SWITCHABLE SURFACTANTS FOR SOIL REMEDIATION

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Abstract

Soil remediation requires technologies to restore contaminated soil to a state that is environmentally acceptable. In most cases, while the soil can be remediated the contaminant itself cannot be reclaimed. Soil washing involves cleaning contaminated soil with a wash solution, generally an aqueous solution of a surfactant. It was proposed that using switchable surfactants for washing oil-contaminated soil will not only help remove the oil from soil, but also aid in the recovery of the oil contaminant from the wash mixture.

Six surfactants were evaluated for their ability to wash Ottawa Sand artificially contaminated with North Sea crude oil. A water wash solution was used as a control. Two commercial surfactants, sodium dodecyl sulfate (SDS) and Triton X-100, and four switchable surfactants, N'-octyl-N,N-dimethylamidine (C8), sodium octyl 4-hydroxy-3-nitrobenzoate (SAS1), sodium 4-(octyoxy) benzoate (SAS2) and sodium laurate (SAS3) were studied. The surfactants were assessed based on their ability to remove oil from the sand and their ability to separate the crude oil from the wash mixture after CO_2 treatment. Oil removal from sand was determined by gravimetric analysis. Oil content in the wash mixture was determined using Solid Phase Extraction and gravimetric analysis. It was determined that switchable surfactants are able to remove North Sea crude oil from sand as well or better than the commercial surfactants and have the added feature of oil separation and recovery from the wash mixture after CO_2 treatment.

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List of Symbols and Abbreviations

atm	atmosphere
C8	N'- octyl-N,N-dimethylamidine
CEC	cation exchange capacity
CMC	critical micelle concentration
$cmol_c$/kg	centimoles of charge per kilogram of soil material
$cm\ s^{-1}$	centimeters per second
ºC	degrees Celsius
g	gram
GC/MS	gas chromatography/mass spectrometry
h	hour
kg	kilogram
L	litre
LC_{50}	lethal concentration to kill 50 % of the population
LD_{50}	lethal dosage to kill 50 % of the population
m^3	cubic meter
min	minute(s)
mg	milligram
M	molar
mM	millimolar
mol	mole
mm	millimeter

O/W	oil-in-water emulsion
ppm	part per million
RT	room temperature (23 ºC)
SAS	switchable anionic surfactant
SAS1	sodium octyl 4-hydroxy-3-nitrobenzoate
SAS2	sodium 4-(octyloxy benzoate)
SAS3	sodium laurate
SDS	sodium dodecyl sulfate
SOM	soil organic matter
UV-Vis	ultraviolet visible spectroscopy
W/O	water-in-oil emulsion
wt %	weight percent

1 Introduction

Water, air, sunlight and soil combine to produce life on earth.[1] Soil, in particular, is essential as it supports the construction of various infrastructures and, of which the most important is, the production of food. Maintaining soil health is vital if we wish to sustain our current quality of life. As industrial productivity has increased, the amount of anthropogenic pollution released into the environment has also increased. Our lands and waterways, which provide many sources of/for life, have also become sinks for waste such as sewage, garbage and chemical waste from industry.[1] Each sink is not independent of the other. Pollution entering the atmosphere for example, will eventually redeposit onto the soil and leach into the water system. A graphical representation (Figure 1), adapted from the U.S. Geological Survey,[2] illustrates how waste from residential, agricultural and industrial activities flows down through the soil column eventually, ending up in the groundwater system.

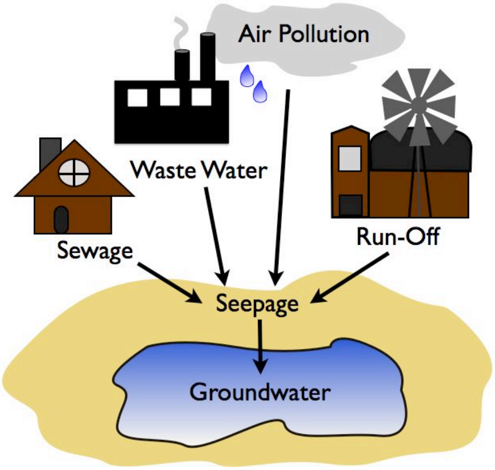


Figure 1: Representation of the interconnection between air, soil and water and the pathways for chemical contamination. (Modified from US Geological Survey, Circular 1225, 1999)

1.1 What is Soil?

Soil is not a single definable entity. Rather, a broad definition of soil could be the following; a complex network of organic and inorganic matter, which together form the medium for growth of food and provide the foundation for shelter.[3] While a universal type of soil does not exist, it is the combination of the various inorganic and organic components which produce the variety of soils found on Earth.

1.1.1 Inorganic Components

Mineral particles (primary and secondary) and rocks (combination of minerals)[3] make up the inorganic components of soil[4,5]. Primary minerals ("minerals unaltered chemically since its deposition and crystallization from molten lava")[4] include quartz and feldspar. Secondary minerals (formed from the weathering of primary minerals) include aluminosilicate minerals such as kaolinite $Al_2Si_2O_5(OH)_4$, and montmorillonite, $M_x(Al, Mg, Fe^{2+})_4Si_8O_{20}(OH)$ (M = Na and Ca), and aluminum oxides such as gibbsite, $[Al(OH)_3]$. These minerals make up what is referred to as the soil texture and are divided into 3 major texture classes: sand, silt and clay.

Sand particles are the largest of the three particle classes, ranging from 2 to 0.05 mm in size. Their single mineral component is quartz (SiO_2).[5] As a result of the larger particle size, the pore diameter between the particles is large, allowing for easy water drainage. Silt particles are composed primarily of quartz, but the particle size is much smaller ranging from 0.05 to 0.002 mm. Unlike sand, the pore diameter between silt particles is much smaller and more numerous prohibiting easy drainage of water.

Clay is the third major particle class, with particle sizes less than 0.002 mm. These particles have a large surface area and a large capacity to adsorb water and other substances, making drainage much more difficult compared to sand and silt.[5] As a result of their size, clay particles behave more like colloids. Unlike sand and silt, clay is not comprised entirely of quartz, but rather tetrahedral and octahedral arrangements of various elements including Al, Mg, K, Fe, Na and Ca. Three major types of clay colloids exist: (1) crystalline silicate clays, (2) noncrystalline silicate clays, and (3) iron and aluminum oxide clays.[5]

An important property of the solid particles in soil is the cation exchange capacity (CEC). Soil colloid particles generally carry a negative charge. There are two sources of the negative charge on silicate clays. The first arises from the negative charge on the oxygen atoms which lie on the outer edge of the silicate crystal.[3] The second arises when an atom of lower positive charge displaces an atom of higher charge in the crystal. For example if an Al^{3+} is replaced by a Mg^{2+} atom, a net negative charge results.[3,5] Due to the negative surface charges, various mineral cations such as Ca^{2+}, Mg^{2+}, K^+, Na^+ can be attracted and released from the surface of the colloid particle.[3] The ability or strength of a soil to attract, hold and release cations is measured by the cation exchange capacity, expressed in centimoles of charge per kilogram of soil material ($cmol_c/kg$).[3] The CEC is measured by titrating a known mass of soil with a solution of ammonium cations. A second titration with a solution containing a different cation, displaces the ammonium cations. The mass of ammonium ions displaced yields the CEC.[3] Many nutrients found in the soil contain the cations mentioned. Therefore, the CEC is also a measure of the soil's ability to attract and release these nutrients.

1.1.2 Organic Components

Organic components in soil are commonly referred to as the soil organic matter (SOM). SOM is important because it retains the majority of water and nutrients found in the soil. Organic matter includes living and dead organisms, plant and animal residues in various stages of decay, and humus.[3] Humus is defined as a "largely amorphous and colloidal mixture of complex organic substances no longer identifiable as tissues".[5] Humic substances, derived from the humus, are complex, polymeric and ill-defined compounds, that is, their chemical and physical properties do not resemble any one specific organic compound[5] and are formed by secondary synthesis reactions.[4] These substances make up 60 to 80 % of the soil organic matter.[5] They are usually dark in colour with molecular weights ranging from 2,000 to 300,000 g/mol. A reproduction of a schematic of humic substance formation[4] is shown in Figure 2. A common pathway (pathway 4, Figure 2) proposed by Selman Waksman[4] suggests humic substances are modified lignins that remain after microbial attack.

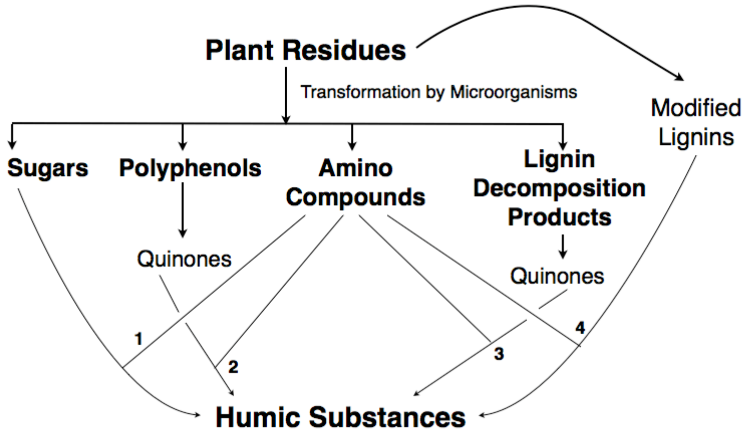


Figure 2: Mechanisms for the formation of humic substances. Modified from F.J. Stevenson, "Humus Chemistry." Copyright © 1982 John Wiley & Sons, Inc.

Humic substances also form colloids, like clay, and can also influence the CEC of a soil. Common functional groups present in humic acids include phenols, carboxylic acids, and alcohols. Depending on the soil pH, these compounds can be deprotonated, and are further sources of negative charge which can interact with the mineral cations present in the soil.

Other organic species are the various macro and microorganisms which can be found in soil. Microorganisms, like bacteria and algae, decompose and dispose of plant and animal remains, forming humus.[3] They are also involved in many nutrient cycles helping to maintain soil health. Macroorganisms, including worms and vertebrates consume organic matter and help to aerate and mix the soil.

Together the inorganic and organic components combine to give us healthy soil to support life on Earth; however, the increase in pollution has put our soil's health in jeopardy and, in so doing, endangers its ability to support life on Earth.

1.2 Soil Contamination

"A contaminant is a substance that can pose or is likely to pose an immediate or long-term hazard to human health or the environment and whose concentration exceeds natural background levels".[6] Soil pollution or soil contamination, in particular, is of increasing concern. In Canada alone, there are over 19,700 documented contaminated sites in the federal government database.[7] Due to the complexity of the soil composition, type of contaminant and the date of the contamination, many of these sites have not been assessed and, therefore, have gone untreated. Soil pollution is a concern on an environmental and economic level. Pollutants in the soil can permeate the soil column and reach the groundwater channels. Groundwater is a major source for drinking water, therefore, diminishing its quality is a concern for all organisms benefitting from clean water. Economically speaking, contaminated soils can reduce the usability of land for development[8] and for agriculture, reducing the potential profits generated for any activity associated with the land. Therefore, reducing soil quality diminishes its ability to provide healthy sustenance (and profit) for inhabitants.

With the increasing knowledge of the impact of contaminants, policies and regulations have been put in place to reduce the quantity of pollutants being dumped, and to ban those which may be causing the most harm. Both the Canadian and United States Governments have issued policies such as the Canadian Environmental Protection Act (CEPA) and established agencies, such as the US Environmental Protection Agency (US EPA) which outline priority pollutants and regulations and which describe how to properly use and dispose of these pollutants.[9,10] Priority contaminants are divided into two major classes: inorganic and organic. Inorganic priority pollutants include lead, cadmium, mercury and arsenic. Organic priority pollutants include polychlorinated biphenyls (PCBs), and petroleum hydrocarbons and polycyclic aromatic hydrocarbons (PAHs). Both inorganic and organic pollutants are found in soil. According to the Canadian Federal Contaminated Sites Inventory[7], petroleum hydrocarbons alone comprise over 30% of contaminants found on the documented soil sites in the Inventory.

However, even with policies and regulations, some contamination will inevitably occur and, as a result, need to be remediated. It is important that the remediation process be undertaken quickly and effectively with the least environmental damage.

1.3 Soil Remediation

The goal of soil remediation is to reduce the risks to the environment and human health posed by contaminants in the soil. This might include containing contamination (in the case of a spill), full or partial removal of contamination to a safe level, restricting access and/or monitoring the site.[11] Ideally, full or partial removal of contamination versus simply containing and/or restricting access to the site is preferred. If full or partial removal is achieved, the land can be reclaimed and re-used.

Various technologies have been developed to address the full or partial removal of soil contamination. These methods have been divided into 3 major classes: biological, chemical, and physical.[6] These classes help to distinguish the basic principles behind the methodologies utilized. The classes are further subdivided into whether they are performed in- or ex-situ. In-situ is always done on site while ex-situ can be done both on or off-site.[12] From these classes, one can find methods such as bioremediation by phytoplankton, soil washing, soil vapour extraction and pyrolysis. Since soil remediation can be quite difficult due to the complexity of the soil matrix and the type of contaminant(s), several methods may need to be implemented to achieve the desired remediation level. For this project, the remediation technique investigated was soil washing.

1.4 Soil Washing

Soil washing is listed under the chemical class of remediation technologies.[6] It is one of the most versatile soil remediation techniques because it can be applied to virtually all target contaminants: petroleum hydrocarbons, metals, PCBs, pesticides, PAHs and non-metallic inorganic compounds.[13] Soil washing is a chemical process, which can be done in- and ex-situ.[14] The goals of soil washing are to remove the contaminant from the soil and to concentrate the contaminants to a smaller volume for further treatment after the remediation has been completed.[14] The removal of the contaminants is accomplished by the scrubbing or "washing" of the soil with a washing solution (water and a chemical additive). The cleaned soil is re-deposited, and the washing solution cleaned and, ideally recycled. Residual sludge (containing the contaminant) and contaminated water are sent to a wastewater facility or similar treatment site. Figure 3 is a schematic adapted from the US EPA[15] outlining the general ex-situ soil washing procedure.

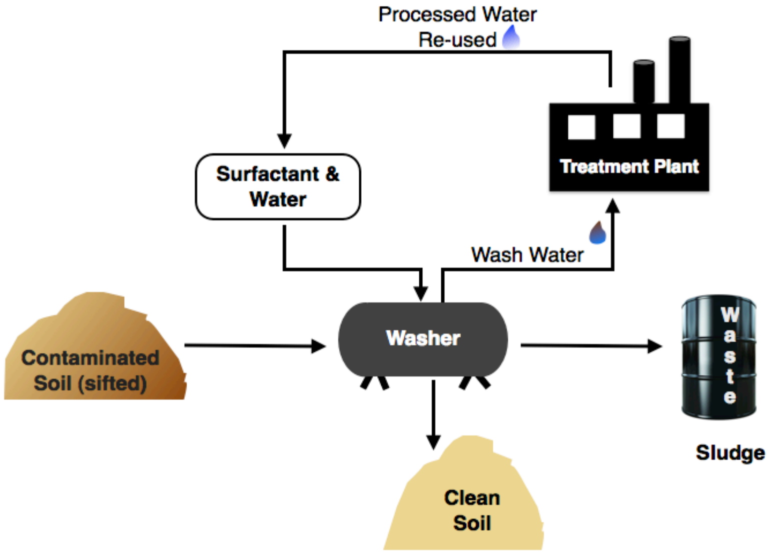


Figure 3: Soil Washing Schematic. Illustrates the polluted soil entering the cycle. It gets washed in the washer with clean soil and sludge as the outputs. The water is then sent for further treatment and re-used in the cycle with the addition of surfactant to continue the process. (Modified from A Citizen's Guide to Soil Washing, US EPA.[15])

1.4.1 Site Characterization

Before any type of soil washing can begin, as with any other remediation technique, the site must be evaluated. Bench tests are conducted on soil samples from the contaminated site to characterize the soil and contaminants present. For soil washing, this also includes tests to evaluate different chemical additives and determine which is most suitable for the washing. Soil characterization is important because its chemical and physical properties can greatly influence the removal efficiency due to the interactions between the soil and the contaminants.[16] Characterization begins with a physical separation of particles within the soil. Typically soil is composed of 3 major particle types and sizes: sand, clay and silt. Particle size is important because it will dictate how easily contaminants will be removed. A large percentage of organic contaminants are associated with or bound to very small silt and clay soil particles; therefore, soil with more fines will be more difficult to remediate. Moreover, the fines tend to disperse into the water and, due to their size, are difficult to remove. If the fines cannot be removed, these particles end up at the treatment facility with the wastewater. Therefore, soil washing is most appropriate for soils that have at least 50 % gravel/sand content (i.e. coastal sandy soils, and soils with glacial deposits).[14] Particle separation is achieved using sieves with the maximum size of particles allowed being 10 to 50 mm. During bench screening tests, only particles with a minimum size of 2 mm are tested for contamination. A 50 % reduction in contamination of the sample with particles greater than 2 mm is considered adequate to proceed with soil washing.[14]

Another important feature of soil is its cation exchange capacity (CEC). Soils with CEC values less than 50 to 100 cmol_c/kg respond better to soil washing.[14] Soil pH is also vital because it can affect both the contaminants and the wash solution. Both CEC and pH are especially important for remediation of metals because they influence the degree of binding of the metal to the soil. For example, at low pH the mobility of a cation is increased, but at high pH, the cation may become bioavailable (as is the case with zinc) and/or sorption of the chemical to the soil is increased.[17]

Partition coefficients are also important for modeling potential outcomes during chemical characterization.[18] Partition coefficients are equilibrium constants that help to determine where a substance will be found in a particular system. The most common partition coefficients used are the soil partition (sorption) coefficient (K_{oc}) and the octanol-water partition coefficient (K_{ow}). The K_{oc}, described by Equation 1[5] is a measure of how much a substance will partition between water and the organic matter in soil.

Equation 1

$$K_{oc} = \frac{\text{mg chemical sorbed/kg organic carbon}}{\text{mg chemical/L solution}}$$

The K_{ow}, described by Equation 2[19] measures the partitioning of a compound between an organic phase (octanol) and an aqueous phase (water). It is often expressed as a logarithm.

Equation 2

$$K_{ow} = \frac{[\text{solute}]_{\text{octanol}}}{[\text{solute}]_{water}}$$

The partition coefficients of a compound can help to determine how difficult it will be to remove from the soil. As a result, chemical characterization is necessary to assess the type of contaminant and the type of soil.

1.4.2 Soil Washing Procedure

First, the soil is screened. Debris and oversized material, not pertaining to the soil are discarded. The soil is then divided into the various fractions: sand, silt and clay. Separation of the fractions allows the largest fraction, sand, to be treated first, while the contaminant is concentrated to the silt and clay, which can be treated or sent for further treatment.[20] Sand is easier to treat because its particles are larger and has a lower organic matter content.[20]

After size separation, any volatile contaminants present in the fractions are removed by heating the soil. The contaminated fraction to be washed is then introduced into a washer. The wash solution, which is composed of water and an extraction agent, typically a surfactant, is added and mixed with the contaminated fraction. Thorough mixing is required to ensure good contact between the soil and the washing solution; this helps to dissolve and disperse the contaminants. Soil washing is usually done with hot water because higher temperatures help to reduce the viscosity of contaminants like oil.[21] Further mixing, washing, rinsing and additional size separation steps may be required. Ideally, the clean soil is then filtered out and the wash water is treated and recycled. Any sludges and contaminated fines (particles too small to settle out of solution) are removed and sent to water treatment facilities.

A measure of soil washing success can be described by the mass reduction percent of the contaminated material, calculated using Equation 3[20]. The mass of the clean products is the mass of the fraction of contaminated soil which has been cleaned to meet regulatory standards.

