Oil Removal and Prevention from Shoreline under Different Environmental Conditions

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ABSTRACT

Oil Removal and Prevention from Shoreline under Different Environmental Conditions

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Marine oil spills frequently occur and cause adverse impacts on the coastal ecosystem and communities. The spilled oil may reach the shorelines and can persist for a long time. The application of surface washing agents is an important shoreline cleanup technique that can help remove stranded oil from substrate surfaces with the advantages of high removal efficiency, low toxicity, and strong economic viability. Herein, in this thesis, the comprehensive literature review was firstly conducted to study the causes and effects of oil spills, transport and fate of the spilled oil, various shoreline cleanup methods, and the use of surface washing agents for shoreline cleanup. Second, the effects of environmental factors on the performance of a commercial surface washing agent were well investigated. Meanwhile, the assessment for this agent was also carried out from aspects of toxicity, detergency, dispersion properties, and field tests. It has the practical implication for the use of surface washing agents in shoreline cleanup. Third, a green and responsive washing fluid was developed by modifying the nanoclay with a nonionic surfactant to washed out the stranded oil on beach sand. The thermodynamic miscibility modeling results had good agreement with the batch test results. The modified nanoclay has the application potential for shoreline cleanup, which can be a desirable alternative to the existing commercial surface washing agents. Fourth, a framework for the evaluation and selection of surface washing agents was also developed to better understand and apply this technique, and it is helpful for future shoreline-cleanup decision making. In addition, a new initiative was proposed with the use of alginate hydrogel coating for emergent shoreline oiling prevention. It provides a unique direction for the future development of green oil spill control strategy.

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LIST OF ABBREVIATIONS

HLB	hydrophilic-lipophilic balance			
LC50	the concentration that is lethal to 50% of the population			
EC50	half maximal effective concentration			
IC50	half maximal inhibitory concentration			
SOR	surface washing agent-to-oil ratio			
Corexit 9580	COREXIT EC9580A			
ANOVA	one-way analysis of variance			
MCDA	Multi-criteria decision analysis			
AHP	Analytic Hierarchy Process			
PROMETHEE	Preference Ranking Organization Method for Enrichment Evaluation			
API	American Petroleum Institute			
WSI	Weight Stability Intervals			

CHAPTER 1. INTRODUCTION

With the rapid development of the economy, the demand and activities for petroleum and related products continue to grow substantially (Dargay and Gately, 2010; Stocker et al., 2018). Oil has become the most important of the energy source all over the world, and both developing and developed countries are more and more dependent on petroleum derivatives to assist people to maintain the high quality of living (Caineng et al., 2009; Khamees, 2021; Moreno-Trejo et al., 2012). Petroleum-based products are closely relevant to every aspect of life, such as heating buildings, powering automobiles and machinery, manufacturing products (eg. plastics), etc. The use of massive oils leads to the frequent storage, transportation, extraction, drilling activities, in which oil spills will inevitably occur, especially in marine environment (Chen et al., 2020a; Ivshina et al., 2015). Marine oil spills refer to the release of crude oil and its relevant products into the ocean by vessels, pipelines, drilling equipment, and so on. This serious environmental problem could do harm to the public health, endanger ecological resources, impede economic development, and affect drinking water (Lyons et al., 1999; Solomon and Janssen, 2010; Teal and Howarth, 1984).

For preparedness and countermeasures, the first priority is to prevent the occurrence of marine oil spills, particularly for some sensitive regions like Arctic, as the spill could induce disastrous or irreversible hazard (Chen et al., 2019a; Eide et al., 2007). Therefore, it is necessary to develop and conduct a series of regulations and preventative measures including inspection, monitoring, and enforcing the training programs to further avoid the spill incident. However, once the marine spill occurs, timely and rapid response tactics should be carried out to minimize the effects of the spilled oil from its sources, containment, and spread (Lee et al., 2015). The offshore cleanup options include manual recovery, shimmers, booms, sorbents, in-situ burning, dispersant and bioremediation, but which method to use need to consider actual environmental factors, access to resources, oil amount and types, expenses, and so on (Grubesic et al., 2017; Li et al., 2019a; Tsocalis et al., 1994). In many cases, some techniques need to be conducted in combination to achieve

better results. However, though the best efforts were made to control and contain the spilled oil, more and less oil may still contaminate the shoreline during the spill incident. For the purpose of protecting these shorelines from being affected by oils, shoreline cleanup is incorporated into the oil spill response.

When the spilled oil reaches the shoreline, the shoreline response methods should be conducted as soon as possible (ECCC, 2016; USCG et al., 2013). There are a wide range of physical, chemical, as well as biological tactics to remove the stranded oil from the shoreline. Various factors such as oil type, geology of beaches, and type and sensitivity of biological communities will influence the response decisions (USEPA, 2016). As an efficient and effective alternative to more aggressive methods (oiled substrates removal and disposal), surface washing agents, also referred as shoreline cleaners, are applied to the affected shorelines to promote the oil removal from beach substrates. These agents are formulated to release but not disperse the stranded oil into the receiving waters in shoreline cleanup. The lifted oil can re-coalesce and form oil slicks on the water surface, which is convenient to be recovered with following methods like shimmers (Koran, 2007). The use of surface washing agent in actual oil spill incidents is very limited as this technique is typically recommended when the traditional cleanup methods are deployed but can not satisfied the cleanup requirements. Besides, the approval for this method from incidentspecific agencies is also required before its application (Bi et al., 2021b). Previous literature generally studied the effectiveness, toxicity, and testing protocols of commercial surface washing agent, but the effects and interactions of different environmental parameter on the performance of the use of these agents are still not clear. Meanwhile, it is also necessary to develop a systematic evaluation and selection framework for surface washing agent to better response in shoreline oil spills.

Therefore, in my study, it is expected to explore the use of surface washing agent comprehensively in a both theoretical and experimental way. Five objectives have been proposed as follows: (i) to conduct comprehensive literature review about the main shoreline cleanup methods and the use of surface washing agents (CHAPTER 2); (ii) to investigate the oil removal from contaminated sand using a commercially available surface washing agent under various environmental conditions (CHAPTER 3); (iii) to develop a green and responsive washing fluid with a non-ionic surfactant modified nanoclay as an alternative to surface washing agent to remove the oil from beach sand (CHAPTER 4); (iv) to develop a framework for evaluation and selection of surface washing agents to cope with shoreline oil spill (CHAPTER 5); (v) to propose a new initiative for emergent shoreline oiling prevention by using the alginate hydrogel coating to avoid the oil adhesion on shoreline substrates (CHAPTER 6). A section for conclusions and future work (Chapter 7) is also included in this thesis.

CHAPTER 2. LITERATURE REVIEW

2.1. Oil spills and shoreline oiling

(Causes and effects) Marine oil spills frequently happen and become serious environmental problems as they will bring a series of detrimental effects to the coastal biota and local communities (Chen et al., 2019a; Fingas, 2016; Zhang et al., 2019). As shown in Figure 2-1, it has been reported that over 100 oil spills occurred since the year of 2000 all over the world (Chen et al., 2019c). The processes of oil exploration, extraction, production, storage, and transportation are usually related to the release of liquid petroleum hydrocarbons to the marine environment (Bi et al., 2020; ITOPF, 2020). Specifically, the released oil may come from the natural seeps, ship collision, equipment corrosion and mechanical failure from offshore platforms or drilling rigs and so on (Boufadel et al., 2014; Lee et al., 2015). The amount of spilled oil from the sources of nature seeps is thought to be considerable, while the fact is that the tankers' operation discharges is the most important contributor to the marine oil pollution, accounting for 45% (Fingas, 2011a). Especially, in 1989, the tanker vessel Exxon Valdez grounded on Bligh Reef in Prince William Sound, Alaska, resulting in approximated 42 million liters of crude oil spilling into the ocean (Ballachey et al., 2014). The oil spill incident causing huge injury to the local habitat, economy, and populations (Monahan and Maki, 1991; Page et al., 2002). In recent years, the 2010 Deepwater Horizon disaster led to over 4.9 million barrels of oil spilling into the surrounding water, and directly affecting 180, 000 km² of ocean (Griggs, 2011).



Figure 2-1 Oil spill incidents around the world since 2000 (Chen et al., 2019c).

(Transport and fate of spilled oil) The characteristics of crude oil are usually complicated due to the fact that they are composed of various components (García and Urbina, 2003). Generally, the oil can be divided into saturates, aromatics, resins, and asphaltenes (Boufadel et al., 2019). The spilled oil in marine environments will be significantly affected by the ocean conditions and its own properties and even stay at sea for months before stranding on the shoreline. It would be taken a series of chemical, physical, and biological processes including photooxidation, emulsification, dispersion, evaporation, and spreading (Bi et al., 2021a; Etkin et al., 2008; Michel and Rutherford, 2013; Taylor et al., 2014). Once the oil spill response cannot be performed quickly, the shoreline will eventually contaminated by the spilled oil from the sea (Bi et al., 2020; Goovaerts et al., 2016). The oil could deposit on different types of shoreline substrates because of the beach characteristics and environmental conditions. Many environmental factors may affect the fate and behavior of oil stranded on the coastal area, however, the properties of oil, shoreline characteristics, and dynamic coastal processes such as tide, currents, wind and so on happened in shoreline are three main reasons (ECCC, 2016). Generally speaking, the

oil residues on shoreline are distributed in three forms: surface oil residues, subsurface residues, and submerged oil mats, and transport through penetration, remobilization and retention (Figure 2-2) (Curtis et al., 2018; Etkin et al., 2008; Lee et al., 2015). To enhance the oil removal and recovery or to prevent oil remobilization, it is necessary to conduct a series of shoreline cleanup methods in oil spill response.



Figure 2-2 The distribution and behavior of stranded oil on shorelines affected by the beach topography and environmental factors (Wang et al., 2020).

2.2. Shoreline cleanup-physical washing, removal and in-situ treatment

(Water washing) The physical method of washing or flooding is the one of most common tactics in shoreline cleanup, and it incudes flooding, water washing with low/high pressure and warm/hot/ambient temperature (Owens et al., 2021). Once this technique is conducted, the water stream should direct the released oil to the adjacent water or collection are for following containment with booms, skimmers or sorbents (Gustitus and Clement, 2017). The specific washing method to be used mainly depends on oil characteristics such as

viscosity and weathering degree (Teal, 1991). For example, the water washing with ambient temperature and low pressure is typically used for the light or unweathered medium oils, while high-pressure, hot wash is often appropriate for use on heavy or weathered oils due to their high viscosity and adhesion (Doerffer, 2013). The very heavy or weathered oil might need further increase of water temperature or/and pressure to improve the oil removal efficiency from shoreline substrates. However, high requirements for water temperature or pressure may generate biological effects on flora and fauna and complicate cleanup operations (ECCC, 2016).

(Manual and mechanical removal) Manual removal refers to the use of manual labor and hand tools to remove the stranded oil on shorelines, which can be conducted effectively in most beach types for small amounts of oil (NPA, 2005). Specific operations include scraping or wiping the oil with sorbents and picking up the oil sediments (Owens, 2011; Pereira and Mudge, 2004). However, this method is usually very inefficient and labor-intensive. In comparison, the mechanical removal is to use a series of mechanical devices to removal the oil and oiled materials, whose efficiency is typically faster than that of manual removal but may produce larger amount of waste (Baker et al., 1993; Fingas, 2011b). It always involves various kinds of earth-moving equipment such as elevating scraper, front-end loader, backhoe, as well as dragline/clamshell, and beach cleaning equipment such as mobile vacuums, off-site sorters, and mobile lifters/sorters and rakes (ECCC, 2016; Jafarinejad, 2016). When using this method, it is necessary to take the trafficability limitation and the accessibility of machines to affected areas into consideration (Chen, 2020; IPIECA and IOGP, 2015).

(Vegetation cutting and vacuum) Manual cutting of oiled vegetation is the method of using scythes, knives, and/or other tools to remove the oiling parts of plants in shoreline cleanup

(Zengel and Michel, 1996). It can be applied on various plants, especially for oiled wetlands, marshes, and seaweeds (Michel and Rutherford, 2014). The goal of the cutting is to decrease potential detrimental effects on wildlife, and the chronic oiling of waterfowl, birds and some fur-bearing mammals lived in marshes is one example (Baker et al., 1993). Besides, vegetation cutting also could enhance the survival and recovery of the oiled plants in some cases, otherwise the oil coated on the leaves may block the passageway for gas exchange (Levine et al., 1995). Vacuum is another shoreline cleanup technique that can remove both onshore pooled oil and nearshore sunken oil through suction (Taylor and Owens, 1997). It can be deployed in combination with flooding or other water washing methods to float and recover the oil (Acosta and Quraishi, 2014). Nevertheless, when it comes to remove the nearshore sunken oil, there is a limitation of poor visibility that may affect the oil removal efficiency of this method. A decanting system for separating the oil from water is necessary when treating high volume of water with oil (Abidli et al., 2020).

(Mixing and sediment relocation) Mechanical mixing of oiled sediments can be divided into the dry mixing and wet mixing based on the presence or absence of water (Dubach et al., 2015a). The former is to improve the oil exposure to air and tides for enhancing the process of natural weathering by tilling, raking, digging and other operations, while the latter refers to float or recover the oil through physically agitating by disc systems, harrow, rakes and so on in the water, thus the floated oil can be collected with skimmers (ECCC, 2016; Owens and Sergy, 2004). The mechanical mixing might influence the local biota living on the sediments. Another in-situ treatment is the sediment relocation which carries oiled substrates to another area with great wave energy or being washed by water (Lee et al., 2003; Sergy et al., 1999). For example, the oiled sediments can be moved from the upper intertidal zone to the lower area, so they can be exposed to the physical process by waves to enhance the oil removal efficiency. However, sediment relocation may not be suitable to treat large amounts of oil as it will cause damage to the other resources (Sergy et al., 2003).

2.3. Shoreline cleanup-chemical treatment

(Dispersants) The use of dispersants is usually considered as an offshore oil spill response, as they are sprayed onto the oil slicks and disperse the oil into water column (Lessard and DeMarco, 2000; Suja et al., 2019). In some early studies, dispersant were used to clean up oiled shorelines, and their effectiveness was not satisfactory (Canevari, 1979). Even now, according to Environment and Climate Change Canada, dispersants still can be applied to release oil from shorelines that promotes the formation of small oil droplets, which would be dispersed into water environment to biodegrade (ECCC, 2016). This kind of agent can reduce the surface tension of the oil, thus fine oil droplets form and are lifted by the waves and/or tides and transported away from the shore. It can enhance the processes of weathering and degradation for the dispersed oil (Fiocco and Lewis, 1999; Lessard and DeMarco, 2000). However, the dispersant is typically not used in shoreline cleanup unless in conditions of high wave or tidal energy (Fingas, 2013).

(Surface washing agents) Surface washing agents, also called shoreline cleaners, are formulated to release the stranded oil from shoreline substrates rather than dispersing it (NWACP, 2020). The surfactants in surface washing agents usually have a higher HLB compared with those of dispersants (Koran, 2007). After the *Exxon Valdez spill* in 1989, the surface washing agent was classified as a separate category in shoreline oil spill response(Schramm, 2000). It can be applied to release oil from the shorelin types of bedrock, manmade structures, and pebble/cooble or boulders (Koran et al., 2005; NOAA, 2010; USCG et al., 2013). The procedure generally includes spraying the agent to the oiled

substrates, soaking for a while, and rinsing off the oil with flush water (Bi et al., 2020; Sullivan and Sahatjian, 1993). In actual application, the tactic is frequent used in combination with some oil collection techniques, such as skimmers and sorbents (Fieldhouse, 2008, 2012).

2.4. Shoreline cleanup-bioremediation

The use of biodegradation is to improve the biodegradation rate of stranded oil by the microorganisms, which use the oxygen to degrade the hydrocarbons into water and carbon dioxide (Pritchard et al., 1992; Venosa et al., 2010). This process can be affected by various factors, including the species and amount of microorganisms, oxygen, nutrients, temperature, oil properties, and so on (Prince et al., 1999). The biological treatment method can be deployed for light and medium oils in a wide range of shoreline types (sand, granule, pebble/cobble...), however, it may take a long time even several weeks to achieve desired oil degradation degree. The biodegradation rate of oil can be further accelerated if this method can be combined with mixing or sediment relocation as these operations can increase the surface area and oxygen amount available for the microorganisms (Lee et al., 2003). Three classes, bioenhancement, bioaugmentation, and phytoremediation, are used to enhance the biodegradation rate. The first approach is he bioenhancement, also referred to as biostimulation, which typically adds nutrients as nitrogen and phosphorus to enhance the oil-degrading activity of the indigenous microbial population at the affected area (Dadrasnia et al., 2020). Sometimes, the local microorganisms might not be enough or able to degrade the oil, bioaugmentation can be applied to accelerate petroleum hydrocarbon degradation (Hosokawa et al., 2009; Simon et al., 2004; Tyagi et al., 2011). The process can introduce living microbes and/or some chemical agents to increase the natural remediation rate, but the inoculated microorganisms can be easily reduced because of inappropriate conditions, so this method had limited application in shoreline cleanup. In addition, the oil biodegradation can also be improved by phytoremediation with the use of the fungi and plants. This technique can remove petroleum hydrocarbons through plant or fungal mechanisms of biodegradation, phytovolatilization, accumulation, and metabolic transformation (Yavari et al., 2015).

2.5. Surface washing agents

The U.S. EPA has already listed 77 surface washing products on the Product Schedule in Subpart J of the National Contingency Plan (USEPA, 2020). There are many commercially available products that can be applied on oiled shorelines, mangroves and seagrasses. However, Corexit 9580, a hydrocarbon-based surface washing agent, is the only one licensed by Environment and Climate Change Canada (Fingas, 2013). Due to concerns over potential adverse effects and lack of sufficient data for performance evaluation, the use of surface washing agents is still limited. Therefore, this section summarized the previous research results of Corexit in terms of its toxicity, laboratory performance, as well as major field tests.

(Toxicity) Detailed information regarding the toxicity of Corexit 9580 is shown in Table 2-1 in which LC50 was used as the indicator for evaluation. It can be seen that the LC50 range varied from 9.06 mg/L for *Mysidopsis* to 10000 mg/L for *Oncorhynchus mykiss* (Rainbow trout) and *Fundulus heteroclitus* (Mummichog), implying *Mysidopsis* was most sensitive to Corexit 9580 (Fingas, 2013; Koran, 2007). Hansen et al. (2014) tested the sensitivity of *Acartia tonsa, Calanus finmarchicus, Calanus glacialis*, and *Corophium volutator* to Corexit 9580, and the corresponding LC50 values with different testing periods were 50.4, 116, 112, and 2267±300 mg/L, respectively. Other studies also reported 96-h

LC50 of Corexit 9580 for *Menidia menidia* (Atalantic Silversides) and *Menidia*, and 48-h LC50 of Corexit 9580 for *Americamysis bahia* (Mysid) were 87 mg/L, 13.2mg/L, and 32 mg/L, respectively (Koran, 2007; Michel et al., 2001). It is known that the 96-h LC50 of weathered oil is typically within 1 mg/L, illustrating Corexit 9580 is less toxic and even non-toxic, and thus would not pose threats to the environment (Chen et al., 2019c; Fingas, 2013). Apart from LC50, EC50, IC50 and fertilization in a given time were also used to evaluate the toxicity of Corexit 9580 for *Skeletonema costatum*, *Vibrio fischeri*, and *Dendraster excentricus*, and results showed this product presented no acute toxicity to the above species (Hansen et al., 2014; Shang et al., 2012).

Affected species	Testing time (h)	LC50 (mg/L)	References
Acartia tonsa	48	50.4	(Hansen et al., 2014)
Calanus finmarchicus	96	116	(Hansen et al., 2014)
Calanus glacialis	144	112	(Hansen et al., 2014)
Corophium volutator	240	2267±300	(Hansen et al., 2014)
Mysidopsis	48	9.06	(Koran, 2007)
Menidia	96	13.3	(Koran, 2007)
<i>Oncorhynchus mykiss</i> (Rainbow trout)	96	10000	(Fingas, 2013)
Fundulus heteroclitus (Mummichog)	96	10000	(Fingas, 2013)

Table 2-1 Toxicity of Corexit 9580 to reference toxicity test species

Menidia menidia (Atalantic Silversides)	96	87	(Fingas, 2013)
Americamysis bahia (Mysid)	48	32	(Fingas, 2013)

From the individual to the cell, researchers assessed the cytotoxicity of three Corexit products, Corexit 9500, corexit 9527, and Corexit 9580, on BEAS-2B epithelial cells of human airway. Compared with the first two agents, no marked change of cell viability was observed as Corexit 9580 concentration increased. It might be a better agent for oil treatment considering the potential adverse effects on human respiratory health (Shi et al., 2013). Similarly, no reduction in cell viability was also observed for lung epithelium cell exposed to Corexit 9580 (Wang et al., 2012). Even though many researchers have worked on the toxicity of Corexit 9580, the current knowledge is still limited and further study on more species and cells is required.

(Laboratory performance) Based on previous studies, up to over 80% of stranded oil could be released from substrates under the treatment of Corexit 9580 in laboratory tests. The detailed washing efficiencies of Corexit 9580 for various oil types under different laboratory test procedures were given in Table 2-2, and they were also illustrated by different colors and height of triangles outside the circle in Fig. 2-3. However, there was an exception for results from Tumeo and Cote (1998), and they reported the treatment with Corexit 9580 only had removed 2.01% of diesel heating oil in tap water and removed 0.69% of oil in seawater, which might be due to the different testing procedure. Koran (2007) used Prudhoe Bay Crude with artificial and natural substrates under various testing methods to test the performance of Corexit 9580, and concluded that the effectiveness was reduced

from artificial materials to natural materials, or in order of Swirling Coupon, Glass Plate, Inclined Trough, and Natural Substrate method. When using the Natural Substrate method, more oil was removed from dry sand (31.4%) than that from wet sand (23.5%). The overall performance of Corexit 9580 was 41% - 44% of oil removed, and similar results were also reported in other literature (Clayton et al., 1995b; Fingas et al., 1990). As to the method of Natural Substrate which can better reflect real field applications, Clayton et al. (1995b) reported Corexit 9580 could achieve higher performance of Bunker C removal with 52.9% for gravel, compared with 21.1% for rip-rap and 23.6% for eelgrass. There are also some studies which focused on the effects of salinity and temperature for different oil types, and the results indicated that the performance of Corexit 9580 was enhanced at higher temperature and at less salinity (Fingas, 2013; Tumeo and Cote, 1998). Fieldhouse (2012) reported the salinity of flush water did not affect the efficiency of Corexit 9580 under different temperature conditions, with over 80% at 22 °C and around 70% at 15 °C for both fresh water and salt water. In addition, Zhang and Liu (1997) also reported the effectiveness of Corexit 9580 ranging from 28.4% to 80.3% with different wetting properties, temperature, washing time and salinity. Therefore, it can be concluded that the effectiveness of Corexit 9580 can be affected by oil types, testing methods, substrates, temperature, salinity, wetting properties, as well as other variables.

