

# **Green Surface-washing Agent and Oily Waste Management for Oil Spill Response**

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## ABSTRACT

### Green Surface-washing Agent and Oily Waste Management for Oil Spill Response

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Oil spills in the marine environment frequently reach the coastal zone where active cleanup strategies may become necessary if the rates of natural weathering and attenuation of the stranded oil are considered inadequate. The application of surface-washing agents (SWAs) is an operational technique that enhances the separation and removal of oil that is adhered to solid surfaces. This study presents a comprehensive review of the current and emerging technologies to treat oiled shorelines using SWAs. The literature review includes a brief description of the characteristics of shoreline oiling and the current available techniques for shoreline treatment or cleanup. It summarizes the basics of surface washing and state-of-the-art efforts to date on oil removal using SWAs at both laboratory and field scales. The development trends of green SWAs for shoreline treatment are further introduced.

To develop the novel green SWA, the use of nanocellulose-based nanofluid as a SWA was studied by investigating its reactivity and effectiveness. Salinity was found to be the most influential factor to facilitate oil removal with the nanofluids. Cations from salt can promote the adsorption of nanocellulose on the oil/water interface by reducing the surface charges. The experimental results revealed the nanocellulose could be effective at low concentrations but an excess of nanocellulose hindered oil removal due to an increase in fluid viscosity. The biotoxicity tests showed that nanocellulose-based nanofluid did not have negative effects on algae growth and introducing nanocellulose into an oiled culture medium can actually mitigate the toxicity of the oil on algae. A comparison in removal efficiency with other surfactants demonstrated the potential value for shoreline cleanup due to the superior effectiveness of nanocellulose-based nanofluids. It was found that the nanocellulose has a high potential for application as a surface-washing agent for shoreline cleanup due to the low cost, low toxicity, and high efficiency.

In addition, the shoreline cleanup operation can generate large amount of oily waste which requires further treatment. It is necessary to develop a programming model for oily waste management. An inexact chance-constrained programming model (ICCP) was developed with the consideration of uncertain environments, which cannot only consider the probability distribution of random variable but also interval parameters. The developed model was applied to a hypothetical oily waste management system. The interval solutions obtained from ICCP model included facilities selection, waste flow allocations, and expected time length under different constraint-violation risks. It is an effective tool to minimize the system cost of oily waste management with uncertainties. The obtained solutions could support the managers for the trade-off between system cost and risk level.

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## LIST OF ABBREVIATIONS

ANOVA	one-way analysis of variance
BC	bacterial cellulose
CCP	chance-constrained programming
CMC	critical micelle concentration
CNC	cellulose nanocrystal
CNF	cellulose nanofiber
DI	deionized
DOM	dissolved organic matter
HLB	hydrophilic-lipophilic balance
ICCP	inexact chance-constrained programming
IL	Ionic liquid
IP	interval-parameter programming
NCP	national contingency plan
OPA	oil-particle aggregate
PAH	polycyclic aromatic hydrocarbon
SDS	sodium dodecyl sulfate
SOR	SWA to oil ratio
SWA	surface-washing agent
UV-Vis	ultraviolet-visible

## CHAPTER 1. INTRODUCTION

Marine oil spills continue to be a major global environmental concern to the petroleum industry, regulators and the public (Arbatan et al., 2011; Lee et al., 2015a; Zhang et al., 2019a). Since 2000, there have been more than 100 onshore and offshore oil spill incidents around the world (ITOPF, 2019) (Figure 1-1). The total discharge of crude oil and its products into marine environments is estimated to be between 1.7 and 8.8 million tonnes per year (Abuodha and Kairo, 2001). The spilled oil primarily comes from natural seeps, offshore drilling and production, transportation losses, and industrial discharges (Zheng et al., 2016). Numerous case studies have documented significant damage to coastal environments caused by oil spilled at sea (Owens et al., 2016a). While natural attenuation of oil (removal by a number of processes including evaporation, biodegradation, etc.) occurs immediately upon its release in the environment, depending on the type of oil spilled and environmental conditions, weathered oil reaching coastal environments may persist and hinder biological functions in the ecosystem for a long time (An et al., 2017; Song et al., 2016). Thus, coastal oiling can result in socioeconomic impacts by disrupting subsistence, commercial and recreational activities and resources (Palinkas et al., 1993). Shoreline treatment and cleanup operations typically are the most expensive and time-consuming component of a spill response; as much as 80–90% of the cleanup costs of a major spill can be attributed to coastal cleanup (Etkin, 2001). This provides incentives for the development of new or improved strategies and methods for treating oil more effectively and efficiently on the shoreline and to accelerate recovery times.

Government has prepared some practice guides regarding shoreline treatment. Many manuals were also proposed by other relevant organizations. The cleanup techniques such as mechanical removal, sorbents, bioremediation, sediment relocation and physical washing have been used to remediate the oil-contaminated shoreline. One of the available techniques is to apply Surface-washing agents (SWAs) which are intended to aid in the removal of stranded oil from surfaces without dispersing it into the surrounding waters; SWAs usually contain surfactants with a higher hydrophilic-lipophilic balance than those

in dispersants (Fingas, 2013a). SWAs are typically applied directly on stranded oils and allowed to penetrate for a certain time period. Oil is then flushed with ambient water to remove the oil and direct it to a controlled area for physical recovery. Since the surface-washing agents are typically applied to a small area of oil in the upper intertidal zone, they can be applied manually using hand-held or backpack sprayers or using large-vehicle or vessel-mounted sprayers. In-situ washing of oiled sediments can also be conducted using a tank or reaction chamber in which the oiled sediments are washed using an agent and the clean sediments then separated and returned to the shoreline, while the used washing solution is collected and treated (Chen et al., 2019a; Chen et al., 2019b). The effluents after washing can be further recovered through appropriate disposal to avoid secondary pollution (Lee et al., 2015a).

SWAs may provide an effective and acceptable alternative to more aggressive techniques, such as oiled sediment removal and disposal. In some circumstances, the application of SWAs can thus positively influence the balance between environmental effects and the net environmental benefits. There are some available commercial SWAs such as Corexit 9580, CytoSol, and PES-51 (Fingas, 2012). Some new SWAs are also under development and testing. The U.S. Environmental Protection Agency (EPA) has approved more than 50 surface-washing agents. The use of SWAs has been reported in many field applications (Fiocco et al., 1991; Michel and Benggio, 1995; Owens et al., 1987; Zengel and Michel, 2013). However, their use has been limited by the lack of operational guidelines for the application of SWAs and concerns over their potential detrimental effects that have influenced the acceptance of this strategy for removing oil from shorelines. The development of cost-effective and advanced surface washing approaches can lead to a more effective and environmentally sound strategy for treatment of oiled shorelines than other physical removal and recovery techniques such as excavation and disposal.

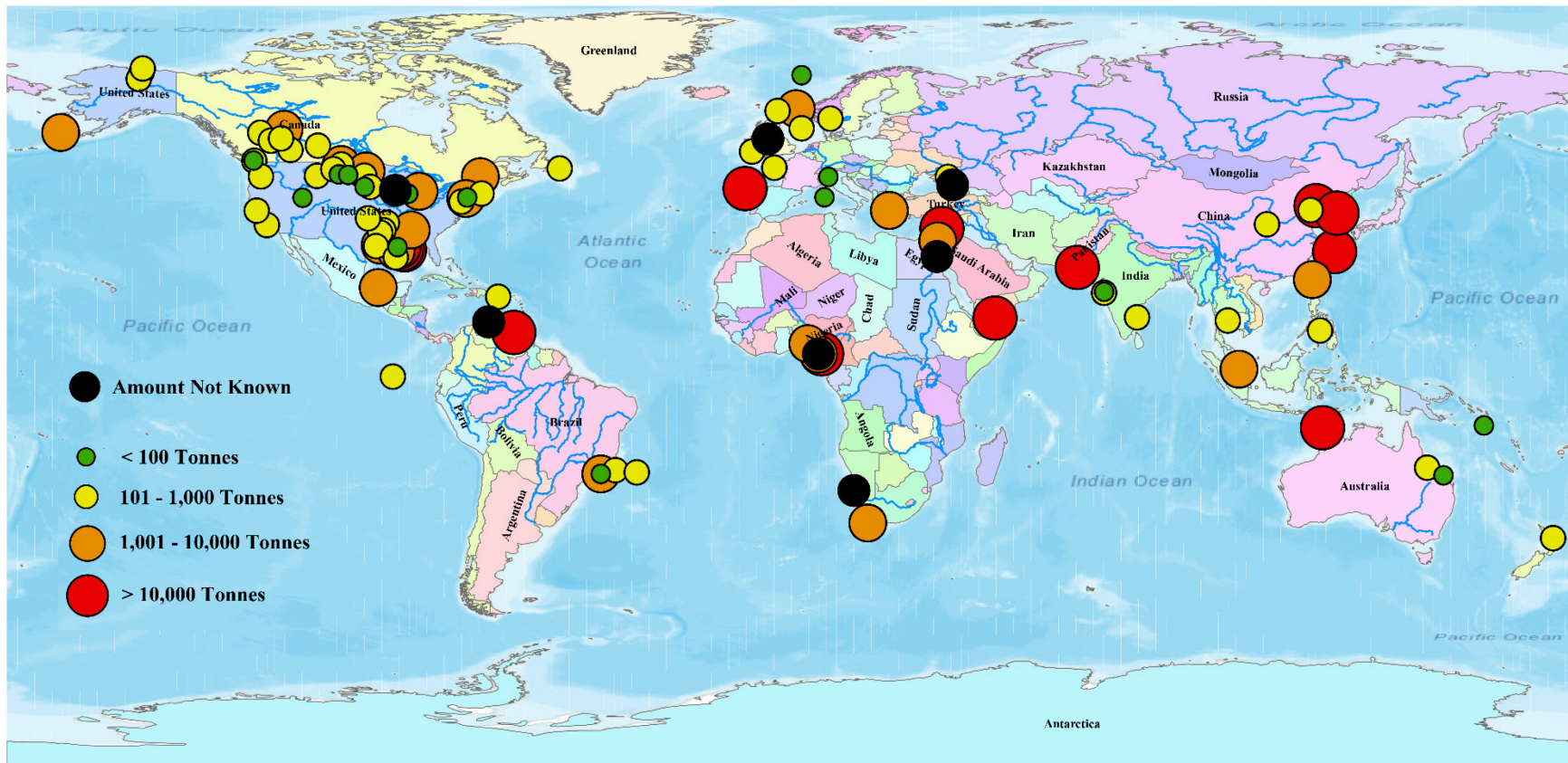


Figure 1-1. Oil spill incidents around the world since 2000.

Another important problem during the shoreline cleanup operation is the management of collected oily waste. Although some documents can provide a brief guideline with the response teams, it is still a difficult problem to consider all the processes in the oily waste management and thus address the problem with the minimum system cost. In addition, the uncertainties that existed in the system make the problem more complicated. Therefore, it is necessary to develop an optimization method for the oily waste management system to assist the managers allocate the resource efficiently with the consideration of various technical, political, economic factors, and system uncertainties. Previously, some researchers have developed a series of optimization model to solve the programming problems with uncertainties, such as fuzzy programming (Zimmermann, 1978), stochastic programming (Huang and Loucks, 2000), interval programming (Li et al., 2006). These methods have been widely used to deal with the uncertainties in the municipal solid waste management (Chen et al., 2014; Chen et al., 2016), water resources management (Guo et al., 2009), energy system (Liu et al., 2019). However, there are no existing studies that have been conducted to address the problems within oily waste management.

Therefore, the aim of this thesis is to develop the tools to enhance the remediation of oiled shoreline affected by oil spill accidents. To achieve this aim, there are three objectives have been proposed as follows:

- Conducting comprehensive literature review to in-depth study the current shoreline cleanup techniques and existing SWAs (CHAPTER 2);
- Developing a novel green SWA with the nanocellulose-based nanofluid (CHAPTER 3);
- Developing an inexact chance-constrained programming model for oily waste management with the uncertain environments (CHAPTER 4).

## CHAPTER 2. LITERATURE REVIEW

### 2.1. Theoretical background of shoreline treatment strategy

#### 2.1.1. Characteristics of shoreline oiling from oil spill

Various transformation processes occur after oil is released into a marine environment, including evaporation, emulsification, and biodegradation. Following spills at sea, oil slicks are often transported to coastal regions due to wind, waves and currents where they can impact the shoreline environment. The oil deposited on shoreline is subjected to a wide range of natural chemical, physical, and biological processes that “weather” the residual oil further without human intervention (Wang et al., 2013). However, the rate of this natural attenuation process may not be an acceptable spill response strategy for environment, social or economic reasons.

Oil can penetrate into the subsurface layers of beach sediments where it becomes trapped by the adhesive force between solid sediment surfaces and potentially isolated from the action of waves and tides (Lee et al., 2015a). Stranded oil on the surface can go through the natural attenuation processes that include dispersion, evaporation, photo-oxidation, biodegradation, and the formation of oil-particle aggregates (OPAs) (IPIECA and IOGP, 2015; Zhu et al., 2001). Biodegradation and photo-oxidation provide a relatively slow pathway for the attenuation of oil on the shorelines. Evaporation, OPAs, and physical dispersion are the primary mechanisms for short-term oil removal.

The oil properties play a critical role in the natural attenuation on shoreline. The oil fraction with low molecular weights attenuates more quickly and easier due to its relatively high



volatility, high dissolution, and low viscosity. n-C11-13 alkanes, C5-6 benzenes, and methyl naphthalene are the components which are most likely removed by evaporation (Wolfe et al., 1994). Low-viscosity oil is relatively easy to be removed by tidal and sea wave due to low shear stress between the oil and sediments on the shoreline. Besides, the low shearing action of oil can also enhance the formation of OPAs which is favorable for oil removal (Omotoso et al., 2002).

The physical environment related to wave energy and shoreline components is another crucial factor that determines the fate of oil. Rashid (1974) conducted field and laboratory tests to study the effects of the coastal processes on the degradation of Bunker C oil. Compared with the laboratory stored samples, the oil removal rate of experimental group could be improved as wave-energy level of the coast increased. The mechanical energy acted on the shoreline consists of natural tides, winds and waves, etc. However, the energy absorbed by the attached oil only depends on the magnitude of mechanical energy, but also can be affected by the attributes of the shoreline. It was found that the depth and rate of oil penetration on the shoreline are impacted by the sediment size and rock types, and the oil penetrated to deeper beach layers were less exposed to the mechanical energy (Owens, 1978).

The difficulty of cleanup varies with the types of shoreline. The examples of beach profiles in a tidal environment are shown in [Figure 2-1](#) (Fingas, 2012). The penetration and retention of oil on these sand and pebble-cobble beaches are different due to different structural and component characteristics. The speed of natural attenuation is also related to the slope of contaminated shoreline. According to a field investigation of oiled beaches by Xia and Boufadel (2011), the higher slope of the beach could enhance the degradation of subsurface oil because the beach with a steep slope was more accessible to the supply of

oxygen and nutrients from sea tide and wave. Environmental temperature can also affect the persistence of oil by changing the oil viscosity. Moreover, in extreme cold environments, the mechanical energy input on the shoreline can decrease due to the formation of ice on the sea or shoreline surface (Owens, 1978).

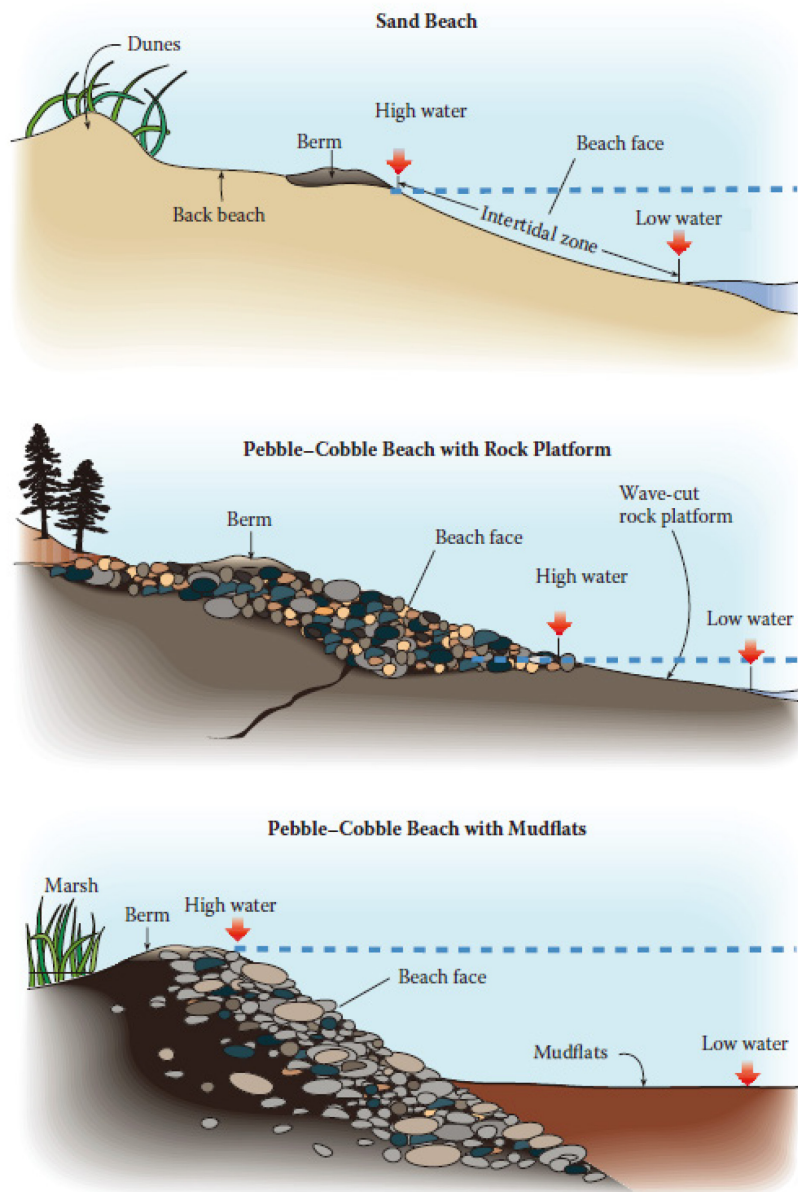


Figure 2-1. Examples of beach profiles in a tidal environment (Fingas, 2012).

As the report on the changes in oil volumes of the beach oiled during *Baffin Island Oil Spill* experiment noted, about 60% volume of stranded oil can be reduced after first 24 h and there was a further 7.5% loss after following 27 days (Owens et al., 1994). Although the concentration of total petroleum hydrocarbons decreased rapidly due to the natural attenuation in the short term, oil residues can remain in the shoreline environment for a long term until the significant change in the physical environment, such as seasonal storms or temperature rise (Owens et al., 2008). Therefore, to clean up the oil on shoreline more effectively in the short-term and long-term period, a number of enhanced-cleanup techniques described in the following section have been evaluated.

### **2.1.2. Shoreline treatment or cleanup techniques**

Oiled shorelines can be treated or cleaned through various physical, chemical and biological techniques. These methods are suitable for oil spill cleanup under different environmental conditions and stages of remedial operations. The major cleaning techniques include manual recovery, mechanical recovery, sorbents, bioremediation, flushing, sediment relocation and surf washing, and surface washing with chemicals. Different treatment approaches are featured by different application requirements and treatment patterns. A comparison of the above shoreline remediation technologies is summarized in [Table 2-1](#) based on the literature and practical experience of experts in oil spill treatment (ASTM, 2009; Dubach et al., 2015; E.H. Owens et al., 2017; IPIECA and IOGP, 2015; Lee et al., 2015a).

- Manual and mechanical recovery

Manual and mechanical recovery are the most direct methods to clean up the shoreline through recovering the stranded oil, which typically requires lots of personnel or machinery

to remove oil physically. The oiled materials are directly removed from the shoreline surface and then collected by personnel or machinery, and the specific cleaning procedure depends on the site condition and oil properties (Owens, 2016; U.S. EPA, 1993). Accessibility is an important factor to determine whether the method can be implemented on the oiled substrates. Mechanical recovery is only available for those sites where vehicle and large machinery can access, and manual recovery is able to be implemented on the shoreline which is accessible on foot (IPIECA and IOGP, 2015; Lee et al., 2015a). The removed oil is stored on site until they are collected for the further treatment. Thus, physical recovery method is typically used to remove non-fluid oil from shoreline, to ensure the removed oil does not spread again during the stored period (IPIECA and IOGP, 2015). However, the intervention of quantities of persons and equipment potentially damage the ecosystem on shoreline (Fingas, 2012; IPIECA and IOGP, 2015; Lee et al., 2015a; Owens, 2016).

- Sediment relocation and surf washing

This remedial strategy is based on the reworking of oiled sediments to break up oil deposits, to facilitate physical oil dispersion, enhance the formation on oil mineral/particle aggregates (OMA/OPA) (Gong et al., 2014; Lee et al., 2003) and to increase oxygen penetration into deep subsurface oil layers. This activity enhances the exposure of the oil to natural removal processes and enhances the rate of oil biodegradation. Under this protocol, oiled beach sediments are rototilled or otherwise mechanically mixed with the use of heavy equipment or relocated from the upper intertidal area of the beach to the surf zone. In the latter procedure which is also known as surf washing or berm relocation, the formation of OMA/OPA reduces the adhesion of the stranded oil to the sediments and promotes its dispersion into surrounding waters while reducing its ability to re-coalesce (Wang et al., 2011). Since the process increases the surface area of the oil and exposes it to

an energetic oxygen rich surf zone over a longer period of time, hydrocarbon dissolution and oil biodegradation rates are enhanced. Generally, sediment reworking is used on sand, cobble or gravel beaches where high erosion rates or low natural sediment replenishment rates are issues (Lee et al., 1997; Lee et al., 2003; Lunel et al., 1996). Sediment reworking may also be used where remoteness or other logistical limitations make sediment removal unfeasible (Lee et al., 2003).

**Table 2-1.** Evaluation on the shoreline cleanup techniques.

<b>Techniques</b>	<b>Cleanup speed</b>	<b>Removal effectiveness</b>	<b>Ease of implementation</b>	<b>Environmental impacts</b>
Natural attenuation	■	■	●	●
Manual removal	◆	●	◆	◆
Mechanical removal	●	●	■	◆
Sorbents	■	◆	◆	◆
Flooding	◆	◆	◆	■
High pressure washing	●	●	■	■
Hot water washing	●	●	■	■
Sediment relocation	◆	◆	◆	◆
Bioremediation	■	◆	●	●
Surface washing agents	●	*	●	*

●: Good performance    ◆: Medium performance    ■: Low performance

\*: Depending on the products or methods

- Sorbents

Sorbents refer to insoluble materials that are able to absorb or adsorb oils (Tiscornia et al.,

2007; Wang et al., 2017). There are some listed sorbent products in the *National Oil and Hazardous Substances Pollution Contingency Plan (NCP)* of the U.S EPA to remove or control the oil discharge (Nichols, 2001). The application range of sorbents is wide and it can be used in all stages of oil spills (Angelova et al., 2011; Oribayo et al., 2017; Wang et al., 2015). In the early stage of the oil spills, the sorbents can be used for preventing further spread of floating oil. It can also be set on nearshore to avoid the oiling of coasts. Furthermore, the shoreside can be covered by the sorbent boom to prevent the removed oil from spreading to sea when the shoreline cleanup is implemented.

Sorbents are also the effective tool to clean up a large area of oiled shoreline. However, it is labour intensive, as the technique requires personnel to cover the oil with large sorbent pads, and then the oil-filled pads have to be manually removed (U.S. EPA, 1993). This method has the great commonality that can be applied on all the shoreline that personnel can access. The sorbent materials are collected when they fill up with oil. However, the disposal of oil-filled sorbents can be expensive and harmful to the environment. Many researchers are studying the new sorbents materials which have better physical performance and are easily disposed. Radetić et al. (2003) developed a recycled wool-based nonwoven material as a new oil sorbent. 88% of oil can be removed through squeezed between rollers, thus achieving more than 5 times reuse. Zhu et al. (2011) manufactured PVC/PS fiber as an oil sorbent through the electrospinning process, which had higher oil-retaining capacity and buoyancy compared with traditional materials. Some renewable materials are also developed. Suni et al. (2004) used cotton grass fibers, the by-product of peat excavation, as the sorbent for oil spill control.

- Bioremediation

Biodegradation is the primary mechanism for the natural attenuation of oil stranded on

shorelines. The microorganisms which can biodegrade petroleum hydrocarbon synthesize the oil into CO<sub>2</sub> and H<sub>2</sub>O through respiration, as shown in [Figure 2-2](#). The biodegradation rate relies on the species and population of the microorganisms, as well as other environmental factors on a shoreline such as air and water temperature, oxygen concentration, nutrient supply and the type and concentration of oil spilled. Therefore, in the natural environment, the biodegradation rate of oil on the shoreline could be slow if lacking the appropriate conditions. Two main approaches, biostimulation and bioaugmentation, are used to accelerate the rate of biodegradation.

