MEMBRANE TECHNOLOGY FOR TREATING DECANTED OILY WASTEWATER FROM MARINE OIL SPILL OPERATIONS: COMPARISON BETWEEN MEMBRANE FILTRATION VS MEMBRANE BIOREACTOR

By

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Abstracts

Accidents from anthropogenic activities such as petroleum transportation and exploration result in marine oil spills, which are particularly challenging to clean up due to quick oil dispersion and emulsification. Current Canadian oil spill regulations require that all liquids collected from an oil spill be taken to shore to an intermediate storage facility for later disposal. The existing spill recovery operation requires many vessels (with limited storage) and frequent trips to the shore. This practice severely constrains the response capacity, and efficiency of oil recovery since most of the liquid collected comprises of water. The inefficiency of the response allows for further oil dispersion and amplification of environmental harm. Onsite treatment of decanted oily seawater would benefit oil recovery operations by increasing vessel storage space and reducing the cycle of trips to shore for disposal. Membrane bioreactor technology has proven to be effective at treating oily wastewater generated from the industry; therefore is a good candidate for onsite treatment of oily wastewater generated from marine oil spills. In this study, the treatment efficiency of a pilot-scale membrane filtrations system (physical treatment only) and a bench-scale membrane bioreactor (MBR), with low hydraulic retention times, were compared for the treatment of oily seawater. The main parameters that were considered in this study were total petroleum hydrocarbons (TPH), petroleum hydrocarbons (PHC), and polycyclic aromatic hydrocarbons (PAH) removal. Both membrane systems evaluated in this study acheived a final oil concentration of less than 15ppm in the treated effluent, which is in line with the MARPOL Annex 1 standard. However, the MBR attained 99.1% TPH removal efficiency with an initial oil concentration of 100 ppm, whereas the physical treatment reached 98.2 % TPH removal efficiency with an initial oil concentration of 30 ppm. 30 ppm was the highest oil concentration that the membrane filtration system could receive before it fouled irreversibly. Most of the PAH concentrations reached below the Canadian water quality standards for both sets of experiments. It is concluded that an MBR system would be a promising onsite treatment option compared to membrane filtration alone for marine oil spill response operations.

List of Abbreviation Used

ASTM   American Society for Testing and Materials

ATP   Adenosine Triphosphate

BOD   Biochemical Oxygen Demand

BSA   Bovine Standard Protein

BTEX   Benzene, Toluene, Ethylbenzene, Xylene

CAS   Conventional Activated Sludge

CCG   Canadian Coast Guards

CFB   Flexibacter-Cytophage-Bacteroids

COD   Chemical Oxygen Demand

CSA   Canadian Shipping Act

DAF   Dissolved Air Flotation

DCM   Dichloromethane

DFO   Department of Fisheries and Oceans Canada

ECCC   Environmental Climate Change Canada

EEZ   Exclusive Economic Zone

EMSA   European Maritime Safety Agency

EPA   Environmental Protection Agency

EPS	Extracellular Polymeric Substances
F/M	Food/Microorganism
GC/MS	Gas Chromatography/Mass Spectrometry
HF	Hollow Fibre
HRT	Hydraulic Rentention Time
IMO	International Maritime Organization
MARPOL	The International Convention for Preparedness of Pollution from Ships
MBR	Membrane Bioreactor
MF	Microfiltration
MLSS	Mixed Liquor Suspended Solids
MLVSS	Mixed Liquor Volatile Suspended Solids
NEBA	Net Environmental Benefit Analysis
OHF	Oil Handling Facility
OLR	Organic Loading Rate
PAC	Poly-Aluminum Chloride
PAH	Polycyclic Aromatic Hydrocarbons
PAN	Polyacrylonitrile
PE	Polyethylene

PHC	Petroleum Hydrocarbons
PLC	Programmable Logic Controller
PPM	Parts Per Million
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene Difluoride
RO	Response Organization
RPM	Rotations Per Minute
RT	Room Temperature
SMP	Soluble Microbial Product
SRT	Sludge Retention Time
SVI	Sludge Index Volume
TC	Transport Canada
TCA	Tricarboxylic Acid
TDS	Total Dissolved Solids
TMP	Transmembrane Pressure
TPH	Total Petroleum Hydrocarbon
UF	Ultrafiltration
US	United States

UV-Vis Ultraviolet-visible

VLSFO Very Low Sulfur Fuel Oil

VOC Volatile Organic Compound

Acknowledgments

CHAPTER 1: INTRODUCTION

1.1. Background

Crude oil is the world's top non-renewable energy resource, with its demand expected to rise in the coming years (Afzal et al., 2019). Over the years, large volumes of oily wastewater from petrochemical extraction, refining and processing, storage, and transportation have been discharged into the environment (Tan et al., 2019; Xu et al., 2018). The wastewater produced is highly recalcitrant and toxic, containing hard-to-degrade compounds. The effluent from the oil and gas industry may contain compounds such as petroleum, petrochemicals, salts, heavy metals, radionuclides, dissolved organic matter, suspended solids, surfactants, sulphides, and ammonia in varying amounts, making this wastewater diverse and complex (Kuyukina et al., 2020; Ghimire & Wang, 2019; Tanudjaja et al., 2019; Yu et al., 2017; Di Bella et al., 2015; Soltani et al., 2010). Pollution from oily wastewater manifests itself in many ways, including contaminating drinking and groundwater resources; causing atmospheric pollution since many of the compounds are volatile; endangering aquatic life; contaminating crop production; destroying natural landscape; and is a danger to human health, as these compounds are carcinogenic and often neurotoxic (Yu et al., 2017; Soltani et al., 2010).

In the event of marine oil spills, liquid petroleum hydrocarbons are discharged into the marine environment due to human activities such as oil transportation and exploration, causing devastation to the local region. The rate at which the oil from marine oil spills spreads into the environment varies depending on multiple factors; it is influenced by ocean currents, temperature, and weather (Mansir & Jones, 2012; EPA, 1999). Canada is at a high risk for oil pollution since nearly 180 vessels carrying more than 80 million tonnes of oil

travel along its 243 000 kilometres coastline (Lee et al., 2020; TC, 2019). Over the past 52 years, six major oil spills have destroyed local ecosystems and communities. Residue from these oil spills still exists today, predominantly from the SS Arrow spill. The SS Arrow spill is the biggest in Canadian history, which led to a rise in scientific and public awareness of the threats of oil spills to coastal systems, marine wildlife, and fisheries. The spill promoted extensive research into enhanced marine environmental protection and effectual emergency response measures (Lee et al., 2020).

The current most common practice for cleaning up oil spills in Canada is mechanical recovery, which involves containing the oil to restrict environmental damage and collecting as much oil as possible. The disadvantage of mechanical recovery is its limitation due to rough weather conditions combined with strong currents and waves, capacity of skimming vessels and storage barges, the thickness of the oil slick, how quickly it spreads, and its state (dissolved or evaporated) (Clearseas, 2020). During mechanical recovery, containment booms are the first line of defence to stop the slick from spreading and reaching sensitive shorelines and habitats (Clearseas, 2020). Once the booms are in place, skimmers and vacuum systems are used to collect the oil from the ocean. Skimmers amass anywhere between 10% and 70% of seawater, consequently filling up 50–60% of the storage space on the barges with water (Liu et al., 2022; SL Ross, 2005). The liquids are gathered in the response vessels, then transferred to storage barges and taken to intermediate storage or final disposal facilities onshore (Clearseas, 2020; IPEICA, 2013). If any component of the waste stream is overwhelmed, response operations have to be ceased until adequate capacity becomes available (IPEICA, 2013).

This research focused on how to increase mechanical recovery efficiency and effectiveness. Natural decanting through gravity separation occurs in the temporary storage barges during clean-up operations. If a treatment system were on board to treat the excess water to reduce the oil concentration to acceptable levels, it would solve the capacity and efficiency issues of the oil spill response regime (Liu et al., 2022; Al-Hawash et al., 2018). Currently, Canada prohibits decanting due to the concern of releasing "priority" PAH contaminants found in oily wastewater back into the marine environment (Adams et al., 2017). The prohibition of discharge from oil spill responders for operational purposes drastically hinders response operations as it limits temporary storage space on barges and requires several cycles of trips to shore to transfer the wastewater to an intermediate storage facility. The lack of response capacity does not allow quick and effective recovery of the spilled oil, instead permits its propagation further into the ocean or shorelines, causing compounding environmental damage.

There are various ways to treat oily wastewater; different treatment strategies are required to remove different components and forms of oil from oily wastewater (Tanudjaja et al., 2019; Brookes, 2005). The traditional methods of treating oily wastewater use physical, chemical, or biological methods, each having its strengths and disadvantages (Abuhasel et al., 2021). These methods' primary problems include long treatment times, high operative costs, high chemical consumption, high energy requirements, and production of secondary pollutants (Capodici et al., 2017; Di Bella et al., 2015). Consequently, researchers' interest has shifted to improving biological treatment as an alternative and more affordable option (Capodici et al., 2017). Recently membrane bioreactors (MBRs) have gained popularity for treating saline wastewater characterized by elevated organic content and petroleum

hydrocarbon (Di Bella et al., 2015). MBRs produce high-quality effluent, have slow sludge production rates, and have a small footprint by having an enhanced ability to remove contaminants and generate smaller amounts of sludge than traditional methods (Ghimire & Wang, 2019; Tan et al., 2019; Capodici et al., 2017; Di Bella et al., 2015). This thesis investigated the use of a submerged hollow fiber (HF) membrane bioreactor as the final polishing step of a treatment train, which would reduce oil concentrations well below 15ppm and eliminate the "priority" PAH contaminants of concern before the water is discharged back into the ocean.

