Investigating centrifuging conditions for sustainable recovery of fuel from oily sludge

Nazanin Motevali

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______________________________ Examiner
Dr. Chunjiang An

______________________________ External Examiner
Dr. Ion Stiharu

______________________________ Supervisor
Dr. Maria Elektorowicz

Approved by ____

Chair of Department of Graduate Program Director

December 13th, 2018 ______________________________________

Dean of Faculty

ABSTRACT

Investigating centrifuging conditions for sustainable recovery of fuel from oily sludge

Nazanin Motevali

One of the most troubling wasted products in both upstream and downstream petroleum industry is oily sludge. Oil sludge is generated in huge amounts through refining, exploration, storage, pipeline and tanker transportation. Such sludge, containing considerable amounts of hydrocarbons, solids, heavy metals, water and other impurities, presents a stable emulsion, which is difficult to treat. An adequate treatment prevents environmental pollution, protect public health, and installation, as well as preserves an adequate tank capacity. On other hand, oil sludge still contains valuable fuel and water, hence in spite of difficulties; the recovery of resources from sludge is a sustainable generation of fuels and recycling water. Centrifuging is one of the available technologies, which is able to break the sludge suspension into phases, while fuel can be recovered. The objectives of this study were to recovery of oil and water, and decrease hazardous volume for disposal using centrifuging process. The investigations were conducted in order to separate fractions, in a sustainable way, i.e. oil be used as a fuel, water be reused in processing, and solids can be treated or disposed efficiently. In order to optimize phase separation and help in fraction recovery, the centrifuging process was modified by various pre-treatment methods. The results showed that the highest quality of oil and water was recovered when centrifuging process was applied with using such additives like ferric chloride, ferrous sulfate and surfactant (Tween 80). Further improvement was achieved when centrifuging three-phase separation was exposed to pre-heating at 55ºC. The calorific value of the recovered fuel increased by 23% comparing to raw oily sludge. Furthermore, an amount sent to disposal decreased by 70%.

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LIST OF ABBREVIATIONS

Name	Definition
$Al_2(SO_4)_3$	Alum
API	American Petroleum Institute
ASTM D95	Standard Test Method for Water in Petroleum Products and Bituminous Materials by Distillation
CEPA 1999	Canadian Environmental Protection Act, 1999
Cmix	Mixture of sludge, which contains all samples except sample C2, and C7
Cmix (C1-C8)	Mixture of all eight types of sludge, which contains sample from C1 to C8
Cr	Chromium
Cu	Copper
EK	Electrokinetics
EOR	Enhanced Oil Recovery
EQA	Environmental Quality Act
$FeCl_3$	Ferric chloride
$FeSO_4$	Ferrous sulfate
$FeCl_3 + FeSO_4$	Mixture of ferric chloride and ferrous sulfate
F/T	Freeze/thaw method
Heavy oil	Typical carbon range from C_8 to C_{50}
IPIECA	International Petroleum Industry Environmental Conservation Association
L	Liter

Light oil	Typical carbon range from C_5 to C_7
LPGC	Liquefied Petroleum Gas Condensate
MEK	Methyl ethyl ketone
mL	Milliliter
mPa	Milli Pascal
MW	Microwave method
NA	No Additives
Ni	Nickel
NO_X	Nitrogen oxides
NSO	Nitrogen sulfur oxygen
O/W	Oil-in-water emulsions
PAHs	Polycyclic Aromatic Hydrocarbons
Pb	Lead
PHCs	Petroleum Hydrocarbons
RCRA	Resource and Recovery Conservation Act
SEO	Surfactant Enhanced Oil Recovery method
SO_X	Sulfur oxides
TGA	Thermogravimetric analysis
TOC	Total Organic Carbon
TPH	Total Petroleum Hydrocarbons
VC	Viscometer
Vol. %	Volume percentage

WOS	Water Oil Separators
O/W	Oil-in-water emulsion
W/O	Water-in-oil emulsions
wt. %	Weight percentage
Zn	Zinc

INTRODUCTION AND RESEARCH OBJECTIVES

Every year, petrochemical industry generates tremendous amount of oily sludge, which originates from different sources including crude oil storage tank bottoms from upstream operations (Kariminezhad and Elektorowicz, 2018a) .

Oily sludge is known as one of the significant waste with a very complex composition and high viscosity. Generally, it contains water-in-oil (W/O) emulsion (oils, water and solids in different proportions depending on its origin and storage conditions) (Chirwa et al., 2017; Lima et al., 2011). It is also classified as a hazardous waste due to a presence of high concentration of petroleum hydrocarbons (PHCs) that has received increasing concerns to the environment and human health (Prakash et al., 2015) .

To date, there is an estimation more than 60 million tons of oily sludge that can be generated every year (Pazoki and Hasanidarabadi, 2017). The statistics also showed that each 500 tons of crude oil processed can produce one ton of oily sludge. This sludge can be disposed of traditionally using land farming and composting (Al-Futaisi et al., 2007). Beside the considerable disposal costs, it has some limitations such as the inability to treat and reduce the level of petroleum contaminants that have an adverse impact on the environment and humans. Hence, the demand for protected and environmentally techniques is essential for petroleum industry to find alternative treatment methods that can manage oily sludge (Battikhi, 2014) .

By breaking the sludge suspension into phases, the separated phases such as oil, water and solids can be treated, reused or disposed in an efficient way. There are many waste recovery and treatment methods to maximize the oil recovery from sludge and to reduce the volume of the hazardous waste (Bhutto and Bazmi, 2005).

Oil recovery could be considered as one feasible method to improve management of fuel supplement. The recovered oil can be reused in the petroleum industry as a processing material or valuable fuel (Hou et al., 2013). Simultaneously, separated water can be forwarded to the wastewater treatment plant for further treatment. In addition, some part of solids material could be solidified and use as road construction materials or embankments minimizing amount sent to the final disposal (Taha et al., 2010).

Centrifugation is one of the conceivable method that has been extensively applied for oily sludge treatment under different speeds, time or temperature conditions. Centrifugation provides a mechanical separation of oil, water and solids particles from oily sludge (Lin et al., 2017) .

Centrifuging process combined with pre-heating and additives (e.g. coagulant, surfactant) can enhance the phase separation of oily sludge in a more effective manner and also reduce its viscosity (Hassanzadeh et al., 2018; Degromont, 2014).

The objective of this research is to develop a centrifugation technique that will lead to the separation of oily sludge phases ready for further recovery and reuse. Then, investigation of the effects of different temperatures and additives to promote the phase separation in a cost effective way have been proposed. It was expected that such approach can significantly reduce the amount of wasted sludge and can recover oil under the form of oil while a high quality of separate water would be preserved.

LITERATURE REVIEW

2.1 Wasted products in the petroleum industry

Over the past decades, the processing of petroleum products has grown dramatically. However, by-products of oil extraction, refinement, transportation and consumption present often sources of environmental pollution (Jackson and Rohlik, 1984). *The Resource and Recovery Conservation Act* (RCRA) defines hazardous waste as a solid waste or combination of solid waste that can pose a potential hazard to human health or the environment by its physical, chemical or infectious characteristics. The term ''solid waste'' is commonly known as any garbage, sludge, refuse from a waste treatment plant including solids, liquid, semi-solids resulting from the industrial activities and processes (LaGrega et al., 2010). According to European Commission and Joint Research Center (2015), waste in a refinery might comprise:

1. Sludge, which is divided into oily (e.g. from tank bottoms sludge) and non-oily (e.g. from wastewater treatment facilities);
2. Miscellaneous liquids, semi-liquids or solid wastes (e.g. contaminated soil, spent catalysts from conversion process);
3. Non-refining wastes (e.g. demolition, domestic and construction)

A summary of major solid wastes and their sources generated from refineries are shown in Table 2-1.

Table 0-1 Major solid wastes and their sources generated by refineries (Jafarinejad, 2016; European Commission and Joint Research Center, 2015; U.S. EPA, 2004)

Types of wastes	Categories	Sources
Oil materials	Oily sludge	Tank bottoms, biotreatment sludge, interceptor sludge, wastewater treatment sludge, contaminated oil materials soils, desatlter sludge
	Solids materials	Contaminated soils, oil spill debris, filter clay acid, tar rags, filter materials, packing, lagging, activated carbon, coke dust (carbon particles and hydrocarbons)
Non-oil materials	Spent catalyst (excluding precious metals)	Catalytic cracking unit, catalytic hydrocracking, hydro treating/hydro processing, polymerization, residue conversion catalyst, catalytic reforming
	Other materials	Resins, boiler feed water sludge, desicants and absorbents, neutral sludge from alkylation plants
Drums and containers		Paint, plastic, metal, glass
Radioactive waste (if used)		Catalysts, laboratory wastes
Scales		Leaded/unleaded scales, rust
Construction/demolition debris		Scrap metal, concrete, asphalt, soil, asbestos, mineral fibers, plastic/wood
Spent chemicals		Laboratory, caustic, acid, additives, sodium carbonate, solvents,
Pyrophoric wastes		Scale from tanks/process units
Mixed wastes		Domestic refuse, vegetation
Waste oils		Lube oils, cut oils, transformer oils, recovered oils, engine oils
Metals		Crude-oil/desalter sludge, spent catalyst fines in catalytic hydrocracking

Refineries generate solid waste and sludge (from 3 to 5 kg per ton of crude processed), a significant portion of that arises from oily sludge and it has received special attention in petroleum industry but other solid waste must also be managed (Islam, 2015; Taiwo and Otolorin, 2009)

Oily sludge is a viscous and thick mixture of water, oil, solids particles and petroleum hydrocarbons and it contains a high concentration of toxic components. Due to its dangerous nature, oil sludge can be troublesome to treat and dispose of. As a result, many efforts are being made to separate the phases to recover the oil retained in the sludge and also to reduce the volume of waste. Therefore, there is a need for oily sludge treatment methods to identify the sources, characteristics, and environmental impact of oily sludge in the refineries in order to(Gonzalez, 2016) :

- Discuss current and available treatment methods;
- Summarize the advantages and limitations of these methods;
- Investigate future improvements to face resource recycling.

2.2 Sources of oily sludge

Large amounts of oily wastes are being obtained from two streams: upstream and downstream operations in petroleum industry. The upstream operation refers to the exploration, extraction, production, transportation, and storage of crude oil, while the downstream operation includes crude oil refining processes and distribution (Ali et al., 2017; Macini and Mesini, 2011).

In the upstream operation, the oily sludge sources consist of crude oil tank bottom sediments, slop oil at oil wells and drilling mud residues. In the downstream operation, there are different sources such as slop oil emulsion solids; sediments at the bottom of rail, truck, or storage tanks; residues from oil/water separator; heat exchange bundle cleaning sludge; excess activated sludge from on-site wastewater biological treatment plants (Cooper at al., 1995). In another classification, the International Petroleum Industry Environmental Conservation Association (IPIECA) has divided the primary sources of oily wastes as illustrated in Table 2-2.

Table 0-2 Different types of oily sludge and their sources (da Silva et al., 2012; IPIECA, 2004)

Types of oily sludge	Primary sources
Oily sludge with detergents or washing liquids, and it is carrying rust and reaction residues	Oily sludge formed during the washing of the equipment used in refineries such as distillation towers, cracking units and hydrotreaters as well as equipment used for catalytic reformation, isomerization, alkylation or delayed coking
Oily sludge tank cleaning operations and with non-mineral skimmed foam and grease	In effluent treatment stations, oily sludge is formed in water-oil separators (WOS), floaters and/or flocculators
Light oily sediments which contain mineral material	In desalter, an oily sludge containing high levels of sediments is formed during the desalinization process
Heavy oily sediments which contain mineral material	In tank bottom used to store the raw petroleum and dark petroleum products (combustible oils, petroleum asphalt cement and lubricants)

Different water-oil separation processes generate oily sludge. In literature, most studies of oily sludge relate to the bottom sediments in crude oil storage tanks. Crude oil is settled in storage tanks where it has a tendency to divide into heavier and lighter petroleum hydrocarbons (PHCs). Usually, the heavier hydrocarbons settle along with water and solids particles and the mixture of oil, solids, and water remained at the storage tank bottom is known as oily sludge (Hu et al., 2013).

More often, a large amount of oily sludge production depends on the refining capacity. Several factors such as oil storage methods, crude oil properties (e.g., density and viscosity), refinery processing scheme and refining capacity have an impact on the quantity of oily sludge generated by the refining process (Islam, 2015).

2.3 Characteristics of oily sludge

The characteristics of oily sludge can provide useful guidelines for selecting alternative treatment methods, determining the hazardous nature of waste and choosing the best disposal method (Krishna et al., 2017).

Oily sludge has a complex composition including oil-in-water O/W, water-in-oil W/O and suspended solids, which is generally characterized as a stable W/O emulsion of water, solids, PHCs, and metals. The W/O emulsion has a high oil concentration and its stability relies on a protective film that prevents water droplets from coalescing with each other. This interfacial film consists of several natural emulsifiers including fine solids, some PHCs components (e.g., asphaltenes and resins), oil soluble organic acids, and other finely segregated materials (Jing et al., 2016; Hu et al., 2013; Sztukowski and Yarranton, 2005).

The range of pH value of oily sludge is normally between 6.5 and 7.5 and its composition varies from one refinery to another and from one oily sludge to another depending on the type of refined crude oil, crude oil source, processing scheme, and equipment (Guo et al., 2011).

Based on several sources, oily sludge contains different ranges of compounds and it varies in composition. It is made up of considerable amount of solids, water and hydrocarbons in which there are many toxic, mutagenic and carcinogenic components such as heavy metals and Polycyclic Aromatic Hydrocarbons (PAHs) (Zhou et al., 2009).

The concentration of water in oily sludge is commonly 30-90%, the concentration of sediments, mostly comprising calcite, halite, kaolinite and quartz, is 4-7%, and the remaining is composed of petroleum hydrocarbons between 5 to 60% (da Silva et al., 2012).

According to Liang et al. (2014), oily sludge comprises 30-50 wt. % oil, 30-50 wt. % water and 10-12 wt. % solids. Mokhtar et al. (2011) state that the contents of solids and hydrocarbons are 5-20 wt. % and 10-30 wt. % respectively and the rest is water. In addition, according to Hu et al. (2013), it contains 30-85 wt. % water, 5-46 wt. % solids and 15-50 wt. % total petroleum hydrocarbons (TPH).

Crude petroleum oil is a complex mixture of hydrocarbons and other organic compounds. In the oily sludge, the petroleum hydrocarbons (PHCs) and other organic compounds generally break into four fractions as following: aliphatics, aromatics, asphaltenes and nitrogen sulfur oxygen (NSO) (Reddy et al., 2011).

In the oily phase of petroleum sludge, there is a high concentration of aromatic hydrocarbons between 25 to 40% and 40 to 60% saturated hydrocarbons, 10 to 15% resins and 10 to 15% asphaltenes (Speight, 2014).

Up to 75% of PHCs in oily sludge is composed of aliphatics, aromatic hydrocarbons, alkanes, cycloalkanes, benzene, toluene, xylenes, naphthalene, phenols, and various polycyclic aromatic hydrocarbons (PAHs) (e.g., methylated derived from fluorine, phenanthrene, anthracene, chrysene, benzofluorene, and pyrene) (Jafarinejad, 2016).

Typically, oily sludge is made up of 40–52% alkanes, 28–31% aromatics, 8–10% asphaltenes, and 7–22.4% resins by mass (Bezza et al., 2015). The stability of oily sludge emulsions depends on asphaltenes and resins since they can act as lipophilic emulsifiers by constituents that contain hydrophilic functional groups (Rondón et al., 2006).

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Due to the varied chemical composition of oily sludge, its physical properties such as viscosity, density, and heat value can change remarkably. The measured properties of oily sludge can change with sampling time, the source of oily sludge and the location of collection (Hu et al., 2013). However, physical properties of oily sludge can be affected by two main factors: polarity and molecular weight of chemical species in the sludge. It is also possible to make an empirical modeling of physical properties as regards to the chemical compositions (U.S. EPA HPV Challenge Program, 2010).

In the components of oily sludge, there is also a diversity of heavy metals, resulting from various sources, their concentrations and species can change over a wide range similar to organic compounds (Hu et al., 2013).

Based on different literature, the metal concentration in oily sludge from different refineries is reported. According to some studies, metal concentrations in oily sludge are 1299 mg/kg for zinc (Zn), 60,200 mg/kg for Fe, 500 mg/kg for copper (Cu), 480 mg/kg for chromium (Cr), 480 mg/kg for nickel (Ni) and 565 mg/kg for lead (Pb) (Jafarinejad, 2016; Marín et al., 2006).

2.4 Impact of oily sludge

All activities and operations in all sectors of refineries and petrochemical plants such as exploration, storage, production, transportation and development can bring wastes and pollution. Solid wastes in these areas have some negative impacts on air, water and soil (Mariano and La Rovere, 2017).

Oily sludge as a major category of solid wastes with a toxicity and hazardous nature can degrade the physical and chemical properties of soils, contaminate surface water and groundwater and also has an adverse impact on public health, air quality and the terrestrial ecosystem (Wuana and Okieimen, 2011).

Oily sludge has a high viscosity, which can be fixed in soil pores, form a continuous cover on soil surface and can be adsorbed onto the surface of soil mineral constituents. These would contaminate soil and has various negative results such as: inhibit seed germination, nutrient cycling, and growth restriction or demises of plants on contact especially and the higher molecular weight of constituents in oily sludge. Their degradation products could stay close to soil surface and make hydrophobic crusts, which reduce water availability and confine water-air exchange (Das et al., 2018).

One of the most widespread soil and groundwater contamination in Canada is PHC. When release to the environment, it can cause significant problems related to their toxicity including transportation of lighter PHC by groundwater or air, fire/explosion hazard, degradation of soil quality, human and environmental toxicity (CCME, 2014).

The presence of PHCs in oily sludge (e.g., PAHs) could lead to many toxic consequences since they could reduce the activity of soil enzymes (i.e. hydrogenase and invertase) and affect the soil microorganisms (Jafarinejad, 2016). They can also enter groundwater causing adverse impacts on aquatic system diversity and the quantity of fish (Wake, 2005).

In addition, after settling in the terrestrial environment for a long period, the weathered chemical residues may arise to resist degradation and desorption, and they interact with soil constituents in a notable time. Long chain alkanes, stable dialkylphthalates and fatty acids could be constituted by covalent bonding among humic polymers (e.g., humins, fulvic acid, and humic acid) and organic compounds in sludge residues in soil with a resistance to microbial degradation.

In extreme cases, PAH could affect the immune system, blood, skin, lungs, spleen and weight loss by generating epoxide compounds with carcinogenic and mutagenic features. Therefore, because of the unsafe nature of oily sludge, there are some regulations such as the RCRA in the Unites States, which have established stringent standards for the management, storage, treatment and disposal of hazardous wastes (Jafarinejad, 2016; U.S. EPA, 1980). In order to protect the environment, health and human life from risks of toxic substances in Canada, *the Canadian Environmental Protection Act, 1999* (CEPA) have set legislations for management of hazardous waste and hazardous recyclable materials. In Québec, *the Environment Quality Act, 2018* (EQA) have implemented regulations tailored to save the environment from the risks of hazardous materials according to the EQA standards.

2.5 Overview of oily sludge management

Waste management plays an important role to achieve sustainable waste management pursuing waste legislation. A waste management is a process that predetermines the methods and activities of waste in line with waste generation and their final release to the environment or dispose off (MVLWB, 2011).

Oily sludge as a major type of solid waste needs the right treatment method. Due to limited on-site storage space, increasing disposal costs, environmental issues and strict legislation, petroleum industries have developed an innovative alternative to treating and managing oily sludge (Hu et al., 2013).

According to the European Commission Directorate-General Environment (2012), a waste management needs a plan with possible elements. The waste management hierarchy is illustrated in Figure 2-1. The aim of the hierarchy is to separate the adverse environmental impacts of the resources and make a recycling system. The hierarchy normally goes down based on the order of the major environmental sight in waste legislation (European Commission and Joint Research center, 2013).