 Table 2-2 Washing efficiencies of Corexit 9580 for various oil types under different

 laboratory test procedures

Methods	Oil type	Substrates	Efficiency	References
Environment	Alberta Sweet	Stainless steel	69% (freshwater)	(Fingas,
Canada,	Mixed Blend	trough	53% (saltwater)	2013)
Inclined	crude oil			
Trough Test				

Environment	Bunker C	Stainless steel	57% (22 °C) 24%	(Guenette
Canada,		trough	(5 °C)	and
Inclined				Fieldhouse,
Trough Test				1998)
Environment	Bunker C	Stainless steel	42%	(Fingas et
Canada,		trough		al., 1990)
Inclined				
Trough Test				
Environment	Bunker C	Stainless steel	Up to 80.3%	(Zhang and
Canada,		trough	(varied with	Liu, 1997)
Inclined			factors)	
Trough Test				
Rotary	Bunker C	Granite tiles	Over 80% (22 °C)	(Fieldhouse,
Mixer			Around 70%	2012)
Method			(15 °C)	
	Bunker C	Stainless steel	47% (overall mean	(Clayton et
		and porcelain	efficiency)	al., 1995b)
		coupons		
Natural	Bunker C	Gravel, rip rap,	52.9% (gravel)	(Clayton et
Substrates		eelgrass	21.1% (rip-rap)	al., 1995a)
			23.6% (eelgrass)	
Environment	Orimulsion	Stainless-steel	27% (22 °C) 15%	(Guenette
Canada,		trough	(5 °C)	and
Inclined				Fieldhouse,
Trough Test				1998)
Natural	Bonny Light		38.2%	(Clayton,
Substrates				1993)
Environment	Prudhoe Bay	Steel and tile	32.2% (steel)	(Koran,
Canada,	crude oil		50.6% (tile)	2007)
Inclined				

Trough Test

Swirling	Prudhoe Bay	Steel and tile	55.4% (steel)	(Koran,
Coupon Test	crude oil		62.5% (tile)	2007)
Glass Plate	Prudhoe Bay	Glass plates	49.7% (smooth)	(Koran,
Test	crude oil	with various	48.3% (fine)	2007)
		surface	40.1% (coarse)	
		roughness		
Natural	Prudhoe Bay	Dry and wet	31.4% (dry sand)	(Koran,
Substrates	crude oil	sand	23.5% (wet sand)	2007)
	Diesel heating	Moderately	2.01% (freshwater)	(Tumeo and
	oil #1	sorted gravel	0.69% (saltwater)	Cote, 1998)
			0.69% (20°C)	
			0.63% (10°C)	



Figure 2-3 Effectiveness of Corexit 9580 on five oil types under different laboratory test procedures and major field trials.

(Field tests) Since U. S. EPA listed surface washing agents as a separate category for oil treatment, some field tests of Corexit 9580 were conducted in real cases, but most of results were not quantified and just declared to be successful or not (Fingas, 2013). As shown in Fig. 2-3 (the inside of the circle) and Table 2-3, from the year of 1989, all 12 field tests of Corexit 9580 were performed in North and South America and its effectiveness was considered to be successful, and 7 trials occurred in USA. The field trials related to both

effectiveness and specific plant sensitivity were conducted. In 1996, Michel et al. (1998) reviewed and reported the treatment of Corexit 9580 on oil spill in M/T Julie N of Portland Harbor, Maine. 50% of oil was removed by combining low-pressure flushing, vegetation cutting as well as other cleanup methods. As the responses to Corexit 9580, the gas exchange, survival and regeneration of oiled Spartina alterniflora in field test were improved, even though the biomass reduced at the final stage of first growing season (Pezeshki et al., 1997). After that, Pezeshki et al. (1998) selected more US Gulf coastal marsh macrophytes due to their sensitivity and ecologically importance. They were oiled with South Louisiana Crude or Arabian Medium Crude and treated by Corexit 9580. The results showed the sensitivity to Corexit 9580 varied with different species, but this surface washing agent could reduce plant tissue death and recover plant stomatal functioning. The application of Corexit 9580 was also successfully performed in the field test of Uruguay (Fingas, 2013). In Canada, it was also reported Corexit 9580 was successfully applied to treat ~10 tons of Bunker C in Quebec and treat another ~1 ton of Bunker C in Nova Scotia in the same year of 1999 (Fingas, 2000). In 2007, Corexit 9580 was successfully applied to the Burrard Inlet, British Columbia shoreline for oil spill clean-up and toxicity evaluation, and proved to be not acutely toxic to Microtox bacteria (Vibrio fischeri), Coho salmon (Oncorhynchus kisutch) and echinoid fertilization (Dendraster excentricus) (Shang et al., 2012). The meso-scale trial of Corexit 9580 was also conducted with Cold Lake Winter Blend dilbit in Gainford, Alberta in 2013, and it was found Corexit 9580 was effective for various stages of weathered oil removal (Taylor et al., 2014).

Table 2-3 Major field tests for the performance of Corexit 9580

Year	Location	Oil type	Effectiveness	References
1989	Disk Island,	Alaska North	65% (surface);	(Fiocco et al.,
	AK, USA	Slope crude	67%	1991)

	•	-	(subsurface)	
1990	Knight Island,	Alaska North	Successful	(Fiocco et al.,
	AK, USA	Slope crude		1991)
1994	Louisiana,	Bunker C, South	Successful	(Pezeshki et al.,
	USA	Louisiana crude		1995)
1994	San Jacinto	Crude oil	Successful	(Michel and
	River, TX,			Benggio, 1995)
	USA			
1994	Puerto Rico,	No.6 fuel oil	Successful	(Michel and
	USA			Benggio, 1995)
1995-	Montegut, LA,	South Louisiana	Successful	(Pezeshki et al.,
1996	USA	crude		1997)
1996	Maine, USA	Bunker C	Varied	(Fingas, 2013)
1997	San Jorge,		Successful	(Fingas, 2013)
	Uruguay			
1999	Quebec, CA	Bunker C	Successful	(Fingas, 2000)
1999	Nova Scotia,	Bunker C	Successful	(Fingas, 2000)
	CA			
2007	Burrard Inlet,	Heavy synthetic	Successful	(Shang et al.,
	BC, CA	crude		2012)
2013	Alberta, CA	Weathered Cold	Successful	(Taylor et al.,
		Lake Winter		2014)
		Blend dilbit		

It can be concluded from the comprehensive assessment of Corexit 9580 that this agent is less toxic compared with other counterparts and thus environmental friendly, and its effectiveness can be up to over 80% but would be affected by various factors. Moreover, Corexit 9580 was successfully used to removed stranded oil from shorelines substrates in many filed trials.

CHAPTER 3. INVESTIGATION INTO THE OIL REMOVAL FROM SAND USING A SURFACE WASHING AGENT UNDER DIFFERENT ENVIRONMENTAL CONDITIONS

3.1. Background

Oil spills are serious environmental problems, which result from oil drilling, pipeline leakage, and tanker accidents (An et al., 2017; Cai et al., 2019; Chen et al., 2019c; ITOPF, 2020). Over 100 major oil spill accidents have been reported all over the world since 2000. For example, the Deepwater Horizon oil spill in 2010 resulted in the release of 4.9 million barrels of crude oil into the surrounding water (McNutt et al., 2012; McNutt et al., 2011). Once oil is spilled into the marine environment, a certain amount of spilled oil may eventually reach the shoreline (Wang et al., 2005). More importantly, the shorelines will be contaminated if the oil spill countermeasures are not immediately conducted, the stranded oil on shoreline may cause extremely detrimental effects on coastal biota (Goovaerts et al., 2016; Rabalais and Turner, 2016). The oiled shoreline can also bring many problems to coastal communities (Li et al., 2018a; Zhang et al., 2019). It is necessary to find effective shoreline cleanup techniques to mitigate the impact of oil spill.

Various shoreline treatment methods such as manual and mechanical removal, chemical treatment, and bioremediation have been employed in different situations (ECCC, 2016). Using surface washing agents for oiled shoreline cleanup is an important technique with the advantages of high oil removal efficiency (particularly for heavily weathered oils), low requirement for temperature and pressure of flush water, and less disturbance to the shorelines (Michel et al., 2001). The washing agents are formulated to help release stranded oil from surfaces and then the released oil can be collected by skimmers or other physical methods. The general purpose of surface washing agents is to lift the oil from substrates,

but without dispersing the oil into water column (Fingas, 2013; Tumeo and Cote, 1998). The application methods for different surface washing agents may vary. Typically, these agents are directly sprayed on the surface of oiled beaches during the low-tide condition, after enough soaking time, the oil is removed by flush water with low pressure and directed to recovery areas (Fingas, 2013). In past decades, surface washing agents have already been applied in many actual spills and field tests. For example, PES-51 and Corexit 9580 were used for the Exxon Valdez spill to treat the oiled shoreline, and the results were declared to be successful (Fiocco et al., 1991). Similarly, it is reported over 60% stranded oil was removed from substrates with Cytosol in San Francisco Bay test, and Alaska North Slope crude oil was also successfully removed from mixed sands and gravels by PES-51 in the test of T/V Exxon Valdez spill (Von Wedel, 2000).

The surface washing agents have been studied in terms of testing protocols and effectiveness in laboratories. The testing protocol using stainless steel troughs as substrates was developed by Environmental Canada (Fingas et al., 1990). Then, Fieldhouse (2012) improved the Environmental Canada Test by using granite tiles and a rotary mixer apparatus to obtain higher precision and repeatable results. The Science Application International Corporation and the Centre de Documentation de Recherche et d'Expérimentation sur les Pollutions Accidentelles des Eaux also developed the swirling coupon method and glass slide method, respectively, for evaluating the effectiveness of surface washing agents (Clayton, 1993; Merlin and Le Guerroue, 1994; Sullivan and Sahatjian, 1993). In addition, U.S. EPA developed the Natural Substrate Protocol with sand or gravel used (Koran et al., 2006). The effectiveness of surface washing agents testing methods and various factors, such as oil type, substrate type as well as operating factors (e.g., mixing speed, mixing time, and SOR) (Chen et al., 2019c; Koran et al., 2009; Luedeker, 2009). However, the influence and

interaction of various environmental factors on the performance of using surface washing agents to treat oiled shoreline are still not clear.

In this study, therefore, the investigation into the oil removal from contaminated sand using a surface washing agent under variable environmental conditions was conducted. In detail, the study was (1) to explore the combined effects of SOR, mixing speed and mixing time on oil removal efficiency with the presence of surface washing agent and determine the optimal operating factors for testing; (2) to investigate the potential effects of four major environmental conditions (temperature, salinity, clay concentration and humic acid concentration) on the effectiveness of a surface washing agent, and (3)to analyze main effects and two-level interactions of above variables based on factorial analysis. The results have significant implications for future application of surface washing agents in the shoreline cleanup.

3.2. Materials and methods

3.2.1. Materials and chemicals

Corexit 9580 was selected as a representative surface washing agent due to its high effectiveness and low toxicity, and it was obtained from COREXIT Environmental Solutions LLC (TX, USA). Crude oil was obtained from Hibernia oil field located in the southeast of St. John's, Newfoundland, Canada, and its basic properties are shown in Table 3-1. Standard washed and high-temperature heated sand (30-40 mesh) was supplied by Millipore (ON, Canada). Sea salt, humic acid and kaolinite were obtained from Sigma Chemical Company (ON, Canada). Hexane was obtained from Fisher Scientific (ON, Canada) at analytical grade. Deionized water was used in all tests.

Origin	Newfoundland, Canada
API gravity	35.0
Flash point (°C)	19
Reid vapor pressure (kPa)	36
Density (g/ml)	0.8430
Pour point (°C)	6
Surface tension (mN/m)	28.8

Table 3-1 Basic properties of crude oil from Hibernia oil field

3.2.2. Experimental procedure and factorial design

The Hibernia oil was aged within a fume hood at 20 °C for 7 days and stored in a closed container before application. All batch experiments were carried out in 20 mL glass vials. 1 g sand was added to each glass vial, and then 4 µL weathered oil were applied drop-wise by micro-syringe onto the sand surface, followed by weathering another 24 h at 20 °C in fume hood. Corexit 9580 was then applied drop-wise by pipette to the oiled sand and allowed to penetrate the oil and contact for 30 min. After that, 15 mL synthetic water with different characteristics were added to vials. The capped vials were put in the New Brunswick Innova 42R Incubator Shaker (Eppendorf, Connecticut, USA) and rotated at different times and speeds. After shaking and decanting liquids, the remaining oil on the sand was extracted with hexane at 300 rpm for 24 h.

Two-level factorial design has been widely applied to investigate the effects of factors and their interactions in environmental processes (Chen et al., 2021c; Wang et al., 2018). In this

study, four environmental characteristics (temperature, salinity, kaolinite concentration and humic acid concentration) that affected oil removal efficiency were tested at two levels (Table 3-2). A full 2⁴ factorial design matrix with triplicate is shown in Table 3-3. "-1" and "1" denoted the low and high levels of each factor, respectively. The response was the oil removal efficiency to show the effectiveness of Corexit 9580 under various conditions.

Symbol	Factor	I I as \$4 a	Level	
	ractor	Units	Low (-1)	High (+1)
А	Temperature	°C	5	20
В	Salinity	wt%	0.5	3.5
С	Kaolinite concentration	mg/L	10	100
D	Humic acid concentration	mg/L	10	60

Table 3-2 Experimental variable factors for chemical properties of flush water

	Co	ded	levels	5	Α	В	С	D
Run number	A	В	С	D	Temperature (°C)	Salinity (wt%)	Kaolinite concentration (mg/L)	Humic acid concentration (mg/L)
1	1	1	1	1	20	3.5	100	60
2	1	-1	1	-1	20	0.5	100	10
3	-1	-1	-1	1	5	0.5	10	60
4	1	-1	1	1	20	0.5	100	60
5	-1	1	-1	-1	5	3.5	10	10
6	1	1	-1	-1	20	3.5	10	10

Table 3-3 Coded levels and corresponding values for factorial design matrix
7	-1	1	1	1	5	3.5	100	60
8	-1	1	-1	1	5	3.5	10	60
9	-1	-1	1	1	5	0.5	100	60
10	1	-1	-1	1	20	0.5	10	60
11	1	1	1	-1	20	3.5	100	10
12	-1	-1	1	-1	5	0.5	100	10
13	-1	-1	-1	-1	5	0.5	10	10
14	-1	1	1	-1	5	3.5	100	10
15	1	-1	-1	-1	20	0.5	10	10
16	1	1	-1	1	20	3.5	10	60

3.2.3. Analytical methods

The concentration of oil in hexane extract was measured using a Thermo ScientificTM Evolution 201 UV-Visible spectrophotometer (MA, USA) at wavelength 220 nm. All batch experiments were conducted in triplicate, and the results were reported as the average value. The data for combined effects of operating factors were analyzed by using SigmaPlot software (Systat Software Inc., CA, USA). The experimental arrangement and results analysis of factorial design were performed using Design Expert 11 (Stat-Ease Inc., MN, USA). Statistical analysis was undertaken through ANOVA for determining the significance of various treatments (p < 0.05) (He et al., 2018; Vitale et al., 2019; Wang et al., 2018).

3.3. Results and discussion

3.3.1. Determination of washing operation factors

In previous studies, it was found that some variables including the volume of oil applied, oil application pattern, and oil-washing agent soak time, did not significantly affect the performance of surface washing agents (Koran, 2007; Koran et al., 2006), and thus their values were fixed in the experiments. Instead, their performance was often sensitive to the variation of SOR, mixing speed, and mixing time. Based on previous literature and our pretest results, these operating factors were analyzed at multiple levels as shown in Table 3-4 (Fieldhouse, 2012; Koran, 2007; Koran et al., 2009; Koran et al., 2005; Luedeker, 2009).

As shown Figure 3-1, the oil removal efficiency became higher as SOR increased. There was a positive correlation between mixing speed and oil removal efficiency with the higher level yielding the higher response. The ceiling effect existed in the effect of mixing time, while there was no additional improvement in the tests with the longest time period (Koran et al., 2009; Luedeker, 2009).

Operating factors	Levels
SOR	1:2, 1:1, 2:1, 5:1
Mixing speed (rpm)	150, 200, 250
Mixing time (min)	5, 15, 30, 60

Table 3-4 Washing operation factors with different levels

The combined effects of these three variables given in Figure 3-1 were further evaluated to determine the optimal combination for oil removal using Corexit 9580. The largest increase in response can be seen as SOR changed from lower (1:2 and 1:1) to higher levels (2:1 and 5:1) at any mixing speed and mixing time. SOR played the most significant role in oil removal efficiency. However, at higher levels, there was less than a 5% increase in oil removal under each combination of these three washing operation factors. Since there is a

large amount of oil to be treated in real world applications, it is necessary to take the cost and toxicology into consideration. Therefore, the SOR of 2:1 was used in the following tests due to a relatively higher oil release and lower cost.

At this selected SOR level, the effects of three mixing speeds just showed a slight increase no matter what levels of mixing time were used. Meanwhile, previous study reported that 200 rpm was already excessively rigorous and resulted in beaker breakage (Koran et al., 2009). Fingas et al. (1990) concluded that a good surface washing agent was supposed to be a poor dispersant, meaning such agent should disperse stranded oil as little as possible to facilitate oil recovery and reduce adverse impacts of dispersed oil in ecologically sensitive areas. However, the high mixing speeds (200 and 250 rpm) in this study, represented high energy of flush water applied in a washing process, could result in more oil dispersed by Corexit 9580, which would lead to less oil recovery and increased oil concentration in the surrounding water. Based on the above considerations, a mixing speed of 150 rpm was determined for later study. Furthermore, ceiling effects of mixing time were observed again in the tests with fixed SOR and mixing speed, and the oil removal efficiency increased from 65.61% to 69.53% as the mixing time period changed from 5 to 30 min. After that, the higher levels of mixing time showed no further effects on oil removal compared with that at 30 min. Also, excessive washing time would result in less efficiency in field treatment. Taking account of these considerations for tests and field practice, a 30min mixing time was selected for the following tests. In summary, SOR (2:1), mixing speed (150 rpm) and mixing time (30 min) were chosen as fixed variables for the following tests.



Figure 3-1 Combined effect of washing operation factors on oil removal.

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3.3.2. Effect of temperature

Temperature is an important environmental parameter which can affect the oil transport as it could change oil properties such as viscosity, directly related to the persistence of the stranded oil (An et al., 2010; Chen et al., 2019c; Qin et al., 2019). The temperature of the natural environment may vary greatly with different regions and time (Chakraborty et al., 2015; Yao et al., 2019). For most of North America, the average shoreline atmospheric temperature throughout the year is at the range of 5- 25 °C, and this temperature range becomes narrower when it comes to shoreline water (Dethier et al., 2012). As shown in Figure 3-2, the oil removal efficiency almost doubled from 33.7% at 5 °C to 63.3% at 25 °C, indicating the effectiveness of Corexit 9580 was improved significantly with increasing flush water temperature. The impact of temperature on removing stranded oil from substrates using surface washing agents was also reported in previous studies (Fiocco et al., 1991; Tumeo and Cote, 1998). Raising flush water temperature appropriately had positive effects on the activity of surfactants in Corexit 9580, which were capable of reducing the interfacial tension between oil and water and facilitating the oil to be removed from substrates surfaces (Koran et al., 2008). More specifically, for the nonionic surfactant components in Corexit 9580, its optimal detergency was related to the phase inversion impacted by the effective size of the hydrophilic head of surfactant compared with hydrophobic tail. The effective size of the head decreased due to the reduction of its hydration when the temperature increased. If the hydrophilic head group was smaller than the lipophilic tail, a water-in-oil emulsion would form changing from the form of oil in water. The minimum interfacial intension existed under the phase inversion condition with equal effective size of head and tail (Aveyard et al., 1985; Koran, 2007).



Figure 3-2 Effect of flush water temperature on oil removal without and with Corexit 9580

Higher water temperature could also reduce the viscosity of oil and Corexit 9580 mixture, making it easier to be flushed and transferred to the water. Previous studies showed the use of hot water washing alone without surface washing agents was also effective for releasing oil into water (Couillard and Tran, 1989). In this study, to determine whether surface washing agent or high temperature played a major role in oil removal, the results of the control tests (no Corexit 9580) were further compared with those with Corexit 9580. It can be found from Figure 3-2 that there was just a slight increase of oil removal efficiency from 22.9% to 24.1% as flush water temperature changed from 5 to 25 °C. The temperature variation in experiments was therefore not the main contributor to oil removal.

3.3.3. Effect of salinity

The salinity is also an important factor to affect the performance of surface washing agents (Luedeker, 2009). The average salinity of seawater is 3.5 wt% but can vary from 3.0 to 3.7 wt%. In nearshore, seawater can be less salty due to the fact that fresh water from rivers and streams flows into the sea (Cao et al., 2020; Lin et al., 2001). In this study, the controlled trials were first. conducted to determine the effects of salinity from 0 to 4.0 wt% on stranded oil in the absence of surface washing agent. As shown in Figure 3-3, the efficiency of oil recovered from sands in these controls was almost the same, around 23%. However, the difference between treatment trials and controls was significant (p<0.05) as oil removal efficiency significantly increased after Corexit 9580 treatment. When the salinity of flush waster increased from 0 to 2.0 wt%, the oil removal efficiency experienced a sharp decrease from 66.3% to 36.1%. Afterwards, there was a gradual reduction of oil removal efficiency as salinity further increased.