There have been numerous MBR studies that have evaluated submerged HF-MBRs for the treatment of oily wastewaters (Capodici et al., 2017; Campo et al., 2016; Cosenza et al., 2017; Di Bella et al., 2015; Kose et al., 2012; Di Trapani et al., 2011). HF membranes are robust systems that allow for aeration in the membrane tank, have high membrane flux due to higher packing densities, and low membrane fouling incidences (Altinbas et al., 2021; Akhondi et al., 2017; Wan et al., 2017). HF membranes were chosen to be tested in the pilot-scale membrane filtration experiments of this study, as there is future potential to add activated sludge into the system to drive aerobic biological processes. Activated sludge refers to biological treatment processes that uses suspended growth of microorganisms to remove contaminants (SSWM, 2019).

Previous studies revealed that although MBRs are proven to be effective in treating oily wastewater from refineries and other aspects of the oil and gas industry, there have not been any studies for its use as an onsite treatment for oily wastewater generated from marine oil spill response (Campo et al., 2017; Capodici et al., 2017; Mannina et al., 2016; Di Bella et al., 2015; Razavi & Miri, 2015; Di Trapani et al., 2014; Sharghi et al., 2013). One of the

main concerns for its use as an onsite treatment system is the long treatment times the biological component will need to effectively remove the harmful components in oil from the incoming emulsified oily wastewater (Webb, 2005). One of the requirements for an onsite oil spill response is fast treatment times; typical hydraulic retention times (HRT) used for oily wastewater treatment are greater than 10h (Soltani et al., 2010). To address this gap, the present study used HRTs of 3 and 6h to test the extent of biological treatment's contribution to the bench-scale MBR system. Alongside the MBR experiments, a pilot-scale membrane filtration set-up was also used to determine oil removal efficiency and maximum oil concentration that the system can handle without adding activated sludge. The performance of the two systems was evaluated to determine the better treatment method and to justify adding activated sludge to the pilot-scale membrane filtration system to improve its performance in terms of removal efficiency and capacity for handling higher initial oil concentration (membrane filtration vs MBR).

MBRs generally operate at high mixed liquor suspended solids (MLSS) concentration (3.5 to 8 g/L) that is achieved through long sludge retention times (SRTs) and biomass acclimation to the wastewater environment to ensure stable conditions in the bioreactor (Ghimire & Wang, 2019; Campo et al., 2017; Capodici et al., 2017; Di Bella et al., 2015; Razavi & Miri, 2015; Di Trapani et al., 2014; Kose et al., 2012; Radjenović et al., 2008; Le-Clech et al., 2006). The greater the MLSS, the lower the organic loading rate (OLR), up to a certain point, and the better the treatment efficiency (Iorhemen et al., 2016; Isma et al., 2014). In an oil spill scenario, there would not be enough time to cultivate a large bacterial population that is acclimated to a particular oily wastewater. To address this issue, the study was conducted using activated sludge collected from an industrial wastewater plant that

treats saline oily wastewater. The activated sludge obtained was not acclimated to the lab saline oily wastewater conditions and was used directly for the experiments. The study was conducted to determine the treatment efficiency of the bench-scale MBR under unsteady state conditions and to determine if it performed better than the membrane filtration experiments.

Lastly, the release of polycyclic aromatic hydrocarbons (PAH) into the environment is a major concern of the Canadian government, which is one of the determining factors prohibiting the release of decanted oily seawater back into the ocean from marine oil spill operations (Adams et al., 2017). There have been numerous MBR studies that assessed the efficiency of this technology in removing total petroleum hydrocarbons (TPH) from oily wastewater sources. However, there is a paucity of information in published literature on the removal efficiency of PAH and other priority contaminants in these systems (Ghimire & Wang, 2019; Tan et al., 2019; Capodici et al., 2017; Campo et al., 2016; Cosenza et al., 2017; Di Bella et al., 2015; Kose et al., 2012; Di Trapani et al., 2011). To address this gap, this thesis investigated the removal of 18 "priority" contaminants, defined by Environmental Climate Change Canada (ECCC), using a membrane filtration system and an MBR. The removal of PAH would render the decanted water non deleterious to marine life. The performance of the two systems was evaluated against each other, and the final PAH concentration results from both systems were compared to that of the freshwater and marine water PAH limits for Canadian water quality standards to justify the use of oil decanting practices in Canada.

1.2. Research Objectives

The ultimate goal of this research, was to investigate different membrane filtration system designs for onsite treatment of decanted oily wastewater for possible integration into Canadian spill response practices. The specific objectives of this thesis were as follows:

- Investigate the use of membrane filtration as an onsite treatment technology for marine oil spill operations by comparing the oil removal capabilities of a microfiltration (MF) membrane filtration and an MBR system operated with MF.
- Determine if the two membrane systems could effectively remove "priority" PAH contaminants from oily wastewater to acceptable Canadian water quality standards and evaluate which system performed the best.
- Evaluate two different HRTs to determine the best operational parameter for oil removal efficiency with MBR treatment.

These objectives were achieved by determining the performance and capacity of both MF membrane filtration and MBR systems. The MF membrane pilot-scale system acted as a physical barrier that allowed the passage of select molecules and blocked the passage of undesirable ones. The MBR bench-scale system had an extra step where biomass in activated sludge contributed to biodegradation and/or acted as an adsorbent that trapped the oil before the wastewater was physically filtered through the membrane. The biological contribution of the MBR system was also determined to assess its impact on oil removal. Both systems were tested for TPH, PHC (F1-F3), and PAH removal efficiencies. Combining activated sludge with the MF-HF membrane unit is a promising treatment technology to be used as part of an onsite treatment train for decanted oily wastewater generated from oil spill response.

1.3. Thesis Outline

This thesis is divided into five chapters. Chapter 1 discusses the project's background, the problem that this research is trying to solve by identifying gaps within the status quo, the research objectives, and the outline of this thesis.

Chapter 2 provides a literature review of the different sources of oily wastewater generated from the petrochemical industry; the cause and effects of marine oil spills; Canadian oil spill response regulation structure; Canadian oil spill response practices; discusses conventional oily wastewater treatment methods; the basics of MBRs; how bacteria degrade hydrocarbons; and lastly, the various operational parameters to consider that affect the biomass within an MBR when treating oily wastewater.

Chapter 3 provides overviews of the materials and methods used to achieve the research objectives. This chapter reviews the methods used for oil characterization, synthetic oily seawater preparation for bench- and pilot-scale experiments, the experimental design for both sets of experiments, and the analytical methods used to evaluate the performance of the experiments.

Chapter 4 presents the results from the pilot-scale MF and bench-scale MBR treatment systems and discusses the treated water quality for the different analyses (TPH, PAH, PHC removal efficiencies) and compares the two membrane system designs with each other.

Chapter 5 summarizes the main findings of the study and indicates further research needs in the subject area. References are also provided in the last section of this thesis.

CHAPTER 2: LITERATURE REVIEW

2.1. Sources of Oily Wastewater

Petroleum oil is a valuable strategic resource for which countries compete aggressively. Anthropogenic activities depend on oil to meet their energy demand, causing the petrochemical industry to thrive, with its demand expected to rise in the following years (Ojagh et al., 2020; Afzal et al., 2019; Xu et al., 2018). With the rise in the use of crude oil, large volumes of oily wastewater from the petrochemical industry have been discharged into the environment, causing serious environmental harm (Tan et al., 2019; Xu et al., 2018). Crude oils are predominantly hydrocarbons, molecules made up of carbon and hydrogen, with hydrogen-to-carbon ratios ranging between 1.5 to 2. There are over 17,000 organic compounds found in crude oil, which can be classified into four main categories: paraffin, aromatics, asphaltenes, and resins (Wang et al., 2016; Brooijmans et al., 2009). Paraffin are saturated linear chains ranging from a single carbon (methane) to waxes, containing more than 40 carbon chains. Aromatic species are benzene rings containing pendant alkyl groups (Wang et al., 2016; Prince & Atlas, 2014). All aromatic compounds contain at least one benzene ring; the unsaturated rings react readily due to the lack of hydrogens. Aromatics are extremely recalcitrant because of their high molecular weight, strong molecular bonds, hydrophobicity, and low water solubility (Ubani et al., 2013). Approximately 15% of crude oil contains heteroatom molecules, such as oxygen, sulphur, and nitrogen, known as polars, asphaltenes, resins, or NSO (Prince & Atlas, 2014).

The drilling, extraction, refining, processing, storage, and transportation of crude oil produce lots of oily wastewater (Afzal et al., 2019; Xu et al., 2018; Yu et al., 2017). Petrochemical wastewater, such as oilfield-produced water, is generated during oil

extraction from onshore and offshore wells, which comprise of high concentrations of artificial surfactants, polymers, radioactive substances, benzenes, phenols, humus, PAHs, and emulsified crude oil and are characterized by high chemical oxygen demand (COD) and low biodegradability (Kuyukina et al., 2020; Ghimire & Wang, 2019; Tanudjaja et al., 2019). Petroleum processing and refinery wastewater can differ vastly in composition depending on the operational units for various products. Oil refineries can produce over 2500 refined products that contain different concentrations of ammonia, sulfides, phenols, benzo, and other hydrocarbons (Kuyukina et al., 2020; Ghimire & Wang, 2019).