(1) Biostimulation: The native microbial turnover of petroleum hydrocarbon can be accelerated by adding nutrients such as nitrogen and phosphorus or changing conditions such as temperature, pH, and oxygen concentration at an oiled site (Tyagi et al., 2011). This process is defined as biostimulation. Most previous biostimulation studies focused on the addition of nutrients to boost the biodegradation rate of microorganisms. The recommended C:N:P ratio of fertilizer for degradation of petroleum hydrocarbons is 100:10:1 according to the experimental results from Nikolopoulou and Kalogerakis (2009). The effect of fertilizer decreases rapidly after the application because it is difficult to maintain the concentration of nutrients under the washing by waves on shoreline. Slow-release fertilizers have been applied to address this issue with improved performance (Lee et al., 1993; Röling et al., 2002).

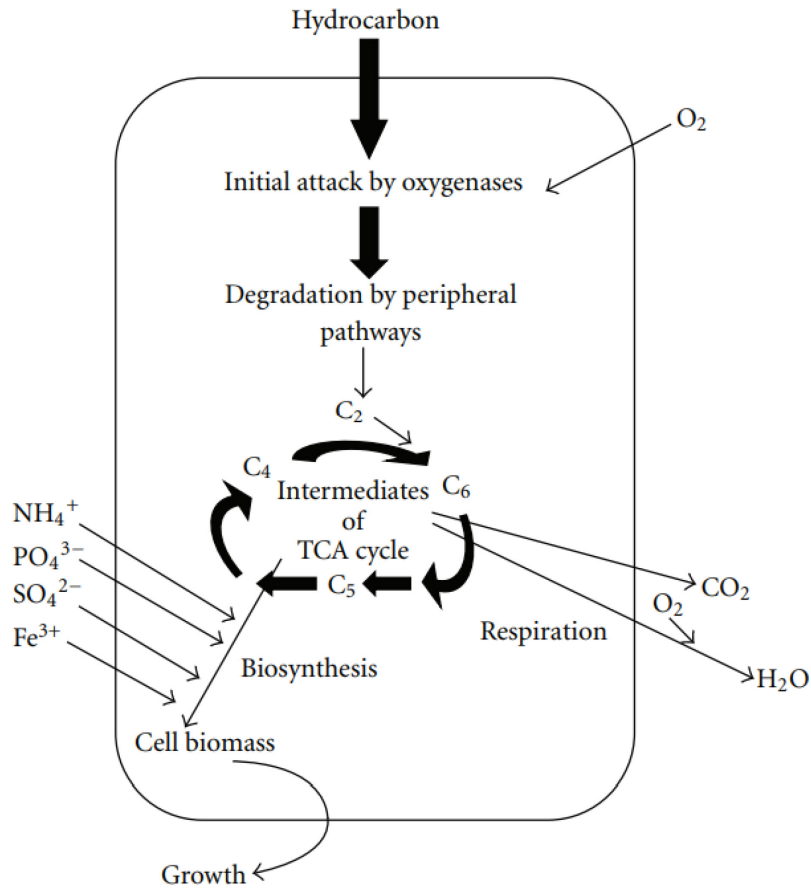


Figure 2-2. Main principle of aerobic degradation of hydrocarbons by microorganisms (Das and Chandran, 2011).

(2) Bioaugmentation: In some cases, the indigenous microbial populations may be insufficient to degrade the petroleum hydrocarbon because the site does not have the oil-degradable organisms or an adequate population size (Adams et al., 2015). Therefore, bioaugmentation is considered as another solution for bioremediation by the introduction of external microorganisms. There are three main methods to implement bioaugmentation: (1) collection of target microorganisms from an oiled site and reinoculation after culturing; (2) culturing and reinoculation of microorganisms which are not from the origin site; (3) introduction of microorganisms which are genetically modified or genetically engineered



related with oil biodegradation (Tyagi et al., 2011; Zawierucha and Malina, 2011). However, the population of inoculated bacterial could decrease rapidly due to inappropriate and changing environmental factors and the competition with indigenous microorganisms, thus, the extent of positive effects may be limited over the long term (i.e., time-scale of response operations) (Margesin and Schinner, 1999).

- Physical washing

For those low-energy shorelines which have a relatively stable physical environment, the oil can be entrapped on the shoreline for a long time (Fingas, 2012). Compared with the passive techniques, surface washing is one of the active treatment techniques which can be used to enhance the removal of oil from shoreline. The nature of surface washing is using additional mechanical energy, kinetic energy and thermal energy, to remove the stranded oil from the shoreline surface. There are several methods which can be used to implement the surface washing on the oiled shoreline. The external energy can be manually implemented through high-pressure or hot-water jet, which refers to high-pressure washing and hot-water washing, respectively. In-situ washing is a method to use machinery to collect and wash oiled materials on shoreline; wastewater generated from the washing process can be collected and treated to avoid the re-pollution. In addition, the oil can also be removed naturally through moving the oiled sediments from low-energy to high-energy environment in shoreline (Owens, 1978). However, these surface-washing methods have their own limitations. The excessive energy from pressure and hot-water washing can also damage the ecological environment, potentially killing the animals and plants living in the intertidal zone (Mearns, 1993). Large machinery required by the sediment relocation or in-situ washing is hard to access areas which are remote or with uneven ground, such as cobbles or boulder beaches.

### **2.1.3. Basics of using surface washing agent**

SWAs are designed to enhance oil removal from the shoreline surface by changing the oil properties or the interfacial properties between water/oil phases. In some early studies, dispersants were used as the shoreline cleaner to clean up oiled shorelines. However, the effectiveness of dispersants as shoreline cleaner was not satisfactory according to the results of previous laboratory and field tests (Canevari, 1979; Little et al., 1986; Owens et al., 1987). Following the *Exxon Valdez spill* incident in 1989, research on the development of SWAs expanded dramatically and they were classified as an independent category (Schramm, 2000). Compared with dispersants, the aim of application of SWAs is to wash oil from solid surfaces without dispersal into the water column as small droplets; thus, in comparison to chemical dispersant formulations, the surfactants in SWAs typically have a higher hydrophilic-lipophilic balance (HLB) (Fingas, 2013b; Koran, 2007; Schramm, 2000). Currently, 57 SWAs are listed by *NCP Product Schedule* of the U.S EPA (U.S EPA, 2019). However, the specific formation of most of these agents is not available due to their complicated components and the requirement of confidentiality (Fingas, 2013b; U.S EPA, 2019). Fingas (2013b) classified six basic groups according to the formation of SWAs: (1) non-ionic or anionic surfactants with HLBs of more than 11 in a low-aromatic hydrocarbon solvent; (2) D-Limonene in various solvents; (3) surfactants mixed with various solvents; (4) surfactants in glycol-type solvents similar to dispersants; (5) detergents with little or no solvent; (6) solvent mixtures.

## **2.2. Laboratory effectiveness tests on surface washing agents**

Apart from the toxicity, the effectiveness in oil removal is another important factor for the evaluation of SWAs. SWAs is one of the five categories of products in the U.S. EPA's NCP product schedule, while the others include dispersants, surface collection agents,

bioremediation agents, and miscellaneous oil spill control agents (U.S EPA, 2019). The performance of the agents is one of the important properties that the manufacturers are required to report to EPA. *Baffled Flask Test* and *Bioremediation Agent Effectiveness Test* were developed by U.S. EPA to provide the normative testing method for the evaluation of the effectiveness of dispersants and bioremediation agents, respectively (Nichols, 2001; Venosa et al., 2002). However, while there is currently no standard test method for SWAs developed by the U.S. EPA; a variety of laboratory testing protocols have been developed by other research organizations to evaluate the effectiveness of SWAs.

### **2.2.1. Test methods**

After the oil spill event *Exxon Valdez spill* in 1989, the SWAs evolved into a separate category of oil spill treatment agents from dispersant (Fingas, 2012). Therefore, testing methods for evaluating the effectiveness of SWAs were needed (Table 2-2). Environment Canada developed the first laboratory test protocol in 1989 (Clayton, 1993). Following an evaluation of 25 test protocols, a steel trough was finally selected as the ideal test substrate due to its repeatability. In the following years, some other laboratory testing methods were successively developed. Science Application International Corporation (SAIC) developed the swirling coupon method to measure the effectiveness of SWAs in 1993. The test substrates (e.g., stainless steel or glass) could be conveniently replaced in this method to evaluate agents' performance under different conditions (Clayton, 1993; Sullivan and Sahatjian, 1993). The Centre de Documentation de Recherche et d'Expérimentation sur les Pollutions Accidentelles des Eaux (CEDRE) in France used an oiled glass slide to evaluate the performance of SWAs, under the "glass slide" method (Clayton, 1993; Francois X. Merlin, 1994). These three testing methods used artificial materials as the substrate. Although the use of artificial materials can help control the testing material variable to

ensure the substrates have a uniform and same surface properties, the natural substrate can be more relevant to materials existing in the shoreline environment.

Fieldhouse (2012) improved the Environment Canada method by using granite tiles as the substrate. The oiled tiles were washed by periodic mixing after adding SWAs and then their removal efficacy was quantified. SINTEF screened two laboratory testing systems, washing robot and washout system (Carlsen and Ramstad, 2007). The slate tiles were artificially oiled and used as the substrate for these two testing systems. The primary difference between the washing robot and washout system is washing method. Pressure nozzle and immersed shaking were applied on the washing robot and washout system, simulating the washing conditions of pressure washing and natural tide, respectively. To select the agents with the best performance of surface washing for remediation of shoreline oiled from the *Exxon Valdez* grounding, the laboratory testing method using commercial aquarium gravel as the substrate was developed by Fiocco et al. (1991). In addition, in 2009, U.S. EPA published a draft testing protocol. A mesh basket was used as the container for the washing of oiled fine sand (Koran et al., 2009). Compared the fixed SOR used in the previous testing methods, DeLorenzo et al. (2017) developed a protocol to evaluate the cleaning performance of the SWAs, in which the chemicals were applied to achieve the optimal efficiency of the identified SWA based on the product manufacturer's instructions. Although several testing protocols have already been developed to evaluate the performance of SWAs, none of these methods has been widely promoted and used as a standard method for evaluation of the effectiveness of SWAs.

Some researchers developed their testing methods for SWAs in order to optimize the variables to improve the performance of agents or evaluate the newly developed agents. To study the effects of the temperature of flushing water on the efficiency of shoreline cleaning

agents, Tumeo and Cote (1998) developed a testing method to measure the percentage of oil removed by water at different temperature after addition of three SWAs respectively. The stainless-steel columns filled with uniformly oiled sand were flushed by water at different temperatures after a specific soaking time with SWAs. However, many details, such as soaking time and flushing time, were not described in this paper. Pereira and Mudge (2004) studied the potential of using biofuel as SWA to clean up the oily shoreline. The experiments were conducted in two scales, a small box (330 × 225 × 200 mm) filled with fine sand, and a plastic container (1200 × 540 × 240 mm) filled with cobbles, gravel, coarse and fine sand, respectively. After the addition of biofuel (day 0), the tidal action was simulated through adding seawater at day 1, 2, 3, 4, and 14; moreover, the oil mixture was collected and analyzed after tidal simulation to determine the percentage of oil removed as time went on. Some testing methods selected breaker or baffled flask as the container in the experiments. Compared with the relatively large size and complicated structure of experimental devices in the previous testing methods, using the breaker or baffled flask as the container can simplify and standardize the testing procedure. Amani (2015) used 2 L beakers as the container to evaluate the performance of four surfactants including two biosurfactants and two commercial surfactants. After stirring the mixture of oiled sand and surfactants for 24 h, the oil removal rate was determined through measuring the oil residual. The baffled flask was used in the testing method developed by Arelli et al. (2018) to optimize the washing condition for selected nine surfactants, improving their hydrocarbon removal efficiencies. The oiled sand was placed into the baffled flask in the shaker, and the oil residual attached on the sand was measured after washing to determine the oil removal efficiency under different testing conditions (Francois X. Merlin, 1994).

Table 2-2. Laboratory testing methods for the effectiveness of SWAs.

Method Name	Oil amount	SOR	Substrate	Weathering time	Soaking time	Washing method	Water volume	Washing magnitude	Washing time	SWAs tested*	References
Environment Canada Inclined Trough Test	150 µL	1:5	Stainless-steel trough	10 min	10 min	Flowing water	10 mL	5mL per 10min	20 min	More than 100 agents	(Fingas, 2012)
SAIC Swirling Coupon Test	48 µL	1:3	Stainless steel or porcelain	18 h	10 min	Shaking	250 mL	-	2 min	Not known	(Clayton, 1993)
CEDRE Glass Slide Test	0.5 g	1:2	Glass slide	20 min	10 min	Spraying	560 mL	28 mL/s	20 s	12 agents	(Francois X. Merlin, 1994)
Beach Washing Test	2.5 g oil/48 g dry rock	1:2.5	Rock	-	1 h	Percolation	100 mL	50 mL/min	2 min	Corexit 9580	(Clayton, 1993; Fiocco et al., 1991)
EPA's Draft Protocol	180 µL	2:1	Sand or gravel	18 h	30 min	Shaking	100 mL	175 rpm	15 min	Aquaclean	(Koran et al., 2009)
SINTEF Washing Robot Test	1 mm depth	1:5 for SWAs 1:25 for dispersants	Shale tiles (10×10 cm)	-	20 min	Nozzle pressure washer	-	14 bars	-	Nine agents	(Øksenvåg et al., 2009)
SINTEF Simulated Shoreline System (SSS) Test	1 mm depth	1:5 for SWAs 1:25 for dispersants	Shale tiles (15×15 cm)	-	20 min	Agitation	2 L	-	30 min	Nine agents	(Øksenvåg et al., 2009)
Improved environment Canada method	1.3 mL	1:1	Granite tiles	30 min	30 min	Mixing	1.3 L	30 rpm	15 min	Six agents	(Fieldhouse, 2012)
-	2-12 mL	1:2 to 1:5	Gravel, rip-rap, and eelgrass	18-22 h; Additional 1-2 h for gravel and rip-rap	3-30 min	Flushing	300 mL	-	-	PES-51 and Corexit 9580	(John R. Clayton et al., 1996)
-	10 g/kg	-	Sand	-	-	Flushing	-	8.11 mL/s	-	Five agents	(Tumeo and Cote, 1998)

Table 2-2. (Continued).

-	200 mL	1:2 to 2:1	Sand	7 days	1 day	Flooding	6 L	1 L for one hour at 1, 2, 3, 4, 14 days after addition of agent.	14 days	Vegetable oil	(Pereira and Mudge, 2004)
-	0.5 g	-	25 g Sea sand	-	-	Shaking	125 mL	400 rpm	10 min	JE1058BS	(Saeki et al., 2009)
-	5.25 g	-	Sand	7 days	-	Shaking	-	50 rpm	24 h	Four agents	(Amani, 2015)
-	-	According to the manufacturer's instruction	Ceramic tiles	10 days	According to the manufacturer's instruction	Flushing	440-625 mL	-	30 s	Four agents	(DeLorenzo et al., 2017)
-	0.5 g to 20 g oil/kg sand	25-500ml SWA	Oiled Sand	10 days	-	Shaking	Water to sand ratio: 1 - 10	80-220 rpm	-	Nine agents	(Arelli et al., 2018)

\*Available from literature.

### **2.2.2. Performance of SWAs in laboratory tests**

A number of SWAs have been tested by the laboratory testing methods summarized in the last section, and the effectiveness results of some representative SWAs using different testing methods are shown in [Figure 2-3](#) (Fingas, 2012; Francois X. Merlin, 1994; Øksenvåg et al., 2009). The removal effectiveness of same SWAs varied using different testing methods. But it is also important to note that the results of effectiveness tests will vary with differences in environmental conditions, including the type of test substrate and oil. Fingas (2013b) summarized the effectiveness of 101 SWAs which were tested by Environment Canada inclined trough method. Comprehensive multi-product test results for the Swirling Coupon method and Glass Slide method were not found from the reviewed literature. Aquaclean was used as the standard testing agent to develop the EPA draft protocol, and its effectiveness ranged from 30-80% under different testing conditions (Koran et al., 2009). Nine agents, including SWAs and dispersants, were evaluated by Shoreline Simulator System (or Washout System), and Washing Robot respectively (Øksenvåg et al., 2009). The results of the effectiveness of agents differed between these two methods and it suggested that the physical conditions can lead to a considerable difference in the results. To better evaluate the performance of the newly-developed SWAs, some testing methods such as Beach Washing Test for Corexit 9580 (Fiocco et al., 1991), sand washing test for JE1058BS (Saeki et al., 2009), and box test for vegetable oil (Pereira and Mudge, 2004) were also developed to study the effects of physical conditions on the agent effectiveness.

The performance of an environmental process can often be impacted by many conditions (Kuo et al., 2018; Morar et al., 2018; Zhang et al., 2019b). The optimization of environmental process can help achieve the maximum benefits in practice (Carvalho et al., 2018; Chen et al., 2018; Guo et al., 2018; Li et al., 2018). The optimization of SWA



performance was studied through designed testing methods by adjusting the physical factors (Arelli et al., 2018; Tumeo and Cote, 1998). Tumeo and Cote (1998) developed the column test to evaluate the effects of the temperature of washing water on the removal rate of three SWAs. Arelli et al. (2018) used laboratory tests to find out the optimal washing conditions including agent concentration, water/sand ratio, mixing rate for nine chemicals as SWAs to enhance the oil removal rate. In addition, similar research was also conducted for exploring the relationship between testing physical conditions and performance of surface washing. Although the factors which can impact the performance of SWAs varied in previous laboratory tests, some general patterns can be summarized as follows.

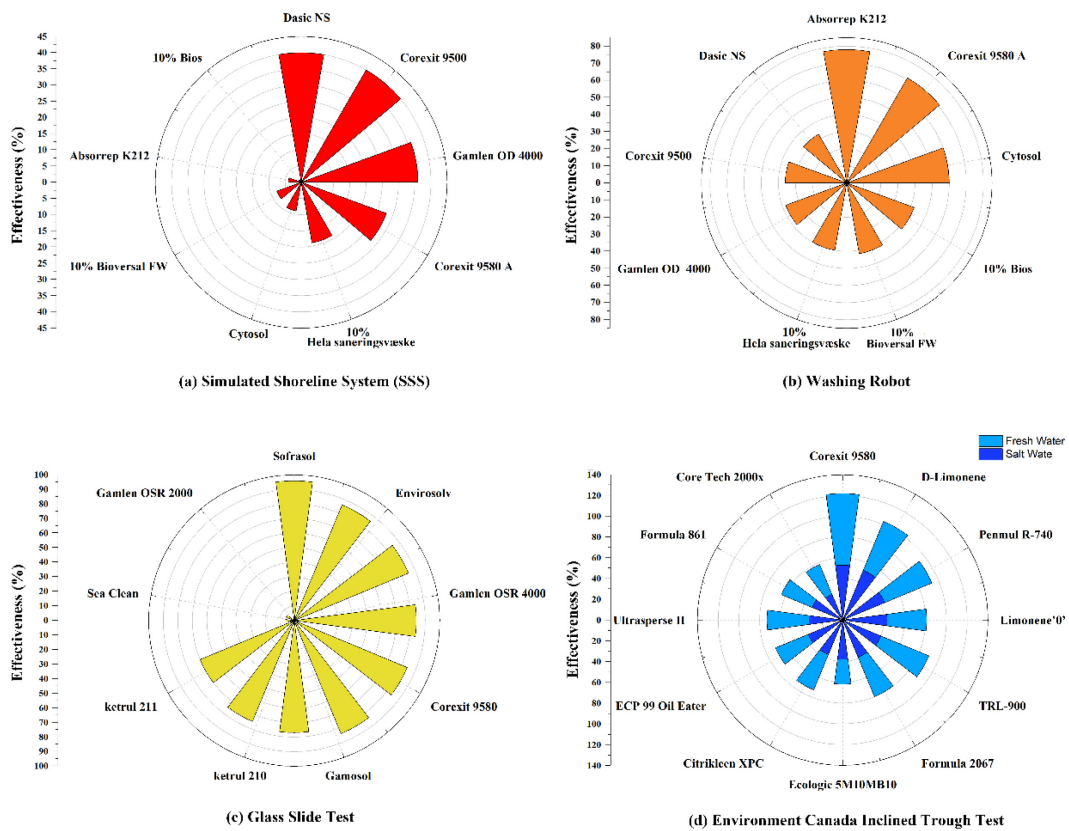


Figure 2-3. Performance of representative SWAs using different testing methods (Fingas, 2012; Francois X. Merlin, 1994; Øksenvåg et al., 2009).

- Temperature

The oil properties such as viscosity and density can affect the persistence of stranded oil and vary significantly as environmental temperature changes. Higher environmental or washing water temperatures effectively enhanced the oil removal in the effectiveness tests of the SWAs (Amani, 2015; Carlsen and Ramstad, 2007; Jézéquel et al., 2009; Tumeo and Cote, 1998). The decrease in oil viscosity caused by the temperature rise reduced the viscous force of the oil and made it more easily to be washed out (Amani, 2015; Sullivan and Sahatjian, 1993). The effects of temperature can be more significant with the aid of SWAs. According to the study by Tumeo and Cote (1998), the overall efficiency losses for PES-51, Corexit 9580, and Grancontrol 'O' were 67%, 9%, and 55% respectively when the flush water temperature dropped from 20 to 10 °C. However, no effects were observed for the sea water without agents.

- Washing method and magnitude

The washing method used in the laboratory tests included shaking, flushing, and pressure washing. Therefore, the methods for quantifying magnitudes of external mechanical energy were different when using the various testing methods. Jézéquel et al. (2009) and Carlsen and Ramstad (2007) studied the effects of pressure of the water jets on the oil removal effectiveness of SWAs based on Washing Robot testing method using pressure washing. Similarly, Arelli et al. (2018) and Koran et al. (2009) applied different mixing rates for washing tests, using a shaker to provide external energy. According to the experimental results, the increase in pressure and turbulent mixing energy accelerated oil removal from substrate surface (Amani, 2015; Arelli et al., 2018; Carlsen and Ramstad, 2007; Koran et al., 2009; Øksenvåg et al., 2009).

- Substrate

The behaviors of the oil on a shoreline are varied with the substrates; thus, the shoreline

with the different substrates requires the different recovery options to address the spilled oil (Lee et al., 2015a). The effects of the substrates on the washing efficiency of SWAs were taken into consideration in some previous studies. Pereira and Mudge (2004) used four substrates (cobble, gravel, coarse sand, and fine sand) to evaluate the effectiveness of vegetable oil as SWA under different conditions. The total removal rate for fine sand and cobble was around 80%, and the rates for gravel and coarse sand were 30% and 47%, respectively. Koran et al. (2009) tested the oil removal efficiency of SWAs for the different oiled substrates (sand and gravel). The oil mass removal from the sand substrate (109.6 mg) was higher than that for gravel substrate (96.1 mg). The effects of the substrates on the surface washing tests can be impacted by several factors, including chemical and physical properties, porosity, and surface-area-to-mass ratio. The oil within the porous medium composed of water-wetted particles is easier to be washed out by water flow than those particles with the oil-wetted surface. Even though the sand has a higher surface-area-to-mass ratio, the lower porosity of the sand makes the penetration of oil harder than gravel, contributing to the high oil removal efficiency of the sand substrate (Koran et al., 2009). However, as shown in the experimental results of Pereira and Mudge (2004), larger cobble substrate had a similar oil removal efficiency. It can be explained by the counteractive effects of lower surface-area-to-mass ratio and higher porosity.

- SWA to oil ratio (SOR)

SOR is an important factor for the oil removal on shoreline. It is expected to use relatively small amounts of SWAs to achieve ideal cleaning effect, thus avoiding the potentially adverse impacts on the biota in the coastal environment caused by the toxicity of agents. Therefore, SOR was set as one of the variables in some washing tests for the optimization of washing conditions. According to the experimental results of the washing tests, the oil removal efficiency can be improved with the increase in SOR. However, the marginal effect existed for the agent dose, although the specific values varied with the testing methods and

agent types. To fairly evaluate the effectiveness of SWAs, those testing methods developed for effectiveness measurement often set the fixed SOR. The SOR in the standard testing method reviewed in this paper ranged from 1:5 to 2:1 (Table 2-2).

- Weathering time

The aim of setting weathering time in the washing tests is to simulate the weathering effects on the persistence of the oil. Oil is typically composed of hydrocarbon and other organics of various molecular weights. The oil viscosity can gradually increase when the stranded time becomes longer due to the evaporation of light-weight fraction in oil; thus, the stranded oil was getting hard to be removed. Pereira and Mudge (2004) studied the weathering process of oil on the testing shale tiles and its effects on the removal efficiency. After 61-days weathering, only 67% of the oil remained on the tiles. In addition, the oil removal efficiency dropped rapidly with the increase in the weathering time under all testing circumstances. The same conclusion was also obtained by using Washing Robot method (Carlsen and Ramstad, 2007).