Figure 3-3 Effect of sea salt concentration of flush water on oil removal without and with Corexit 9580

Obviously, the increase of ionic strength of flushing water presented an inhibitory effect on the desorption of crude oil with the use of surface washing agent. This trend may be attributed to the ionic effects which related directly to the salinity, and interactions with the substrate surfaces (Tumeo and Cote, 1998). The relevance of the adsorption of organic matter and ionic strength is largely due to the Helmholtz double layer that refers to the close field charge structure surrounding oiled substrates. It was also found the double layer of ions at the surfactant monolayer interface was greatly compressed, slowing down about one third of the velocity of the surfactant counter-ion charge movement at interface (Eicke and Meier, 1996). In this case, the addition of sea salt to the wash water resulted in the ionic strength enhancement. The Helmholtz double layer would be even more compressed and therefore further hinder the movement of surfactant counter-ion. This might be the main reason for the obvious reduction of oil removal with increasing salinity at lower levels. However, it is impossible for the double layer to be compressed indefinitely, instead, the amount of space that can be compressed gradually decreases as more sea salt is added, causing the rate of response reduction gradually decreases and even becomes stable. Overall, as the salinity of flush water increased, the tendency of non-polar mixture of oil and Corexit 9580 to enter the increasingly polar water environment would decrease a lot.

3.3.4. Effect of kaolinite concentration

Clay mineral is a widespread constituent in both shoreline and nearshore areas. Due to its strong sorption affinity, large surface area, and as high cation exchange capacity, clay can often affect the pollutant transport in the aqueous solution (Zhao et al., 2014). Previous research mainly focused on the desorption of petroleum compounds from the clay materials using surfactants (Li et al., 2016a). The effect of flush water with clay minerals on oil removal after the treatment of surface washing agent is still not clear. In this study, kaolinite was selected as the representative clay mineral and the flush solution with clay was used to wash the oiled sand. The results showed the oil removal efficiencies for the control tests without any treatment were significantly different with those after Corexit 9580 treatment.



Figure 3-4 Effect of kaolinite concentration of flush water on oil removal without and with Corexit 9580

As shown in Figure 3-4, if only using the kaolinite solution to wash the oiled sand, about 23% of crude oil could be released into water and there was almost no variation of oil removal efficiency within the kaolinite concentration range of 0 to 100 mg/L. The weathered crude oil has been already tightly bonded with sand surface and thus would be less affected by the kaolinite in the flush water. Nevertheless, when Corexit 9580 was applied to this process, much higher proportion of oil, ranging from 54.18% to 70.11%, was removed. However, the oil removal efficiency experienced a drop of around 16% as kaolinite concentration in flush water increased. It may be related to the fact that some Corexit 9580 or its effective constituents were partly adsorbed on kaolinite during the

washing process. In this way, less Corexit 9580 would function normally remove the oil from the sand, causing an efficiency reduction for this kind of surface washing agent.

3.3.5. Effect of humic acid

Humic substances derived from the decay of organic materials, commonly exist in the natural environment and they also have the impact on the transport of pollutants (Zhao et al., 2019). In this study, the effect of humic acid concentrations of flush water ranging from 10 to 100 mg/L on the oil removal using Corexit 9580 was investigated. As shown in Figure 3-5, it can be concluded that adding humic acid to the flush water could release more oil from the sand compared with that only using deionized water to wash the mixture of oil and Corexit 9580. There was a slight increase from 64.2% to 79.1% of oil removal efficiency as humic acid, the response change gradually became stable around 78%. The control tests showed a large amount of oil was still retained on the sand surface and little change can be seen in terms of percent of oil released when only using different concentrations of humic acid solution without Corexit 9580 treatment.



Figure 3-5 Effect of humic acid concentration of flush water on oil removal efficiency without and with Corexit 9580

The enhanced removal of oil can be explained by the synergistic solubilization by humic acid and Corexit 9580, facilitating more oil release from sands. The surface active compounds in Corexit 9580 were known to be nonionic (Tumeo and Cote, 1998). The synergistic effects of nonionic surfactants and humic acid on the solubility of polycyclic aromatic hydrocarbons has been reported in previous study (Cho et al., 2002). During the washing process, the sorption of humic acid on the surface of lifted oil in water made the mixture surface negatively charged (Cai et al., 2017; Zhu et al., 2015). Meanwhile, humic acids also had strong affinity to quartz which is the main component of the sand, thus the electrostatic repulsion prevented re-adsorption of oil on substrates and then improved the

performance of Corexit 9580 (Jada et al., 2006; Pitois et al., 2008).

3.3.6. Factorial analysis of the influencing factors

From the above discussion, it can be concluded that oil removal efficiency using Corexit 9580 was influenced by the flush water properties of temperature, salinity, kaolinite concentration and humic acid concentration. These factors may interact with each other and affect the oil recovery efficiency. Environmental modeling can often help analyze the environmental process (Chen et al., 2020b; Huang et al., 2019; Li et al., 2019b; Roberts et al., 2019; Shen et al., 2017). In this study, the effects of these environmental factors were analyzed based on factorial design. According to the effect of hierarchy principle, a system is usually dominated by main effects and low-ordered interactions, and high-order interactions may be less significant (Li et al., 2011). Therefore, only individual factors and two-factor interactions were considered in factorial analysis because they may have the most significant effects. The relationship of oil removal efficiency and the four parameters can be expressed by below polynomial equation:

Oil removal efficiency (%) = +43.01+6.54*A-10.34*B-2.30*C+1.43*D-3.36*A*B -0.86*A*C+1.36*A*D+0.31*B*C-3.44*B*D-0.38*C*D

where A, B, C, D were temperature (°C), salinity (wt%), kaolinite concentration (mg/L), humic acid concentration (mg/L), respectively.



Figure 3-6 Normal plot of residuals on oil removal efficiency.



Figure 3-7 Pareto chart of effects on oil removal efficiency.

The normal plot of residuals given in Figure 3-6 presented an almost straight line, implying that experimental data was in a normal distribution. In order to distinguish main effects and interactions of all components, the Pareto chart of effects in Figure 3-7 was used to visualize the positive or negative effects of parameters by different colors. A decreasing order of significance was observed, represented by the height of the column. The ANOVA was also performed and shown in below Table 3-5. The F-value of model was 19.19 and the P-value was 0.0022, indicating the model was statistically significant. In addition, the value of R² was 0.9746, showing a high reliability of the regression model for the interpretation of experimental data. It can be seen that the effects of individual factors A-temperature, B-salinity, and interactions of temperature and salinity (AB), salinity and humic acid concentration (BD) were significant terms.

Source	Sum of	Degree of	Mean	F-value	P-value	Standardized	Contribution
	square	freedom	square			effects	(%)
Model	2927.33	10	292.73	19.19	0.0022		
Α	684.08	1	684.08	44.85	0.0011	13.08	22.78
В	1711.06	1	1711.06	112.18	0.0001	-20.68	56.97
С	84.73	1	84.73	5.56	0.0650	-4.60	2.82
D	32.06	1	32.60	2.14	0.2036	2.86	1.09
AB	180.63	1	180.63	11.84	0.0184	-6.72	6.01
AC	11.70	1	11.70	0.7669	0.4213	-1.71	0.39
AD	29.76	1	29.76	1.95	0.2213	2.73	0.99
BC	1.54	1	1.54	0.1008	0.7637	0.62	0.05
BD	188.93	1	188.93	12.39	0.0169	-6.87	6.29
CD	2.30	1	2.30	0.1505	0.7140	-0.76	0.08

Table 3-5 ANOVA for full factorial model on oil removal with Corexit 9580

Residual 76.26 5 15.25

Cor total 3003.59 15

Table 3-5 also summarized the standardized effects and contributions of variables and their interactions. It can be found that temperature (A) and humic acid concentration (D) had positive effects on the desorption of weathered oil, indicating that higher levels of these factors would be favorable for oil release from the sand. However, salinity (B) and kaolinite concentration (C) showed negative effects on oil removal efficiency as concentration of either sea salt or kaolinite increased.

As shown in Table 3-5 and Figure 3-8, Factor A-temperature had the largest positive effect on the release of oil from substrate with a contribution of 22.78%. It indicated that increase in flush water temperature could improve the effectiveness of Corexit 9580. The positive effect of temperature can be explained by above mentioned surfactant activity enhancement and mixture viscosity reduction. Therefore, during the cleaning of oiled shoreline, flush water in appropriately higher temperature can help achieve a better oil removal performance in the use of Corexit 9580. When applied in cold region, the flush water can be heated to reach a certain temperature. However, too high temperature may have detrimental effects on resident microorganisms, plants and even animals on shoreline (Holloway, 1991). By contrast, the largest negative effects can be seen from the factor Bsalinity, with a contribution of 56.97% to the overall performance. It suggested that an increase in sea salt concentration of flush water reduced the effectiveness of Corexit 9580, which was due to ionic effects. The ionic strength of flush water increased with addition of sea salt, resulting in less oil released from substrates. In this way, fresh or low-salinity water could be a good alternative to seawater to wash out Corexit 9580-treated oil from substrates for small-scale oil spill. In the case of large-scale oiled shoreline cleanup, the use of seawater as flush water is inevitable. The salinity of seawater for washing Corexit 9580treated oil on sands should be as low as possible. In the field application, if the treated area is close to the estuary, it would be better to use fresh water in rivers (less than 0.05 wt% in salinity) or seawater with low salinity for treatment, because the salinity of estuaries is usually at a lower range of 0.05 to 3.0 wt% (Tansel et al., 2014).

As shown in Figure 3-9, the effect of factor C-kaolinite concentration was insignificant. The stranded oil has been already adsorbed on sand surface before washing process, thus it was difficult for kaolinite to uptake oil from substrates but could affect the well balanced Corexit 9580 to reduce its effectiveness. Therefore, a little negative effect of kaolinite concentration on oil removal efficiency was observed. Similarly, the factor D-humic acid concentration had almost no effect on the response, and its contribution for the system performance was only 1.1%.



Figure 3-8 Main effects and significant two-level interaction effects plot for oil removal

The effect plots of insignificant two-level interactions are also given in Figure 3-9, and the parallel lines were the indication of no interactive effects of factors. Only the effects of salinity and kaolinite concentration (BC) presented parallel lines, implying there was no interaction between them. Although the interactions of temperature and kaolinite concentration (AC), temperature and humic acid concentration (AD), as well as kaolinite concentration and humic acid concentration (CD) had positive or negative effects on cleaning performance of Corexit 9580, their contributions to model response were low to

0.39%, 0.99% and 0.08%, respectively, which were not as significant as the other two interactions. Among these three insignificant combinations, the interaction between temperature and humic acid concentration (AD) showed a positive effect, because the oil desorption efficiency improved more at high-level humic acid concentration with increasing flush water temperature. It indicated that the temperature played a more significant role in removing Corexit 9580 treated oil from substrates compared to humic acid.



Figure 3-9 Insignificant effects of single factors and two-level interactions for oil removal

As shown in Figure 3-8, it was interesting to note that the effect of humic acid concentration (D) was insignificant. However, its interactive effect with salinity (B) was significant and exhibited the most negative interactive effect on oil removal with the exception of salinity. As humic acid concentration varied from low to high levels, the absolute value of slope increased, suggesting the presence of humic acid in flush water further inhibited the performance of Corexit 9580 when the salinity was higher and higher. This interaction could be attributed to the fact that ionic strength in flush water was enhanced by adding more sodium ions from humic acid salts (Singh and Singhal, 2012). Also, significant negative effect was observed from the interaction of temperature and salinity (AB). It can be seen that the effect of temperature was less noticeable at higher salinity than that at a lower level, indicating that the involvement of more sea salt was unfavorable for oil removal as temperature increased (Fingas et al., 1990).

3.4. Summary

This is the first study to comprehensively investigate the influence of flush water characteristics on the performance of a surface washing agent. A preliminary test was conducted to obtain optimal combinations of operating factors of SOR 2:1, mixing speed 150 rpm, and mixing time 30 min. The results of single-factor experiments showed that high temperature and humic acid concentration of flush water contributed to the enhanced performance of a surface washing agent, while salinity and kaolinite concentration could inhibit its performance. The factorial analysis revealed the main effects of temperature and salinity, and the interactive effects of temperature and salinity as well as salinity and humic acid concentration that were significant to the washing efficiency of the surface washing agent. The results have important implications for the use of surface washing agents to assist oil removal. The determined factors can be used to improve the efficiency of surface washing agent and provide the decision support for field applications

CHAPTER 4. TREATMENT OF OILED BEACH SAND USING A GREEN AND RESPONSIVE WASHING FLUID WITH NONIONIC SURFACTANT-MODIFIED NANOCLAY

4.1. Background

Marine oil spills frequently occur as the result of the ship collisions, equipment corrosion, and mechanical failure during oil exploitation, transportation, and storage (Chen et al., 2019a; Feng et al., 2021; Zhang et al., 2019). They bring huge economic losses and cause detrimental effects on the coastal ecosystem (Bi et al., 2021b; Lee et al., 2015). After experiencing a set of physical, chemical, and biological processes, the spilled oil may finally reach the shoreline with the wind, currents, and tides (Wang et al., 2020). The stranded oil is highly weathered and persistent; appropriate response methods are therefore required to successfully remove the oil from the substrates.

The response strategies and tactics usually deployed to treat impacted shorelines include mechanical removal, sediment relocation, bioremediation, and so on (ECCC, 2016; Hammouda et al., 2021; Saborimanesh and Mulligan, 2015). However, some treatment methods are plagued by low removal efficiency, high manpower, equipment, and monetary requirements, and complex operations (Dicks et al., 2002). The use of a surface washing agent is a viable alternative for oil spill response. However, the concerns about its toxicity should be considered, as this kind of agent is typically formulated with organic solvents and other additives (Fingas, 2013). The release of the surface washing agent into the environment may therefore affect the coastal biota. For example, Baxter et al. (2018) reported the lethal and sublethal effects of two commercial products (Accell Clean SWA and PES-51) with and without crude oil on grass shrimp at both the larval and adult stages. Rial et al. (2010) found that mussels, sea urchins, and mysids were extremely sensitive to

CytoSol (a commercial surface washing agent) after the treatment of oiled substrate. Meanwhile, it is also expected the effluent after surface washing can be easily treated and would not cause secondary pollution. Therefore, it is necessary to develop an effective, nontoxic, and easily treated washing fluid for shoreline cleanup.

Clay materials, technically referred to as nanoclays, have been used for pollution control due to their abundant availability, nontoxic nature, and low cost (Sarkar et al., 2019). However, raw nanoclays may not be able to remove high levels of pollutants; the modification of such nanoclay may therefore enhance its contaminant removal efficiency. Ogunlaja and Pal (2020) prepared cetyltrimethyl ammonium bromide (CTAB)-modified bentonite nanoclay to delay the inversion process from water/oil to oil/water emulsion. The similar nanoclay was treated with zwitterionic surfactant cocamidopropyl betaine (CAPB) by Abdel Ghafar et al. (2020) to remove the Pb^{2+} and Reactive Yellow 160 from water. Nyankson et al. (2015) reported on the use of the halloysite clay nanotubes loaded with various combinations of Tween80, dioctyl sodium sulfosuccinate (DOSS), Span 80, and modified soybean lecithin phosphatidylinositol to achieve high oil-dispersion effectiveness. Bentonite, modified with hexadecyltrimethyl ammonium (HDTMA) chloride, was also developed to remove 2, 4, and 6-trichlorophenol from effluents (Anirudhan and Ramachandran, 2014). It should be noted that some cationic and anionic surfactants, such as quaternary ammonium compounds and DOSS, are often involved in the modification of nanoclay; this may have toxic effect on the environment (Li and Brownawell, 2010; Mulligan et al., 2001). In comparison, the modification of nanoclay with nonionic surfactants (such as Tween 80), as opposed to their ionic counterparts, is more environmentally friendly (Biswas et al., 2019). However, recent research has mainly focused on the use of surfactant-modified nanoclay for pollutant adsorption, while its potential for oiled shoreline cleanup was not comprehensively studied.

Therefore, the aim of this study is to develop a green and responsive washing fluid with nonionic surfactant-modified nanoclay to remove the oil from beaches. First, the modified nanoclay was characterized using a series of analytical methods to investigate the changes in its structural, chemical, and surface properties. Batch surface washing tests were then conducted to study the effects of the operational parameter (washing rate) and environmental conditions (temperature, salinity, pH, and nanoclay concentration) on sand cleanup. Factorial analysis was conducted to analyze the contributions of both individual effects and two-level interactions to the overall performance. After washing the oiled sand, the nanofluid effluents were further treated with calcium chloride to separate the oiled nanoclay from water. The thermodynamic miscibility model was also used to explore how concentration and temperature influenced oil/water miscibility in the presence of the modified nanoclay.

4.2. Materials and method

4.2.1. Materials and chemicals

Both the nanoclay (hydrophilic bentonite) and the food-grade nonionic surfactant (Tween 80) were purchased from Sigma Aldrich (ON, Canada). Shell Rotella® T4 conventional diesel engine oil (15W40) was used as the representative oil in all tests; its physical properties are given in Table 4-1. Standard washed and ignited sand (30-40 mesh) was provided by Millipore Sigma (Oakville, Canada). Other chemicals, including sea salt, hydrochloric acid (HCl), and sodium hydroxide (NaOH), were also obtained from Sigma Aldrich (ON, Canada). Analytical grade hexane was purchased from Fisher Scientific (ON, Canada). Deionized water was used in all batch tests.

Table 4-1 Physical properties of Shell Rotella® T4 conventional diesel engine oil.

Shell Rotella®	T4	conventional	diesel	engine	oil	(15W40)

Туре	Diesel engine oil
Density (g/cm ³)	0.88
API°	29.3
Fresh Viscosity (cP)	257.08
Weathered Viscosity (cP) (7 days)	258.60

4.2.2. Modification of nanoclay with the nonionic surfactant

First, three grams of nanoclay were mixed with 50 mL deionized water; ultrasonic treatment was then conducted until the nanoclay was thoroughly dispersed. Three grams of Tween 80 were mixed with 50 mL deionized water and then added into the nanoclay dispersion. The resulting mixture was shaken at 300 rpm at 20°C for 48 h. After that, centrifugation with 10000 rpm was conducted for 20 min to recover the nonionic surfactant-modified nanoclay from the mixture. The resulting precipitates were then washed three times with deionized water to remove residual surfactant. The solids were then put into an oven and dried at 60°C for 24 h. Finally, the resulting nanoclay was ground and sieved to pass through a 200 mesh to get the modified nanoparticles.

4.2.3. Batch surface washing tests and factorial design

The engine oil was weathered within a hood at 20°C for 7 days; the result showed that there was no evaporation loss during the weathering process. The aged engine oil (oil/sand ratio: 0.5 g / 100 g) was dissolved in hexane and then mixed with sand for the preparation of oiled substrates. The mixture was homogenized for 10 min in an ultrasonic bath before the

hexane was evaporated in a hood at room temperature for 24 h. The oil sand was stored in a closed container prior to application (within 72 h). The modified nanoclay was used to form stable dispersions with ultrasonicator (30% amplitude) for 30 min. All batch tests were conducted in 20 mL glass vials, in which there was 1 g oiled sand and 15 mL modified nanoclay dispersions. Surface washing was then conducted by putting capped vials in the New Brunswick Innova 42R Incubator Shaker (Eppendorf, Connecticut, USA) at 300 rpm for 24 h. The liquid was then decanted and 15 mL of hexane were added to extract the residual oil from the sand for later analysis.

Factorial design is frequently used to explore the influences of parameters and their interactions on the cleanup processes (Bi et al., 2020; Chen et al., 2021c; Liu et al., 2020). Herein, a full 2⁴ factorial experiment design was performed to assess the effects of four environmental factors (temperature, salinity, pH, and modified nanoclay concentration) and their interactions on the washing efficiency of the modified nanoparticles. There were 16 test runs, all of which were conducted in triplicate. As shown in Table 4-2, the upper and lower levels of each factor were denoted by "1" and "-1", respectively. The oil removal efficiency of the modified nanoclay under different variables was the response of the factorial design.

Symbol	Fastar	11	Level			
	Factor	Units	Low (-1)	High (+1)		
А	Temperature	°C	5	25		
В	Salinity	wt%	0.5	3.5		

Table 4-2 Experimental variable factors for modified nanoclay dispersion.

С	рН		4	10
D	concentration	mg/L	100	800

4.2.4. Responsive separation of washing effluent

Ten grams of the aforementioned oiled sand were put into a conical flask, and 150 mL of stable nanofluid at 800 mg/L were mixed with the sand at 300 rpm for 24 h to remove the stranded oil. Then, 15 mL of washing effluent were poured into the vials, and the concentrations were adjusted with the addition of calcium chloride at 0, 0.1, 0.2, and 0.3 M. After 3 and 24 h, the turbidity and oil concentration of the supernatant at different calcium chloride concentrations were measured. The micromorphology of sediment aggregation (the settled oiled nanoclay) at the bottom of the vials was also studied.

4.2.5. Analytical methods

The zeta potentials of raw and modified nanoclay suspensions at different salinities and pHs were measured using a Malvern Zetasizer Nano ZS (Malvern Instruments, Worcestershire, USA) at 25°C. X-ray diffraction (XRD) analysis of the crystalline structures of the samples was conducted using a Philips X' Pert PRO diffractometer (Almelo, Netherlands) with Cu-K α radiation in 2 θ mode from 10° to 120°. The surface morphologies of the pristine and functionalized nanoclay were characterized by a Hitachi S-3400N scanning electron microscope (SEM, Tokyo, Japan), and energy dispersive spectroscopy (EDS, JEOL-JMS 5310 LV) was carried out to determine the elemental compositions of the samples. Fourier transform infrared spectroscopy (FTIR) was carried out using the Invenio S FTIR spectrophotometer (Bruker Optics, Ettlingen, Germany) in the wavenumber range 4000 – 400 cm⁻¹ to identify the functional groups and structural changes of the modified nanoclay. Thermogravimetric analysis (TGA) was conducted

using a Q500 Thermogravimetric Analyzer (Lukens Drive, Delaware, USA) under a nitrogen atmosphere from 30 to 1000°C with a heating rate of 10°C/min. The oil concentrations were determined with a UV–Visible spectrophotometer (Agilent Cary 3500, USA) at a wavelength of 284 nm. The ORION AQ3010 turbidimeter (Thermo Scientific, Canada) was used to determine the turbidity of the washing fluid. The micromorphology of the sediment in the washing effluent was obtained using a fluorescence microscope system (ESC-350, ACCU-SCOPE, USA).