Once extracted, crude oil must be carried from extraction wells to oil refineries; after the finished product is obtained, it must be delivered from refineries to distributors. Today, oil tankers are the only option to transport crude oil across oceans worldwide. Between filling and drawing crude oil from and into the oil tankers, the hulls are cleaned with salt water to remove hydrocarbons from the tankers' walls. This operation generates a shipboard industrial effluent known as "slop," distinguished by elevated salt, hydrocarbon, and other organic contaminant concentrations (Kuyukina et al., 2020; Campo et al., 2017).

Marine oil pollution caused by the illegal discharge of bilge water and oil spill accidents from tankers or offshore drilling platforms has become an increasingly serious environmental and safety issue (Han et al., 2019). It has been reported that approximately 140 large spills occurred between 1907 and 2014, releasing over seven million tons of oil into the marine environment. The most common oil spill response method is mechanical containment and recovery, which is known to generate large amounts of oily wastewater; the volume of oily wastewater generated from oil spill response operations is contingent on the type and volume of spilled oil, oil characteristics, weather conditions, and response time

(Hosseinipooya et al., 2022). Oil products contain volatile organic compounds (VOCs), PAHs, and other toxic compounds that affect the growth and reproduction of marine organisms, consequently reducing their diversity (Mansir & Jones, 2012).

2.2. Marine Oil Spills

The rate at which the oil from marine oil spills spreads into the environment varies depending on ocean currents, temperature, and weather (Mansir & Jones, 2012; EPA, 1999). The occurrence of oil spills causes severe environmental damage, with many short- and long-term repercussions (Mansir & Jones, 2012). Some short-term effects of these events are direct harm to wildlife in the area; it increases the mortality rate in animals such as birds, marine mammals, and fish. The oil damages animals' fur insulation and water repellency, subjecting them to harsh elements. Due to the lack of protection from the cold water, the animals exposed to the oil often die from hypothermia (NOAA, 2020). Marine mammals exposed to the oil spill inhale the oil, which causes lung and immune function damage, and reproductive disorders (NOAA, 2020; Mansir & Jones, 2012). Fish, shellfish, and corals are not immediately exposed to the oil; these animals come into contact with it once it mixes into the water column. The harmful compounds eventually begin to bioaccumulate in fish, making them unsafe for human consumption (NOAA, 2020). Long-term damages from oil spill adversely affect native vegetation, wildlife, and the food chain and negatively alter the local environment's chemical and physical aspects (Han et al., 2019; Mansir & Jones, 2012).

Canada's coastline is over 243 000 kilometres long, making it the longest coastline in the world. Roughly 180 vessels carrying more than 80 million tonnes of oil travel through Canada's Exclusive Economic Zone (EEZ), putting Canada at a high risk of oil spill

incidents (Lee et al., 2020; TC, 2019). Over the past 52 years, there have been six major oil spills that have devastated local ecosystems and communities:

- 1970: The SS Arrow tanker ran aground in the Atlantic Ocean near Nova Scotia off Chudabucto Bay, spilling around 10 million litres of fuel oil, making it Canada's largest oil spill (Clearseas, 2020; SOPF, n.d.).

- 1970: The Irving Whale oil barge sank off Prince Edward Island's north coast with a cargo of oil on board.

- 1979: The Kurdistan broke in two, spilling 7 500 tonnes of oil into the southern entrance of Cabot Strait (SOPF, n.d.)

- 1988: A tug crashed with the Nestucca fuel barge off the coast of Washington state, spilling 875 430 litres of fuel oil that washed ashore, reaching parts of British Columbia. This oil spill was the largest spill on Canada's pacific coast (Clearseas, 2020; SOPF, n.d.).

- 1990: The Rio Orinoco carrying 9,080 tonnes of liquid asphalt, ran aground on the south shore of Anticosti Island in the Gulf of St. Lawrence, spilling 200 tonnes of fuel oil (SOPF, n.d.)

- 2016: The Nathan E. Stewart tugboat ran aground off Bella Bella, BC, spilling 110 000 litres of diesel fuel. This is Canada's most recent significant oil spill (Clearseas, 2020)

Residue from these oil spills still present today, particularly from the SS Arrow, the largest oil spill in Canadian history, led to an increase in scientific and public awareness of the threats of oil spills to coastal systems, marine wildlife, and fisheries. The call for enhanced

marine environmental protection and effectual emergency response measures was made evident (Lee et al., 2020).

The present research will focus on oily wastewater generated from marine oil spills that are physically and chemically complex. New strategies for more effective and efficient oil spill clean-up operations are needed to improve the status quo. Before assessing current technologies and the proposed technology for oily wastewater treatment, a good understanding of the current Canadian oil spill operations is needed.

2.3. Canadian Oil Spill Response Regulation Structure

The Canadian environmental response system is responsible for developing and administering policies, regulations, and programs to protect the marine environment, lessen the effects of marine pollution incidences in Canadian waters, and ensure general public security. One of the most significant programs under the Environmental Response Systems' mandate is Canada's Marine Oil Spill Preparedness and Response Regime (TC, 2019). Environmental response systems work with other federal agencies and departments, including Transport Canada (TC), Fisheries and Oceans Canada (DFO), the Canadian Coast Guards (CCG) and Environment Canada, to establish guidelines, regulatory framework, and mechanisms for the oil spill preparedness and response regime (TC, 2019). TC is the lead federal regulatory agency responsible for the Regime, which relies on the collaboration between government and industry. The industry is obligated to take sufficient preventative actions and ensure an efficacious response plan and preparedness are available under the polluter responsibility principle. It is the responsibility of the Federal Government to ensure the fulfillment of public interests (TC, 2019).

2.3.1. Canada Shipping Act

Under the guidance of the Canada Shipping Act, 2001 (CSA 2001), the Arctic Waters Pollution Prevention Act, and international conventions and standards established by the International Maritime Organization (IMO), TC regulations and standards provide the framework for the department's comprehensive marine safety, pollution prevention, enforcement, and oil spill preparedness and response programs.

CSA 2001 is the primary legislation supervising Canadian and foreign ships' activities in Canadian waters. The responsibility of managing CSA 2001 is split between The Minister of Fisheries and Oceans and the Minister of Transportation. It is stated in the CSA 2001 regulations that the party accountable for a pollution incident is liable for shouldering preparedness measures, paying for the repairs, and alleviating damages to the marine environment. Various ships and oil handling facilities (OHFs) are required to have an Oil Pollution Emergency Plan in place with a government-certified response organization (RO). ROs are Canadian-based, private-sector organizations obligated to be certified by the Federal Government by proving their competence in preparing and responding to marine ship source pollution (TC, 2019). TC ensures that industry, vessels, and OHFs have a suitable level of preparedness available for responding to marine oil spill incidents in Canada of up to 10 000 tonnes within a reasonable time frame, contingent on operating environments, covering marine regions south of 60◦N latitude. The Regime is developed on the principle of cascading resources, meaning that in the event of a spill, the resources of a particular region can be supplemented with those from other areas or international partners, as needed. The CCG also reserves a substantial preparedness capacity to accompany the Regime capability. CCG's capacity functions as a "safety net" that can offer

instant response capability where needed and is accountable for responding to marine spills north of 60Ṅ latitude (TC, 2019).

2.3.2. International Maritime Organization Convention and Standards

The international conventions and standards developed by the IMO and its members, including Canada, strive to promote worldwide cooperation in mitigating pollution and the risk of major incidents. The conventions and standards address matters such as ship construction, training and crew qualifications, and navigation safety. The international agreements that allow Transport Canada to accomplish its roles in the prevention and preparedness of marine oil pollution incidents are the following:

The International Convention for the Preparedness of Pollution from Ships (MARPOL) aims to eliminate intentional marine pollution and reduce accidental discharges of pollutants from shipping operations. International regulation regarding the discharge of oil from vessels is contained in Annex I of the MARPOL Convention. MARPOL prohibits the discharge of oil or oily mixtures into the sea, except when the content of undiluted effluent does not exceed 15ppm. However, there is a stipulation under the MARPOL convention for discharge in the case of oil spill operations, such that the regulation shall not apply to "the discharge into the sea of substances containing oil, approved by the Administration when being used for the purpose of combating specific pollution incidents in order to minimize damage from pollution. Any such discharge shall be subject to the approval of any Government in whose jurisdiction the contemplated discharge will occur" (IPIECA, 2013). In Canada, it is illegal to discharge decanted water from marine oil spill response due to the concern of the "priority" PAH contaminants found in crude oil (ClearSeas, 2020; Adams et al., 2017; IPEICA, 2013).

International Convention on Oil Pollution Preparedness, Response and Cooperation is a framework that permits Canada to support major incidents in other member states when requested and to obtain assistance from international colleagues when needed (TC, 2019).

TC establishes the guidelines and regulatory structure for marine oil spill preparedness and response. TC is responsible for ensuring the following:

- Effective and responsive legislation,

- Potential polluters pay for preparedness,

- Polluter pays for reasonable response costs,

- The partnership with industry,

- Comprehensive contingency plans,

- Mutual agreements with neighbours (TC, 2019).

2.3.3. The Canada Fisheries Act

The Fisheries Act is the primary federal legislation to manage and protect fisheries resources. The Act prohibits the discharge of deleterious substances into water frequented by fish or any place where the harmful substances may enter the waters frequented by fish. Deleterious substances are described as any substance that, if added to any water, would degrade or change the water quality in a way that could directly or indirectly harm fish, fish habitat, or humans through fish consumption (TC, 2010). Petroleum products such as oil, gas, diesel, grease, and oily mixtures are one of the substances considered to be deleterious (Canada, 2022). Part III of the Oil Pollution Prevention Regulations specified the general prohibitions and exceptions concerning oil and oily mixture discharges. The regulations state, "No oil or oily mixtures shall be discharged from a ship in waters under Canadian

jurisdictions." Waters under Canadian jurisdiction are divided into various zones with different restrictions regarding oil discharges.