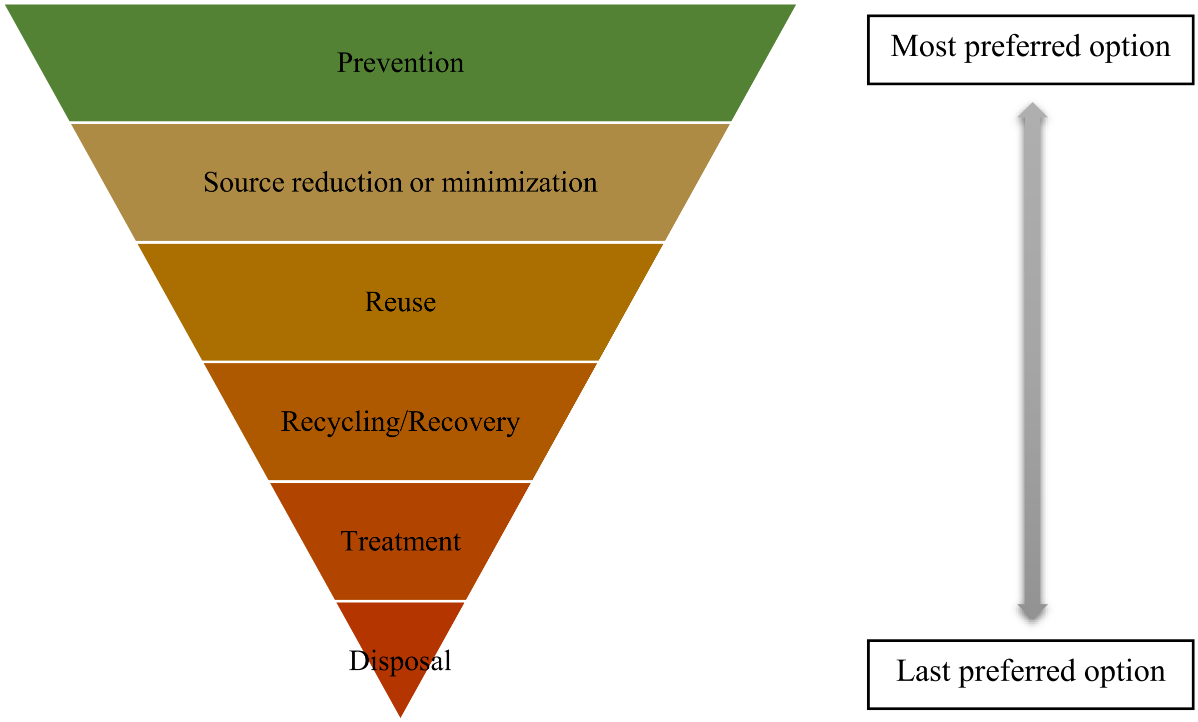

Figure 0-1 Waste management hierarchy

The examples of each elements of the hierarchy are shown in Table 2-3.

Table 0-3 Elements of waste management plan with their examples (Jafarinejad, 2016)

Elements of waste management plan	Some examples in the petroleum industry
Prevention	Keeping hazardous and nonhazardous wastes separate, design of new or modified operations and processes, determination of sludge and water content for feedstock
Source reduction or minimization	Using of gravel packs and screening for reduction of volume of solids/sludge generation in E&P sector, proper operation of equipment
Reuse	Reuse of oily sludge in process units (e.g., cocking) as part of the feed due to their oil content
Recycling/Recovery	Recovery of oil from tank bottoms via centrifuging and filtering, recycling catalyst and coke fines, and valuable product recovery from oily sludge with solvent extraction
Treatment	Thermal, physical, chemical and biological processes
Disposal	Incineration, biodegradation, composting, landspreading, landfarming, landfilling

Following Hu et al., (2013), oily sludge management is an important challenge to industry players in the petroleum industry. The right treatment and disposal methods for oily sludge depends mainly on the physical and chemical properties of the sludge, the availability of facilities and regulatory requirements. Prior to final disposal, sludge is generally de-oil or dewatered (e.g., centrifuging).

According to Kwon and Lee (2015), the first step to management of oily sludge is to prevent the generation of oily sludge and apply some technologies to decrease the volume of oily sludge production, and then use the effective treatment methods by focusing on recovery of valuable fuels and water from oily sludge to eventually dispose the unrecoverable residues.

Various techniques have been developed for management of oily sludge including oil recovery, dewatering and disposal. In order to reduce the volume of waste and develop it more environmentally friendly, recovery and recycling have been taken into account as an acceptable and sustainable management method for oily sludge. The separated oil from oily sludge is considered as oil recovery, which is valuable for other uses in petroleum industries. There are several methods (practical and not) as shown in Fig. 2-2.

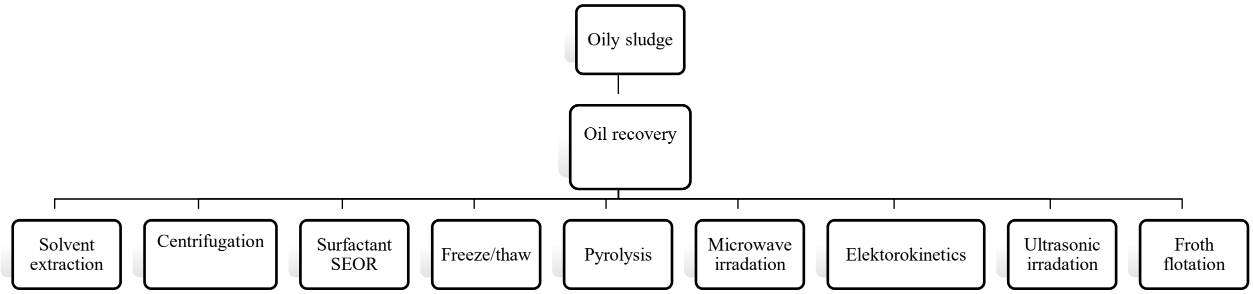

Figure 0-2 Overview of oil recovery methods from oily sludge (Hu et al., 2013)

2.6 Recovery of oil from sludge

Due to the high oil concentration in sludge, oil recovery from sludge is considered as one of the feasible environmental options. Moreover, it can also reduce its contamination and decrease the volume of hazardous waste disposal. However, each method has its own advantages and disadvantages, which have been summarized and compared in Table 2-4 based on their advantages and limitations. It should be noted that some of these methods only have been used on a laboratory scale such as: electrokinetics, ultrasonic irradiation, freeze/thaw, froth flotation and the rest have been used on a field scale (Jafarinejad, 2016; Bahadori, 2013).

Table 0-4 Main features of oily sludge treatment methods (Jahromi and Elektorowicz, 2018; Jafarinejad, 2016; Hu et al., 2013)

Method	Advantages	Limitations
Solvent extraction	Lower energy requirements, easy cleaning of oil storage facilities, recycling of extraction solvents, easy to apply, fast and efficient	Large amount of organic solvents is used, high cost and not environmentally sound
Surfactant SEOR	Easy to apply, fast and efficient,	High cost, chemical surfactants could be toxic, surfactants need to be removed from recovered oil
Freeze/thaw	Easy to apply, short treatment duration, suitable for cold regions	Lower efficiency, cost could be high due to high energy consumption for freezing
Pyrolysis	Fast and efficient, recovered oil can be upgraded, large treatment capacity	High capital, maintenance, and operating cost, high consumption of energy, and not suitable for oily sludge with high moisture content
Microwave irradiation	Very fast and efficient, no need of chemical addition	Special designed equipment, high capital and operating cost, high consumption of energy, small treatment capacity
Electrokinetics	Enhancement in horizontal and vertical separation of oil and water, no need of chemical addition	Not easy to apply, long treatment duration, few industrial applications in a pilot scale
Ultrasonic irradiation	Effective technique for removing adsorbed materials from solids particles, separating solids from liquid in high-concentration suspensions,	High cost of equipment and maintenance, small treatment capacity
Froth flotation	Easy to apply, no intensive energy requirement	Relatively low efficiency, large amount of water is used, not suitable for treating oily sludge with high viscosity
Centrifugation	Clean appearance and mature technology, easy to apply, fast start up and shut down, does not occupy much space, high throughput, minimal odor problems, economically viable for the treatment of large amounts of sludge	High capital and maintenance cost, high energy consumption, noise problem, pre-treatment requirement,

2.6.1 Solvent extraction

According to El-Nadi (2017), solvent extraction is one of the common techniques for separation and recovery of components based on their solubility in different immiscible liquids such as water and organic compound.

Al-Zahrani and Putra (2013) investigated that solvent extraction is widely used in the petroleum industry. It can combine oily wastes with an appropriate portion of solvent to make certain about ideal miscibility, while unwanted impurities such as water and solids are rejected and can be separated by centrifugation or gravitational settling. In order to separate oil from solvent, the oil and solvent mixture is then sent for distillation.

Jafarinejad (2016) studied that some factors affect the oil recovery efficiency such as solvent-to-sludge ratio, temperature, mixing and type of solvent. By increasing solvent-to-sludge ratio, the quality and quantity of recovered oil can ameliorate.

Due to Zubaidy and Abouelnasr (2010), some organic solvents like methyl ethyl ketone (MEK) and liquefied petroleum gas condensate (LPGC) at a solvent-to-sludge ratio of 4:1 have the most oil recovery rate, measuring 39% and 32% respectively.

Fisher et al. (1997) reported that high temperature can speed up the extraction process, but it can cause a loss of PHCs and solvent by evaporation, in contrast, a lower temperature not only reduces the process cost but also decreases the efficiency of oil recovery. Mixing and heating can cause improvement in the dissolution of sludge organic components in solvent.

In general, Hu et al. (2013) found that solvent extraction is an efficient method to separate oily sludge into oil in a short period. It is also capable of treating a large volume of sludge.

2.6.2 Surfactant enhanced oil recovery (SEOR)

Surfactant enhanced oil recovery is a well-known and effective technique to treat a large volume of oily sludge. Surfactant, known as a surface-active agent, has a tendency to reduce the surface tension between two liquids phases or between a liquid and solids, which originated from polar-nonpolar structure of its molecules. Its molecule contains both a hydrophilic (water loving) group, and a hydrophobic (water hating) group. The hydrophilic group are polar and can interact and dissolve in the water and enhance the solubility of PHCs. The hydrophobic group are non-polar and have an affinity to the molecules of oil, which decrease the surface tension and increase the mobility of PHCs (Hu et al., 2013)

Some chemical surfactants such as sodium dodecyl sulphate (SDS), Triton X-100, Tween 80 are capable to increase the concentration of non-polar compounds (PHCs) in aqueous phase. However, using chemical surfactants may have some disadvantages such as toxicity, resistance to biodegradation and a high cost. Therefore, one should take into account some factors like cost, ability to recycle, oil recovery, public and environmental regularity (Hu et al., 2013; Myers, 2005).

2.6.3 Freeze/thaw

Demulsification is a process for water removal from water-in-oil emulsions (W/O). According to Rajaković et al. (2006), a freeze/thaw method (F/T) was introduced as a demulsification method, which is successful for dewatering, with approximately 90% of water removal from W/O emulsion. It can be noted that freeze/thaw is a feasible method for handling oily wastes such as oily sludge, especially those located in cold regions like Canada with natural freezing.

In this method, demulsification is performed under two different mechanisms. Firstly, the water in emulsion stands frozen ahead of the oil phase, while in the second mechanism, the oil becomes frozen ahead of the water phase (Rajaković and Skala, 2006). The following sequences, describe the freeze/thaw demulsification for W/O emulsion:

a) Original emulsion,

b) Water droplet freezing, expansion and coalescing,

c) Oil phase freezing to form a solids cage,

d) Water droplets freezing and expanding to break the cage,

e) Emulsion thawing and water droplets coalescing,

f) Gravitational delamination.

Some factors such as water content, solids content, freezing and thawing temperature, duration, salinity of aqueous phase, presence of surfactants can affect the performance of freeze/thaw on demulsification. For instance, it was reported that the dewatering rate at -40° C was higher than -20° C and the lower thawing temperature makes the dewatering process better. In general, besides the advantages of freeze/thaw treatment, there are some requirements that should be taken into consideration such as freezing time and related costs. Furthermore, this is a slow process that needs a high energy and high cost. Therefore, it is more preferable for cold regions with natural freezing conditions (Hu et al., 2013).

2.6.4 Pyrolysis

Pyrolysis is a process in which organic matter is decomposed by heating at high temperatures in the absence of oxygen. Charcoal, organic liquids, gas and water are produced with different ratios of this process. Their ratio and their amount depend on the operating temperature, heating rate, time remaining, the type of raw material and chemical additives, characteristic of oily sludge (i.e. water content) (SATBA, 2018).

According to several studies, it has been reported that pyrolysis can be applied for fuel recovery from oily sludge. It has been investigated that the total organic carbon content (TOC) in oily sludge (around 80%) in the temperature range of 327 to 450 ˚C could be turned into usable hydrocarbons when applying pyrolysis. It has also been found that near 70-84% of the oil could be separated from oily sludge in the temperate range of 460 to 650 ˚C using a fluidized bed reactor, which is one of the types of reactors for the pyrolysis process (Schmidt and Kaminsky, 2001).

Pyrolysis of oily sludge produces some lower greenhouse gases (i.e. NOx and SOx) and also it can enable heavy metals to concentrate in solids product. The liquids generated from the pyrolysis process could be easily stored and transported. In spite of its advantages, it should be noted that this method requires a high energy and high operation cost for a large-scale implementation. For example, due to a high water content of oily sludge, some treatment is needed for dewatering the oily sludge before pyrolysis, which increases the overall cost of the process (Jafarinejad, 2016).

2.6.5 Microwave irradiation

Distinctive features of microwave (MW) irradiation including selective heating, fast processing rate, energy efficiency, capable to enhance the quality of product and environmentally friendly can make this method agreeable for treatment of materials (Jones et al., 2002).

MW irradiation in the electromagnetic spectrum occurs in the wavelengths range from one meter to one millimeter at corresponding frequencies of 300 MHz (100 cm) to 300 GHz (0.1 cm) (International Radiation Protection Association, 1981). The microwave system is made up of a microwave source (i.e. magnetron), a heating controller and an applicator to deliver the power to material. The characteristics of microwave such as penetrating radiation, fast heating, selective heating of materials and controllable electric field distributions provide opportunities for processing of different materials (Thostenson and Chou, 1999).

A heating in microwave could be generated by energy through penetrating the material with the electromagnetic field and molecular interaction. This heating can affect the demulsification of W/O emulsion by increasing the temperature, which results in the viscosity reduction, the rapid settlement of water droplets, and breaking the heavy hydrocarbons into lighter ones (Shang et al., 2006).

Oily sludge demulsification is affected by several factors including water-oil ratio, pH, salt, microwave power and duration (Tyagi and Lo, 2013). For example, Xia et al (2004) found that inorganic salt could advantageously affect the demulsification efficiency and enhance the light transmittance of separated water from emulsion.

The short heating time, easy controller and high-energy efficiency could make the microwave irradiation more beneficial in comparison with other heating techniques. However, on the industrial scale for oily sludge, this treatment needs special equipment with high operating cost and it is unable to treat heavy metals (Jafarinejad, 2016).

2.6.6 Electrokinetic phenomena

Electrokinetics (EK) is a process that is handled by applying direct electric current. It contains a low-intensity direct current source with a positively charged electrode (anode) and a negatively charged electrode (cathode) located in colloidal medium. When current is applied, it can cause electro osmosis of the liquid phase as well as migration of ions and electrophoresis of charged particles. All above mentioned phenomena like electrolysis reactions, electro-migration, electroosmosis and electrophoresis result in EK (Elektorowicz et al., 1996).

According to Elektorowicz et al. (2006), in the EK system, three-phase separation of oily sludge (water, oil and solids) can be observed. For instance, one of the mechanisms that takes place in EK system is breaking the colloidal aggregates in oily sludge by electrical field, which leads the separated liquid phase (water and oil) to move toward the cathode area, while, solids phase and colloidal particles move toward the anode area.

Jahromi and Elektorowicz (2018) treated oily sludge using EK technique with a novel implemented controller that increases sludge demulsification and an amelioration of the quality of separated phases.

Elektorowicz and Habibi (2005) applied the EK process to treat oily sludge to reduce the water content by 63%, and light hydrocarbons content by 43%, and when combining the EK with surfactant, the light hydrocarbons content could be reduced to until 50%.

Kariminezhad and Elektorowicz (2018) used an electrokinetic method to investigate the effects of different types of electric currents. CDC, PDC, IDC and DDC currents were applied to examine its potential in phase separation. Their results illustrated that DDC had the highest efficiency to separate the different phases of oil sediments.

In general, the performance of EK treatment can be affected by different factors such as electrical potential, pH, resistance and spaces among electrodes. It can be noted that the EK system requires less energy for oil recovery, but most of the EK studies for treatment of oily sludge were done on a lab scale. Tests on industrial scale requires further investigations (Jahromi and Elektorowicz, 2018; Jafarinejad, 2016).

2.6.7 Ultrasonic irradiation

A sound wave with a frequency greater than the upper limit of human hearing (<20 kHz) is called ultrasound. Some great features of ultrasound such as reducing the stability of water-in-oil emulsions, separation solids from liquid in high concentration suspensions and removing adsorbed materials from solids particles made this method usable in petroleum industry (Mason and Peters, 2002). Ultrasonic irradiation can affect the cavitation collapse that results in breaking the oscillating cavitation bubbles, and conduct the erosion of contaminant film related to solids particles and penetrates into the inner region of solids matrix (Li et al., 2013).

Ultrasonic irradiation shows high potential in oil recovery from oily sludge. According to Zhang et al. (2012), the oil recovery from oily sludge was reported up to 80% at a power of 66W, with a frequency of 20 kHz after 10 min. In addition, an oil recovery higher than 95% was obtained by applying a frequency of 28 kHz and a power of 400W in 15 min (Jin et al., 2012).

It can be said that many factors like temperature, power, frequency, time, intensity, solids particle size, salt and water sludge can change the efficiency of oil recovery from oily sludge. In spite of the high oil recovery, this method generates a large volume of wastewater with a large amount of unrecoverable PHCs and salts that require a high overall cost of removal. Another limitation of ultrasound is the high cost of equipment and maintenance in industry. Therefore, it is mostly used on a lab scale and can only be applied to a small volume of oily sludge (Jafarinejad, 2016).

2.6.8 Froth flotation

Froth flotation is a process in which hydrophobic particles are separated selectively from hydrophilic ones (Fuerstenau et al., 2007). This method is applied in mineral processing, mining and oily wastewater treatment plants (Salmani Nuri et al., 2017).

Ramaswamy et al. (2007) investigated the recovery of oil from oily sludge applying froth flotation process and achieving up to 55% of recovered oil in 12 min. The process involved in this method consists of capturing oil droplets or solids particles in an aqueous slurry and conducting flotation and collection in a froth layer (Urbina, 2003).

Effects of oily sludge properties (e.g., viscosity, density), surfactant, time and initial amounts of oil were studied in detail for the performance of recovered oil from oily sludge by froth flotation method (Jafarinejad, 2016).

It can be noted that froth flotation is a low cost and simple method for handling oily sludge, but it is unable to treat heavy metals. Due to a high viscosity of oily sludge, it needs some pre-treatments to decrease its viscosity and remove coarse solids particles. It also requires a large volume of water for the treatment of oily sludge (Jing et al., 2016).

2.6.9 Centrifugation

The centrifugation method is usually applied in the industry for separating components like liquids or removing solids. Oily waste such as oily sludge, which contain high amounts of solids, oil, and water, can be processed by centrifugation (Bahadori, 2013).

The acceleration at centripetal force of centrifuge makes the substances of higher density (solids particles) separate along the radial direction and settle at the bottom of the centrifuge tube. By the same concept, the substances with lower density (oil and water) tend to float (Taiwo and Otolorin, 2016). After centrifugation, a three-phase separation can be observed, of which solids residues sit in the bottom layer, water in the middle and oil in the upper layer. The recovery of oil can be done from the upper layer (Zheng et al., 2017).