4.2.6. Miscibility modelling

From a thermodynamic point of view, a miscible blend that typically satisfies the free energy of mixing (ΔG) is less than or equal to zero while its second derivative value regarding its composition $(\frac{\partial^2 \Delta G}{\partial \phi^2})$ is greater than zero (McGlashan, 2007). A theoretical model based on the Flory-Huggins theory was developed and is widely applied to solvent/solvent and solvent/polymer mixtures in many chemical processes (Flory, 1942; Huggins, 1942). This theory has also been reported to be valid for chain-like alkanes and water (Haji-Akbari et al., 2015). The equation can be expressed as follows:

$$\Delta G = \chi_{12} R T \phi_1 \phi_2 + R T (n_1 \ln \phi_1 + n_2 \ln \phi_2)$$
(1)

where χ_{12} is the parameter of the Flory–Huggins interaction; R is the universal gas constant; T is the temperature; ϕ_1 and ϕ_2 are the respective molar concentrations of the components 1 and 2; and n_1 and n_2 are the respective molecule numbers of components 1 and 2. However, the conventional Flory-Huggins theory cannot sufficiently address the system in the presence of nanoparticles. Zhang et al. (2018) therefore developed a systematic thermodynamic model to examine the effects of surfactant modified nanoparticles on the miscibility of oil-water system. The free energy of mixing for the system, with addition of the modified nanoclay, is defined as:

$$\Delta G = \Delta G_{\rm flu} + \Delta G_{\rm np} \tag{2}$$

where ΔG_{flu} is the free energy from the interaction between the water phase and the modified nanoclay and ΔG_{np} is the free energy from the contribution of the modified nanoclay. The addition of the nanoclay changed the characteristics of the water phase but had almost no effect on the oil phase, and so the influence of the oil phase on the system was considered small. Therefore, free energy between water and oil can be ignored and Equation (2) can be presented as follows:

$$\Delta G_m = \frac{\phi}{v_p} (1 - \phi) p(\frac{r_{\rm NP}}{r_0}) \frac{3r_{NP}^2}{2\sqrt{v_1 v_2} r_0^2} + \chi_{\rm flu} \phi(\frac{r_0}{r_{\rm NP}}) (1 - \phi) + \frac{\phi}{v_p} [ln \phi + p(\frac{r_{\rm NP}}{r_0}) \frac{4\phi - 3\phi^2}{(1 - \phi)^2}]$$
(3)

where ϕ is the weight fraction of the modified nanoclay; $r_{\rm NP}$ is the radius of a single nanoparticle; r_0 is the monomer radius; v_p , v_1 , and v_2 are the volume of a single nanoparticle, surfactant, and water, respectively; and $\chi_{\rm flu}$ is the parameter of the Flory– Huggins interaction between water and nanoparticles. This equation assumes that the modified nanoclay is spherical and hydrophilic when the model is applied to pure water (no change in salinity). Detailed information on this thermodynamic model is presented elsewhere (Zhang et al., 2018).

4.3. Results and discussion

4.3.1. Characterization of nonionic surfactant-modified nanoclay

The XRD patterns of the nanoclay before and after the modification by the nonionic surfactant are presented in Figure 4-1 (a). The measurements for raw nanoclay showed some obvious reflection peaks at 6.01°, 19.78°, and 34.95°, corresponding to the d₀₀₁, d₁₀₀,

and d₀₀₆ basal planes, which are characteristics of the Na-montmorillonite structure (Ramil et al., 2020). The main component of this nanoclay is implied to be Na-montmorillonite. Post-modification, the basal spacing of d₀₀₁ increased from 14.549 Å to 16.446 Å, indicating structural changes in the nanoclay, which was attributed to the fact that the nonionic surfactant intercalated into the interlayer space of the nanoparticle (Nourmoradi et al., 2012).

FTIR characterization is a useful tool for indicating the presence of nonionic surfactant in the nanoclay. As shown in Figure 4-1 (b), both raw and modified nanoclay were examined with the FTIR, and they both displayed the typical absorption bands of montmorillonite. The peak at 3617 cm⁻¹ was related to the structural -OH stretching vibrations in the Al-OH and Si-OH of the nanoclay (Putra et al., 2009). The sharper absorption at 1645 cm⁻¹ was the result of the deformation vibrations of the interlayer water molecules (Alkaram et al., 2009). The IR band observed at 996 cm⁻¹ was due to the stretching vibration of Si-O groups, while the band of 515 cm⁻¹ was attributed to the typical bending vibrations of layered Al-O-Si networks (Eren et al., 2009). However, in addition to the above characteristic bands, some new absorption bands were observed in the modified nanoclay. The peaks at 2927 and 2848 cm⁻¹ in the spectra of the treated nanoclay were attributed to the asymmetric and symmetric stretching vibrations of C-H group in the methylene groups; their bending vibrations were observed at 1468 cm⁻¹ (Moslemizadeh et al., 2016). The new absorption band at 1345 cm⁻¹ corresponded to the plane vibration of the -OH groups (Tunc and Duman, 2008). The appearance of new peaks indicated that the surfactant was successfully intercalated in the layers of the nanoclay.

The TGA test was conducted for both raw and modified nanoclay to examine whether the surfactant had been loaded onto the nanoclay; the results are shown in Figure 4-1 (c). The

TGA profiles of pristine nanoclay showed a mass loss of 8.44% between 30 and 160°C, which was due to the removal of moisture from the surface and the crystal lattice (Dos Santos et al., 2018). However, the mass loss of modified nanoclay was only 3.67% in the same temperature range, indicating that moisture contents decreased as the surfactant was successfully intercalated into the nanoclay (Hojiyev et al., 2017). The mass loss of 2.71% for raw nanoparticles with temperature change from 160 to around 700°C was due to the dehydration of coordinated water and the dehydroxylation of the crystal network (Baxter et al., 2018). In this stage, the nanoclay loaded with nonionic surfactant had obvious influences on the TGA profile. Firstly, its mass loss decreased slightly until the temperature reached around 300°C. As the temperature further increased to around 500°C, the mass of the modified nanoclay decreased steeply due to the thermal degradation of the surfactant (Owoseni et al., 2014). The mass weight values for both nanoclays gradually approached a constant as the temperature continued to increase from 700 to 1000°C, corresponding to the organic carbonaceous residues (Xie et al., 2001). The mechanism of mass loss implied that the surfactant was loaded onto the nanoclay.

SEM measurement was also performed to study the surface morphology of both the pristine and modified nanoclay. As shown in Figure 4-1 (d) and (e), their surfaces greatly varied and showed irregular structures with different size distributions. Without the modification of the surfactant, the nanoclay presented a relatively more massive and aggregated morphology as well as a greater surface area (Figure 4-1 (d)). In comparison, the modified nanoclay showed less agglomeration but smoother surfaces, and there were many tiny flakes with severely crumpled structures (Figure 4-1 (e)). These observations imply that the interlayer of the nanoclay was expanded and intercalated with the surfactant. EDX analysis was carried out as well to investigate the composition of both nanoclays (Figure 4-1 (f)). The major elements of the raw nanomaterial were Si and O, at 24.88 and 50.15%, respectively. However, the attached surfactant on the nanoclay increased C compared to Si to become the second largest component at about 23.06%. The changes in composition further indicated that the surfactant successfully modified the nanoclay.



Figure 4-1 XRD patterns (a), FTIR spectra (b), TGA thermograms (c), SEM images (d, e), and EDX weight percentage of elements (f) for pristine and modified nanoclay.

4.3.2. Batch surface washing tests under different conditions

(Effect of washing time) Washing time is a key parameter in batch surface washing tests as it directly affects both the oil removal efficiency and the energy consumption during the washing process. It is therefore necessary to explore the optimum washing time. As shown in Figure 4-2, the rate of oil removal at 20°C, salinity of 0 wt%, pH 7, and the nanoparticle dose of 800 mg/L presented a rapid growth from 22.5 to 71.1% as the washing time increasing from 0.5 to 24 h. This may be due to the greater availability of binding sites on the surface of modified nanoclay related to hydrophobic interactions between engine oil

and nonionic surfactant tails (Nourmoradi et al., 2012). After that point, washing time had only a slight effect on the oil removal efficiency of this surface washing process, as the percentage of removed oil increased by just 7% over the next 24 h. On one hand, the available active sites on the surface of the modified nanoclay declined significantly during the first 24 h due to the fact that most of them were already occupied by engine oil (Shirzad-Siboni et al., 2015). On the other hand, the remaining binding sites also became harder to access due to the repulsive forces both between oil molecules on the modified nanoclay and between the previously discussed molecules and oiled sand in the bulk phase (Kyzas et al., 2012). Therefore, the washing time of 24 h was selected for the following batch experiments.



Figure 4-2 Effect of washing time on oil removal efficiency.

(Effect of temperature) Temperature is a key factor which can affect the transport and behavior of pollutants (Yu et al., 2020; Zhao et al., 2017). Hence, in this study, the effect of temperature on the oil removal efficiency of the modified nanoclay was determined by increasing the temperature from 5 to 30°C for a washing time of 24 h, salinity of 0 wt%, pH 7, and the nanoparticle dose of 800 mg/L; the data are presented in Figure 4-3. It is obvious that the percentage of removed oil showed a significant increase from 44.2% at 5°C to 71.4% at 20°C. This may be due to the swelling effect within the internal structure of the modified nanoclay, the rapid rate of oil molecular diffusion, and the reduced van der Waals forces between organic pollutants and their substrates at higher temperatures (Li et al., 2018b; Wang et al., 2019a). Another explanation is that the increased temperature reduced the thickness of the boundary layer surrounding the nanoparticles, meaning that the mass transfer resistance of the engine oil also declined, which was beneficial for oil removal (Aytas et al., 2009). As the temperature further increased from 20 to 30°C, there was only a marginal increase in oil removal efficiency, under 4%. This may be because the adsorptive force between the active nanoparticle sites and the engine oil was weakened as the temperature continued to increase. Overall, a higher temperature led to a higher oil removal efficiency. Changes in temperature also could influence the viscosity of the nanofluid, which could therefore affect oil removal. Thus, viscosity changes in nanoparticles were measured as a function of temperature (Figure 4-4). The results showed that the increase in temperature led to a decrease in the viscosity of the nanofluid. This reduction in viscosity would mitigate the sorption between the modified nanoclay and the sand, resulting in the release of more engine oil (Li et al., 2017a).



Figure 4-3 Effect of temperature on oil removal efficiency.



Figure 4-4 The effect of temperature on viscosity of the nanofluid.

(Effect of salinity) The washing process is usually conducted with nearshore sea water, making salinity an important factor for consideration during the surface washing process. In the current study, batch tests were performed at a washing time of 24 h, temperature of 20°C, pH 7, and the nanoparticle dose of 800 mg/L to study how salinity affected the washing capacity of the nanofluid. As shown in Figure 4-5, the increment of salinity on modified nanoclay fluid enhanced oil removal to a greater or lesser extent. Within the salinity range of 0.5 to 1.5 wt%, the nanofluid showed a higher level of oil removal efficiency. In fact, up to 83% of the oil was released from the sand surface at 1 wt% salinity. However, when the salinity increased further, the oil removal percentage showed a slightly decline from 79.5 to 76.4%; this was still higher than the oil removal percentage for fresh water (around 70%). Anirudhan and Ramachandran (2014) reported similar results with
higher NaCl (the primary component of sea salt) concentrations yielding higher pollutants removal. Based on the surface chemistry, the existence of electrolytes like NaCl could greatly compress the electric double layer, creating a beneficial environment for the engine oil and modified nanoparticles to approach each other, resulting in increased oil removal efficiency (Manohar et al., 2002). The zeta potential values of the nanofluid in the presence of various salinity conditions were also measured (Figure 4-5); the zeta potential was - 36.57 mV without sea salt. However, its value experienced a sharp increase to under -8 mV once sea salt was added. With the increase of salinity from 0.5 to 4 wt%, the overall slight decrease can be seen in the values of zeta potentials, which varied from -7.34 mV to -3.64 mV. Low zeta potentials indicated a decrease in repulsive molecular force and the formation of aggregation; the former can enhance the oil's interaction with nanoparticles while the latter would reduce the number of binding sites on the surface area, thus inhibiting oil removal. The high oil removal efficiency found at various salinities is an advantage of applying such cleanup by shores.



Figure 4-5 Effect of salinity on oil removal efficiency.

(Effect of pH) The pH of the modified nanoclay fluid is an another important factor in surface washing, as it may affect the pollutant transport (An and Huang, 2012; Yin et al., 2021). Herein, the effect of aqueous phase pH on oil removal efficiency was investigated over the pH range 3-11 while keeping other conditions at a washing time of 24 h, temperature of 20°C, salinity of 0 wt%, and the nanoparticle dose of 800 mg/L. It can be seen from Figure 4-6 that there were two peak values for oil removal efficiency at 72.8 and 82.4%, which correspond to the pH 3 and 11. Other studies have reported the similar results when using organo-clay for anionic pollutant removal (Baouch et al., 2020). To better understand this phenomenon, the zeta potential of the modified nanoclay fluid at different pH levels was also tested. It is an indicator to reflect the electrokinetic properties of the nanoparticle surface. As shown in Figure 4-6, the zeta potential values of nanofuild were

negative over the entire pH range. At pH3, the nanoparticle surface was much less negatively charged (-15.73 mV) because the existence of abundant protons make the negatively charged sites (Si-O⁻) and silanol groups (Si-OH) on modified nanoclay more protonated, forming Si-OH₂⁺ (Chen and Zhao, 2009). Therefore, electrostatic repulsion between the oil adhered to the sand and the modified nanoclay can be reduced via proton neutralization in the bulk phase, resulting in high oil removal efficiency. As the pH increased, the modified nanoparticles became more ionized as well as negatively charged, making it more difficult for oil droplets with negative charges to reach the binding sites on the nanoparticles, causing lower oil removal (Brito et al., 2018). However, it is worth mentioning that the washing efficiencies of the nanofuild increased from 66.3 to 82.4% when pH values were greater than 8. This may be due to the dominance of other processes, including hydrogen bonding, ion-dipole interactions, and hydrophobic partitioning (Anirudhan and Ramachandran, 2014).



Figure 4-6 Effect of pH on oil removal efficiency.

(Effect of modified nanoclay concentration) To explore the effects of modified-nanoclay concentration on oil removal efficiency, batch experiments were carried out; other parameters remained the same (washing time of 24 h, temperature of 20°C, salinity of 0 wt%, pH 7) while the modified nanoclay concentration was increased from 0 to 1600 mg/L, and the results are shown in Figure 4-7. Overall, the percent of oil removed from sand increased from 48.6 to 72.2% as the concentration of modified nanoclay increased. The high oil removal efficiency can be explained by the extra active sites afforded from more modified nanoparticles. More specifically, larger amounts of modified nanoclay could provide greater surface area, resulting in an increase of available binding sites on the nanoparticles' surfaces, which can absorb more engine oil, achieving high removal efficiency (Dos Santos et al., 2018; Yin et al., 2021). Previous studies have reported that

surface tension could be affected with changes in nanofluid concentration (Estellé et al., 2018). Therefore, the surface tension of the modified nanoclay fluid was measured throughout the above concentration range. It also can be seen from Figure 4-7 that there is an opposite trend in the surface tension, decreasing from about 73 mN/m at 0 mg/L to around 44 mN/m at 1600 mg/L. The reduction in surface tension with the increase in the modified nanoclay concentration is favorable for oil removal. However, at higher concentrations (above 800 mg/L), oil removal efficiency slightly increased, by around 2%, and then became stable. This phenomenon may be attributed to the fact that the aggregation of nanoparticles formed with increasing concentrations, reducing the total surface area of the modified nanoclay and limiting further increases in oil removal efficiency. Hence, the particle size distribution of modified nanoclay suspension at different concentrations was characterized (Figure 4-8). At 800 mg/L, the test sample had a good dispersion with only one size peak at 513.3 nm. However, when the concentration was increased to 1600 mg/L, there was an additional size peak at 2590 nm, indicating that the aggregation of the modified nanoclay occurred and inhibited the effectiveness of nanoparticle.



Figure 4-7 Effect of modified nanoclay concentration on oil removal efficiency.



Figure 4-8 Size distribution of the modified nanoclay dispersion at 800 and 1600 mg/L.

4.3.3. Factorial analysis of washing influencing factors

The environmental processes can be impacted by various factors and their interactions (He et al., 2020a; Shen et al., 2017; Stampoulis et al., 2020). This study showed that the

efficiency of modified nanoclay in the removal of oil can be affected by various factors, including temperature, salinity, pH, and nanoclay concentration. All above factors may have effects on the final amount of oil removal, but higher order interactions would be less necessary (Li et al., 2011). Therefore, two-level factorial analysis was performed to investigate the statistical significance of both single parameters and the interactions between several parameters in terms of the oil removal efficiency of the modified nanoclay. The relationship between the responses of four variables (A, temperature; B, salinity; C, pH; D, modified nanoclay concentration) was given by the following polynomial equation:

Oil removal efficiency (%)=57.53+4.68A+14.64B+5.17C+6.09D-2.22AB+0.3519AC-0.7819AD-1.13BC+1.60BD+0.4456CD (4)

The points of residuals demonstrated an approximately straight line, illustrating that the experimental data showed the fitness of this model (Figure 4-9). As shown in Table 4-3, ANOVA was conducted to assess the significance of the model and quantify the contributions of the individual factors as well as their two-level interactions to the response. The model was clearly significant, as the F-value and P-value were 143.93 and <0.0001, respectively. The R² of 0.9992 demonstrated that the factorial regression equation was highly reliable. It showed that all single factors (A, B, C, and D) as well as the interactions of temperature with salinity (AB) and salinity with modified nanoclay concentration (BD) had significant effects on the response.



Figure 4-9 Normal plot of residuals on oil removal efficiency.

Source	Sum of	Degree of	Mean	F-value	P-value	Standardized	Contribution
	square	freedom	square			effects	(%)
Model	4954.71	10	495.47	143.93	< 0.0001		
А	350.91	1	350.91	101.93	0.0002	9.37	7.06
В	3427.22	1	3427.22	995.57	< 0.0001	29.27	68.93
С	427.35	1	427.35	124.14	0.0001	10.34	8.60
D	594.26	1	594.26	172.63	< 0.0001	12.19	11.95
AB	78.54	1	78.54	22.82	0.0050	-4.43	1.58
AC	1.98	1	1.98	0.5755	0.4823	0.70	0.04
AD	9.78	1	9.78	2.84	0.1527	-1.56	0.20

Table 4-3 ANOVA for a full factorial model on oil removal with modified nanoclay

BC	20.36	1	20.36	5.92	0.0592	-2.26	0.41
BD	41.12	1	41.12	11.94	0.0181	3.21	0.83
CD	3.18	1	3.18	0.9230	0.3808	0.89	0.06
Residual	17.21	5	3.44				
Cor total	4971.92	15					

As shown in Table 4-3 and Figure 4-10, all four individual factors had positive effects on the oil removal efficiency of the modified nanoclay, with salinity (B) being the most significant, offering the largest contribution (68.93%) to the overall system. This means that the salty nanoparticle fluid is favorable for washing, because the reduction of fluid zeta potential resulted in a decrease in repulsion but an increase in the interactions between the oil and nanoparticles. Therefore, using seawater along with the modified nanoclay in washing to achieve higher oil removal from substrates showed good performance. Nanoparticle concentration (D) was the second largest model term, but its contribution was only 11.95%, much smaller than that of salinity. This indicated that an appropriate concentration increase in real-world applications could improve the effectiveness of the modified nanoclay in removing oil. However, as previously discussed, a concentration that is too high may lead to only a slight increase in oil removal, as the nanoclay would aggregate and reduce its surface area, limiting further increases in removal efficiency. The factors of temperature (A) and pH (C) also had positive and significant effects on the response, but only contributed 7.06 and 8.60% to the overall performance. In applications, however, a limited enhancement of treatment efficiency could be associated with high energy consumption for increasing the fluid temperature, and adjusting fluid pH to become either extremely acid or extremely basic could cause some other risks.



Figure 4-10 Main effects and significant interactive effects of influencing factors on the oil removal efficiency.

The significant two-level interactions are presented in Fig. S4 (f) and (e); the non-parallel lines mean that the two parameters showed some interactive effects (Chen et al., 2019b; Wang et al., 2018). As can be seen, only the interactive effects of temperature with salinity (AB) and salinity with modified nanoclay concentration (BD) were significant for oil removal efficiency; their contributions to the overall system were only 1.58 and 0.83%, respectively, much less than those of the four main effects. The interaction of temperature and salinity had a negative influence on the effectiveness of the modified nanoclay, as the effect of temperature became less remarkable at higher levels of salinity. Additionally, the value of the oil removal percentage remained relatively stable, at around 70%, in high salinities as the temperature increased, which suggested that salinity played a more important role in removing oil than temperature. This is consistent with the above data indicating that salinity offered the largest contribution. It also implied that raising the temperature at high salinities during the washing process may be not a good way to enhance the oil removal. The increase of salinity and the nanoparticle concentration exhibited positive interactive effects on the treatment response. As the nanoclay concentration increased from 100 to 800 mg/L, the slope of the relationship between salinity and oil removal efficiency increased. It indicated that the presence of more nanoclay could further enhance the treatment response as the salinity varied from low to high. This phenomenon might be attributed to the joint effects of more available binding sites and the reduction of the repulsion between oil and nanoparticles. Other effect plots of no or insignificant interactions are shown in Figure 4-11. It is obvious that the lines for temperature with pH (AC) and pH with concentration (CD) were almost parallel, meaning that no interactions occurred. The two-level interactions of temperature with concentration (AD) and salinity with pH (BC) had negative influences on the model response; their contributions to the performance of the modified nanoclay were only 0.20 and 0.41%, respectively, and both



P-values were above 0.05, indicating that the two model terms were insignificant.

Figure 4-11 Insignificant effects of two-level interactions on oil removal efficiency.

4.3.4. Ionic strength-responsive separation of washing effluent

After the washing process, the effluents need be treated to separate the modified nanoclay with engine oil from the water to avoid secondary pollution. Ionic strength-responsive separation is featured by good efficiency and easy operation (Zhou et al., 2020). In the present study, the ionic strength of effluent was adjusted with calcium chloride, and the

separation results are given in Figures 4-12 and 13. The turbidity of the washing fluids was measured for evaluating the separation efficiency. The initial turbidity ranged from 850 to 857 NTU, indicating that the nanoclay fluids were homogeneous and turbid. After 3 h, as shown in Figure 4-12 (a), the supernatant turbidity of the washing effluent decreased to 788 NTU without the addition of calcium chloride, while those of effluents with additional 0.1, 0.2, and 0.3 M calcium chloride exhibited dramatic reductions to 19.2, 16.8, and 21.0 NTU, respectively. These photographs also show that the addition of calcium chloride made the supernatant much clearer than it was in the absence of the agent. With no treatment, turbidity remained very high after 24 h, at about 600 NTU, but all supernatants with the addition of calcium alginate became clearer and reached lower levels of turbidity, under 5 NTU (Figure 4-12 (b)). However, no obvious difference was observed with different amounts of the responsive separation agent, indicating that 0.1 M calcium chloride was enough to effectively aggregate the suspended matters for later treatment; its efficiency in terms of turbidity reduction was more than 99%. This significant decrease in turbidity was attributed to the fact that the addition of calcium chloride increased the ionic strength of the solution, causing the compression of the diffused layer associated with the oiled nanoparticle (Mui et al., 2016). Therefore, the zeta potential on the surface decreased and the repulsions between the oiled nanoclay diminished, meaning that the van der Waals forces played a major role and made the suspended matter attract and form aggregations at the bottom (Matusiak et al., 2021; Teh et al., 2016).