### **2.3. Field tests of surface washing for oil removal**

#### **2.3.1. Field tests of SWAs-aided oil cleanup**

The toxicity and performance of SWAs can be determined through regulatory laboratory tests designed to verify the safety and effectiveness of the agents approved for operational use. Through the approval by the corresponding organizations, the agents can be tested in small- to large-scale field trial studies with controlled releases of oil. In this review, the total of 16 field trials from 1970 to 2011 were summarized, including the evaluation of about seven types of SWAs, as shown in Table 2-3.

In the early stages of shoreline surface cleanup operations using chemical agents, the concept of SWAs had yet to be developed. Thus, Canevari (1979) analyzed the potential of water-compatible dispersants to clean oiled shoreline surfaces in the laboratory in addition to the conduct of large-scale field tests. Initial results showed that the surface of the oiled shoreline was cleaned through the application of a hydrocarbon-based surfactant; but the oil also penetrated deeper subsurface where it was retained for an extended period. However, it appeared that an application of the washing stream with mixed water-based surfactants avoided this problem; as the oil was effectively removed and flushed away from the sand particles. Despite this preliminary evidence, numerous other researchers noted the limitations of using dispersants to clean oiled shoreline environments. Little et al. (1986) and Owens et al. (1987) reported the field tests for two dispersants, BP 1100X and Corexit 7664, in Wales, UK, and Cape Hatt, Baffin Island, Canada, respectively. The testing results showed that the addition of these two dispersants did not significantly increase the oil removal, and even probably exacerbated the oil retention compared with the untreated plots.

After the *Exxon Valdez* spill in 1989, the concept of SWAs were recognized and they were classified as a separate category of oil-treatment agents by U.S. EPA (Fingas, 2013b). To clean up the oiled shoreline caused by *Exxon Valdez* spill, Corexit 9580 was evaluated by laboratory testing as well as a number of other chemical agents (Fiocco et al., 1991). The full-scale field test and demonstration were conducted in Prince William Sound on Disk Island and Knight Island, respectively. Both tests were successful in verifying the effectiveness of Corexit 9580 as a SWA to treat oiled shoreline surface. The results of the field test in Disk Island showed that the 65% of oil attached to the surface of shoreline and 67% of oil penetrated the subsurface of shoreline, were removed by adding the agent, compared with the untreated reference with the rates of 61% for surface and 27% for subsurface correspondingly. Similarly, to test the performance of the newly developed

SWA, Cytosol, a field test was conducted in San Francisco Bay (von Wedel, 2000). About 60% retained oil was removed through passive removal after the addition of agent. Brodersen (1999) reported the field test for removing eight-year weathering oil by applying PES-5 for a gravel beach in Latouche Island in Prince William Sound oiled following the *Exxon Valdez* grounding. About 43% and 78% of the oil were removed after two months and one year of treatment, in contrast with the figure 26% and 44% for untreated site, respectively.

Salt marshes are one of the most ecologically important and sensitive coastal ecosystems to oil spills. Field tests have been conducted on salt-marshes to study the oil-removing performance of chemical agents. Pezeshki et al. (1997) conducted the full-scale field tests to investigate the potential of Corexit 9580 to remove oil from marsh vegetation. Three groups were set in this test: (1) no oil and no SWA, (2) oiled, and (3) oiled and cleaned by Corexit 9580. The stomatal conductance and transpiration of the salt-tolerant plants were monitored for 65 days after application and the results showed that even though the marsh vegetation did not recover to a “no oil” status, the death rate and respiration rate were significantly improved compared to the untreated groups. The application of SWAs (PES-51 and Cytosol) on oiled salt marshes was evaluated on the marsh shoreline of Northern Barataria Bay, Louisiana, impacted by *Deepwater Horizon* Oil Spill (Zengel and Michel, 2013). Although the addition of these two agents increased the mobilization of oil, the major proportion of oil remained on the marsh plants. Therefore, a decision was made not to apply the chemicals on an operational scale on the basis of the pilot-scale tests.

Through the review of the field tests of SWAs, it was found that most applications of SWAs were successful in removing the oil from shorelines, apart from those field trials which used chemical dispersant formulations. In some cases, the dispersants even exacerbated the

oiled condition after the application of chemicals which increased the mobility of the oil and its penetration into deeper subsurface layers, thus extending its retention time within the sediments (Little et al., 1986). Dispersants designed to emulsify the oil to accelerate its degradation are typically hydrocarbon-based surfactants which have a lower value of HLB. In addition, the systematic evaluation of oil removal in the field tests was a challenge because it was difficult to control the multitude of environmental variables, and oil degradation varied with spatial distribution due to the heterogeneous nature of the sediments (Little et al., 1986). Therefore, the evaluation of SWAs in most field trials was performed based on qualitative observations.

### **2.3.2. Guidelines for field application of SWAs**

Oil spill response manuals can provide guidance for the selection of treatment techniques according to the stage and extent of the spill (ASTM, 2009; Dubach et al., 2015; E.H. Owens et al., 2017). The application of SWAs is now a recognized spill response technique for the treatment of oiled shorelines. Even though the toxicity of SWAs depends on the specific washing agent, most agents are moderately toxic to aquatic organisms. Therefore, approval from the appropriate regulatory agencies is necessary before the implementation of SWAs (Whitney, 1994). Some guidelines have stated the appropriate circumstances for using washing agents to aid spill cleanup (E.H. Owens et al., 2017).

The shoreline and oil types are the primary factors to determine the effectiveness of SWAs, which are also taken into consideration by response guidelines. Chemical agents are typically applied on low porosity materials, such as sand, bedrock, and fixed manmade structures. Applying agents on a high porosity shoreline (pebbles, cobble or boulder without a sand matrix) could make oil/water emulsion penetrate into the deeper subsurface and increase the difficulty of follow-up cleaning procedure (International, 2017; IPIECA

and IOGP, 2015). Moreover, SWAs are more suitable for the high-viscosity or weathered oil on the shoreline (Robertson and Maddox, 2003). The oil and chemicals could be flushed onto the adjacent water if applying the agents on the shoreline if large amounts of floating oil are released. Besides, some specific considerations to recover the oil removed by SWAs and avoid the impacts from natural environment (rain, snow, or tides) during operation, are also included to ensure the agents can achieve the optimal performance when using them on shoreline (International, 2017; IPIECA and IOGP, 2015; Robertson and Maddox, 2003).



Table 2-3. Field tests for the effectiveness of SWAs.

Year	Location	Shoreline type	Spill name	Oil rate	Oil type	Application rate	Agents	Application method	Washing method	Effectiveness	References
1970	Tampa Bay, FL, USA	-	<i>Delian Apollo</i>	-	Bunker C	-	Water-based dispersant	Fire hose mixed with sea water	Flushing	Successful	(Canevari, 1979)
1980	Sandyhaven Pill, Wales, UK	Sandy beaches	Test only	0.25 L/m <sup>2</sup>	Crude oil	10%, 1:1	BP 1100WD	Sprayers	Natural tidal	Not effective	(Little et al., 1986)
1980	Sandyhaven Pill, Wales, UK	Sandy beaches	Test only	0.25 L/m <sup>2</sup>	Crude oil	2%, 1:20	Corexit 7664	Sprayers	Natural tidal	Not effective	(Little et al., 1986)
1982	Cape Hatt, NWT, Canada	Mixed sand/gravel beach	<i>Baffin Island</i> experiment	-	Lagomedio crude	-	BP 1100X	Spray	Tidal	Not effective	(Owens et al., 1987)
1982	Cape Hatt, NWT, Canada	Mixed sand/gravel beach	<i>Baffin Island</i> experiment	-	Lagomedio crude	-	Corexit 7664	Firehose and eductor	Tidal	Not effective	(Owens et al., 1987)
1989	Disk Island, AK, USA	-	Test only	2.5 gal/100 ft <sup>2</sup>	Alaska North Slope (ANS) crude	1 gal/100 ft <sup>2</sup>	Corexit 9580	-	Seawater flush	65% for surface; 67% for subsurface	(Fiocco et al., 1991)
1990	Knight Island, AK, USA	Bedrock	<i>T/V Exxon Valdez</i>	-	Alaska North Slope (ANS) crude	1 gal/100 ft <sup>2</sup>	Corexit 9580	-	Spot-washing	Successful	(Fiocco et al., 1991)
1994	Puerto Rico, USA	Carbonate-cemented sandstone	<i>T/B Morris J. Berman</i>	1 L/m <sup>2</sup>	No. 6 fuel oi	4-6 L/10 m <sup>2</sup>	Corexit 9580	Hand sprayer	Ambient flush	Successful	(Michel and Benggio, 1995)
1994	Puerto Rico, USA	Carbonate-cemented sandstone	<i>T/B Morris J. Berman</i>	1 L/m <sup>2</sup>	No. 6 fuel oi	4-6 L/10 m <sup>2</sup>	PES-51	Hand sprayer	Ambient flush	Successful	(Michel and Benggio, 1995)

Table 2-3. (continued).

1995	San Francisco Bay, USA	-	Test	-	-	-	CytoSol	Spray	Passive wash	Over 60%	(von Wedel, 2000)
1995-1996	Point aux Chiens Wildlife, USA; Management Area, Montegut, Louisiana, US	Salt marsh	-	2 L/m <sup>2</sup>	South Louisiana crude	0.33 L/m <sup>2</sup>	Corexit 9580	Spray	Flushing	Successful	(Pezeshki et al., 1997)
1997	Sleepy Bay, Prince William Sound, AK, USA	Mixed sand/gravel each	<i>T/V Exxon Valdez</i>	-	Alaska North Slope (ANS) crude	-	PES-51	Air knives	Flushing	Over 57%	(Brodersen, 1999)
2001	Texas City, USA	-	<i>M/V Genmar Hector</i>	-	-	-	PES-51	Garden-type sprayer	High-pressure hot water	Successful	(Thumm et al., 2003)
2010	Northern Barataria Bay, LA, USA	Salt marsh	<i>Deepwater Horizon</i>	-	Crude oil	-	PES-51	Spray	Flushing	Not significant	(Zengel and Michel, 2013)
2011	Northern Barataria Bay, LA, USA	Salt marsh	<i>Deepwater Horizon</i>	-	Crude oil	-	Cytosol	Spray	Flushing	Not significant	(Zengel and Michel, 2013)

## **2.4. Recent advances in the formulation of washing agents**

### **2.4.1. Advances in SWA surfactant-based formulations new surfactants**

Surfactants are another component which play critical roles in the SWAs for shoreline treatment and they have been applied as additives for soil washing for the remediation of contaminants including heavy metals, PAHs, and hydrocarbons (Mulligan et al., 2001). The typical molecules of the surfactant have a hydrophobic tail and a hydrophilic head; therefore, these surfactants are able to reduce the interfacial tension between the oil/water phases to release the oil from the attached surface. The synthesis of conventional surfactants from crude or seed oils may generate high levels of greenhouse gases. To achieve sustainable goals, in recent years, there is a trend to generate less toxic and more effective surfactants from renewable raw materials and by the use of biological processes which is more environmentally acceptable (Rebello et al., 2014).

- Surfactants synthesized from renewable materials

Surfactants generally consist of two critical components, hydrophobes and hydrophiles. At present, a variety of renewable biomass is used as the raw materials for surfactant production. The renewable materials providing hydrophobics include fatty acids (FAs) derived from plants and triglycerides (TGs) derived from animals, and they can be used to generate a variety of surfactants or surfactant precursors through different chemical transformations (Rebello et al., 2014). Moreover, the renewable raw materials to produce hydrophiles can include glycerol, carbohydrates, and organic acid. While the synthesis and application of surfactants based on the renewable materials have been developed, to date, industrial production is limited by the availability of raw materials (Kjellin and Johansson, 2010). The production of the renewable raw materials (total 926 tons/year in 2004) far less than the production of the crude oil (3600 tons/year in 2004) (Kjellin and Johansson, 2010). Furthermore, the results of life cycle assessment

showed the greenhouse gas emissions from the production of surfactants could be reduced by replacing petroleum-based with renewable materials (Fogliatti et al., 2014; Patel et al., 1999), but these chemically synthesized surfactants may be more expensive to produce.

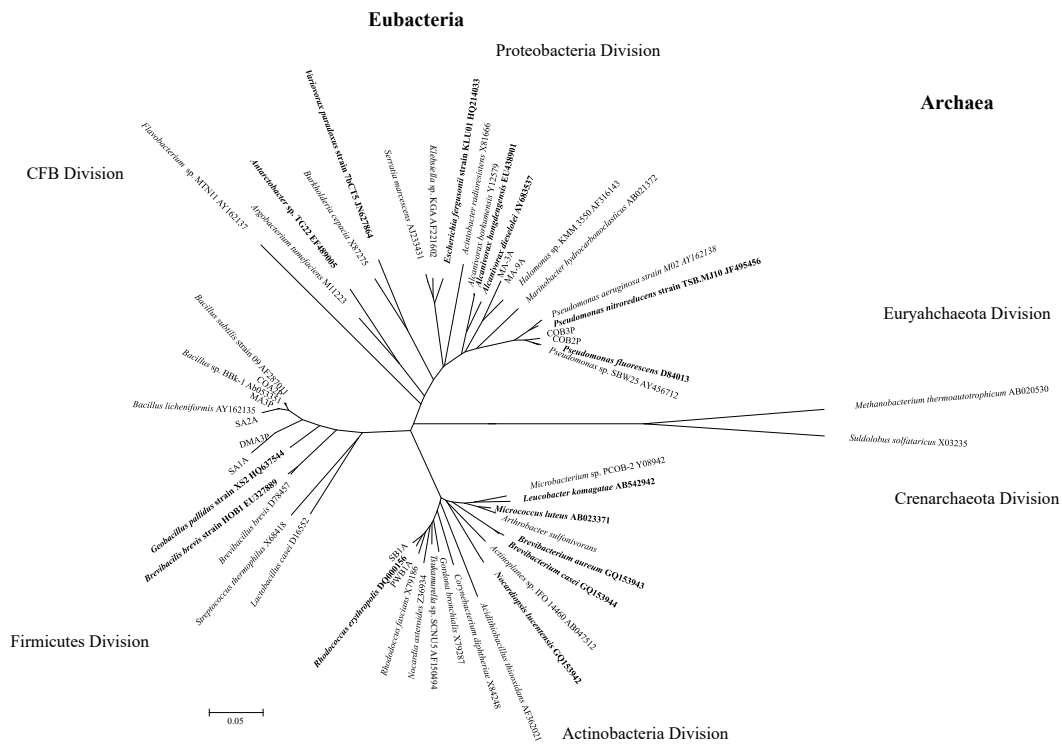
- Biosurfactants

Biosurfactants are the amphiphilic molecules produced from microorganisms, which have high surface activity to reduce the interfacial tension between two liquid phases (Banat, 1995; Cai et al., 2014). Compared with the chemical surfactants, the biosurfactants with the lower critical micelle concentration (CMC) are more effective (Zhang et al., 2012; Zhu et al., 2016) and may be less toxic (Bezza and Chirwa, 2017). Biosurfactants derived by microorganisms sustained on renewable resources are considered to more environmentally friendly than surfactants produced from petroleum hydrocarbons. Based on the molecular structure and sources, the biosurfactants can be categorized as glycolipids, lipopeptides, polymers, phospholipids, and particulate biosurfactants.

A variety of biosurfactants have been produced for the cleanup of oiled storage site and oiled soil. The enhanced remediation using biosurfactant is driven by two primary mechanisms related to the reduction in the interfacial tension between water and oil phases: (1) physical washing-out aided by the increasing mobility and solubility after the addition of the agent; and (2) biodegradation enhancement (Pacwa-Płociniczak et al., 2011). Enhancement of oil biodegradation rates has been well illustrated in batch experiments (Zhu et al., 2016).

A variety of biosurfactants were produced by novel bacteria strains and studied for their potential use in petroleum pollution control. Screening the biosurfactant-producing bacteria is the first step to obtain high-performance biosurfactants and [Figure 2-4](#) shows

the phylogenetic tree of some representative bacteria. *Bacillus* is often used to produce the lipopeptide biosurfactant. Some other bacterial species were also studied. Cai et al. (2016) used the biosurfactant from *Rhodococcus erythropolis* SB-1A as an oil spill dispersant, showing better performance than conventional dispersants, Corexit 9500 and Corexit 9527. de Souza et al. (2018) isolated biosurfactants from *Cunninghamella echinulate* to remove the petroleum hydrocarbon from an oiled site, and the results showed the high performance on oil removal (98.7% removal for diesel and 92.3% removal for kerosene).



**Figure 2-4.** Phylogenetic tree based on 16S rDNA sequence from representative biosurfactant producers isolated in the study of Cai et al. (2015) and those published in the literature.

Some studies proved the higher efficiency of biosurfactants for oil remediation than synthesized surfactants. According to experimental results from Chaprão et al. (2015), about 10% more oil was washed out from sand by using biosurfactant produced by

*Bacillus* species for the 24-h washing test compared to the chemical surfactants (Tween 80 and TritonX-100). A similar conclusion was also drawn by Ayed et al. (2015). The biosurfactant produced by *Bacillus amyloliquefaciens* showed the better performance on solubilizing diesel than SDS and Tween 80, which is an important property for biodegradation enhancement.

Some researchers tested the performance of cell-free broth rather than extracted biosurfactants and explored its potential on the cost reduction. Chaprão et al. (2015) compared the performance of cell-free broth and isolated biosurfactant produced by *Bacillus*, and the results proved their similar oil degradation efficiency. Similar results were also obtained by de França et al. (2015) and they found the removal rate of hydrocarbons after 24-h washing test with the addition of biosurfactant and broth was 76.89% and 85.00%, respectively. This trend has also been observed in many previous studies (Batista et al., 2010; Coimbra et al., 2009; Santos et al., 2013; Silva et al., 2010). The direct use of cell-free broth instead of isolated biosurfactant can reduce 30-35% of the cost for biosurfactant production without the performance reduction (Chaprão et al., 2015).

#### **2.4.2. SWA formulations based on the use of lower-toxicity solvents and vegetable oils**

Solvents are a crucial component within SWAs and other surfactant-based agents to enhance their performance. The primary mechanism of the solvent is reduction of oil viscosity to aid its detachment the oil from the substrate so it can be effectively removed by the water flushing for on-water recovery to avoid reoiling (Clayton, 1993).

The conventional organic solvents such as ketones, amines, and esters used in chemical industry are typically highly toxic and therefore there is a potential concern when used in SWA products for oil removal on shorelines. To address this issue, “green solvents”

are now considered an option for use in SWAs. “Green solvents” are defined in the chemical field as solvents that have low impacts on the health and safety which are readily degraded by microorganisms (Capello et al., 2007). These chemicals are typically derived from plants, animals, and microorganisms, rather than that extracted and purified from crude oil. CytoSol, a commercial SWA product composed of vegetable oil methyl esters and bioremediation agent, was developed using the above criteria to remove the oil from the substrate surface (von Wedel, 2000).

Vegetable oils have also been widely applied as an extraction agent for the remediation of specific components of oil in contaminated soil (Table 2-4). The potential use of vegetable oil to treat oiled substrates was also verified through laboratory tests by Pereira and Mudge (2004). They demonstrated that 96% and 70% of oil can be removed from oiled sand through simulated tidal action after the addition of pure vegetable oil and recycled waste cooking oil, respectively. Pannu et al. (2004) used peanut oil to extract the polycyclic aromatic hydrocarbons (PAHs) from soils. The extraction efficiency of anthracene can reach over 90% by using peanut oil with concentrations from 2.5% to 20%. The peanut oil was also used for the remediation of contaminated soil with the combination of ten PAHs, and the extraction efficiency can be enhanced with the increase in peanut oil temperature (51.5% at 20 °C and 81.4% at 60 °C). The performance for the commensurate peanut oil can be promoted through implementing multiple extractions instead of single extraction. The double extraction (2×5 wt% oil) and single extraction (10 wt% oil) removed 91.4% and 85% of PAHs, respectively. Gong et al. (2005) and Gong et al. (2006) investigated the potential of using sunflower oil for PAHs removal from contaminated soil. The results of batch experiments showed most PAHs (81-100%) within contaminated soil were dissolved into sunflower oil (Gong et al., 2005). The following column experiments further confirmed the effectiveness of sunflower oil on the remediation of contaminated soils. Similar removal efficiency (90%) was obtained through the addition of sunflower oil for

different levels of contamination. For higher PAHs concentration, the higher volume of washing oil would be required to achieve similar effects (Gong et al., 2006).

Several researchers also reported the enhanced biodegradation of PAHs within the contaminated soils by the use of vegetable oil (Pizzul et al., 2006, 2007a; Pizzul et al., 2007b; Scherr et al., 2009). The addition of vegetable oil makes the oil released from soil, increasing the bioavailability; thus, the biodegradation of the PAHs can be significantly enhanced. It was found that the increase in the biodegradation rate reached 15%-90% after the amendment of 1-5 wt% vegetable oil, compared to the unamended operations.

Vegetable oil can also be used with other treatment methods in remediation. Bogan et al. (2003) used corn oil with unsaturated lipids and palm kernel oil to pre-treat the PAHs-contaminated soil, thus enhancing the removal of PAHs by following treatment with Fenton reagent. Fenton reagent with hydrogen peroxide ( $H_2O_2$ ) and ferrous iron (typically iron(II) sulfate,  $FeSO_4$ ) as catalyst can be used to oxidize organic contaminants (Usman et al., 2016). The vegetable oil can help on the release of PAHs from soil, and the  $H_2O_2$  and Fe (II) are also soluble in oil. Therefore, the oxidation effects of Fenton reagent on the PAHs within contaminated soils was significantly improved.

It should be noted even though most PAHs can be removed from contaminated soil by vegetable oil, some oil remains in the treated soil, which could lead to potential risks. Gong et al. (2008) studied the effects of PAHs contaminated soil on plant growth after treatment. The results proved that the remained sunflower oil inhibited the plant growth and that the *Brassica rapa* was more sensitive than the *Avena sativa*. To avoid the effects caused by the extracted oil and to achieve cost-effectiveness, Gong et al. (2007) developed a method to recycle and reuse the vegetable oil used in the extraction of oiled



soil. The total removal rate for PAHs within used oil can reach 68.1-93.5% by the adsorption of activated carbon in the column tests. Therefore, using activated carbon to treat vegetable oil after the extraction of PAHs can make the vegetable oil recyclable and reusable, also reducing the environmental impacts.

#### **2.4.3. Application of ionic liquids as SWAs**

Ionic liquids (ILs) are organic salts with melting points lower than 100 °C. ILs have an extremely low volatility, incombustibility and stability, compared with the conventional organic solvents (Cvjetko Bubalo et al., 2015; Ninomiya et al., 2015). Many ILs such as dialkyl imidazolium, dialkylpyridinium, and alkylammonium salts have their surface-active ability due to their amphiphilicity (Smirnova and Safonova, 2010). With such a unique property, the application of ILs in enhanced oil recovery, oil transportation, and oil spill remediation have been studied in recent years.

Pereira et al. (2014) reported 65.7% of the oil can be recovered after flushing with 2 wt% water-based 1-ethyl-3-methylimidazolium tosylate solution, while a 32% recovery rate was obtained for using 2 wt% NaCl solution. Moreover, the interaction between the aromatic fractions of crude oil and this IL promoted the wettability of the substrate to increase the oil recovery rate. Hezave et al. (2013) observed the dynamic interfacial tension (IFT) between water-based 1-dodecyl-3-methylimidazolium chloride and crude oil varied with temperature, salinity, and IL concentration. The IL solution could significantly reduce the IFT between water and oil and such effect has good tolerance to high salinity, unlike the traditional surfactants. Sakthivel et al. (2016; 2017) reported that the water-based IL solutions containing imidazolium, lactam, and alkyl ammonium IL recovered 17-23% more oil from the core than sodium dodecyl sulfate (SDS), and the performance of ILs solution could be further improved through the increase in the salinity. Rodríguez-Escontrela et al. (2016) designed and synthesized a new surface-active IL (tributylmethylphosphonium dodecylsulfate) for the enhanced oil recovery.

The IFT between crude oil and water was significantly reduced to 0.08 mN/m by adding this new IL, compared with SDS and other previously-developed surface-active ILs (all above 1 mN/m). The performance of ILs was significantly affected by the types of groups on the head and tail of IL molecules and the length of alkyl chain length. The longer alkyl chain of ILs showed more reduction on the IFT between crude oil and solution (Sakthivel et al., 2016).