Equation 3

$$\text{mass reduction (\%)} = (1 - \frac{\text{feed soil (tons) - clean products (tons)}}{\text{feed soil (tons)}}) * 100\%$$

1.4.3 In-Situ vs. Ex- Situ

Soil washing can be done both on and off-site. In-situ soil washing is done on-site without the removal of material and requires pumping the washing solution down into the contaminated unexcavated zone. The washing solution is then pumped through the contaminated zone and pumped back up to the surface. Treatment times for this type of washing vary from less than 1 year to between 1 and 3 years.[13] One limitation to this type of washing is the permeability of the soil in its undisturbed state. If the permeability is less than 4-10 cm s^{-1}, the soil is considered unsuitable for in-situ washing; the washing fluid is not able to penetrate and reach the contaminated site. Therefore, ex-situ soil washing may be required. [22]

Ex-situ soil washing requires the excavation of the soil, which is then processed either at a different location or at a clean-up station on site. Equipment used for ex-situ soil washing can be broken down into the following modules[21]: (1) a screening machine that can remove oversized particles; (2) a module to remove the contaminants, i.e. perform the washing; (3) a wastewater treatment module in which any dispersed soil and contaminants are removed from the water; (4) a residual management module, to handle the actual contaminants either by recycling, desorption, bioremediation or stabilization for landfills; (5) a volatile emission control module; and (6) a wash water storage and management module. Some processes recycle more than a million gallons of water per day. Treatment times for ex-situ washing are less than a year.[23] Limitations to this technology include: (1) the space required for the unit installation; (2) infrastructure on or near site which can prevent soil excavation; and (3) treatment may create anaerobic conditions in the soil which can induce chemical transformation(s) of the contaminants, increasing their toxicity.[23] Limitations to both ex- and in-situ washing include: soil composition, soil organic matter content (can affect soil-contaminant-wash fluid interactions), location of contamination within the soil (the depth of the contamination increases the cost) and the possibility to produce large volumes of contaminated wash water depending on the volume of soil that needs remediation and the types of contaminants.

1.5 Components of Soil Washing: The Contaminant and The Chemical Additive

1.5.1 The Contaminant: Crude Oil

Crude oil is the collective term used to describe the "complex mixtures of hydrocarbons and other compounds in the form of solids (bitumen, tars), liquids and gases (natural gases), extracted from the topmost layer of the Earth's crust".[24] Carbon is the most abundant element comprising of 85% of the mass of crude oil, with hydrogen next at 13% and other elements such as sulfur, nitrogen, oxygen, lead, copper, chromium, nickel and vanadium rounding out the last 2%.[24] While crude oil cannot be described by one specific and well defined organic compound, its contents can be grouped into four classes of compounds, abbreviated as SARA: saturated compounds, aromatics, resins and asphaltenes (complex mixtures rich in aromatic and heterocyclic compounds)[25, 26]

Crude oil composition depends on the biological source material (biomass) and the geological conditions under which it was converted to oil.[24] Oil reservoirs can be found all over the world including: Canada (eg. Alberta and Saskatchewan), the United States (eg. Texas), South America (eg. Venezuela), Russia, the Middle East (eg. Saudi Arabia) and parts of Africa and China.[24]

Given the diversity of compounds, crude oils can be classified as light, medium, heavy and any variation in between. To better determine the difference between a light and heavy crude, the American Petroleum Institute has assigned an API gravity to all oils, described in Equation 4. Light crude oils have an API gravity greater than 31.1 and heavy crudes have an API gravity lower than 22.3 (water has an ºAPI equal to 10).[24]

Equation 4

$$^{\circ}\text{API}=\frac{141.5}{\text{specific density}}-131.5$$

Crude oil found naturally in the soil may not necessarily be considered a soil contaminant[27], but it can become problematic if it migrates towards the groundwater level. Crude oil migration depends on the properties of the oil such as its density and viscosity, and the soil properties such as its permeability. Denser oils will sink until they reach an impermeable layer. Less dense crude oils will tend to float at the interface between the water-saturated and unsaturated zones and spread horizontally in the direction of groundwater flow.[28] It only takes 1 g of oil to contaminate 1 m^3 of groundwater to 1 ppm.[28] Therefore, if the crude oil has been removed from its natural source and is spilled as a result of processing or transportation, it can be considered a soil contaminant, because it could have a negative impact on the surrounding environment.

1.5.2 Why Crude Oil?

Everyday we come into contact with products directly and indirectly derived from crude oil such as fuel oil and plastics.[24] The U.S. Energy Administration, estimated Canadian oil production in 2008 to be 3.4 million barrels per day with a consumption rate of 2.3 million barrels per day with the remaining barrels being exported primarily to the U.S.[29, 30]

The high demand for oil and its derivatives means that crude oil obtained from land and sea drilling needs to be transported and stored. Transportation from the oil fields to the consumer involves as many as 10 to 15 transfers, from oil tankers to pipelines to tank trucks.[30] Oil spills in Canada are attributed mainly to pipeline transfers.[30] As a result of the numerous transfers, the probability for leaks and spills is increased.

Oil spills are not a thing of the past. The BP oil spill off the coast of Louisiana in 2010 is only a recent reminder of the ever-present dangers associated with our dependence on crude oil. To prevent oil spills, legislation and operating codes have been put in place and high fines are associated with cleanup in the event of a spill. Cleanup costs in Canada average \$20 per L of oil spilled and worldwide the cost ranges from \$20 to \$200 per L, depending on the oil and location.[30]

The economic impact is not the only downfall to an oil spill. There is also an impact on the habitats and ecosystems in the affected and surrounding areas. An oil spill near a marsh has a significant impact on the wildlife and vegetation. Marshes are habitats for many marine and bird life and are rich in vegetation, which trap oil.[30] Marshes are also more difficult to access, which inhibits the cleanup process. It may be years before a marsh is able to recover.[30]

Various organizations around the world maintain records on oil spills. In Canada, Environment Canada maintains a database and in the United States, the Coast Guard keeps a similar database for spills in navigable waters.[30] However, statistics relating to the size or volume may be misleading because of inconsistencies in reporting procedures. Often the total amount of oil may be unknown.[30] Overall, the cost of crude oil spills is widespread and significant given the impact on the environment, society, the economy and the oil companies responsible.

1.5.3 The Chemical Additive: Surfactants

Soil washing requires the use of a chemical additive that promotes the release of the contaminant from the soil and into the water. This project focused on surfactants as the chemical additive used to remove crude oil from contaminated soil.

1.5.3.1 What are Surfactants

Surfactants are ubiquitous chemicals used in a variety of industries: detergents and cleaners, pharmaceuticals and food and packaging.[31] They are amphiphilic molecules composed of a hydrophilic and a hydrophobic moiety[32] and are used to help reduce the surface tension between two interfaces. Surfactants can be divided into three different classes, depending on the form their hydrophilic portion takes when added to water; they are: non-ionic, anionic or cationic.

In soil washing, surfactants are used to liberate the oil from the soil by reducing the surface tension between the oil and the water, as well as decreasing the attraction between the contaminant and the soil. Laboratory- and field-scale tests have shown that surface-washing agents are able to liberate as much as 90 to 95% of the oil from surfaces such as rocks.[30]

1.5.4 Properties

Surfactants can be viewed as "performance" chemicals, meaning they are designed to carry out a specific function.[33] As not all surfactants are equal and interchangeable, the specific application determines the choice of surfactant. Properties associated with the performance of a surfactant, are its critical micelle concentration, emulsification ability, the hydrophile-lipophile balance, biodegradability and toxicity.

1.5.4.1 Critical Micelle Concentration & Emulsification

At low concentrations in solution, the surfactant is present as monomers. If the surfactant concentration is increased, the monomers begin to accumulate and at a certain concentration, form aggregates known as micelles. This is known as the critical micelle concentration (CMC).[33] Micelle formation dramatically affects the physical properties of the solution, such as surface tension and conductivity. The CMC can be determined by measuring a physical property of the solution, for example surface tension, as a function of surfactant concentration. The point at which there is a break in the curve is the critical micelle concentration.[33]

In soil washing, the CMC is important because it helps to distinguish the two mechanisms used to describe the process of oil removal from soil using surfactants. The two mechanisms are mobilization and solubilization and occur below and above the CMC. During mobilization, surfactant monomers accumulate at the soil-water interface, increasing the contact angle between the soil and the contaminant. The contact angle is the degree of contact a liquid at equilibrium makes with the other phases with which it is in contact; usually a solid substrate and a gas.[33] Repulsive forces between the soil particle surface and the surfactant hydrophilic group release the oil from the soil particles.[34] Solubilization of the contaminant, occurs above the CMC. In this mechanism, the micelles are formed, providing for the partitioning of the contaminant from the soil surface into the hydrophobic core of the micelles.[34]

An emulsion is a heterogeneous system consisting of at least one immiscible liquid dispersed in another in the form of small droplets, usually with a diameter of <0.1 mm.[31] Emulsions are classified by differentiating between the dispersed phase and the continuous phase. In most cases, water will be one of the phases, therefore emulsions can be described as either an oil-in-water (O/W) or water-in-oil (W/O). Soil washing results in O/W emulsions. Emulsions are generally not very stable; hence surfactants are used as emulsion stabilizers. Emulsification of oil in water by surfactants is the principle behind using surfactants for soil washing.

1.5.4.2 Hydrophile-Lipophile Balance

The concept of the Hydrophile-Lipophile Balance (HLB) was developed to correlate the chemical structure of a surfactant with its surface activity.[31] The HLB value can help to determine which surfactant should be used in a particular application. The HLB is calculated using empirical formulas. These formulas generate numbers from 0 to 20 on an arbitrary scale. Surfactants with high HLB values are very water-soluble, act as good detergents, and stabilize O/W emulsions. Surfactants with a low HLB tend to be less water-soluble and are suitable for stabilizing W/O emulsions. Table 1 gives the various HLB ranges with their associated applications[31].

Table 1: HLB Ranges and their general applications

HLB Range	*General Application*
2-6	W/O Emulsions
7-9	Wetting and spreading
8-18	O/W Emulsions
13-15	Detergency
15-18	Solubilization

Detergency is particularly important for soil washing. Detergency describes the "process of removing unwanted material from the surface of a solid by various physiochemical and mechanical means related to surfactant action".[31] Therefore, surfactants with HLB values within 13-15 would be considered ideal for soil washing.

1.5.4.3 Biodegradability and Toxicity

Both a surfactant's biodegradability and its toxicity are important factors when considering surfactants for soil washing. Biodegradation may be defined as the "removal or destruction of the chemical compounds through the biological action of living organisms".[31] Toxicity, on the other hand, describes the harmfulness of a compound. It can be described as acute or chronic and is generally expressed as an LD_{50} or LC_{50}, the dosage or concentration required to kill 50 % of a target population.[19] Surfactants employed in soil washing should be biodegradable and possess the lowest possible acute and chronic toxicity.

General structural factors that promote biodegradability in surfactants, are: increased linearity in the hydrophobic portion, terminal position of a phenyl ring, and fewer oxypolyethlene groups. Structural factors, which decrease toxicity are: decreased linearity of the hydrophobic group, central position of the phenyl ring, and a greater number of oxyethylene groups. Evidently factors promoting biodegradability also promote toxicity, therefore, the art of surfactant design is finding the structure, which carries out the desired function and poses the least amount of environmental risk.

1.6 Switchable Surfactants

As noted earlier, surfactants are performance compounds designed to perform one particular function. Switchable surfactants, however, have the ability to perform two particular functions upon application of a trigger. The switchable surfactants developed by Jessop and co-workers[35] can be reversibly converted between a form with surface activity, and a form with greatly reduced or even negligible surface activity to a molecule upon the application or removal CO_2.

The first class of switchable surfactants was cationic and based on long alky chain amidines.[35]. When treated with 1 atmosphere of CO_2 the neutral amidine, which is a good demulsifier, is converted into an amidinium bicarbonate salt, which acts as an emulsifier, Figure 4. To date, these switchable surfactants have been found to have the ability to stabilize alkane/water emulsions, and to have potential utility in emulsion polymerization and in the crude oil industry.

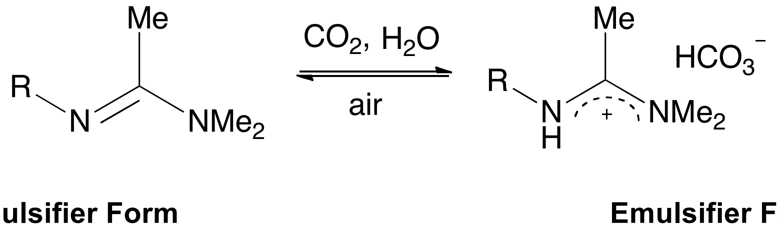


Figure 4: Examples of cationic switchable surfactants. R = $C_{12}H_{25}$, $C_{16}H_{33}$. The amidine in its neutral form (L) acts as a demulifier and when protonated the amidinium bicarbonate salt (R) acts as an emulsifier.

Switchable anionic surfactants (SAS) have also been developed. Here, the principle is reversed. The surfactant is active in its salt form, like the cationic surfactants, but is transformed to its non-surfactant form by the addition of 1 atmosphere of CO_2. Application of heat removes the CO_2 and the molecule reverts back to its surfactant form. Figure 5 is an example of an anionic switchable surfactant developed in the Jessop Group.[36]

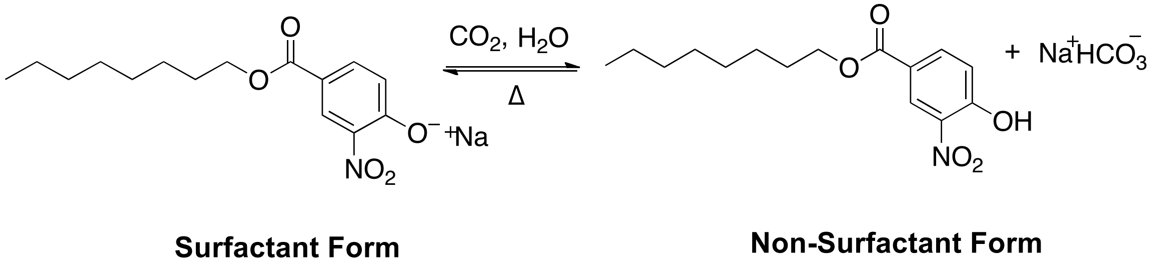


Figure 5: An example of an anionic switchable surfactant: as the salt (L) it acts as a surfactant and when protonated, it precipitates out of water and no longer functions as a surfactant (R).

1.7 Research Objectives

It is proposed that the switchable surfactants can be used to improve the soil washing process. Figure 6 outlines how the switchable surfactants (cationic or anionic) can be introduced into the current model for soil washing. After the washing is completed and the soil has been separated, the washing solution will be brought into a separator. Depending on the surfactant, air or CO_2 would be introduced, causing the surfactant to be "turned off" and resulting in the separation of the crude oil and surfactant from the wash water. The crude can then be reclaimed and recycled, while the wash water and surfactant can be re-introduced into the washing cycle.

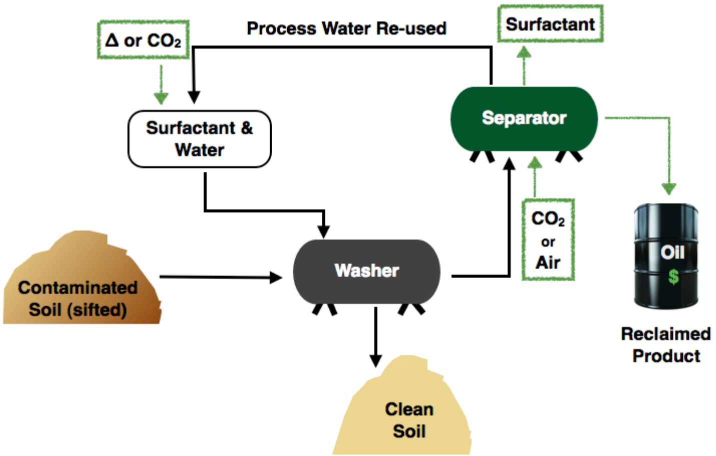


Figure 6: Proposed Solution for Soil Washing using Switchable Surfactants. The start of the cycle is the same. The difference is the inclusion of a separator which will introduce either CO_2 or air, depending on the type of surfactant. This will cause the separation of surfactant, contaminant and water, all of which could be re-sold or re-used. (Modified from A Citizen's Guide to Soil Washing, US EPA.[15])

Research objectives included the following: (1) developing a method to demonstrate and compare the washing ability of both commercial and switchable surfactants; (2) determining the efficiency of the separation and recovery of crude oil from water and; (3) determining the efficiency of surfactant separation, recovery and reuse.

2 Model System & Method Development

2.1 Introduction

To determine the applicability of the switchable surfactants developed by Jessop and co-workers versus surfactants currently on the market for soil washing, a method was needed. This method would need to be able to differentiate the surfactants based on their ability to first wash oil off soil and then separate the oil from the water. Method development was based on finding a representative soil/crude oil sample system on which the washing could be done. Ottawa Sand was chosen as a representative soil matrix and the oil contaminant was North Sea crude oil.

Analysis of this soil/crude oil system was divided into two parts. First, the sand/oil sample was analyzed to determine the ability of the surfactants to remove oil from the soil. Next, the wash mixture (oil, surfactant and water) was analyzed to determine the ability of the surfactants to separate oil from the wash water. The present chapter describes the initial stages of the method development.

2.2 Experimental

Sources of reagents and supplies are listed in Chapter 3. The procedures outlined were developed by modifying methods reported in literature.[26, 32, 37]

2.2.1 Sand Contamination

Artificial sand contamination by crude oil was achieved by adding either 0.53 g (for 1 wt%) or 2.5 g (3.8 wt%) of North Sea crude oil to a 400 mL beaker. Tetrahydrofuran (THF) was added to dissolve the oil. Enough Ottawa Sand, 53 g and 62 g was added to achieve a contamination level of 1.0 wt% and 3.8 wt% (oil on sand) respectively. The mixture was stirred with a spatula and left to sit overnight to allow evaporation of THF. Afterwards, the sand was broken up, mixed in the beaker and transferred to an amber vial.

2.2.2 Washing

A sand washing experiment included a wash with water, a commercial non-switchable surfactant and a switchable surfactant. 0.5 wt% solutions of the surfactants were prepared by adding 0.056 g of surfactant to 11 g of water in 20 mL vials. 5 g of artificially contaminated sand was added to each vial containing the wash solution (water and surfactant). A stir bar was added to the vials, and the samples were stirred for 2 h after which the samples were left to settle overnight (Figure 7).

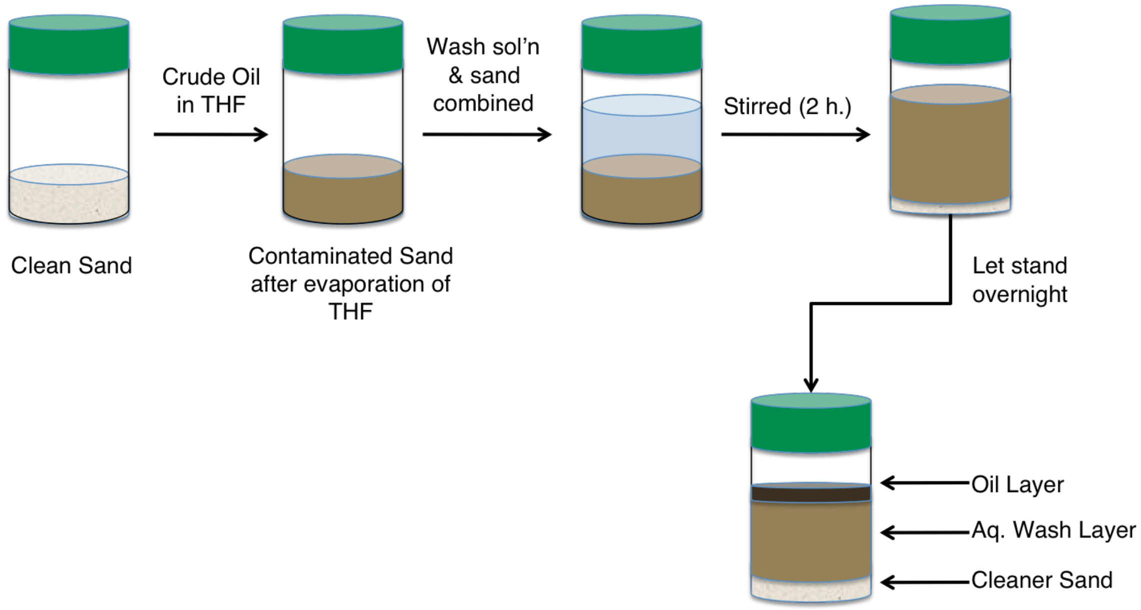


Figure 7: Illustration of the method of sand contamination and sand washing. Clean sand was contaminated with crude oil dissolved in THF and left to evaporate. A 5 g sample was added to a 20 mL vial containing the surfactant solution. The sample was stirred for 2 h and left to sit overnight.

2.2.3 Sand Analysis

Four 10 mL extractions using hexanes were carried out. 10 mL of hexanes were added to the vial containing the washed sand. The sand sample was stirred for 10 minutes, and the hexanes layer was collected using a pipette. Each extract was collected separately and analyzed by UV-Vis spectroscopy (Figure 8).