Canada's EEZ is adjoining the territorial sea of Canada, the EEZ has as its inner limit the outer limit of the territorial sea, and the outer limit of the EEZ is 200 nautical miles from the baseline of Canada's territorial seas. Canada's internal waters comprise of waters on the landward side of the baseline of Canada's territorial seas. Internal waters are divided into two categories:

- Division I includes fishing zones 1, 2, and 3 and internal waters not within a shipping safety control zone.
- Division II: include territorial sea and portions of fishing zones 4, 5, and 6 that are not within a shipping safety control zone.

Canada's inland waters are considered to be all the rivers, lakes, and other navigable fresh waters.

When discussing zones, the following need also to be considered:

- Shipping safety control zones: are described as the areas of arctic waters in Schedule II and zones specified in Schedule I of the Shipping Safety Control Zones Order.
- Fishing zones 1, 2, and 3: are marine areas adjoining the coast of Canada designated by the Ocean Act and the Fishing Zones of Canada Order.
- Special areas: are described in the MARPOL Convention Annex I.

The ban on the discharge of oil or oily mixtures is withdrawn in emergency situations where it is inevitable or necessary. The following situations are examples of when a ship is exempt

from the discharge regulations set out by the Prevention of Pollution from Ships and for Dangerous Chemicals Regulations:

- If the discharge of oily waste is intended to save lives or halt the instant loss of a ship.

- If the discharge is the consequence of a navigation accident or equipment damage unless the accident results from no ordinary practice actions.

- When slight leakage happens because of underwater operational machinery components.

- If the discharge is for scientific research into pollution reduction or control, competent authorities must grant permission to run these sorts of experiments.

In general, a maximum of 5 ppm of an oily mixture can be discharged from a ship into Division I waters only:

- When the ship's engine has just been stopped, the vessel continues going through the water, still creating a wake.

- No oily mixture is derived from the cargo pump room bilges or is mixed with oil cargo residues.

- The discharge is filtered through equipment, resulting in an undiluted effluent of a maximum of 15ppm oil concentration. It activates an alarm and a discharge-stopping device as soon as the effluent concentration surpasses 5ppm when oily mixtures are discharged in inland waters or when it surpasses 15ppm in Fishing Zones 1, 2, and 3 or in internal waters that do not include Canada's inland waters.

Discharge should not be mixed with chemicals or other substances presented into oily wastewater to evade oil concentration detection that surpasses oil content limits specified in the regulations (TC, 2010).

2.4. Canadian Oil Spill Response Practices

Current practices for cleaning up oil spills in Canada involve containing the oil to restrict environmental damage and collecting as much oil as possible. Containment booms are the first line of defence to stop the slick from spreading and reaching sensitive shorelines and habitats (Clearseas, 2020). Once the oil is contained, the responders evaluate various response measures to minimize the damage to people and the environment; this is done through a Net Environmental Benefit Analysis (NEBA). Before a NEBA analysis, responders determine potential scenarios for the spill for a specific location. Once the scenarios have been determined, the possible impacted environmental and community assets are identified and prioritized. NEBA is subsequently used to balance the tradeoffs and choose a suitable response option to mitigate a potential spill's effect on the assets (NEBA, n.d.) NEBA helps the responders assess safety issues, societal impacts, and environmental considerations to determine the ideal response approach (NEBA, n.d.)

There are four different approaches that Canadian responders can choose from:

- Natural Recovery
- Chemical Oil Dispersants
- In-situ burning
- Mechanical Recovery

Natural recovery allows the spilled oil to disperse naturally and is generally used when the weather conditions are harsh or when the spill occurs far from shore. Strong winds, ocean currents, and waves create unsafe conditions for responders and make mechanical recovery challenging or impossible. Under severe weather conditions, the oil disperses and breaks down more quickly. Once the oil is sufficiently dispersed, the ocean's indigenous bacteria can degrade it, breaking it down into a less harmful substance. When natural recovery is chosen, the response teams still closely monitor the spill in case additional measures need to be taken later on (Clearseas, 2020).

Chemical oil dispersants are an internationally used response method; however, they are currently under study in Canada. Dispersants are valuable when used to treat large slicks, to limit the effect of oil on sensitive habitats, wildlife, or shorelines, and respond to oil spills that occur during harsh weather conditions. Chemical oil dispersants are applied to a spill using an aircraft or vessel equipped with spraying arms to rapidly break down oil into small droplets. The natural bacteria then degrade the small droplets in the ocean (Clearseas, 2020). Dispersants used in any country must be tested by respective government agencies and approved. In Canada, ECCC has approved only two products, an oil dispersant and a shoreline treating agent. They are not approved for general use; therefore, their use is assessed on a case-by-case basis (Clearseas: Research Spotlight, 2020).

In-situ burning is used once the oil has been concentrated in an enclosed area using fire-resistant booms. The oil is ignited to burn it off from the water's surface. In-situ burning is used under calm weather conditions for spills away from shorelines and populated areas. This method is effectively used to reduce a thick slick of oil quickly. In-situ burning is used in Canada on a case-by-case basis (Clearseas, 2020). Canada's response capacity is

generally hindered by the lack of available tools to respond to an oil spill quickly, unlike other countries. The use of majority of the response tools are used on a case-by-case basis and need approval by the government once an oil spill scenario has been assessed.

Mechanical recovery is Canada's most frequently used method for responding to oil spills. After the booms have concentrated the oil in an enclosed area, skimmers are deployed to collect it. Skimmers can collect anywhere between 10-70% water depending on weather conditions and oil properties. Wave conditions resulting from changing weather contribute to variations in oil thickness, shearing of slick surface and mixing of oil with underlying water. The oil's viscosity also plays a key role in the efficiency of skimmers in collecting oil. For instance, light crude oils do not easily accumulate in thick layers on the surface of oleophilic skimmers; as a result, a lot of water gets collected. On the other hand, heavy and viscous crude oils are sticky and difficult to remove from the surface of skimmers; as a consequence, once the skimmers are saturated, it begins to accumulate more water (ClearSeas, 2020; Lee et al., 2015; IPEICA, 2013).

Since the skimmers collect an enormous amount of water, approximately 50-60% of the storage space on the barges is taken up by seawater. All fluids collected on the barges are transported to shore to intermediate storage facilities before being transferred to final disposal sites (TC, 2020; IPEICA, 2013). If any part of the waste stream is overwhelmed, response operations must be halted until sufficient capacity becomes available (IPEICA, 2013). The inefficiency of skimmers drastically constrains the response capacity and efficiency, requiring additional storage barges and frequent trips back to shore to dispose of the wastewater. The lack of capacity results in the propagation of oil further into the

ocean or the shoreline, where it wreaks havoc on wildlife, human health, and the local economy, resulting in compounding environmental harm (Liu et al., 2022).

This research will focus on how to increase mechanical recovery efficiency and effectiveness. Decanting wastewater collected from marine oil spill operations is proven to increase the response capacity of clean-up operations. European Maritime Safety Agency (EMSA), including members of the European Union and some of the adjoining countries such as Norway, Iceland and candidate Member States, allows for decanting surplus water from oil spill clean-up operations to maximize onboard storage space. The excess water discharged from the vessel to the marine environment must obey the international MARPOL standard of oil content of 15ppm or less (EMSA, 2010). The US also allows for decanting of oily wastewater as long as the effluent concentration is less than 15ppm. Although the US authorizes decanting practices, permits must be obtained before this response method is used (ISCO, 2022; PWSRCAC, 2017). While Europe and the US allow for decanting practices, Canada prohibits it due to the concern of releasing "priority" PAH contaminants found in oily wastewater back into the marine environment (Adams et al., 2017). The prohibition of discharge from oil spill responders for operational purposes drastically hinders response operations as it limits temporary storage space on barges and requires several cycles of trips to shore to transfer the wastewater to an intermediate storage facility. The lack of response capacity does not allow quick and effective recovery of the spilled oil, instead permits its propagation further into the ocean or shorelines, causing compounding environmental damage.

This research proposes using a membrane bioreactor as a part of a decanting system on a barge to treat the oily wastewater collected by skimmers to increase the capacity and

efficacy of response operations. The HF-MBR aims to reduce the discharge's oil concentration to less than 15ppm and eliminate the "priority" PAH contaminants from the oily wastewater. Before analyzing the effectiveness of MBRs in treating oily wastewater, other conventional oily wastewater treatment methods will be discussed, along with an introduction to the main functions of an MBR system.

2.5. Conventional Oily Wastewater Treatment Methods

Conventional oily wastewater treatment methods can be classified into three approaches, chemical, physical, and biological (Bhattacharyya et al., 2022; Abuhasel et al., 2021).

2.5.1. Physical Treatment Methods

Gravity separation is a simple and low-cost method that uses the difference in density between oil and water to promote separation. It is most effective at treating low-density and viscosity oils due to the greater density distinction between the oil and water (Ubani et al., 2013; Stewart & Arnold, 2009). This process is suitable for separating free and dispersed oil (Abuhasel et al., 2021). Gravity separation, however, requires a large area for setup and is not effective at separating emulsified oil (Bhattacharyya et al., 2022; Abuhasel et al., 2021; Han et al., 2019).