**Table 2-4.** Application of green solvents and ionic liquids as washing agents.

Agents	Target Components	Performance Testing	References
Corn oil or palm kernel oil	PAHs	Remediation of PAHs with Fenton's reagent	(Bogan et al., 2003)
Peanut oil	PAHs	PAHs removal	(Pannu et al., 2004)
Sunflower oil	PAHs	PAHs removal	(Gong et al., 2005; Gong et al., 2006)
Rapeseed oil	PAHs	Biodegradation of PAHs	(Pizzul et al., 2006, 2007a; Pizzul et al., 2007b)
Sunflower oil	PAHs	Recycled potentials	(Gong et al., 2007)
Canola oil	PAHs	Biodegradation of PAHs	(Scherr et al., 2009)
1-dodecyl-3-methylimidazolium chloride	Crude oil	Core flooring test	(Hezave et al., 2013)
1-ethyl-3-methylimidazolium tosylate	Crude oil	Core flooring test	(Pereira et al., 2014)
Imidazolium, pyridinium, and thiazolium ILs	Crude oil	Viscosity modifiers	(Subramanian et al., 2015)
Alkyl ammonium ILs	Crude oil	Core flooring test	(Sakthivel et al., 2016)
Tributylmethylphosphonium dodecylsulfate	Crude oil	Core flooring test	(Rodríguez-Escontrela et al., 2016)
Ethoxylated octadecylammonium tosylate	Crude oil	Dispersion	(Atta et al., 2016)
Imidazolium-based ILs	Crude oil	Asphaltene dispersion	(Atta et al., 2017)
Imidazolium and lactam ILs	Crude oil	Core flooring test	(Sakthivel et al., 2017)
Choline laurate	Crude oil	Dispersion	(Shah et al., 2019)

Besides the use of ILs in oil recovery, ILs have been used in the oil spill control. Atta et al. (2016) applied the amphiphilic ionic liquid in oil-spill dispersant, and the

dispersion efficiency of the ethanol-based IL solution reached 80%. Shah et al. (2019) used choline laurate to replace the conventional organic solvent in dispersants. The dispersion effectiveness reached about 83% by using IL-based biosurfactant (a binary mixture of choline laurate and lactonic sophorolipid). Subramanian et al. (2015) studied the effect of four ionic liquids diluted by toluene on crude oil. A maximum of 35% reduction in the oil viscosity was observed by adding dodecylpyridinium chloride. The effects of ILs had a positive correlation with the alkyl tail length and anion charge density. The use of ILs on the crude viscosity reduction was also proved by Atta et al. (2017). They used imidazolium cation and organic salt anions to develop new ILs and tested their performance for the dispersion of asphaltene of Arabic heavy crude oil. The better performance on the asphaltene dispersion was achieved by the increase in the hydrophobicity of IL. The head of IL molecules can affect the charge transfer interaction including van der Waals forces and  $\pi$ - $\pi$  stacking, thus resulting in the change of crude viscosity. The recent research efforts on the application of green solvents and ionic liquids as washing agents are summarized in [Table 2-4](#).

#### **2.4.4. SWA formulations based on organic acids**

Organic acids refer to acidic organic matters, such as carboxylic acids and sulfonic acids. Unlike the strong inorganic acids, organic acids are weak acids that cannot be completely hydrolyzed. Many organic acids exist widely in the natural environment, especially in the soil, caused by the plant and microbial secretions (Hu et al., 2018). They can be used as environmental-friendly agent in the washing of petroleum contaminants. An et al. (2010) investigated the effects of five short-chain organic acids on the desorption of pyrene within the water-soil system. The experimental results showed that the existence of organic acid could promote the desorption of pyrene. Moreover, the adsorption of pyrene positively depended on the organic acid concentration and negatively depended on the pH. Ling et al. (2009) reported the

availability of phenanthrene and pyrene were significantly promoted after the addition of citric or oxalic acid. More PAHs can be extracted from the soil after treatment and the extracted amount increased with the high concentration of organic acids. In addition, some studies investigated the role of root exudate in the desorption of PAHs. Wang et al. (2014b) tested the effects of low molecular weight organic acids from the root exudates of mangrove plants on the removal of PAHs. It was found that the concentration of low molecular weight organic acids was related to the PAHs concentration, and the removal rates of 4- and 5-ring PAHs were positively correlated with the all six organic acids (benzoic, maleic, succinic, lactic, malic and citric acids). Organic acids can form complexes with metal ions and hence the existence of organic acids could potentially change the binding among pollutants, solid surface and other soil organic matter (SOM). The organic acids such as, carboxylates, from root exudates facilitated the mobility of petroleum hydrocarbons within sediment, and provided energy sources and nutrients for the microorganisms; thus, the degradation of petroleum hydrocarbons can be improved through the increased bioavailability and microbial activity (Martin et al., 2014). Organic acids could also be used with surfactants to enhance the desorption of PAHs from sediments. An et al. (2011) studied the combined effects of rhamnolipid biosurfactant and four short-chain organic acids (acetic acid, oxalic acid, tartaric acid, and citric acid) on the desorption of phenanthrene. It was found that the desorption of phenanthrene was improved by the combined use of biosurfactant and organic acids. The citric acid presented the most significant improvement. More anions could be provided for complexing by citric acid in comparison with other unary or binary acids. It would result in the enhanced release of metals and organic matter from soils, carrying more associated phenanthrene molecules. These studies suggest that organic and acidic properties of organic acids may benefit the development improved SWAs formulation. D-Limonene, one type of organic acids, has been used as the major component of some SWAs (Fingas, 2013b).

## 2.5. Oily waste management

Many documents and tools have been drafted by governments and other organizations to provide the guidelines of oily waste management for the response groups, as shown in Table 2-5. The main work procedure for the oily waste management mainly consists of waste collection and minimization, temporary storage, transportation, intermediate storage, and treatment (REMPEC, 2010). Many on-site prevention and treatment techniques have been developed and deployed to minimize waste generation and reduce the waste which is required to be treated off site (IPIECA, 2014). Sorbents can be set along the nearshore to avoid the spread of oil slicks. In-situ washing methods, such as surface washing and sand flushing, are preferred in first response instead of techniques which are required to be further treated, such as manual and mechanical removal. Bioremediation could be applicable for some sites, depending on the environmental conditions and characteristics of oily wastes. The application of these clean-up techniques can reduce the subsequent workload of oiled shoreline remediation by minimizing the waste generation.

**Table 2-5.** Summary of published guidelines for oily waste management.

Document	Reference
Disposal and waste management guidance for the northwest area	(RRT/NWAC, 2020)
Oily waste management manual	(CEDRE, 2016)
Disposal of oil and debris	(ITOPF, 2014)
Oily waste minimization and management	(IPIECA, 2014)
Guidelines on oily waste management	(REMPEC, 2010)
Guidelines and strategies for oily waste management in arctic regions	(Polaris Applied Sciences, 2009)

## **2.6. Knowledge and research gaps**

Many recent efforts have been made in the use of SWAs for the treatment of oiled shorelines but there remains a significant knowledge gap in the adequate understanding of SWAs-aided cleaning processes and operational applications. Further study is required for making sound strategic plans and operational response decisions. The future challenges and recommendations are as follows.

### **(1) Development of more effective and environmentally friendly SWAs**

Many SWAs have been produced for the treatment of oiled shorelines. The major components of currently available SWAs include surfactants and solvents, which are mostly chemically synthesized. Although the toxicity of some SWAs is moderate, they can still have a potential adverse impact on the shoreline environment after application. Certain environmental impacts were observed in the use of SWAs for the cleanup of oiled marsh and mussel beds in shoreline (Michel et al., 2001). For better public acceptance, a greater emphasis should be given to the development of efficient, biodegradable, and low-toxicity SWAs from renewable biomass resources. From a sustainable view, the production of such SWAs also needs to involve low energy consumption and waste generation. The good biodegradability of green SWAs can also accelerate the biodegradation of contaminants by providing microorganisms with nutrients, thus removing more contaminants. The new SWAs derived from natural environment or biological process will be of great interest for future study and the corresponding oil removal performance needs to be evaluated.

To date, SWA toxicity studies have largely focused on comparisons between individual species under a variety of test conditions. It is important to note that organisms within shorelines may vary considerably between different geographic locations. Some species in a shoreline environment can be particularly vulnerable to chemicals such as SWAs.

But the species in the current toxicity tests of SWAs are limited and there is a need to obtain more results about a wider range of organisms and to understand ecosystem-level effects due to trophic dynamics. Furthermore, in terms of toxicity, SWAs will interact with the oil in the treatment process, altering its fate and behaviour and thus its bioavailability. It is important to consider the toxicity of both SWA products alone and the mixture of oil and SWAs. Understanding the potential adverse effect of SWAs in the food chain can also help better evaluate their toxicity. Due to regulatory considerations, toxicity studies on SWAs have been focused on the provision of LC50 values. An improved understanding of the mechanisms responsible for SWA toxicity would provide important information to support the production of less toxic products. For example, the major proteins, enzymes and genes impacted by SWAs are still not clear. It is expected to explore the toxicity of SWAs from a new biophysical, biochemical and molecular perspective.

## (2) Performance of SWAs under various environmental and operational conditions

Most previous studies of SWAs were conducted in simulated environments. Only limited environmental and operational factors such as temperature, washing method, oil and substrate characteristics have been considered (Clayton, 1993; Fingas, 2012; Koran et al., 2009; Øksenvåg et al., 2009; Sullivan and Sahatjian, 1993). SWAs can be considered for future applications in the field with more complicated environments. Oiled shorelines may embrace a wide range of physical environments and ecosystems from warm, sediment-rich, low-wave conditions in a bay to cold, nutrient-limited, high-energy wave conditions in the Arctic. In particular, there is a changing environment for shorelines as a result of anthropogenic activities and climate change (Aguilera et al., 2018). Many factors related to the properties of water, sediment, and atmosphere can influence washing efficiency. Moreover, such environmental factors can also present the interactive effects on the environmental process. That can support science-based decision making for the use of SWAs. It is necessary to well characterize the

environmental conditions of oiled shoreline and analyse the individual and interactive impacts of various environmental factors on the washing efficiency. In addition, different operational strategies can be used in SWA-assisted treatment. To achieve better performances, the operation can be optimized to achieve the maximum efficiency under certain conditions.

### (3) Comprehensive assessment of SWAs for shoreline treatment

There is a range of SWAs that can be used in shoreline treatment. It may be challenging to select the most appropriate SWA from many options for specific environmental scenarios. At first, various testing methods have been used to evaluate the performance of SWAs at different scales. However, there is still no uniform testing protocol that has been widely accepted and applied for inter-calibration of different test protocols. Some available testing methods did not adequately consider the application conditions, while some others are too complicated for operation and can be difficult for completing a large number of testing runs. It is desired to develop a well-accepted testing method which can be easily applied under different laboratory conditions and used for comparison among the results from different studies. Secondly, the selection of washing agents requires the demonstration of efficacy, reliability, cost, toxicity and other environmental effects. A comprehensive index system considering multiple factors can be used for the evaluation of SWAs based on different considerations. That will help systematically analyse the socio-economic and environmental impacts of given SWAs and policies for a specific region. A database can also be built to support decision making.

### (4) Combination with other oil spill response technologies

A shoreline response operation is an integrated process including many treatment procedures and methods, which are often used together for achieving the best performance. A single technology can hardly solve the shoreline treatment challenge on



its own. A diversified portfolio can help provide flexibility and lower risk in application. For instance, the sorbent booms and skimmers can be set along the shoreline before floating oil arrives. If the oil has contaminated the coast, the proper techniques can be implemented by considering the actual situations. Natural attenuation and bioremediation would be recommended when the shoreline has relatively high-level ambient energy (temperature, wind, and wave) and low-level oil contamination. For further cleanup, more aggressive methods, such as high temperature/pressure washing and application of SWAs can be used. However, after treatment, the removed oil is transferred into the surrounding water and it needs to be recovered to prevent oiling or re-oiling of adjacent shorelines. Some methods such as booms, skimmers and decanting can be used to collect this released oil. When collected oil-water mixture needs to be recycled in applications, some pre- or post-treatment methods such as oil separation and advanced oxidation can be used to improve the treatment efficiency. Therefore, it would not be recommended to implement SWAs as the sole practice a shoreline response. Many other types of oil spill treatment methods may be used with SWAs to achieve the overall treatment target criteria. In an integrated process, the advantages of various methods can also be combined to complement each other. However, there is limited information on the strategies that combine SWAs and other methods. When designing the combined process for a shoreline response, both the cleaning efficiency and socio-economic impacts based on the different treatment target criteria and site conditions should be considered.

#### (5) Guideline and decision support for field application

The previous guidelines only provide a general recommended approach for the use of SWAs in shoreline treatment but does not consider other factors such as the procedure, cost, impact, and management associated with an operation. An application guide for SWA-aided shoreline treatment can be developed to consider all of these aspects to enhance the resilience of an oil spill decision and management system. The engineering

design of a SWA-aided treatment process involves more than simply applying identical results of washing and other parameters from previous studies. For a better large-scale application, it would be valuable to conduct some meso-scale tests using the same components and conditions as those in on-site application. Moreover, an operational endpoint indicator should be determined based on the considerations of multiple SWA performances such as removal efficiency and cost. The optimal conditions for the use of washing agents in shoreline treatment would be identified. In addition, a decision support system (DSS) is a useful tool which employs a methodology for multi-stage decision making in an engineering or process design (Pastori et al., 2017; Xu et al., 2018). The modelling approach can be used to generate different practice options in terms of their impacts on the overall performance. The best practices to ensure maximum performance of SWA-aided shoreline treatment should be identified and implemented. At the same time, key stakeholders need to be closely consulted to ensure effective knowledge translation and identification of most appropriate solutions for end users. The guideline and DSS can be provided to oil spill response managers to demonstrate the effects and consequences of SWAs practice options for different oil types in different coastal environments.

#### (6) Programming model for oily waste management system

It could be difficult to dispose of all the waste on the site by applying in-situ treatment methods; especially in cases that generate large volumes of oily waste. The waste might need to be sent to off-site treatment facilities for further disposal. The facilities that can be used for oily waste treatment include cement plants (use oily waste as a raw alternative material), soil washing, facilities, pyrolysis facilities, and landfills (CEDRE, 2016). Moreover, waste storage sites could be required if the amount of collected waste exceeds the waste treatment capacity of existing facilities. Although the documents can provide a brief guideline with the response teams, it is still a difficult problem to consider all the processes in the oily waste management and thus address the problem

with the minimum system cost. A programming model for oily waste management system could be a effective tool to support the decision makings of repose group.

## CHAPTER 3. EXPLORING THE USE OF CELLULOSE NANOCRYSTAL AS SURFACE-WASHING AGENT FOR OILED SHORELINE CLEANUP

### 3.1. Background

Accidental releases of oil in marine waters from petroleum exploration and production activities, vessel operations, and land-based sources have been a global issue of concern for decades (National Research Council, 2003). Thousands of oil spills have resulted in millions of tonnes of petroleum and related products being released into the oceans over last fifty years (An et al., 2017; ITOPE, 2019). A series of physical, chemical, and biological processes including evaporation, emulsification, photo-oxidation, and biodegradation occur after the oil spills on the sea. In many cases, slicks of this weathered oil are transported to coastal regions by wind, waves, tides, and currents (Geng et al., 2020; Lee et al., 2015b), where it can become stranded on shorelines. As this oil is weathered further by evaporation, photo-oxidation, and biodegradation processes the residual oil becomes more recalcitrant and thus, more environmentally persistent and difficult to remove (Boufadel et al., 2019; Owens et al., 2016b).

To mitigate the environmental impacts of spilled oil on the intertidal zone ecosystems, many novel materials have been developed to remediate the spilled oil, such as sorbents (Saleem et al., 2018; Yati et al., 2016) and dispersants (Rongsayamanont et al., 2017). In addition, various treatment techniques have been developed to aid oil removal on shorelines, including physical removal (including the use of sorbents) or washing, sediment relocation, and bioremediation (Lee, 2000; Owens, 2011; Sun et al., 2019). With the exception of bioremediation, deployment of these active remediation strategies can be demanding logistically due to the need for specialized heavy equipment, waste treatment facilities and large numbers of personnel on site that could

impact the health and survival of shoreline organisms. Although bioremediation treatment has a low environmental impact, it cannot reach high removal rate in a short time and its performance depends on the conditions of oiled sites (Bidgoli et al., 2019; Cao et al., 2020).

Surface-washing agents (SWAs) are an option to accelerate the removal of stranded oil by altering the rheological properties of oil or the interfacial properties between the oil/water phases. After the *Exxon Valdez* incident in 1989, SWAs were considered to be in a separate category of response options from dispersants (Schramm, 2000). Currently more than 50 SWAs are listed in the National Contingency Plan (NCP) Product Schedule in the United States (U.S EPA, 2019) as potential options for use during an oil spill response. Although the composition of most commercial SWAs is confidential, the main constituents typically consist of surfactants and solvents. As these components may be harmful, there are concerns about the potential impacts of these chemical agents on shoreline organisms and nearby coastal populations (Chen et al., 2019a; Chen et al., 2019c). To address these concerns there is a need to consider new formulations of SWAs that are more effective, economical, and environmentally friendly.

Cellulose is the most abundant organic compound in the world, forming the main structural component of plants (Dufresne, 2013). Nanocellulose, cellulose particle at a nano scale is attracting interest due to its low cost, low toxicity, biodegradability and its ability to alter physiochemical properties (Kargarzadeh et al., 2017). According to different manufacturing methods and material properties, nanocellulose can be divided into three types; cellulose nanocrystal (CNC), cellulose nanofiber (CNF), and bacterial cellulose (BC). Recent research has indicated the potential application of nanocellulose materials for oil spill remediation and enhanced oil recovery for oil exploitation. Korhonen et al. (2011) found that nanocellulose aerogel with TiO<sub>2</sub> coating can selectively adsorb oil from water phase, which make a potential green oil spill sorbent.

Similarly, Cervin et al. (2012) used vapor phase deposition to treat nanocellulose aerogel with octyltrichlorosilane, transferring the hydrophilic to a hydrophobic properties, which led to improved performance with respect to oil and water separation. Wei et al. (2016) investigated the potential of nanocellulose for enhanced oil recovery in oil exploitation, and their results demonstrated that adding nanocellulose into flooding water can reduce the interfacial tension between the oil/water phases and transfer water into a shear-thinning fluid (Li et al., 2017; Molnes et al., 2017; Molnes et al., 2016). Although the potential of using nanocellulose for remediation has been reported, there has yet to be any relevant studies investigating the effectiveness of nanocellulose-aided surface washing for the cleanup of oiled shorelines.

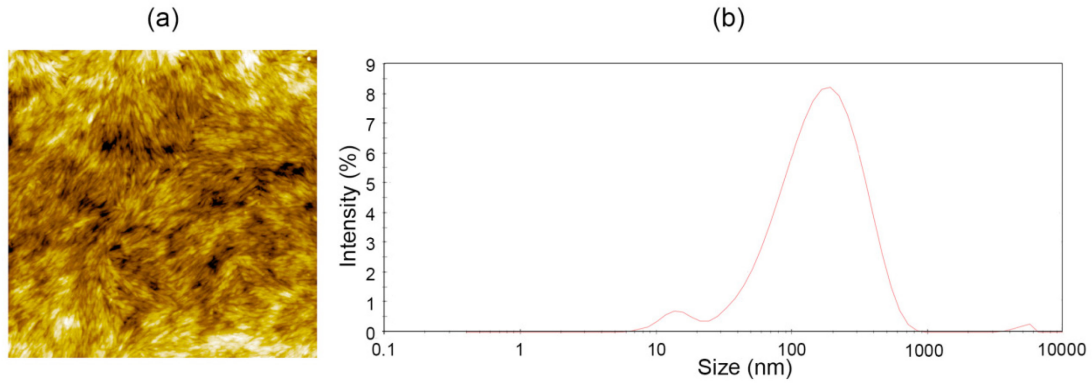
In this chapter, the potential use of nanocellulose-based nanofluid as a SWA has been investigated. Batch tests were performed to assess efficiency and the effects of influencing factors of the SWA on removal performance were evaluated by factorial design. A biotoxicity test was conducted to compare the toxicity of oil, nanocellulose, and their mixture. In addition, the performance of nanofluid was compared with selected commercial surfactants to further investigate its potential application as a shoreline cleanup agent.

## **3.2. Materials and method**

### **3.2.1. Materials**

The oil used in this study was Shell Rotella® T4 conventional diesel engine oil (15W40). The CNC was obtained from CelluForce (Montreal, Canada). The physical properties of the engine oil and the CNC-based nanofluid provided by the manufacturers are shown in [Table 3-1](#) and [Figure 3-1](#). Pre-washed and calcinated quartz standard sand was obtained from MilliporeSigma (Oakville, Canada). All the other

chemicals, including sea salt, humic acid sodium salt, n-hexane and surfactants (Tween 20, Tween 80, sodium dodecyl sulfate (SDS), and Triton X-100) were obtained from Sigma-Aldrich (Oakville, Canada).



**Figure 3-1.** Characteristics of CNC particles:(a) atomic force microscopy (AFM) image and (b) particle size distribution.

**Table 3-1.** Characteristics of the test engine oil and CNC.

Properties	Value
<i>Engine oil</i>	
Density at 15 °C	0.878 g/mL
Kinematic Viscosity at 40 °C	118 mm <sup>2</sup> /s
Viscosity index	133
Sulfated ash	1%
Total base number	10.1 mg KOH/g
Flash point	234 °C
Pour point	-36 °C
<i>CNC</i>	
Density of CNC	0.7 g/cm <sup>3</sup>
Z-average size	109.5 nm
Polydispersity index	0.495
Gram molecular weight	14,700 - 27,850

### 3.2.2. Preparation of oiled sand

A standard washed and calcinated sand was used for the preparation of the oiled sand (4 g-oil/kg-sand) used in this study. It was prepared by adding the engine oil dissolved in hexane to the sand followed by homogenization for 5 minutes in an ultrasonic bath

and removal of the solvent by evaporation in a fume hood at 20 °C for 48 h. The oiled sand was stored in amber glass bottles at refrigerator for later use.

### 3.2.3. Sand washing and experimental design

All the washing tests were conducted in 20 mL vials with 1 g oiled sand and 15 mL nanofluid. The vials were placed into a shaker run at 300 rpm under the designated temperature for 24 h to remove the oil. The liquid phase was removed after washing and the sand was gently flushed by deionized (DI) water to remove the residual nanofluid. To avoid the influence of water on the following extraction process, the sand was placed in the drying oven overnight at 50 °C. The samples were then extracted by adding 15 mL n-hexane and shaking the sample for 24 h. The oil concentration in hexane was quantified by Thermo Scientific Evolution 201 ultraviolet–visible (UV-Vis) spectrophotometer. Based on the full scanning results, 284 nm<sup>-1</sup> was selected as the reference wavelength to establish the calibration standards for oil quantification. For each batch of experiments, the oil amount for the oiled sand was also determined by this method to provide a baseline for the calculation of removal efficiency. Therefore, the oil removal efficiency can be calculated by Eq. (3-1):

$$RE = \left( \frac{Oil_T - Oil_R}{Oil_T} \right) \times 100\% \quad (3-1)$$

where, RE is oil removal efficiency,  $Oil_R$  is the amount of oil residue on sand, and  $Oil_T$  is the total amount of oil on sand.

Factorial design has been used to examine the effect of factors and their interactions (Chen et al., 2020; Yao et al., 2019; Zhao et al., 2019; Zhao et al., 2020). In this study, a 2<sup>4</sup> factorial design was conducted to better understand the individual and interactive effects of four environmental factors on oil removal efficiency. Four factors, including temperature, nanocellulose concentration, salinity, and dissolved organic matter (DOM) concentration, were taken into consideration and the levels of each factor and coded



levels are shown in Table 3-2 and Table 3-3. Each set of experiments was based on the design in Table 3-2 and was carried out in triplicate to assure data quality. Humic acid sodium was added to account for the influence DOM in seawater. In addition, single-factor experiments were carried out to investigate the influence of each of the four factors at different levels on the oil removal efficiency. The other three factors were set as standard level when conducting a single-factor experiment for one variable. The standard reference level for temperature, CNC concentration, salinity, and DOM concentration were 20 °C, 0.15 wt.%, 3.5 wt.%, and 0, respectively.