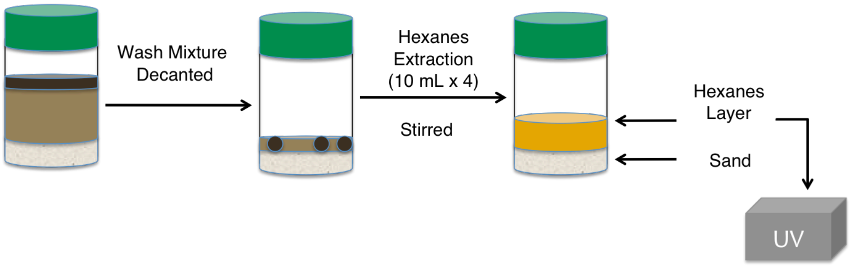


Figure 8: Schematic illustrating the sand analysis. After the washing is completed, the wash mixture is decanted. 5 extractions are carried out with hexanes. Each extract is collected separately and analyzed by UV-Vis.

A calibration curve of North Sea crude oil in hexanes (Figure 9) was created to quantify the concentration of oil extracted by hexanes after washing. The absorbance was recorded at 297 nm to avoid any spectral interferences with the absorbance of the switchable surfactant, SAS1.

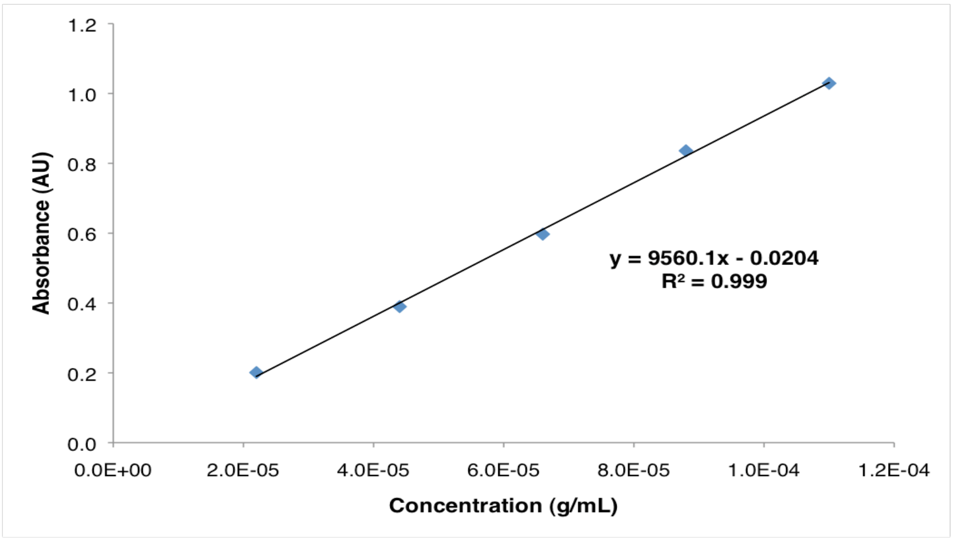


Figure 9: Calibration curve of North Sea crude oil diluted in hexanes.

2.2.4 Wash Mixture Analysis

After washing, the wash mixture was decanted into a separate 20 mL vial. The vial was capped with a septum. CO_2 was introduced into the sample by bubbling for 1 h. The vial was then turned upside down, clamped on a retort stand, and left for 1 h. The aqueous layer was collected in a another 20 mL vial by piercing of the septum with 2 syringe tips. Four extractions were done with 10 mL of hexanes and combined. The combined extract solution was analyzed using UV-Vis spectroscopy, Figure 10. The amount of oil present in the hexanes was calculated using the same calibration curve used for the sand analysis (Figure 9).

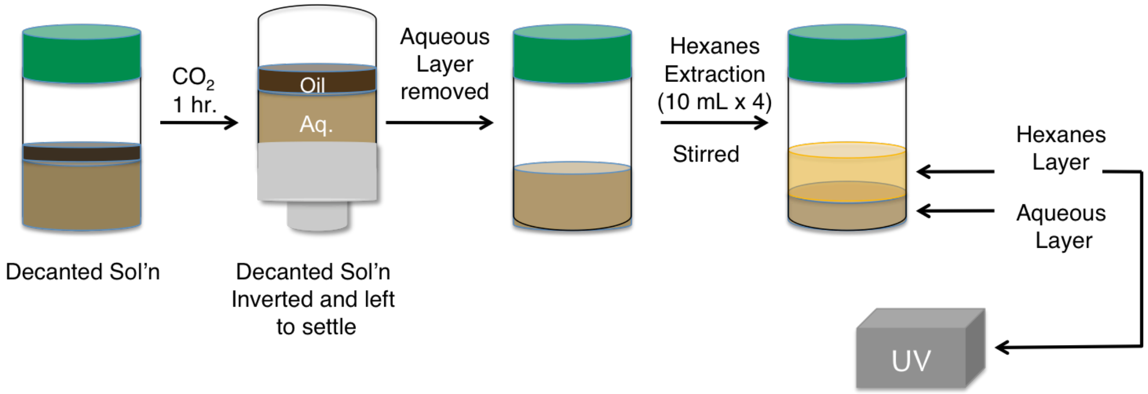


Figure 10: The decanted solution is treated with CO_2 for 1 h and inverted and left to settle for 1 h. The aqueous layer is removed using a syringe tip and a liquid-liquid extraction is carried out. The hexanes layer is removed and a UV-Vis spectrum is taken to determine the oil content remaining in the water after CO_2 treatment.

2.3 Results from Method Development

Analysis of the results obtained from the sand washing experiments was contingent upon the development of a representative real contaminated soil sample. Two model contaminated soil systems were investigated. The first system consisted of a single component contaminant, a model soil matrix and a surfactant solution. The second replaced the representative contaminant with crude oil.

2.3.1 Model System #1: 1-methylnaphthalene

The contaminant chosen was 1-methylnaphthalene and the model soil matrix was Ottawa sand. 1-methylnaphthalene was chosen because it belongs to the family of polycyclic aromatic hydrocarbons, which are marker compounds, found in crude oil. Furthermore, its structure would allow for easy detection by any UV-visible spectroscopic method. Ottawa Sand is typically used in laboratory studies as a reference material for soil and as a result was chosen as the initial model soil matrix. Two surfactants were used. Sodium dodecyl sulfate (SDS) was chosen as the representative commercial non-switchable surfactant and the switchable surfactant was N'-octyl-N,N-dimethylamidine (C8). For this system, the objectives were to determine the absorption of the contaminant by the sand and what effect, if any, the surfactant would have on solubilizing the contaminant, i.e. bringing it from the sand into the aqueous surfactant solution.

Fluorescence spectroscopy was chosen as the method of analysis. Fluorescence data would provide insight into contaminant composition as well as elucidate the effect of addition of sand and surfactant based on the changes in concentration of the contaminant. Initially this appeared to be the case because, as seen from Figure 11, there is a drop in the concentration of 1-methylnaphthalene in the presence of both surfactants; suggesting the uptake of the contaminant into the micelles of each surfactant. However, upon closer inspection of the C8 curve, the excitation wavelength at 224 nm in the 1-methylnaphthelene excitation spectrum had disappeared. This was a result of interference from the C8 surfactant's broad absorbance in the 240 - 220 nm region of the spectrum (Appendix, Figure 31). Excitation using wavelengths of lower energies was not pursued because it was thought light scattering would be increased due to the small Stokes' shift.[38] Because of the interference presented by the switchable surfactant, this method of analysis was abandoned.

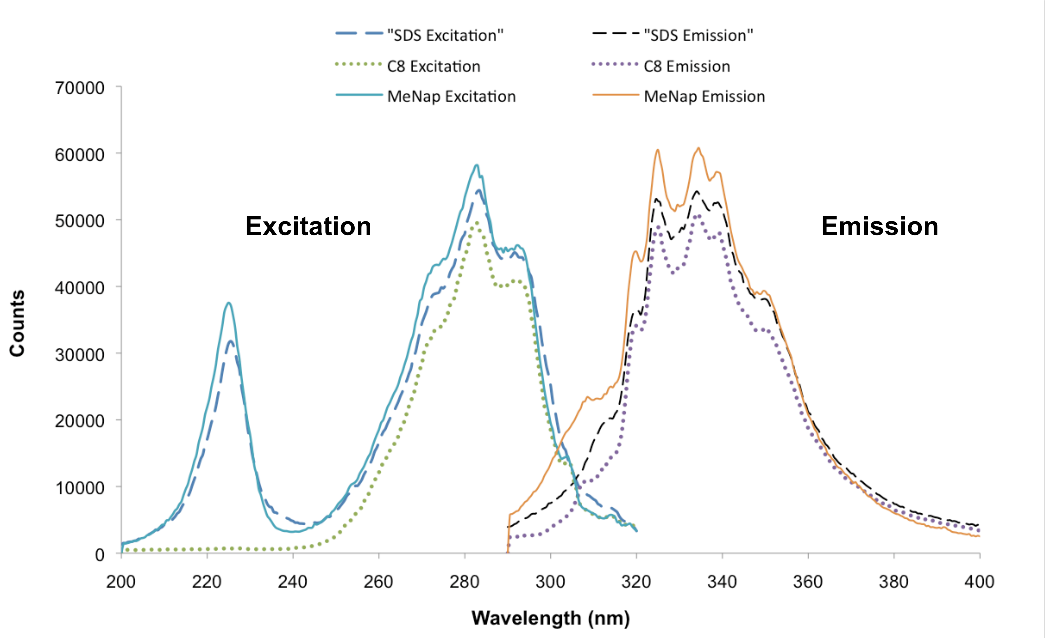


Figure 11: Fluorecence spectra of a 1.0x10^{-6} M solution of 1-methylnapthalene alone, in the presence of SDS and in the presence of C8. It can be seen that the characteristic peak at 224 nm is gone in the C8 solution.

2.3.2 Model System #2: Crude Oil

Using crude oil as the model system provided advantages over using 1-methylnapthalene. It was thought that developing an analytical method based on a contaminant consisting of one component would not be representative of a multiple component contaminant like crude oil. This limitation was avoided by changing to a sample system containing crude oil and Ottawa Sand. Also, a switchable anionic surfactant was incorporated into the analysis along with the switchable cationic surfactant C8.

Qualitative experiments were first done using both cationic and anionic switchable surfactants as well as SDS. Sand contamination levels reported in literature range from 0.1 to 92 mg of oil/g of soil.[26,32,39] For the qualitative experiments, sand contamination levels of 1.0 and 3.8 wt% oil on sand (i.e. 10 and 38 mg of oil/g of soil), were chosen. Experiments using the cationic surfactant were done on the 1.0 wt% sand and the 3.8 wt% sand was treated with the anionic surfactant. All qualitative sand washing experiments included a wash with water, the switchable surfactant and SDS.

2.3.2.1 Qualitative Experiments: Cationic Surfactant

A 5 g sample of contaminated sand was washed with water, a 1 % C8 solution and an equimolar (with respect to the C8) SDS solution. The samples were stirred on a stir plate for 30 minutes, followed by another 30 minutes with carbon dioxide bubbling.

Initial qualitative results using visual assessment of the sand samples suggested that a 1 wt% C8 solution did not remove the oil as effectively as SDS (Figure 12a). However, after increasing the amount of C8 (to 3% by mass relative to water), a change began to occur (Figure 12b); the sand was becoming cleaner and oil appeared to be pulled off the sand and into the aqueous phase.

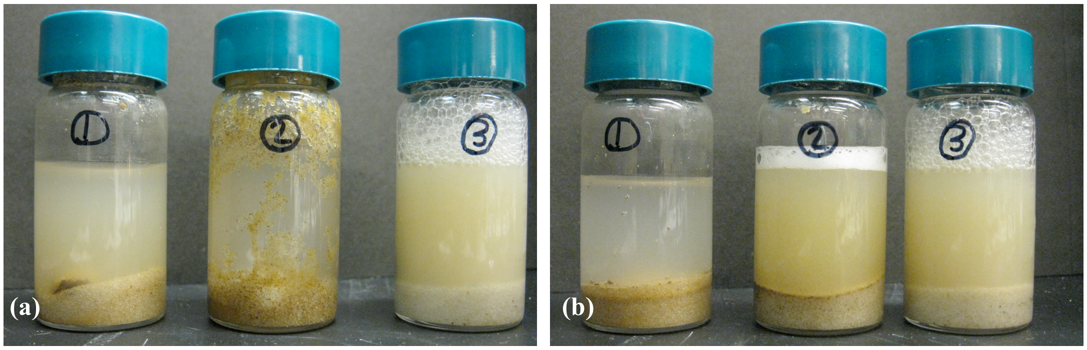


Figure 12: Washing of 1 wt% oil on sand samples with (1) Water, (2) C8 and (3) SDS. (a) The C8 and SDS solutions are equimolar and there is no visual change in the C8 vial. (b) After further addition of C8 (up to 3 wt%) the changes in the sample appear to be similar to SDS.

It was determined that this contamination level was too low for the sand washing application considering that immediate or even slightly weathered soil with crude oil would have a higher contamination level, therefore further experiments were carried out on the 3.8 wt% contaminated sand. Also, it was decided, based on literature[32] that the 1 wt% surfactant solution was too concentrated. Therefore the new surfactant concentration was reduced to 0.5 wt%.

2.3.2.2 Qualitative Experiments: Anionic Surfactant

The anionic switchable surfactant used was sodium octyl-4-hydroxy-3-nitrobenzoate (SAS1). Samples of 3.8 wt% sand were treated with 0.5 wt% solutions of SAS1 and SDS, as well as with water, as a control. Results from the washings are shown in Figure 13.

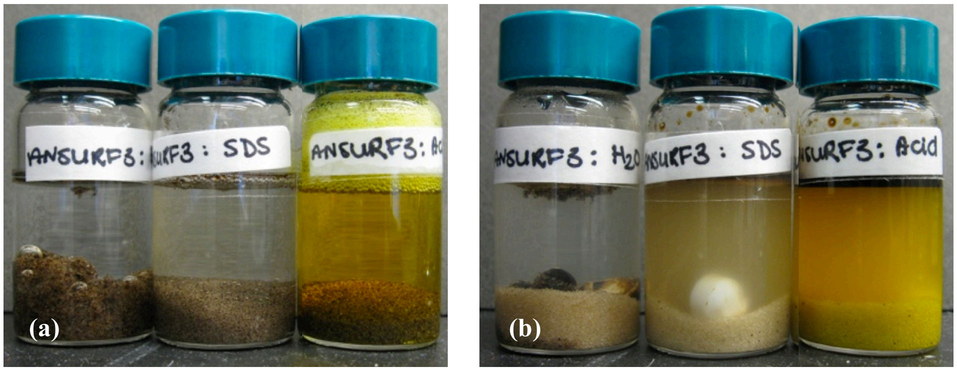


Figure 13: Washing of 3.8 wt% oil on sand samples with (1) Water, (2) SDS and (3) SAS1. (a) The 5 g samples before washing has commenced. (b) The samples after washing was completed. It can be seen that both surfactants performed adequately at removing the oil from the sand.

2.3.2.3 Qualitative Sand Washing Conclusions

The qualitative experiments suggest that using sand contaminated with crude oil would be a sufficient model system for the method development. As a result, initial washings demonstrated that switchable surfactants both cationic and anionic can work similarly to a commercial surfactant for the sand washing application. However, work with the C8 switchable surfactant was abandoned for the following reasons: 1) it is a cationic switchable surfactant and typically cationic surfactants are not used for soil washing due to their affinity for the soil[17] and; 2) the amount of surfactant necessary to achieve a similar result with C8 was much higher (3 wt% vs. 0.5 wt%), therefore it would not be a desirable alternative. Focus was directed to the anionic surfactants for further quantitative analysis.

2.3.3 Quantitative Experiments

In typical soil washing experiments reported in literature,[26, 32, 37] determining the remaining oil on the sand after washing is enough to assess the surfactant's ability to remove oil from the soil. Yet the appeal of the switchable surfactants is their ability not only to facilitate the removal of the contaminants from the sand, but then, upon a trigger, to separate the contaminant (and surfactant) from the water. To better understand these two functional properties, the analysis was split into two parts: 1) sand analysis (how much oil was left on the sand after washing) and 2) wash mixture analysis (how effective is the CO_2 treatment at separating the oil (and surfactant) from the wash water).

2.3.3.1 Sand Analysis

The sand analysis method developed (Section 2.2.3) was successful in determining the washing performance of the surfactants. Results indicated that SDS and SAS1 were performing equally well at washing the oil off the sand with a removal percentage of 92 ± 5 % for SDS and 91 ± 3 % for SAS1.

2.3.3.2 Wash Mixture Analysis

The wash mixture contains the two most important components of the system: the surfactant and crude oil (the contaminant). To demonstrate the benefit of the switchable surfactants for this application, their ability to "turn off" and cause of the separation of the surfactant and contaminant from the water needed to be determined and quantified. Assessment of this "switchability" can be based on the following variables: oil removal percentage (how much oil is separated from the water after CO_2 treatment), the oil recovery after CO_2 treatment, how much surfactant can be recovered, and can how many times can the procedure can be repeated.

The separation of the oil from the water using CO_2 was investigated first. It was determined that this separation is possible using CO_2, but the degree of separation was still unknown. Closer inspection of the analytical method developed (Section 2.2.4) revealed that the removal percentage could not be calculated because the amount of oil present in the wash mixture before was not recorded, only the amount after CO_2

treatment. Therefore an accurate removal percentage of oil from the water could not be calculated. Furthermore, this method assumed that all the oil would partition into the hexanes layer and after qualitative experiments, this was found to not be the case. It was decided to move in a different direction for the analysis of the sand and the wash mixture.

2.3.4 Conclusions from Method Development

Several conclusions can be drawn from the method development experiments. First, the washing method does establish which surfactants are working for the application. A recommended change was to eliminate the overnight standing period. Originally the samples were left to sit overnight to permit the settling of fines in the sample without the influence of added machinery like a centrifuge. However, Ottawa Sand contains a small amount of fines which would not cause any interferences, therefore there was no need for such a long settling period.

Upon closer inspection of the washings, it was evident that water alone was washing the sand just as well as the surfactant solutions. Because the Ottawa Sand contains no organic matter and the contaminated sand samples had not been treated to mimic real contaminated soil having been exposed to environment, it was decided that the contaminated sand samples should also be weathered (i.e. heat treated) to better mimic real contaminated soil. This was investigated and is discussed in Chapter 4.

The organic solvent extraction using hexanes and spectroscopic analysis proved satisfactory for the determination of surfactant performance, but it was not sufficient for the quantitative analysis of the wash mixture. A new method that would permit the quantitative analysis of both the sand and the water mixture was needed.

3 Experimental

This outlines the final method developed and executed using the anionic surfactants presented in this thesis for the preparation of the sand samples, the execution of the sand washings and analysis of the sand and wash mixture.

3.1 Source of Reagents and Supplies

CO_2 (99.9%, Praxair (Belleville, Ontario)) and nitrogen (99.998%, Praxair) were used as received. Sodium dodecyl sulfate (99%) was received from J.T. Barker (TekniScience, Terrebonne, Quebec). Triton X-100 and 1-methylnaphthalene were used as received from Sigma Aldrich Chemical Company (Oakville, Ontario). Ottawa Sand was purchased from EMD Chemicals (VWR, Mississauga, Ontario). North Sea crude oil was provided by Chevron Energy Technology Company (San Ramon, California). Solvents were purchased from either Fisher Scientific (Whitby, Ontario) or Caledon Labs (Georgetown, Ontario). All other chemicals were purchased from Fisher Scientific. Deionized water was obtained using a Millipore Synergy UV (SYNSV0000) filtration system (Millipore, Jaffrey, New Hampshire). All chemicals acquired from commercial sources were used as received unless specified.

Switchable surfactants were synthesized in the laboratory. N'-octyl-N,N-dimethylamidine (C8) was prepared according to literature.[35] Octy-4-hydroxy-3-nitrobenzoate (SAS1) was prepared in house by Dr. J. Harjani by previously reported methods.[36, 41] The sodium salt was made in-situ using sodium bicarbonate monohydrate during surfactant solution preparation. The switchable carboxylate salts of 4-octyloxy benzoic (SAS2) and lauric acid (SAS3) were prepared by mixing the acid with sodium hydroxide under reflux, followed by isolation of the white solid product.[41]

3.2 Instrumentation

Conductivity was measured using a Jenway 470 Conductivity meter (Jenway, Burlington, New Jersey). Fluorescence data were acquired using a PTI Fluorimeter with an 814 Photomultiplier Detection System and LPS-220B Xenon Arc Lamp Power Supply (Photon Technology International, London, Ontario). UV-Visible Spectroscopy data was obtained using an Agilent 8453 UV-Vis Spectrometer (Agilent Technologies, Mississauga, Ontario).