In order to improve oil recovery, promote the performance of centrifuging system and decrease energy consumption prior to centrifugation, there is a need to decrease the viscosity and the demulsification of the sludge. These last two processes can be achieved by pre-heating or adding additives (Dehaghani and Badizad, 2016; Zolfaghari et al., 2016).

The three-phase horizontal decanter centrifuge (tricanter) is a suitable centrifuge type for treatment of oily sludge with continuous three phase separation. In this centrifuge, it is possible to separate light liquid phase (oil), a heavy liquid phase (water) and a solids phase (Nahmad, 2012).

Generally, centrifugation is a good technique to separate liquid-liquid-solids mixtures with different densities. It does not occupy much space. It can make a basic mechanical separation for oil, water and solids particles from oily sludge with the advantages of simplicity, clean operation, low costs for industrial implementation, and low environmental impact (Hu et al., 2013).

2.6.9.1 Screening of additives to enhance centrifuging performance

Oily sludge need to be changed through sludge pre-treatment with additives, such as demulsifiers, coagulants, surfactants, etc to enhance the process of separation (Zheng et al., 2017; Nahmad, 2012).

a. Demulsifier (addition of surfactant)

Demulsifiers are surface-active agents that are used due to a low cost, simple pre-treatment method, and high recovery ratio. Surfactants are amphiphilic compounds, which consist of hydrophobic and hydrophilic moieties in the molecules. There are many utilizations of surfactants for the increase in the hydrocarbons solubility and the hydrocarbons mobility. In the petroleum industry, surfactant has been used to increase the solubility of petrol and its by-products. Some additives such as sodium dodecyl sulphate, Triton X-100, Tween 80 can increase the concentration of PHCs in the aqueous phase (Ramirez Guerrero, 2017;Hu et al., 2013; Mulligan, 2009).

According to Omar et al., (2002), by introducing surfactants for petroleum wastes, the oil recovery could be improved. Enhanced oil recovery (EOR) by surfactant could be carried out through some procedures such as lowering interfacial tension between oil and aqueous solution spontaneously, reducing rheological properties of interfacial interface between oil and aqueous solution and spontaneous emulsification (Myers, 2005; Rudin et al., 1994).

b. Coagulants

Hydrocarbons and mineral fine particles having a small size within a diameter from 20 µm, express surface charge (e.g. negative) which is a main contributor to form stable emulsions. Coagulation is the process in which the surface charge of emulsions is neutralized by means of three-valent cations (e.g. iron and aluminum); therefore, the resultant energy between electrostatic forces and Van der Waals force changes permitting decreasing thickness of the diffuse double layer and the flocculation process. The most common coagulants are ferrous chloride, ferric sulfate and alum (Karamalidis and Voudrias, 2001). The effect of coagulant salt on emulsion breakdown of oily sludge can be carried out by adding small amounts of $CaCl_2$ in the concentration range of 0.01-0.5 M, in order to enhance emulsion destabilization and centrifugation performance with oil removal efficiency by 92-96% (Cambiella et al., 2006).

The objective of this study is to evaluate the oil recovery efficiency of the centrifuging approach for oily sludge treatment. Water removal is also the main objective of the treatment since it decreases a volume for disposal and makes leaching from disposal sites.

EXPERIMENTAL

Chapter three introduces the detailed procedures for the treatment of oily sludge by centrifuging method. It also covers the parameters affecting the treatment, devices employed and all experimental measurements.

3.1 Methodological approach

In this study, the centrifuging process was applied to the viscous water-in-oil sludge in order to optimize oil recovery.

Centrifugal processes at lab scale focused on a three-phase separation using three volumes to assess the scale-up efficiency. After centrifugation, the feasibility of the formation of three phases with respect to different pre-treatments and volumes were observed. The three phases, including solids, water, and oil were assessed and recovered oil was quantified. The methodological steps are shown in Fig. 3-1.

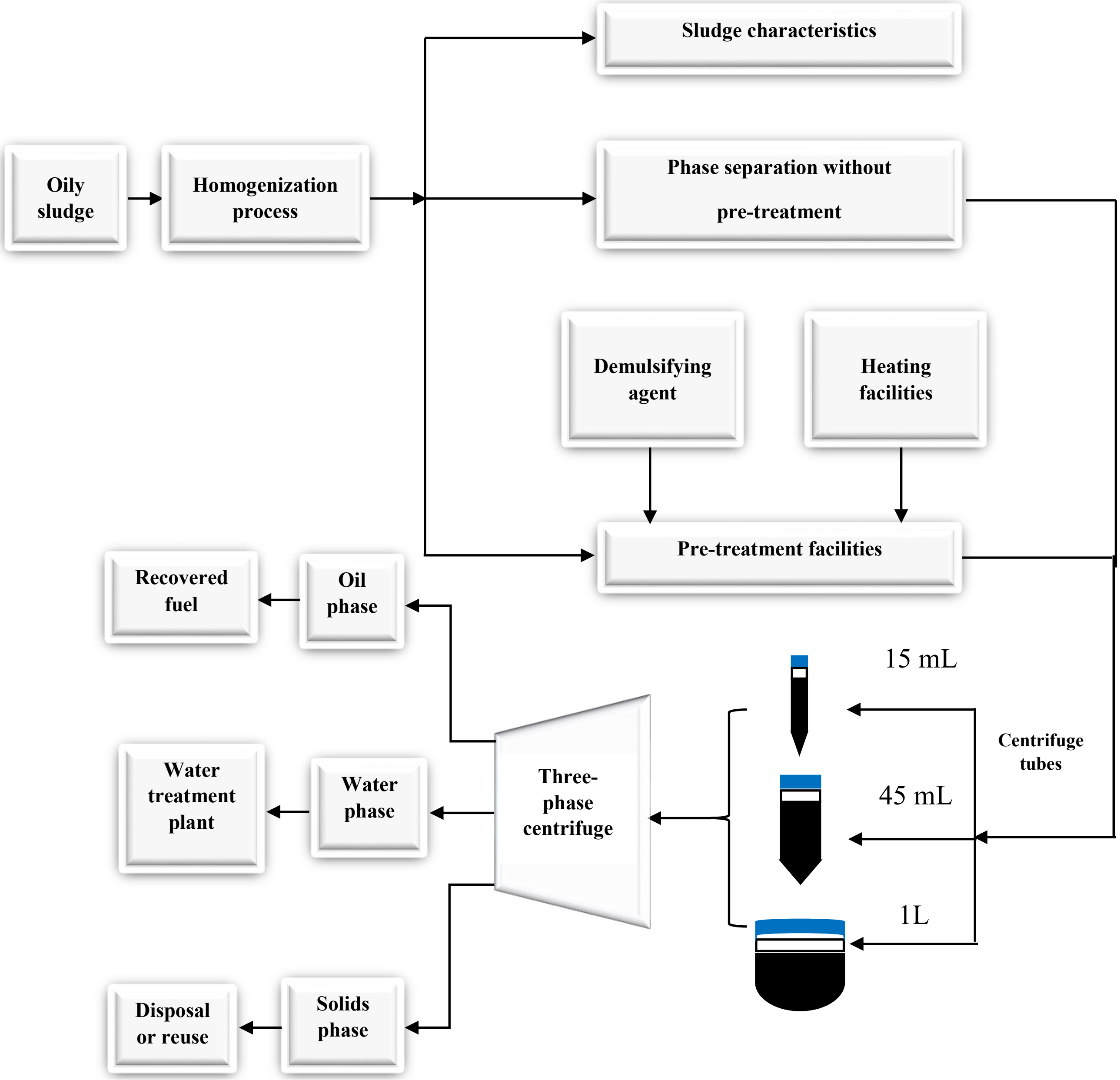

Figure 0-1 General scheme of research methodology

The diagram (Fig. 3-1) shows that oily sludge is initially homogenized. The oily sludge is then characterized, after which is then mixed with demulsifying agents. In order to reduce its viscosity, in a pre-treatment tank, hot steam is introduced to the mixture and an adequate speed centrifuge is applied to separate the components. For comparison purposes, the centrifuging of oil sludge was conducted without a pre-treatment.

Since the main aim of this work is to establish the optimal conditions for oil recovery from sludge using centrifuging process, the following stages of work were conducted:

1. Phase 1: Characterization of petroleum oily sludge was collected from bottom storage tanks;
2. Phase 2: Conducting oil recovery from sludge by centrifuging at a small scale:
    a. Stage 1: Oil recovery without pre-treatment;
    b. Stage 2: Examining the optimal temperature for oil recovery using centrifuging with pre-heating only;
    c. Stage 3: Identifying the pre-treatment conditioners to optimize oil removal from sludge.
3. Phase 3: Scaling up the centrifugation process;
    a. Stage 1: Study without conditioning
    b. Stage 2: Study with conditioning

3.1.1 Materials

The oily sludge used in this tests was collected from the bottom of crude oil storage tanks in an oil extraction field. Sludge sent in eight buckets of 20L showed varying properties (Figure 3-2). A comparative study was conducted on samples from each bucket as well on a composite oil sludge consisting of a mixture of samples originating from each bucket. Oil sludge samples taken from each of the eight buckets were labelled: C1, C2, C3, C4, C5, C6, C7, C8, respectively, while the composite sample was Cmix.

The samples were mixed manually before being taken from the bucket for tests. Each sample was initially characterized with respect to water, light hydrocarbons, heavy hydrocarbons, and solids contents.

Figure 0-2 Oily sludge sample stored in a 20 L bucket

3.1.2. Equipment

a. ***Centrifuge***

Centrifuging is one of the technological methods that can separate sludge on two or three phases. A centrifuge is a device that circulates liquids in a rotation around a fixed axis by means of a rotor. Spinning the samples at high speeds, the centrifuge utilizes a strong centripetal force and under gravitational force (G-force), applies the principle of sedimentation, causing the denser substances to separate and gravitate towards the bottom of the centrifuge tube. At the same time low-density substances travel to the center and top of centrifuge tube (Miller, 1992).

The centrifugal process thus permits oily sludge components to be separated according to their densities. There are different types of centrifuging operation units, however the study lab was equipped with vertical centrifuging tubes. The centrifugation for small scale was carried out by IEC-HN-SII three-phase centrifuge designed for continuous and heavy-duty services (Figure 3-3). The HN-SII centrifuge is able to spin various emulsions such as oily samples. It has variable speed control, direct reading tachometer, 60-minute automatic timer and continuous run mode, manual dynamic electric brakes, 4x250mL maximum capacity, 4,650rpm maximum speed with fixed angle rotor and 6,225 maximum G-force (force x gravity) (Scientific equipment repair, 2018). Another series of tests (1L) were conducted utilizing a Centrifuge Thermo Scientific Sorvall ST 40 (Fig. 3-4). Sorvall ST 40 has a maximum capacity of 4 liters (4 x 1000mL), maximum speed of 5300rpm, maximum G-force of 5590 and a maximum timer range of 9 hours, 59 minutes (Fischer Scientific, 2015).

The range of chosen parameters for centrifugation tests were as follow: 2000 rpm for rotation speed, 15 minutes for centrifugation time and 21°C for the centrifugation temperature (Huang et al., 2014; Philemon and Benoît, 2013).

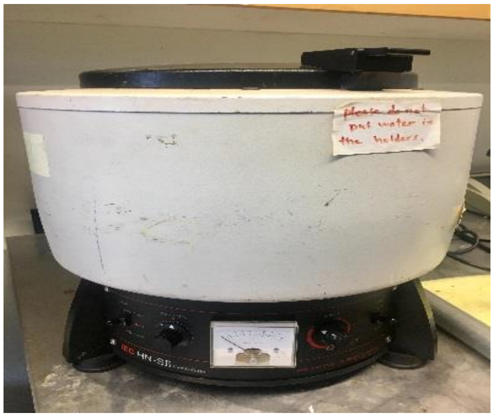

Figure 0-3 IEC-HN-SII benchtop centrifuge

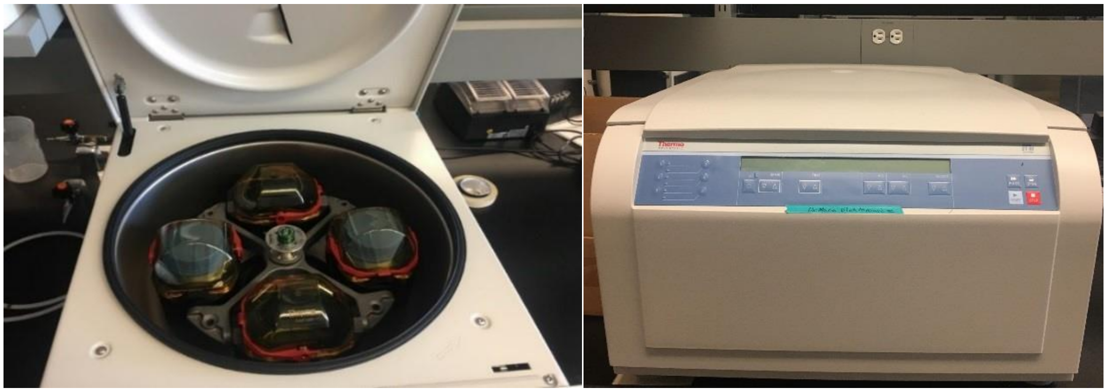

Figure 0-4 Centrifuge Thermo Scientific Sorvall ST 40 for 1-liter test

b. Thermogravimetric analyzer (TGA)

Thermogravimetric analysis is a method that tracks the temperature increase of the sample and measures any loss of mass in the constituent sample. This measurement can be applied to characterize any material and provide information about phase changes due to decomposition, oxidation, or dehydration (TA Instruments, 2006).

In this study, a TGA Q500 with autosampler was used to define the presence of other fractions in separated phases (water, light and heavy hydrocarbons).

Analyses were carried out under H_2 that allows the analysis of 16 samples simultaneously.

c. Viscometer

A viscometer was used to measure viscosity samples before and after centrifuging. It allowed for an assessment of the impact of viscosity on the effectiveness of phase separation. Viscometer (VC), vibro-viscometer SV-10 (Fig. 3-5) in NanoQam Research Centre, UQAM, Montreal (QC) was applied. Two thin sensor plates, shown in Fig. 3-7, are applied, utilizing electromagnetic force to vibrate the sample fluid at their natural frequency of 30 Hz. Evaluating the relationship between the degree of electric current and the viscous resistance of the sample in maintaining the sensor places at a constant vibration amplitude, viscosity is then calculated.

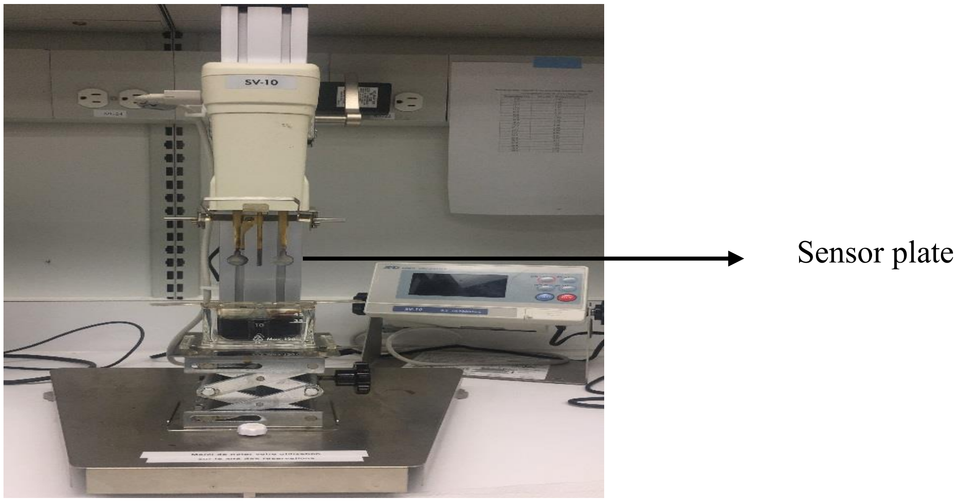

Figure 0-5 Viscometer in NanoQam lab

3.2 Phase 1: Characterisation of oily sludge

The knowledge of the preliminary characteristics of oily sludge defines the complexity of material to treat. Therefore a characterization of sludge in an isolated bucket was conducted to define the differences between sludge properties and their potential impact on the centrifugation process.

3.2.1 Characteristics of oily sludge: Sample C1, C2, C3, C4, C5, C6, C7, C8

Oily sludge samples taken from each of the eight buckets were analyzed individually with respect to water, light oil, solids, and heavy oil contents. The characterization of a composite sample Cmix (C1 to C8), as well as a Cmix (C1, C3, C4, C5, C6, C8), were also conducted.

a. Water content (vol. %):

The water content of the oil samples was measured according to ASTM-D95 by applying the Soxhlet method. An amount of 20-25g of samples C1, C2, C3, C4, C5, C6, C7, and C8 was transferred into a 250mL PYREX™ short neck glass vessel and 24/40 standard taper joint, where 100mL of toluene (solvent) was added. Then, the components of the apparatus were assembled as illustrated in Fig. 3-6.

The adequately clean condenser tube and trap ensured free drainage of water into the bottom of the trap. The heater was adjusted and target materials were heated under reflux with a water-immiscible solvent and co-distilled with the water-in-oily sludge sample. Condensed solvent and water were continuously separated in a trap. The water was settled in the graduate section of the trap and the solvent returning to the still, then, the volume of trap water in graduated cylinders was read. Finally, the water content (by volume percentage) in the samples was calculated in accordance to (ASTM, 2002) (Eq. 1):

$$Water\ content\ \% = \frac{(Volume\ in\ water\ trap, ml) - (Water\ in\ solvent\ blank, ml)}{Volume\ of\ test\ sample, ml} \times 100\% \qquad (1)$$

In order to convert the volume percentage of water content to weight percentage, the water density of 1g/mL was applied to Equation (2):

$$Weight\ percentage\ of\ water\ content = [\text{Density of water}\left(\frac{\text{g}}{\text{mL}}\right) \times \text{Volume of water content (mL)}] \qquad (2)$$

Figure 0-6 Typical assemblies for measuring water content by solvent extraction method (ASTM D95)

b. Light oil (wt. %) content:

In order to determine the amount of light oil inside the oily sludge, a sample of a known weight was put in an oven (Fig. 3-7) at 105°C for 24 hours. The reduction in its weight was equal to the moisture and light hydrocarbon constituent in the sludge. The light hydrocarbon content (wt. %) was calculated from Eq. 3, while water content was measured as above:

$$Light\ hydrocarbon\ content\ \% = \frac{Reduced\ mass\ in\ g}{Mass\ of\ remained\ \ sample\ in\ g} \times 100\% - Water\ Content\ in\ wt\% \qquad (3)$$

Figure 0-7 Sludge samples dried in oven at 105°C

c. Solids content (wt. %):

Solids (sediment, ash, and organics) content was measured based on the previously dried sample with some adjustments. A dried sample was placed in a furnace at 550°C for 120 minutes. The residue showed the solids content of the sludge as weight percentage:

$$Solids\ content\ \% = \frac{Residue\ remaining\ after\ burning\ in\ g}{Mass\ of\ tested\ sample\ in\ g} \times 100\% \qquad (4)$$

d. Heavy oil content (wt. %):

After measuring the water content, light hydrocarbon content, and solids content, the nonvolatile hydrocarbons content - which is equal to the heavy hydrocarbon content in the sludge - can be calculated in weight percentage as follows:

$$Heavy\ hydrocarbon\ content\ \% = 100 - (light\ hydrocarbons\ content + solids\ content + water\ content) \qquad (5)$$

3.2.2 Characterization of mixed sludge (Cmix)

Cmix refers to the mixture of sludge, which contains all samples except sample C2, and C7, which were predominantly used for small-scale tests. The characteristics of sample Cmix was measured three times based on the methods described in section 3.3.1. The characteristics of Cmix was carried out by using a previously described method. Briefly, for determining water content, ASTM D95 was applied and a known amount (20g) of Cmix sample was weighed and placed in an extraction thimble to which 100mL of toluene was added. Cmix and solvent were heated under reflux, which co-distilled with the water in the sample. Condensed solvent and water were continuously separated in a trap. The water was settled in a graduated cylinder and the final water volume was then used in calculating the water content.