Figure 4-12 The turbidity and photographs of the supernatant with different dosages of

calcium alginate after 3 h (a) and 24 h (b).

The oil concentrations of the supernatant and the aggregations of oiled nanoclay at the bottoms of vials with various amounts of calcium chloride were investigated after 3 and 24 h (Figure 4-13). After 3 h, the oil concentration for the non-treated fluid was around 165 mg/L; the other three fluids showed much lower oil concentrations in the supernatants, about one fifth as much as that of the fluid without calcium chloride. The oil concentrations of all four supernatants, both with and without the calcium chloride, continued to decrease after 24 h. However, only a 16.1% reduction was seen from the nanoclay fluid that received no treatment. The calcium chloride enabled the supernatant to reach very low levels of oil concentration, especially in the 0.3 M calcium chloride (5.33 mg/L). This suggested that the released oil from the sand was adsorbed on the modified nanoclay, and the presence of the divalent cation decreased the stability of the oiled nanoparticles and led to a much more effective aggregation, reducing the oil concentration in the supernatant (Schaumann et al., 2015). The microscopic images of the sediments are presented in Figure 4-13, and it is obvious that the particle sizes were still well distributed in absence of calcium chloride, even after 24 h, though they showed a higher particle density. The addition of calcium chloride made the oiled nanoclay form larger and more irregular aggregations that quickly settled to the bottom. The dose of calcium chloride affected the morphology of the sediments, especially during the first 3 h, with similar spheres for 0.1 M, irregular flocs for 0.2 M, and different rods for 0.3 M. As time further increased to 24 h, the differences in the morphology of the precipitations gradually diminished as more and more oiled nanoclay aggregated and settled to the bottom, with previously settled flocs.



Figure 4-13 The oil concentrations of the supernatant and microscope images of the

sediments with different dosages of calcium alginate after 3h (a) and 24 h (b).

4.3.5. Miscibility modeling for washing fluid with modified nanoclay

Miscibility is a critical state of the system and its main characteristic is homogeneity (Sharma, 2005). A high degree of fluid miscibility is closely related to better interphase mass transfer (Ayirala and Rao, 2006). Therefore, the miscibility of the modified nanoclay fluid directly affected the effectiveness of nanoparticles with high miscible state yielding high oil removal efficiency. To explore how the modified nanoclay contributed to this fluid miscibility, the aforementioned thermodynamic model was applied to describe oil/water miscibility in the presence of nanoparticles. As shown in Figure 4-14, the free energy of mixing for the system with the addition of nanoclay was calculated with concentrations ranging from 50 to 1600 mg/L and a temperature range of 5 to 30 °C. The miscibility state was greatly enhanced as the concentration of the modified nanoclay increased to about 1200 mg/L. After that, further increases in the nanoparticle concentration kept the system miscibility stable, and possibly led to detrimental effects. This is consistent with the batch test results for concentrations; oil removal efficiency especially showed almost no change as the concentration of nanoparticles increased from 1200 to 1600 mg/L. Overall, it can be inferred that the addition of the modified nanoclay within a certain value had positive effects on fluid miscibility of the system. Additionally, the contribution of temperature to the miscible state may not be as large as that of concentration, but it still cannot be neglected in this system. As temperature increases, the absolute values of the free energy of mixing become larger, implying increases in the fluid miscibility of the system. More specifically, higher temperature ranges were observed to be more beneficial to the miscibility state as compared to lower temperature ranges, as in the comparison between the cases of 5-15 °C and 15-25 °C. The results of the miscibility modeling and batch surface washing tests are in good agreement, and this thermodynamic model considering the presence of modified

nanoparticles could provide a theoretical support for understanding the effects of concentration and temperature.



Figure 4-14 Calculated free energy of mixing with the modified nanoclay concentrations at temperatures from 5 to 30°C.

4.4. Summary

This is the first time that nonionic surfactant-modified nanoclay was used as a green and responsive washing fluid in oil spill remediation. The analysis, based on the increased basal spacing (d₀₀₁) in XRD, the emergence of new peaks in FTIR, the thermal degradation of surfactant in TGA, morphology changes in SEM, and varying element weight percentages in EDX, indicated that the surfactant was successfully loaded onto the nanoclay. The effectiveness of the washing nanofluid was impacted by the single factors of washing time, temperature, salinity, pH, and modified nanoclay concentration. Two-level factorial analysis revealed that salinity was the most significant factor, contributing 68.93% to the

response. It also indicated that the interactions of temperature with salinity and salinity with modified nanoclay concentration were significant. Ionic strength-responsive separation was performed with the addition of calcium chloride, which dramatically reduced the turbidity and oil concentration in the supernatant for subsequent treatment. In addition, the results of thermodynamic miscibility modelling also showed the good agreement with experimental results. Overall, the nonionic surfactant-modified nanoclay has great potential in terms of oil cleanup, offering a desirable alternative to the existing washing agents. Further study is expected to access its effectiveness in large-scale applications under complicated environmental conditions.

CHAPTER 5. A FRAMEWORK FOR THE EVALUATION AND SELECTION OF SHORELINE SURFACE WASHING AGENTS IN OIL SPILL RESPONSE

5.1. Background

Oil exploration, production, transportation, and consumption activities can lead to the occurrence of oil spills with adverse impacts on the socio-economy and ecological resources (Cai et al., 2019; Chen et al., 2019a; Chen et al., 2021c; Fingas, 2016; NRC, 2003; Zhu et al., 2020b). More seriously, once the spilled oil reaches the shoreline, the coastal biota will be heavily affected by the stranded oil (Deis et al., 2017; Goovaerts et al., 2016; Wang et al., 2020). Compared with offshore spill response, shoreline cleanup operations typically are much more difficult, complicated, laborious, and expensive (Etkin, 2000; Tarpley et al., 2014; Ye et al., 2020). ECCC (2016) classified the shoreline cleanup countermeasures into categories of natural recovery, physical washing or removal, physical in-situ treatment, and chemical or biological treatment. As a form of a chemical treatment method, the application of surface washing agents is done to lift, but not disperse, the stranded oil to the water surface for follow-up recovery (Bi et al., 2020; Fingas, 2013). Some surface washing agents can also accelerate the natural attenuation of oil adhered to the substrate through the addition of bioremediation enhancers. It is necessary to study this technique in depth for better coping with shoreline oil spills.

Previous studies mainly focused on the evaluation of surface washing agents in laboratories and their application in experimental field-scale projects or in actual shoreline oil spill responses. A series of effectiveness testing protocols, including Inclined Trough test, Rotary Mixer method, Swirling Coupon test, Glass Plate test, and Natural Substrates method, were developed in laboratories to quantify the amounts of different oils lifted from various substrates treated with surface washing agents (Clayton et al., 1995a; Fieldhouse, 2012; Fingas et al., 1990; Guenette and Fieldhouse, 1998; Koran, 2007). Besides, the U.S. EPA Baffled Flask Test (BFT) was used to measure the dispersion properties of surface washing agents (Sorial et al., 2004). This method was further modified by Fieldhouse (2008) to test these agents under higher energies. Complementary field-scale experiments for using surface washing agents have also been conducted. For example, Corexit 9580 was tested for its ability to remove Dilbit crude oil from rock tiles (Taylor et al., 2014). In terms of surface washing agent treatment for actual spill response, it began with the application of PES-51 and Corexit 9580 on the oiled shoreline in the Exxon Valdez spill, and the application was reported to be successful (Fiocco et al., 1991). Corexit 9580 was successfully used during response to the Westridge spill in Burrard Inlet as a final treatment action to remove the coat to trace of Albian Heavy synthetic crude oil from a cobble-pebble shoreline (Shang et al., 2012; Stantec, 2012). Besides, commercial surface washing agent products were also used in some other oil spill incidents, such as Morris J. Berman oil spill, Cosco Busan oil spill, and Deepwater Horizon oil spill (Ford et al., 2009; Zengel and Michel, 2013).

Surface washing agents have been used on a limited basis for shoreline cleanup and the approval for their application is required from incident-specific agencies (Michel et al., 2001). During shoreline oil spill cleanup process, confirmation of the appropriateness of using surface washing agents and selection of the most suitable one are two critical issues as both of them have direct impacts on decision process, cleanup effectiveness, and coastal environment. Previous literature came up with some criteria or minimum requirements for the use of surface washing agents (NWACP, 2020). A flow chart was also developed by USEPA (2002) to illustrate the specific contexts for desirability of using surface washing agents. However, there is no good tool to illustrate all possible scenarios in which surface washing agents may be considered given all relevant factors. If surface washing agent

treatment is adopted as a part of shoreline cleanup countermeasures, the next problem will be selection of a suitable product, which is a complicated decision-making procedure. Therefore, it is necessary to propose a systematic evaluation and selection system of surface washing agents in shoreline cleanup.

Surface washing agent selection is a process of inspecting and evaluating potential products from technical, environmental, and economical perspectives in order to determine the best one for the specific conditions of given shoreline cleanup. MCDA techniques have been developed to address similar problems in a wide range of research areas such as energy development and management, solid waste management, supplier selection, site selection, and material selection (Abdullah et al., 2019; Asif and Chen, 2020; Doustmohammadi and Babazadeh, 2020; Kumar et al., 2017; Mardani et al., 2017; Pereira et al., 2019; Sarkkinen et al., 2019; Wu et al., 2018b). However, the MCDA methodology has not yet been applied to the selection of surface washing agents.

In this study, an incident specific evaluation and selection framework for the selection and use of surface washing agents is developed to better cope with oil spills. In detail, the study was (1) to review and illustrate all kinds of shoreline cleanup techniques and their frequent combinations in actual oil spill responses; (2) to develop a decision tree to help responders to determine the possible scenarios for applying surface washing agents by taking oil collectability, shoreline types, oil types and amount, stranded oil position, and removal requirements into account; (3) to come up with a new MCDA method to evaluate surface washing agent products from the perspectives of toxicity, effectiveness, minimal dispersion, demonstrated field tests, and cost to choose the most preferred one; and (4) to illustrate a case study of surface washing agent selection for a particular oil spill and analyzes its results. The evaluation and selection framework for the use of surface washing agents has

significant implications for future shoreline-cleanup decision making.

5.2. Methodology

5.2.1. Research framework

As shown in Figure 5-1, the analytical processes of the study framework can be divided into four stages. In the first stage, the oil spill background was introduced, and then a series of shoreline cleanup countermeasures were summarized according to the literature review. Based on various factors (shoreline characteristics, type/amount/weathering conditions of stranded oil, cleanup requirements), a targeted decision tree was developed to illustrate all possible scenarios for surface washing agent treatment in shoreline response.

After choosing this technique to cope with stranded oil on shorelines, a novel hybrid MCDA model was developed during the second stage to select the most appropriate surface washing agent product. Firstly, the alternatives and criteria for surface washing agent evaluation were defined. Then, the combined weights of criteria were calculated based on objective weights by entropy method and subjective weights by AHP method, and the PROMETHEE was also established. The third stage consisted in combining the PROMETHEE method with entropy-AHP weighting method to rank alternatives. Afterwards, sensitivity analysis was conducted to check the robustness of the model outcome. Finally, the last stage presented the results and discussion of the model and the conclusions of the study were drawn.



Figure 5-1 Analytical processes of the study framework.

5.2.2. Entropy-AHP method

The combined weights of criteria for surface washing agent products evaluation were

calculated through the entropy-AHP method. The integrated weighting method has been widely applied in various fields since it was first used in decision making for ship investment (He et al., 2020b; Yu et al., 2020; Zhong, 2000). Recently, Feizi et al. (2017b) came up with an entropy-AHP approach for assigning weights of factors in mineral potential mapping. This hybrid method was also conducted in the aviation fuel consumption reduction to investigate the comparative importance of criteria (Singh et al., 2019). In addition, Du et al. (2020) proposed this method integrated with extension theory for evaluating and ranking alternatives in heavy-duty machine tool remanufacturing. Compared with either entropy method or AHP method, the entropy-AHP approach could compensate the deficiencies of individual methods to get more reasonable, reliable, and accurate outcomes (Soleimani Damaneh and Zarepisheh, 2009; Zhao et al., 2018). The entropy-AHP weighting method was not adopted in the context of oil spill response for evaluating the performance of surface washing agent products.

(Entropy method for objective weights) The concept of entropy was first introduced into the information theory by Shannon (1948) to quantify the uncertainty of systems. For the decision matrix, the entropy weight can be obtained by calculating the degree of difference and information entropy of the indicators (Kundu and Ghoshal, 2019; Soleimani Damaneh and Zarepisheh, 2009; Wu et al., 2018a). Generally, a greater entropy of an evaluated criteria denotes a smaller weight of the criteria, and vice versa (Aggarwal, 2019). The result of the entropy method is objective and effective as it avoids the human intervention on the weights of criteria (Zhou et al., 2012; Zhu et al., 2020a). However, using this method alone may not accurately reflect the importance of attributes, especially in practical engineering applications (Cui et al., 2018; Zhou and Li, 2020). The calculation steps of entropy weighting method consists of the following steps (Chen, 2019; Kang and Lee, 2007):

1. Establish the decision matrix $D = x_{ij}$ with m surface washing agent products and n

criteria, where i = 1, 2, ..., m; j = 1, 2, ..., x_{ij} is the measured value of j^{th} criterion of i^{th} surface washing agent.

2. Normalize the decision matrix $D = x_{ij}$ into the corresponding matrix $R = p_{ij} \cdot p_{ij}$ is calculated as follows:

$$p_{ij} = \frac{x_{ij}}{\sum_{i=1}^{m} x_{ij}} \tag{1}$$

3. Calculate the entropy of criteria based on the following equation:

$$E_j = -\frac{\sum_{i=1}^m p_{ij} \ln p_{ij}}{\ln m} \qquad (2)$$

where E_j is the entropy value of j^{th} criterion, ranging from 0 to 1 (Zhu et al., 2020a).

4. Calculate the weight of criteria by the following equation:

$$w(e)_j = \frac{1-E_j}{\sum_{j=1}^n (1-E_j)}$$
 (3)

where $w(e)_j$ is the entropy weight value of j^{th} criterion.

(AHP method for subjective weights) AHP is a practical MCDA method which can decompose the decision problem in a form of hierarchical structure with different levels, such as target, criteria, and alternatives (Ossadnik et al., 2016). Pairwise comparisons are performed based on experts' experiences, knowledge, preference and understanding of evaluation systems to derive priorities of criteria and alternatives (Feizi et al., 2017a; Kamaruzzaman et al., 2018). Moreover, a consistency check will be conducted to exclude the inconsistent judgement and increase the credibility of the weights calculated by AHP method (Jain et al., 2018; Si et al., 2020).

The basic calculation steps are summarized as follows:

1. Construct a hierarchical structure by decomposing the surface washing agents evaluation problems into three levels: the goal for suitable surface washing agent selection, the criteria for evaluating the surface washing agent products, and the alternatives to surface washing agent products for evaluation.

2. Apply the pairwise comparison by expert group, and the preferences were standardized using the nine-point scale (Saaty, 1987). A comparison matrix $A = a_{ij}$ was established and expressed as follows:

$$A = \begin{bmatrix} 1 & \cdots & a_{1n} \\ \vdots & \ddots & \vdots \\ a_{n1} & \cdots & 1 \end{bmatrix} \quad (4)$$

where a_{ij} is the relative importance between criterion i to criterion j.

3. Calculate the subjective weight of each criterion based on below equation:

$$w(a)_j = \frac{b_j}{\sum_{k=1}^n b_k} \quad (5)$$

where $w(a)_j$ is the AHP weight value of j^{th} criterion; $b_j = (\prod_{j=1}^n a_{ij})^{\frac{1}{n}}$.

4. Check the consistency of judgment matrix by the following equation,

$$C.R. = \frac{\lambda_{max}}{(n-1)R.I.} \quad (6)$$

where λ_{max} is the maximum Eigen vector; R.I. is the random index. Only if the value of C.R. is less than 0.1, the judgement matrix can be considered consistent and the weights for evaluation criteria can be considered acceptable (Akaa et al., 2016).

(Combination weighting method) The objective weight determined by entropy method and the subjective weight calculated by AHP method are comprehensively considered through the equation (7) to get the combined weights for criteria.

$$w_j = \frac{w(e)_j \times w(a)_j}{\sum_{j=1}^n w(e)_j \times w(a)_j}$$
(7)

where w_j is the combined weight value of j^{th} criterion.

5.2.3. **PROMETHEE method**

The PROMETHEE method, an outranking method of MCDA, was proposed for decision-

making based on pairwise comparisons of alternatives regarding each criteria (Mareschal et al., 1984). With various advantages, this method has been successfully applied in many real-life problems. There are four versions of PROMETHEE method (I, II, III, and IV), and each version has its own characteristics and applicability (Brans and De Smet, 2016; Nikouei et al., 2017). Considering the nature of surface washing agent selection, PROMETHEE II was selected to rank the surface washing agent products because of its characteristic of complete ranking. The application of PROMETHEE II method involves five steps (Behzadian et al., 2010; Vulević and Dragović, 2017):

1. Determine the performance difference of every two surface washing agent products for each criterion by pair-wise comparison based on the following equation (8):

$$d_i(m,n) = p_i(m) - p_i(n)$$
 (8)

where $d_j(m,n)$ is the performance discrepancy; $p_j(m)$ and $p_j(n)$ denote the performance values of alternatives m and n in terms of criterion j.

 Choose the preference function. This function represents a function of discrepancy for each pair evaluation for each criterion as:

$$P_i(m,n) = F_i(d_i(m,n))$$
(9)

where $P_j(m, n)$, ranging from 0 to 1, represents the preference of alternative m over n regarding the criterion j. The closer the value gets to 1, the bigger the difference between m and n is

3. Calculate the global preference index.

$$\pi(m,n) = \sum_{j=1}^{k} P_j(m,n) w_j$$
(10)

where the integrated preference index $\pi(m, n)$ denotes the degree of m is preferred to n for all criteria.

4. Calculate the outranking flows.

$$\emptyset^{+}(m) = \frac{1}{n-1} \sum_{x \in A} \pi(m, x)$$
(11)

$$\emptyset^{-}(m) = \frac{1}{n-1} \sum_{x \in A} \pi(x, m) \quad (12)$$

where n is the number of alternatives; $\phi^+(m)$ and $\phi^-(m)$ denote the outflow and inflow of alternative m, respectively.

5. Calculate the net flow and rank the surface washing agent products

$$\emptyset(m) = \emptyset^+(m) - \emptyset^-(m) \ (13)$$

where $\emptyset(m)$ represents the net outranking flow regarding every alternative. The surface washing agent product with the highest value of $\emptyset(m)$ is the most preferred one.

5.2.4. A novel entropy-AHP PROMETHEE method

In order to address the problem of surface washing agent products selection in oil spill response, a novel MCDA tool by using entropy-AHP weighting method and PROMETHEE II ranking method was developed to prioritize the surface washing agents. The process on how to use the entropy-AHP PROMETHEE method can be summarized as follows:

- 1. Determine the surface washing agent candidates and the corresponding criteria.
- 2. Establish and normalize the decision matrix.
- 3. Calculate the combined weights of criteria based on entropy-AHP method.
- 4. Choose the preference function and calculate the integrated preference index.
- 5. Determine the outflow and inflow of each alternative.
- 6. Obtain the net outranking flow of each surface washing agent product.
- 7. Rank the products according to their net flow values.

5.3. Results and discussion

5.3.1. Possible scenarios for the use of surface washing agents

(Shoreline cleanup techniques) The objective of shoreline cleanup techniques is to remove

the stranded oil or to accelerate the natural recovery of oiled shorelines while reducing the adverse impacts of cleanup operations on surrounding environment (ExxonMobil, 2014; MERRAC, 2005). Basically, shoreline cleanup tactics can be classified into several broad categories of methods: natural recovery, physical recovery and removal, in-situ treatment (physical methods), and chemical and biological treatment (ECCC, 2016). As shown in Figure 5-2, each category can be subdivided into more specific response tactics. Only natural recovery does not involve any cleanup activities on a shoreline, leaving stranded oil to a series of natural processes such as evaporation, biodegradation, photooxidation, dissolution, and washing through wave, current, and tidal action to remove oil (Fingas, 2012; Owens et al., 2003; USEPA, 2016). Generally, natural recovery is suitable for small spills, light oiling, exposed shorelines, and/or remote sites (ECCC, 2016; USEPA, 2016). Physical recovery methods mainly refers to remobilizing oil by washing or flushing the oiled substrates with different pressure and/or temperature of the water, and then the floating oil is collected by skimmers or sorbents (MERRAC, 2005). Physical removal may include manual/mechanical removal, vacuuming, vegetation cutting, and sorbents (ECCC, 2018). For in situ treatment, both mixing and sediment relocation could accelerate the natural removal processes by breaking down oil deposits physically, and then enhance stranded oil removal and shoreline recovery (Dubach et al., 2015b). However, Owens et al. (1987) reported burning was not a practical in situ treatment technique for oil removal in shorelines. When chemical or biological methods are used, various agents such as surface washing agents, dispersants, solidifiers, and biological agents would be added to enhance stranded oil removal and/or accelerate natural processes (Michel et al., 2001; Walker et al., 1999). These agents are regulated by responsible agencies, and appropriate approvals and compliance are usually required before their application (Owens, 2011; Owens and Sergy, 2008). With various shoreline treatment techniques, the selection of an appropriate one is often based on a series of factors: shoreline types, the amount and characteristics of stranded oil, environmental sensitivity, logistics, waste generation, government approval, and so on (ECCC, 2016; Fingas, 2016; Owens, 2011; Owens et al., 2003).

The application of surface washing agents can be a good choice when weathered oil is stranded on the shoreline and other methods are not effective in removing oil, as this method has features such as high oil removal and recovery, low requirements for logistics, and less disturbance to the shore zone (Bi et al., 2020; Fingas, 2013; Michel et al., 2001). The surface washing agent is formulated to release as much of oil as possible from substrate surfaces, then the lifted oil can be recovered by physical removal operations (Tumeo and Cote, 1998). Typically, it is sprayed on the oiled beaches during low-tide phases, then the flush water is used to rinse the surface to lift the oil that will be directed to specific area for recovery. In actual applications, this technique is generally used in combination with other shoreline cleanup methods to achieve treatment goals (Colcomb et al., 1997; Michel et al., 2017).