3.3 Artificial Sand Contamination & Weathering

Sand samples were prepared to achieve an initial contamination of 3.8 ± 0.1% oil on sand. North Sea crude oil (3.7 - 4.8 g) was added to a pre-weighed 400 mL beaker. Tetrahydrofuran (THF) was added to solubilize the oil. Enough Ottawa Sand was then added (94 - 127 g) to achieve the desired weight percent contamination on the sand. The beaker was left uncovered overnight at room temperature to allow the THF to evaporate. Afterwards, the sand was broken up and mixed in the beaker. The beaker was then left uncovered for a further time period so that the total evaporation time was at least 24 hours.

After the sand was left to sit for at least 24 hours, it was transferred to a pre-weighed Petri dish which was placed into an oven at 110 ºC for another 24 hours.[34] The Petri dish was removed and cooled to room temperature. The Petri dish and sample mass was recorded and the sand was transferred into a 100 mL amber vial for storage. The new contamination level ranged between 2.6 and 3.1 wt % oil on sand.

3.4 Sand Washing

Sand washings were carried out at room temperature (23 ºC) and at 50 ºC. The following procedures describe how the surfactant solutions were prepared and the sand washings were carried out.

3.4.1 Surfactant Solutions

A surfactant concentration of 0.5 wt % was chosen based on the work done by Urum et al.[32] The non-switchable surfactants used were SDS and Triton X-100. The switchable surfactants used were sodium octyl 4-hydroxy-3-nitrobenzoate (SAS1), sodium 4-(octyloxy) benzoate (SAS2) and sodium laurate (SAS3). Deionized water was used as a control. Structures and critical micelle concentrations of the surfactants used are presented in Table 2.

For the room temperature washing, the surfactant solutions or wash solutions were prepared by adding 0.25 g of surfactant to a 50 mL volumetric flask. Deionized water was added to achieve a total mass of 50 g. If necessary the solution was sonicated to dissolve the surfactant. The SAS1 solution preparation was slightly varied. In the case of this surfactant, 0.25 g of the octy-4-hydroxy-3-nitrobenzoate was added, then sodium carbonate (0.84 g) was added to a achieve a 1:8 octy-4-hydroxy-3-nitrobenzoate : carbonate mole ratio. Deionized water was again added to achieve a total mass of 50 g.

For the washings done at 50 ºC, the deionized water was first heated in a 150 mL beaker in a water bath to 50 ºC, then added to the surfactant. Sonication was not needed to further dissolve the surfactant.

3.4.2 Sand Washings (Room Temperature and 50 ºC)

The sand washing procedure was adapted from Urum et al.[42] All sand washings were done in triplicate. Samples were prepared by adding approximately 5.0 g of the contaminated sand to a 20 mL vial, followed by 10 g of the desired surfactant solution. A stir bar was also added.

The vials were capped with Teflon® lined lids. The samples were shaken by hand for 20 seconds, placed in a 150 mL beaker and then stirred at 470 rpm for 1 hour, re-shaken for another 20 seconds and stirred for another hour. For the washings at 50 ºC, the samples were placed directly into the water bath, which was previously heated to 50 ºC. The samples were left to stand briefly to let the solution settle. Figure 14 illustrates the sand washing process.

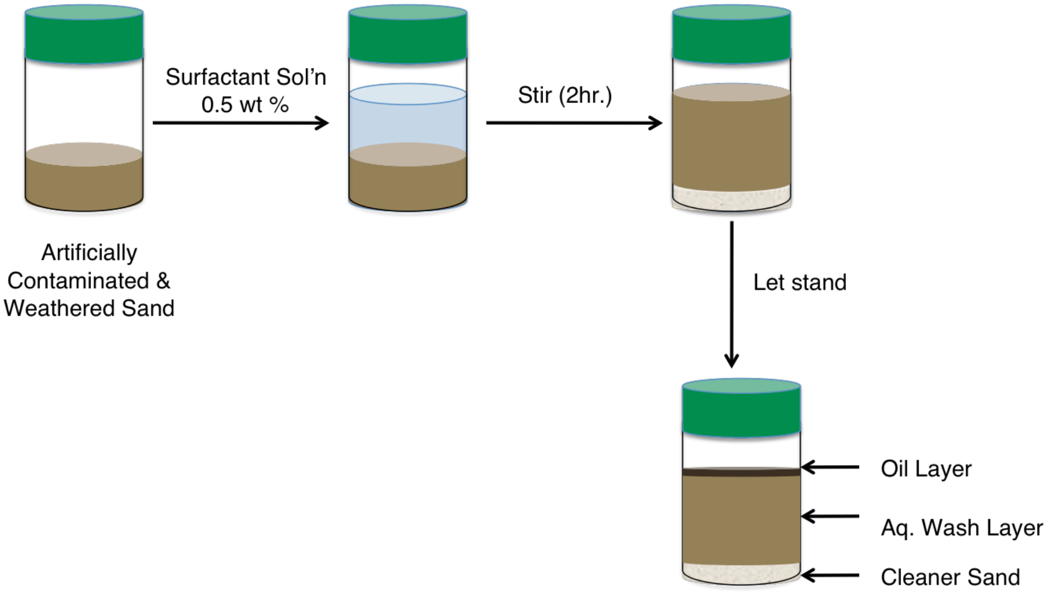


Figure 14: The sand washing process at room temperature. Artificially contaminated sand was placed in a 20 mL with a Teflon lined cap. The surfactant solution was added, the mixture is stirred for 2 hours and a cleaner sand sample with the oil contained in the aqueous layer was observed.

3.5 Analysis

The analysis was split into two parts. Part I was the analysis of the sand after washing. This analysis would determine the efficiency of the surfactant at removing the oil from the sand. Part II was the analysis of the wash mixture, i.e. the decant (or supernatant liquid) from the washing. Analysis of the aqueous portion would determine the amount of oil in the surfactant solution before and after addition of CO_2.

3.5.1 Analysis of the Sand via Solvent Extraction

After the washing was completed, the wash mixture was decanted into a separate 20 mL vial and the mass was recorded. This initial decanted solution will be referred to as the first decant. The sand was then rinsed with 50 mL of deionized water and the rinses were combined in a 100 mL Wheaton jar, henceforth referred to as the rinse solution.

A solvent extraction was carried out on the sand using 10 mL of a 1:1 dichloromethane:hexanes solution (organic solvent). Five, 10 mL extractions were carried out. The first two extractions were stirred for 20 min, and the following three extractions were stirred for 10 min. All extractions were combined in a pre-weighed 100 mL roundbottom flask. The organic, oil containing layer was transferred out of the vial by pipette, passed through a pipette containing a glass wool plug, to remove any solid particles, and into the roundbottom flask. The solvent was then removed by rotary evaporation and the mass of oil was determined gravimetrically. Figure 15 illustrates the process.

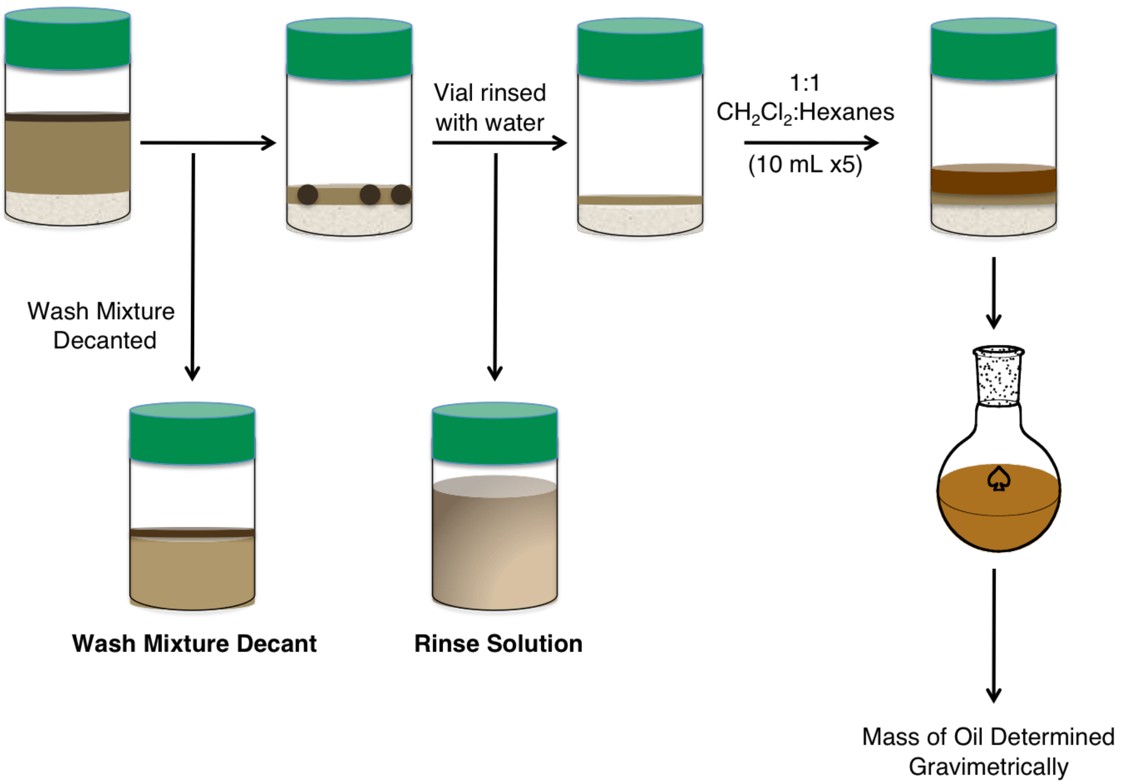


Figure 15: Schematic of solvent extraction of remaining oil from washed sand. The wash mixture was decanted and stored in a separate 20 mL vial. The vial is then rinsed with deionized water and the rinses are stored in a 100 mL Wheaton jar. The remaining oil on the washed sand was then extracted 5 times with a 1:1 DCM:hexanes solution. The extracts were combined in a 100 mL roundbottom, the solvent is removed using rotary evaporation and the mass of oil is determined gravimetrically.

3.5.2 Analysis of the Wash Mixture

As mentioned in Section 3.5.1, there were two aqueous portions (wash mixture decant and rinse solution), which were analyzed separately. The wash mixture decant was used to analyze the effect of CO_2 treatment and the rinse solution was used to verify the total amount of oil present in the wash mixture.

3.5.2.1 CO_2 Treatment

Solid Phase Extraction (SPE) was used to determine the amount of oil present in the aqueous solution before and after CO_2 treatment. The analysis of the three samples was done in parallel. Three 3 mL Supelclean™ ENVI-18 SPE Tubes were placed on a Supelco Preppy SPE Manifold and conditioned with 4 mL of 2-propanol followed by 5 mL of distilled water. The wash mixture decant was briefly shaken to homogenize the sample. A 2 mL aliquot was taken from the wash mixture using a syringe and added to the SPE tube. The oil was washed through the column using a 80:20 [160 mL : 40 mL] methanol:water solution (aqueous solution). The surfactant solution that was washed off the column was kept in 20 mL vials for potential future analysis. The column was then dried under vacuum for 5 min.

The oil was then eluted with the organic solution of 1:1 dichloromethane:hexanes [400 mL : 400 mL]. The eluant was transferred quantitatively to a pre-weighed 25 mL roundbottom flask. The solvent was removed using rotary evaporation and the mass of oil was determined gravimetrically. Figure 16 illustrates this procedure.

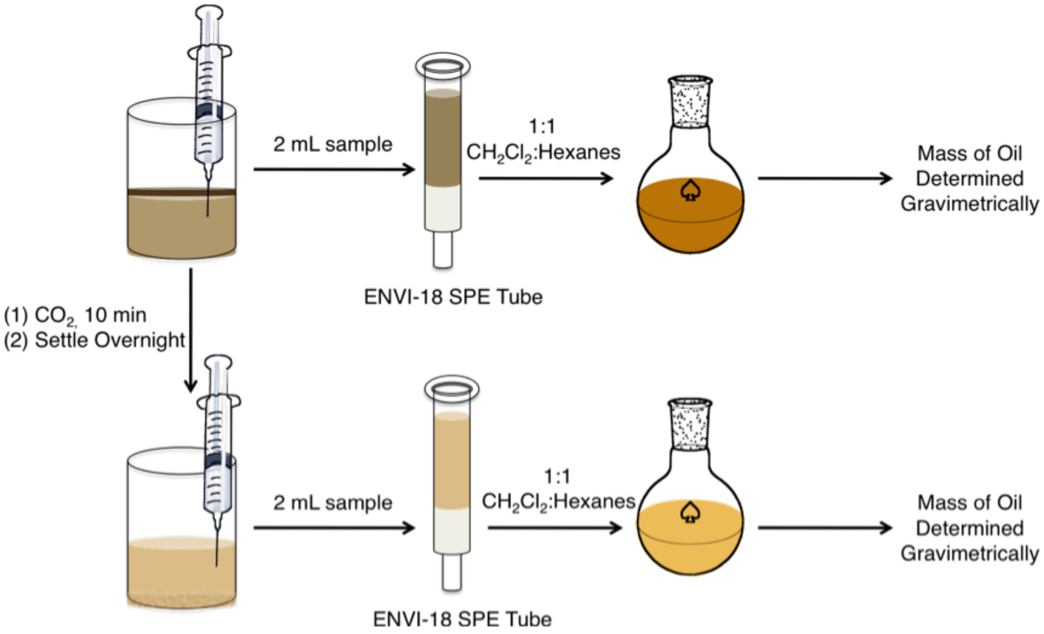


Figure 16: Schematic of SPE treatment on aqueous samples before and after CO_2 treatment. In both cases, a 2 mL sample was taken and passed through a 3 mL SPE tube. The oil, previous retained on the column, was eluted with the organic solvent and transferred to a 50 mL roundbottom. The solvent was removed with rotary evaporation and the mass of oil was determined gravimetrically

Following the first SPE treatment, the vial containing the decant was capped with a rubber septum. CO_2 was bubbled into the vial using a syringe at a flow rate of 3 to 5 mL min^{-1} for 10 min. A separate syringe was used as a vent source. After 10 min, the vials were re-capped with the Teflon® lid and left to settle overnight. The SPE procedure was repeated to analyze the amount of oil remaining the water after CO_2 treatment (Figure 16).

3.5.2.2 Analysis of Rinse Solution

To verify that the total oil content in the wash mixture, the SPE treatment was done on the rinse solution. In this case, 20 mL Supelclean™ ENVI-18 SPE tubes were used. The same procedure employed in Section 3.5.2.1 was carried out, except the amount of solvent needed was adjusted accordingly. Again, surfactant solutions were retained but were stored in 100 mL Wheaton jars.

The Wheaton jars containing the original rinse solutions were then rinsed with the organic solution to collect any oil remaining on the walls of the jar. Magnesium sulfate was added to the jars to remove any residual water. This solution was then added to the SPE tube during the elution of the oil. A final rinse of the tube was done with the organic solvent. The eluant was transferred quantitatively to a pre-weighed 100 mL roundbottom flask. The solvent was removed using rotary evaporation and the mass of oil was determined gravimetrically.

3.6 UV-Vis Spectroscopy Analysis

The fate of the surfactant throughout the process is also important. The loss of surfactant after washing and the amount remaining in the water after CO_2 treatment was determined using UV-Vis Spectroscopy. A brief experiment was done using the switchable surfactant, SAS1. A calibration curve (Figure 17) was created by diluting a 2×10^{-2} M stock solution of the SAS1 surfactant solution with the 80:20 methanol:water aqueous solution. Absorbance values were recorded at 400 nm.

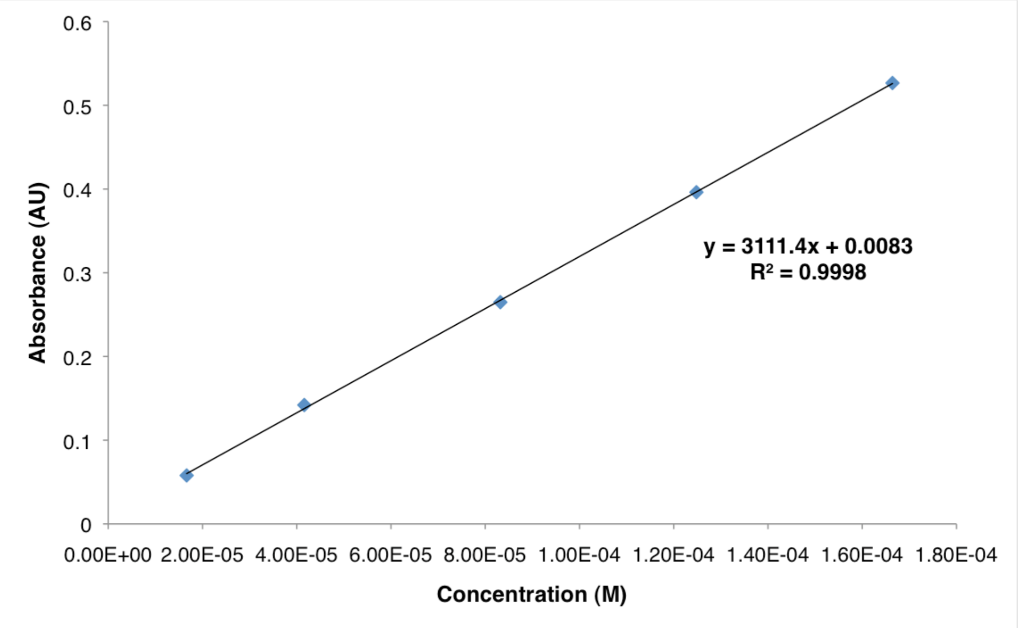


Figure 17: SAS1 Calibration Curve. Created in an 80:20 methanol:water solution. Samples were diluted 50 μL in 3.0 mL

4 Results & Discussion

This chapter describes the selection of the materials used as well as the results from the sand washings done at room temperature (23 ºC) and 50 ºC as outlined in Chapter 3.

4.1 Analytical Methodology

Solid Phase Extraction (SPE) is a popular sample preparation method for aqueous samples.[40] In principle, an analyte of interest contained in a complex sample matrix is concentrated onto a solid phase sorbent and can then be eluted and analyzed separately. The entire separation is based on the affinity of a particular analyte of interest for the solid phase sorbent. A sample is passed through a tube containing the packed sorbent, which has been pretreated to accept the aqueous sample. The analyte remains on the sorbent while impurities and interfering compounds are washed away with the conditioning solvents. Rinsing with the appropriate solvent or solvent system elutes the analyte, which can undergo further spectroscopic or gravitmetric analysis without interferences.

This sample preparation method was ideal for the wash mixture analysis. Oil content before and after CO_2 could be determined and the efficiency of CO_2 treatment for the separation could be calculated. Furthermore, the surfactant solution could also be analyzed separately without oil interferences.

4.2 Material Selection

4.2.1 Surfactants

The structures and critical micelle concentrations (CMC) of all surfactants used are included in Table 2. Two commercial surfactants, SDS and Triton X-100 were selected to determine a benchmark from which the results of the switchable surfactants could be compared. SDS is a fairly ubiquitous anionic surfactant used in a variety of different products from everyday detergents to personal care products such as shampoos. It has also been reported in the literature as a common reference surfactant. Also, SAS3 contains a C12 chain and it was thought that using SDS could potentially offer insights into structural benefits for the sand washing. Triton X-100 is a non-ionic, biodegradable and widely used surfactant found in many household and industrial cleaners.[43] It is part of the family of alkylphenol "polyethoxylates" ($RC_6H_4(OC_2H_4)_xOH$) which have been reported in soil washing literature.[33, 34] Triton X-100 is similar to SAS1 and SAS2 with respect to the aryl functionality. It was included to offer some further insight into the behaviour of SAS1 and SAS2.

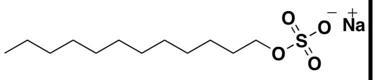
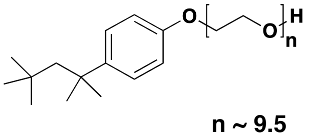
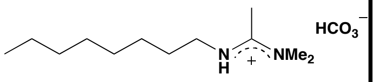
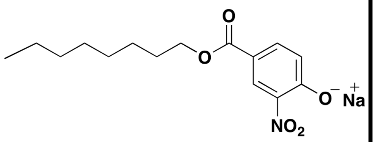
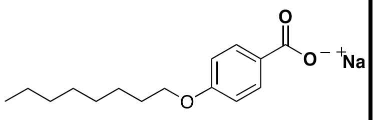
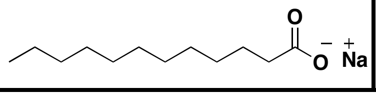
The switchable surfactants used are of two classes of surfactants: cationic and anionic (Table 2). The cationic switchable surfactant studied was the N'-octyl-N,N-dimethylamidine (C8). It is composed of an amidine head group and an alkyl chain length of eight. Previous work in the Jessop Group has been done using this class of surfactant where the chain length varied from 12 to 16 carbons.[35] It was thought that having a chain length of 8 carbons instead of 12 would increase the water solubility of the surfactant.