To ascertain the presence of light hydrocarbon, the weighted (40g) of sludge was placed in an aluminum dish and heated to 105°C in a ventilated incubator for a duration of 24 hours. The lost mass was attributed to light hydrocarbons evaporation in sludge. As water content was measured previously, the light hydrocarbon content (in wt. %) was calculated using Equation (3).

Solids fraction was determined by placing a dried sample of Cmix (105°C) into a furnace at 550°C for 120 minutes. The subsequent residue revealed the solids content of the sludge, which was calculated using Equation (4).

Heavy oil content in Cmix sample was calculated after measuring the water content, light hydrocarbon content, and solids content. It was calculated in weight percentage using Equation (5).

3.2.3 Characterization of composite sample (Cmix (C1-C8))

Cmix (C1-C8) refers to the mixture of all eight sludge buckets, which contained samples C1 to C8. The standardized method D95 was applied to measure the water content of the oily sludge. 20g sample of oily sludge was heated. When 100mL of toluene (solvent) was co-distilled with water, the condensed liquid (water) was transferred to a graduated cylinder and the volume of water was measured. Presence of light hydrocarbons were obtained from resulting loss of weight by heating 40g sludge sample at 105°C for 24 hours. The light hydrocarbon content (in wt. %) was calculated using Equation (3). The solids content was measured according to the method described in section 3.3.1. The dried sample (at 105°C) was heated in a muffle furnace at 550°C for 30 min and the remaining material was weighed. The solids content was calculated using the Equation (4). After measuring the water content, light hydrocarbon content, and solids content, the heavy oil content was calculated using Equation (5).

3.3 Phase 2: Investigation of oil recovery at small scale

In this study, the centrifugation tests considered three-scale volumes, namely, 15mL, 45mL, and 1L. The range of chosen parameters for centrifugation tests were as follows: rotation speed 2000 rpm, centrifuging time 15 min, temperature 21 °C. The centrifugation was carried out by IEC-HN-SII three-phase centrifuge (Fig. 3-3).

3.3 Phase 2, Stage 1: Centrifuging at small scale without pre-treatment

To identify the appropriate treatment method, samples of the oily sludge were tested in two tubes sizes of 15ml and 45mL at lab small scale.

3.3.1 Centrifuging at small scale in 15mL tube: Sample C1, C2, C3, C4, C5, C6, C7 and C8

Equal volumes of oily sludge samples C1, C2, C3, C4, C5, C6.C7, and C8 were poured in 15mL cone-shaped centrifuging tubes. Each tube had an accurate and distinct graduation number. The mouth of each tube was covered with a liquid-resistant rubber stopper to prevent any risk of splashing. Centrifuging tubes were placed in centrifuge device IEC-HN-SII (Fig. 3-3), and exposed to 2000rpm for 15 minutes. Evidenced in Fig. 3-8, the initial centrifuging process separates the oily sludge samples into three phases of oil, water, and solids, respectively in each tube. The volume of each phase was visualized on the graduated scale on each tube and was considered the total volume for calculation of the percentage of each separated fraction.

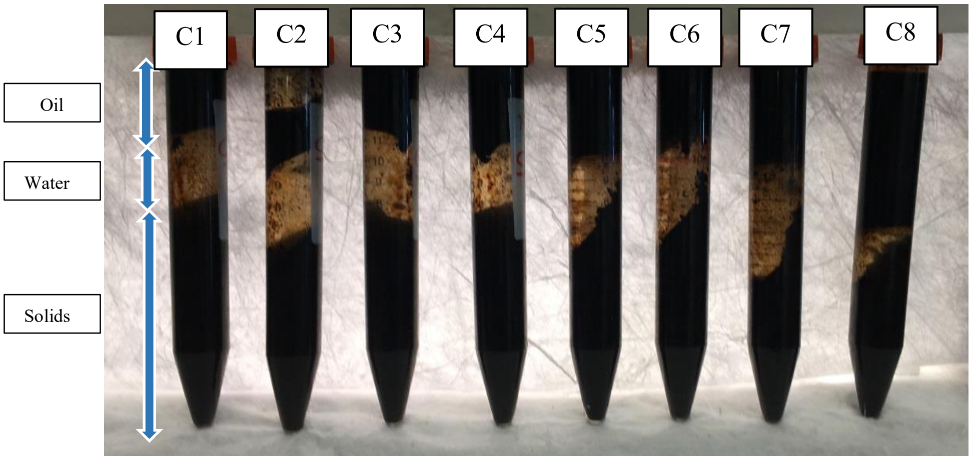

Figure 0-8 Eight samples after centrifuging at ambient temperature in 15 mL centrifuge tubes

3.3.2 Centrifuging at small scale in 45 mL tube: Sample C1, C2, C3, C4, C5, C6, C7, and C8

In the following series of tests saw the volume of samples increased to 45mL (Fig. 3-9). Samples C1, C2, C3, C4, C5, C6, C7 and C8 were homogenized and poured in 45mL centrifuging tubes. The centrifuge device IEC-HN-SII (Fig. 3-3) was set to 2000rpm and 15 minutes. After centrifugation, the volume of each phase was measured and recorded.

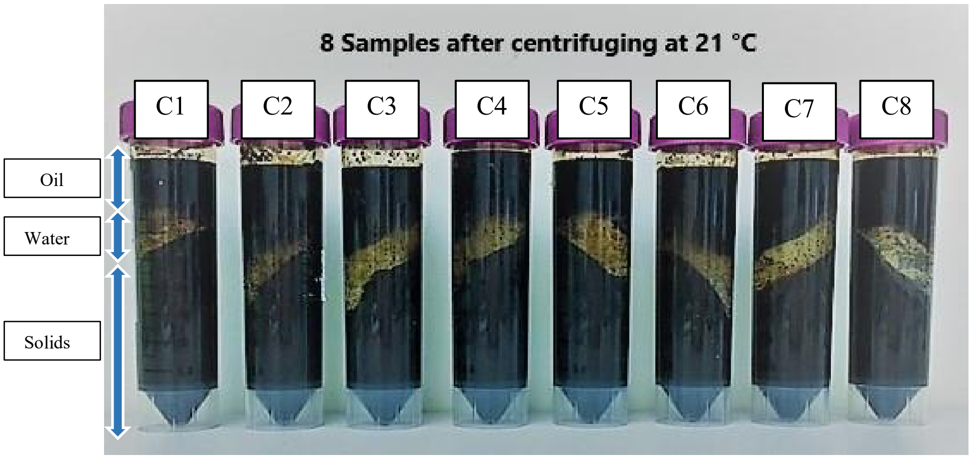

Figure 0-9 Eight samples after centrifuging at ambient temperature in 45 mL centrifuge tubes

3.3.3 Centrifuging at small scale in 45 mL tube: Sample Cmix

Cmix refers to the mixture of sludge, which contains all samples except sample C2, and C7. Similar to the section 3.3.2, the sample Cmix was poured in 45mL tubes and centrifuged to a speed of 2000rpm for 15 minutes. The volume of each phase was then recorded after centrifuging process.

3.4 Phase 2, Stage 2: Centrifuging at small scale with pre-treatment

In this study, sludge was conditioned before centrifuging by heating with different additives and centrifuged with speed of 2000 rpm for 15 minutes.

3.4.1 Centrifuging at small scale with pre-heating

The heating process was aiming to address the effect of temperature on oily sludge treatment to enhance the water and oil removal and disposal processes. The effect of heating on eight oily sludge samples (C1-C8) with different ratios of water, oil and solids components was then evaluated.

Centrifuging was conducted at four different temperatures: 21, 40, 55 and 70° C. Water bath Blue M Magni-Whir1 MW-1120A-1 (Fig. 3-10) was used to control temperature. Samples were subjected to centrifuging process at 2000 rpm for a 15 minute duration and were immediately applied to the water bath. For this study, speed and time were operated manually using centrifuge IEC HN-SII (Fig. 3-3).

Figure 0-10 Adjusting the temperature of centrifuge tubes using bath for oily sludge samples with Blue M Magni-Whir1 MW-1120A-1 water bath

After centrifuging at four different temperatures, the volume of each phase for samples C1-C8 was measured and recorded based on the visual scale (Fig. 3-11, 3-12, 3-13 and 3-14).

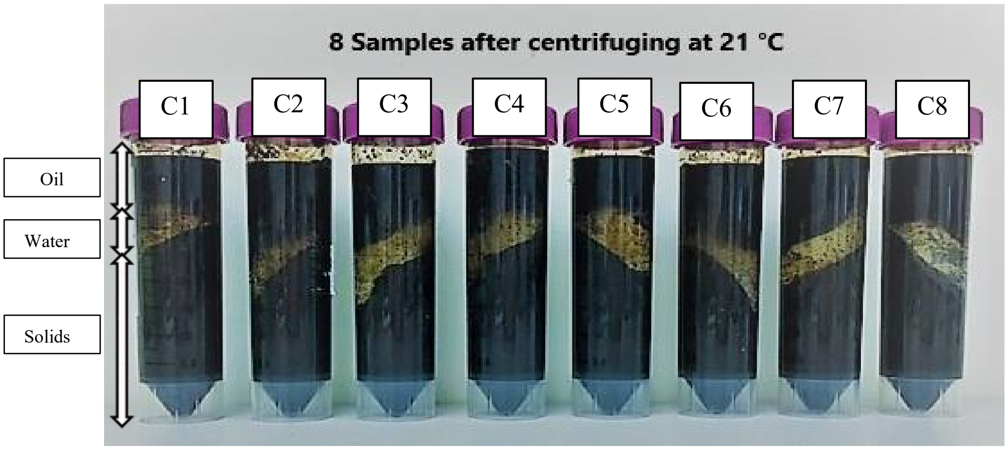

Figure 0-11 Eight samples after centrifuging at 21 °

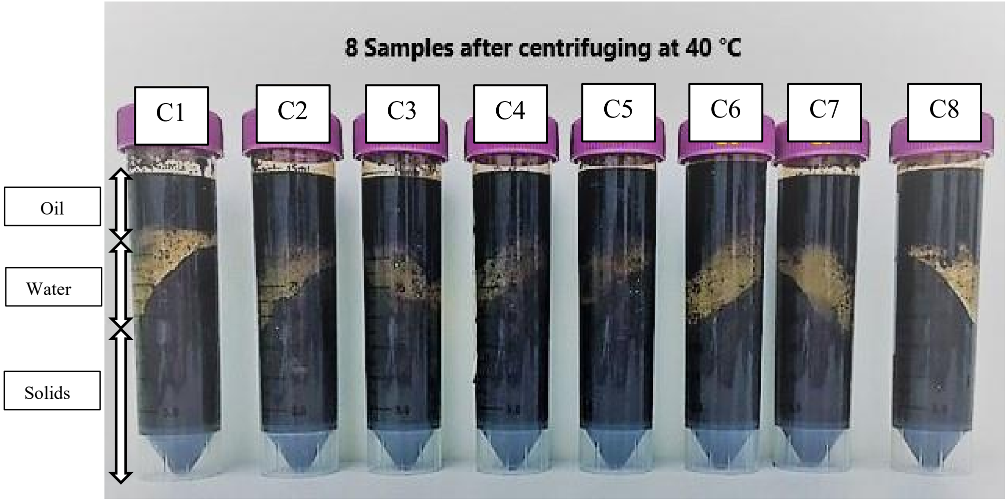

Figure 0-12 Eight samples after centrifuging at 40 °C

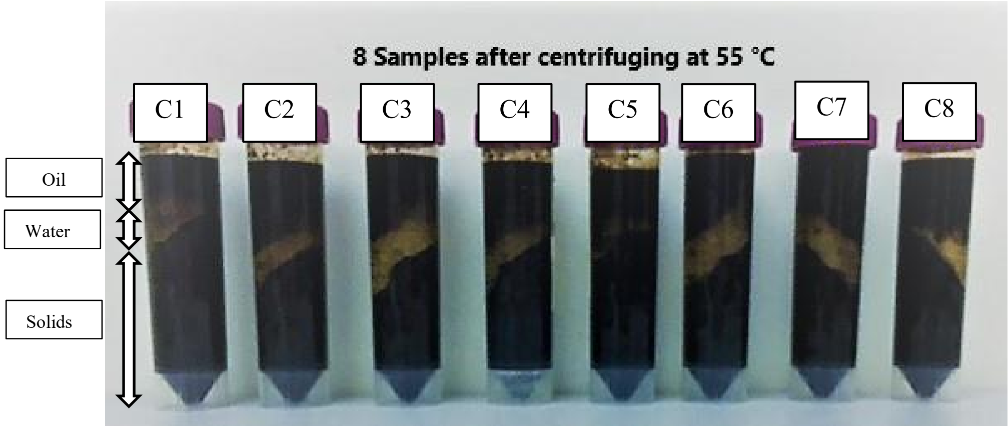

Figure 0-13 Eight samples after centrifuging at 55 °C

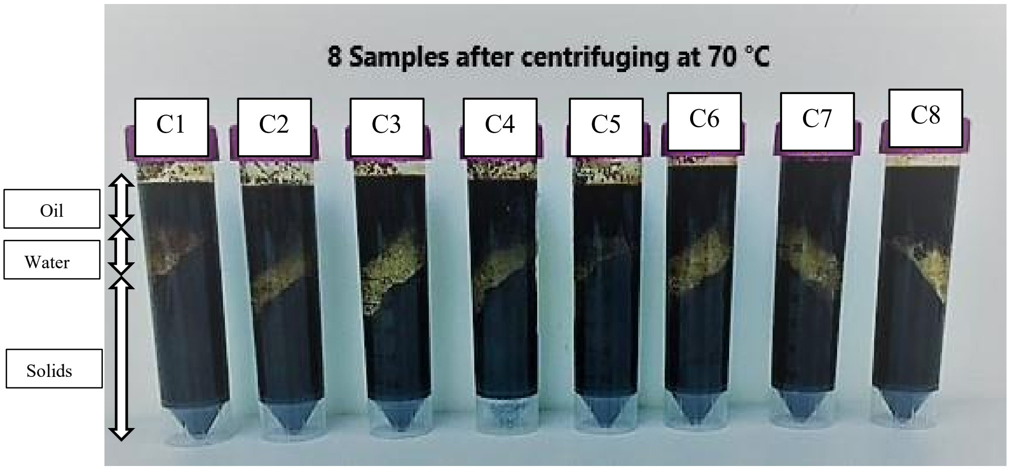

Figure 0-14 Eight samples after centrifuging at 70 °C

3.4.2 Centrifuging at small scale with different additives

In order to achieve an optimal centrifuge performance, different demulsifiers have been utilized. The aim of this section is to evaluate the impact of adding chemical agents before the centrifuging process to ameliorate the separation process.

The additives used in this study included the following three groups: surfactants, coagulants and polymers. Some of the features of these additives are mentioned in Table 3-1. These features were introduced based on preliminary studies on wastewater.

Table 0-1 Common features of different additives (López-Vizcaíno et al., 2012; Bratby. J, 2006)

Additives	**Type of additives**	**Common features**
ferric chloride	Coagulant	Effective in clarification, good turbidity removal, sludge dewatering agent
ferrous sulfate	Coagulant	Reduces the repulsive forces between colloids, effective in clarification, sludge dewatering agent
alum	Coagulant	Effective in clarification, sludge dewatering agent, good turbidity removal
polyacrylamide	Polymer	Enhances oil recovery, improves sludge dewatering
sodium metasilicate	Coagulant	Demulsifying, dispersing, wetting and penetrating, anti-corrosion protection to metals, water retention agent
lime	Coagulant	Contributes to the clarity of the water, stabilizing sludge
calcium chloride	Coagulant	Better effectiveness of separation, reduction in turbidity
cationic polymer	Polymer	Increases the dewaterability of sludge, filters fine colloids
clay	Coagulant	Sludge dewatering, absorbs a wide variety of contaminants
Tween 80	Surfactant	Reduces surface tension, enhances the oil recovery and reduces the burden of hydrocarbon contamination
sodium dodecyl sulfate	Surfactant	Reduces surface tension, changes the interfacial tension of water and oil, has an ability to decontaminate and washes oily sludge
aluminum oxide	Coagulant	Improves the production of hydrocarbons, good purification of water
sodium carbonate	Surfactant	Reduces surface tension, accelerates the breakup of oil slicks into numerous small droplets,
Triton x-100	Surfactant	Reduces surface tension, inhibits anaerobic and some aerobic sludge organisms,

This experiment sought to investigate the impact different additives had on the enhancement of phase separation. The additives were ferric chloride ($FeCl_3$), ferrous sulfate ($FeSO_4$), and alum ($Al_2 (SO_4)_3$ were implemented. All are commonly used for coagulation process in wastewater treatment plants to help with the flocculation process and to remove water from municipal sludge. It was presumed that these coagulants might demulsify oil sludge too; however, tests were required to assess an impact of these compounds for oil recovery.

Four samples C2, C5, C7, and C8 were tested to assess the effect of using additives on the centrifuging process. Ferric chloride ($FeCl_3$), ferrous sulfate ($FeSO_4$), a mixture of ferric chloride and ferrous sulfate (Mix ($FeCl_3$+$FeSO_4$) and alum ($Al_2(SO_4)_3$) were used and compared with the sample without additives (NA). About 45mL of the oily sludge sample was placed in 100mL beaker. The demulsifier was then well mixed with sample concentration (1:150) until complete miscibility. From here the mixture was transferred into conical shaped tubes and centrifuged at 2000rpm for 15 minutes. After centrifuging, the phase separation of mixtures were examined to evaluate the effect of chemical additives. An identical process was applied to control sample without additives for comparison.

The effect of additives on Cmix were also examined at a further stage. Thirteen different additives were chosen and directly added to Cmix samples before centrifuging. The following additives were chosen based on the literature review and company's suggestions: ferrous sulfate, ferric chloride, alum, polyacrylamide, sodium metasilicate, lime, calcium chloride, cationic polymer, clay, Tween 80, sodium dodecyl sulfate, aluminum oxide, sodium carbonate.

3.4.3 Centrifuging at small scale with combined conditioning

The next stage of the investigation sought to capitalize on the benefits of the used treatment processes by combining heat treatment and by using the available additives.

According to the results of heat treatment, a 55˚C temperature showed the best effect when applied to thirteen samples with different additives.

The effect of combined conditioning was examined on Cmix. Thirteen different additives were applied, of which were chosen in section 3.4.2. A blank sample of sludge without additives was selected for comparison.

Certain amounts of each additive was poured into sludge and mixed well. Equal amounts of prepared mixtures were placed into conical shaped and graduated tubes. The tubes then were transferred into a water bath Blue M Magni-Whir1 MW-1120A-1and and preheated to 55°C.

Following the water bath, the mixtures were centrifuged at 2000rpm for 15 minutes. The three-phase separation was then observed, as shown in Figures 3-15, 3-16 and 3-17.