**Table 3-2.** Coded levels and corresponding values for factorial design matrix.

Number	Coded levels				A	B	C	D
	A	B	C	D	Temperature (°C)	CNC concentration (wt.%)	Salinity (wt.%)	DOM (mg/L)
1	-1	-1	-1	-1	10	0.1	0	0
2	-1	-1	-1	1	10	0.1	0	20
3	-1	-1	1	-1	10	0.1	3.5	0
4	-1	-1	1	1	10	0.1	3.5	20
5	-1	1	-1	-1	10	0.3	0	0
6	-1	1	-1	1	10	0.3	0	20
7	-1	1	1	-1	10	0.3	3.5	0
8	-1	1	1	1	10	0.3	3.5	20
9	1	-1	-1	-1	20	0.1	0	0
10	1	-1	-1	1	20	0.1	0	20
11	1	-1	1	-1	20	0.1	3.5	0
12	1	-1	1	1	20	0.1	3.5	20
13	1	1	-1	-1	20	0.3	0	0
14	1	1	-1	1	20	0.3	0	20
15	1	1	1	-1	20	0.3	3.5	0
16	1	1	1	1	20	0.3	3.5	20

**Table 3-3.** High and low levels for the 2<sup>4</sup> factorial design.

Factor	Temperature A (°C)	CNC concentration B (wt.%)	Salinity C (wt.%)	DOM D (mg/L)
High level (+1)	20	0.3	3.5	20
Low level (-1)	10	0.1	0	0

After washing with nanofluid, the samples were analyzed by Fourier transform infrared (FTIR) spectroscopy by an Optics Tensor 27 spectrometer (Bruker, USA). In addition, an Agilent Cary 670 spectrometer with liquid nitrogen cooled focal plane array detector was used to map the distribution of attached oil on the surface of sand particles and evaluate the effect of nanofluid on oil removal. The peaks at 2954, 2924, and 2854  $\text{cm}^{-1}$  corresponding to  $\text{CH}_3$ ,  $\text{CH}_2$ , and  $\text{CH}$  stretching bonds were used as reference wavelengths of engine oil in the analysis (Ancheyta, 2016).

#### **3.2.4. Biotoxicity test**

The biototoxicity tests were implemented to assess the level of potential detrimental environmental effects associated with the use of the CNC-based nanofluid as SWA. In recognition of green algae as a primary producer in the food chain that plays a central role in the aquatic ecosystem, *Chlamydomonas reinhardtii* - strain CPCC 243 from the Canadian Phycological Culture Center (CPCC, University of Waterloo, Canada) was selected as the test organism for biototoxicity tests in this study. The algae were cultured in Bold's Basal Medium (BBM) under a cycle of 12 h light and 12 h darkness. Different amounts of engine oil were evenly mixed with BBM to achieve various concentrations in the cultured environment. 50 mL oiled BBM, 50 mL BBM with cultured algae, and 7 mL CNC-based nanofluid (DI water for control groups) were mixed together at the beginning of the tests. Cell density was determined under a Zeiss Axio Observer Z1 microscope (Zeiss, Denmark), and chlorophyll concentrations were calculated from absorption measurements made with a Cary-300 double beam UV-visible spectrophotometer (Agilent Technologies, USA) at 663 nm and 645 nm (Jeffrey and Humphrey, 1975). These two indicators were measured at 72 h and 96 h for each testing group to evaluate the impacts of CNC on oil toxicity to algae.

### 3.2.5. Comparison with commercial surfactants

To verify the effectiveness of CNC nanofluid in oil removal, a washing test was implemented in comparison to commercial surfactants. 0.15 wt.% CNC-based nanofluid with 3.5 wt.% sea salt was selected as the reference in this test. The selected surfactants included anionic surfactant (SDS) and nonionic surfactants (Tween-20, Tween-80, and Triton X-100). The cationic surfactants were not taken into consideration in this study because of the low efficiency caused by its strong sorption into sand particles (Chu, 2003). The properties of surfactants used in the test are shown in Table 3-4. The washing and measurement procedures were same as described in section 2.3.

Table 3-4. Properties of selected surfactants.

Surfactants	Chemical nomenclature	Molecular weight	Critical micelle concentration (CMC)
SDS	Sodium dodecyl sulfate	288	2.3 g/L
Triton X-100	4-(1,1,3,3-Tetramethylbutyl)phenyl-polyethylene glycol	625	0.2 g/L
Tween-20	Polyoxyethylene (20) sorbitan monolaurate	1228	16 mg/L
Tween-80	Polyoxyethylene (80) sorbitan monooleate	1310	74 mg/L

### 3.2.6. Data Analysis

To ensure the quality and reliability of the results, each group of experiments was conducted in triplicate and the average values were applied in the data analysis. The standard deviation (sample variances) were calculated and displayed as error bars in related figures. Minitab (Minitab, LLC., USA) was applied to design the experiments and analyse the data in factorial design. Also, one-way analysis of variance (ANOVA) with least significance difference test was performed to identify treatments that were statistically different ( $p < 0.05$ ). OPUS 7.2 software (Bruker Optics Inc., USA) and CytoSpec 2.0 (Cytospec, USA) were used to process FTIR and mapping data.

### 3.3. Results and discussions

#### 3.3.1. Factorial analysis of environmental factors influencing oil removal

A two-level full factorial design was conducted in this study to identify the effects and interactions of four factors (temperature, CNC concentration, salinity, and DOM concentration) on the oil removal efficiency. The residue analysis was implemented and the corresponding plots are shown in [Figure 3-2](#). The sparsity-of-effects principle demonstrated that the response was mainly controlled by the primary effects and low-order interactions; therefore, only single factor and two-factor interactions were taken into consideration in this factorial analysis. The results of factorial design and its ANOVA are shown in [Figure 3-3](#) and [Table 3-5](#), respectively. The regression equation derived from the experimental data described the effect of these factors as follows:

$$\text{Oil removal efficiency} = 0.4716 + 0.00769A - 0.283B + 0.04402C - 0.00638D + 0.01210AB - 0.001444AC + 0.000112AD - 0.0048BC + 0.00841BD + 0.000537CD.$$

The coefficient of determination, R-squared and adjusted R-squared, for the regression model were 0.9026 and 0.8762, respectively. The p value for lack-of-fit was 0.066, showing the good fit of the model ( $p > 0.05$ ). The significant effects included C–salinity, A–temperature, D–DOM concentration, and interaction AC, CD, and BD ([Figure 3-3](#)).

Table 3-5. ANOVA table for analysed factors and their two-way interactions.

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	10	0.235646	0.023565	34.27	<0.001
Linear	4	0.217042	0.054261	78.91	<0.001
Temperature	1	0.090951	0.090951	132.27	<0.001
CNC	1	0.000313	0.000313	0.46	0.504
Salinity	1	0.105222	0.105222	153.02	<0.001
DOM	1	0.020557	0.020557	29.90	<0.001
2-Way Interactions	6	0.018603	0.003101	4.51	0.002
Temperature*CNC	1	0.001758	0.001758	2.56	0.118
Temperature*Salinity	1	0.007666	0.007666	11.15	0.002
Temperature*DOM	1	0.001512	0.001512	2.20	0.147
CNC*Salinity	1	0.000035	0.000035	0.05	0.824
CNC*DOM	1	0.003397	0.003397	4.94	0.032
Salinity*DOM	1	0.004236	0.004236	6.16	0.018
Error	37	0.025442	0.000688		
Lack-of-Fit	5	0.006761	0.001352	2.32	0.066
Pure Error	32	0.018680	0.000584		
Total	47	0.261087			

\*DF: degree of freedom; Adj SS: adjusted sums of squares; Adj MS: adjusted mean squares.

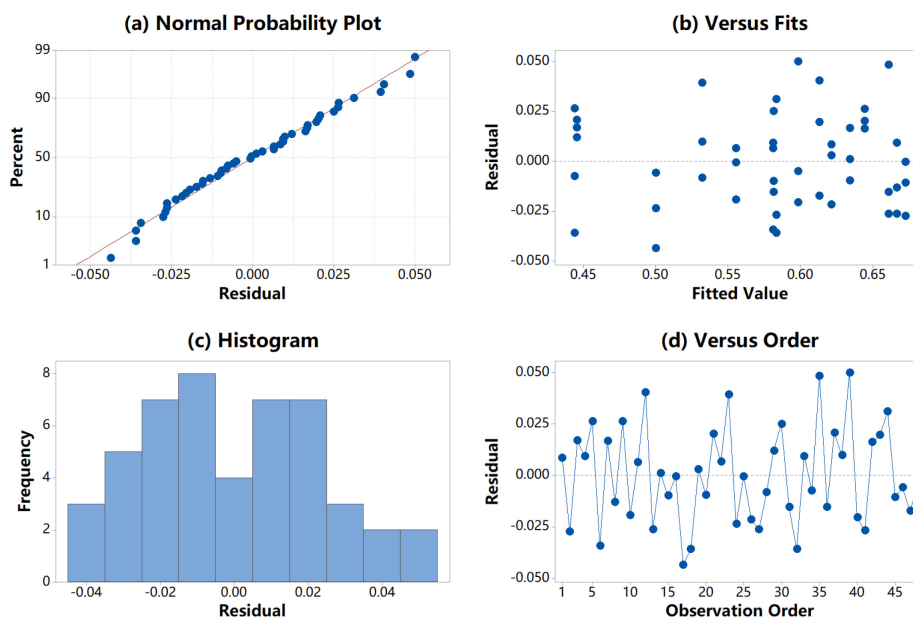


Figure 3-2. (a) Normal probability plot, (b) residual versus fitted value, (c) histogram plot, and (d) residual versus observation order.

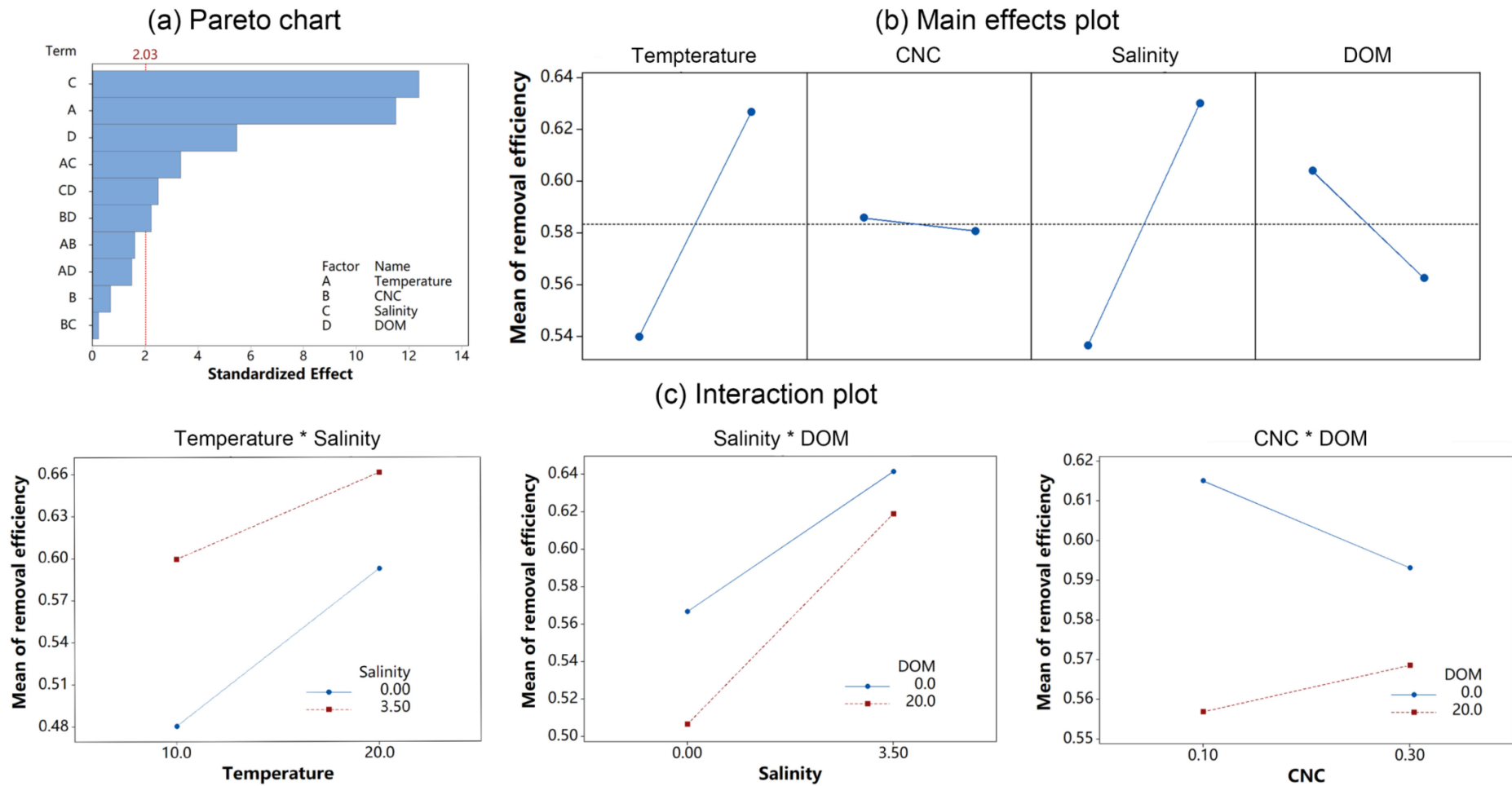


Figure 3-3. Results of factorial design for oil removal efficiency. (a) Pareto chart, (b) main effects plot, and (c) interaction plot.

Salinity (sea salt concentration) was found to be the most significant factor to influence the oil removal efficiency according to the results of factorial analysis. The removal efficiency was 62.8% with the high level of salinity and was 53.0% for the low level (Figure 3-3). Although the average salinity of seawater is 3.5 wt.%, the salinity in nearshores area may vary due to the discharge of freshwater from land-based runoff and estuaries. The two salinity levels which were selected to evaluate the efficiency of nanocellulose in this study correspond to seawater (3.5 wt.% sea salt) and freshwater respectively. The results demonstrate that the use of nanocellulose could be more applicable on marine coastlines compared to freshwater environments, such as rivers and lake shores. It also suggests that seawater could be used to prepare the nanocellulose-based nanofluid in site.

Temperature is an important parameter of seawater which had a positive effect on the oil removal efficiency using the nanocellulose-based nanofluid. The sea surface temperature varies considerably by region and latitude and during different seasons because of the influence of solar radiation. Direct sunlight can stabilize the sea surface water above 30 °C throughout the year in equatorial regions but the temperature would be only around -2 °C in polar regions (NASA Earth Observations, 2020). The long-term global average value is 16.1 °C according to the observation data of NASA's Aqua satellite (NASA Earth Observations, 2020). Based on this, 10 and 20 °C were applied as low and high levels of temperature in this factorial design to analyze the effect of environmental temperature. The removal efficiency was improved from 53.3 to 62.5% when temperature was raised from 10 to 20 °C, which may be due to decreased oil viscosity.

DOM is wide spread coastal waters, mainly consisting of humic acid, fulvic acid, and phenols, which are derived from estuaries, land-based runoff, and plankton (Cessna, 2008). In this study, humic acid salt was selected as the representative material to explore the

potential effects of DOM on removal efficiency. In previous studies the concentration of humic acids used was typically 2-16 mg/L to simulate the effect of DOM in seawater (Curcio et al., 2010; Furukawa et al., 2009; Wang et al., 2014a). In this investigation the low and high levels of DOM were set as 0 and 20 mg/L for the factorial design. The main effect of DOM is shown in [Figure 3-3](#) which illustrates that the humic acid salt was negatively correlated with the removal efficiency of the nanocellulose-based nanofluid.

The effective concentration of CNC-based nanofluid on oil removal is an important parameter to evaluate the potential for large-scale applications. 0.1 wt.% and 0.3 wt.% were selected as the low and high levels of CNC concentration to identify the effect on oil removal efficiency. The result of factorial analysis showed that the effect was not significant ( $p>0.05$ ), which suggests that the application of a CNC-based nanofluid on oil removal can be effective at low concentrations.

The two-factor interactive effects were analyzed and results are shown in [Figure 3-3](#). The significant interactive effects included AC, CD, and BD according to ANOVA. For the interaction between A (temperature) and C (Salinity), the removal efficiency at a high temperature were all higher than the figures for low levels, but the difference was relatively small when using seawater compared with DI water. Although the existence of DOM showed negative effects on removal efficiency for all concentrations of CNC and salinity, these effects were reduced with the high concentrations. This suggests that the ions from sea salt and humic acid might have interactions with the dispersed CNC particles.

To further investigate the effects of these four factors on removal efficiency, the single-factor experiments were implemented and the reference levels for each factor were set based on the previous analysis. The standard reference levels for temperature, CNC



concentration, salinity, and DOM concentration were 20 °C, 0.15 wt.%, 3.5 wt.%, and 0, respectively. The reference levels were fixed for others while one of the factors was been evaluated. The results of the single-factor experiments are described in following sections.

### 3.3.2. Effect of salinity on oil removal

Removal efficiency was increased with the increase of salinity (Figure 3-4). The introduction of a small amount of sea salt showed only a negligible effect, but there was an increase on removal efficiency at sea salt concentration more than 0.5 wt.%. The increasing trend ended at 2 wt.% and the response stabilized at around 70%. The FTIR analysis demonstrated the effectiveness of salt-added nanofluid on oil removal as shown in Figure 3-5. The absorbance of the oiled sand at the reference wavelength for hydrocarbon (2954, 2924, and 2854  $\text{cm}^{-1}$ ) was significantly reduced after washing by nanocellulose-based nanofluid. Moreover, sand washed with CNC nanofluid in seawater showed lower peaks in comparison with samples washed only with CNC nanofluid.

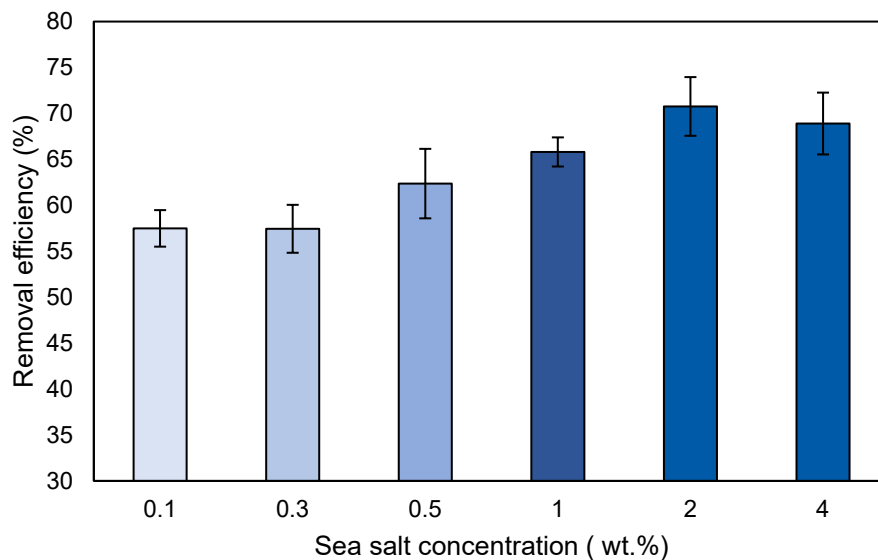
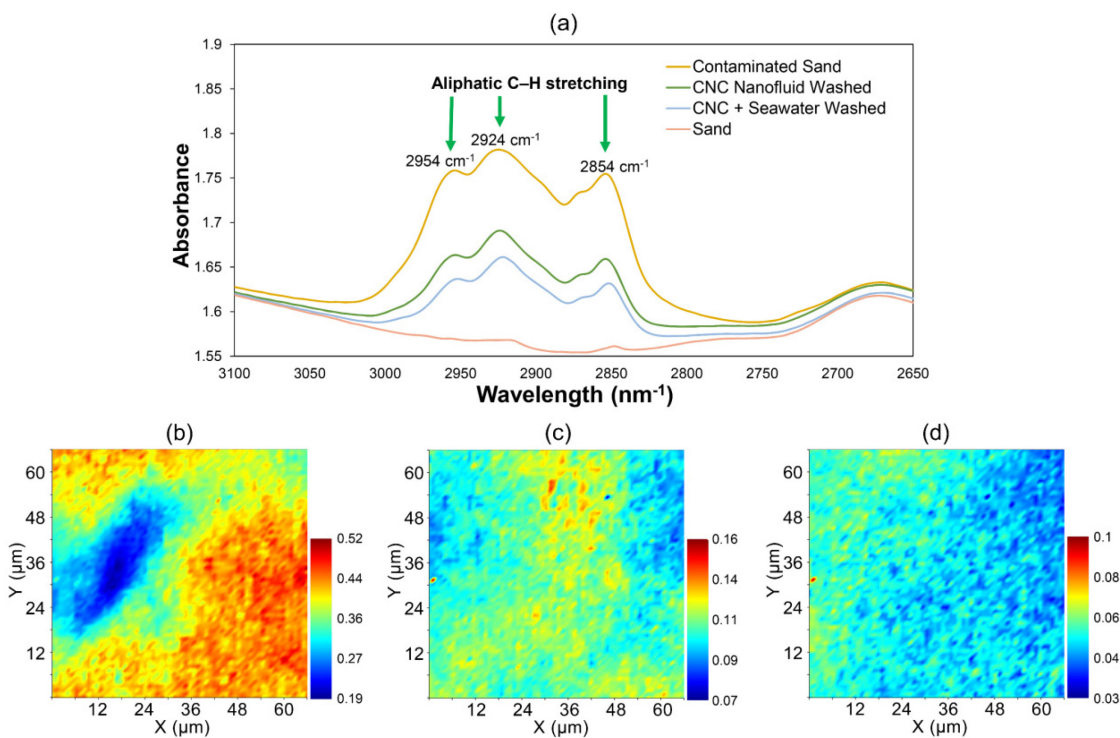


Figure 3-4. Effect of salinity on removal efficiency of nanofluid.



**Figure 3-5.** FTIR spectrum analysis: (a) FTIR absorbance spectra for sand, oiled sand, and nanofluid-washed sand from 3100  $\text{cm}^{-1}$  to 2650  $\text{cm}^{-1}$ ; (b, c, d) FITR mapping results for aliphatic C-H (2924  $\text{cm}^{-1}$ ) for oiled sand, CNC nanofluid washed sand, and CNC + seawater washed sand.

This result suggests that not only should nanocellulose-based nanofluid be applicable for shoreline cleanup in a saline environment, but using seawater to prepare the washing fluid may further enhance the efficiency of CNC nanofluid for cleanup. The amount of petroleum hydrocarbons was significantly reduced by the 0.15 wt.% CNC nanofluid prepared by seawater. The zeta potentials of nanofluid were significantly affected by addition of sea salt. The positive ions in sea salt, such as  $\text{Na}^+$  and  $\text{Ca}^{2+}$ , may be adsorbed on the nanocellulose surface, leading to the compression of the electric double layer. The resultant decrease in the repulsion force between particles leads to the aggregation and reduction of the viscosity of the nanofluid, which has been observed in previous studies (Molnes et al., 2016; Zhong et al., 2012).

There are several possible explanations for why salinity might enhance oil removal with nanocellulose-assisted washing. First high levels of salinity may compress the electrical double layer of CNC particles as well as the oil droplets to facilitate the formation of oil particle aggregates OPAs that promote removal of attached oil (Le Floch et al., 2002). Le Floch et al. (2002) observed OPA formation in laboratory under different seawater salinities. The results demonstrated that more than 75% of OPAs were formed in seawater (3.4 wt.% sea salt) while only 10% were formed in DI water. Second, salinity may also enhance the formation of a Pickering emulsion which is stabilized by solid particles. Wang et al. (2016) found that salinity has a positive effect on the formation of CNC-stabilized oil-in-water Pickering emulsion. The existence of 0.1 wt.% salt increased the emulsion volume from 24.1% to 90.1%; however, the emulsion volume stabilized at around 60% when the salt concentration was between 0.2 to 2 wt.%. Kalashnikova et al. (2012) found that the sulfate ester groups from the production of nanocellulose results in strong acid surface charges, hindering the formation of stable oil in water emulsion stabilized by nanocellulose; in other words, it suppressed adsorption at the interface. Their study demonstrates that the Pickering emulsion can only be formed while the nanocellulose had a low surface charge density ( $0.03 \text{ e/nm}^2$ ). The addition of salt can limit electrostatic repulsions and enhance nanocrystal stabilization at the oil/water interface.

### **3.3.3. Effect of temperature on oil removal**

Higher temperatures considerably enhanced the oil removal efficiency of the nanofluid as shown in [Figure 3-6](#). Oil removal efficiency of nanofluid was 74.9% at 25 °C but 60% at 5 °C. As temperatures increase the corresponding decrease in the viscosity of the oil and nanofluid improved the mobility and solubility of hydrocarbons. Decreasing viscosity can facilitate the release of attached oil and the formation of emulsions, thus improving the oil

removal from oiled sand. In addition, temperature is a major parameter that influences the oil behaviour on the sand particle surface through its effect on oil viscosity (Stoffyn-Egli and Lee, 2002). At lower oil viscosities and at higher temperatures, the energy needed to break oil into smaller droplets and the adhesion force between sand and oil are lower. In addition, previous studies report that an increase in temperature could reduce the zeta potential of silica and make it more negative in various systems including quartz, sodium kaolinite, and other minerals (Dai and Chung, 1995). The higher surface charges caused by the temperature rise could lead to a greater electrostatic repulsion between sand particles and oil droplets, preventing the re-adsorption of removed oil.