The second class of surfactant studied was the anionic switchable surfactant. These surfactants were based on two different classes of compounds. SAS1 is a nitroparaben derivative and SAS2 and SAS3 are both salts of carboxylic acids. SAS2 was chosen to further explore the carboxylic acid functionality and the possibility that the aryl ring would help to solubilize more compounds. SAS3 is a common fatty acid, sodium laurate. Its ability to switch has been investigated for the purpose of coagulation of latex particles[44] and it was thought that the possibility of promoting the switch with CO_2 could be explored.

4.2.2 Surfactant Concentration

Surfactant concentration plays an important role in soil washing. Two mechanisms at work during soil washing have been reported.[34] The first is mobilization and occurs above and below the surfactant's CMC. The second is solubilization and occurs above the CMC. To determine the appropriate concentration for the initial studies it was decided to operate above the CMC initially to ensure that both mobilization and solubilization mechanisms were available for all surfactants and false negatives would be avoided. For our initial experiments, 1 wt% was chosen because it is above the CMC for all the surfactants studied (see Table 1). The CMC values of SAS3[47] SDS[45] and Triton X-100[43] were found in literature. The CMC values of SAS1 and SAS2 were determined experimentally (see Appendix).

Table 2: Surfactants (non-switchable and switchable) studied for sand washing

Surfactant	*Structure*	*MW (g/mol)*	*Solubility (mg/L)*	*CMC (mM)*	*CMC (m/L)*	*CMC wt %*
SDS Sodium dodecyl sulphate		288.4	150 000[72]	8.0 [45]	2300	0.23
Triton X-100 octylphenol ethoxylate		625	soluble[46]	0.24[46]	150	0.015
C8 N'-octyl-N,N-dimethylamidine		222.3	N/A	N/A	N/A	N/A
SAS1 sodium octyl 4-hydroxy-3-nitrobenzoate		318.1	N/A	2.8 *	890	0.089
SAS2 sodium 4-(octyloxy) benzoate		272.3	N/A	14 *	3800	0.38
SAS3 Sodium Laurate		222.3	12 000[73]	24[47]	5300	0.53

* Determined experimentally. See Appendix.

4.2.3 Ottawa Sand

One of the specific objectives of the project was to establish a method to screen the washing performance of individual surfactants. As was described in the Introduction, soil is a complex, heterogeneous matrix composed of rock, mineral and organic compounds as well as a variety of microorganisms. These components can interact with the surfactant and the contaminant; for example, organic matter in the soil, such as humic acids, can protonate the surfactant reducing its effectiveness. This magnifies the effect of heterogeneity, which would make differentiating surfactants purely based on washing performance more difficult.

To simplify comparisons of surfactants, Ottawa Sand was chosen as a model "soil" matrix for the washing studies. Ottawa Sand is typically used in laboratory studies as a reference material for soil. It is a nonporous silica sand which contains little organic matter with particle size ranging from 0.1 to 1.0 mm[48, 49], making it an ideal model "soil" for the initial soil washing experiments presented in this thesis. Comparisons of key surfactants identified in this work will need to be repeated with real samples, including organic matter content, in future work.

4.2.4 Crude Oil

Crude oil was the contaminant under investigation as a result of concern for crude oil contamination of soil near petrochemical or processing operations, and resulting from oil spills. Previous applications of the switchable surfactants investigated in the Jessop Group[35] include use with crude oil emulsions, leading to the suggestion they may work as washing agents. A light crude, North Sea Crude Oil, was chosen as the best candidate for this work because its low viscosity would make it easier to work with initially. Its properties are listed in Table 3.

Table 3: North Sea Crude Oil Properties

Property	*Value*
API Gravity	19.5
Specific Gravity	0.937
Viscosity at 40 ºC (cSt)	129
Viscosity at 100 ºC (cSt)	11.22

4.3 Sand Contamination & Weathering

Artificially contaminated sand was weathered for these studies. Weathering is an important process in the artificial contamination of the sand because it best mimics real environmental samples. In real soil washing applications, the soil is generally not remediated right after the contamination. Therefore, it is exposed to the elements and becomes aged. This weathering process increases the binding of the contaminant to the soil and makes remediation more difficult.[37]

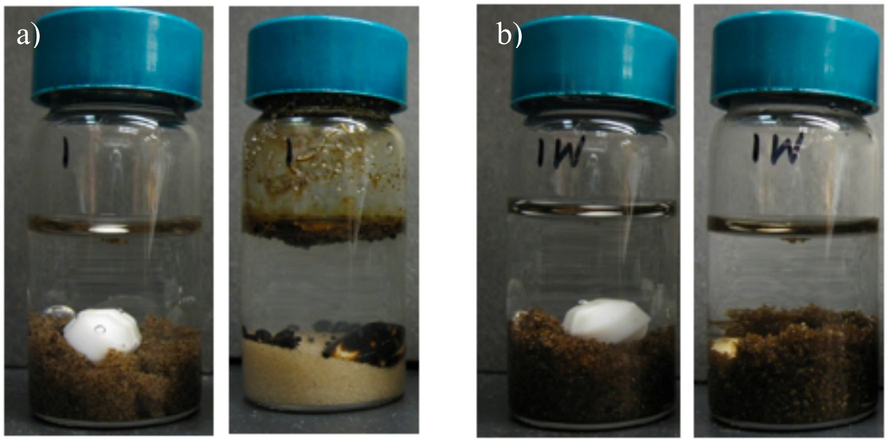
Various batches of sand were created for the samples described in this thesis (Table 4). The batch weight (total mass of the oil and sand), as well as the oil mass in the sample before and after weathering is listed. The average percent mass of oil lost during weathering was 26 %.

Table 4: North Sea Crude Oil contaminated sand. Contamination levels before and after weathering (Air dry, 24hrs followed by heating at 110 °C for 24 hrs).

Batch Number	*Batch Weight (g)*	*Oil Mass Before Weathering (g)*	*Oil Mass After Weathering (g)*
1*	40.9	1.6	1.0
2	89.8	3.3	2.3
3	127.2	4.7	4.0
4	101.7	3.9	3.0

* This sample was split into two batches, only half the batch was weathered.

Separate washing experiments on unweathered contaminated sand showed that water alone was able to remove the oil from the soil. To demonstrate the difference between weathered and unweathered sand, a batch of sand was created (Batch 1) where half the batch was weathered and half the batch was left unweathered. Three samples from each batch were taken and washed according to the procedure outlined in Chapter 3. Figure 18 shows the washing done on unweathered and weathered sand. Water was able to remove 59 % of the oil in the unweathered case and only 4 % after weathering.



Unweathered Sand Washed **Weathered Sand Washed**

Figure 18: Before and after the washing of (a) unweathered sand with water and (b) weathered sand with water. It is evident that the weathering has altered the binding of the oil on the sand, making it more difficult to remove with water alone.

The experiments presented only illustrated an evident physical change of the sand samples after weathering. Yet, the chemical composition of the oil also changes. Urum et al.[26, 37] conducted gas chromatography/mass spectroscopy (GC/MS) experiments on soil samples that they had artificially contaminated and then weathered. They report that most carbon compounds lower than C_{16} were reduced to trace levels or lost. The loss of these components increased the proportion of higher molecular weight components. This resulted in contaminated soil with oil of higher molecular weight, density and viscosity, leading to the greater binding strength of crude oil to soil.[37] This is consistent with the difference observed in the samples shown in Figure 18, where, after weathering of the sand, water alone was not able to remove oil from the sand. While the method of weathering done by Urum et al. was different than the method used in this thesis, it is expected that similiar trend would be observed. Investigation into the chemical composition of the contaminated sand samples before and after weathering by GC/MS is recommended for future work.

4.4 Sand Washing Experiments

4.4.1 Room Temperature

While soil washing is typically done at elevated temperatures, initial washing experiments were done at room temperature (23 ºC). The room temperature (RT) experiments would determine the surfactants' performance without the aid of heating, which should maximize the washing performance difference between surfactants. Elevated temperatures increase the efficiency of soil washing because the viscosity of the oil is reduced which helps to solubilize the oil.[21, 37] Furthermore if the switchable surfactants performed well at room temperature, it would increase the desirability of these chemicals because their usage could potentially reduce energy costs associated with the washing.

Figure 19 shows the samples using water and all the surfactants before washing has commenced and at the completion of the washing. Typically, two or three distinct layers are apparent after washing: (1) sand on the bottom, (2) an opaque, tan coloured aqueous layer, and (3) in some cases, a thin oil layer is observed on the top. From the photos it can be seen that all surfactants are in fact removing oil from the sand during washing. The removal of oil by water alone was insignificant compared to that by aqueous solutions of the surfactants. SAS1 visually appeared to remove the most oil from the sand, as the washed sand is the whitest of the six samples.

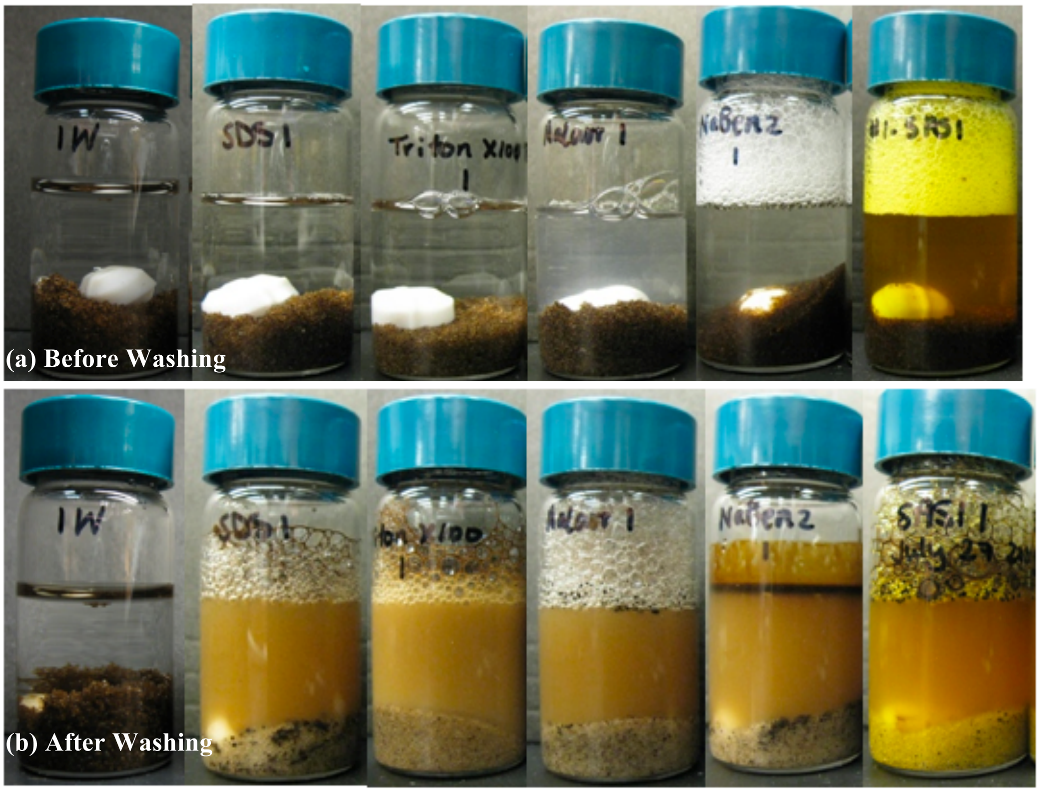


Figure 19: Photos of the RT washings (a) before washing has commenced and (b) at the completion of the 2 h washing period for (L to R): Water, SDS, Triton X-100, SAS3, SAS2 and SAS1.

To determine the residual oil on the sand after washing, an organic solvent extraction was performed. The mixture of dichloromethane and hexanes in a 1:1 volume ratio was chosen because it removed the most oil from the sand, compared to either solvent on its own. The procedure is outlined in Chapter 3.5.1. Equation 5 was used to calculate the percent removal of oil from sand.

Equation 5

$$\%\ \text{Removal} = \left(1 - \frac{\text{mass of oil remaining on sand}}{\text{total expected mass of oil}}\right) \times 100\%$$

where $$\text{Total Expected Mass of Oil} = \text{Wt}\ \%_{\text{Oil on Sand}}\ \text{x Sample Mass}$$

At room temperature SAS1 removed the most oil from the sand (82 %) compared to the rest of the candidates (Figure 20).

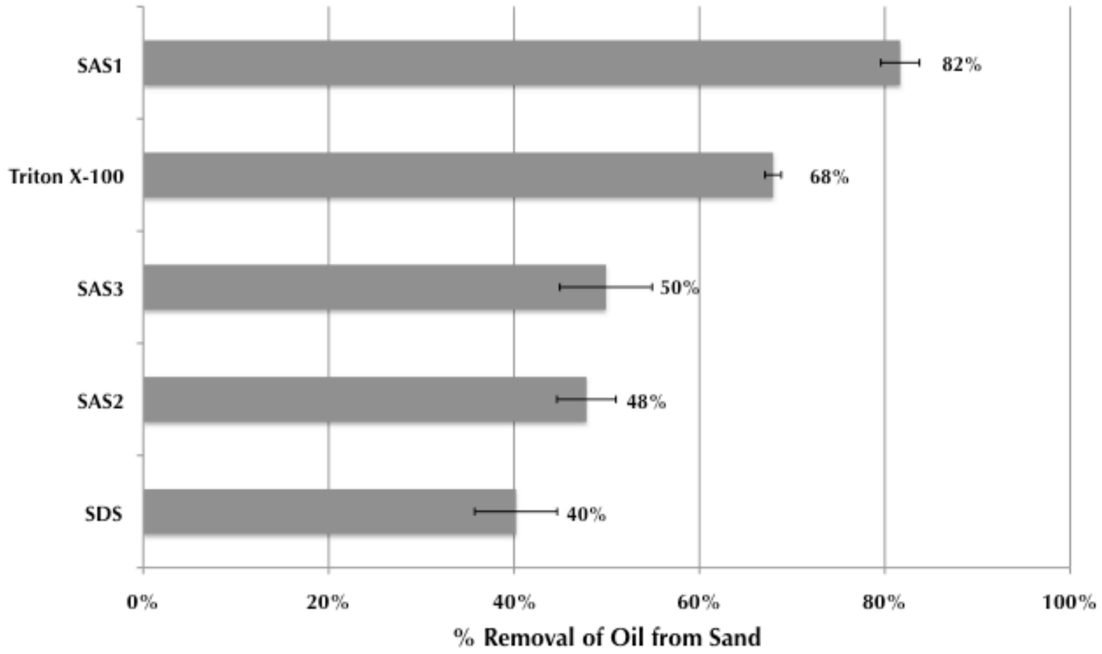


Figure 20: Comparison of the average % removal of oil from sand by the surfactants after sand washings at room temperature. (Error bars represent the standard deviation. n = 3)

Given that the switchable surfactants performed well compared to the commercially available non-switchable surfactants, it was decided to investigate how the surfactants would perform at an elevated temperature.

4.4.2 Elevated Temperature (50 ºC)

Soil washing is typically carried out at elevated temperatures.[21] The increase in temperature reduces the viscosity of hydrocarbons present and increases their mobility and interactions with the surfactant.[21, 37] 50 ºC was chosen for the investigation of the effect of elevated temperature on the efficiency (i.e. the ability to remove oil from the sand) of the surfactants.[32, 37] Figure 21 shows the sand samples before washing has commenced and at the completion of the washing done at 50 ºC. At this temperature, all the surfactants performed much better than at room temperature, with the average removal percentage increasing from 58 % to 92 % (Figure 22). There was also a dramatic increase in the rate of decolouration of the sand. Within 3 min, there was already a change in the sand colour as oil was being pulled into the aqueous layer. After 20 min, the washing was essentially completed, but was continued for the full 2 h to allow a comparison between the 50 ºC and room temperature washings. Again, three distinct layers were observed, although the oil layer was more pronounced in the 50 ºC washings.

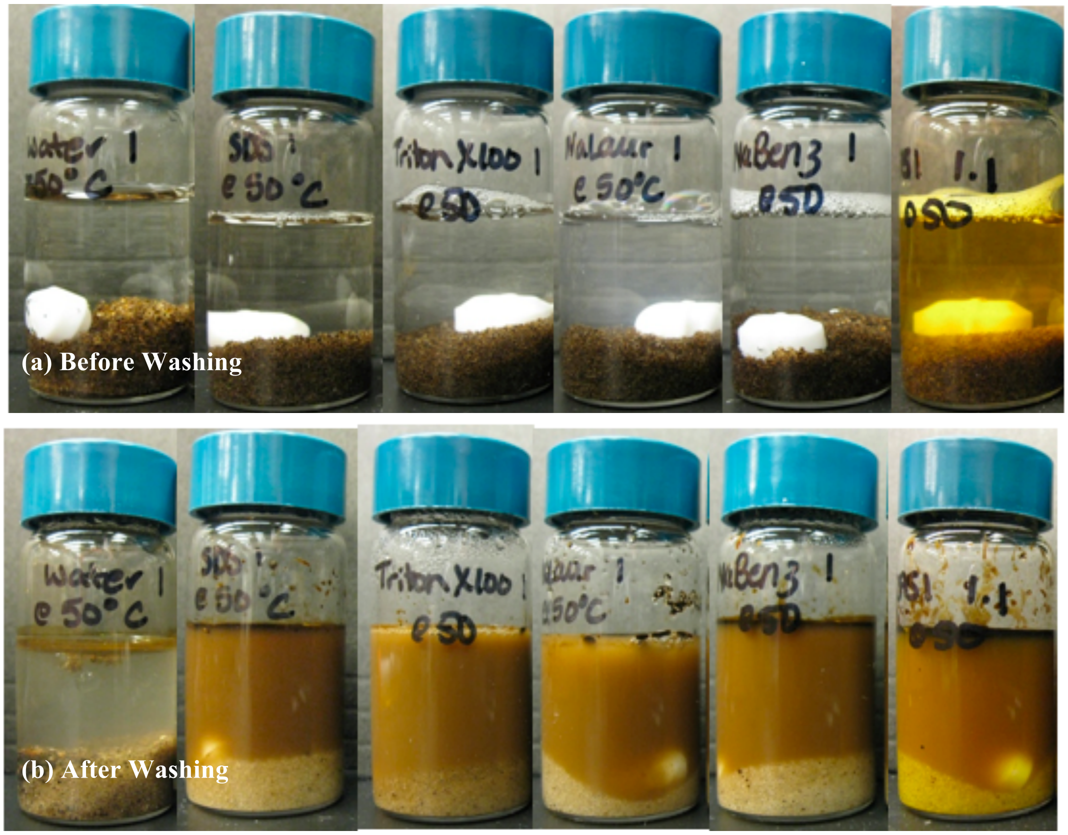


Figure 21: Photos of the room temperature washings (a) before washing has commenced and (b) after the 2 h of washing was completed for (L to R): Water, SDS, Triton X-100, SAS3, SAS2 and SAS1.

Qualitatively, while the washing performance of all the surfactants was increased at the elevated temperature, temperature alone was not sufficient to remove the oil completely. This was evident by washing only with water at 50 ºC. While there was some decolouration of the sand resulting in oil present in the water layer, this difference was not as significant compared to the change when a surfactant is added. Therefore, it is the combination of surfactant solution and increased temperature that enhances oil removal. For the samples with surfactant, the aqueous layer was darker (compared to the room temperature washings) and the sand samples for all surfactants are clean and white. Again, SAS1 was the best surfactant overall with a removal percent of oil from sand of 97 % (Figure 22).