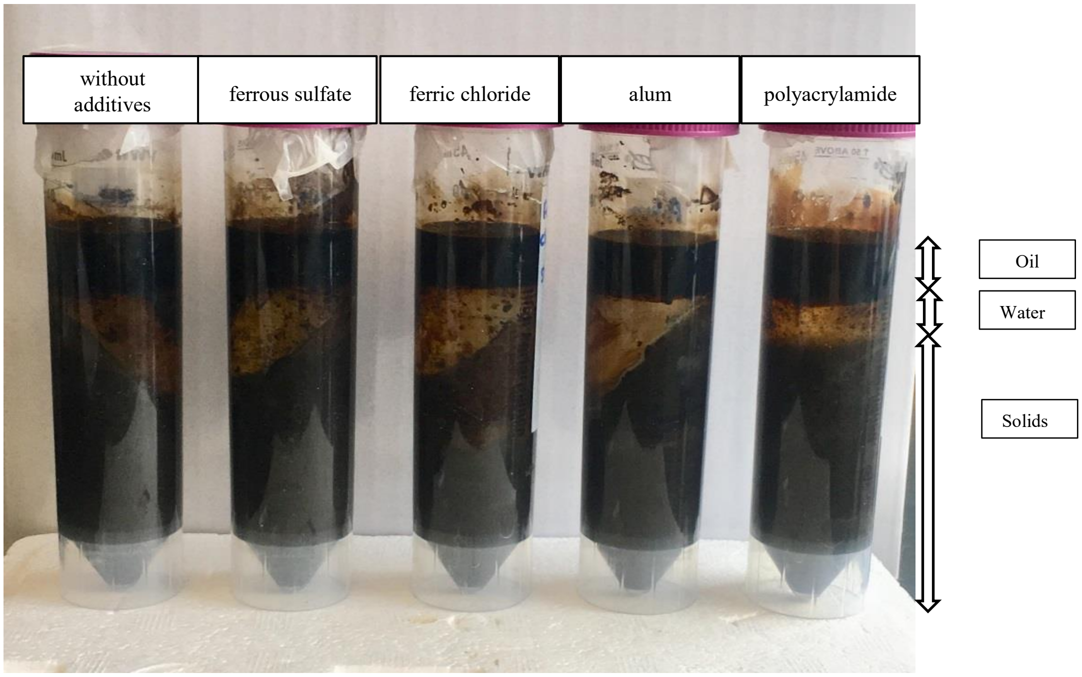

Figure 0-15 Sample Cmix after centrifuging with the effects of pre-heating at 55 °C and additives (ferrous sulfate, ferric chloride, alum, and polyacrylamide) and without additives

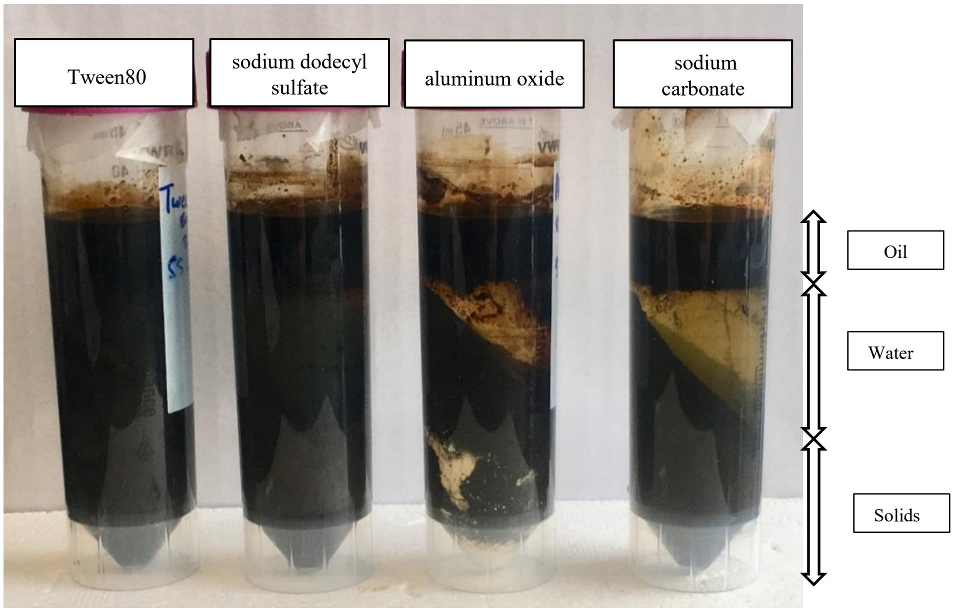

Figure 0-16 Sample Cmix after centrifuging with the effects of pre-heating at 55 °C and additives (Tween80, sodium dodecyl sulfate, aluminum oxide, and sodium carbonate)

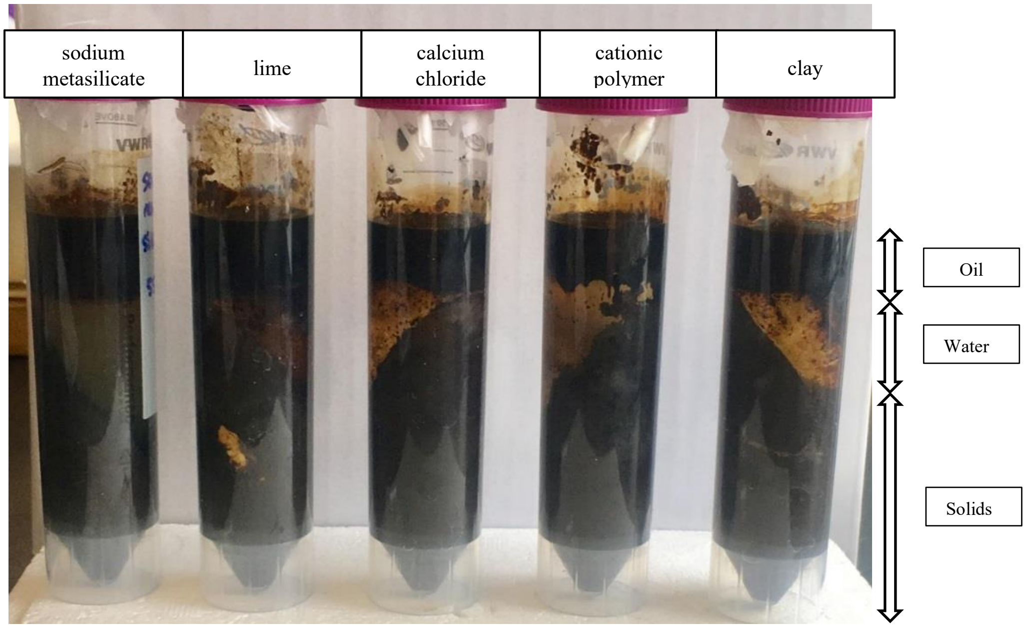

Figure 0-17 Sample Cmix after centrifuging with the effects of pre-heating at 55 °C and additives (sodium metasilicate, lime, calcium chloride, a cationic polymer, clay)

3.5 Phase 3: Scale-up the centrifuging process

Small-scale centrifuging tests was processed on sample volumes of 15mL and 45mL respectively. The objective of this section was to scale up the centrifuging process both with and without conditioning to optimize oil recovery.

3.5 Phase 3, Stage 1: Scale-up centrifuging process without conditioning

One-liter samples of oily sludge was taken from samples C2, C5, C7 and C8 (total 4 liters) and were submitted to the centrifuging process without pre-treatment for specific characteristics. Samples were centrifuged using Thermo Scientific Sorvall ST 40 (Fig. 3-4) applying the same centrifuging conditions.

After the centrifuging process, the volume of each phase was measured whilst monitoring occupied space (Fig. 3-18). The containers for 1L volume, however, were not transparent enough to observe the water/oil interface. Therefore, oil and water phases were poured in a separatory funnel, and after a few hours, when the separation interface appeared, the volume of each fraction was measured (Fig. 3-19). The weight of the remaining solids in the container was measured as the reduction in weight of samples before and after centrifugation.

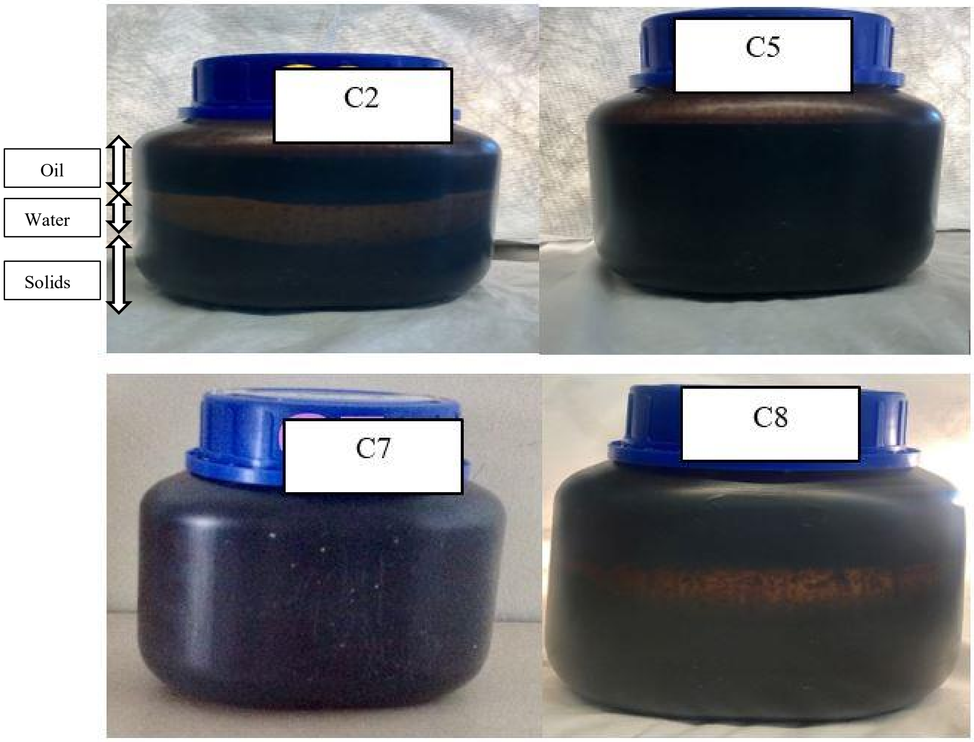

Figure 0-18 Samples C2, C5, C7 and C8 after 1L-volume centrifuging test

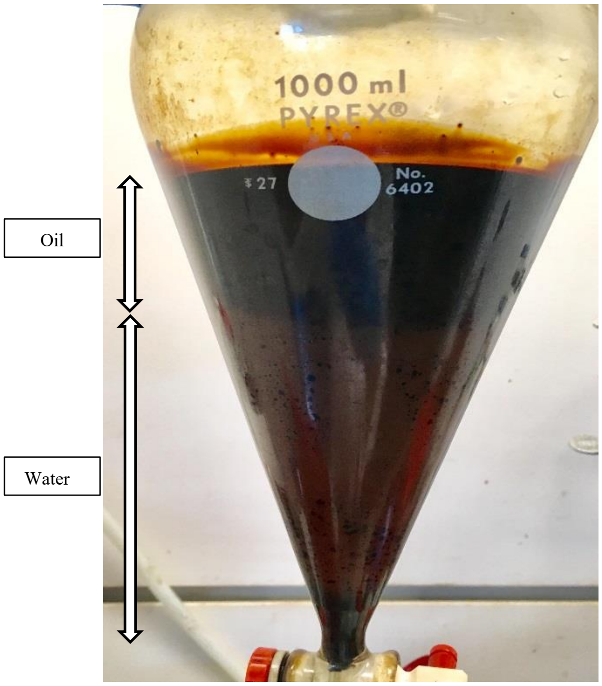

Figure 0-19 Phase separation between oil and water in a separatory funnel

3.5 Phase 3, Stage 2: Scale-up centrifuging process with conditioning

In this section, the effect of additives on centrifuging Cmix at medium scale (4 x 1L) was examined. The speed of centrifuge Thermo Scientific Sorvall ST 40 had been adjusted at 2000rpm and exposure time of 15 minutes. Based on favourable separation at small-scale (phase 3.4.2), the following four additives were chosen: ferric chloride, ferric chloride+ferrous sulfate, polyacrylamide and Tween 80. Certain amounts of each additive were mixed with sludge samples before centrifuging. Three-phase separation was observed with the effect of additives after centrifuging process (Fig. 3-20 - Fig. 3-23).

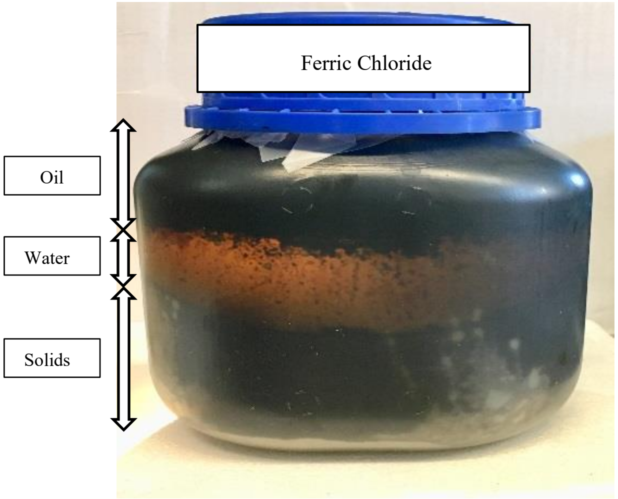

Figure 0-20 Sample Cmix after 1L-volume centrifuging with the effect of ferric chloride

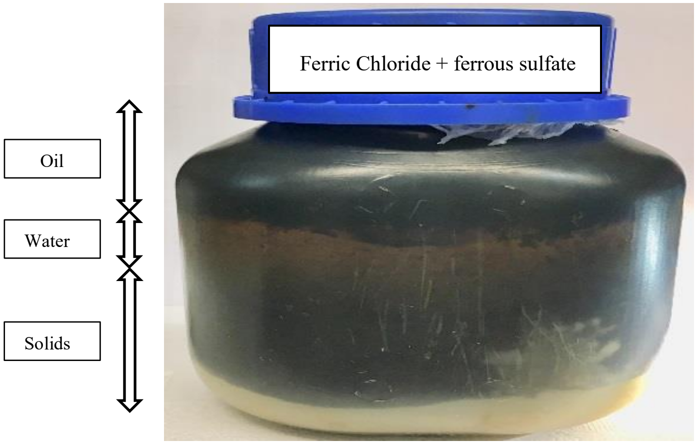

Figure 0-21 Sample Cmix after 1L-volume centrifuging with the effect of ferric chloride + ferrous sulfate

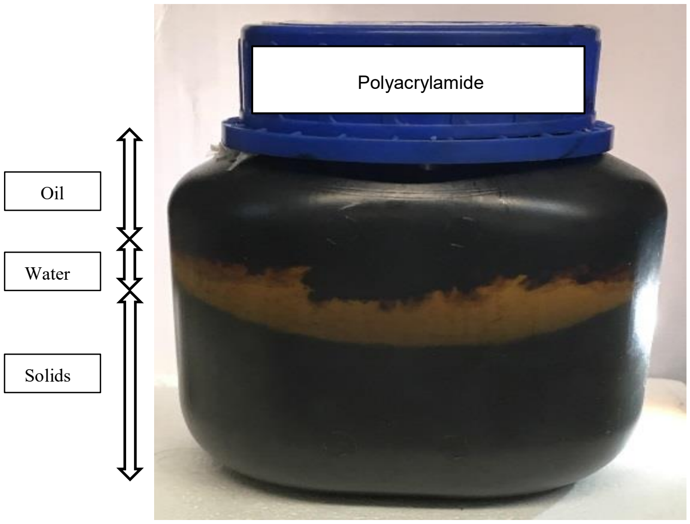

Figure 0-22 Sample Cmix after 1L-volume centrifuging with the effect of polyacrylamide

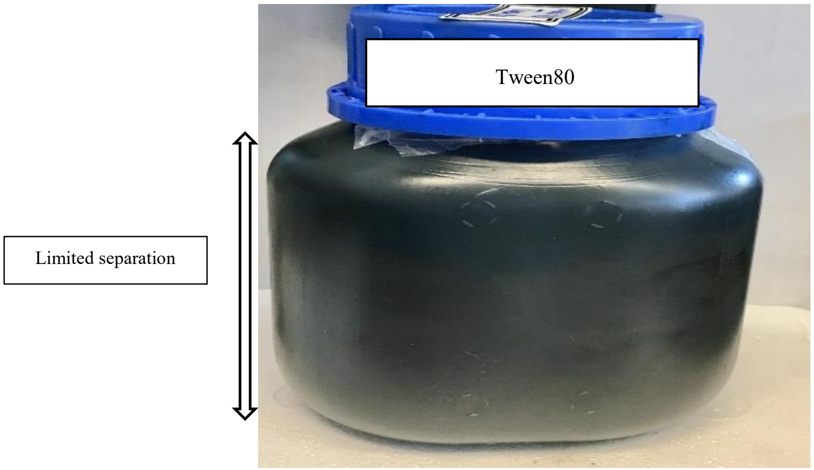

Figure 0-23 Sample Cmix after 1L-volume centrifuging with the effect of Tween80

This method can now be applied to full scale. However, scaling up the cost from lab scale to full scale is irrelevant and does not provide realistic data.

3.6 Liquid seepage from oil sludge

As mentioned previously, besides a recovery of oil, the centrifuging process also separates water and solid fractions. If the solid fraction is to be sent for disposal, an assessment of the liquid seepage from solids should be conducted. The results of seepage (wettability) are particularly important when considering methods of sludge disposal and their cost. Many landfills do not accept materials with evident seepage of liquids; others dispose it for higher price due to necessity of additional pre-treatment.

In order to determine liquid seepage, a direct wetting method of solids was carried out.

Figures 3-24 to 3-26 present the extend of liquid seepage out of solids for samples C2, C7 and C8 before and after centrifuging. About 15g of solids separated from each sludge sample was placed on filter paper with a determined diameter for 1 hour. A radius of wettability of solids phase was shown on each filter paper.

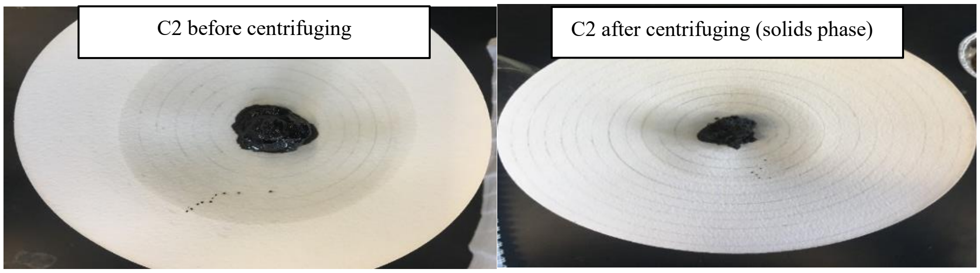

Figure 0-24 Liquid seepage for sample C2 before and after centrifuging test (solids phase)

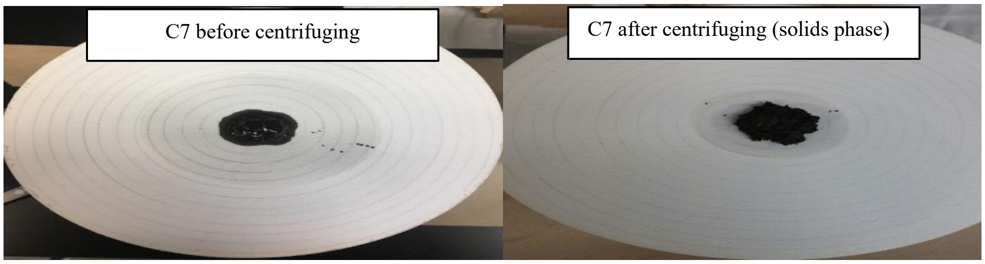

Figure 0-25 Liquid seepage for sample C7 before and after centrifuging test (solids phase)

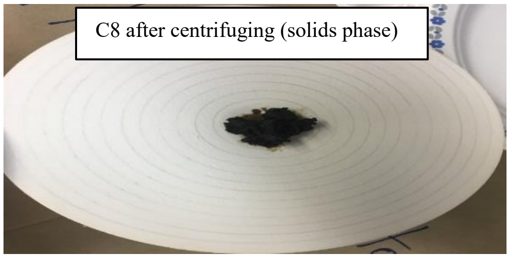

Figure 0-26 Liquid seepages for sample C8 after centrifuging test (solids phase)

3.7 Thermogravimetric analysis (TGA)

The aim of this section is to provide information about the content of various constituents in separated phases such as water, heavy oil and some light oil fractions, as well as the quality of separated oil. TGA was used by TGA Q500 to assess the contents of fractions in 1L centrifuged separated oil and solids phases of samples C2, C5, C7, and C8. TGA also was used to evaluate the thermal properties of the solids for all combinations of Cmix with four additives (ferric chloride, mixture of ferric chloride + ferrous sulfate, polyacrylamide and tween 80).