Dissolved air floatation (DAF) is a physical treatment system that presents pressurized air at the base of a basin, and as the fine bubbles rise, it attaches to the oil droplets, carrying oil to the top of the tank (Abuhasel et al., 2021). Since oil density is lighter than water, the layer of scum remains separated from the water and is skimmed off (Yu et al., 2017). DAF produces a high-quality effluent that is effective at separating emulsified oil; additionally, it requires a much smaller footprint than gravity separation. One disadvantage of this

system is the high operational cost due to the generation of bubbles (Bhattacharyya et al., 2022; Nieuwan et al., 2018; Yu et al., 2017; Saththasivan et al., 2016).

Adsorption is a method where a solid adsorption material with suitable porosity and high surface area is utilized to absorb medium- to small-sized oil droplets from contaminated water (Abuhasel et al., 2021; Ghimire & Wang, 2019; Han et al., 2019). Conventional adsorption materials, such as zeolite and activated carbon, have a high cost, long adsorption times, and limited adsorption capacity. Currently, research has been focused on developing cheaper new materials, such as foam, biomass, metal-organic framework, chitosan, cotton, sponge, and magnetite nanoparticles, to increase adsorption capacity. Although adsorption methods are easy to use and effective, they generate by-products that need further treatment (Bhattacharyya et al., 2022; Abuhasel et al., 2021).

Filtration is another physical treatment option that permits the passage of water through a porous media and retains emulsified or dispersed oil droplets in the membrane tank. Examples of membrane materials are mesh, porous hydrogel, aerogel, textile, and membranes (Han et al., 2019). This method can also recover oil and remove other pollutants from the wastewater. Some disadvantages of this process are the high energy requirement and frequent media cleaning or replacement because of fouling events (Bhattacharyya et al., 2022; Mohammadi et al., 2020; Kundu et al., 2018).

2.5.2. Chemical Treatment Method

Coagulation and flocculation is a chemical treatment method where a flocculant is added to the wastewater to counteract the negative charges of the emulsified or dispersed oil droplets by neutralizing their charge to help link particles to form larger flocs (Abuhasel et

al., 2021; Yu et al., 2017; Wen et al., 2016). This process is easy to use and has lower capital and operational cost than DAF and biological technologies (Abuhasel et al., 2021; Zhao et al., 2020; Yu et al., 2017; Wen et al., 2016). The effectiveness of coagulation and flocculation relies on flocculant type, dosage, and the wastewater's initial oil concentration, temperature and pH. Both inorganic and organic flocculants are used for the treatment of oily wastewater. Some commonly employed cheap and simple-to-use inorganic flocculants are aluminum sulfate, polymerized ferrous sulfate, and poly-aluminum chloride (PAC); however, they display low flocculation efficiency and typically require wastewater pH adjustment. Organic flocculants, such as polyacrylamide, can achieve higher flocculation at lower dosages than inorganic flocculants and can be effectively used at wide pH ranges. The problem with organic flocculants is that they present a hazard to the environment and human health as they are challenging to biodegrade (Bhattacharyya et al., 2022; Abuhasel et al., 2021). Major disadvantages of the coagulation and flocculation method as a whole are that it produces large quantities of sludge that require secondary treatment and do not work effectively when surfactants are present (Abuhasel et al., 2021; Zhao et al., 2020; Han et al., 2019; Yu et al., 2017; Wen et al., 2016).

2.5.3. Biological Treatment Methods

Biological treatment methods rely on bacterial metabolism to break down hydrocarbons. Conventional activated sludge (CAS) is an aerobic biological treatment that uses suspended microbial floc to treat emulsified or dissolved oil in wastewater (Adetunji & Olaniran, 2021; Han et al., 2019). It is an inexpensive process that does not require adding chemicals during treatment; however, it requires a large area, long treatment times, and has low treatment capacity (Han et al., 2019; Kundu et al., 2018).

In biofilm treatment methods, a biofilm is formed by growing microorganisms on a filter material or carrier; when the wastewater contacts the biofilm, the microorganisms metabolize the organic pollutants, using them as nutrients (Han et al., 2019). The support material of the biofilm protects the microorganisms from harsh wastewater conditions, such as high pollutant concentrations and mechanical stress, increasing the survival rate of the immobilized cells and their pollutant biodegradation capabilities. Immobilizing microorganisms in an appropriate matrix is advantageous for treating heavy oil-polluted wastewater (Bhattacharyya et al., 2022; Adetunji & Olaniran, 2021; Lee et al., 2001). Although this method is very effective, the multiple cell layers that develop on the carrier material cause diffusion resistance of substrate and nutrients to the microorganisms, limiting operational time and decreasing treatment effectiveness (Kundu et al., 2018). Novel technologies that use biofilms include moving bed bioreactors (MBBR) and sequential batch biofilm reactors (SBBR) (Bhattacharyya et al., 2022; Han et al., 2019).

Each treatment method effectually treats certain aspects of the complex oily wastewater generated from the petroleum industry. Therefore, integrating different traditional treatment methods into a single train is the only way to meet discharge or water reuse standards for oily wastewater (Bhattacharyya et al., 2022; Abuhasel et al., 2021). Typically, the first step in an integrated system is a physical treatment to remove free and dispersed oil, followed by either a chemical or biological treatment to remove emulsified oil (Kuyukina et al., 2020). The standard methods for treating oily wastewater cannot be used as standalone systems as they require a lot of space, have high energy consumption, have long treatment times, and produce secondary pollutants; therefore, it is crucial to find new

technologies to overcome these limitations (Bhattacharyya et al., 2022; Abuhasel et al., 2021; Cosenza et al., 2017).

2.6. Membrane Bioreactor for Oily Wastewater Treatment

A membrane bioreactor is a promising treatment that can easily be integrated with other advanced technologies that have proven to be effective at treating oily wastewater generated from the petrochemical industry. A membrane bioreactor combines biological and physical treatments; it is easy to operate, generates high-quality effluent, and has slower sludge production than CAS (Ghimire & Wang, 2019; Han et al., 2019; Tan et al., 2019; Iorhemen et al., 2016; Zhidong et al., 2009; Judd & Judd, 2006.).

2.6.1. HF Membrane

Membranes are semi-permeable barriers through which selectivity between species can be obtained to separate unwanted and wanted particles. They allow the passage of desired species and block the passage of undesirable ones (Kang et al., 2019). Membrane technology is capable of removing stably dispersed oil droplets (<10 µm) in wastewater (Gao et al., 2021; Dickhout et al., 2017).

Ideally, the membranes must be able to maintain their integrity for a wide range of chemicals, pH, and heat and have sufficient mechanical strength to accommodate changes in membrane flux (Han et al., 2019; Kang et al., 2019). There are various ways to prepare membranes depending on the morphology required to treat different types of wastewater; for oily wastewater treatment, HF polymeric membranes are typically prepared using phase inversion or electrospinning (Ismail et al., 2020). Phase inversion changes the thermodynamic state of a homogenous polymer solution by contacting it with another phase

(liquid or vapour); this promotes the formation of the solid phase helping produce a microporous polymeric membrane (Tang et al., 2021; Chanupanich et al., 2005). Electrospinning produces nano to micrometre-sized ultra-thin spun polymer fibres forming either a nonwoven or persistent web of nanofibers with an intricate pore structure (Barani et al., 2021). Electrospinning creates high porosity membranes with relatively uniform pore sizes and distribution, which are highly interconnected compared to membranes created through phase inversion (Ahmed et al., 2015).

Some common materials used to create polymeric membranes are polyvinylidene difluoride (PVDF), polyethylene (PE), polyacrylonitrile (PAN), and polytetrafluoroethylene (PTFE) (Ismail et al., 2020; Baig et al., 2021). Polymeric membranes are hydrophobic and thus susceptible to high membrane fouling rates; the manufacturers modify the membranes to improve their performance (Ismail et al., 2020). The hydrophobicity of the membranes is altered through surface modifications using hydrophilic polymers or by coupling various manufacturing techniques to enhance the membrane performance. The resulting hydrophilicity aids in preventing oil droplets from blocking the membrane surface, improving treatment efficiency and extending the membrane's life (Zulkefli et al., 2021; Mutamin et al., 2012; Chanupanich et al., 2005). The membrane surface is modified to have the same charge as the foulants in the wastewater, which creates repulsive electrostatic forces that decrease fouling events (Yang et al., 2021; Zhou et al., 2009). MF and Ultrafiltration (UF) membranes are most commonly used for oily wastewater treatment due to their low-pressure operation capabilities (Abuhasel et al., 2021; Tanudjaja et al., 2019).

Hollow fibre (HF) membranes are the favoured membrane configuration for oily wastewater treatment since they are compact modules with self-supporting structures with high membrane surface area, meaning they can handle higher membrane flux. Additionally, they are capable of movement with the help of aeration. Previous studies established that aeration intensity improves the hydrodynamics of the membrane filtration system; air bubbles alter the structure of the fouling layer, resulting in a decrease in specific resistance (Wibisono et al., 2014; Cabassud et al., 2001). In other words, membrane fouling is reduced through inter-fibre interactions and bubbles scouring the membrane surface, resulting in mechanical erosion of the foulant layer (Pourbozog et al., 2017; Bréubé et al., 2006). Selecting an optimum air flow rate is essential for treatment efficiency; a higher aeration flow rate than the critical value has exhibited to have no effect on system performance, whereas a low aeration flow rate does not provide good hydrodynamic conditions for the membranes (Bouhabila, 2001; Ueda et al., 1996). The location of aerators in the HF membrane filtration system was also studied, the results indicated that the injection of air at the bottom of the membrane fibre improved the overall system performance (Guibert et al., 2002). Lastly, HF membranes can be backwashed, reducing pore blocking and prolonging the membrane's life (Obotey et al., 2020; Salahi et al., 2015; Kose et al., 2012; Judd, 2010; Radjenović et al., 2008; Frederickson et al., 2005).