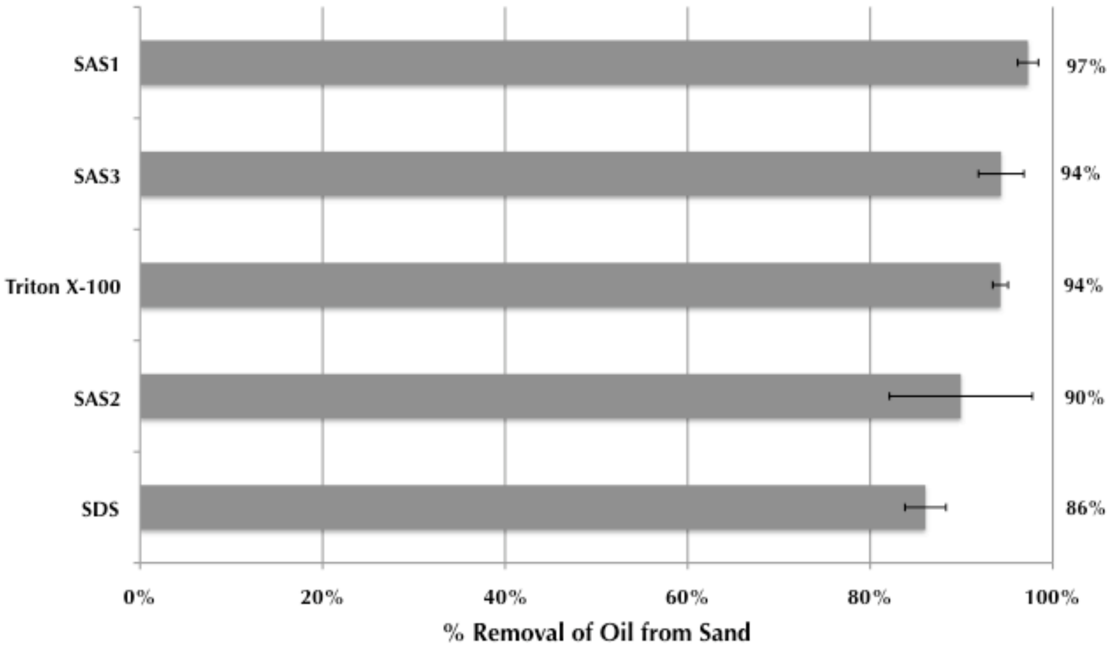


Figure 22: Comparison of the average % removal of oil from sand of the surfactants after sand washings done at 50 ºC. (Error bars represent the standard deviation. n = 3)

4.4.3 Sand Washing Conclusions

For this project, it was necessary to develop a method that could discriminate various surfactants (commercial and switchable) based on their ability to wash crude oil from sand. From the results of sand washings performed at room temperature and 50 ºC, it can be concluded that this method was successful at discriminating the surfactants based on their washing performance. It also demonstrated that the switchable surfactants are useful for the sand washing with removal percentages of 82 %, 50 % and 48 % (at RT) and 97 %, 94 %, 90 % (at 50 ºC) for SAS1, SAS3 and SAS2 respectively.

4.5 Processing of the Decanted Wash Mixture

A key reason for considering the use of a switchable surfactant over a commercially available non-switchable surfactant is the potential to recover the contaminant and the surfactant through the switching properties of the surfactant. Determination of the possibility for contaminant recovery was the primary objective for the processing of the wash mixture.

During the washing process, the surfactant facilitates the emulsification of oil in water. In typical soil washing operations, this wash mixture containing the valuable crude oil and surfactant materials is generally disposed or sent for further treatment. Treatments may include aeration, filtration, adsorption using activated carbon, reverse osmosis and electrodialysis.[19, 50] These treatments of the wash mixture will recover the water, but the surfactant and contaminant are non-recoverable due to biodegradation or subsequent treatments. Both the contaminant and the surfactant are potentially valuable components. If one or both could be recovered and re-used, it would not only reduce waste, but it may, in the case of the oil, result in revenue which could offset the cost of remediation. This is where the switchable surfactants may find their utility.

Separation of the crude oil from the wash mixture is achieved when the surfactant becomes inactive upon application of a trigger. Rendering the surfactant inactive (i.e. it no long exhibits surface active properties) destabilizes the emulsion, causing it to "break." This destabilization affords the natural separation of the oil from the water. For the purpose of this thesis, "breaking the emulsion" describes the formation of distinct and continuous phases that do not recombine upon simple shaking or stirring even after a period of days. The decanted wash mixtures created during the sand washing with the surfactants were used to investigate the separation or "breaking" of the emulsions (Figure 23). A good separation, for this thesis, is defined as a distinct separation between water, oil and surfactant, where the components exist as continuous and independent phases.

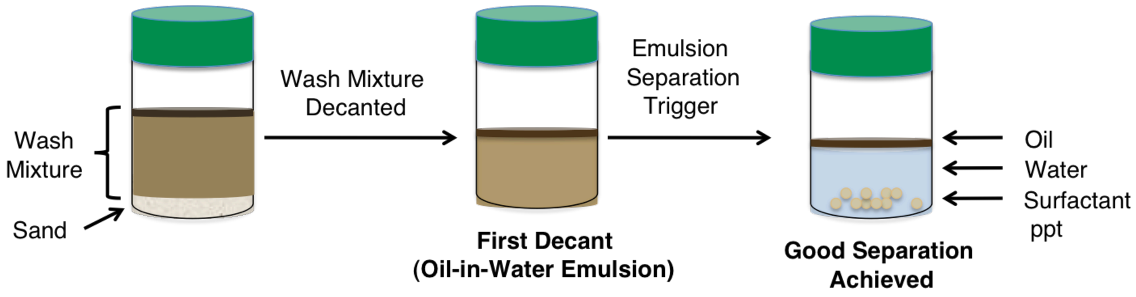


Figure 23: After the sand washing, the aqueous layer is decanted into a 20 mL vial. This decant is an oil-in-water emulsion. To "break" the emulsion, the appropriate trigger for the surfactant is applied. The last vial on the right illustrates what a good separation would ideally look like.

4.5.1 Commercial Surfactants

Emulsions of commercial charged surfactants, either cationic or anionic, can be broken by increasing the ionic strength; accomplished by the addition of salt. While this process is effective and fairly simple, there are drawbacks. Salting out of the surfactant produces a salty solution, which can be disposed, but the salt is lost. This salty solution can be treated, and the water and salt can be recovered by desalination, but this is expensive and uses energy.

4.5.1.1 Breaking the Emulsion with Salt

The samples containing emulsions created with SDS (an anionic surfactant), were broken by salting out SDS with the addition of NaCl, until a distinct separation was observed. That is, water formed the continuous lower layer and oil formed the continuous layer on top. The samples were left to settle overnight, but separation began almost immediately after salt addition. Figure 24 shows the wash mixture decants from

SDS washings done at RT and 50 ºC. At both temperatures, the separation of oil from water was achieved; there is visually no oil remaining in the water layer, and it is not emulsified upon shaking or stirring. However, there did not appear to be a definitive separation between SDS and the oil. The tan coloured layer above the water is not a clean, oil phase, but rather a mass of oil adhered to solid surfactant particles. Furthermore, the water layer contains salt and cannot be re-introduced into the washing cycle until it is desalinated. Therefore, this process dramatically reduces the recovery of surfactant, NaCl and the contaminant oil, and the water would have to undergo further treatment before being reused or disposed.

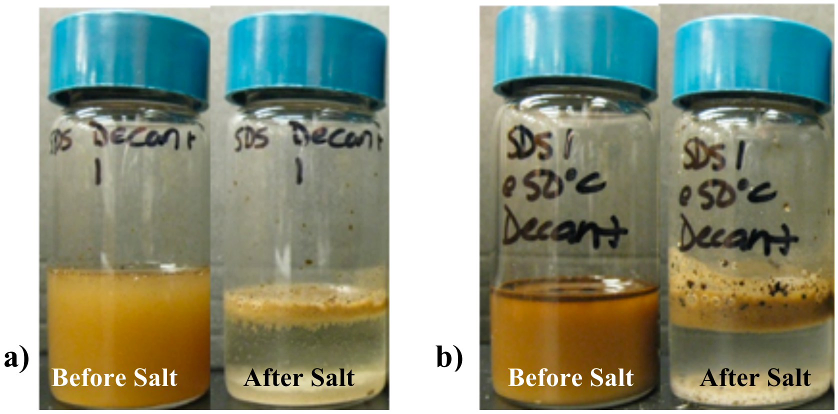


Figure 24: Photos of the wash mixture decants from the (a) RT washings and (b) 50 ºC washing before and after salt addition. After salt addition, the water phase is on the bottom, excess salt and a fraction of surfactant particles are on the bottom of vial and the top layer is a mass of oil adhered to surfactant particles.

Triton X-100 on the other hand is a non-ionic surfactant. Typically, emulsions created using neutral surfactants are more difficult to break. As confirmation, two wash mixture decants from sand washing with Triton X-100 were tested to identify which method, if any, would cause the emulsion to break. One wash mixture was treated with NaCl and the other was heated to 50 ºC. When NaCl was added, even to saturation, distinct, continuous and immiscible phases were not observed (Figure 25). This was also the case for the sample that was heated. It was concluded that these emulsions could not be broken by conventional methods. The experiments using Triton X-100 provided a scenario opposite to SDS, where facile oil recovery is not achieved.

Figure 25: Photo of the wash mixture decant from a RT washing using Triton X-100 before and after salt addition. Even at saturation, the emulsion has not broken. Two distinct, continuous and immiscible phases are not observed.

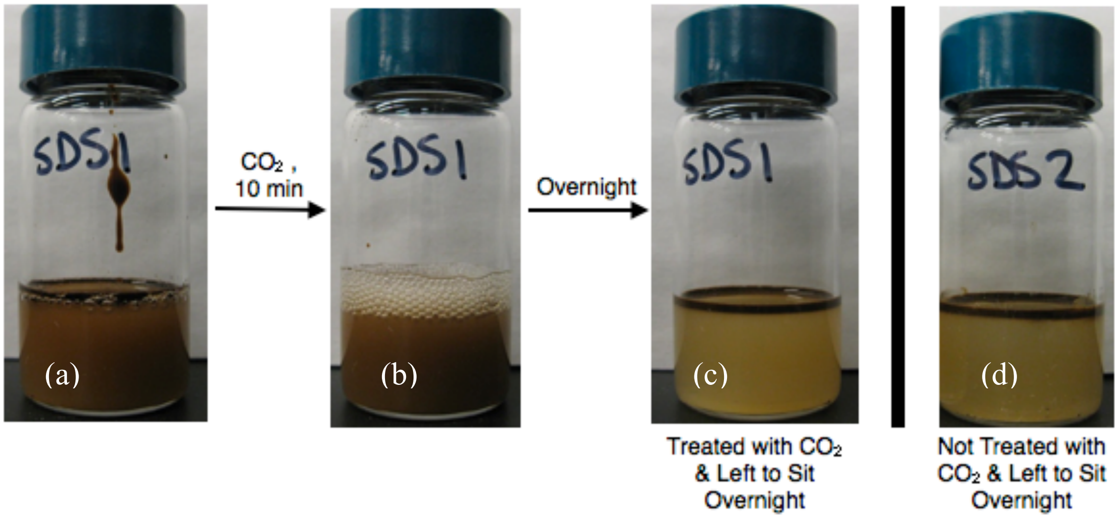
4.5.1.2 Breaking the Emulsion with CO_2

As CO_2 is the trigger used for the switchable surfactants, a control experiment using carbon dioxide as the trigger for emulsion "breaking" for the commercial surfactants was done to determine if it would have any influence on these emulsions. Two samples were prepared, one was treated with CO_2 for 10 min and left to stand overnight, and the other was left untreated. Solid Phase Extraction analysis (Chapter 3.5.2.1) was done on the aqueous layer of both samples. The mass of oil in the aqueous layer and percent removal of oil (Equation 6) from the aqueous layer for both SDS and Triton X-100 samples is presented in Table 5. In both cases, CO_2 effectively had no influence on either the SDS or Triton X-100 samples with respect to removing oil from the aqueous layer. Visual observations (Figure 26) support this conformation because there is no apparent difference in the samples with and without CO_2 treatment for the SDS sample.

Table 5: Mass of oil in the aqueous layer before and after treatment as well as % removal of oil from the aqueous phase.

Surfactant	*Original Decant (before treatment)*		*After Sitting Overnight*		*% Removal*	
			With CO_2	*Without CO_2*		
	1	2	1	2	1	2
SDS	5.2 mg	4.9 mg	1.5 mg	1.4 mg	71 %	71 %
Triton X-100	13.2 mg	10.7 mg	3.8 mg	3.2 mg	71 %	70 %

While a removal percentage of 71% suggests there is a decline in oil mass in the samples, the decline is neither rapid nor permanent. The separation that is observed in Figure 26 is a result of the oil creaming out of the bulk mixture. Creaming describes the movement of the oil droplets towards the surface while the water molecules move downward into the bulk.[31] Eventually, enough droplets will accumulate at the interface that they will coalesce and two distinct and continuous phases will form. In the SDS result presented, the separation was not permanent because if the vials were disturbed in any way, the oil would be once again emulsified and separate immiscible phases were not achieved; the oil had not been permanently separated from the aqueous phase. Therefore, CO_2 did not offer any benefit with respect to the breaking of emulsions created using the commercial surfactants studied.



Treated with CO_2 & Left to Sit Overnight

Not Treated with CO_2 & Left to Sit Overnight

Figure 26: From L to R, a decant from a washing with SDS is bubbled with CO_2 for 10 min. This sample is left to sit overnight. The sample (c) is then compared to a similar sample (d) which has not been treated with CO_2. Samples (c) and (d) are visually identical.

4.5.1.3 Conclusions for Commercial Surfactants

Experiments carried out using the commercial surfactants established two scenarios for oil separation from the wash mixture as a result of breaking the emulsions using a separation trigger. One scenario involved emulsions created using SDS. Separation of the crude oil and water was achieved by the addition of NaCl. The other scenario involved emulsions created using Triton X-100. In this case, separation of the crude oil and water was not achieved by conventional means. The next step was to determine if the switchable surfactants would offer another scenario, which would allow for the separation and recovery of the crude oil from the wash mixture using CO_2.

4.5.2 Anionic Switchable Surfactants

The "breaking" of the emulsions formed during the sand washing using the anionic switchable surfactants, was achieved by injection of CO_2 into the sample for a period of time, called the "bubbling time". The "bubbling time" for these experiments was 10 min (Section 3.5.2.1). During this time, the mixture became turbid and a colour change was observed (medium brown to cream). The turbidity was attributed to the precipitation of the surfactant. Addition of CO_2 into the mixture decreases the pH of the system, shifting the surfactant equilibrium towards the protonated, water insoluble form (Figure 5). After 10 min, precipitation of the surfactant was considered complete; foaming had ceased and the components (oil, water and surfactant) no longer formed an emulsion. A slight variation in precipitation time was observed. For SAS2, precipitation occurred almost immediately upon bubbling; for SAS1 and SAS3, it was over at least 6 min.

Separation of the phases did not however, occur as rapidly as it did in samples with SDS treated with NaCl. Initially, the mixture was cloudy; a good separation was not achieved immediately after bubbling. The treated wash mixtures were left to stand overnight, after which separation of the crude oil and surfactant from water did occur. A faster separation could be achieved by centrifuging the solution. After the overnight standing period, it was observed that the surfactant had clumped together and either risen to the top of the solution or settled at the bottom and the oil had adhered to the surfactant particles and the walls of the vial. Figure 27 and Figure 28 show the wash mixture decants before and after CO_2 treatment for the room temperature and 50 ºC washings.

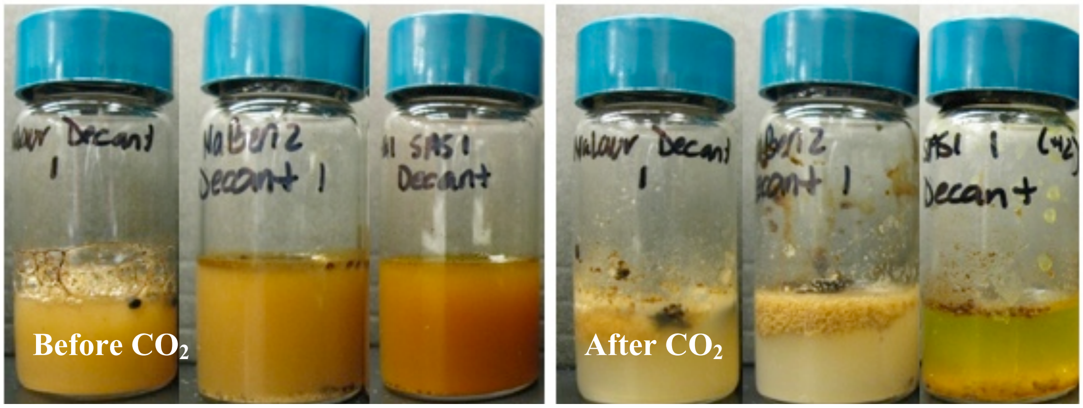


Figure 27: Photos of the decants from the room temperature washings before and after overnight standing following CO_2 treatment for (L to R): SAS3, SAS2 and SAS1. The surfactant particles have clumped together and either floated to the top and/or remained at the bottom of the vial. The oil has adhered to the walls of the vial and the surfactant particles.

While CO_2 treatment was done at room temperature for both the room temperature and the 50 ºC washings, the decants are not the same. The decants from the 50 ºC washings resulted in a better separation of the three phases: oil, surfactant and water (Figure 28). In the room temperature experiments, while the emulsion is broken and the surfactant and oil have separated from the water, there is no distinct separation of the oil from the surfactant. Further treatment would be needed to separate the oil from the surfactant.

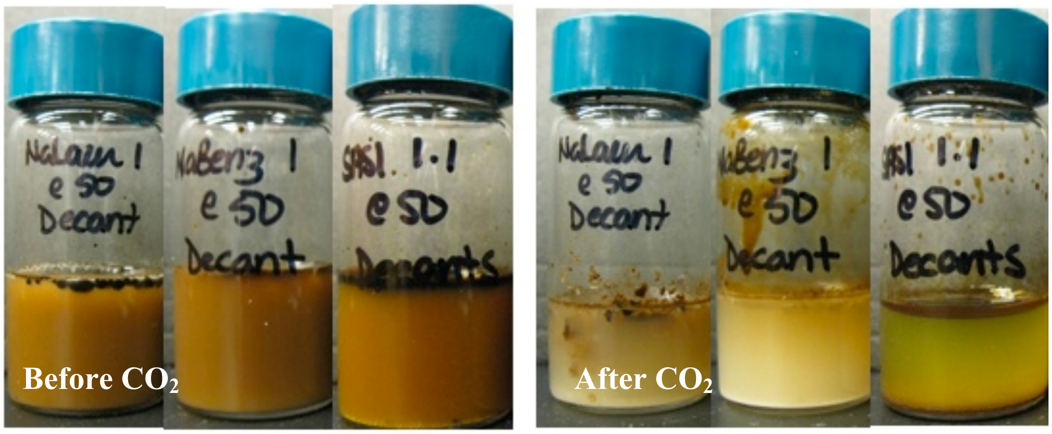


Figure 28: Photos of the decants from the 50 ºC washings before and after overnight standing following CO_2 treatment for (L to R): SAS3, SAS2 and SAS1. The surfactant particles have not clumped together as much as in the room temperature washings. The oil can still be found adhered to the walls of the vial and the surfactant particles (SAS3 and SAS2) or as a continuous phase on top (SAS1).

Visual inspection of the wash mixture decants after CO_2 treatment from the 50 ºC washings suggests that there is a better separation between all three phases. The oil does not appear to adhere as much to the surfactant particles and forms a layer on the top of the aqueous phase. This is particularly evident for the SAS1 surfactant. Having a better separation of the oil from both the surfactant and water should make oil recovery much easier, which is one of the desired objectives for this project. Even though it may appear that the separation of the surfactant from the water is not as good, as might be the case with SAS2 and SAS3, this may not be a major concern as long as the oil can be removed, because both the water and the surfactant would be recycled back into the process for further washing.

The switchable surfactants then, offer a separation scenario in between the ones presented by SDS and Triton X-100 (Figure 29). On one hand, emulsions made with SDS break to give a more complete separation of the surfactant and contaminant components from the water, but this process involves adding salt, which would need to be removed from the water. Emulsions made with Triton X-100, do not offer a complete and distinct phase separation. The switchable surfactants offer a fairly good separation of the surfactant and oil from the water, and they also use a benign and inexpensive emulsion breaking trigger, namely CO_2, to cause the separation. The water would require little treatment before reuse.