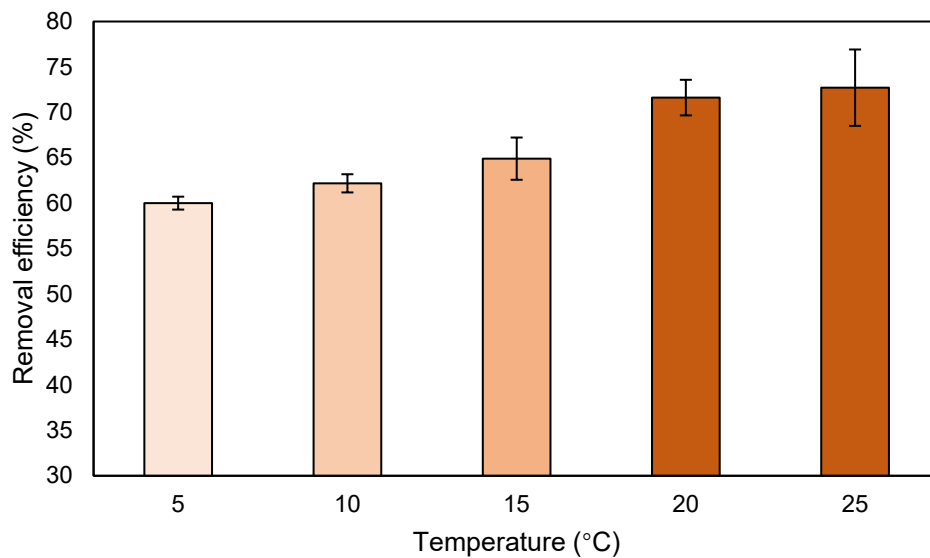


Figure 3-6. Effect of temperature on removal efficiency of nanofluid.

Another finding was that additional improvements in efficiency were not observed at temperatures exceeding 20 °C. For example, the removal efficiency was 64.9% at 15 °C, 71.6% at 20 °C and 72.7% at 25 °C. Similar results were obtained by Sørensen et al. (2014) when they studied the interaction between sediment and oil droplets, the largest amount of oil adsorbed to sediment occurred at 5 °C, and there was little difference between the values

at 10, 15, and 20 °C. The improvement on oil removal by increasing temperature involves several mechanisms including dissolution, viscosity reduction, and emulsion. Although the overall removal efficiency of a nanofluid can be increased with higher temperatures, the stability of Pickering emulsions stabilized by nanocellulose may be affected under high temperatures (Gestranius et al., 2017). However, this should not be a factor under real-world conditions, where the maximum sea surface temperatures around 30 °C (NASA Earth Observations, 2020).

#### **3.3.4. Effect of CNC concentration on oil removal**

CNC concentration had a negative effect on oil removal efficiency over the range of test conditions evaluated under this study. The highest removal efficiency in this test was 71.5% at the lowest (0.02 wt.%) concentration (Figure 3-7). It decreased slightly with an increase in CNC concentrations from 0.02 to 0.5 wt.%. However, the removal efficiency drastically dropped to 31.6% at 1 wt.% CNC concentration. Although the negative effects were observed at high CNC concentrations which increased the viscosity, the oil removal can be improved when CNC concentration was less than 0.5 wt.%. This suggests that nanofluid washing can be effective in extremely low CNC concentrations, which would support its application as a low-cost technique for shoreline cleanup.

The production of CNC normally involves sulfuric hydrolysis of cellulose from natural sources, such as plants, animals, and microorganisms (Kalashnikova et al., 2012). Sulfuric hydrolysis can produce crystalline particles with enhanced hydrophilic surface properties. The sulfate ester groups on the particle have a higher surface charge following treatment, which enhances the stability of the colloidal solution of nanocellulose.

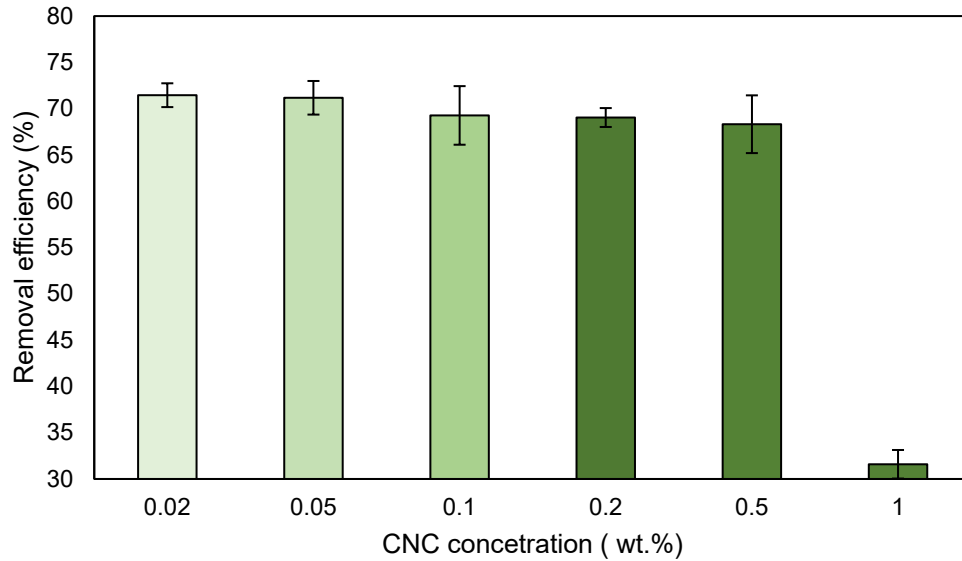


Figure 3-7. Effect of CNC concentration on removal efficiency of nanofluid.

However, a highly charged nanoparticle surface is not a favourable condition for hydrocarbon removal because the electric repulsion can also prevent the nanoparticles from adsorption on the surface of oil droplets that have same negative charges, thus hindering the formation of Pickering emulsions. Moreover, the electroviscous effects can result into the increase in viscosity of the fluid, which are caused by the distortion of the ionic double layers when the fluid is flowing (Hubbe et al., 2017). Although the surface charges of CNC and associated effects can be mitigated by adding salts into nanofluid, the viscosity of nanofluid can be substantially increased with the increase in the CNC concentration. Molnes et al. (2016) analyzed the rheological properties of CNC-based nanofluid, and found the viscosity of 1.0 wt.% nanofluid ranged from 1.3 to 1.6 cP under various ionic strengths which was higher than 0.89 cP of water at 25 °C. In their experiments, the gel-like CNC aggregations were observed at the 1.0 wt.% CNC nanofluid with seawater; the high concentration aggregations hindered oil diffusion and reduced oil removal. Therefore, it is necessary to determine an appropriate CNC concentration based on the oil loading to achieve maximum removal efficiency.

### 3.3.5. Effect of DOM on oil removal

The increase in DOM concentration in nanocellulose-based nanofluid reduced the oil removal efficiency; a trend shown in Figure 3-8. The removal efficiency gradually decreased from 69.2 to 62.5% when the humic acid salt concentration increased from 1 to 40 mg/L. The addition of humic acid can suppress the effects of sea salt and improve the stability of CNC-based nanofluid, thus hindering oil removal.

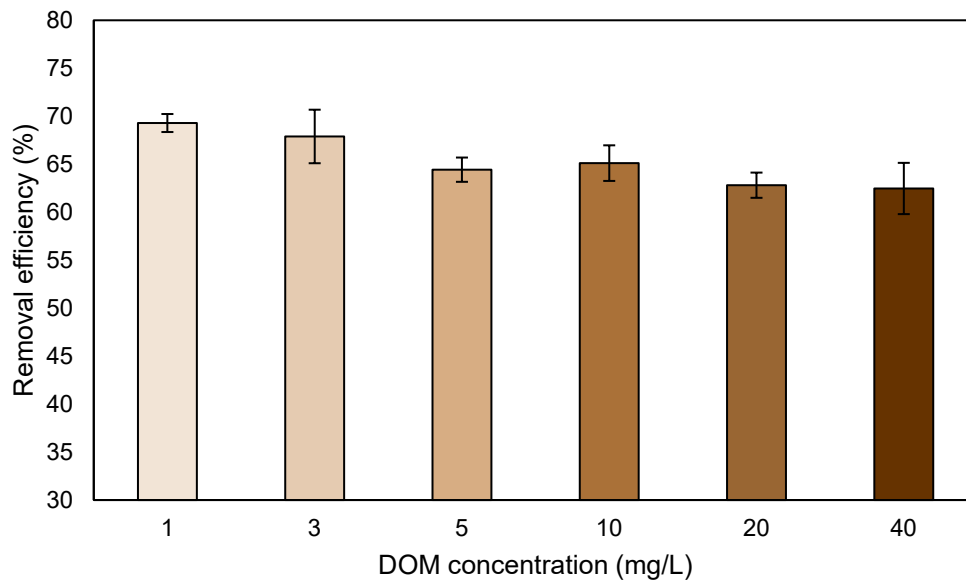


Figure 3-8. Effect of DOM concentration on removal efficiency of nanofluid.

Some previous studies have reported this interaction between humic acid and colloidal system (Jiang et al., 2012). Kretzschmar et al. (1993) studied the effects of humic substances on flocculation of kaolinitic soil clays. The results showed that the negative charge and high molecular weight of humic acid stabilized colloidal clay solutions through electrostatic and steric stabilization, respectively. Cai et al. (2017) found that the presence of humic acid reduced the settling rate of marine sediment particles due to the strong affinity of humic acid to clay surfaces. The sorption of humic acid can increase the negative

charge of the particles to a condition where stronger double electrode layer repulsion leads to more stable dispersion. These concepts are also applicable nanocellulose nanofluids which has negative surface charges. The addition of humic acid salt can make surface charges of CNC particles more negative and prevent their adsorption at the oil/water interface, suppressing the formation of Pickering emulsions. In addition, an increase in negative surface charges can also contribute to a more stabilized colloidal solution. The study conducted by Molnes et al. (2016) demonstrates that the increase in the shear viscosity of CNC nanofluid can be achieved by electroviscous effects that enhance negative surface charges. These studies support the finding in this study that humic acid can weaken the positive effects of salts on oil removal, resulting in a lower removal efficiency.

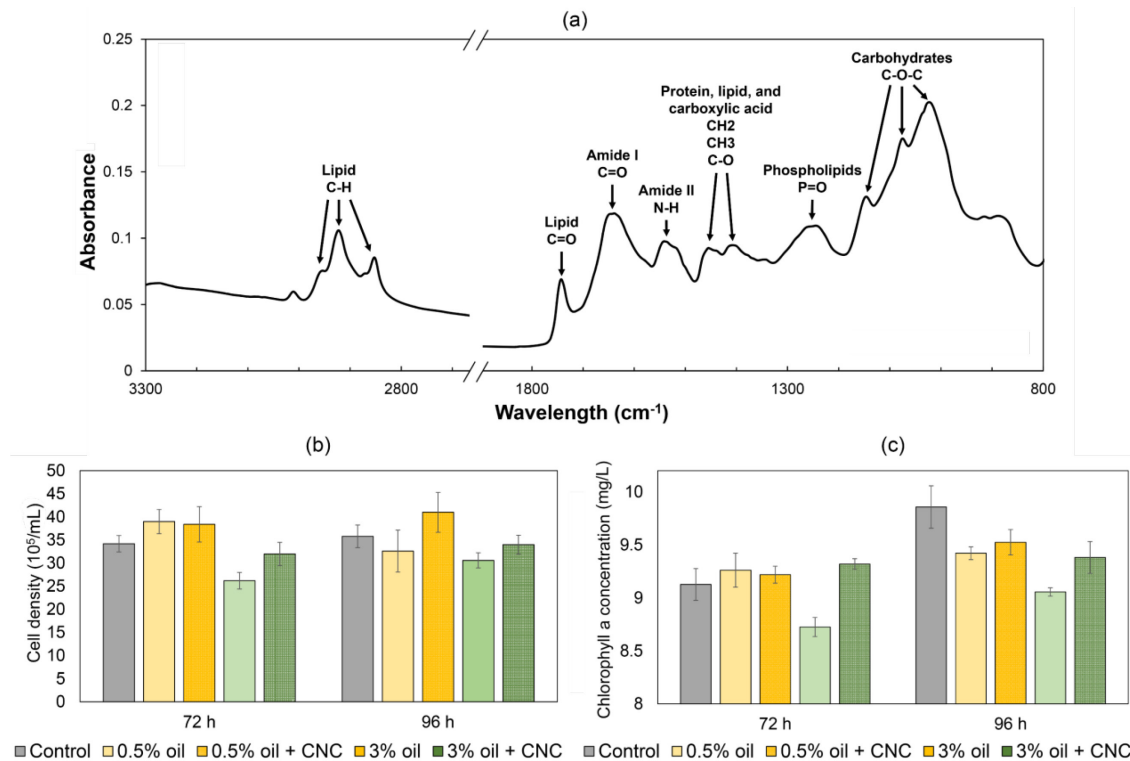
### **3.3.6. Biotoxicity test**

Biotoxicity tests were performed to evaluate the toxicity of oil and the potential effects of CNC nanofluid on a community of algae. The composition of the green algae *Chlamydomonas reinhardtii* CPCC 243 was analyzed by FTIR and the spectra are shown in Figure 3-9 (a). The FTIR spectra demonstrated the distribution of macromolecular in algae cells and these peaks mainly reflect three main components in green algae including lipids ( $3000\text{-}2800\text{ cm}^{-1}$  and around  $1740\text{ cm}^{-1}$ ), proteins ( $1724\text{-}1490\text{ cm}^{-1}$ ) and carbohydrates ( $1200\text{-}1000\text{ cm}^{-1}$ ). Previous study have shown that green algae can uptake hydrocarbons when they are exposed to engine oil, causing an increase in the characteristic peak of lipids in FTIR analysis of oil-exposed algae (Pietroletti et al., 2010; Ramadass et al., 2015). Previous studies have also made similar observations of changes in the bands for Amide I and II proteins due to oxidative stress caused by oil accumulation in cells (Sano et al., 2010; Xin et al., 2019). Ramadass et al. (2015) found that 0.8-3.5% of unused motor oil could increase the level of antioxidant enzymes such as superoxide dismutase, catalase, and peroxidase in algae, but inhibitive effects were observed combined with the cessation of algae growth at 4.5% oil concentration.



The algae were exposed to 0.5 and 3% engine oil with or without nanocellulose. The cell density and chlorophyll concentration were measured at 72 and 96 h; the results are illustrated in Figure 3-9. Cell density is a widely-used indicator to evaluate the toxicity of specific chemicals and water quality (Pavlić et al., 2005). Control groups without any chemicals were set as the reference to determine the growth-inhibition effects of 0.5% and 3% oil and exposure to CNC (Figure 3-9). The low concentration oil (0.5%) showed a positive effect ( $p < 0.05$ ) on the algae growth. The cell density at 0.5% oil concentration with or without nanocellulose was higher than control groups at 72 h. The stimulation of algae growth at low concentration of oil has also been observed in previous study (Phatarpekar and Ansari, 2000). Indeed, green algae have been reported to have the ability to utilize low concentrations of organic pollutants as a carbon source, while high concentrations inhibited their growth (Gattullo et al., 2012; Ramadass et al., 2015). High concentrations of oil (3%) in this study resulted in inhibition of growth and the addition of CNC suppressed the effect ( $p < 0.05$ ). Higher cell density was observed for groups treated by CNC compared with 3% oil only groups at 72 and 96 h.

Chlorophyll a concentration is an important indicator to evaluate algae biomass. Only the Chlorophyll a concentration in the test with 3% oil was lower than the level for the control groups at 72 h. The results for the other experimental groups showed positive effects on chlorophyll a synthesis. The oil droplets in BBM reduced the exposure levels of light to the algae. To mitigate this shading effect, the algae cells increased their chlorophyll concentration to compensate (Semchenko et al., 2012; Steinman et al., 2017). However, this increase in chlorophyll synthesis to compensate for the reduction in light levels could not outweigh the negative impacts caused by the toxicity of the high concentration (3%) of oil.



**Figure 3-9.** (a) FTIR absorbance spectra for the green algae, and its toxicity response under different concentration of oil with or without CNC: (b) cell density and (c) chlorophyll a concentration.

At 96 h, all experimental groups had a lower Chlorophyll a concentration compared to the control groups. The ranking from high to low at 96 h was control > 0.5% oil + CNC > 0.5% oil > 3% oil + CNC > 3% oil. Although there was a slight increase, 3% oil resulted in the lowest Chlorophyll a concentration among all groups at 96 h. It is well documented that oil exposure can impact biochemical processes in algae cells. For example, the membrane permeability of algae can be increased in the presence of hydrocarbons, leading to a compromise of the electrochemical gradient across the thylakoid membrane (Piehler et al., 2003). In addition, formation of an oil layer around algae cells can inhibit gas diffusion (Ramadass et al., 2015). The mitigation effects of CNC on oil toxicity were also observed as higher Chlorophyll a concentrations were observed in the oiled groups treated with CNC at 96 h.

The addition of CNC did not have significant effects on the algae growth at the low oil concentration because the algae cells can tolerate the low concentration organic compounds and even utilize them as carbon sources to facilitate the growth (Gattullo et al., 2012; Ramadass et al., 2015). However, the results of both the algal cell density and chlorophyll a tests showed the mitigating effects of CNC on oil toxicity at the higher oil concentration (3%). The results show that CNC-based nanofluid do not have negative effects on algae growth and that its introduction may reduce the level of toxicity to algae associated with oiled sediments. It is hypothesized that the absorbance of CNC to the surface of oil droplets might effectively reduce the bioavailability of oil to the algae cells.

### 3.3.7. Comparison with commercial surfactants

The removal efficiency of the CNC-based nanofluid was compared with commercial surfactants and the results are shown in Figure 3-10. All surfactants were tested at their critical micelle concentration (CMC) and compared with 0.15 wt.% CNC in seawater.

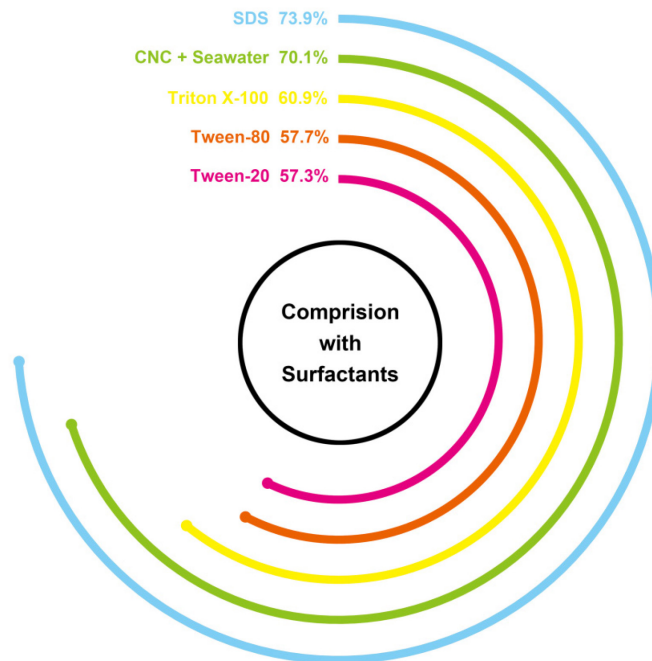


Figure 3-10. Comparison of removal efficiency of CNC nanofluid and selected commercial surfactants.

SDS, an anionic surfactant, had the highest efficiency among all commercial test agents, removing 73.9% of the oil attached to the sand. The efficiency of the nonionic surfactants were lower; the removal rates for Tween-20, Tween-80, and Triton X-100 were 57.3, 57.7, and 60.95%, respectively. The relatively low efficiency of nonionic surfactants may be due to their adsorption on the sand (Chu, 2003). In comparison, CNC-based nanofluid was able to remove around 70% of the oil, demonstrating that it provides relatively comparable results to commercial surfactant products. Given its lower toxicity, concentration requirements and potential higher levels of public acceptance (as they are derived from plants material); in comparison to the commercial surfactant formulations evaluated, the results of this study support further investigation on the production and use of a CNC-based nanofluid based SWA.

### **3.4. Summary**

In this chapter, the potential application of a nanocellulose-based nanofluid as a novel environmental-friendly agent for oiled shoreline cleanup was investigated. The results of factorial analysis and single-factor experiments revealed that salinity and temperature were two factors that positively correlated to oil removal efficiency. The existence of salts in the CNC nanofluid reduced the surface charge and electric repulsion between CNC particle and oil droplets, improving the oil removal by enhancing the adsorption of nanocellulose on the oil/water interface. High temperatures can reduce the viscosity of the nanofluid and oil; which favoured the mobility and removal of oil on sand. The addition of DOM (humic acid) had negative effects on washing because of a high affinity of humic acid molecules to the CNC can result into a higher surface charge of nanocellulose, weakening the positive effects of the salts. Even though the experimental results showed that excessively high CNC concentrations can hinder the removal of oil due to increased viscosity, the low concentration of CNC in seawater can effectively clean the oiled sand. The biotoxicity tests suggest that adding a CNC can mitigate the oil toxicity to green algae, increasing the cell density and chlorophyll concentration compared with the groups with only oil. In addition, the removal efficiency using a nanocellulose-based nanofluid was compared with that of commercial surfactants and the results showed a higher removal efficiency for the

nanofluid on washing the oiled sand. Overall, the nanocellulose has a high potential to be applied as a SWA for shoreline cleanup due to the low cost, low toxicity, and high efficiency in a marine environment. Future studies are also expected to further explore nanocellulose-assisted oil removal mechanisms under other environmental conditions and investigate its performance in large-scale tests.

## CHAPTER 4. AN INEXACT CHANCE-CONSTRAINED PROGRAMMING MODEL FOR OILY WASTE MANAGEMENT

### 4.1. Background

Increasing number of oil exploration, production, and transportation activities for decades have resulted into the higher risks in oil spill accidents all over the world. Thousands of oil spills have resulted in millions of tonnes of petroleum and related products being released into the oceans and land over last fifty years (National Research Council, 2003). After the oil spilled at sea, a series of physical, chemical, and biological processes, including evaporation, photo-oxidation, and biodegradation, can rapidly degrade the light hydrocarbons (Lee et al., 2015b). However, the residual oil could be transported to shorelines by wind, waves, and currents. This oil that becomes stranded on shorelines continues to attenuate and weather, but typically at lower rates compared to an open-sea environment. The weathering process of oil makes the spilled oil more environmentally persistent and hard to remove (Boufadel et al., 2019; Owens et al., 2016b). In addition, although the amount of oily waste depends on the oil properties, climate and geological conditions of the spill site, it can be more than 30 times that of the spilled oil in extreme cases based on the records of previous accidents. Therefore, the management of shoreline oily waste is necessary to mitigate its negative effects on coastal environments (National Research Council, 2003).

Although the documents can provide a brief guideline with the response teams, it is still a difficult problem to consider all the processes in the oily waste management and thus address the problem with the minimum system cost. Therefore, the aim of this chapter is to develop an inexact programming model for oily waste management with uncertainties

and conduct a case study. In detail, a mathematical model for oily waste management will be established to quantify the system cost. Based on this model, an interval chance-constraint programming method, which can consider the uncertainties of both parameters in objective function and right-hand side constraints, will be introduced to select the waste management facilities and allocate the waste flows. The developed model will be applied in a case study to verify its applicability. The obtained solutions at different violation probabilities will be further discussed about the tradeoff between the system cost and risk.

## **4.2. Methodology**

### **4.2.1. Statement of problem**

In oily waste management, it necessary to set temporary storage facilities which can provide the space for preliminary sorting and storage of waste generated from nearby working sites (REMPEC, 2010). The temporary storage sites can be used for the pre-treatment to ensure the waste meet the entry criteria of subsequent treatment or storage facilities. Use of existed treatment facilities is prior. Setting up new treatment plants are only considered in the case of major oil spills, could be expensive and time-consuming. The potential facilities which can be directly used for oily waste treatment include cement plants, soil washing facilities, pyrolysis facilities, and landfill.

The oiled sand can be used as an alternative raw material in cement work, but the oiled sand has to be used in specific ratio and its oil content need to be limited and to ensure the quality of the cement products are not affected. The washing and pyrolysis facilities are the relatively mature techniques for soil remediation (Hamby, 1996). The washing equipment is widely existed in construction and mining industries, which can be used as the alternative

facilities for oiled sand treatment (REMPEC, 2010). Chemical reagents and solvents can be applied to improve the washing efficiency. If the washed sand meets the relevant standards, it can be reused as the fill material in construction works. However, it might require secondary washing or landfilling for some batches that does not pass the sampling inspection. Another limitation of this method is that the wash water must be properly managed after use due to the high organic contents. Pyrolysis can remove the organic contamination from sand by thermal decomposition in the inert environments (IPIECA, 2014). The by-products decomposed from the oil include gas, carbon, and ash, that have potential to be reused as energy sources or construction materials. However, the installation and operation expenditures are relatively high compared with other methods.