3.8 Water properties' assessment

One of the major parameters of reclaimed water properties is its pH. In order to examine the pH value, separated water from each sample of 1L Cmix volumes was filtered first by syringe filters (Fig. 3-27). This was carried out both with and without the effects of four different additives (ferric chloride, mixture of ferric chloride + ferrous sulfate, polyacrylamide and Tween 80). The Fisher Scientific Accumet AR25 pH meter was then applied to a 45mL volume sample.

Turbidity and clarity - other important indices of water quality – were also assessed. Turbid water requires an advanced treatment in Wastewater Treatment Plant. Figure 3-27 shows evident differences between water samples generated by centrifuging with and without the presence of additives. Ferric chloride and its mixture with ferrous sulphate show the highest water clarity. The water without additives and with Tween 80 show colored and turbid water.

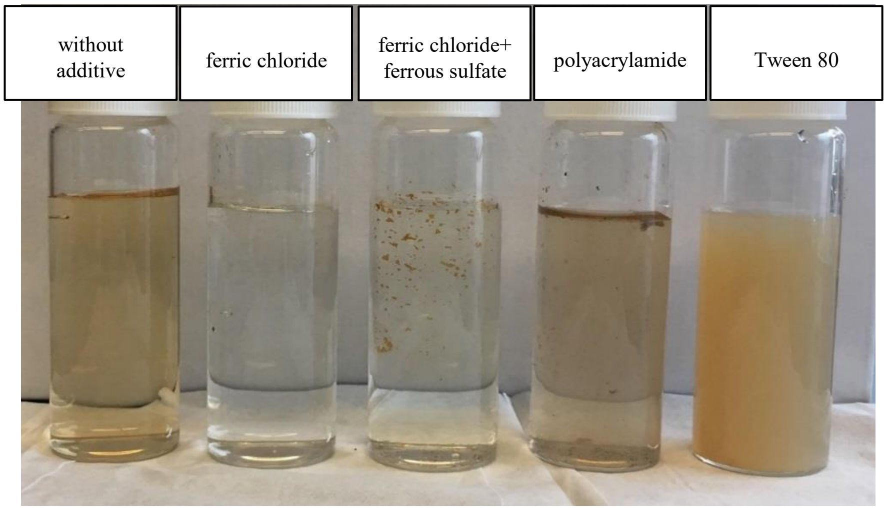

Figure 0-27 Filtered water of sample Cmix with and without the effect of four different additives after centrifuging

3.9 Viscosity measurement

The effect of additives on viscosity was then investigated. The 1L sample of Cmix was firstly mixed with the additive; a high-speed centrifugation was then used to separate the phases. After centrifuging, the separated oil and oily water underwent a viscosity measurement by vibro-viscometer SV-10 (Fig. 3-5).

3.10 BS&W – Basic Sediments and Water analysis

The quality of oil depends on the amount of its impurities present. Water and solids are among important oil's impurities, therefore BS&W analysis is recommended at full scale for their assessment. ASTM standard D4007 revealed the BS&W analysis in the recovered oil sludge (Cmix) with additives. The separated oil phase was centrifuged at 2000rpm for 15 minutes using the laboratory centrifuge IEC-HN-SII to determine the BS&W content. The recovered oil samples using different additives (ferric chloride, ferric chloride+ferrous sulfate, polyacrylamide, Tween 80) are shown in Fig. 3-28.

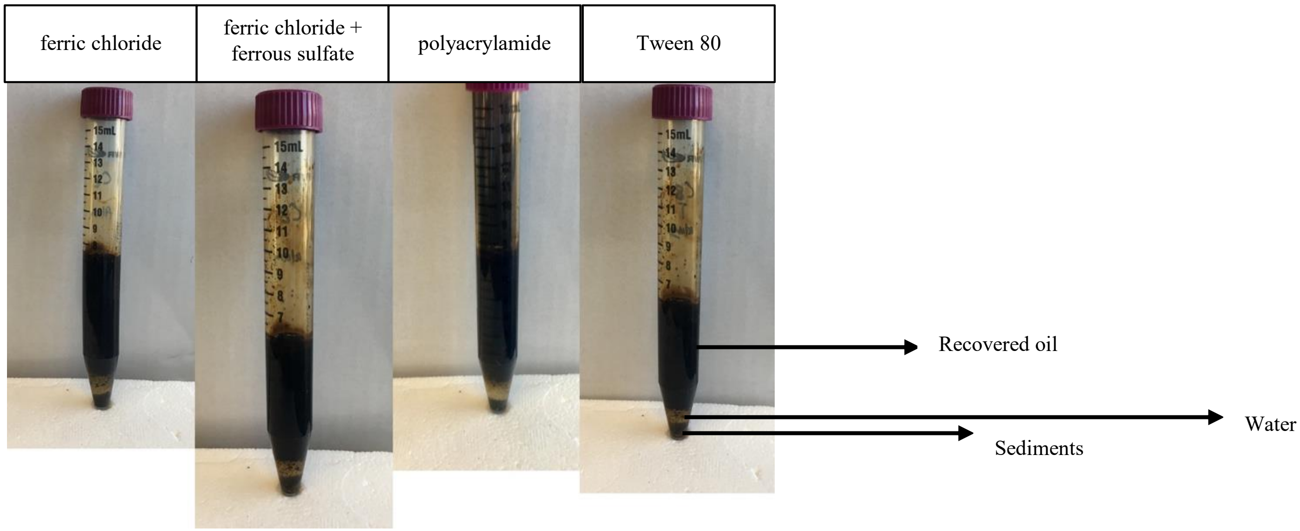

Figure 0-28 Laboratory BS&W analysis for an oil sludge Cmix with four different additives

EXPERIMENTAL RESULTS AND DISCUSSION

This chapter presents the results of tests conducted in Phase 1, 2 and 3.

4.1 Phase 1: Characteristics of oily sludge

4.1.1 Characteristics results of sample C1, C2, C3, C4, C5, C6, C7, and C8

The lowermost oily sludge provided in 8 buckets was extracted from the same tank at the same time; however, results showed a difference in their characteristics. Bottom tanks are cleaned sporadically and thus, certain stratification of sludge takes place over a period of time. Subsequently, a variation of sludge phases ratios can be expected in samples C1 to C8. However, is unknown if such differences could influence the recovery of oil. Overall, Table 4-1 shows a variation of water content between 46% and 35%, a solids content between 33% and 24%, a light oil content between 15% and 2% and a heavy oil content between 30% and 16%. Water content represents the highest constituent of the sludge, the light oil the lowest. Usually water, due to its high affinity to sludge components, brings significant troubles to sludge management. Water increases the volume of sludge disposal and moreover, the presence of water in recovered oil decreases its calorific value.

Table 0-1 Initial content of eight oily sludge samples (C1-C8)

Samples	Water content%	Light oil content%	Heavy oil content%	Solids content%
C1	46.11	1.91	26.64	25.34
C2	37.34	9.74	24.94	27.98
C3	42.77	3.49	29.87	23.87
C4	39.64	6.70	26.01	27.65
C5	44.87	8.23	16.79	30.11
C6	40.35	5.71	25.07	28.87
C7	43.26	7.53	16.03	33.18
C8	34.88	14.91	21.61	28.60

4.1.2 Characteristics results of mixed sludge (Cmix)

The study also required conducting tests with composite samples consisting of a mixture of sludge taken from different buckets. According to Table 4-2, sludge Cmix comprises approximatively 32.22% of water, 23.57% of solids, 13.92% of light oil and 30.28% of heavy oil. In this case, water still represents the highest fraction, followed by heavy oil, solids and light oil.

Table 0-2 Test results for the properties of mixed sludge (C mix)

Sample	Water content %	Light oil content %	Heavy oil content %	Solids content %
Cmix	32.22	13.92	30.28	23.57

The characterization analyses showed that the water content in oil sludge samples C1-C8 and sample Cmix (Tab. 4-1 and Tab. 4-2) varied from 32% to 47%. These samples also contained a mixture of other components such as hydrocarbons, which were also present in the solid phase. The volume of solids is also significant to sludge. The mineral phase in solids represents a significant issue in practice due to abrasive nature of such components, leading to potential damages on centrifuging equipment. Some fine mineral components might show colloidal behavior. Water-in-oil emulsion with a fraction of solids usually presents problems for centrifuging process. The application of modifiers (e.g. coagulant) would be required to neutralize the colloidal fraction of solids.

4.1.3 Characteristics results of mixed eight sludge samples (Cmix (C1-C8))

Sample Cmix (C1-C8) approximately comprises 40.16 % of water, 23.63 % of solids, 4.88 % of light oil and 31.31% of the heavy oil (Tab. 4-3).

Table 0-3 Test results for the properties of mixed eight sludge (C mix (C1-C8))

Sample	Water content %	Light oil content %	Heavy oil content %	Solids content %
Cmix (C1-C8)	40.16	4.88	31.31	23.63

It was found that the characteristics of Cmix (C1-C8) were situated somewhere between properties of Cmix and individual samples C1 to C8.

The tests were repeated three times and data provided in the figures is an arithmetical average of three measurements. Standard deviation for water, light oil, heavy oil and solids measurements were found to be 5.59, 5.23, 4.95 and 3.06, respectively.

4.2 Phase 2, Stage 1: Centrifuging results at small scale without pre-treatment

4.2.1 Centrifuging results at small scale in 15 mL tube: Samples C1, C2, C3, C4, C5, C6, C7, and C8

The results for 15mL after centrifuging for the water phase (Fig. 3-8) showed that the highest water extraction occurred in samples C7 and C6 while C8 had the lowest (Tab. 4-4).

As presented in Table 4-4, sample C8 had the highest oil content by a value two times larger than of other samples, while the lowest oil content was represented by sample C3. In terms of the solids content, the highest values were obtained by both samples C1 and C4, and the lowest value by C8.

Table 0-4 Water content, oil content and solids content in eight samples after centrifuging at ambient temperatures in 15mL volume

Samples	**Three phase separation percentage**		
	Water content%	**Oil content%**	**Solids content%**
C1	25.60	20.40	54.00
C2	28.70	18.60	52.70
C3	29.30	17.10	53.60
C4	23.50	22.50	54.00
C5	26.40	24.20	49.40
C6	26.40	24.50	49.10
C7	34.20	28.30	37.50
C8	13.50	54.10	32.40

4.2.2 Centrifuging results at small scale in 45 mL volume: Sample C1, C2, C3, C4, C5, C6, C7, and C8

Of the 45mL samples tested, the results demonstrated that the highest water extraction was related to sample C6 while the lowest being sample C7 (Tab. 4-5). The highest and lowest percentages of oil content were obtained in samples C2 and C1, respectively. Samples C5 and C6 contained the highest and the lowest solids.

Table 0-5 Water content, oil content and solids content in eight samples after centrifuging at ambient temperatures in 45mL volume

Samples	**Three phase separation percentage**		
	Water content%	**Oil content%**	**Solids content%**
C1	43.10	17.50	39.40
C2	41.90	23.80	34.30
C3	42.70	23.50	33.80
C4	41.70	21.50	36.80
C5	32.00	18.70	49.30
C6	45.80	23.60	30.60
C7	28.80	22.90	48.30
C8	30.40	22.80	46.80

4.2.3 Centrifuging results at a small scale in 45 mL tube: Sample Cmix

Table 4-6 illustrates three-phase separation of 45 mL sample Cmix. After centrifuging, the sample mix contained 23.47 % water, 17.36% oil and 59.17% solids.

Table 0-6 Three-phase separation percentage in sample Cmix after centrifuging at ambient temperatures in 45mL volume

Sample	**Three phase separation percentage**		
	Water content%	**Oil content %**	**Solids content %**
Cmix	23.47	17.36	59.17

In conclusion, the percentage of water extraction in Cmix is low compared with C1-C8. It was revealed that the solids content increased after centrifuging. It was also speculated that the colloidal solids fraction might have an affinity to water, which does not facilitate separation. Subsequently, a conditioning of sludge has to be proposed before the centrifuging process.

4.3 Phase 2, Stage 2: Test results for small scale centrifuging with pre-treatment

4.3.1. Test results for the effect of four different temperatures on oily sludge samples centrifuging

The effect of temperature on fractioning was investigated by applying four different temperatures, namely 21, 40, 55 and 70 °C, to each of the eight sludge samples (C1-C8).

Table 0-7 Water content under various heating conditions in eight samples after centrifuging

Samples	**Water content % (visual assessment after centrifuging)**			
	21˚C	**40 ˚C**	**55˚C**	**70˚C**
C1	43.10	34.80	39.50	34.80
C2	41.90	34.50	35.40	54.30
C3	42.70	55.00	50.80	50.80
C4	41.70	40.60	51.70	47.30
C5	32.00	36.60	53.30	41.40
C6	45.80	64.50	54.40	51.30
C7	28.80	32.80	37.50	65.60
C8	30.40	53.30	67.90	53.30

According to Table 4-7, the removal of water was enhanced with the increase of temperature: the highest water removal was observed at 55 ˚C. Sample C8 had the highest amount of water removal at 55 ˚C in comparison to other samples. The temperature enhanced water removal from the colloidal system. The lowest removal of water was observed in sample C7 at 21 ˚C. This study showed that the centrifuging process can be processed with the separation of oily sludge on three phases. Water separation was evidently dependent on the pre-treatment and sludge properties. The results showed that there is an optimal temperature at which centrifuging is found to be more efficient. The highest temperature (e.g. 70 ˚C) results in the evaporation of water, which is not helpful in the centrifuging process. Multifarious parameters play an important role in the efficacy of the centrifuging process. Thus, a continuous characterization of each oil sludge system is not a practical procedure.

Table 4-8 showed the highest values regarding the oil content at 21, 40, 55 and 70 °C were obtained by samples C2, C4, C3 and C7 respectively. The highest oil content was observed after centrifuging sample C4 at 40°C.

Table 0-8 Oil content under various heating conditions in eight samples after centrifuging

Samples	**Oil content % (visual assessment after centrifuging)**			
	21˚C	**40 ˚C**	**55˚C**	**70˚C**
C1	17.50	19.30	19.60	25.50
C2	23.80	30.20	32.20	30.60
C3	23.50	32.20	33.50	31.50
C4	21.5	37.50	32.60	32.00
C5	18.70	32.50	21.50	27.50
C6	23.60	20.10	25.50	30.40
C7	22.90	23.50	30.30	32.50
C8	22.80	25.50	25.20	32.30

4.3.2. Effect of different additives on oily sludge demulsification and separation process

According to Tables 4-9 and 4-10, in terms of water content, C2 subjected to $FeCl_3$+$FeSO_4$ shows the highest percentage of water extraction (45.98%), while C2 subjected to $Al_2 (SO_4)_3$) showed the lowest percentage of water extraction (11.11%).

Considering oil extraction, C5 (NA) and C5 ($FeCl_3$+$FeSO_4$) showed the same percentage of oil (44.12%) recovery which was the highest of all other samples, while C5 ($Al_2 (SO_4)_3$), showed the lowest percentage (22.22%). Regarding solids content, C2 ($Al_2 (SO_4)_3$) and C5 ($Al_2 (SO_4)_3$) were identical, both measured the highest percentage of solids content (61.11%), while C5 ($FeCl_3$+$FeSO_4$) was the lowest (23.53%). It was assumed that in C5 oil has been successfully extracted from both solids and water fractions. In fact, centrifuging forces applied to the sludge without additives have a comparative oil recovery, although water recovery is increased. It seems that the centrifuging process transform W/O stable emulsion to O/W emulsion, while the addition of conditioners affects also O/W emulsion in a subsequent step, leading to a better water fraction separation. Alum producing long chains of $Al\text{-}OH_x$ increases the volume of solids fraction.

Table 0-9 Comparison of three-phase separation after centrifuging with & without additives for samples C2 and C5

Phase	**C2**					**C5**				
	NA	**FeCl3**	**FeSO4**	**Mix (FeCl3 +FeSO4)**	**Al2(SO4)3**	**NA**	**FeCl3**	**FeSO4**	**Mix (FeCl3 +FeSO4**	**Al2(SO4)3**
	1	**2**	**3**	**4**	**5**	**1**	**2**	**3**	**4**	**5**
Water%	30.12	33.13	32.35	45.98	11.11	29.41	23.53	39.16	32.35	16.67
Oil%	30.12	30.12	29.41	28.74	27.78	44.12	35.29	24.10	44.12	22.22
Solids%	39.76	36.75	38.24	25.29	61.11	26.47	41.18	36.75	23.53	61.11

Table 0-10 Comparison of three-phase separation after centrifuging with & without additives for samples C7 and C8

Phase	**C7**					**C8**				
	NA	**FeCl3**	**FeSO4**	**Mix (FeCl3 +FeSO4)**	**Al2(SO4)3**	**NA**	**FeCl3**	**FeSO4**	**Mix (FeCl3 +FeSO4)**	**Al2(SO4)3**
	1	**2**	**3**	**4**	**5**	**1**	**2**	**3**	**4**	**5**
Water%	23.53	30.12	25.00	41.18	22.22	22.22	22.22	22.22	22.22	18.75
Oil%	35.29	30.12	31.25	29.41	27.78	27.80	33.33	33.33	27.78	37.5
Solids%	41.18	39.76	43.75	29.41	50.00	50.00	44.44	44.44	50.00	43.75

It can be concluded that pre-treatment with a mixture of ferric chloride and ferrous sulfate could enhance the separation of water and oil in comparison to other additives. However, solids responded very well to alum.

The effect of additives on Cmix was also examined. According to Tab. 4-11 it appears that among all samples, Cmix had the best response in terms of water extraction (25%) to Tween 80 and polyacrylamide, while the worst extraction (10%) was observed when the cationic polymer was applied. Cmix with ferrous sulfate showed the best oil content extraction (29%), while Cmix with sodium metasilicate had the lowest percentage (11%).

However, the highest separation of solids content (69%) was obtained when the cationic polymer was applied to Cmix, whilst Cmix and Tween 80 had the lowest percentage of separation

(49%). The cationic polymer, usually applied for the thickening of sludge solids, demonstrated a high affinity to solids in oil sludge.

Table 0-11 Three-phase separation percentage after centrifuging in a 45mL tube for sample Cmix using a different additive

Sample with & without additives	**Three phase-separation percentage**		
	Water content %	**Oil content %**	**Solids content %**
C_{mix} (without chemical)	23	16	61
C_{mix} (ferrous sulfate)	17	29	54
C_{mix} (ferric chloride)	21	28	51
C_{mix} (alum)	18	22	60
C_{mix} (polyacrylamide)	25	19	56
C_{mix} (sodium metasilicate)	24	11	65
C_{mix} (lime)	18	21	61
C_{mix} (calcium chloride)	25	16	59
C_{mix} (cationic polymer)	10	21	69
C_{mix} (clay)	18	23	59
C_{mix} (Tween 80)	25	26	49
C_{mix} (sodium dodecyl sulfate)	20	19	61
C_{mix} (aluminum oxide)	18	19	63
C_{mix} (sodium carbonate)	22	20	58

It can be noted that both Tween 80 and ferrous sulfate have a successful effect on the separation of water and oil among all other additives.

4.3.3 Effect of combined conditioning on centrifuging process

Combinations of the optimum temperature (55 ˚C) and thirteen additives were tested. Table 4-12 presents the effect of using thirteen additive agents with pre-heated oily sludge at 55 ˚C on centrifuging the Cmix sample (Fig. 3-15, 3-16 and 3-17). It illustrates that Cmix (cationic polymer) occupies the highest place of all regarding water content measuring (41%). In contrast, Cmix (polyacrylamide) took the lowest place (16%). In terms of oil content, Cmix (ferric chloride) and Cmix (Tween 80) show 35% and 32% extraction values, respectively. However, Cmix (calcium chloride) expresses the lowest percentage (15%) of oil recovery. Furthermore, Cmix (polyacrylamide) has the highest solids content (64%) while Cmix (ferric chloride) has the lowest (34%).