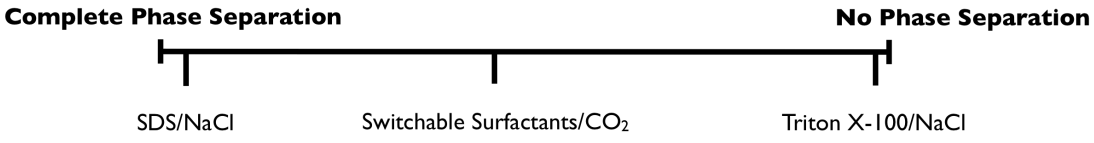


Figure 29: Qualitative comparison of the quality of phase separation after breaking of the oil-in-water emulsions stabilized by surfactants presented in this thesis.

4.5.3 Quantitative Evaluation of the Phase Separation

Solid Phase Extraction analysis (SPE), described in Chapter 3.5.2.1, was used to quantify the phase separation, that is, how much oil was present in the aqueous layer before and after CO_2 treatment. The removal percentage of oil from the aqueous phase was calculated using Equation 6, where the oil mass is the mass of oil found in the 2 mL aliquot taken for the SPE analysis. The results for the commercial surfactants were presented with respect to the traditional treatment used to cause phase separation. The results are tabulated in Table 6.

Equation 6

$$\% \text{ Removal} = (1 - \frac{\text{Oil Mass}_{\text{After CO2}}}{\text{Oil Mass}_{\text{Before CO2}}}) * 100\%$$

Table 6: Evaluation of the % Removal of Oil from the Bulk Aqueous Phase

Surfactant		***Room Temperature***			***50 °C***		
	Treatment	*mg_{oil}/mL_{aq} before treatment*	*mg_{oil}/mL_{aq} after treatment*	*% Removal of Oil from Aq. Phase*	*mg_{oil}/mL_{aq} before treatment*	*mg_{oil}/mL_{aq} after treatment*	*% Removal of Oil from Aq. Phase*
Commercial							
SDS	NaCl	1.7	0.35	79	9.8	0.25	98
Triton X-100	N/A	5.8	--	Non-recoverable	11	--	Non-recoverable
Switchable							
SAS1	CO_2	2.6	0.48	81	4.4	0.32	93
SAS2	CO_2	2.2	1.0	55	6.7	0.73	89
SAS3	CO_2	1.4	0.63	55	11	0.5	95

From the results, it is evident that for all three switchable surfactants at 50 ºC 89 % or more of the oil is separated from the wash mixture by CO_2 bubbling. This is consistent with the qualitative data collected from the images of the decants before and after CO_2 treatment, where it appeared that the decants from the 50 ºC washings had better separation between the components (Figure 27 and Figure 28). At room temperature, SAS1 had 81 % of the oil separated while separation for SAS2 and SAS3 was not as efficient. Finally it can be noted that at room temperature, recovery of the oil from wash mixture using SAS1 and CO_2 was as efficient as SDS with salt addition. At 50 ºC recovery of the oil from wash mixture using SAS1 and CO_2 was only a small percentage lower than the recovery using SDS with salt addition. Therefore, not only are the switchable surfactants able to remove oil from the sand like their non-switchable counterparts, but separation of the oil and the surfactant from the water using CO_2 is possible.

4.6 Fate of the Oil

A major component of determining the applicability of the switchable surfactants was to develop a method that would allow for the discrimination of the various surfactants (commercial and switchable). The accuracy of the results obtained from each procedure was contingent on the accuracy of the method. Figure 30 summarizes the location of oil throughout the sand washing and analysis for SAS1 at 50 ºC. The calculations are presented in the Appendix.

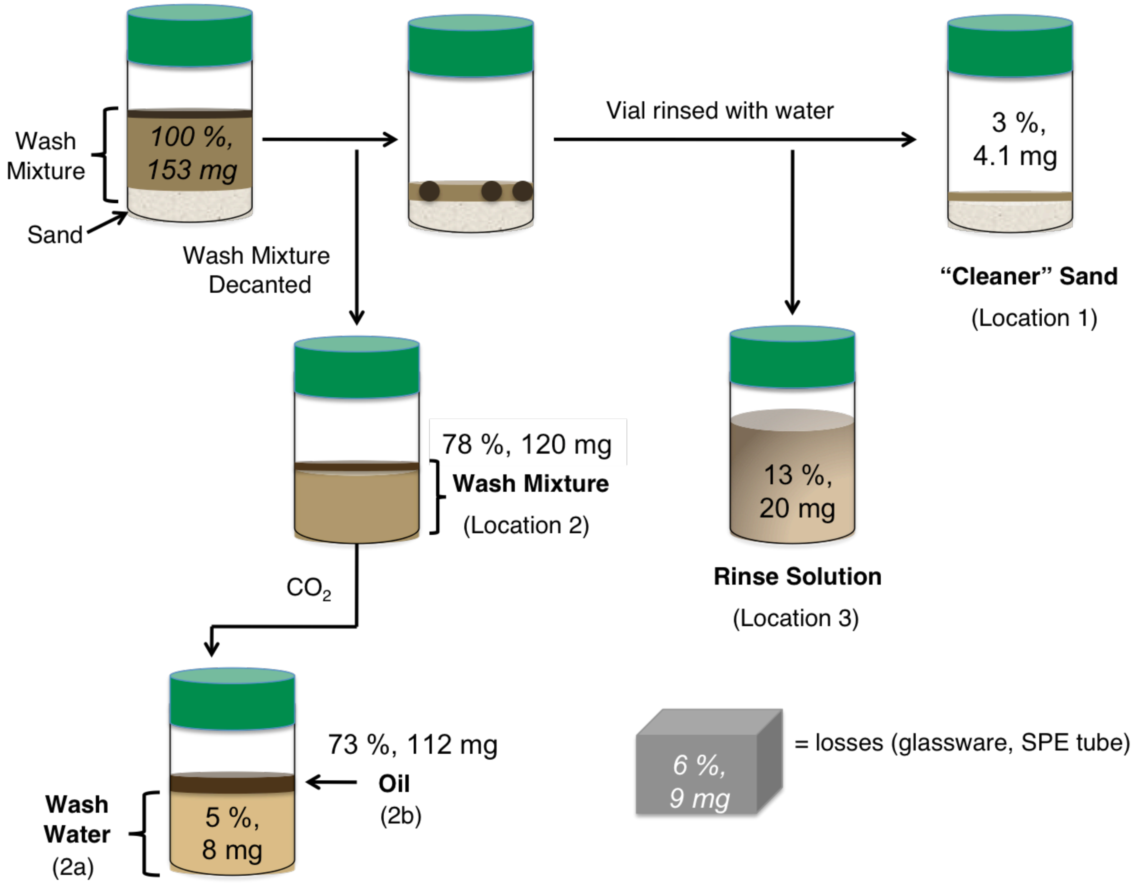


Figure 30: Average percent of the mass of oil throughout the sand washing and analysis for SAS1 at 50 ºC (Table 8, entry 3). See Appendix for calculations.

From Figure 30, it can be seen that the oil originally on the sand is, after the washing procedure, and before CO_2 treatment located in three places 1) some of it remains on the sand; 2) some of it is in the wash mixture decant; and 3) some of it is in the rinse solution. After CO_2 treatment, the oil in the wash mixture is further subdivided into the wash water (2a) and in a separate oil phase (2b).

If the analytical methods are accurate, then the amount of oil determined to be in those three locations should add up to the total amount of oil originally on the oil (minus small amounts lost on the sides of glassware and SPE tubes). If this mass balance is found to be correct, then we can be confident that the analytical methods are not dramatically under-reporting or over-reporting the oil quantities. Table 7 and Table 8 report the average masses recorded from the various analytical methods.

Masses of oil determined in locations 1 and 3 are reported as directly measured (Section 3.5.1 and Section 3.5.2.2 respectively). The mass for the oil in the wash mixture decant (location 2) was calculated using Equation 7 because only 2.0 mL of the mixture was analyzed. It was assumed that the density of the wash mixture would be similar to that of water because water is the continuous phase. Hence, the density of the 2 mL sample was assumed to 1.0 g/mL.

Equation 7

$$\text{Total Mass of Oil in Wash Mixture Decant (g)} = \frac{\text{Oil Mass}_{\text{In 2mL sample}}(g)}{2g} * \text{Mass of Wash Mixture Decant (g)}$$

Table 7: Mass of oil recorded in the various locations, 1,2, and 3 at RT. All masses are in mg. Average and standard deviation reported (n = 3).

Entry	*Surfactant*	*Total Oil in Sample*	*Oil Mass in Location 1*	*Oil Mass in Location 2*	*Oil Mass in Location 3*	*Total Oil Mass (1+2+3)*	*Mass Balance** (%)*
1	SDS	**132 ± 0.51**	79 ± 3.2	14 ± 1.1	38 ± 6.7	**131 ± 4.8**	**99**
2	Triton X-100*	**157 ± 1.2**	50 ± 2.1	50 ± 6.1	44 ± 4.5	**144 ± 3.8**	**92**
3	SAS1	**134 ± 6.2**	25 ± 1.2	23 ± 1.8	60 ± 10	**107 ± 12**	**80**
4	SAS2	**134 ± 0.71**	70 ± 5.0	20 ± 2.7	47 ± 4.3	**137 ± 2.0**	**102**
5	SAS3	**132 ± 0.16**	66 ± 0.87	12 ± 1.7	34 ± 11	**112 ± 12**	**84**

*Studies with Triton X-100 were done on Batch 3 while Batch 2 was used for the other surfactants.
** Mass Balance = (1+2+3)/(Total Oil in Sample) * 100

Table 8: Mass of oil recorded in the various locations, 1, 2 and 3 at 50 °C. All masses are in mg. Average and standard deviation reported (n =3).

Entry	***Surfactant***	***Total Oil in Sample***	***Oil Mass in Location 1***	***Oil Mass in Location 2***	***Oil Mass in Location 3***	***Total Oil Mass (1+2+3)***	***Mass Balance** (%)***
1	SDS	**152 ± 0.35**	21 ± 2.2	86 ± 4.7	22 ±0.35	**128 ± 5.0**	**84**
2	Triton X-100	**151 ± 0.15**	8.7 ± 0.84	101 ± 0.47	21 ± 2.3	**131 ± 4.0**	**87**
3	SAS1	**153 ± 0.37**	4.1 ± 1.3	39 ± 4.5 [#]	20 ± 11	**63 ± 17**	**41**
4	SAS1	**157 ± 0.25**	6.3 ± 0.69	140 ± 5.9		**146 ± 5.9**	**93**
5	SAS2	**152 ± 1.1**	15 ± 7.8	58 ± 9.2[#]	45 ± 5.1	**119 ± 1.9**	**78**
6	SAS3	**151 ± 0.53**	8.5 ± 2.5	90 ± 8.6[#]	17 ± 1.1	**116 ± 9.2**	**77**

** Mass Balance = (1+2+3)/(Total Oil in Sample) * 100 %

Oil mass is inaccurate due to the heterogeneous dispersal of the oil in the wash mixture

A high amount of oil left on the sand occurs for the surfactant that has a low removal percentage (Figure 20 and Figure 22). For example, the removal percentage of SAS2 at RT was 48 %, indicating that 52 % of the oil remained on the sand (Table 7, entry 4). The reverse is true for a high removal percentage. Overall for both the room temperature and the 50 ºC washings, the mass balance is good to excellent for all but one experiment (Table 8, entry 3). Losses are attributed to residue remaining on the walls of the jars, the caps and the SPE columns.

Comparing the results, however, from the room temperature and 50 ºC washings, the following observation was made: the mass balance is lower for 50 ºC washings, particularly for SAS1. The mass balance for SAS1 is dramatically lower compared to the other surfactants at 50 ºC (41 % vs. 77 %). The source of error may lie with analysis of the wash mixture decant (location 2). In this procedure, a 2 mL aliquot is taken from the middle of wash mixture after shaking. It is assumed that the sample is homogenous and the aliquot representative of the total oil contained in the sample. For the room temperature experiments, this was generally a reasonable assumption. Also, the total amount of oil in the wash mixture was lower than the amount of oil in the rinses, so errors in this measurement would have a small impact on the mass balance. For the 50 ºC washings, the wash mixture had a significantly higher amount of oil, making it more difficult to homogenize the mixture by shaking before sampling. This is consistent with the observation of a more pronounced oil layer (Figure 28). Also, the higher amount of oil means that errors in this measurement would have a larger impact on the mass balance.

To confirm that the oil is in fact removed with the aqueous phase and has not been lost, a separate washing was performed where the wash mixture treatment with CO_2 was omitted. The total aqueous portion (wash mixture and rinses) was passed through a 20 mL SPE tube. SAS1 was the surfactant used because it had the largest drop in apparent percent recovery. The total oil recovered after this procedure was 146 ± 11 mg (93 %); confirming that the oil removal efficiency is not reflected by the mass balance results in Table 8 (column 5, entries 3, 5 and 6).

Given the discrepancy associated with the wash mixture analysis, it is recommended for future work to study the efficiency of CO_2 treatment separately, after the mass balance of the oil has been confirmed, minimizing the errors associated with the method.

The location of the oil in the wash mixture sample after CO_2 treatment for SAS1 (Figure 30, 2a and 2b) was determined by using the total was mixture data for from Table 8, entry 4 and the percentage of oil recovered from Table 6, entry 3. Attempts to directly measure the oil in top layer after CO_2 treatment (2b) by physical separation (pipetting or decanting) was unsuccessful owing to the presence of surfactant in the oil layer.

4.7 Fate of the Switchable Surfactants

Thus far, the emphasis has been on the fate of the oil, but the fate of the surfactant is equally important. The surfactant is valuable and its recovery is an important aspect of this process. In contrast, the recovery of the commercial surfactants studied is difficult for SDS and very unlikely, for Triton X-100. For the switchable surfactants, the recovery is possible although the extent however of recovery needs to be determined.

When discussing surfactant recovery it is important to determine location of the surfactant during the washing and separation processes. The potential losses of the surfactant during washing include a) adsorption onto the surface of the sand during the washing process and b) uptake into the oil droplets. The remaining surfactant after these losses should be in the aqueous phases of the wash mixture decants and rinse solutions. Determining how much surfactant is lost is necessary to establish washing parameters such as the amount of surfactant necessary to carry out various washing cycles and therefore the price associated with the surfactant use. The loss of surfactant to the sand is expected to be minimal because the switchable surfactants are anionic and due to the repulsion of the negatively charged head group with the negative charges on the surface of the sand[3], there should be little adsorption.

SAS1 was chosen for this investigation because of its performance and because it has a chromophore. Surfactant samples retained from the SPE experiments of a room temperature and 50 ºC washing, as well as samples from a control washing over clean sand were analyzed. The washing of clean sand with the surfactant would determine if there would be any loss to the sand. It was found that only 0.45 % of the SAS1 remained on the sand after washing. Therefore loss to the sand is not a major sink for the surfactant.

Next, the amount of surfactant lost during washing as result of uptake by the oil was determined using surfactant solutions samples retained during SPE analysis. The loss was calculated using the difference between the concentration of SAS1 solution before washing and the concentration in the wash mixture (Table 9). For both RT and 50 ºC washing, over 70% of the surfactant concentration is lost as a result of washing. This suggests that sand washing using SAS1 will possibly require the addition of more surfactant for further wash cycles.

Table 9: Concentration of SAS1 remaining in aqueous phase before CO_2 treatment

Sample	***Concentration (M) of Surfactant Remaining in Aqueous Phase***	
	Room Temperature	***50 °C***
SAS1 Stock Solution	2.15×10^{-2}	2.15×10^{-2}
Before CO_2 (after washing)*	6.11×10^{-3}	4.67×10^{-3}
Loss of Surfactant Before CO_2	71 %	78 %

*Concentration in rinse solutions was included

CO_2 treatment of the wash solution causes the separation of the crude oil because of the precipitation of the surfactant. The precipitation facilitates surfactant recovery (the surfactant can be collected and reused), and minimizes the amount of treatment which must be done to the wash water before disposal.

The SPE samples of the surfactant solution collected after CO_2 were used to determine the amount of surfactant remaining in the water. Table 10 shows the surfactant concentration before and after CO_2 treatment as well as the percent reduction of surfactant in the aqueous phase after CO_2 treatment.

Table 10: Concentration of SAS1 remaining in aqueous phase after CO_2 treatment

Sample	***Concentration (M) of Surfactant Remaining in Aqueous Phase***	
	Room Temperature	***50 °C***
Before CO_2 (after washing)	6.11×10^{-3}	4.67×10^{-3}
After CO_2	3.57×10^{-4}	9.66×10^{-5}
% Reduction of Surfactant in the aqueous phase after CO_2	94%	98%

The results show that the CO_2 treatment was effective at reducing the surfactant concentration in the aqueous phase. A percent reduction of greater than 90% for both the room temperature and 50°C washings suggests that the surfactant can be recovered and water could be reused with minor treatment. Isolation and analysis of the precipitate was not done at this time. It is recommended for future work to isolate and weigh the precipitate to confirm the percent recovery of the surfactant. It would be worthwhile to investigate the recycling of the recovered precipitate to determine the number of subsequent washings one batch of surfactant can achieve.

4.7.1 Suitability of switchable surfactants for soil washing

Soil washing is not a closed system. Surfactants used will come into contact with the environment either through adsorption to the soil or as a result of their water solubility. The suitability of the switchable surfactants for soil washing should be assessed not only on the parameters used for the washing (concentration, temperature, etc.) but also on the overall effect the switchable surfactants will have once released into the environment. A comprehensive comparison can be made using a qualitative life cycle assessment (LCA) based on methods described by Guinée and co-workers and Allan and Shonnard[51]. The LCA is a multivariate analysis that offers an informative comparison between chemicals used for a given process. The variables or metrics used for the assessment are: acidification potential (AP), ozone depletion potential (ODP), aquatic toxicity (FAETP), smog formation potential (SFP), global warming potential (GWP), human toxicity by ingestion (INHTP), human toxicity by inhalation (INGTP), persistence (PER), bioaccumulation (ACCU) and abiotic depletion potential (ADP).

A qualitative LCA analysis was performed to assess the environmental impact of using switchable surfactants for soil washing. Four scenarios were explored: 1) not washing the sand (i.e. the environmental effect of leaving the North Sea crude oil in the environment); 2) washing with SAS1; 3) washing with SAS2 and; 4) washing with SAS3. The degree of concern of the environmental impact of each metric was assigned a colour. The three major degrees were low (green), moderate (yellow) and high (red). The ideal scenario would be the one that has the most green squares, indicating the least adverse impact of that scenario on the environment. A description of each metric with its corresponding impact for each scenario is described below. It should be noted that much of the data needed to calculate the factors are not available yet; therefore the factors should be used as guidelines rather than absolutes. The results are summarized in Table 11.

Table 11: Life Cycle Analysis of Soil Washing

Scenario	*ADP*	*AP*	*FAETP*	*EP*	*GWP*	*INHTP*	*INGTP*	*HHE*	*ODP*	*SFP*	*PER*	*ACCU*
1	🟩	🟩	🟥	🟩	🟩	🟨	🟥	🟥	🟩	🟩	🟥	🟥
2	🟩	🟩	🟥	🟩	🟥	🟩	🟩	🟥	🟩	🟩	🟩	🟨
3	🟩	🟩	🟩	🟩	🟥	🟩	🟩	🟩	🟩	🟩	🟩	🟨
4	🟩	🟩	🟩	🟩	🟥	🟩	🟩	🟩	🟩	🟩	🟩	🟨

Legend: 🟩 low 🟨 moderate 🟥 high

4.7.1.1 Scenario Assessment

Acidification Potential (AP): the potential of a gaseous compound to form acid rain relative to an equal mass of sulfur dioxide. (SO_2).[52]

There is little risk of acidification potential for all the scenarios because no volatile compounds having the potential to form acid rain are released.

Eutrophication Potential (EP): the potential to cause over fertilization of water relative to phosphate.

There is little risk of eutrophication potential for all the scenarios because no volatile compounds having the potential to over fertilize water.

Aquatic Toxicity (FAETP): considers the toxicity of a particular compound to fresh waters. The potential of a compound to exhibit toxic effects on aquatic life has been related to its log K_{ow}. The aquatic toxicity for the analysis presented in this thesis, was estimated based on log K_{ow} of the various surfactants.

Jessop, Hodson and co-workers[53] have studied the relationship between aquatic toxicity and the log K_{ow} of the switchable surfactants. They determined that switchable surfactants with log K_{ow} close to 4 or less were not of critical concern. For this LCA analysis, even though the log K_{ow} values for all three switchable surfactants was close to 4, SAS1 was flagged as posing the largest threat. This assignment was based partly on its partition coefficients and partly on its structure. SAS1 is a nitro version of a paraben ester. Paraben esters are of concern because they have been shown to have adverse effects on aquatic life[54] and the corresponding acid (4-hydroxy-3-nitrobenzoic acid) of SAS1 has been shown to inhibit chloroplast development in linseed and oat seedlings[55] Aquatic toxicity (mild or severe) should always be considered when choosing a surfactant (switchable and non-switchable) because a fraction of the surfactant will be water soluble, and will therefore eventually enter wastewater channels and affect local aquatic life.