The use of landfills is necessary for oily waste management. Although these treatment methods can nearly eliminate the waste by recycling, there are still some residues require further landfilling after treatment. In addition, oiled sand can be directly transported to landfill after stabilisation, but the oily waste needs to mix with domestic waste to avoid the impacts caused by the oil leachate and allow the biodegradation of oil. Therefore, the landfill has the capacity limit for the entry of oiled sand. The constraints are determined by the capacity of the landfill and the characteristics of the oily waste. In general, it is not difficult to deal with the waste generated from the shoreline affected by the small and medium oil spill accident. However, the intermediate storage sites might be needed to temporarily store the waste that beyond the treatment capacities in major oil spill accident. The intermediate storage sites are usually located close to the oiled shoreline or corresponding treatment facilities, which can provide the buffering function and convenient access for the further transports. After waste collection stage, the oiled sand at the storage sites can be gradually transported to treatment facilities.



Therefore, it could be a problem for decision makers to select the treatment and storage facilities and allocate the material flows between them in the oily waste management. For example, the storage facilities can still be used although the total capacities of available treatment facilities can satisfy the disposal demand for the generated waste, because cost for using some plants could be more expensive than storing the waste and treating them by other cost-effective methods when the facilities are available. The treatment methods are varied by the facilities, which have different efficiency, capacity, capital expenditures, and operation expenditures. In addition, the location of the facilities affects the transport cost which is another important factor that need to be taken into consideration in oily waste management. The response groups must decide which candidate facilities in the proposal will be used to dispose of the oily waste and how allocate waste between the selected facilities, to minimize the system cost and make sure the decisions comply the technical constraints.

#### **4.2.2. Modeling formulation**

After the preliminary cleanup and collection on the oiled site, because the capacity of on-site storage is limited and also waste is constantly produced at waste collection stage, the collected wastes stored at temporary storage site must be transported to further treatment or storage. Therefore, the response group need to propose the optimum scheme based on the information of existing facilities that are able to receive generated waste. The waste can be potentially transferred from temporary storage sites ( $i$ ) to treatment facilities ( $k$ ), intermediate storage site ( $j$ ), and landfill ( $l$ ).

However, due to different applicability to oily waste, these facilities could require different opening cost to improve or purchase the equipment. Operation cost is another important factor to affect the selection of the facilities, which is the average cost of disposing of per

tonne waste for treatment or landfilling disposal or the average cost of storing per tonne waste per period at the intermediate storage site. However, the operation costs of the untreated waste at landfills are much higher than the residue waste from treatment plants due to the direct landfilling requires the pre-treatment of stabilization or solidification.

To avoid the extra cost by using the treatment facilities which have high initial investment or operation cost, the intermediate storage sites can be prepared to receive the waste that exceed the existing treatment capacity. After the waste collection stage, which means that no new waste would be generated and need to be transported from temporary storage sites, the waste stored at intermediate sites can be gradually transferred to available treatment facilities. Therefore, there are two periods which must to be taken into consideration in this programming problem if the intermediate storage sites are used, waste collection and destocking. In waste collection stage, the main waste flow is from temporary storage sites to treatment facilities, intermediate storage sites, and landfills. In destocking stage, the main waste flow is from intermediate storage sites to treatment facilities and landfills. To minimize the system cost, the manager must consider opening cost, transportation cost, treatment operation cost, storage cost, landfilling cost in these two periods at the same time. The parameters and decision variables used in the developed model are described as follows:

- Parameters:

$f^{\pm}$  = expected system cost (\$);

$FCS_j^{\pm}$  = fixed cost of opening storage facility  $j$  (\$);

$FCT_k^{\pm}$  = fixed cost of opening treatment facility  $k$  (\$);

$FCL_l^{\pm}$  = fixed cost of opening landfill  $l$  (\$);

$LC^{\pm}$  = Time length of waste collection stage (days);

$LS^{\pm}$  = length of time period for destocking stage (days);

$TC_{ik}^{\pm}$  = transportation cost for transporting waste from temporary storage site  $i$  to treatment facility  $k$  (\$/ton);

$TC_{ij}^{\pm}$  = transportation cost for transporting waste from temporary storage site  $i$  to storage facility  $j$  (\$/ton);

$TC_{il}^{\pm}$  = transportation cost for transporting waste from temporary storage site  $i$  to landfill  $l$  (\$/ton);

$TC_{kl}^{\pm}$  = transportation cost for transporting waste from treatment facility  $k$  to landfill  $l$  (\$/ton);

$TC_{jk}^{\pm}$  = transportation cost for transporting waste from intermediate storage facility  $j$  to treatment facility  $k$  (\$/ton);

$TC_{kl}^{\pm}$  = transportation cost for transporting waste from treatment facility  $k$  to landfill  $l$  (\$/ton);

$OPS_j^{\pm}$  = operation cost of intermediate storage facility  $j$  for storage of wastes (\$/ton/day);

$OPT_k^{\pm}$  = operation cost of treatment facility  $k$  for treatment of wastes (\$/ton);

$OPL_l^{\pm}$  = operation cost of landfill facility  $l$  for treatment of wastes (including stabilization) (\$/ton);

$OPTL_l^{\pm}$  = operation cost of landfill facility  $l$  for final disposal of waste residue treated at treatment facility  $k$  (\$/ton);

$W_i^{\pm}$  = waste collection rate at source  $i$ ;

$p_{i,W}$  = admissible probability of exceeding the expected waste generation rate;

$CS_j^{\pm}$  = capacity of intermediate storage facility  $j$  (ton);

$p_{j,CS}$  = admissible probability of violating the capacity of intermediate storage facility  $j$  (ton);

$CT_k^{\pm}$  = capacity of treatment facility  $k$  (ton/day);

$p_{k,CT}$  = admissible probability of violating the capacity of treatment facility  $k$ ;

$CL_l^{\pm}$  = daily capacity of landfill  $l$  (ton/day);

$p_{l,CL}$  = admissible probability of violating the daily capacity of landfill  $l$ ;

$FCL_l^\pm$  total capacity of landfill  $l$  (ton);

$p_{l,FCL}$  = admissible probability of violating the total capacity of treatment facility  $l$ ;

$TR_k^\pm$  = residue rate of waste treated at treatment facility  $k$ .

- Decision variables:

$O_j^\pm, O_k^\pm, O_l^\pm$  = the binary integer variables for deciding if the storage facility  $j$ , treatment facility  $k$ , and landfill  $l$  were opened;

$x_{ij}^\pm, x_{ik}^\pm, x_{il}^\pm$  are the waste flow from temporary storage site  $i$  to intermediate storage facility  $j$ , treatment facility  $k$ , and landfill  $l$  at waste collection stage (ton);

$x_{kl}^\pm$  is the waste flow from treatment facility  $k$  to landfill  $l$  at waste collection period (ton);

$A_{jk}^\pm, A_{jl}^\pm$  are the waste flow from storage facility  $j$  to treatment facility  $k$  and landfill  $l$  at destocking period (ton);

$A_{kl}^\pm$  is the waste flow from treatment facility  $k$  to landfill  $l$  at destocking stage (ton);

The cost function of the oily waste management system can be formulated based on the above description:

$$\min f^\pm = f_1^\pm + f_2^\pm + f_3^\pm + f_4^\pm + f_5^\pm \quad (4-1)$$

(a) Opening cost for treatment facilities, intermediate storage sites, and landfills:

$$f_1^\pm = \sum_{j=1}^j FCS_j^\pm O_j^\pm + \sum_{k=1}^k FCT_k^\pm O_k^\pm + \sum_{l=1}^l FCL_l^\pm O_l^\pm \quad (4-1a)$$

(b) Transportation cost at waste collection stage:

$$\begin{aligned}
f_2^\pm = & LC^\pm \sum_{i=1}^i \sum_{k=1}^k x_{ik}^\pm TC_{ik}^\pm + LC^\pm \sum_{i=1}^i \sum_{j=1}^j x_{ij}^\pm TC_{ij}^\pm \\
& + LC^\pm \sum_{i=1}^i \sum_{j=1}^j x_{il}^\pm TC_{il}^\pm + LC^\pm \sum_{i=1}^i \sum_{j=1}^j x_{kl}^\pm TC_{kl}^\pm
\end{aligned} \tag{4-1b}$$

(c) Operation cost for treatment facilities, intermediate storage sites, and landfills at waste collection stage:

$$\begin{aligned}
f_3^\pm = & LC^\pm \sum_{i=1}^i \sum_{k=1}^k x_{ik}^\pm OPT_k^\pm + LC^\pm \sum_{i=1}^i \sum_{j=1}^j \frac{1}{2} x_{ij}^\pm LC^\pm OPS_j^\pm \\
& + LC^\pm \sum_{i=1}^i \sum_{j=1}^j x_{il}^\pm OPL_l^\pm + LC^\pm \sum_{i=1}^i \sum_{j=1}^j x_{kl}^\pm OPTL_{kl}^\pm
\end{aligned} \tag{4-1c}$$

(d) Transportation cost at destocking stage:

$$f_4^\pm = LS^\pm \sum_{j=1}^j \sum_{k=1}^k A_{jk}^\pm TC_{jk}^\pm + LS^\pm \sum_{i=1}^i \sum_{j=1}^j A_{jl}^\pm TC_{jl}^\pm + LS^\pm \sum_{i=1}^i \sum_{j=1}^j A_{kl}^\pm TC_{kl}^\pm \tag{4-1d}$$

(e) Operation cost for treatment facilities, intermediate storage sites, and landfills at destocking stage:

$$\begin{aligned}
f_5^\pm = & LS^\pm \sum_{j=1}^j \sum_{k=1}^k A_{jk}^\pm OPT_k^\pm + LS^\pm \sum_{j=1}^j \sum_{k=1}^k \sum_{l=1}^l \frac{1}{2} LS^\pm (A_{jk}^\pm + A_{jl}^\pm) OPS_j^\pm \\
& + LS^\pm \sum_{i=1}^i \sum_{j=1}^j A_{jl}^\pm OPL_l^\pm + LS^\pm \sum_{i=1}^i \sum_{j=1}^j A_{kl}^\pm OPTL_l^\pm
\end{aligned} \tag{4-1e}$$

Constraints are important to ensure the obtained results are applicable in the real-world problem. The constraints are considered in this study include facilities selection, mass balance, and facility capacity. In addition, to consider the constraints violation risk for this problem, some of right-hand-side parameters are assumed as the random variables with interval value, including waste generation rate  $W_i^\pm$ , capacity of intermediate storage sites  $CS_j^\pm$ , treatment facilities  $CT_k^\pm$ , and landfills  $CL_l^\pm$ .  $p_i$  ( $p_i \in [0, 1]$ ), in the superscript of these

parameters, are the admissible probability of violating the constraints  $i$ .

- Constraints of facility selection

The binary integer variables will be applied to determine whether the candidate facilities will be used in the oily waste management as shown in [Eqs. (4-11f) -(4-11h)]. In addition, at least 1 treatment facility and 1 landfill should be opened to meet the minimal demand.

$$O_j^\pm = \begin{cases} 0, & \text{if the storage facility } j \text{ is deployed;} \\ 1, & \text{if otherwise} \end{cases}, \quad \forall j \quad (4-1f)$$

$$O_k^\pm = \begin{cases} 0, & \text{if the treatment facility } k \text{ is deployed;} \\ 1, & \text{if otherwise} \end{cases}, \quad \forall k \quad (4-1g)$$

$$O_l^\pm = \begin{cases} 0, & \text{if the landfill } l \text{ is deployed;} \\ 1, & \text{if otherwise} \end{cases}, \quad \forall l \quad (4-1h)$$

$$\sum_{k=1}^k O_k^\pm \geq 1 \quad (4-1s)$$

$$\sum_{l=1}^l O_l^\pm \geq 1 \quad (4-1t)$$

- Mass balance at waste collection stage

The constraints are set to describe the mass balance at waste collection stage of oily waste management. Eq. (4-11i) ensures the generated waste can all be disposed or stored, and Eq. (4-11j) ensures all residual waste from treatment facilities can be properly landfilled.

$$\sum_{i=1}^i \sum_{j=1}^j x_{ij}^\pm + \sum_{i=1}^i \sum_{k=1}^k x_{ik}^\pm + \sum_{i=1}^i \sum_{j=1}^j x_{il}^\pm \geq (W_i^\pm)^{(1-p_{i,W})}, \quad \forall i \quad (4-1i)$$

$$\sum_{l=1}^l x_{kl}^\pm = TR_k^\pm \sum_{i=1}^i x_{ik}^\pm, \quad \forall k \quad (4-1j)$$

- Capacity constraints for intermediate storage sites, treatment facilities, and landfills at waste collection stage

The facilities for oily waste management can only receive the amount of waste within their capacities. Eq. (4-11l) and (4-11m) reflect the daily capacity constraints for treatment facilities and landfills respectively. For intermediate storage sites, there is no daily capacity limits but the total amount of received waste during waste collection stage have to be less their total storage capacity [Eq. (4-11k)]. In addition, the binary variables for determining whether the facilities are used are added into the right-hand side of the inequations of facilities capacity constraints to prevent waste from flowing to unopened facilities. In other words, for all unopened facilities, the waste flows between all sources and these facilities must be zero.

$$\sum_{i=1}^i x_{ik}^{\pm} \leq O_k^{\pm} (CT_k^{\pm})^{(p_{k,CT})}, \quad \forall k \quad (4-1l)$$

$$LC^{\pm} \sum_{i=1}^i x_{ij}^{\pm} \leq O_j^{\pm} (CS_j^{\pm})^{(p_{j,CS})}, \quad \forall j \quad (4-1k)$$

$$\sum_{i=1}^i x_{il}^{\pm} + \sum_{k=1}^k x_{kl}^{\pm} \leq O_l^{\pm} (CL_l^{\pm})^{(p_{l,CL})}, \quad \forall l \quad (4-1m)$$

- Mass balance at destocking stage

At destocking stage, the out flow from intermediate storage sites must be equal to amount of the received waste during waste collection stage. The mass balance of storage sites is defined by Eq. (4-1n), and Eq. (4-1o) describes the materials flow of residual waste from treatment facilities.

$$LS^{\pm} \left( \sum_{k=1}^k A_{jk}^{\pm} + \sum_{l=1}^l A_{jl}^{\pm} \right) \geq LC^{\pm} \sum_{i=1}^i x_{ij}^{\pm}, \quad \forall j \quad (4-1n)$$

$$\sum_{l=1}^l A_{kl}^{\pm} = TR_k \sum_{j=1}^j A_{jk}^{\pm}, \quad \forall k \quad (4-1o)$$

- Capacity constraints for treatment facility and landfill at destocking stage

Eq.(4-1p) and Eq.(4-1q) reflect the daily capacity of treatment facilities and landfills respectively.

$$\sum_{j=1}^j A_{jk}^{\pm} \leq O_k^{\pm} (CT_k^{\pm})^{(p_k, CT)}, \quad \forall k \quad (4-1p)$$

$$\sum_{j=1}^j A_{jl}^{\pm} + \sum_{k=1}^k A_{kl}^{\pm} \leq O_l^{\pm} (CL_l^{\pm})^{(p_l, CL)}, \quad \forall l \quad (4-1q)$$

- Nonnegative constraints

$$\begin{aligned} x_{ij}^{\pm} &\geq 0, & \forall i, j \\ x_{ik}^{\pm} &\geq 0, & \forall i, k \\ x_{il}^{\pm} &\geq 0, & \forall i, l \\ x_{kl}^{\pm} &\geq 0, & \forall k, l \\ A_{ik}^{\pm} &\geq 0, & \forall i, k \\ A_{il}^{\pm} &\geq 0, & \forall i, l \\ A_{kl}^{\pm} &\geq 0, & \forall k, l \end{aligned} \quad (4-1u)$$

### 4.2.3. Solution method

The model for the oily waste management system is described in section 4.2.2. The solution method is important to obtain optimized results of the programming problem. Before introducing the solution method of the proposed model, interval programming (IP) and chance-constrained programming (CCP) must be introduced at first. The IP have been by studied by previous researchers (Chen and Huang, 2001; Liu and Wang, 2007). The general form of IP model is:



$$\min f^\pm = \sum_{j=1}^n c_j^\pm x_j^\pm \quad (4-2a)$$

Subject to

$$\sum_{j=1}^n a_{ij}^\pm x_j^\pm \leq b_i^\pm \quad (4-2b)$$

$$x_j^\pm \geq 0 \quad (4-2c)$$

Where,  $c_j^\pm$ ,  $b_i^\pm$ , and  $x_j^\pm$  are interval parameters or variables. However, IP is not effective when dealing with the probability-distributions parameter in right-hand side. Therefore, inexact chance-constrained programming (ICCP) has been developed by combined IP and CCP to solve the problem (Guo et al., 2008). To convert the IP to ICCP model, each constraint  $i$  must be fixed with a certain level of probability  $p_i \in [0, 1]$ , and the conditions are imposed to ensure the constraint is satisfied with at least a probability of  $1 - p_i$ . Therefore, ICCP can be organized as follows:

$$\min f^\pm = \sum_{j=1}^n c_j^\pm x_j^\pm \quad (4-3a)$$

Subject to

$$\Pr\left(\sum_{j=1}^n a_{ij}^\pm x_j^\pm \leq b_i^\pm\right) \geq 1 - p_i, \quad \forall j \quad (4-3b)$$

$$x_j^\pm \geq 0 \quad (4-3c)$$

The optimized solution of this ICCP problem can be more complicated when coefficient  $c_j^\pm$  have different signs. However, when they have same sign, the bound of cost function can be easily found by obtaining the upper and lower bound by solving the two sub-models

which are separated from the original model (Guo et al., 2008). Thus, the sub-model for the upper bound ( $f^+$ ) is (assume that all the parameters in the model are larger than or equal to 0, which is same to the conditions of the proposed model in this study):

$$\min f^+ = \sum_{j=1}^n c_j^+ x_j^+ \quad (4-4a)$$

Subject to

$$\Pr\left(\sum_{j=1}^n a_{ij}^+ x_j^+ \leq b_i^-\right) \geq 1 - p_i, \quad \forall j \quad (4-4b)$$

$$x_j^\pm \geq 0 \quad (4-4c)$$

The sub-model for lower bound ( $f^-$ ) is:

$$\min f^- = \sum_{j=1}^n c_j^- x_j^- \quad (4-5a)$$

Subject to

$$\Pr\left(\sum_{j=1}^n a_{ij}^- x_j^- \leq b_i^+\right) \geq 1 - p_i, \quad \forall j \quad (4-5b)$$

$$x_j^\pm \geq 0 \quad (4-5c)$$

By solving these two sub-models, the upper and lower bounds for ICCP can be obtained, which is also applicable for the programming model of oily waste management developed in this study. Although the binary variables are applied in the right-hand side of some constraints, it does not affect the solutions of the bounds of the interval variables. The only effect of binary variables in the model is to prevent the waste from flowing to unopened facilities. In other words, it converts the capacity of unopened facilities to zero. According to the algorithm, the established model of oily waste management can be divided into two

sub-models. By solving them, the solutions corresponding to upper bound ( $f^+$ ) and lower bound ( $f^-$ ) of the original problem can be obtained respectively.

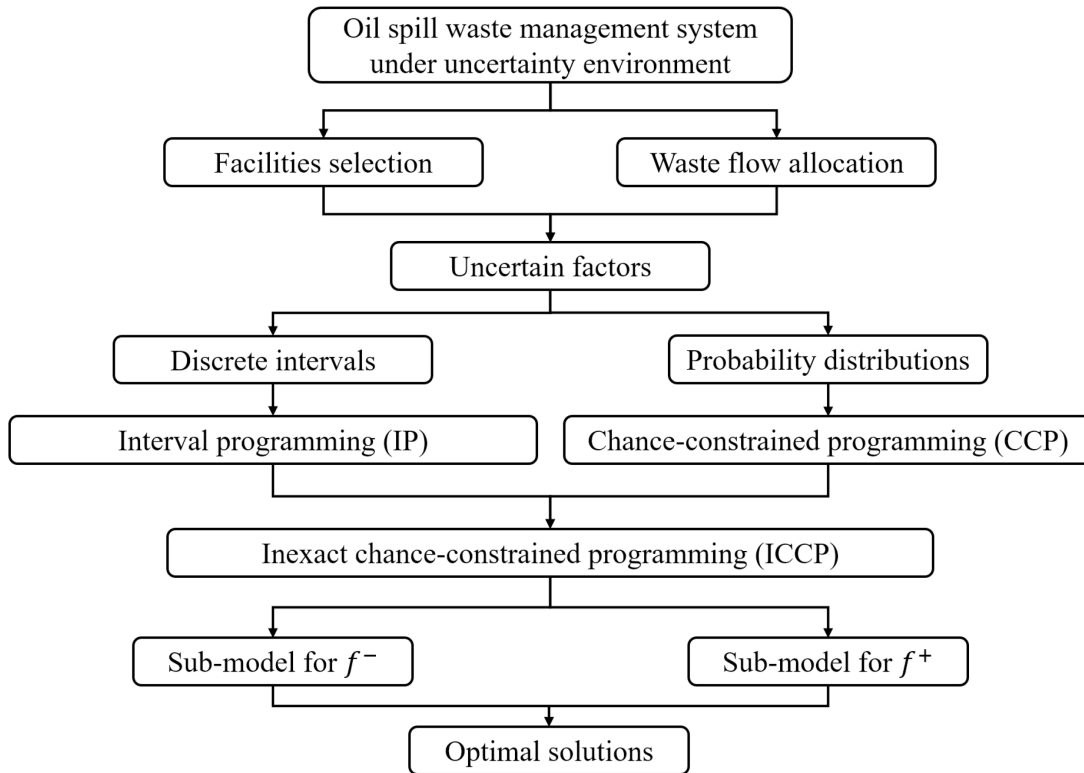


Figure 4-1. Framework of inexact chance-constrained programming for oily waste management under uncertain environments.

The optimal solutions for the decision variables, including the facilities selection and waste flow allocations at waste collection and destocking stages can be obtained by solving the sub-models. Figure 4-1 illustrates the framework of ICCP for oily waste management system with uncertainties. This model considers the interval parameters and random variables at the same time, which provide a valuable reference for managing oily waste under uncertain environments and aid the works of managers to make optimal decisions at the complex situations.

### 4.3. Case study

A hypothetical problem, as shown in [Figure 4-2](#), is proposed in this study to illustrate the application of developed model in oily waste management system. To dispose of the oily waste generated from this oil spill accident, three temporary storage sites are set up to collect and sort the waste generated on site. Each temporary storage sites would send a certain amount of waste to further disposal facilities every day depending on the amount of they collect. According to the information obtained by the response group, the nearby treatment facilities which are available to receive the oily waste include 1 cement plant, 1 pyrolysis facility, and 1 soil washing plant. Two landfills can accept the stabilized waste and waste residues after treatment. Moreover, 3 sites have been assessed and can be used as the intermediate storage sites.

Two different stages must be considered in the oily waste management, waste collection and destocking. At waste collection stage, the collected waste is preferentially sent to opened treatment facilities or landfill (after stabilization). However, the waste generation rate could exceed the capacity of treatment plants; this part of waste is transported to intermediate storage sites to wait the further disposal. When the shoreline cleanup operation was completed and no new waste generated on site, the management system moves to destocking stage to dispose of the stored waste at intermediate storage sites. The manager must select the proper facilities and optimize the waste flow for these two periods to minimize the system cost of the oily waste management.

To consider the uncertainties in the system, all the parameters in the system are interval value. In addition, to study the impacts of risk levels of constraints on the system cost, some of parameters are assumed to be random variables with normal probability

distribution, including the amount of daily collected waste at temporary storage sites, daily capacity of treatment facilities and landfills, and capacity of intermediate storage sites. 3 violating probability ( $p_i$ ) are assessed respectively in this study, including 0.01, 0.05, 0.10. Table 4-1 showed the interval values of these parameters at three different  $p_i$  levels. In addition, the data for other parameters, such as transportation cost and operation cost, fixed opening cost, and residue rate of facilities, are provided in Table 4-2 and Table 4-3 respectively.