2.6.2. Membrane Bioreactor

The bioreactor component contains activated sludge, which degrades hydrocarbons using microbial metabolism. The bioreactor permits greater precision control and management of biodegradation factors, including temperature, pH, oxygen, nutrients, and homogenous distribution of hydrophobic contaminants and biomass concentration (Kuyukina et al.,

2020). MBRs allow for higher mixed liquor suspended solids (MLSS) concentration and sludge retention times (SRT) than CAS, allowing the biomass to develop, adapt, and biodegrade oil more effectively (Bhattacharyya et al., 2022; Radjenović et al., 2008; Sutton, 2006). The treatment efficiency of the system can be controlled through operational parameters, such as mixed liquor suspended solids (MLSS), aeration rate, hydraulic retention time (HRT), sludge retention time (SRT), and membrane flux, to achieve optimal treatment conditions that improve membrane performance (Abuhasel et al., 2021; Adetunji & Olaniran, 2021; Tanudjaja et al., 2019; Iorhemen et al., 2016; Guo et al., 2012; Ji & Zhou, 2006; Le-Clech et al., 2006). Biodegradation is an essential feature of MBR that significantly affects the permeate quality when treating oily wastewater. MBRs are inoculated with activated sludge that contains bacteria that metabolize organic compounds in raw water.

Before discussing operational parameters that control the treatment efficiency of an MBR in depth, it is essential to understand the key biodegradation process that occurs within the bioreactor.

2.7. Biodegradation of Hydrocarbons by Bacteria

Since the discovery of the first hydrocarbon-degrading bacteria, over 175 genera of oil-degrading bacteria have been found. Bacteria from various phyla, such as Proteobacteria, Flexibacter-Cytophaga-Bacteroides (CFBs), Actinobacteria, and Cyanobacteria, were isolated from different environments, and their effectiveness at metabolizing hydrocarbons was established. Xu et al., 2018 summarize the main petroleum hydrocarbon biodegradation profiles of different bacteria (as shown in Table 2.1). The biodegradability of oil components generally declines in the sequence of n-alkanes, branched-chain alkanes,

branched alkenes, low-molecular-weight n-alkyl aromatics, monoaromatics, cyclic alkanes, PAHs, and asphaltenes (Xu et al., 2018; Das & Chandran, 2011; Yang et al., 2009). Alkenes and alkynes are linear unsaturated molecules uncommon in crude oils but are abundant in refined products such as gasoline (Prince & Atlas, 2014). Crude and refined oils are complicated products with varied physical and chemical properties depending on their composition and proportion. A slight variation in constituents can lead to an overall change in physical properties and chemical toxicity (Yang et al., 2009). Each bacterial strain can metabolize a specific type of hydrocarbon (Bhattacharyya et al., 2022; Godfrin et al., 2018). Most bacteria in a genus can only degrade a small range of hydrocarbons with similar structures. For instance, a genus can metabolize alkanes containing different carbon chain lengths, while another can utilize aromatic hydrocarbons with similar characteristics. A single bacterial strain or genus cannot degrade every oil component because of its complicated composition. For example, Alcanivorax metabolizes straight-chain or branched alkanes; Cycloclasticus is known for consuming PAH as a carbon source (Wang et al., 2016; Brooijmans et al., 2009). Effective biodegradation of various hydrocarbons found in oily wastewater involves a mixed population of hydrocarbon-metabolizing bacteria with adequate tolerance to environmental changes within a reasonable range for favourable microorganism activity (Bhattacharyya et al., 2022; Wang et al., 2016; Yang et al., 2009).

Table 2.1. Petroleum hydrocarbon biodegradation profile of bacteria (Xu et al., 2018)

Petroleum Hydrocarbon Components	Bacterial Species	Main Degradation Profile
Aliphatics	Dietzia sp.	n-alkanes (C6-C40)
	Pseudomonas sp.	n-alkanes (C14-C30)
	Oleispira antartica	n-alkanes (C10-C18)
	Rhodococcus ruber	n-alkanes (C13-C17)
	Geobacillus thermodenitrifican	n-alkanes (C15-C36)
	Rhodococcus sp.	Cyclohexane
	Alcanivorax sp.	n-alkanes and branched alkanes
	Gordonia sihwensis	Branched and normal alkanes
Aromatics	Achromobacter xylosoxidans	Mono-/polyaromatics
	Aeribacillus pallidus	Mono-/polyaromatics
	Mycobacterium cosmeticum	Monoaromatics
	Pseudomonas aeruginosa	Monoaromatics
	Cycloclasticus	Polyaromatics
	Neptunomonas naphthovoran	Polyaromatics
	Bacillus Licheniformis	Polyaromatics
	Bacillus mojavensis	Polyaromatics
Resins and asphaltenes	Sphingomonas, Sphingobium, and Novosphingobium	Polyaromatics
	Pseudomonas sp.	Resins
	Pseudomonas spp.	Asphaltenes
	Bacillus sp.	Asphaltenes
	Citrobacter sp.	Asphaltenes
	Enterobacter sp.	Asphaltenes
	Staphylococcus sp.	Asphaltenes
	Lysinibacillus sp.	Asphaltenes
	Bacillus sp.	Asphaltenes
	Pseudomonas sp.	Asphaltenes

Before bacteria can start metabolizing hydrocarbons, it needs to be able to access them easily. The proteins and lipids on the microbial cell surface and the biosurfactants that the cell produces, in the form of extracellular polymeric substances (EPS) and soluble microbial products (SMP), are used to access hydrocarbons at a wide range of pH, temperatures, and salinities (Abuhasel et al., 2021). Biosurfactants are essential substances that increase the efficiency with which bacteria absorb petroleum hydrocarbons (Xu et al., 2018; Ubani et al., 2013). The bacteria must first attach itself to the oil droplet with the help of pili or flagella. It then secretes biosurfactants of diverse molecular sizes and chemical nature that emulsify the oil droplet to increase the oil-water surface area and its solubility (Bhattacharyya et al., 2022; Godfrin et al., 2018; Ubani et al., 2013; Brooijmans et al., 2009). Table 2.2 shows the different types of biosurfactants that bacteria produce. Bacterial biosurfactant production is natural, non-toxic, biodegradable, and cost-effective for assisting in the solubilization of oily wastewater during biodegradation (Mapelli et al., 2017; Ubani et al., 2013). Once the bacteria have solubilized the oil, they can absorb and metabolize the hydrocarbon (Bhattacharyya et al., 2022; Karlapudi et al., 2018).

Table 2.2. Biosurfactants produced by hydrocarbon-degrading bacteria

Bacteria	Biosurfactant	Reference
P. aeruginosa	Rhamnolipids	(Karlapudi et al., 2018; Das & Chandra, 2011)
Rhodococcus sp.	Trehalolipids, Glycolipids	(Karlapudi et al., 2018; Floris et al., 2018)
B. licheniformis	Peptide-lipid	(Karlapudi et al., 2018)
P. fluorescens	Viscosin, Rhanmolopids, Glycolipids, Lipopeptides	(Karlapudi et al., 2018; Floris et al., 2018; Tripathi et al., 2018; Das & Chandra, 2011)
B. subtilis	Surfactin, Glycolipids, Lipopeptide, Glycopeptide, $^{\varepsilon}$-poly-L-lysine	(Karlapudi et al., 2018; Floris et al., 2018; Tripathi et al., 2018; Das & Chandra, 2011)
Microbacterium sp.	Carbohydrate-protein-lipid	(Karlapudi et al., 2018)
A. borkumensis	Glycolipids, Glucose lipids, Trehalose lipids	(Maneerat et al., 2005)
P. nautica	Polymeric biosurfactants, lipid-carbohydrate-protein, Glycolipids, Rhamnolipids	(Maneerat et al., 2018)
Marinobacter sp.	Carbohydrates: lipids complex, phospholipopeptide	(Tripathi et al., 2018)
S. saprophyticus	Glycolipid	(Tripathi et al., 2018)
B. circulans	Lipopeptide	(Tripathi et al., 2018)
B. mojavensis	Lipopeptide	(Tripathi et al., 2018)
B. megaterium	Lipopeptide	(Tripathi et al., 2018)
Marinobacter sp.	Carbohydrates: lipids complex, phospholipopeptide	(Tripathi et al., 2018)
S. saprophyticus	Glycolipid	(Tripathi et al., 2018)
B. circulans	Lipopeptide	(Tripathi et al., 2018)
B. mojavensis	Lipopeptide	(Tripathi et al., 2018)
B. megaterium	Lipopeptide	(Tripathi et al., 2018)
S. lentus	Glycolipid	(Tripathi et al., 2018)
E. cloacae	EPS (emulsifier-stabilizing agent in food)	(Tripathi et al., 2018)

2.7.1. Biodegradation of Linear Hydrocarbon Chains

O_2 activates the aerobic alkane degradation pathway. Mono-oxygenases are alkane-activating enzymes that can overcome the low chemical reactivity of hydrocarbons by producing reactive oxygen species. When methane is oxidized, it becomes methanol, then is successively converted into formaldehyde, and finally into formic acid. The newly formed formic acid can then be transformed into CO_2 or integrated for the biosynthesis of multi-carbon compounds through the monophosphate or serine pathway, depending on the microorganism (Bhattacharyya et al., 2022; Xu et al., 2018; Rojo, 2009).