Ozone Depletion Potential (ODP): the decrease in stratospheric O_3 caused by quantitative release of a gaseous chemical, relative to CFC-11 (CCl_3F).

Smog Formation Potential (SFP): the ability of a volatile organic compound to contribute to smog formation relative to a standard mixture of organic gases.[56]

There was little risk of ODP and SFP for all four scenarios because no volatile (halogenated) compounds would be released which would attribute to ozone depletion or smog formation.

Global Warming Potential (GWP): the amount a volatile compound will contribute to global warming over time with respect to and equal mass CO_2. This factor also considers the amount of CO_2 emitted as a result of chemical process, as well as the amount of CO_2 generated from energy consumption.[56]

The GWP of Scenario 1 was flagged as a low concern because it was assumed that the oil would have been weathered before washing, therefore there is no difference to GWP as a result of leaving the oil on the soil. The surfactants themselves would not directly affect the GWP because they are non-volatile. However, other factors such as heating the wash water, the CO_2 used for the switching, the CO_2 released when the recovered oil is burnt as fuel as well as the cost associated with running the soil washing equipment all contribute to the GWP of soil washing using the surfactants.

Human Toxicity by Ingestion (INHTP): considers the concentration of a chemical in water as described by the LD50 value, relative to toluene.

The LD50 values for the surfactants or similar compounds are not significant to contribute to the risk of acute toxicity to humans by ingestion.

Human Toxicity by Inhalation (INGTP): considers the concentration of a chemical in water as described by the LC50 value, relative to toluene.

The surfactants are non-volatile and were not considered a concern for INHTP for Scenarios 2-4. For Scenario 1, INHTP was considered of moderate concern as some volatile components in the crude oil do linger and may pose a threat to humans by inhalation.

Human Health Effects (HHE): INGTP and INHTP only consider acute toxicity and do not consider other possible side effects such as the risk of estrogen mimicry. SAS1 is of moderate concern to human health. While an LD50 is not currently available for SAS1, it has been suggested that paraben esters have estrogenic effects[57-59] and anti-androgenic activity (inhibiting testosterone-induced transcription)[60]. It is unclear if the nitro versions of paraben esters exhibit these effects. Also because of estrogenic effects have not been reported for the parent acids, it is possible that cleavage of the ester group (which is likely to occur in the environment but not necessarily immediately) would reduce the risk of estrogenic effects.

Persistence (PER): how long the chemical is expected to remain in the environment. Persistence can be predicted by looking at factors such as atmospheric degradation, degradation in aqueous environment and aerobic and anaerobic biodegradation. The Boethling Index[61] is used to estimate the aerobic biodegradation lifetime of a chemical based on the type and number of functional groups. The persistence of all three switchable surfactants was estimated to be on the order of weeks and determined not to be of concern. The persistence for the crude oil was not determined but can be assumed to be of high concern because of the various non-volatile, complex compounds such as asphaltenes which will not degrade easily.

Bioaccumulation (ACCU): the potential of a chemical to bioaccumulate indicated by the log K_{ow} of a chemical.

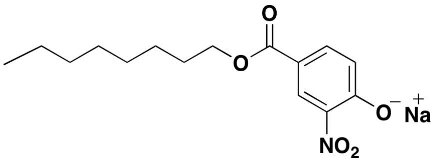
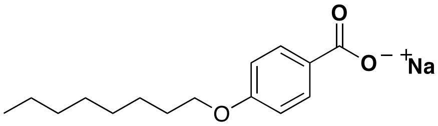
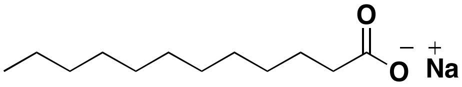
When considering the accumulation potential, it is useful to know where the chemical will end up (air, water, or soil) once released into the environment. Partition coefficients indicate the degree of partitioning of a chemical between two phases. The two partition coefficients of interest for the surfactants are the log K_{ow} (partitioning of a compound into octanol and water) and the log K_{oc} (partition coefficient of a compound into soil) presented in Table 12. Low log K_{ow} and log K_{oc} values indicate the compound is more hydrophilic and high values indicate the compound is more hydrophobic. Hydrophobic compounds are of concern because they will partition in the fatty tissues of organisms and can accumulate over time.

Log K_{ow} values for the compounds were calculated using an ALOGPS 2.1, an online software program developed by Tetko et al. [62,63] Estimated log K_{oc} values were using calculated by taking the logarithm of the simplified relationship developed by Karickhoff[64] (Equation 8).

Equation 8

$$K_{oc} = 0.41 * K_{ow}$$

Table 12: log K_{ow} and log K_{oc} of the switchable surfactants studied for sand washing. Log K_{ow} was calculated using the online software ALOGPS 2.1. Log K_{oc} was calculated using Equation 8.

Surfactant	***Structure***	***Log K_{ow}***	***Log K_{oc}***
SAS1 sodium octyl 4-hydroxy-3-nitrobenzoate		4.54 ± 1.06	4.15
SAS2 sodium 4-(octyoxy) benzoate		4.51 ± 1.16	4.12
SAS3 Sodium Laurate		4.30 ± 0.86	3.91

Both partition coefficients of all the surfactants fall between 3.91 and 4.55, suggesting that the surfactants exhibit some hydrophobic nature and will have the possibility to bioaccumulate. Therefore they were all considered moderate risks.

The accumulation potential for oil was rated as high because it is expected that the log K_{ow} of the crude oil would be higher than 4.5 due to the number of hydrophobic components.

Abiotic Depletion Potential (ADP): is a measure of resource depletion. It estimates the risk of depletion of an element relative to antimony.[52] Elements classified as abundant such as carbon, hydrogen, oxygen, nitrogen and sodium are not considered.

The ADP of all four scenarios was determined to be of low concern because they also contain elements of abundance and therefore there is little risk of depletion.

Cost is also an important factor. At the present time, a cost estimate is not provided. Not all the information is available to accurately determine a cost associated with the manufacture and production of the surfactants. It is expected that manufacturing costs would decrease as a result of economies of scale.

4.7.1.2 Scenario selection

From Table 11, it was determined that Scenario 1, (not washing the sand and leaving the crude oil), is not favourable. Half of the factors were determined to be of moderate to high concern. This is a result of the cumulative adverse effects that the various components (at varying concentrations) found in the crude oil have on human, animal and plant activity.

While SAS1 was shown to be the best switchable surfactant with respect to sand washing and oil separation after CO_2 treatment, particularly at RT, the LCA analysis suggests that SAS1 may be an unlikely candidate for a real-life soil washing application. This scenario could be improved if it was shown that the fraction of SAS1 remaining in the water would not pose a significant threat to surrounding, aquatic, plant and human life.

Scenarios 3 (SAS2) & 4 (SAS3) are identical. However, including the sand washing performance and oil separation after CO_2, Scenario 4, using SAS3 (sodium laurate) would be the best.

5 Conclusions

The switchable surfactants presented have been shown to be able to remove crude oil from sand and afford subsequent separation of the crude oil from the water upon CO_2 treatment.

5.1 Influence of Surfactant Structure

Surfactant properties are directly correlated to the surfactant structure. The impact of the structures of the switchable surfactants on their washing ability and their efficiency of oil and surfactant separation and recovery will be discussed.

5.1.1 Effect on Washing

At RT and 50 ºC the switchable surfactant trend for washing performance is the same SAS1>SAS3>SAS2. The removal percentages however, are significantly different. At RT the values are, in order of the trend: 82 %, 50 %, 48 % compared to: 97 %, 94 %, and 90 % at 50 ºC. It is expected that increasing the concentration of SAS3 would enhance its performance by ensuring its concentration is well above its CMC (Table 2). Structurally it appeared that the nitroparaben derivative (SAS1) afforded the best oil removal from sand at both temperatures. At 50 ºC, both aliphatic and aromatic carboxylates (SAS3, SAS2) performed well.

As a result of the similarity in removal percentages of the switchable surfactants at 50 ºC it would be worthwhile to perform a GC/MS study, similar to Urum and co-workers[26, 37], on the crude oil remaining on the sand before and after the organic solvent extraction. This analysis might demonstrate an affinity of the surfactant for certain types of compounds, which would provide further insight into the effect of surfactant structure on sand washing.

5.1.2 Effect on the separation of oil from water after CO_2 treatment

The surfactant trends for the percent removal of oil from the bulk aqueous phase are as follows: at RT, SAS1 (80 %) > SAS2 (55 %) = SAS3 (55 %) and at 50 ºC: SAS1 SAS3 (95 %) > SAS1 (93 %) > SAS2 (89 %). At RT, the difference between surfactant performance at oil separation from the water is more pronounced than at 50 ºC. Coupling this data with the performance of the surfactants at sand washing suggests that it the nitrophenol functionality of the hydrophilic moiety of SAS1 enhances the surfactant's ability to cause oil and water mixing and separation, especially at RT. It is recommended to conduct GC/MS or LC/MC analyses to support this hypothesis.

5.1.3 Surfactant Selection

As described in Section 4.7.1.2, based on surfactant performance (at RT and at 50 ºC), removal of oil from the bulk aqueous and life cycle analysis, SAS3, sodium laurate is the best switchable surfactant for soil washing.

6 Future Work

Soil washing using switchable surfactants could be very promising. Before a pilot scale test is performed, washing parameters such as surfactant concentration and recovery and washing temperature should be optimized. It is also recommended to test the switchable surfactants at the optimized parameters on various real soil matrices to assess how the performance of the switchable surfactants is affected.

6.1 Surfactant Concentration

Ideally, the least amount of surfactant needed to achieve a removal percentage of at least 90 % is desirable. Environmentally, using less surfactant preferred. Reduction in the amount of material reduces the risk to the environment because it is expected that less surfactant will enter the environment. Economically, less material translates into a lower operating cost. While the percent recovery after the separation process may be reduced, lower surfactant loading would still be favoured. If the surfactant remains in the wash water instead of precipitating out, this might offset the amount of surfactant that will need to be added for further washing cycles. An investigation into determination of the optimal surfactant concentrations is recommended.

6.2 Washing Temperature

The temperature at which the washing takes place might also affect the minimum effective surfactant concentration. At 50 ºC, it was shown that the surfactant performed better at removing oil from the sand. Crude oil separation from the wash mixture was also affected by the increased washing temperature; offering a better separation, particularly for SAS1. It is possible that reducing the surfactant concentration and increasing the washing temperature might provide the ideal soil washing scenario. It would be worthwhile to further investigate the effect of increased temperature on the soil washing system, both for the washing and subsequent separation with CO_2.

6.3 Oil Recovery

Analysis into improvement of oil recovery is suggested. It is recommended the series of experiments illustrated in Figure 30 be performed on a larger scale to verify the percentages assigned.

6.4 Real Soil Matrices

This project focused solely on the washing of Ottawa Sand. Further research should test soil matrices of varying sand, silt, clay and organic matter content as well as soils at various stages of weathering, to determine how the switchable surfactants respond. It would be advisable to test different crude oils to assess the surfactant's behaviour when in contact with contaminants of different, density, adsorption and hydrocarbon distribution. Chemical characterization by GC/MS of the crude oil samples before and after weathering is also suggested. This could provide insight into which compounds are preferentially removed upon treatment with the switchable surfactants.

Appendix

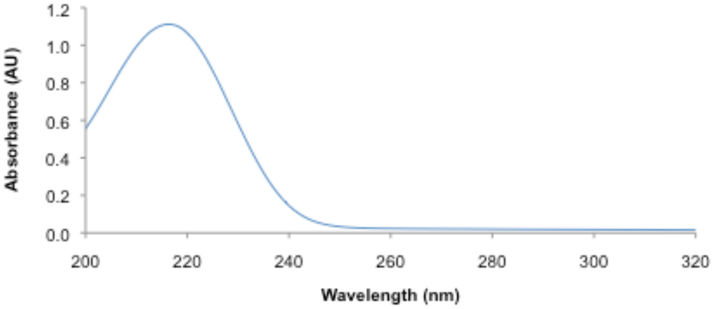


Figure 31: UV-Vis Spectrum of C8 taken in hexanes. λ_{max} is observed at 215 nm.

CMC Measurements

The critical micelle concentrations of SAS1 and SAS2 were determined by measuring the change in conductivity with surfactant concentration. The curves with the CMC values are shown below.

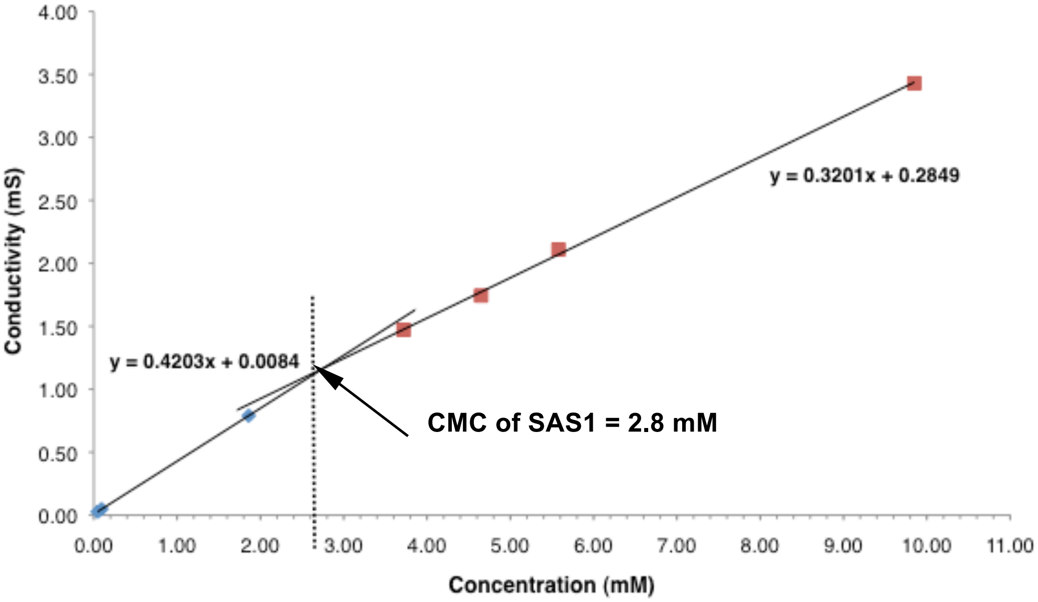


Figure 32: CMC of SAS1 determined by measuring conductivity as a function of surfactant concentration.

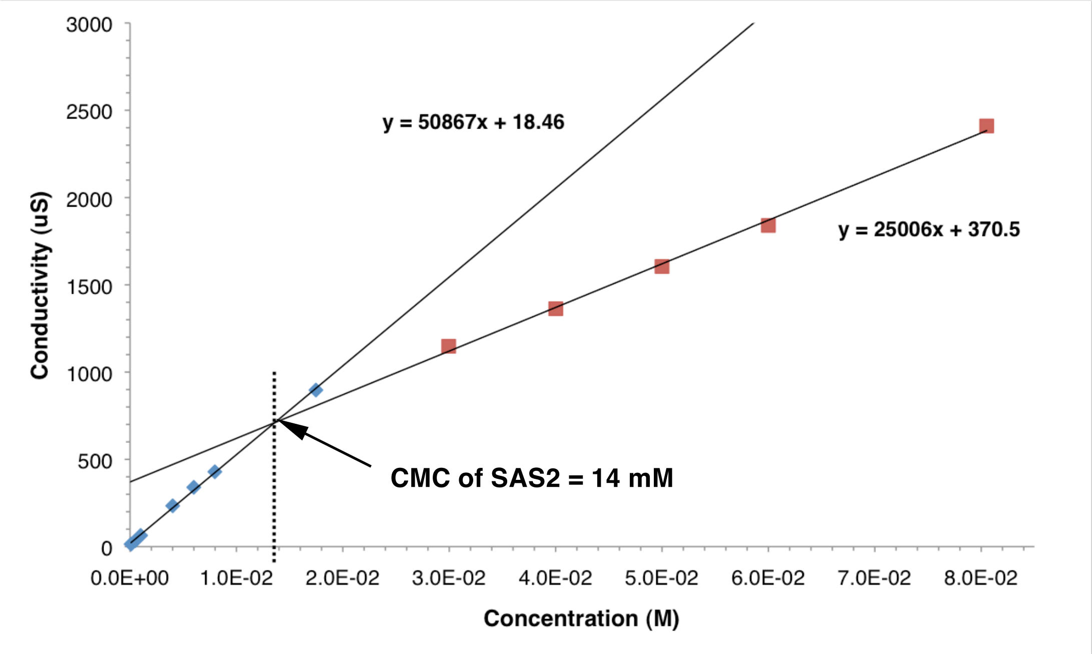


Figure 33: CMC of SAS1 determined by measuring conductivity as a function of surfactant concentration.

Mass Balance Calculations

Figure 34 is a recreation of Figure 30 where all the calculations for the percentages associated with each location of oil have been included. The values are summarized below.

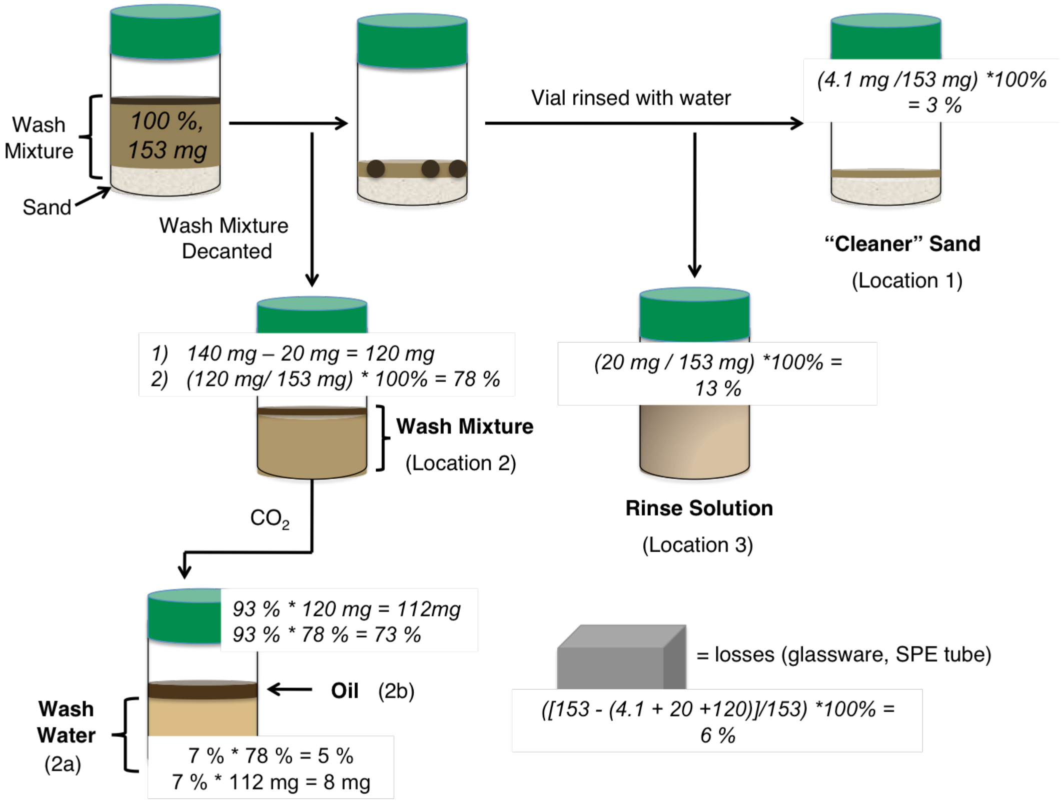


Figure 34: Recreation of Figure 30, including calculations for mass balance.

Variable	Value	Reference in Thesis
Mass of oil in the sample	153 mg	Table 8, entry 3
Mass of oil remaining on sand	4.1 mg	Table 8, entry 3
Mass of oil in rinses	20 mg	Table 8, entry 3
Mass of oil in total aqueous portion	140 mg	Table 8, entry 4
Mass of oil in the wash mixture	120 mg	calculated
Percent of oil removed from wash mixture (after CO_2)	93 %	Table 6, entry 3
Percent of oil remaining in wash mixture	7 %	calculated
Mass of oil found in top layer of wash mixture after CO_2 (2b)	112 mg	calculated
Mass of oil found in wash mixture after CO_2 (2a)	8 mg	calculated

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