Table 0-12 Three-phase separations after centrifuging in a 45mL tube of sample Cmix with various additives and after pre-heating at 55 °C

Sample with & without additives	**Three phase-separation percentage with pre-heating at 55 °C**		
	Water%	**Oil%**	**Solids%**
Cmix (without chemical)	37	17	46
Cmix (ferrous sulfate)	28	30	42
Cmix (ferric chloride)	31	35	34
Cmix (alum)	28	29	43
Cmix (polyacrylamide)	16	20	64
Cmix (sodium metasilicate)	40	22	38
Cmix (lime)	32	24	44
Cmix (calcium chloride)	35	15	50
Cmix (cationic polymer)	41	19	40
Cmix (clay)	33	17	50
Cmix (Tween 80)	30	32	38
Cmix (sodium dodecyl sulfate)	39	25	36
Cmix (aluminum oxide)	39	25	43
Cmix (Sodium Carbonate)	35	20	45

Interestingly, ferric chloride and Tween 80 in combination with pre-heating at 55 ˚C showed an agreeable enhancement in the separation of water and oil respectively. It was concluded that additives in a combination with pre-treatment, e.g. pre-heating, had an important impact on phase separation by centrifuging.

4.4 Phase 3: Results of the scale-up centrifuging process for oil and water recovery

4.4.1 Phase3, stage 1: Scale-up centrifuging process without conditioning

After a study of feasibility of the centrifuging recovery of oil and water for a volume of 45mL, an investigation took place for 1L sludge volume. Results of centrifuging on such a large scale showed differences in separation of phases as water, oil, and solids (Fig. 3-18). Amounts of separated water in Sample C2 and C8 were higher than for C5 and C7, however, lower comparing to small-volume tests. Furthermore, the water was not clear and contained oil droplets and represented an oil-in-water emulsion. Usually such water requires further treatment, nevertheless, oil recovery reached 29% and 38% for C2 and C8, respectively. Solids content was observed higher (56%) in sample C2.

No phase separation was observed in samples C5 and C7. Emulsions in C5 and C7 preserved their stability after centrifuging in provided conditions. Both samples had a similar viscosity but one much lower than oil separated from samples C2 and C8 (Tab. 4-13). It was concluded that higher sludge volume requires a higher speed and pre-treatment for an effective centrifuging, which means higher operational costs.

Table 0-13 Three-phase separation percentage after centrifuging in 1L- volume for samples C2 and C8 in natural conditions

Samples	**Three phase-separation percentage**		
	Water%	**Oil%**	**Solids%**
C2	14	29	56
C8	15	38	47

4.4.2 Phase 3, Stage 2: Scale-up centrifuging process with the effect of conditioning

Table 4-14 illustrates the three-phase separations of sample Cmix at 1L volume. The highest water content extraction of (30%) from Cmix was observed when ferrous sulfate and ferric chloride were applied; in contrast, the sample Cmix with polyacrylamide experienced the lowest water removal (18%). It was also noted that the highest oil contents of (33%) and (32%) were observed in Cmix (ferric chloride) and Cmix (Tween80). While Cmix (polyacrylamide) had the lowest oil content of (30%) (Fig. 3-20, 3-21, 3-22 and 3-23).

Table 0-14 Three-phase separations after centrifuging sample Cmix with four different additives in 1L -volume

Sample with additives	**Three phase-separation percentage**		
	Water%	**Oil%**	**Solids%**
Cmix (ferric chloride)	26	33	41
Cmix (ferrous sulfate +ferric chloride)	30	31	39
Cmix (polyacrylamide)	18	30	52
Cmix (Tween 80)	29	32	39

As a result, it is interesting to note that Tween 80 and ferric chloride had a good effect on the separation of water and oil phases at both small and large scale (1L–volume).

Table 4-15 demonstrates the three-phase separations of sample Cmix considering 1L-volume with the effect of surfactants. The highest water and oil extractions i.e. 27.27% and 31.82%, respectively, were observed when Tween 80 was applied to Cmix.

It was noted, that Cmix with Triton x-100 has a high oil content of 22.1% in comparison to sample Cmix without additives at the large scale (17.56%).

Table 0-15 Three-phase separations after centrifuging of sample Cmix (without additives) and with the effects of surfactants in 1L -volume

Samples	**Three phase-separation percentage**		
	Water %	**Oil %**	**Solids %**
Cmix (without additives)	26.14	17.56	56.25
Cmix (Triton x-100)	24.34	22.10	53.55
Cmix (Tween 80)	27.27	31.82	40.91

As a result, it can be concluded that surfactants Tween 80 and Triton x-100 have a good effect on separation of oil phases at the large scale (1L–volume).

4.5 Characterization of separated fraction

4.5.1 Test results for the liquid seepage before and after centrifuging

According to Table 4-16 and Figure 4-1, sample C2 before centrifuging had the highest wettability due to its liquid seepage, and it is interesting to note that C8 after centrifuging has shown no seepage (Fig. 3-24, 3-25 and 3-26).

Table 0-16 Radius of wettability of solids phase – liquid seepage before & after centrifuging in 1L-volume

Samples	The radius of wettability due to liquid seepage (cm)
C2 before centrifuging	1.50
C2 after centrifuging	1.00
C7 before centrifuging	1.65
C7 after centrifuging	1.40
C8 before centrifuging	1.50
C8 after centrifuging	1.00

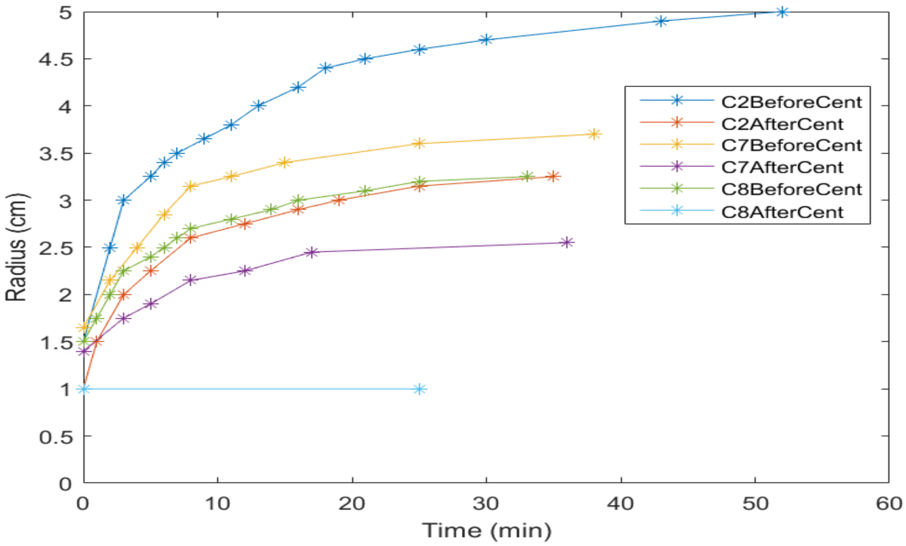

Figure 0-1 Trend of liquid seepage for samples C2, C7 and C8 before and after centrifuging

The results of seepage (wettability) are particularly important in deciding the method of sludge disposal according to estimated cost. Many landfills do not accept materials with an evident seepage of liquids, others increase the costs of disposal due to the necessity of additional pre-treatment of such materials. Furthermore, oil and water recovery decrease amount of waste sent for disposal. Based on this study, it was assumed that disposal volume decreased roughly by 70%, leading to a decrease of disposal costs ranging from 200 to 450 CAD per metric ton. Furthermore, such material, without leaching, is manageable and easier to transport. Moreover, it can be used for further transformation, or reused as a value-added-product.

4.5.2 TGA results for separated oil and solid phases

The visual and physical assessment of phase separation as defined in Chap. 3 (Fig. 3-18) did not sufficiently assess the efficacy of the method with respect to the final product purity. Subsequently, more advanced methods such as Thermogravimetric, viscosity and calorific value analyses were applied.

Thermogravimetric analysis (TGA) was used to assess the purity, i.e. remaining other fractions, in separated oil sludge components. Centrifuged large sample C2 has a visible vertical separation on three phases: top light oil zone, middle water zone and bottom solids' zone (Fig. 3-18). Top oil fraction and bottom solid fractions were then subjected to TGA assessment. Similar analysis was applied to other large samples. TGA showed that all separated fractions contained some water (Fig. 4-2, 4-3); however, in the case C2, more water was observed in the oil fraction and some oil in the solid fraction. Furthermore, the bottom fraction of sample C5 contained more water after centrifuging than that C2. It was also visible that the top fraction of sample C8 (Fig. 4-

3) contained much less heavy oil fractions than the C8 sample at the bottom. A similar observation can be associated with sample C7 (Fig. 4-3).

In summary, there are differences in phase separation in each sample. However, all samples responding positively to the centrifuging process.

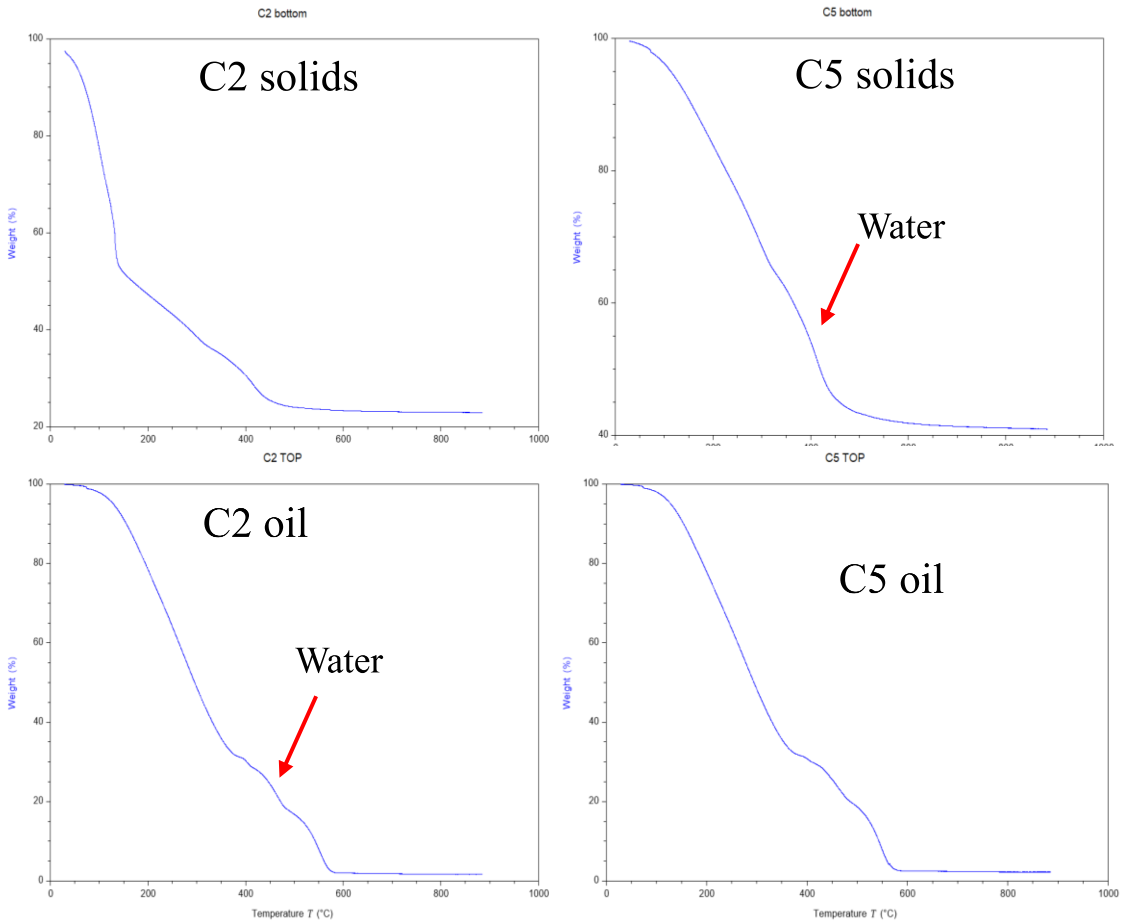

Figure 0-2 TGA results of samples C2 and C5 after centrifuging for solids and oil phases

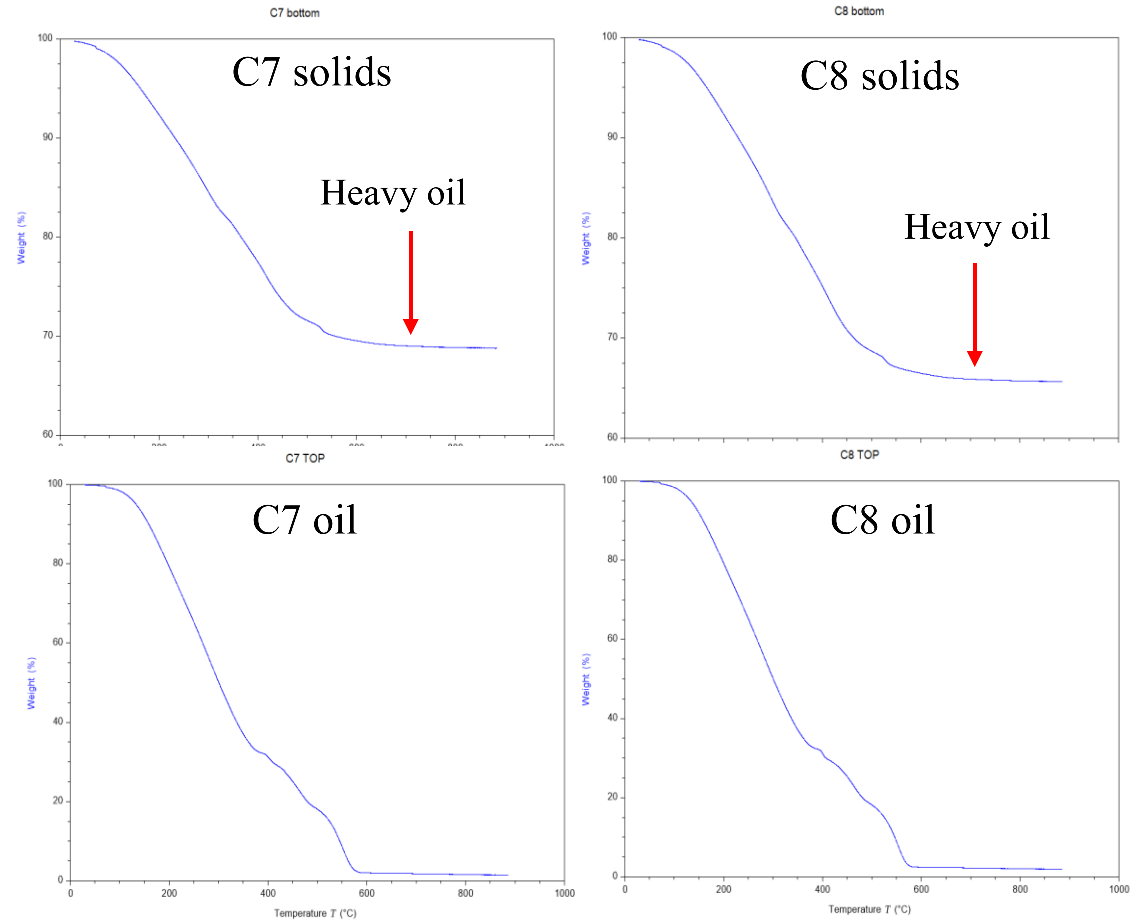

Figure 0-3 TGA results of samples C7 and C8 after centrifuging for solids and oil phases

Results from TGA allows to conclude that centrifuging demulsifies the W/O sludge and makes separation of phases, but separated phases contain various fractions of impurities at a moderate level. In order to improve efficiency of the centrifuging process, the application of additives was suggested. The additives found to be the most suitable at a small centrifuging scale, were applied to the large scale.

Subsequently, TGA assessed efficiency of additives such as ferric chloride, a mixture of ferric chloride and ferrous sulfate, polyacrylamide and Tween 80 when used in conjunction with Cmix 1L-volume. Solid phase, after centrifuging exposed to TGA, showed how much the oil recovery from solids can be improved by using a particular additive.

The lowest amount of remaining heavy oil was found in the solid phase treated with ferric chloride (Fig. 4-4). The remaining oil in the solids phase (from the lowest to highest) was found by TGA in the following: sludge with ferric chloride < sludge with Twee80 < sludge with mixture of $FeCl_3$ and $FeSO_4$ < sludge with polyacrylamide (Fig. 4-4).

Regarding the water and oil presence, the minimum weight loss (30%) was observed in the case of using polyacrylamide. Using a mixture of ferric chloride and ferrous sulfate revealed better separation of phases (Fig. 4-4). Conversely, Tween 80 treated sludge showed the most weight loss (42%). Fig. 4-4 shows the presence of hydrocarbon and water in the solids phase of treated centrifuged sample. These results showed that centrifuging supported with simple coagulants can improve the separation of phases in oily sludge.

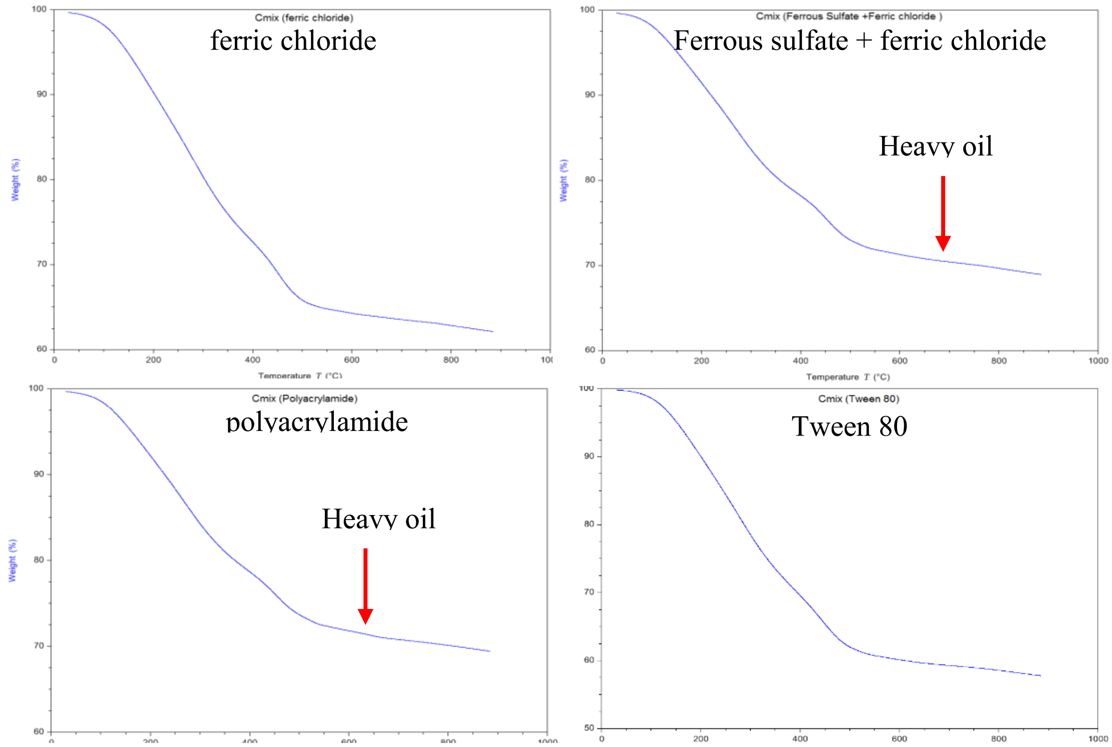

Figure 0-4 TGA results for solids phase after centrifuging sample Cmix with the effect of ferric chloride, ferrous sulfate+ferric chloride, polyacrylamide and Tween 80 in 1 L volume

4.5.3. Quality of recovered water with respect to pH, sample Cmix with additives at large scale

Centrifuging process with the support of additives allowed for a better recovery of water. However, a characterisation of such water was necessary to assess its further application for direct use or a potential treatment.