N-alkanes comprising two or more carbon atoms are usually degraded by first oxidizing the terminal methyl group to form a primary alcohol for terminal oxidation. It is then further oxidized to form corresponding aldehydes, and lastly, it is transformed into a fatty acid. The fatty acids are then coupled with CoA and processed by b-oxidation to render acetyl-CoA (Bhattacharyya et al., 2022; Xu et al., 2018; Rojo, 2009). Acetyl CoA may be used for many other biochemical processes, such as the tricarboxylic acid (TCA) cycle, to produce adenosine triphosphate (ATP). Oxidation of subterminal n-alkanes occurs by converting alkane groups into secondary alcohols and turning them into corresponding ketones. A Baeyer–Villiger mono-oxygenase then oxidizes it to generate an ester. An esterase further hydrolyzes it to alcohol and a fatty acid. Terminal and subterminal oxidation can exist simultaneously in select microorganisms (Bhattacharyya et al., 2022; Al-Hawash et al., 2018; Brzeszcz & Kaszycki, 2018; Xu et al., 2018; Das & Chandran, 2011; Rojo, 2009). The biodegradation pathway of alkanes by aerobic bacteria, as illustrated by Brzeszcz & Kaszycki, 2018 is shown in Figure 2.1.
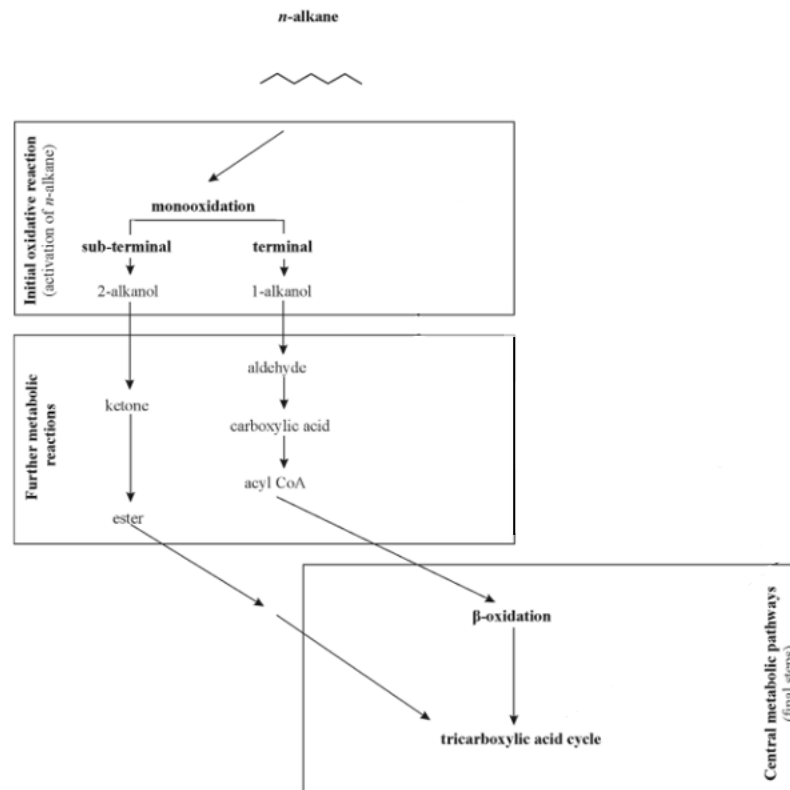
Figure 2.1. Biodegradation pathways of alkanes by aerobic bacteria (modified from Brzeszcz & Kaszycki, 2018)

2.7.2. Biodegradation of Aromatic Hydrocarbons

PAHs in oil are extremely resistant to biodegradation due to the inherent stability of aromatic rings. PAHs are toxic, carcinogenic, and persistent in oil-polluted regions. Although PAHs are difficult to biodegrade, it is not impossible since they are of biological origin. PAHs are composed of two or more aromatic rings with various branches and aromatic groups (Bhattacharyya et al., 2022; Wang et al., 2018). Some well-known bacteria that can metabolize PAHs are Arthrobacter, Burkholderia, Mycobacterium, Pseudomonas, Sphingomonas, and Rhodococcus (Brooijmans et al., 2009).

Naphthenes are the simplest polycyclic aromatic compounds that comprise parent compounds such as cyclopentane, cyclohexane, and decalin, along with their alkylated

analogues (Prince & Atlas, 2014). They are composed of two fused benzene rings; their chemical formula is $C_{10}H_8$ (Bhattacharyya et al., 2022; Wang et al., 2018; Ubani et al., 2013). One of the ways bacteria break down this component is to oxidize Naphthalene with mono-oxygenase and dioxygenase attack of the aromatic ring, which yields the intermediate compounds of dihydrodiol. The bacteria utilize the dioxygenase reaction to oxidize Naphthalene to D-trans-1,2-dihydroxy-1,2-dihydronaphtalene, then the dehydrogenase enzyme is used to catalyze the previous intermediate to 1,2-dihydroxynaphthalene (Travkin & Solyanikova, 2021; Li et al., 2019; Xu et al., 2018; Wang et al., 2016; Ubani et al., 2013). The dihydroxylated PAH then goes through cleavage by breaking the aromatic ring to create carboxylated compounds, which, if further oxidized by enzymes, are directed to the tricarboxylic acid cycle (Bhattacharyya et al., 2022; Travkin & Solyanikova, 2021; Li et al., 2019; Das & Chandran, 2011). The metabolism of Naphthalene is shown in Figure 2.2. Bacteria similarly degrade other aromatics. Figure 2.3 shows the overall biodegradation process of any hydrocarbon by bacteria.

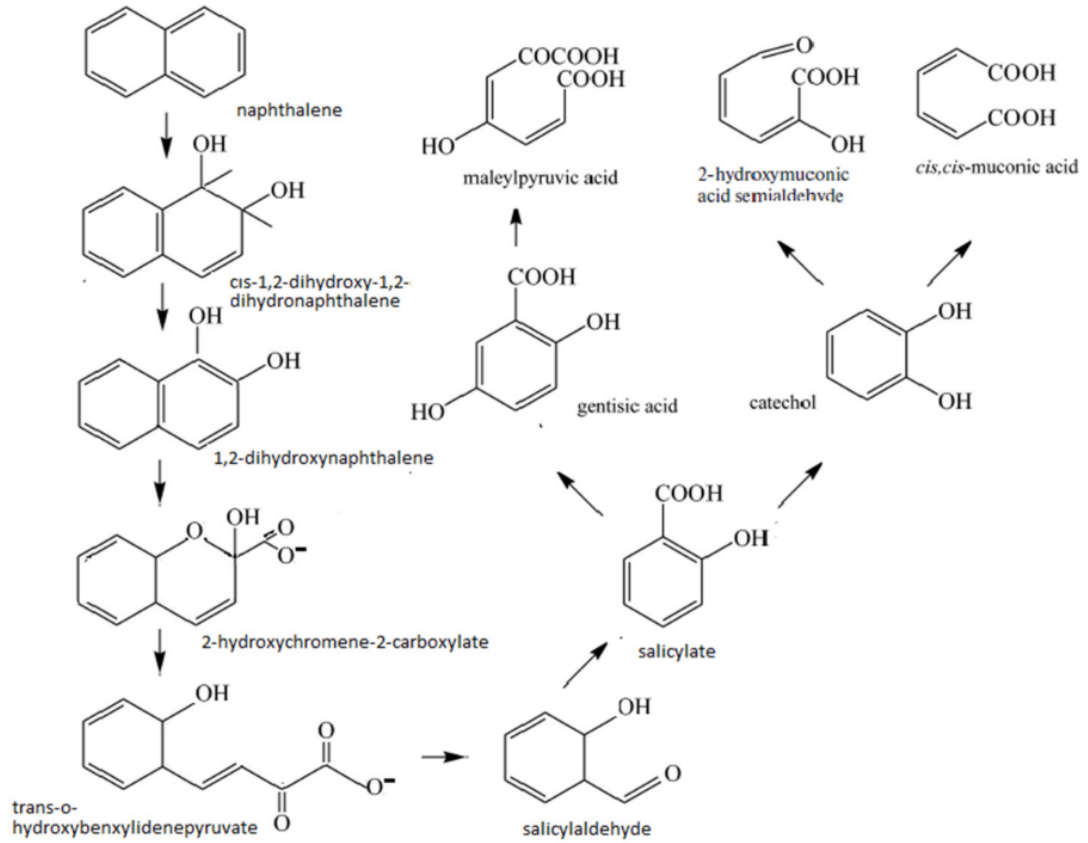**Figure 2.2. Biodegradation pathway of PAH by aerobic bacteria (Travkin & Solyanikova, 2021)**
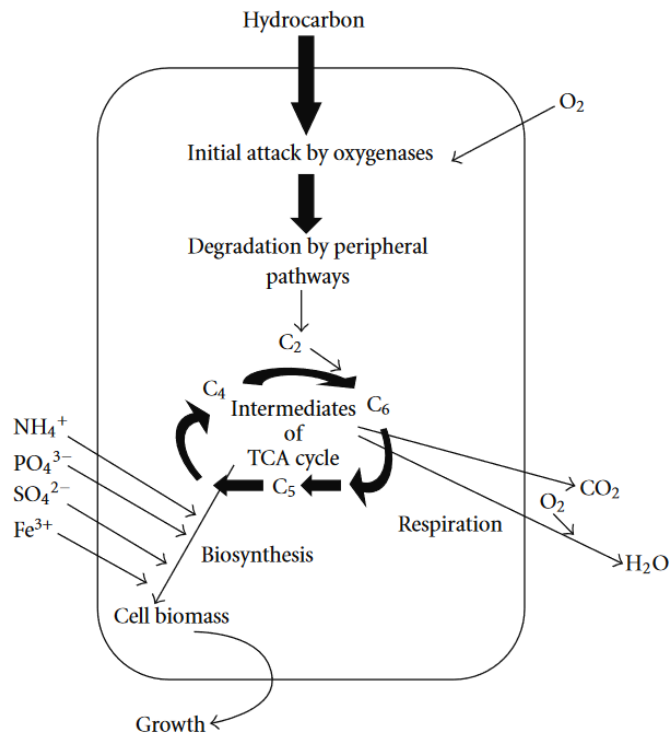
Figure 2.3. Biodegradation pathway of hydrocarbon by bacteria (Das & Chandran, 2011)

Biological processes are an essential part of MBRs; therefore, it is key to understand the effects of wastewater characteristics and the mechanism required to control microbial activity in the bioreactor (Ubani et al., 2013). The bacteria must be able to synthesize enzymes that catalyze the metabolism of hydrocarbons, converting them to simpler or less toxic compounds (Ubani et al., 2013). Unlike biodegradation in nature, there are limited resources within a bioreactor (Prince & Atlas, 2014). Microbial activity relies on parameters such as wastewater composition, pH, temperature, aeration, F/M ratio, hydraulic retention time, and sludge retention time (Bhattacharyya et al., 2022; Adetunji & Olaniran, 2021; Cao et al., 2020).