Figure 5-2 Shoreline cleanup methods and their frequent combinations in spill response.

(Decision tree for the use of surface washing agents) There are two different types of surface washing agents. One is the "lift and disperse" product which disperses oil into the water column. The other is the "lift and float" product that lifts but not disperses oil, thus the released oil can float and be collected (DeLorenzo et al., 2017). The decision tree is only applicable for determining the appropriateness of "lift and float" surface washing agent products, and it is assumed that the government has approved their use. The purpose of the decision tree is to assist oil spill responders in considering the possible scenarios for the use of surface washing agents, based on initial evaluation of oil collectability, shoreline types, oil types and volume, trapped oil position, and removal requirements (ECCC, 2016; NWACP, 2020; USEPA, 2002). However, the possible scenarios for using surface washing

agents do not mean this tactic is bound to be used in real cases as it is generally recommended when the conventional tactics have been attempted and failed to satisfy the cleanup objectives.

According to the decision tree given in Figure 5-3, six circumstances (red leaf nodes of decision tree) can be identified for possible application of surface washing agents. Specifically speaking, the root node of decision tree determines whether the stranded oil can float on the water surface and be contained or not. If the API gravity of the weathered oil is greater than about 7 (lighter than seawater), the oil will float, otherwise it will sink (Usher, 2006). The bucket test can be performed to see if the removed oil would float so it can be contained when remobilized (USEPA, 2002). Then, the next consideration is the shoreline types, classified by Sergy (2008) for oil spill response, which were divided into several categories in this decision tree: bedrock or solid manmade shoreline, permeable manmade or pebble/cobble or boulder beaches, marsh or wetland, and other shoreline types. The first possible scenario for using surface washing agents is when heavily weathered oil or heavy crude is stranded on the bedrock and solid manmade shorelines, while this method is still applicable for a small amount of spilled oil when it comes to the permeable manmade or pebble/cobble or boulder beaches (second circumstance) (ECCC, 2016). For lighter oils, if flooding or water washing is used for shoreline cleanup, there will be other two scenarios that may consider applying surface washing agents: enhance the oil removal and reduce temperature and/or pressure of flush water (Koran et al., 2009; NWACP, 2020; Walker et al., 1993). Fifthly, the application of surface washing agents can be further considered for the oiled marsh or wetland if the affected area is accessible from the marsh fringe (USEPA, 2002). Moreover, it is also appropriate to consider surface washing agents as an option when the oil is stranded on shorelines inaccessible to other treatment methods (i.e., mechanical removal), but it can be flushed and the flush water can be collected (Michel et

al., 2001; Walker et al., 2003).



Figure 5-3 Decision tree for the consideration of surface washing agent application.

5.3.2. Selection and quantification of decision-making criteria

Once spill responders decide to apply the surface washing agent to cope with oiled shorelines, it is necessary to comprehensively evaluate potential surface washing agent products to determine preferences, as the U.S. EPA has already licensed over 70 surface washing agents in the Subpart J of the National Contingency Plan (USEPA, 2020). The selection system of surface washing agent products requires taking into consideration multiple factors such as effectiveness, toxicity, cost, demonstrated field tests, and dispersion ability (Chen et al., 2019c; Fingas, 2000, 2013; Michel et al., 2001; Shang et al., 2012). It is desirable to select the indicators that have greater effects on the weighting and

ranking processes (Du et al., 2020; Karimi et al., 2020). Therefore, the determination of the criteria for this MCDA model was mainly based on literature review and analysis combined with experts' suggestions. As shown in Table 5-1, a scientific and practical criteria system for surface washing agent selection was established, which includes toxicity, effectiveness, minimal dispersion, demonstrated field tests, and cost.

Criteria	Unit	Evaluation values	Definition		
Toxicity	ppm	1: below 10 ppm	LC50 of surface washing agent for aquatic species over a period of time		
		2: 11-50 ppm			
		3: 50-100 ppm			
		4: 100-150 ppm			
		5: above 150 ppm			
Effectiveness	%	1: below 30 %	The ability of the surface washing		
		2: 30-40 %	agent to lift oil off substrates (an		
		3: 40-50 % 4: 50-60 % 5: above 60 %	effective one leaves little oil		
			adhered to the substrate; usually in		
			context of oils with higher		
			adhesion and viscosity)		
Minimal	%	1: above 30 %	The tendency of a surface washing agent to disperse oil into the		
dispersion		2: 20-30 %			
			surrounding water rather than		
		3: 10-20 %	lifting and re-floating the oil removed (a good surface washing		
		4: 5-10 % 5: below 5 %			
			agent should be a poor dispersant)		

Table 5-1 An evaluation index system for surface washing agents evaluation.
Demonstrated		1: seldom	The number of tests and/or
field tests		2. rarely	applications of a surface washing
		2. Turory	agent (proven to work in actual
		3: sometimes	responses or experiment field-
		4: frequently	scale projects)
		5: often	
Cost	\$/m ²	1: above 30	Surface washing agent material
		2: 20-30	cost per unit area for treatment
		3: 10-20	
		4: 5-10	
		5: below 5	

5.3.3. Scenario analysis

(Case study site description and alternative identification) The oil tanker named Sea Empress ran aground at Milford Haven, United Kingdom (Latitude: 51.71, Longitude: - 5.03) on February 15, 1996 and spilled 72,000 tons of crude oil and 480 tons of heavy fuel oil (Harris, 1997). Over the following weeks, the surrounding coastline with various beach types (rocky shore, sand, boulders, cobbles, mud, etc.) was heavily oiled (Colcomb et al., 1997). The affected area has great environmental importance and many beaches were also popular tourist attraction. Compared with most crude oils, the heavy fuel oil is more viscous and persistent, potentially having more serious impacts on shoreline and cleanup. Suppose that there is 1000 m² of boulders beach with low-energy regimes, which was heavily oiled. The approval for application of surface washing agent was obtained from U.K. regulatory authority. An environmental tradeoff was conducted to prove the use of surface washing agent is better than leaving the oil on the boulders. Also, other shoreline cleanup tactics have been tried and failed to effectively remove the stranded oil. The surface washing agent was selected as a countermeasure to address the heavy oiling condition of the boulder beach.

Considering the cleanup objective and the condition of oiling site, six commercially available surface washing agent products were chosen for evaluation: Corexit 9580, PES-51, Cytosol, Accell Clean SWA, CN-110, and Biosolve. Detailed information about each of the products is provided in Table 5-2. Although the PES-51 is in the category of miscellaneous oil spill control agents on the NCP product schedule, it was considered as a surface washing agent in our study based on its mechanism for removing oil and its past use in that capacity (e.g., Prince William Sound). To avoid unnecessary commercial dispute, the above surface washing agents were labeled as A1 ~ A6, which will not affect the ranking of alternatives calculated by the integrated MCDA tool.

Surface	Toxicity	Effectiveness	Dispersion ability	Field	Cost
washing agents	(ppm)	(%)	(%)	tests	(\$/m ²)
Corexit 9580	59.5	52.9 (Koran,	14.45	12	23.68
(A1)		2007)	(Luedeker, 2009)		
PES-51 (A2)	77	30.4 (Koran,	5	6	2.05
		2007)	(Fieldhouse, 2008)		
Cytosol (A3)	431	74 (Von	4.9	8	3.23
		Wedel, 2000)	(Fieldhouse, 2008)		
Accell Clean	41.5	45.3	17.3 (assumption)	1	14.42
SWA (A4)		(assumption)			
CN-110 (A5)	32247.5	39.2	26.5 (assumption)	0	1.72
		(assumption)			
Biosolve (A6)	5	27.5 (Koran,	25.97	1	1.16
		2007)	(Luedeker, 2009)		

Table 5-2 The data for each criterion of six surface washing agents

(Construction and normalization of the decision matrix) As shown in Table 5-2, the data for each criterion of the six surface washing agent products were gathered and computed. Some data such as toxicity had major discrepancies for different alternatives. For example, LC50 could range from 3.6 to 12,300 ppm for Mysid Shrimp, or from 6.4 ppm to 52,200 ppm for Inland silversides. Therefore, based on experts' suggestion, the values of criteria were evaluated by a fixed scale with five points for better precision and higher effectiveness of assessment (Table 5-3). The decision matrix D was also constructed by the following equation (14) with six alternatives and five criteria:

$$D = \begin{bmatrix} x_{11} & x_{12} & \cdots & x_{15} \\ x_{21} & x_{22} & \cdots & x_{25} \\ \vdots & \vdots & \ddots & \vdots \\ x_{61} & x_{62} & \cdots & x_{65} \end{bmatrix} = \begin{bmatrix} 3 & 4 & 3 & 5 & 2 \\ 3 & 2 & 5 & 4 & 5 \\ 5 & 5 & 5 & 4 & 5 \\ 2 & 3 & 3 & 2 & 3 \\ 5 & 2 & 2 & 1 & 5 \\ 1 & 1 & 2 & 2 & 5 \end{bmatrix}$$

where d_{ij} represents the evaluation values of i^{th} alternative with j^{th} criterion. Then, the decision matrix was normalized according to the equation (2) to obtain the corresponding matrix R,

	г0.16	0.24	0.15	0.28	ר0.08
	0.16	0.12	0.25	0.22	0.20
D –	0.26	0.29	0.25	0.22	0.20
К –	0.11	0.18	0.15	0.11	0.12
	0.26	0.12	0.10	0.06	0.20
	$L_{0.05}$	0.06	0.10	0.11	0.20

Table 5-3 The evaluation values for each criterion of six surface washing agents

Surface	washing	Toxicity	Effectiveness	Minimal	Demonstrated	Cost
~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~		10110103			2 • • • • • • • • • • • •	0000

agents			dispersion	field tests	
Corexit 9580 (A1)	3	4	3	5	2
PES-51 (A2)	3	2	5	4	5
Cytosol (A3)	5	5	5	4	5
Accell Clean	2	2	2	2	2
SWA (A4)	Z	5	5	Z	3
CN-110 (A5)	5	2	2	1	5
Biosolve (A6)	1	1	2	2	5

(Combined weights for evaluation criteria)

(1) Objective weight by entropy method

Firstly, the entropy value E_j of j^{th} criterion can be calculated by equation (2). For example, the detailed calculation of E_1 is as follows:

$$E_{1} = -\frac{\sum_{i=1}^{6} p_{i1} \ln p_{i1}}{\ln 6} = -\frac{0.16 \times \ln 0.16 + 0.16 \times \ln 0.16 + 0.26 \times \ln 0.26 + 0.11 \times \ln 0.11 + 0.26 \times \ln 0.26 + 0.05 \times \ln 0.05}{\ln 6}$$

=0.937

In the same calculation, the values of E_2 , E_3 , E_4 , and E_5 were obtained, and they are 0.942, 0.962, 0.936, and 0.973, respectively. Then, the objective weight $w(e)_j$ can be obtained by equation (3) as follows:

$$w(e)_1 = \frac{1 - E_1}{\sum_{j=1}^5 (1 - E_j)} = \frac{0.063}{0.063 + 0.058 + 0.038 + 0.064 + 0.027} = 0.252$$

The same goes for $w(e)_2$, $w(e)_3$, $w(e)_4$, and $w(e)_5$, which are 0.232, 0.152, 0.256, and 0.108, respectively.

(Subjective weight by AHP method)

The pairwise comparison results of five criteria conducted by all experts were aggregated,

indicating the importance of one criterion over another. Then the subjective weights of attributes $w(a)_j$ were calculated based on the equation (5), and they were 0.355, 0.248, 0.157, 0.196, and 0.044, respectively. In order to avoid the inconsistence of experts' judgments, the consistency check was performed by equation (6). The value of C.R. is less than 0.1, indicating the judgement is consistent and the subjective weight obtained by AHP method is acceptable.

(Combined weight)

The objective weight and subject weight of each criterion for surface washing agent products were considered comprehensively by the combination weighting method to obtain more reasonably evaluation, and the final weights w_j were determined by equation (7) as follows:

$$w_{1} = \frac{w(e)_{1} \times w(a)_{1}}{\sum_{j=1}^{5} w(e)_{1} \times w(a)_{1}} = \frac{0.06 \times 0.40}{0.06 \times 0.40 + 0.12 \times 0.03 + 0.26 \times 0.03 + 0.15 \times 0.17 + 0.10 \times 0.13} = 0.396$$

In the same way, w_2 , w_3 , w_4 , and w_5 could also be calculated as shown in Table 5-4.

Criteria	Combined weight (<i>w_j</i>)
Toxicity	0.396
Effectiveness	0.255
Minimal dispersion	0.106
Demonstrated field tests	0.222
Cost	0.021

Table 5-4 Combined weight for five criteria.

(Rank alternatives) Firstly, the differences between each pair of surface washing agents in

terms of each criterion were calculated based on equation (8). The deviations of any two potential surface washing agents are presented in Table 5-5. The next step was the selection of the preference function that is to define the preference of one surface washing agent over another with respect to each above criterion. Considering the criteria properties, the V-shape criterion preference function was employed to equation (9) to obtain the preferences as shown in Table 5-6. Then the corresponding preference index can be obtained by incorporating the criteria weight using the equation (10), and the values of preference index are presented in Table 5-7.

Pair	Taulaita	Effe direction and	Minimal	Demonstrated	Cast
comparison	Ioxicity	Effectiveness	dispersion	field tests	Cost
A1A2	0	2	-2	1	-3
A1A3	-2	-1	-2	1	-3
A1A4	1	1	0	3	-1
A1A5	-2	2	1	4	-3
A1A6	2	3	1	3	-3
A2A1	0	-2	2	-1	3
A2A3	-2	-3	0	0	0
A2A4	1	-1	2	2	2
A2A5	-2	0	3	3	0
A2A6	2	1	3	2	0
A3A1	2	1	2	-1	3
A3A2	2	3	0	0	0
A3A4	3	2	2	2	2
A3A5	0	3	3	3	0

Table 5-5 Difference of any two surface washing agents with respect of any criterion

A3A6	4	4	3	2	0
A4A1	-1	-1	0	-3	1
A4A2	-1	1	-2	-2	-2
A4A3	-3	-2	-2	-2	-2
A4A5	-3	1	1	1	-2
A4A6	1	2	1	0	-2
A5A1	2	-2	-1	-4	3
A5A2	2	0	-3	-3	0
A5A3	0	-3	-3	-3	0
A5A4	3	-1	-1	-1	2
A5A6	4	1	0	-1	0
A6A1	-2	-3	-1	-3	3
A6A2	-2	-1	-3	-2	0
A6A3	-4	-4	-3	-2	0
A6A4	-1	-2	-1	0	2
A6A5	-4	-1	0	1	0

Table 5-6 Preference of one surface washing agent over another surface washing agent with respect to each criterion by V-shape criterion preference function (p=3).

Pair	Tovisity	Effectiveness	Minimal	Demonstrated	Cost	
comparison	Toxicity	Effectiveness	dispersion	field tests	Cost	
A1A2	0	0.67	0	0.33	0	
A1A3	0	0	0	0.33	0	
A1A4	0.33	0.33	0	1	0	
A1A5	0	0.67	0.33	1	0	
A1A6	0.67	1	0.33	1	0	

A2A1	0	0	0.67	0	1
A2A3	0	0	0	0	0
A2A4	0.33	0	0.67	0.67	0.67
A2A5	0	0	1	1	0
A2A6	0.67	0.33	1	0.67	0
A3A1	0.67	0.33	0.67	0	1
A3A2	0.67	1	0	0	0
A3A4	1	0.67	0.67	0.67	0.67
A3A5	0	1	1	1	0
A3A6	1	1	1	0.67	0
A4A1	0	0	0	0	0.33
A4A2	0	0.33	0	0	0
A4A3	0	0	0	0	0
A4A5	0	0.33	0.33	0.33	0
A4A6	0.33	0.67	0.33	0	0
A5A1	0.67	0	0	0	1
A5A2	0.67	0	0	0	0
A5A3	0	0	0	0	0
A5A4	1	0	0	0	0.67
A5A6	1	0.33	0	0	0
A6A1	0	0	0	0	1
A6A2	0	0	0	0	0
A6A3	0	0	0	0	0
A6A4	0	0	0	0	0.67
A6A5	0	0	0	0.33	0

Surface washing	A 1	A 2	13	A /	15	16
agent products	AI	AL	AJ	A4	AJ	AU
A1	-	0.244	0.073	0.437	0.428	0.778
A2	0.092	-	0	0.365	0.328	0.604
A3	0.441	0.520	-	0.801	0.583	0.906
A4	0.007	0.084	0	-	0.192	0.337
A5	0.286	0.265	0	0.410	-	0.480
A6	0.021	0	0	0.014	0.073	-

Table 5-7 Preference index incorporated with the criteria weights.

Finally, the positive outranking flow, negative outranking flow, and net flow for each surface washing agent product were calculated using equations (11) - (13) (Table 5-8). The positive flow indicates the extent of the selected surface washing agent dominating others, while the negative flow shows the extent of the selected surface washing agent dominated by others. The complete ranking of surface washing agent products depends on the magnitude of net flow values that is the balance of positive and negative flows. The preferred surface washing agent is the one with highest value of net flow. Therefore, A3 can be regarded as the optimal alternative as it had the largest net flow value. However, it should be noted that the most suitable surface washing agent product obtained by this evaluation method is incident-specific, and it does not mean this surface washing agent is better than other products in other oil spills.

Table 5-8 Positive flow, negative flow, and net flow of each alternative.

Surface	washing	Positive	flow	Negative	flow	Not flow (1)	
agent products		$ \emptyset^+(A) $		$\phi^{-}(A)$			
A1		0.3923		0.1688		0.2231	
A2		0.2774		0.2225		0.0551	
A3		0.6494		0.0148		0.6345	

A4	0.1248	0.4052	-0.2805
A5	0.2880	0.3215	-0.0333
A6	0.0217	0.6208	-0.5987

5.3.4. Sensitivity analysis

The outranking results may change by varying the weights of criteria (Gupta et al., 2019). Therefore, it is necessary to perform the sensitivity analysis by changing the weight of each criterion (toxicity, effectiveness, minimal dispersion, demonstrated field tests, and cost) independently to check the robustness of the priority rank obtained by the model. Additionally, the sensitivity analysis could help decision makers to evaluate the maximum change of criteria weights that would not alter the current rank of surface washing agents (Sindhu et al., 2017). In order to investigate the variation in overall ranking, the weight of each criterion varied while keeping other four criteria changing according to the original scores. The results of five scenarios are illustrated in Figure 5-4.

As shown in Figure 5-4(a), the sensitivity of net flows of six surface washing agent products was assessed by changing the criterion of toxicity. The toxicity is the most important criteria with the weight value of 39.6%; A3 is the most favored surface washing agent product while A6 is the least favored one. The overall sequence of six alternatives will not change with the weight value of toxicity varying from 22.75% to 46.10%, and the weight variation range without altering rankings is called WSI. A4 will overtake A5 to rank fourth when the weight of toxicity is reduced to less than 22.75%. By contrast, when its weight is incremented to about 56% or more, A5 will outrank A1 and A2 as the second favored option. Overall, it is obvious that only the net flows of A3 and A5 show growing trends while others decline to different extent with the increasing weight of toxicity.

In the second chart (Figure 5-4(b)), the net flow changes of alternatives were observed as the weight of effectiveness varied. Effectiveness has been determined to be the second most significant indicator for evaluation of surface washing agents with 25.5%, and it has the WSI with the range of 5.69% to 53.96%. The chart also indicates the positions of A3 and A6 are robust enough throughout the change in weight of effectiveness. The order of other alternatives would vary if the weight value is outside of the WSI. Figure 5-4(c) and (d) present the influence of weights in the criteria of minimal dispersion and demonstrated field tests on the ranking of surface washing agent products, respectively. The initial weights of minimal dispersion and demonstrated field tests are 10.6% and 22.2%, respectively, and their WSIs are also very different with the former between 3.49% and 26.12% and the latter between 15.62% and 55.33%. It is worth mentioning that the alternative of A1 will exceed A3 to become the most preferred surface washing agent as the weight value of demonstrated field tests continues to increase to 64.56%.

As shown in the last chart (Figure 5-4(e)), the sensitivity of outcomes was observed against changes in cost criterion, the least important one for assessment of surface washing agents with only 2.1%. The overall sequence will not alter only if the weight of cost is less than 14.12%, otherwise, it will change with the modification of cost weight. Especially, the second favored A1, at the initial ranking, will be outranked by A2, A5, A6, and A4 successively to be least preferred option with the weight value of cost rising. Similar to other criteria (except for the weight of demonstrated field test over 64.56%), A3 keeps the top priority among other surface washing agents no matter what the weight value of cost is.

Overall, it can be summarized from the above sensitivity analysis that the alternative A3 remains its leading ranking order in surface washing agent selection for this oil spill incident, unless the weight of demonstrated field tests is large enough in which case A1



may outrank A3 to be the most favored alternative. Therefore, the robustness and stability of this model are verified.

Figure 5-4 Sensitivity analysis based on changes in five criteria.

5.3.5. Implications for shoreline spill response

(Research implications) This developed evaluation and selection framework for surface washing agents used in shoreline oil spill cleanup has a series of research implications. Firstly, it was the first time to develop a decision tree for exploring the scenarios that are appropriate to use surface washing agents by considering site conditions and cleanup requirements. Secondly, multiple factors presented direct or indirect effects on the selection of surface washing agent products. This study established the evaluation index system of surface washing agent products only containing top five influential indicators (toxicity, effectiveness, minimal dispersion, demonstrated field tests, and cost) on the basis of literature review and suggestions from experts from shoreline cleanup industry. According to their relative importance for surface washing agent evaluation, these indicators could be prioritized in each oil spill using combined entropy-AHP weighting method. Thirdly, one outranking MCDA model was developed to rank the surface washing agent products, and the sensitivity analysis was conducted for validation of the model and corresponding results. The present study presented an opportunity for comprehensive evaluation and application of surface washing agents in oil spill response with the consideration of various influential factors. The established theoretical model can be used to narrow the significant gap and provides a good foundation for future research about surface washing agents.