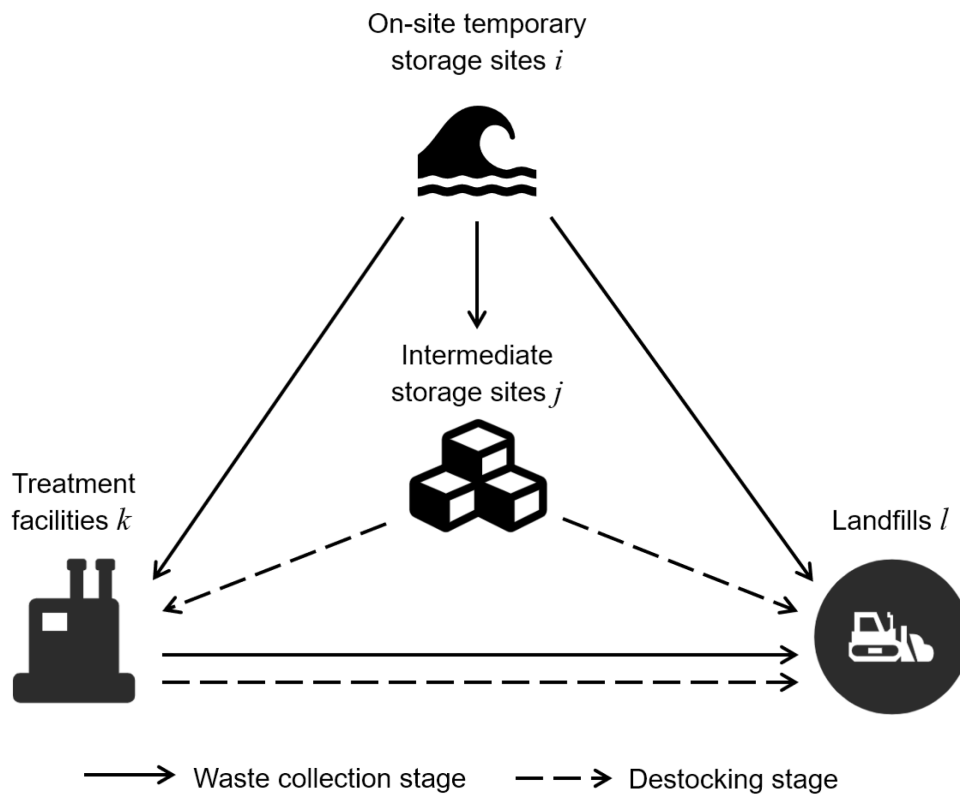


Figure 4-2. A hypothetical oily waste management system ( $i = 1, 2; j = 1, 2, 3; k = 1, 2, 3;$  and  $l = 1, 2, 3$ ).

**Table 4-1** Information of the constraints at three different violating probability ( $p_i= 0.01$ , 0.05, and 0.1).

Parameter	Probability of violating the constraints ( $p_i$ )		
	0.01	0.05	0.1
Waste generation rate (ton/day)			
$W_1$	[90, 95]	[80, 85]	[65, 68]
$W_2$	[115, 120]	[95, 101]	[75, 82]
Treatment Capacity (ton/day)			
$CT_1$	[24.5, 28]	[30.8, 32.5]	[32, 34.4]
$CT_2$	[36, 38.5]	[44.3, 46.8]	[47.8, 50]
$CT_3$	[30.5, 35.6]	[38.7, 42.4]	[40.2, 46.3]
Storage Capacity (ton)			
$CS_1$	[4200, 4600]	[5000, 5400]	[5380, 5800]
$CS_2$	[6000, 6400]	[6500, 6900]	[7650, 8000]
$CS_3$	[5400, 5800]	[6000, 6350]	[6300, 6750]
Landfilling Capacity (ton/day)			
$CL_1$	[54.2, 60.8]	[64.9, 68.5]	[69.4, 78.3]
$CL_2$	[24.5, 28.7]	[34.4, 39.5]	[40, 47.7]
$CL_3$	[64, 68.2]	[72, 78.3]	[80, 86.4]

Table 4-2. Data of transportation cost at waste collection and destocking stages.

Waste collection stage			Destocking stage		
Waste source	Waste destination	Value (\$/ton)	Waste source	Waste destination	Value (\$/ton)
From temporary storage sites $i$ to intermediate storage sites $j$			From intermediate storage sites $j$ to treatment facilities $k$		
$TC_{ij}^{\pm}$	$i = 1, j = 1$	[5.7, 6.8]	$TC_{jk}^{\pm}$	$j = 1, k = 1$	[8.9, 10.7]
	$i = 1, j = 2$	[11.7, 14.0]		$j = 1, k = 2$	[10.0, 12.0]
	$i = 1, j = 3$	[14.4, 17.3]		$j = 1, k = 3$	[14.1, 17.0]
	$i = 2, j = 1$	[14.6, 17.5]		$j = 2, k = 1$	[6.3, 7.6]
	$i = 2, j = 2$	[10.8, 12.9]		$j = 2, k = 2$	[6.0, 7.2]
	$i = 2, j = 3$	[8.2, 9.9]		$j = 2, k = 3$	[14.4, 17.3]
From temporary storage sites $i$ to treatment facilities $k$				$j = 3, k = 1$	[12.6, 15.2]
$TC_{ik}^{\pm}$	$i = 1, k = 1$	[12.0, 14.4]		$j = 3, k = 2$	[7.2, 8.7]
	$i = 1, k = 2$	[7.2, 8.7]		$j = 3, k = 3$	[20.6, 24.7]
	$i = 1, k = 3$	[19.0, 22.8]	From intermediate storage sites $j$ to landfill $l$		
	$i = 2, k = 1$	[15.6, 18.7]	$TC_{jl}^{\pm}$	$j = 1, l = 1$	[6.3, 7.6]
	$i = 2, k = 2$	[5.7, 6.8]		$j = 1, l = 2$	[15.2, 18.3]
	$i = 2, k = 3$	[24.1, 28.9]		$j = 1, l = 3$	[21.3, 25.5]
From temporary storage sites $i$ to landfill $l$				$j = 2, l = 1$	[12.0, 14.4]
$TC_{il}^{\pm}$	$i = 1, l = 1$	[11.7, 14.0]		$j = 2, l = 2$	[8.9, 10.7]
	$i = 1, l = 2$	[18.1, 21.7]		$j = 2, l = 3$	[10.0, 12.0]
	$i = 1, l = 3$	[21.6, 26.0]		$j = 3, l = 1$	[18.1, 21.7]
	$i = 2, l = 1$	[18.9, 22.6]		$j = 3, l = 2$	[14.1, 17.0]
	$i = 2, l = 2$	[19.7, 23.6]		$j = 3, l = 3$	[10.0, 12.0]
	$i = 2, l = 3$	[18.1, 21.7]	From treatment facilities $k$ to landfill $l$		
From treatment facilities $k$ to landfill $l$			$TC_{kl}^{\pm}$	$k = 1, l = 1$	[6.3, 7.6]
$TC_{kl}^{\pm}$	$k = 1, l = 1$	[6.3, 7.6]		$k = 1, l = 2$	[6.3, 7.6]
	$k = 1, l = 2$	[6.3, 7.6]		$k = 1, l = 3$	[13.4, 16.1]
	$k = 1, l = 3$	[13.4, 16.1]		$k = 2, l = 1$	[13.4, 16.1]
	$k = 2, l = 1$	[13.4, 16.1]		$k = 2, l = 2$	[14.6, 17.5]
	$k = 2, l = 2$	[14.6, 17.5]		$k = 2, l = 3$	[15.2, 18.3]
	$k = 2, l = 3$	[15.2, 18.3]		$k = 3, l = 1$	[8.0, 9.6]
	$k = 3, l = 1$	[8.0, 9.6]		$k = 3, l = 2$	[8.0, 9.6]
	$k = 3, l = 2$	[8.0, 9.6]		$k = 3, l = 3$	[18.0, 21.6]
	$k = 3, l = 3$	[18.0, 21.6]			

Table 4-3. Data of time length, fixed opening cost, operation cost, and residue rate.

Parameter	Value	Parameter	Value
<i>Time length</i>			
Waste collection stage (day)		Destocking stage (day)	
$LC^{\pm}$	[90, 100]	$LS^{\pm}$	[150, 180]
<i>Intermediate storage sites j</i>			
Fixed cost (\$)		Operation cost(\$/ton/day)	
$FCS_1^{\pm}$	[150000, 180000]	$OPS_1^{\pm}$	[1.5, 1.8]
$FCS_2^{\pm}$	[200000, 240000]	$OPS_2^{\pm}$	[1, 1.2]
$FCS_3^{\pm}$	[170000, 204000]	$OPS_3^{\pm}$	[1.2, 1.4]
<i>Treatment facilities k</i>			
Fixed cost (\$)		Operation cost (\$/ton)	
$FCT_1^{\pm}$	[300000, 360000]	$OPT_1^{\pm}$	[275, 330]
$FCT_2^{\pm}$	[700000, 750000]	$OPT_2^{\pm}$	[310, 350]
$FCT_3^{\pm}$	[500000, 600000]	$OPT_3^{\pm}$	[300, 360]
Residue rate			
$TR_1^{\pm}$	[0.15, 0.18]		
$TR_2^{\pm}$	[0.3, 0.36]		
$TR_3^{\pm}$	[0.25, 0.3]		
<i>Landfills l</i>			
Fixed cost (\$)		Operation cost (\$/ton)	
$FCL_1^{\pm}$	[500000, 650000]	$OPL_1^{\pm}$	[420, 504]
$FCL_2^{\pm}$	[300000, 400000]	$OPL_2^{\pm}$	[380, 456]
$FCL_3^{\pm}$	[600000, 720000]	$OPL_3^{\pm}$	[390, 468]
Operation cost for residue waste (\$/ton)			
$OPTL_1^{\pm}$	[40, 48]		
$OPTL_2^{\pm}$	[32, 38.4]		
$OPTL_3^{\pm}$	[35, 42]		



## 4.4. Results and discussion

### 4.4.1. Facility selection

Figure 4-3 shows the results of facilities selection and time length of destocking stage obtained from ICCP model under different  $p_i$  level. The intermediate storage site 2 is selected for all risk level due to its relatively low operation cost and large capacity. The use of the intermediate storage site 2 can meet the waste storage demand in most case apart from the extreme case at  $p_i = 0.01$ . The additional intermediate storage site 3 is used to store the oily waste exceed the treatment capacity. The technical constraint is set to ensure at least 1 treatment facility and landfill can be opened to dispose of generated waste.

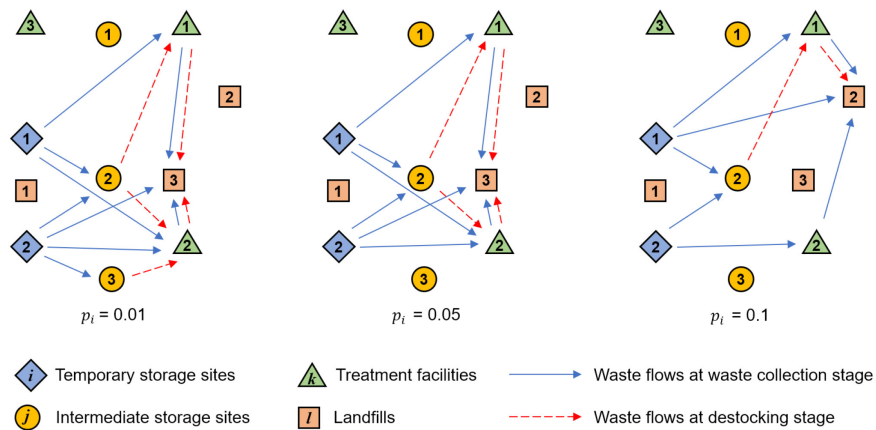


Figure 4-3. Directions of waste flow allocation for upper and lower bounds under different admissible probability of violating constraints  $p_i$ .

Treatment facility 1 and 2 is always used and it is be opened at all risk levels because of the low unit price of treatment cost. The landfills can receive the residual waste from treatment plants and waste after stabilization. At least 1 landfill must be open to receive the residual waste. However, direct landfilling of stabilized waste could be the last choice due

to the high unit price compared with treatment facilities. Therefore, only 1 landfill would be used at all risk level to meet the minimal requirement, thus avoiding extra cost. The model trend to increase redundancy of the system by increasing the available capacity when it takes low violation risk.

#### 4.4.2. Waste flow allocation

Allocation of waste flows between these facilities is necessary to minimize the transportation cost. Table 4-4 and Table 4-5 demonstrate the solutions of waste allocation obtained from the ICCP model for waste collection and destocking stage respectively. Figure 4-3 demonstrated the direction of waste flow allocation for upper and lower bounds at different  $p_i$  level. As the increase of  $p_i$  level, more facilities are used to deal with the generated oily waste, causing more transporting routes and more complicated allocation problems. Due to the high opening cost, the amount of waste sent to each treatment facility or landfill is equal to their maximum daily capacity at waste collection stage. It can be noticed that some of stabilized oily waste from temporary storage sites are transported to landfill in every case even though the unit operation cost for landfilling stabilized waste is much higher than treatment facilities.

For instance, landfill 2 receives the oily waste from temporary storage site 1 when  $p_i = 0.1$ . However, no any wastes are sent to landfill from intermediate storage sites at destocking stage ( $A_{jl} = 0, \forall j, l$ ). This is an effect strategy to reduce the system cost for oily waste management. At waste collection stage, landfilling stabilized waste can decrease the amount of the waste stored at intermediate storage sites and the number of intermediate storage sites required to be opened. However, use of this method does not give any benefits on cost at destocking stage due to its higher unit operation cost in comparison with other treatment methods.

Table 4-4. Solutions of waste flow allocations at waste collection stage.

Waste flow (ton/day)	Waste source	Waste destination	$p_i = 0.01$	$p_i = 0.05$	$p_i = 0.1$
From temporary storage sites $i$ to intermediate storage sites $j$					
$x_{ij}^{\pm}$	$i = 1$	$j = 1$	0	0	0
	$i = 1$	$j = 2$	[60, 62]	[36.32, 54.20]	[3.06, 18.97]
	$i = 1$	$j = 3$	0	0	0
	$i = 2$	$j = 1$	0	0	0
	$i = 2$	$j = 2$	[0, 9.11]	[0, 6.19]	[25, 34.2]
	$i = 2$	$j = 3$	[14.94, 47.87]	0	0
From temporary storage sites $i$ to treatment facilities $k$					
$x_{ik}^{\pm}$	$i = 1$	$k = 1$	[24.5, 28]	[30.8, 32.5]	[32, 34.4]
	$i = 1$	$k = 2$	[0, 10.5]	[0, 11.19]	0
	$i = 1$	$k = 3$	0	0	0
	$i = 2$	$k = 1$	0	0	0
	$i = 2$	$k = 2$	[25.5, 38.5]	[35.62, 44.3]	[47.8, 50]
	$i = 2$	$k = 3$	0	0	0
From temporary storage sites $i$ to landfill $l$					
$x_{il}^{\pm}$	$i = 1$	$l = 1$	0	0	0
	$i = 1$	$l = 2$	0	0	[17.03, 27.54]
	$i = 1$	$l = 3$	0	0	0
	$i = 2$	$l = 1$	0	0	0
	$i = 2$	$l = 2$	0	0	0
	$i = 2$	$l = 3$	[46.63, 52.45]	[50.51, 59.39]	0
From treatment facilities $k$ to landfill $l$					
$x_{kl}^{\pm}$	$k = 1$	$l = 1$	0	0	0
	$k = 1$	$l = 2$	0	0	[5.16, 5.76]
	$k = 1$	$l = 3$	[4.2, 4.41]	[4.88, 5.54]	0
	$k = 2$	$l = 1$	0	0	0
	$k = 2$	$l = 2$	0	0	[15, 17.21]
	$k = 2$	$l = 3$	[11.55, 12.96]	[14.04, 15.95]	0
	$k = 3$	$l = 1$	0	0	0
	$k = 3$	$l = 2$	0	0	0
	$k = 3$	$l = 3$	0	0	0

Table 4-5. Solutions of waste flow allocations at destocking stage.

Waste flow (ton/day)	Waste source	Waste destination	$p_i = 0.01$	$p_i = 0.05$	$p_i = 0.1$
From intermediate storage sites $j$ to treatment facilities $k$					
$A_{jk}^{\pm}$	$j = 1$	$k = 1$	0	0	0
	$j = 1$	$k = 2$	0	0	0
	$j = 1$	$k = 3$	0	0	0
	$j = 2$	$k = 1$	[24.5, 28]	[21.79, 30.80]	[16.84, 29.54]
	$j = 2$	$k = 2$	[8.83, 14.67]	[0, 2.75]	0
	$j = 2$	$k = 3$	0	0	0
	$j = 3$	$k = 1$	0	0	0
	$j = 3$	$k = 2$	[8.96, 26.59]	0	0
	$j = 3$	$k = 3$	0	0	0
From intermediate storage sites $j$ to landfill $l$					
$A_{jl}^{\pm}$	$j = 1$	$l = 1$	0	0	0
	$j = 1$	$l = 2$	0	0	0
	$j = 1$	$l = 3$	0	0	0
	$j = 2$	$l = 1$	0	0	0
	$j = 2$	$l = 2$	0	0	0
	$j = 2$	$l = 3$	0	0	0
	$j = 3$	$l = 1$	0	0	0
	$j = 3$	$l = 2$	0	0	0
	$j = 3$	$l = 3$	0	0	0
From treatment facilities $k$ to landfill $l$					
$A_{kl}^{\pm}$	$k = 1$	$l = 1$	0	0	0
	$k = 1$	$l = 2$	0	0	[2.52, 5.32]
	$k = 1$	$l = 3$	[4.2, 4.41]	[3.27, 5.54]	0
	$k = 2$	$l = 1$	0	0	0
	$k = 2$	$l = 2$	0	0	0
	$k = 2$	$l = 3$	[7.09, 12.96]	[0, 0.99]	0
	$k = 3$	$l = 1$	0	0	0
	$k = 3$	$l = 2$	0	0	0
	$k = 3$	$l = 3$	0	0	0

#### 4.4.3. Trade-off between system cost and constraint-violation risk

Figure 4-4 illustrates the costs of the proposed oily waste management system under different  $p_i$  level. The system cost is \$  $[5.92, 8.26] \times 10^6$  when  $p_i = 0.1$ . However, the figures are \$  $[7.59, 10.46] \times 10^6$  and \$  $[9.13, 12.64] \times 10^6$  for  $p_i = 0.05$  and 0.01 respectively. More capitals would be spent to the redundant design if the system does not allow the high system risks. Lower system cost can be achieved at higher  $p_i$  level; however, it results into lower system reliability. The manager needs to analyze and estimate the additional cost and environmental impacts required to deal with the cases with violating constraints and deciding the acceptable constraint-violation probability. The trade-off between system cost and risk have to be considered and decided by the response group to minimize the cost under the controllable risks. This model provides an effective tool for decision maker to assist their strategic planning in the oily waste management.

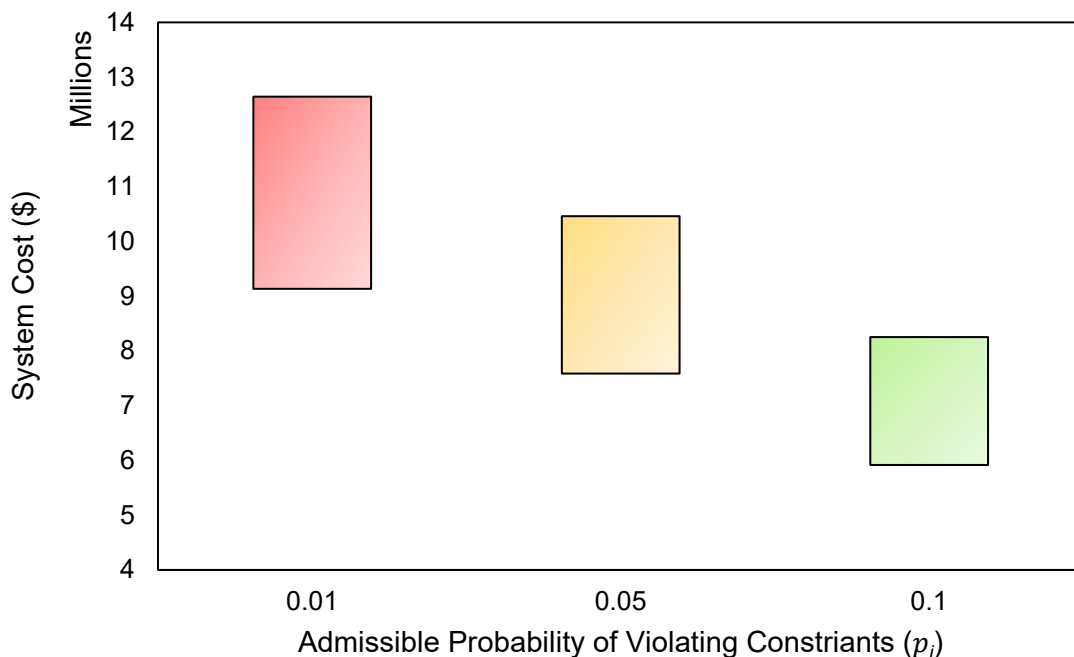


Figure 4-4. System cost under different admissible probability of violating constraints  $p_i$ .

#### 4.5. Summary

An inexact chance-constrained programming model (ICCP) has been developed to manage the oily waste generated from the cleanup of the shoreline affected by oil spill accidents. To consider the uncertainties in the system, this model combined interval programming and chance-constrained programming. All the parameters are interval values corresponding their variation ranges in the system, and probability distribution of the constraints are considered in the model to assess the system cost under different constraint-violation risk  $p_i$ .

A case study is provided in this study to demonstrate the application of the developed model. The obtained solutions include the facilities selection and waste allocation for waste collection and destocking stages under different risk levels. The binary integer variables correspond the selection of facilities; other interval variables represent the waste flows and time length of destocking stage. These solutions can provide a good guideline with managers to analyze the trade-off between system cost and constraint-violation risks. The developed model has high application potential as job-aid tool to manage the oily waste generated from the remediation operations on the oil-spilled shoreline.

## CHAPTER 5. CONCLUSIONS

### 5.1. Summary

In this thesis, a comprehensive literature review was conducted to provide the background knowledge about the existing SWAs and shoreline cleanup techniques. A database was built for the performance of existing SWAs including effectiveness and toxicity, based on the previous studies. These data could assist the development of decision support tools for oiled shoreline treatment in the future. Following that, the potential of using a novel nanocellulose-based nonfluid as SWA was demonstrated. Its efficiency and potential impacts of environmental factors were evaluated through batch tests. The comparison with commercial surfactants and biotoxicity tests proved the high application potential of nanocellulose-based nanofluid due to its high efficiency and low toxicity. The results proved the feasibility of using nanocellulose-based nanofluid as SWA in the oiled shoreline treatment, providing a potential green option for the oiled shoreline treatment. In addition, an inexact chance-constrained programming model for oily waste management was developed in this thesis. A case study was given to demonstrate the application of developed model. The interval solutions under different risk levels were obtained, providing decision support on the trade-off between system cost and constraint-violation risks for oily waste management under uncertain environments. Overall, these studies contributed to the development of knowledges and techniques in the field of shoreline cleanup.

## **5.2. Recommendations for future research**

- It is expected to further explore nanocellulose-assisted oil removal mechanisms under other environmental conditions and investigate its performance in large-scale tests.
- The addition of nanoparticles could enhance the performance of surfactants. The combining use of nanocellulose and surfactants will be explored in future study.
- For the model developed in CHAPTER 4, only the minimization of system cost was considered in the programming. It can be further improved by taking the other performance aspects into the consideration to comprehensively examine the environmental impacts, cost, and time length at the same time.



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## PUBLICATIONS

### Peer-reviewed journal articles

- (1) **Chen, Z.K.**, An, C., Yin, J., Owens, E., Lee, K., Zhang, K., Tian, X., 2021. Exploring the use of cellulose nanocrystal as surface-washing agent for oiled shoreline cleanup. *J. Hazard. Mater. (Elsevier)* 402, 123464. (Adapted into CHAPTER 3).
- (2) **Chen, Z.K.**, An, C., Boufadel, M., Owens, E., Chen, Z., Lee, K., Cao, Y., Cai, M., 2020. Use of surface-washing agents for the treatment of oiled shorelines: Research advancements, technical applications and future challenges. *Chem. Eng. J. (Elsevier)* 391, 123565. (Adapted into CHAPTER 2).
- (3) **Chen, Z.K.**, An, C., Fang, H., Zhang, Y., Zhou, Z., Zhou, Y., Zhao, S., 2020. Assessment of regional greenhouse gas emission from beef cattle production: A case study of Saskatchewan in Canada. *J. Environ. Manage. (Elsevier)* 264, 110443.
- (4) Hao, J., **Chen, Z.K.**, Zhang, Z., Loehlein, G., 2020. Quantifying construction waste reduction through the application of prefabrication: a case study in Anhui, China. *Environ. Sci. Pollut. Res (Springer)*, in press, DOI: 10.1007/s11356-020-09026-2.
- (5) Tian, X., An, C., and **Chen, Z.K.**, 2020. Assessing the impact of urban form on the greenhouse gas emissions from household vehicles: A review. *J. Environ. Inform. Let. (International Society for Environmental Information Sciences)* 3 (2), 70-85.
- (6) Hao, J. Maria, F. D., and **Chen, Z.K.**, 2020. Comparative study of construction and demolition waste management in China and the European Union. *Detritus (CISA Publisher)*, accepted in July 2020 (Manuscript ID: DJ-19-115.R2).

### Conference abstracts

- (1) **Chen, Z.K.**, An, C., 2020. Investigating the potential application of biomass-derived nanoparticles in oiled beach cleanup. 70th Canadian Chemical Engineering Conference (CCEC 2020). October 25-28, 2020.
- (2) Bi, H., An, C., Chen, X., and **Chen, Z.K.**, 2020. Performance of a surface washing agent impacted by environmental conditions. 70th Canadian Chemical Engineering Conference (CCEC 2020). October 25-28, 2020.