Figure 4-5 presents the pH value of Cmix (1L-volume) using four different additives. Cmix (polyacrylamide) has the maximum pH value of (7.48), while, Cmix (ferric chloride) has the minimum pH value measuring (5.90). Water treated with ferric chloride might then undergo further treatment depending on its final application.

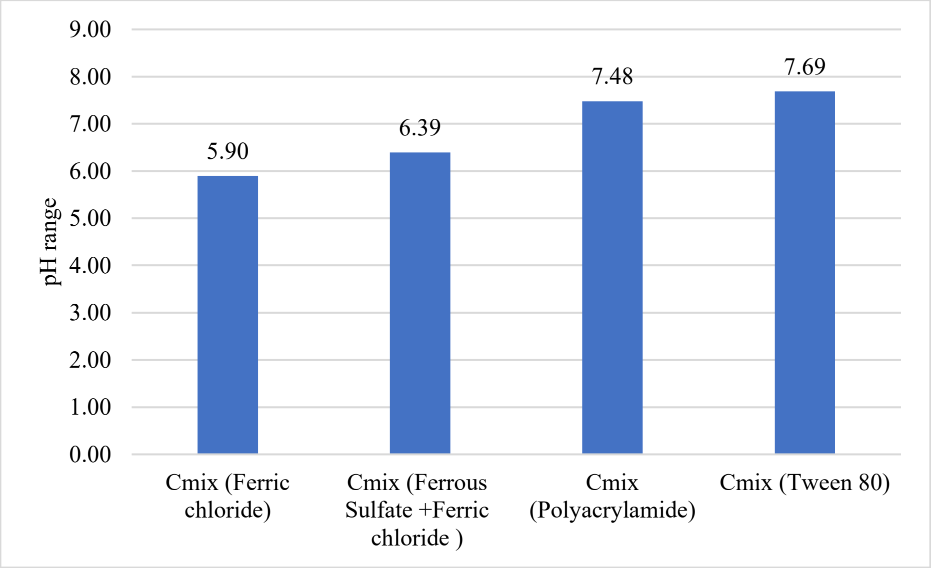

Figure 0-5 Comparison of water phase pH for sample Cmix with the effect of four additives after centrifuging 1L- volume

Ferric chloride and its mixture with ferrous sulphate show the highest water clarity. The water without additives and with Tween 80 show colored and turbid water.

4.5.4 Viscosity of phases separated from sample Cmix treated by centrifuging with additives

The viscosity tests were conducted to additionally assess an efficiency of phase separation in the presence of thirteen different additives. As it can be seen in Tab. 4-17, in terms of water phase, Cmix with cationic polymer has the maximum viscosity (39.70 mPa.s) which means a high content of oil in water. While, Cmix with lime has the minimum viscosity (7.10 mPa.s). It is also shown that oil phase of Cmix with lime has a maximum viscosity (43.60 mPa.s) due to the formation of a new matrix (non-Newtonian fluid). It might be partially due to a high content of oil in the sample and partially due to lime's affinity to resins, which in turn might change the rheological properties of the matrix. However, Cmix with sodium dodecyl sulfate has the lowest viscosity (22.60 mPa.s) showing a high content of water.

Table 0-17 Effect of thirteen additives on the viscosity of sample Cmix sludge components after centrifuging

Samples	**Viscosity after centrifuging at 24°C**	
	Oil-water phase (10^{-3} Pa.s)	**Oil phase (10^{-3} Pa.s)**
C_{mix} (without additive)	16.60	38.30
C_{mix} (ferrous sulfate)	13.50	29.90
C_{mix} (ferric chloride)	15.10	29.80
C_{mix} (alum)	15.30	42.90
C_{mix} (polyacrylamide)	20.20	26.00
C_{mix} (sodium metasilicate)	13.90	33.10
C_{mix} (lime)	7.10	43.60
C_{mix} (calcium chloride)	14.40	29.50
C_{mix} (cationic polymer)	39.70	43.20
C_{mix} (clay)	13.40	39.40
C_{mix} (Tween 80)	14.20	27.70
C_{mix} (sodium dodecyl sulfate)	16.90	22.60
C_{mix} (aluminum oxide)	18.20	34.30
C_{mix} (sodium carbonate)	14.30	26.40

It can be concluded that centrifuging process improved separation of sludge phases by reducing the viscosity. However, their impurity was still high. It was also found that using additives such as lime and sodium dodecyl sulfate resulted in the lowest viscosity in water and in oil phases, respectively.

Table 4-18 shows the results of viscosity for oil and water phases after the three-phase separation of samples Cmix (1L volume for each) using four different additives. These results show much better separation of phases than the tests at a small scale. These measurements confirmed that in spite of the oil phase separation, water still contained varying amounts of viscous substances, particularly in the case of polyacrylamide; this water should have an additional treatment. Once more, it has shown that treatment with ferric chloride gives the highest oil recovery with the highest purity (80 mPa.s). Other additives show similar viscosity lower by 16% to 23% viscosity comparing to the centrifuging with $FeCl_3$.

Table 0-18 Viscosity results of water and oil phases for 1L- volume centrifuging with the effect of additives for the sample Cmix

Samples	**Viscosity after centrifuging at 24 °C**	
	Water phase (10^{-3} Pa.s)	**Oil phase (10^{-3} Pa.s)**
Cmix (ferric chloride)	1.32	80.4
Cmix (ferric chloride + ferrous sulfate)	1.18	67.3
Cmix (polyacrylamide)	5.49	61.1
Cmix (Tween80)	1.13	67.4

The tests at large scale (1L) showed the same tendency which has been already observed at the smaller scale. Water fraction after centrifuging Cmix with polyacrylamide showed the highest viscosity. However, water separation at a large scale with additives seems to be more efficient, having a water viscosity a little above 1 mPa.s. The same can be concluded for oil separation; the top separated fraction when Cmix was combined with ferric chloride reached a significantly high quality with oil viscosity of 80 mPa s.

It can be concluded that the purity of recovered oil without additives is sufficient, but with water and solid phases still containing a remaining oil fraction. To increase the quality of recovered water and solids, additives should be applied; it seems that an addition of simple coagulants might be the most cost-effective.

4.5.5 Test BS&W for Cmix 1L- volume centrifuging with additives

BS&W is a standard test of oil quality applied in the petroleum field (Chap. 3, 3-10 and Fig. 3-28). According to Figure 4-6, the recovered oil samples contained around 3-5% of water and around 1 % of sediments.

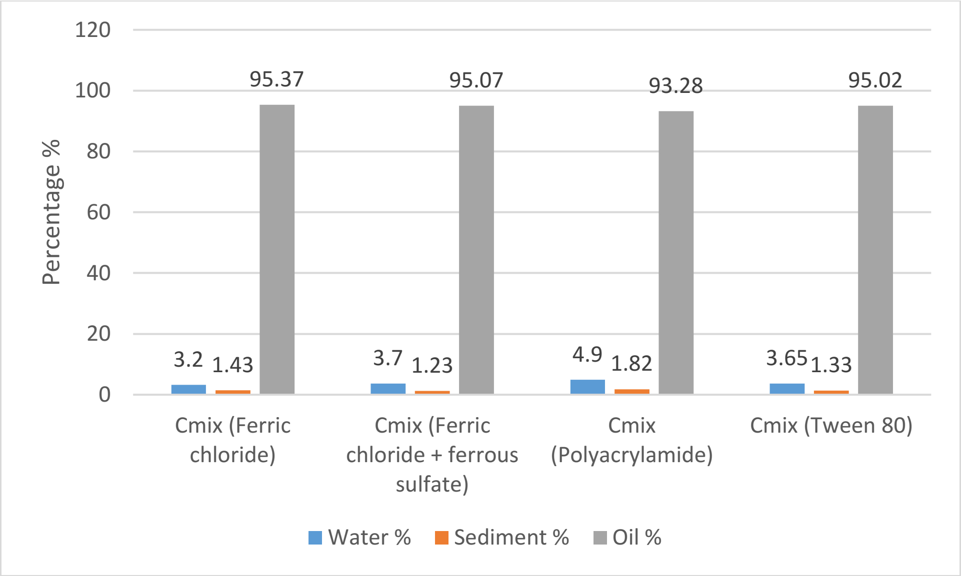

Figure 0-6 Comparison of BS&W after centrifuging sample Cmix with the effects of additives for1L- volume

Considering that total BS&W should be less than 3% for a superior quality of oil, the above results showed rather a moderate quality of the recovered oil. The best recovery found to be by application of ferric chloride as an additive to centrifuging process.

4.5.6. Calorific value of recovered oil

The oil sludge samples before and after centrifuging underwent the tests for assessing their suitability of use as a fuel. For this reason calorific values were measured. The raw oil bottom tank sludge before any treatment had the calorific value of 13,851 kJ/kg. The recovered oil by centrifuging process without additives increased in calorific value by almost 23% to 17,872 kJ/kg.

Overall, it can be concluded that centrifuging process with additives can recover oil, water and solids from wasted, hazardous materials. Oil can serve as a fuel, water can be returned to industrial processes and solids can be used as a valuable filling material.

CONCLUSIONS AND CONTRIBUTIONS

5.1 Conclusions

Three-phase separation in oil bottom tank sludge was achieved by centrifuging process at both small (15mL, 45ml volume) and large scale (1L volume). The recovery of oil, water and solids was observed.

The results showed that the centrifuging process worked better when a pre-treatment was implemented. Pre-treatment of oil sludge with additives (e.g. ferric chloride, or its mixture with ferrous sulfate as well as Tween 80), while a high speed centrifuging was applied, improved phase separation by centrifugation process. The study also showed that such three-phase separation might be more effective when combined with pre-heating, while an optimum temperature for pre-heating was found to be 55°C. Furthermore, the calorific value of separated oil increased by 23% when centrifuging was applied to wasted W/O (water-in-oil) sludge.

The recovered solid phase had the highest quality when ferric chloride was used.

The recovered oil had the highest quality when ferric chloride or no additives were applied.

The recovered water had the highest quality when ferric chloride or mixture of ferric chloride with ferrous sulphate were used.

The volume for potential disposal of sludge was reduced by 65 to 70 %.

A leaching from solids was prevented which improved the quality and management of such material, and decreased the disposal costs.

Overall, the modified centrifuging process permitted to recover new resources from sludge due a sustainable generation of fuels and recycling water.

After completion of this thesis, it is noteworthy to mention the following contributions:

1. Define an optimal heat value of 55° C for oils sludge pre-treatment in the view of water recovery.
2. Showing differences in the affinity of various oil sludge samples to different additives.
3. Demonstrating the methods of combining pre-treatment techniques in order to improve recovery of separated phases.

5.2 Future works

Concerning the fact that the functionality of the results is dependent on treatment volume, it is required to confirm the experimental conditions at a larger scale in future.

In the light of the experimental results obtained from the present study on the oily sludge treatment by centrifuging method, the following recommendations are suggested in order to improve future endeavors in this area:

1. Improving the quality of separated water in order to reuse this water directly after treatment and redirect to an adequate operation unit;
2. Proceed with an advanced removal of water and solids from in recovered oil by using different ratios of additives and different speeds of the centrifuge device;
3. Applying a 20L volume and pilot scale centrifuging process to adjust the lab scale results

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Appendix

Appendix 1

A) Effect of additives on centrifuging process (45mL tube)

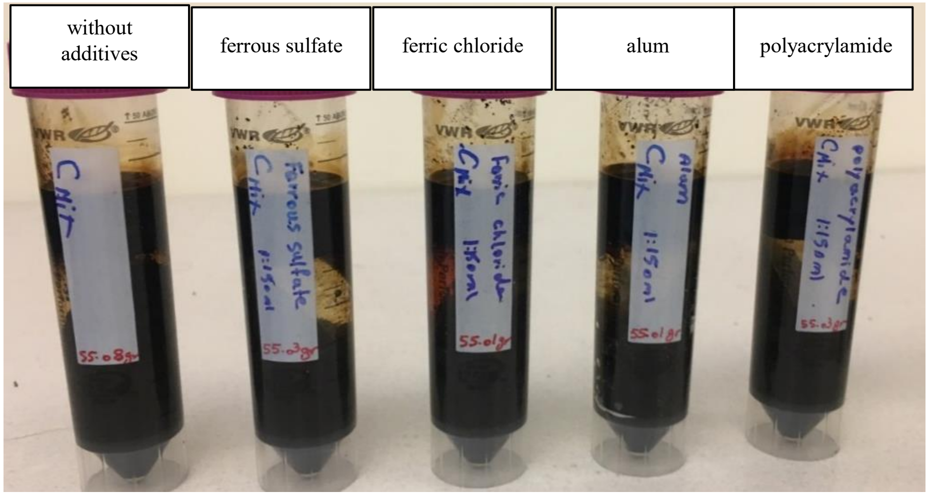

Figure 1 Sample Cmix after centrifuging without and with additives (ferrous sulfate, ferric chloride, alum, and polyacrylamide)

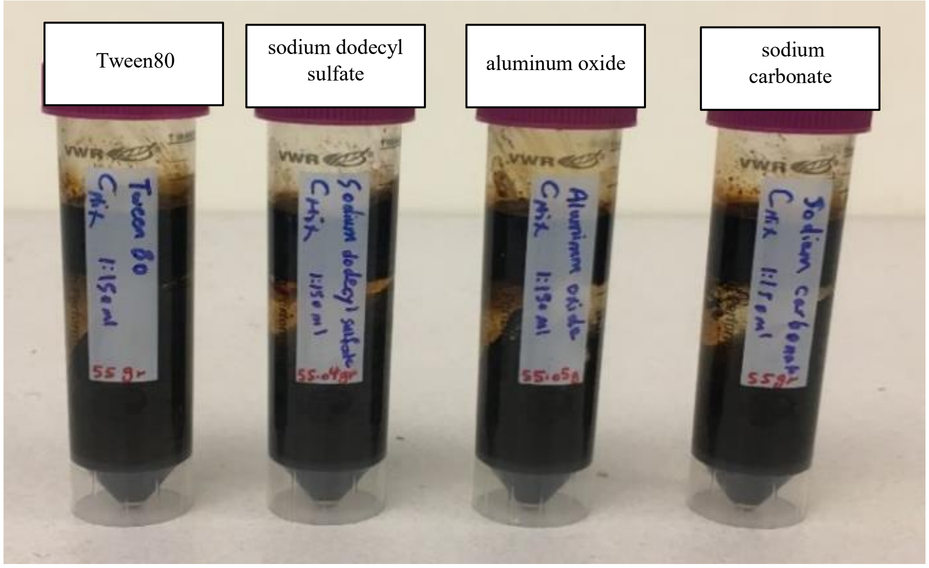

Figure 2 Sample Cmix after centrifuging with additives (Tween80, sodium dodecyl sulfate, aluminum oxide, sodium carbonate)

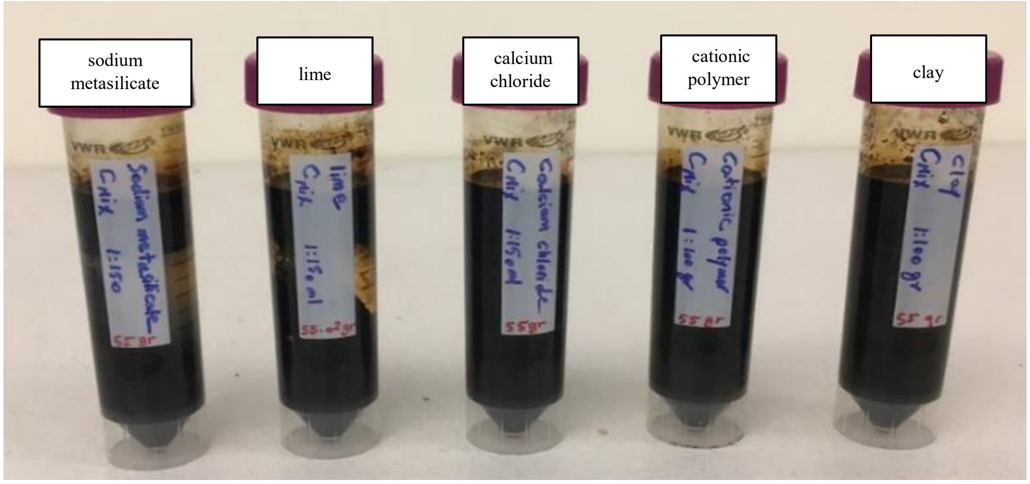

Figure 3 Sample Cmix after centrifuging with additives (sodium metasilicate, lime, calcium chloride, a cationic polymer, clay)

B) Characteristics of oily sludge

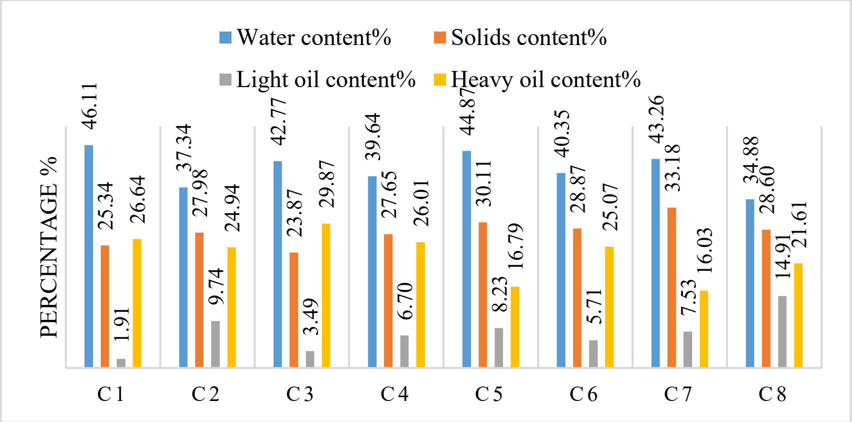

Figure 4 Comparison of water, solids as well as light and heavy oils contents in eight oily sludge samples (C1 to C8)

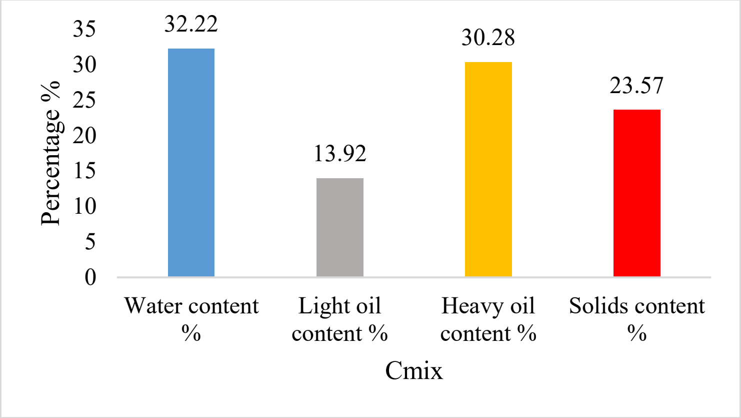

Figure 5 Comparison of water, solids as well as light and heavy oil contents in sample Cmix

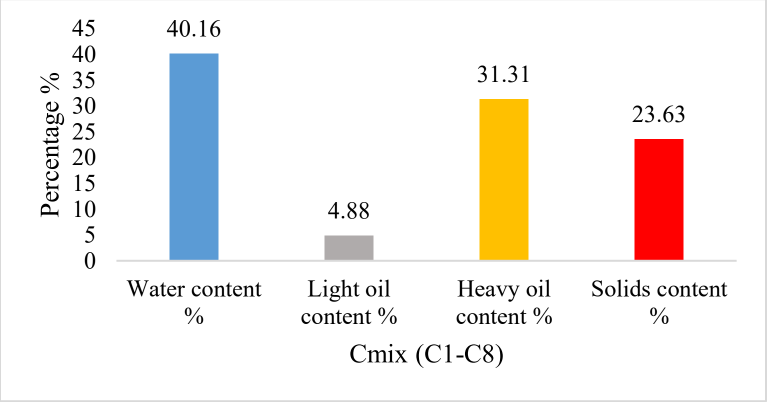

Figure 6 Comparison of water, solids as well as light and heavy oils contents in sample Cmix (C1-C8)