(Practical implications) The present work also has the following practical implications. Firstly, the decision tree could assist the environmental authorities and response teams in identifying and considering shoreline cleanup conditions suitable for surface washing agent application. It can also be a viable response tool to guide the decision-making process to determine whether surface washing agent is worthy of further consideration. In addition, one significant advantage of the decision tree is that it includes all the possible scenarios for using surface washing agents, thus the decision tree may be analyzed and used by responders to adopt the application of surface washing agents as a part of shoreline spill response. Secondly, the combined weighting technique can be utilized to obtain the weights of criteria with the merits of reducing the subjectivity of experts' judgements and improving the objectivity of decision-making process. In real cases, the weights of all criteria could

change with different affected sites and different preferences of experts, so the final ranking of the alternatives may vary in different contexts. Thirdly, the selection model incorporating MCDA method is suitable for dealing with the problem of choosing the most desirable surface washing agent product to cope with the stranded oil, providing the valuable references for assessment and selection of surface washing agents in field application. It should be noted that some other considerations such as hydraulic conditions, meteorological conditions, and environmental sensitivity also need to be taken into account in real oil spill response. Once the use of surface washing agents is adopted for shoreline cleanup, this system would also help decision makers to target the most important factors for selecting the most appropriate surface washing agent.

5.4. Summary

This is the first study to construct a framework for the evaluation and selection of surface washing agents to cope with shoreline oil spills. An incident-specific decision tree was developed to guide oil spill responders to analyze all possible scenarios applicable for using surface washing agent s. The suitability of surface washing agent treatment is related to various factors, including oil collectability, shoreline character, types and amount of stranded oil, as well as cleanup requirements. Based on the combination of theoretical modeling and empirical study, this study presented an integrated MCDA method for selecting the most appropriate surface washing agent product from five perspectives of toxicity, effectiveness, minimal dispersion, demonstrated field test, and cost. That is also a reliable scientific management method for real shoreline oil spill response. The model was applied to a hypothetical case with six alternatives. The results of the case study indicated A3 was technically, ecologically, and economically the most preferred option for this shoreline cleanup incident among the six surface washing agent products considered. Meanwhile, sensitivity analysis also illustrated the results obtained by the model was robust

and stable. Overall, the proposed framework can be used to evaluate, improve, and develop surface washing agent -aided shoreline treatment, and help decision makers better understand this technique and choose a more reasonable alternative in field applications.

CHAPTER 6. EXPLORING THE USE OF ALGINATE HYDROGEL COATING AS A NEW INITIATIVE FOR EMERGENT SHORELINE OILING PREVENTION

6.1. Background

Marine oil spills are often reported as a result of activities associated with oil exploration, production and transportation (An et al., 2017; Chen et al., 2019a; ITOPF, 2020; Zhang et al., 2019). Once oil is released into the marine environment, it can undergo various transformation processes including evaporation, oxidation, aggregation, emulsification, and biodegradation (Cao et al., 2020; Lee et al., 2015; Mulligan and Yong, 2004; Saborimanesh and Mulligan, 2015). The spilled oil may reach the shoreline, and then the stranded oil can persist for a long time, exerting many negative effects on the coastal ecosystem (Bi et al., 2020; Michel et al., 2013; Wang et al., 2020). To mitigate the impact of shoreline oiling, various shoreline cleanup methods, such as mechanical removal, surface washing, chemical treatment, and bioremediation have been used for the affected areas (Chen et al., 2019c; Chen et al., 2021c; ECCC, 2016). Typically, the operations of shoreline treatment and cleanup during the spill response are expensive, which can account for 80-90% of the total cleanup cost (Chen et al., 2021b; Etkin, 2001). This provides incentives for preventing the spilled oil from reaching shores. The main prevention method at present is to deploy oil booms along the potentially affected shoreline (Li et al., 2016b; Wong and Barin, 2003). However, the application of oil booms and its effectiveness can be limited by poor weather conditions (Fingas, 2011c). In addition, the used booms have to be properly disposed of, which is expensive and has some other environmental risks (Fingas, 2011b; Pagnucco and Phillips, 2018). Therefore, the new prevention techniques which are easily-implemented, effective, and environmentally friendly need to be developed.

The coating with special wetting properties has the great potential for environmental applications (Lu et al., 2020d). For example, Yang et al. (2015) developed a novel polyelectrolyte-fluorosurfactant complex/SiO₂ nanocomposite coating with superhydrophilicity and superoleophobicity on stainless steel meshes. Boakye-Ansah et al. (2016) fabricated the 1H,1H,2H,2H-perfluorooctyltriethoxysilane coating for oil/water separation. A superhydrophilic/superoleophobic coating with photocatalytic activity through spray-casting was also proposed by Lu et al. (2020b). However, using synthetic materials can cause some problems in terms of complex preparation process, relatively high cost, and toxic raw materials.

Recently, there is an increasing interest in developing low-cost green coatings (Chen et al., 2019b; Li et al., 2019d). Sodium alginate is a linear and unbranched polysaccharide naturally derived from brown sea algae (Wang et al., 2019b). The alginate contains biodegradable massive oxygen-containing groups (-COONa and -OH), exhibiting the excellent hydration ability (Li et al., 2019c). It has been widely studied as it is a low-cost, biodegradable, and commercially available coating material. Cai et al. (2019) prepared alginate coatings via electrostatic interaction between cationic polyethyleneimine (PEI) and anionic sodium alginate. Matsubayashi et al. (2017) also used a similar method by using PEI as the cationic crosslink agent to assemble the alginate hydrogel coating. However, the use of corrosive or expensive materials for pre-modifying the surface was not economical and environmentally friendly. Although some previous findings are encouraging, the knowledge about functionalized alginate hydrogel coatings is still limited. A number of issues about the coating mechanism and performance are poorly understood. There is still a gap between the available green coating technique and the increasing need for shoreline oiling prevention.

Therefore, in our study, a novel shoreline oil-repellent coating technique will be developed to prevent the shoreline from the impact of spilled oil. The detailed objectives are (i) to develop a novel and green alginate hydrogel coating method to prevent the shoreline substrate from oiling; (ii) to characterize the substrate coated with alginate hydrogel; and (iii) to comprehensively evaluate the oil-repellent performance of this green coating using continuous, batch and tank tests. The proposed method represents an integration of innovative efforts beyond established approaches in oil pollution control and a new initiative for emergent oil spill response.

6.2. Materials and methods

6.2.1. Materials and chemicals

Sodium alginate, anhydrous calcium chloride (CaCl₂), and Oil Red O at analytical grade were purchased from Sigma Chemical Company (ON, Canada). Hibernia Crude, Shell Rotella® T4 conventional diesel engine oil (15W40), and Cold Lake Blend were used as representative oils in this study with properties shown in Table 6-1. The Marina natural gravel was obtained from Rolf C. Hagen, Inc. (QC, Canada) and the fraction passing through the 6 mm sieve but recovered by the 4 mm sieve was used as the representative shoreline substrate for this study. Sea salt and hexane were obtained from Fisher Scientific (ON, Canada). Deionized water was used to prepare the solutions and the artificial seawater (3.5 wt% sea salt) was used in all tests.

			American		
Oil Type	т	Density (g/cm ³)	Petroleum Institute	Fresh Viscosity	Weathered
	Type			(cP)	Viscosity (cP)
			(API) gravity (°)		

Table 6-1 Physical properties of Hibernia Crude, engine oil, and Cold Lake Blend

Hibernia	Light crude	0.87	34.1	15.66	25.50
Engine oil	Diesel engine oil	0.88	29.3	257.08	258.60
Cold Lake Blend	Heavy crude	0.92	21.8	218.99	1602.00

6.2.2. Preparation of the alginate hydrogel-coated gravels

The alginate hydrogel-coated gravel was fabricated using ionic gelation and self-assembly methods. First, 10 g of sodium alginate were dissolved in deionized water and stirred constantly to form a clear and viscous solution (2 wt%). A certain volume of sifted gravel was immersed into the sodium alginate solution for 5 min using a dip-coating method, and the treated gravel was then impregnated with 500 mL of a calcium chloride solution (10 wt%) for 10 min by in-situ ionic gelation. The coated gravel used in this study was obtained after repeating the aforementioned steps once more with the same solutions. The resulting gravel was dried for 24 h at 23°C with 15% relative humidity for later use.

6.2.3. Continuous oil-repellent experiments

Before the continuous tests, a commercial product (MicroCure DTO 30, Cytonix, United States) was applied using fold microfiber by the simple cross-hatch pattern to make the glass column and conical flasks oleophobic. An oil-in-water emulsion containing engine oil (0.06 wt%) and artificial seawater was prepared using a high-speed homogenizer (Ultra-Turrax T25, IKA, Staufen, Germany) operating at 10,000 rpm for 10 min (Chen et al., 2021a). Meanwhile, both pristine and coated gravels were prewetted with artificial seawater for 10 min, and the excess seawater on the surfaces was then wiped off. The same volumes of coated and uncoated gravels were placed separately into the 50 mL oleophobic

glass columns, which were fixed above the oleophobic conical flasks. Next, 50 mL of above homogeneous and stable emulsion was poured into each column gradually. It flowed through the coated and pristine gravels and eventually seeped into the conical flasks. This process was repeated 4 times in this study. Cycle 0 indicated the original state of emulsion, and cycle 1 signified that the coating process had taken place. After each specific cycle, the sample (1 mL) in conical flasks was collected in triplicate for analysis.

6.2.4. Batch oil-repellent experiments

The Hibernia oil, engine oil, and Cold Lake Blend were weathered in a fume hood at 22 °C for seven days until the weathering states of the Hibernia oil and Cold Lake Blend achieved 10% and 7% mass loss, respectively. The engine oil showed no evaporation loss during the weathering process. The three weathered oils were then stored in a closed amber glass bottle before application. All washing tests were conducted in 20 mL glass vials. Three grams of the coated and pristine gravels were put into separate glass vials. Next, 20 µL of fresh or weathered engine oil were added by pipette onto the gravel surface, and the vials were placed into the fume hood at 22 °C for another 24 h. Then, 15 mL of artificial seawater were added to the vials, which were then put in the Incubator Shaker (Innova 42R, Eppendorf, USA) to wash the oiled gravels at 300 rpm for 15 min. When the washing process was completed, the washed gravels were taken out of the vials and rinsed slowly with artificial seawater to remove the oil that did not really adhere to both gravels. The rinsed gravels were then extracted with 15 mL of hexane at 300 rpm for 24 h.

6.2.5. Performance evaluation using the laboratory shoreline tank simulator

The laboratory shoreline tank simulator was built to investigate the efficiency of the proposed oil preventive approach. The simulator consisted of a simulation tank module, a

pumping module, a water storage and distribution module, and a programmable logic controller module with specially designed software (see the schematic representation in Figure 6-1). The chamber of the simulation tank module had three sections, namely, a large central section, a left section, and a right section, which represented a beach, groundwater sinks, and the ocean, respectively. The internal dividers were mesh screen sandwiched in a stainless-steel frame. The gravels (about 18 L) were laid inside the central section at a slope of 28° with a 13×13×2 cm pit for the oiled pristine gravel in the control test and the oiledcoated gravel in the coating test. Then, the two pre-weathered and Oil Red O-dyed engine oil (42.87 g for the control test and 41.59 g for the coating test) were mixed with the pristine gravel (503.24 g) and the coated gravel (501.63 g), respectively. The oiled pristine gravel was layered on the pit for the control test, while the oiled-coated gravel was used for evaluating the oil preventive capacity. The period of each artificial tidal cycle was 2 h, and three tidal cycles were conducted for each test. The groundwater flow was set to 0 in both tests. As shown in Figure 6-1, when the test started, the artificial seawater was pumped from the feed tank into the "ocean" side of the tidal simulation chamber at the low water level (0.1 m). After about 20 minutes, the seawater rose to the point where the oiled gravels were layered. The oiled zone was flooded continuously until the high water (0.26 m) was reached. At this time, a pre-weighed oil spill absorbing pad was used to remove the oil floating on the artificial seawater surface. This was then put into the fume hood for 24 h to evaporate the water, leaving only the remaining oil. The pad with only the oil was weighed again to determine the removal amount of floated oil. It should be noted that the oil absorbing pad was only used in the first tidal cycle as no floated oil was detected on the surface of artificial seawater in the following two cycles. However, samples were still taken at three different points in the oiled zone at the end of each cycle to measure the amount of oil residue. The whole process was recorded by a camera, and the stranded oil on the gravel after each falling tide was also photographed.



Figure 6-1 Schematic diagram of the laboratory shoreline tank simulator.

6.2.6. Analytical methods

The gravels were thoroughly ground to a fine powder for X-ray diffraction (XRD) analysis, and the mineralogical composition of the gravels was obtained using the Philips X' Pert PRO diffractometer (Almelo, Netherlands) equipped with a Cu K α tube and an Ni filter (λ = 0.15418 nm) at a scanning speed of 5°/minute in 2 θ mode between 10° and 120°. The surface morphologies of the untreated and coated gravel samples were characterized using a Hitachi S-3400N scanning electron microscope (SEM, Tokyo, Japan). Energy-dispersive X-ray spectroscopy (EDX) analysis was conducted using Jeol 35-cf equipped with EDAX system attached to the FESEM system (Tokyo, Japan). Fourier transform infrared spectroscopy (FT-IR) was also performed using the Invenio S FTIR spectrophotometer (Bruker Optics, Ettlingen, Germany). The contact angle was measured using an optical goniometer instrument (VCA Optima, AST Products, Inc., Billerica, USA) at an ambient temperature of 22 °C. Diiodomethane was used as the standard liquid for oil contact angle measurement. The volume of the probing liquids was predetermined as 0.5 µL, and the shapes of drops and contact angles were recorded using VCA Optima Series analysis software. The concentration of Hibernia oil, undyed and dyed engine oil, and Cold Lake Blend in the hexane were quantified using a Thermo Scientific Evolution 201 UV–Visible spectrophotometer (Weltham, MA) at the wavelength of 224, 284, 513, and 230 nm, respectively. All experiments were carried out at least in triplicate, and the average values were reported as the results.

6.3. Results and discussion

6.3.1. Characterization of the alginate hydrogel-coated gravel

The XRD pattern of the pristine gravel is shown in Figure 6-2(a), and the mineralogical phases in the gravel were identified. The narrow peaks indicated that the powder of the gravel was comprised of crystal structures. It exhibited the strongest diffraction peak at about 27° , illustrating the most abundant crystalline phase in the gravel was the quartz containing the elements of silicon and oxygen (Ramil et al., 2020; Yang et al., 2021). When fabricating the alginate hydrogel-coated gravel, the pristine gravel was first placed into a sodium alginate solution. The sodium alginate molecules could be absorbed into the gravel due to the relatively high viscosity of the solution, which endowed the surface of the gravel with negative charges (Abubakr et al., 2009). Consequently, the treated gravel was immersed into the calcium chloride solution to form insoluble hydrogel through the crosslinking of the sodium alginate with the Ca²⁺ (Mokhena and Luyt, 2017). It is mainly because the carboxylate segments of the sodium alginate (-COO⁻) were bound by the Ca²⁺ via an ion-exchange mechanism between the -COONa/Ca²⁺ (Ayub et al., 2019). To improve the deposition of the calcium alginate on the gravel, one further coating cycle was

necessary for the layer-by-layer self-assembly process, and the resulting coated gravels were presented in Figure 6-2 (b) (Gao et al., 2018; Wang et al., 2019b). More coating means a higher degree of calcium alginate deposition; however, too many cycles may cause the unnecessary consumption of chemical materials with limited performance improvement.

The surface morphologies of both pristine and coated gravels with different magnifications were further observed. As shown in Figure 6-2 (c) and (d), the pristine gravel had a relatively smooth surface, while the surface of the coated gravel at same magnification was featured by numerous microstructures after the deposition of the alginate coating, which greatly increased the surface roughness. The surface morphology of the modified gravel at higher magnifications is described in Figure 6-2 (e) and (f). There were some cracks on the very rough surface, which may have been due to the partial collapse of the polymer network during dehydration (Pasparakis and Bouropoulos, 2006). The surface roughness played an important role in enhancing the wetting properties of the modified gravel because the special wettability of the surfaces was closely associated with the combination of surface chemical composition and roughness (Liu et al., 2013). When the hydrophilic surface was immersed in water, the water tended to enter the spaces with a high degree of roughness, and the trapped repulsed liquid repelled the oil on the oil/water/solid interface, thus the alginate hydrogel-coated gravel could protect the surface from oiling.



Figure 6-2 The XRD pattern of the pristine gravel (a); Digital photograph of coated gravels (b); SEM image of the pristine gravel (c); SEM images of the modified gravel at different magnifications (d, e, f); EDX spectrum of the hydrogel coating (g); Elemental distribution of Ca (h), Cl (i), and O (j) on hydrogel coating; FTIR spectra for sodium alginate (blue line) and calcium alginate (red line) (k).

The results of EDX are presented in Figure 6-2. As shown in Figure 6-2 (g), the peaks of calcium (Ca), chloride (Cl), oxygen (O), and sodium (Na) were observed, indicating the hydrogel coating was mainly composed of these four elements. The element of Cl accounted for 42.34% as the weight percentage, while the Ca and O contents of this coating were 27.62 and 29.53%, respectively. Only trace amount of Na was detected, implying most Na⁺ in alginate was replaced by Ca²⁺ via ion-exchange during the coating process.

The elemental mapping of Ca, Cl, and O was analyzed as shown in Figure 6-2 (h)-(j), suggesting that these elements were uniformly distributed on the coating matrix. As shown in Figure 6-2 (k), chemical bonds within the hydrogel coating were also examined through FTIR analysis. The peaks at 3275 cm⁻¹ for sodium alginate and 3385 cm⁻¹ for calcium alginate in the spectrum were due to the stretching vibrations of -OH groups (Pongianyakul, 2009). For weak peaks towards 2908 and 2916 cm⁻¹ in both alginate, they can be attributed to the -CH group antisymmetrical stretching vibration (Huang and Wang, 2018). There were two characteristic peaks of symmetric and asymmetric stretching of -COO group at 1593 and 1402 cm⁻¹ for sodium alginate and 1598 and 1442 cm⁻¹ for calcium alginate, respectively. These two peaks were related to ion crosslinking exchange as their peaks shifted to a higher wavenumber (Cho et al., 2014). This could be due to the strong electrostatic interaction between Ca^{2+} and carboxylic groups of the alginate. The peaks at 1023 and 1012 cm⁻¹ are the results of the stretching vibration of C-O band. In sodium alginate, the C-O vibration of -COO group was weak and no absorption peak appeared. However, the stretching vibration peak of C-O of the alginate membrane that appeared at 1270 cm⁻¹ was attributed to the reaction between carboxyl and Ca ion ("C-O-Ca-O-CO-" group structure), which enhanced the C-O vibration (Ribeiro et al., 2004). These changes indicated that Ca^{2+} formed an "egg tray" structure with the sodium alginate molecular chain.

The water contact angle (WCA) and underwater oil contact angle (UOCA) of the pristine and coated gravels were further measured to systematically investigate the surface wetting behavior (Lu et al., 2020c). It can be seen from Figure 6-3 (a) and (b) that the water droplet had a WCA of \sim 32.40° on the pristine gravel. The droplet spread very quickly on the coated gravel with a WCA of \sim 7.10°, indicating its remarkable surface water wettability. This phenomenon can be explained by the combination of the hydrophilic nature and microscale mesh structure of the calcium alginate hydrogel coating (Matsubayashi et al., 2017; Wang et al., 2019b). A comparison with the UOCA of the pristine gravel immersed in water is shown in Figure 6-3 (e). When the diiodomethane droplet contacted and left the modified gravel surface, it separated from the surface instead of remaining on it, as shown in Figure 6-3 (f)–(h). This showed the coated gravel had excellent underwater oleophobicity with low adhesion. Calcium alginate has intrinsic oxygen-containing groups, thus the microscale structure of the surface could be filled with the polar water to form a hydrated layer that strongly repelled the non-polar oil, resulting in the underwater oleophobic properties. Here, the Cassie equation was applied to explain the underwater wetting behavior of the oil droplets in the oil/water/solid three-phase system (Cassie and Baxter, 1944):

$$\cos\theta_2 = f\cos\theta_1 + f - 1 \tag{1}$$

Where θ_2 and θ_1 are the UOCAs on the coated and pristine gravels, respectively, and f represents the area fraction of the solid surfaces directly in contact with the oil. According to the equation, the hydration layer formation means the surface of the coated gravel had a small area fraction (f) that led to a small contact opportunity for the oil with the coated surface. This would result in a high UOCA (θ_2) or even allow the oil to leave the surface in water. The modified gravel also displayed a low oil adhesion within the small contact area, further improving the underwater oleophobicity. These characteristics endowed the coated gravel with a high oil-repellent performance, which can facilitate the oil repellence.



Figure 6-3 Digital photo of a water drop on the pristine gravel with WCA of \sim 32.40° in air (a); the coated gravels with WCA of \sim 7.10° in air (b); a diiodomethane (MI) drop on the pristine gravel with OCA of \sim 25.20° in air (c); the coated gravels with OCA of \sim 52.00° in air (d); a MI drop on the pristine gravel with UOCA of \sim 144.30° in water (e); the process of a MI drop contacting and leaving the coated gravel (f), (g), and (h).

6.3.2. Continuous oil-repellent performance of alginate hydrogel-coated gravels

The continuous experiments were conducted with an oil/water emulsion flowing through the pristine and coated gravels. The concentrations of the collected emulsions in the conical flasks after each cycle were measured and recorded (Figure 6-4). The oil concentrations of the initial emulsions for the original and coated gravels were 23.60 and 22.85 mg/L, respectively. After one cycle, the concentration of the collected emulsion flowing through the pristine gravel was 16.55 mg/L, approximately 7 mg/L less than that of cycle 0, while there was a smaller decrease (about 4 mg/L) in the collected emulsion for the coated gravel compared with the initial emulsion. It indicated that some oil droplets adhered to both kinds of gravel during the flowing process. However, compared with the pristine gravel, the concentration of the collected emulsions from the coated gravel was higher. Thus, the oil adhered less to the coated gravels because the alginate hydrogel coating enabled the gravels to be oleophobic underwater. The concentrations of the collected emulsions for both gravels continued to decrease during the next few cycles, but those of the coated gravel were always higher in concentration than those of the pristine gravel.



Figure 6-4 Oil concentrations of collected emulsion in conical flask after each cycle, and the oil mass balance for pristine and coated gravels in continuous oil-repellent experiments.

In the continuous tests, it was hard to determine the final oil adhesion content (m) of the

two kinds of gravel based only on the difference in the initial oil amount (m₀) and the amount of oil from the collected emulsion flowing through them (m₅). Besides from the oil adhering to the surface of the gravel, there were two other parts: the amount of oil microdroplets on the glass columns and conical flasks during the experiments and the residual oil on gravels. The latter included the oil microdroplets that did not really adhere to the gravel, while the micron-sized droplets lacked sufficient gravity to fall into the conical flask with the emulsion. Therefore, the exact amount of oil stranded on both the original and coated gravels after five cycles could be determined by a mass balance analysis. First, the control experiment without gravel for the same volume of oil emulsion was prepared, and the amount of oil adhering to both the glass columns and conical flasks (m_c) was calculated based on the difference between the emulsion concentration before and after the test and the emulsion volume. For the coating group, two kinds of gravel were collected and rinsed with the same volume of artificial seawater to remove the micron-sized oil droplets on their surface. The oil mass of the artificial seawater after rinsing both gravels (masw) was also recorded. Based on the obtained data, the mass balance equation was written to determine the actual oil adhering to the pristine and coated gravels as:

$$m_0 - m_5 = m_c + m_{ASW} + m$$
 (2)

where m_0 is the oil mass in initial emulsion for both gravels; m_5 is the oil mass of collected emulsion after 5 cycles for both gravels; m_c is the total oil mass stranded on both glass columns and conical flasks; m_{ASW} is the oil mass in artificial seawater that rinsing gravels; m is the actual oil mass adhered on pristine or coated gravels.

The results for both the pristine and coated gravels are also presented in Figure 6-4, which shows that the final oil adhesion content (m) could be calculated using equation (2), with

158.5 μ g for the original gravel and 9 μ g for the modified gravel. The amount of oil flowing through the gravels was the difference between the initial mass (m₀) and the blank oil mass (m_c), with 664 μ g for the pristine gravels and 619.5 μ g for the coated gravel. Therefore, the percentage of oil stranded on the gravel was the ratio of oil adhesion content (m) and actual oil flowing through gravels (m₀ - m_c). In comparison, only 1.5% of the oil adhered to the surface of the alginate hydrogel-coated gravel, while up to 23.9% of the oil remained on the pristine gravel, indicating that the coated gravels had excellent oil-repellent properties. It can therefore be inferred that when the calcium alginate hydrogel coating is applied on shoreline substrates in oil spill incidents, considerably less spilled oil will be absorbed by the shoreline due to the oil-repellent ability of the coated substrates, thus dramatically reducing the difficulty of oil cleanup and recovery.

6.3.3. Performance of alginate hydrogel-coated gravels in batch oil-repellent tests

Batch washing tests were conducted to see how much oil remained on the gravel after a 15-minute washing with artificial seawater. To explore the effects of oil type and weathering status on the oil-repellent performance, the fresh and weathered Hibernia oil, engine oil, and Cold Lake Blend were used, which were corresponding with light crude oil, diesel engine oil, and heavy crude oil, respectively. Figure 6-5 shows the percentage of oil residue after washing with two different gravels, three oil types, and two weathering statuses. It can be seen that independent of the kind of oil or weathering status, only a very small amount (below 1%) of oil remained on the coated gravel after washing compared to that of the pristine gravel with up to around 84%. The results indicated that the coated gravel had very high oil-repellent efficiency (over 99%). Before washing, both the dry pristine and the coated gravels were oleophilic with an oil contact angle of 25.20° and 52.00° in air, respectively, as shown in Figure 6-3 (c) and (d). The addition of artificial seawater made the stranded oil depart readily and quickly from the coated surfaces. The modified

surface was hydrophilic due to its large amounts of hydroxyl groups and numerous microstructures. The seawater could enter and fill the surface microstructure of the coated gravel with high roughness and then form a hydration layer to detach the stranded oil from the surface (Liu et al., 2012; Tang et al., 2020).



Figure 6-5 Oil residue percentage of both pristine and coated gravels for different types of oil and weathering status in batch oil-repellent tests

As shown in Figure 6-5, the percentages of oil residues on the pristine gravel varied dramatically according to the different types of oils, but that of the modified gravel remained almost the same regardless of the oil type. For the original gravel, the percentage of oil residue after washing increased considerably when the oil became more viscous and adhesive, from below 20% for the Hibernia oil to over 80% for the Cold Lake Blend.

However, the coated gravel showed high oil-repellent efficiency for both the light and heavy oils as the permeate medium was still the artificial seawater. Additionally, an oil spill response takes 6 to 72 hours depending on the location and size of the incident site . Spilled oil experiences the most rapid changes in its physical properties within the first 48 hours (King et al., 2017).

Weathering was also considered in the present study. The results for the Hiberina oil and Cold Lake Blend were impacted by their weathering status, and the percentage changes in mass were 10 % and 7%, respectively, based on previous literature (Fingas, 1999; Fingas, 2015). In particular, 72.83% of the fresh Cold Lake Blend remained on the pristine gravel, while the weathered oil residual percentage increased to 84.22%. The reason is that during the weathering process the light oil components were lost due to evaporation, resulting in the increasing viscosity of the Cold Lake Blend from 219 to 1602 cP (Table 6-1). The adhesion of oil to shoreline substrates is dependent on the characteristics of oils, particularly the viscosity (Bi et al., 2021b; Boufadel et al., 2019). However, there was no significant difference in the viscosity of the engine oil before and after the weathering process, so the values of the oil residue on the pristine gravel were almost the same, at around 35%.

Overall, it can be concluded that stranded oil on coated gravel would be easy to removeby surface washing regardless of the oil type or its weathering status, which is particularly favorable for shoreline cleanup. In real oil spill cases, once the spilled oil from marine is set on the shoreline, such as the intertidal zone, the oil will become increasingly sticky and adherent due to its exposure to sea winds; thus, it will be very resistant for removal by cold or warm water flushing (Michel et al., 2013). Other shoreline cleanup methods such as sediment relocation, mechanical removal, and water washing with high temperature and

pressure can be deployed. However, they are typically complicated, laborious, expensive, and toxic, and the result is frequently not satisfactory (Dicks et al., 2002; ECCC, 2016; Etkin, 2000). If the calcium hydrogel coating could be applied to shoreline substrates before oil is stranded, the oil could be easily flushed or washed with almost no damage to the affected zone.

6.3.4. Environmental stability of the alginate hydrogel-coated gravels

There may be a concern for the de-crosslinking of the network in the seawater environment, which would affect the oil repellence of the coated gravel, thus the environmental stability of the alginate hydrogel-coated gravels was also evaluated (Kakita and Kamishima, 2008; Lu et al., 2020a). To be specific, the coated gravel was immersed in the artificial seawater and oscillated at 300 rpm for different time periods from 1 to 24 h. Then, the treated gravels with non-treated pristine and coated gravel were used to conduct the aforementioned washing tests to investigate the effect of environmental factors on the oil-repellent performance of the coating (Figure 6-6). As seen, the percentage of oil residues on the coated gravel remained at very low levels (under 2%) for 24 hours of immersion and shaking in artificial seawater, in comparison with that of the pristine gravel with 31.0% of oil residue. The coated gravel retained its oil-repellent properties in the salt solution for 24 hours, implying good stability in high ionic strength environments. This can be ascribed to the fact that a tight "egg-box" structure was formed by the combination of the Ca^{2+} ions and the -COO⁻ groups in the polygluronate units of the calcium alginate. Furthermore, the unit has a strong ability for auto-cooperative binding of Ca^{2+} ions and acts as a stable crosslinking structure within the coating (Bajpai and Sharma, 2004; Li et al., 2017b; Smidsrød, 1974).

However, an exchange could still take place with the Na⁺ ions and the small number of the

cross-linked Ca²⁺ ions that diffuse out from the egg-box buckled structure into the artificial seawater, resulting in partial de-crosslinking (Balanč et al., 2016; Shoichet et al., 1996). However, in this study, this kind of de-crosslinking was too slight to reduce the oil-repellent stability of the coated gravel. In addition, it would have created a loose structure of the coating on the gravel for more water to fill instead of destroying the networks on the surface, thus promoting the maintenance of oil-repellent properties of the coated gravel (Li et al., 2017b). Therefore, the oil residue percentages stayed almost the same, particularly during the first eight hours. After 16 h, the stability of the coating gravel was slightly affected as the amount of the oil residue increased due to the further decrosslinking. This suggests that the application of calcium alginate coating to the shoreline substrate should be at the right time and in the right place. Relevant studies indicated that the spilled oil along the shoreline can be identified by boats, airplanes, and space-borne satellites, including synthetic aperture radar (Clemente-Colón and Yan, 2000; Garcia-Pineda et al., 2017). Additionally, the amount of oil reaching the beach can be quantified and the location of the impacted area can be predicted by simulations of oil transport (Boufadel et al., 2014; Zhai et al., 2020). Therefore, before the spilled oil runs aground with the tide, the shoreline substrates could be coated with the calcium alginate hydrogel to prevent the substrates from oiling. Even though the oil is stranded on the coated substrates, it would be easily washed away by surface washing.



Figure 6-6 Oil residue percentage of coated gravels after immersing at different times.

6.3.5. Performance evaluation based on the laboratory shoreline tank simulator

To further prove the feasibility of the alginate hydrogel coating on shoreline substrates, tests were conducted using the laboratory shoreline tank simulator. The side views of the tank simulator at low tide (0.1 m) and relative high tide (0.24 m) are presented in Figure 6-7(a) and (b). As shown in Table 6-2, a certain amount of dyed engine oil was mixed with the pristine gravel and the coated gravel to form oiled gravels with an initial oil/gravel ratio of 85.23 mg/g and 82.91 mg/g, respectively. These were put into the pit of the shoreline with 40.6% porosity in the tank, as shown in Figure 6-7 (c) and (d). During the first cycle, the artificial seawater gradually flowed over the oiled gravels to the highest level. Only 0.12 g of the oil was lifted from the pristine gravel to the water surface in the control test, which is shown in Figure 6-7 (e), while 13.68 g of the oil floated from the coated gravel in the coated g
repellent ability in compared to that of the pristine gravel because around 33% of the oil was lifted by the seawater from the surface of the coated gravel recovered by the oil-absorbing pads. Based on the amount of oil floated, it can be inferred that almost all the oil remained on the pristine gravel or entered the subsurface in control test, and two thirds of the oil was either left on the coated gravel or went into the subsurface in coating test. The sample analysis for oiled zone in that pit was conducted after each cycle to determine how much oil was stranded on the pristine and coated gravels. Table 6-2 and Figure 6-7 (g), (i) and (k) show that the oil/gravels ratio in the control test declined from 18.88 to 11.56 mg/g with the cycles. Assuming that the oil residues were evenly distributed in that oiled pit during the whole process, it can be inferred that the oil remaining on the pristine gravel decreased from 9.50 g after one cycle to 5.82 g after three cycles. In contrast, as shown in Figure 6-7 (h), (j) and (l), the oil/gravel ratio of the coated gravel stayed almost same for each cycle, at around 1 mg/g, indicating that only 0.46 g of the oil remained on the gravel after three cycles. The amount of oil entering the subsurface in the two cases could thus be calculated using equation (3):

$$m_{total} = m_{floated} + m_{gravels} + m_{penetration} \tag{3}$$

where m_{total} is the total mass of oil applied to gravels; $m_{floated}$ is the mass of floated oil to surface; $m_{gravels}$ is the mass of oil remaining on pristine or coated gravels in the pit after three cycles; $m_{penetration}$ is the mass of oil penetrating into the subsurface after three cycle.



Figure 6-7 Side views of the tank at low tide (0.1 m) (a) and relative high tide (0.24 m) (b); top views of the artificial shoreline in tanks within 3 cycles for initial states of oiled pristine 134

(c) and coated gravels (d); immersion of oiled pristine (e) and coated gravels (f) at high tide of the first cycle; pristine (g) and coated gravels (h) after the first cycle; pristine (i) and coated gravels (j) after the second cycle; and pristine (k) and coated gravels (l) after the last cycle.

The penetration results for the control and coating tests are provided in Figure 6-7. Almost 37 g of the oil from the pristine gravel entered the subsurface, accounting for 86 % of the total applied oil. For the coated gravels, less oil (66%) penetrated into the deeper substrates compared to the control test. The main reason for the penetration of most of the oil in both tests is that the well-sorted gravel was used as the shoreline substrates, and there were large inter-connected pore spaces where the oil could readily penetrate. Shoreline oil penetration is highly dependent on the shoreline's characteristics, particularly in terms of the porosity and permeability of the substrates (Etkin et al., 2008; Harper et al., 1995; Zhao et al., 2019). Even in this case, the laboratory shoreline tank simulator test still proved that the alginate hydrogel coating could make more stranded oil floated, resulting in considerably less oil remaining on the substrate and penetrating into the subsurface.

	Control test	Coating test
Gravel	Pristine gravel	Coated gravel
Applied oil amount m _{total} (g)	42.87	41.59
Gravel weight (g)	503.24	501.63
Initial oil/gravel ratio (mg/g)	85.23	82.91
Floated oil m _{floated} (g)	0.12	13.68
Oil/gravel ratio after first cycle (mg/g)	18.88	0.99
Oil/gravel ratio after second cycle (mg/g)	12.10	1.09
Oil/gravel ratio after third cycle (mg/g)	11.56	0.92
Oil remaining on gravels mgravels (g)	5.82	0.46
Oil penetration mpenetration (g)	36.93	27.45

Table 6-2 Transport of applied oil in the laboratory shoreline tank simulator

6.4. Summary

In this study, the use of alginate hydrogel coating was proposed as a new initiative for emergent shoreline oiling prevention. The alginate hydrogel-coated gravels showed high surface roughness, as well as remarkable water wetting and low-oil-adhesion properties. There was a low oil adhesion on the coated gravels in the continuous test with oil/water emulsion flow, indicating the excellent oil-repellent properties of coated substrate. The results of the batch oil-repellent tests were independent of the kind or weathering degree of the oil used and oil can be easily washed out from the coated gravels. The coated gravels had good environmental stability and the slightly partial de-crosslinking of alginate structure would not reduce the oil repellence performance. Moreover, the performance of the alginate hydrogel-coated gravel was further proved in the laboratory shoreline tank simulator, in which more stranded oil floated to the water surface and less oil remaining on gravels and entering into the subsurface in the tests with coated artificial shoreline. The developed shoreline oil-repellent coating technique has important implications for oil spill response which can be used in field applications.

Some recommendations for the use of the proposed emergent shoreline oiling prevention method can also be obtained based on the testing results. First, the proposed method is not suitable for sandy and mud beaches even though they have very fine substrates and tightlypacked sediments that are less permeable to oil. This is because it will be difficult for sand and mud to be coated evenly, and they may aggregate with the calcium alginate hydrogel or change the location due to the tides and waves. The larger particle size of the beach substrate is more favorable for coating application. It should be noted that pebbles, cobbles and boulders may be large enough to be coated, but these kinds of beaches are also permeable, so partial oil may still penetrate into the subsurface from the coated substrate. Second, this proposed oil prevention method can be used for the bedrock shorelines, such as bedrock ramp and bedrock platforms, and some solid manmade shorelines, including structures for moorage (docks, wharfs, and marinas) and concrete seawall, as such substrates are impermeable and less affected by waves. Third, the alginate coating material using in this study is derived from the biomass in the ocean. The material itself is green and will not cause toxic effects on the shoreline biota. After emergent application, the coating materials can be degraded under natural conditions. Therefore, the use of alginate hydrogel coating in oiling prevention also represents a sustainable way in shoreline pollution control. Further research is also required to evaluate its performance under complicated shoreline environment and determine the optimal application conditions.

CHAPTER 7. CONCLUSIONS

7.1. Conclusions

In this study, oil removal and prevention from shoreline during oil spills under different environmental conditions was comprehensively studied. Firstly, the comprehensive literature review was conducted to study the causes and effects of oil spills, transport and fate of the spilled oil, various shoreline cleanup methods, and the use of surface washing agents for shoreline cleanup. It improved the understanding of the oil spill and its responding tactics and provided the instruction for surface washing agents.

Second, the investigation into the oil removal from contaminated sand using a surface washing agent under variable environmental conditions was conducted. A preliminary test was conducted to obtain the optimal combination of operating factors of surface washing agent-to-oil ratio (SOR) 2:1, mixing speed 150 rpm, and mixing time 30 min. The results of single-factor experiments showed that high temperature and humic acid concentration of flush water contributed to the performance of a surface washing agent, while salinity and kaolinite concentration could inhibit its performance. The factorial analysis revealed the main effects of temperature and salinity, and the interactive effects of temperature and salinity as well as salinity and humic acid concentration that were significant to the washing efficiency of the surface washing agent.

Third, a green and responsive washing fluid was developed by modifying the nanoclay with a nonionic surfactant to wash the stranded oil on beach sand. A series of characterization results showed changes in the basal spacing, absorption peaks, thermal degradation, surface morphology, and element weights after modification, indicating the surfactant was successfully loaded onto the nanoclay. Batch tests were conducted to illustrate that the factors of washing time, temperature, salinity, pH, and the modified nanoclay concentration enhanced the effectiveness of the nanoparticle fluids to varying degrees. The two-level factorial analysis revealed that the factor of salinity was the most significant environmental factor with the contribution of 68.9% to the oil removal efficiency. It also indicated the interactions of temperature with salinity and salinity with the modified nanoclay concentration were significant to the response. The separation tests suggested the addition of calcium chloride could dramatically reduce the turbidity and the oil concentration in the supernatant for following treatment. Besides, the thermodynamic miscibility model was applied to describe oil/water miscibility in the presence of the modified nanoclay, and the results were also shown to agree very well with experimental results. The nonionic surfactant-modified nanoclay in this study has great potential in shoreline cleanup, which can be seen as a desirable alternative to the existing commercial surface washing agents.

Fourth, a framework for evaluation and selection of surface washing agents in oil spill incidents was constructed to better understand and apply this technique. A decision tree was firstly developed to illustrate all possible scenarios which are appropriate to use surface washing agents in consideration of oil collectability, shoreline character, types and amount of stranded oil, and cleanup requirement. Based on literature review, theoretical modeling, and experts' suggestions, an integrated MCDA method was then come up to select the most preferred surface washing agent from five aspects of toxicity, effectiveness, minimal dispersion, demonstrated field test, and cost. Its suitability and rationality were proved by a hypothetical case. In addition, sensitivity analysis was performed by changing the weight of each criterion independently to check the priority rank of alternatives, and it also verified the robustness and stability of this model. The presented framework has significant implications for future research and application of surface washing agents in the shoreline

cleanup.

In addition, the use of alginate hydrogel coatings was proposed as a new initiative for emergent shoreline oiling prevention. The alginate hydrogel-coated gravels showed high surface roughness, as well as remarkable water wetting and low-oil-adhesion properties. There was a low oil adhesion on the coated gravels in the continuous test with oil/water emulsion flow, indicating the excellent oil-repellent properties of the coated substrate. The results of batch oil-repellent tests showed that independent of the kind or weathering degree of the oil used, oil can be easily washed out from the coated gravels. The coated gravels had good environmental stability and the slightly partial de-crosslinking of alginate structure would not reduce the oil repellence performance. Moreover, the performance of the alginate hydrogel-coated gravel was further proved with a laboratory shoreline tank simulator, in which more stranded oil floated to the water surface and less oil remained on gravels and entered into subsurface. This proposed oiling prevention method can be used not only for shorelines but also for coastal piers, seaports, and solid manmade shorelines. The coating material is derived from the biomass in the ocean and can be degraded under natural conditions. This study may provide a unique direction for the future development of green oil spill control strategy.

7.2. Recommendations for future research

- (1) It is expected to conduct more field tests for both commercial surface washing agents and newly developed modified nanoclay in terms of effectiveness, as the environmental conditions in fields will be more complicated.
- (2) Future study may also focus on not only the oil removal efficiency of washing agents, but also their testing protocols, toxicity, dispersion ability, etc.
- (3) The developed washing fluid with nonionic surfactant-modified nanoclay for beach

sand treatment is required to be evaluated with different oil types and weathering status to further prove its effectiveness. Meanwhile, it is also necessary to conduct the toxicity tests for some representative species to quantify impacts of washing fluid on the environment.

(4) The alginate hydrogel coating was proposed in shoreline oiling prevention, and its effectiveness and environmental stability were evaluated with batch tests and a simulation tank test under lab conditions. It is necessary to assess its performance under a complex shoreline environment and determine the optimal application conditions.

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PUBLICATIONS

Peer-reviewed journal articles

(1) **Bi, H.**, An, C., Chen, X., Owens, E., Lee, K., 2020. Investigation into the oil removal from sand using a surface washing agent under different environmental conditions. *Journal of Environmental Management (Elsevier)* 275, 111232. (Adapted into CHAPTER 6).

(2) **Bi, H.**, An, C., Owens, E., Lee, K., Chen, Z., Mulligan. C.N., Taylor, E., Boufadel, M., 2021. A framework for the evaluation and selection of shoreline surface washing agents in oil spill response. *Journal of Environmental Management (Elsevier)* 287, 112346. (Adapted into CHAPTER 5).

(3) **Bi**, **H.**, An, C., Mulligan. C.N., Wang, Z., Zhang, B., Lee, K., 2021. Exploring the use of alginate hydrogel coating as a new initiative for emergent shoreline oiling prevention. *Science of the Total Environment (Elsevier)* 797, 149234. (Adapted into CHAPTER 6).

(4) **Bi, H.**, An, C., Mulligan. C.N., Zhang, K., Lee, K., Yue, R., 2021. Treatment of oiled beach sand using a green and responsive washing fluid with nonionic surfactant-modified nanoclay. *Journal of Cleaner Production (Elsevier)*, under review (Manuscript Number: JCLEPRO-D-21-16798). (Adapted into CHAPTER 4).

(5) Yue, R., An, C., Ye, Z., **Bi, H.**, Chen, Z.K., Liu, X., Zhang, X., 2021. Cleanup of oiled shoreline using a dual responsive nanoclay/sodium alginate surface washing agent *Environmental Research (Elsevier)*, under review (Manuscript Number: ER-21-4948).

Conference abstracts

(1) **Bi, H.**, An, C., et al. (2020). Investigation into the oil removal from sand using a surface washing agent under different environmental conditions, Multi-Partner Oil Spill Research Initiative (MPRI) Student Research Forum. November 13, 2020.

(2) **Bi, H.**, An, C., et al. (2020). Performance of a surface washing agent impacted by environmental conditions. 70th Canadian Chemical Engineering Conference (CCEC 2020). October 25-28, 2020.

(3) Chen, Z.K., An, C. Tian, X., and **Bi, H.** (2020). Investigating the potential application of biomass-derived nanoparticles in oiled beach cleanup. 70th Canadian Chemical Engineering Conference (CCEC 2020). October 25-28, 2020.