2.8. Operational Parameters

2.8.1. Effects of Temperature

Temperature affects the physical characteristics and chemical composition of hydrocarbons. It determines the hydrocarbons that persist after evaporation and influences the extent of oil exposure by affecting the oil surface area available to microorganisms for biodegradation. At low temperatures, the viscosity of oil increases, reducing the volatilization of toxic short-chain alkanes and oil solubility (Al-Hawash et al., 2018; Yang et al., 2009; Radjenović et al., 2008; Atlas, 1991). Decreasing temperatures reduce the biodegradation rate due to lower bacterial enzymatic activity (Atlas, 1991). Higher temperatures decrease oil viscosity and increase the volatilization of benzene, toluene, ethylbenzene and xylene (BTEX) components, the solubility of oil and the rate of microbial metabolism (Alsalhy et al., 2016; Iorhemen et al., 2016; Das & Chandran, 2011; Radjenović et al., 2008; Le-Clech et al., 2006). The preferred temperatures for optimal microbial biodegradation activity are within the range of 30 to 40 °C; higher temperatures

typically increase the toxicity of hydrocarbons to the bacteria (Bhattacharyya et al., 2022; Al-Hawash et al., 2018; Atlas, 1991).

Alsalhy et al., 2016 investigated the effects of feed water preheating times (i.e., 15, 30, and 45 min) at a temperature of 45 °C on oil removal in oil refinery wastewater using an MBR. The activated sludge concentration for the experiment set was 1000 mg/L MLSS. The oil concentration decreased by 95% with three days of hydraulic retention time when using preheating time of 15 min. The system removed 100% of the oil when using preheating times of 30 and 45 min. Increasing the preheating temperature to 55 °C increased the speed of oil removal. In addition to oil removal, Alsalhy et al., 2016 measured the effects of preheating on COD removal. The COD concentration was reduced by 50%, 58%, and 64% when using preheating times of 15, 30, and 45 min, respectively, at a temperature of 45 °C. Increasing the preheating temperature to 55 °C considerably increased COD removal efficiency. The COD removal increased to 52%, 63%, and 71% for preheating times of 15, 30, and 45 min, respectively. The increase in temperature and preheating time removed the volatile substances from the wastewater and promoted the biodegradation of hydrocarbons by making them more accessible to bacteria. A similar study by Al-Malack et al., 2007 confirmed the results (Bhattacharyya et al., 2022).

2.8.2. Effects of pH

The pH of wastewater affects the microbial biodegradation of hydrocarbons; it impacts processes such as cell membrane transport, catalytic reaction balance, and enzymatic activity. Most heterotrophic bacteria favour neutral to alkaline pH in the range of 7.2–8.5 (Al-Hawash et al., 2018; Radjenović et al., 2008). Previous studies have found that the microbial mineralization of naphthalenes and octadecanes may occur at a pH of 6.5.

Phenanthrenes were biodegraded in liquid media effectively at a pH range of 6.5–7.0 by bacteria such as Burkholderia cocovenenas. Pseudomonas aeruginosa was capable of biodegradation of crude oil in water up to a pH of 8.0 (Bhattacharyya et al., 2022; Al-Hawash et al., 2018).

2.8.3. Effects of Salinity

Salinity is another factor affecting microorganisms in an MBR in terms of growth and floc rheology. The enzymatic activity of microorganisms can be severely inhibited due to toxic effects from fluctuating salinity. Varying influent salt concentrations can also impact the structure of the microbial consortia within the bioreactor (Al-Hawash et al., 2018; Wang et al., 2018; Cosenza et al., 2017; DeTemmerman et al., 2017; Bassin et al., 2011; Reid et al., 2006). A sharp salinity increases osmotic pressure on the cell membrane, causing dehydration and eventual plasmolysis, decreasing sludge settleability and bioflocculation (Capodici et al., 2020; Ferrer-Polonio et al., 2016). The toxic effects of salinity can be overcome by gradually acclimating the bacteria to the high saline conditions (Bhattacharyya et al., 2022; Campo et al., 2017; Capodici et al., 2017; Mannina et al., 2016; Di Bella et al., 2013; Di Trapani et al., 2011; Reid et al., 2006).

In recent years, many studies have considered using a hydrocarbon-degrading microbial consortium that can tolerate saline environments to optimize the treatment process when treating saline oily wastewater (Capello et al., 2016). Halophilic and halotolerant marine microorganisms have been used to inoculate MBRs to improve biodiversity and enhance the efficacy of biodegradation for saline oily wastewater treatment (Bhattacharyya et al., 2022; Tan et al., 2019; Cosenza et al., 2017; Sharghi et al., 2013; Lefebvre & Moletta, 2006).

2.8.4. Effects of Aeration

Oxygen supply is critical for aerobic degradation as it functions as a terminal electron acceptor in the hydrocarbon metabolism process, making aeration an important parameter to consider in MBR treatment of wastewater, as it is directly related to DO concentration within the bioreactor (Bhattacharyya et al., 2022; Al-Hawash et al., 2018; Iorhemen et al., 2016; Ubani et al., 2013; Yang et al., 2009; Radjenović et al., 2008). It is understood that the mass of oxygen needed to metabolize a hydrocarbon load is approximately 0.3 g of oxygen per gram of oil oxidized (Yang et al., 2009).

Biomass features, such as SMP and EPS, impact the organics removal rate due to their effect on oxygen transport. SMP is soluble and hence exists in the liquid phase, whereas EPS is attached to cells and thus exists in the solid phase. The quantity of EPS varies with changes in the microbial state and bioreactor operation conditions. Oxygen must first permeate the liquid layer surrounding the flocs and then diffuse through the floc matrix (EPS) to access the active spots on the bacterial cell membrane. Poor sludge properties due to over-aeration caused by weak floc structure and a low sludge volume index (SVI), resulting in dispersion of bacteria in the MBR that leads to poor biodegradation (Iorhemen et al., 2016; Radjenović et al., 2008). On the other hand, low aeration can create anaerobic conditions causing excess microbial SMP and EPS production (Du et al., 2020; Xiaoguang et al., 2017; Wang et al., 2014; Sheng et al., 2010). Thus, finding the optimal aeration rate is vital to provide microorganisms with enough oxygen to perform metabolic processes and simultaneously not disturb floc formation (Bhattacharyya et al., 2022).

Additionally, aeration generates unsteady-state shear at the membrane surface via turbulent eddies, fibre oscillations, particle scouring, and recirculation of content in the bioreactor,

which contribute to a reduction of cake layer formation on the membrane surface, consequently reducing membrane fouling (Akhondi et al., 2017; Iorhemen et al., 2016; Radjenović et al., 2008). If aeration is inadequate, the membranes are more susceptible to clogging or blocking by bacterial EPS and SMP production, which causes uneven flow distribution, disrupting permeate production by obstructing permeate flow through the membrane (Bhattacharyya et al., 2022; Akhondi et al., 2017).

2.8.5. Effects of Nutrients

The development of heterotrophic bacteria relies on nutritional elements and an electron acceptor, such as oxygen, for biodegradation involving aerobic bacteria (Ubani et al., 2013; Das & Chandra, 2011; Yang et al., 2009). The absence of any of these elements hinders the growth and metabolism of the microorganism. Bacteria responsible for degrading hydrocarbon require a fixed nitrogen source, such as NH_3, NO_3-, NO_2- (inorganic), and some organic nitrogen sources. Phosphorus is another critical nutrient for the microbial population as it is utilized to synthesize adenosine triphosphate (ATP), nucleic acids, and cell membrane components (Bhattacharyya et al., 2022; Ubani et al., 2013; Das & Chandra, 2011).

The activated sludge in MBR requires a balance between the food entering the bioreactor and the bacteria in the bioreactor for optimal system performance. A high F/M ratio indicates more food than microorganisms available to consume the food. When the F/M ratio is high in bioreactors, the bacteria are active and proliferate quickly, but they are also more distributed. Dispersion provides an environment in which the bacteria does not form adequate, big, dense flocs and, as a result, frequently leads to poor settling (Al-Hawash et al., 2018; Atlas, 1985). A low F/M ratio indicates that the microbes are plentiful, but there

is a limited food supply. When food is scarce, bacteria begin to produce a thicker slime layer, lose their motility, and cluster together to form a dense floc that settles readily (Al-Hawash et al., 2018). At a high sludge age and MLSS concentration, the MBR systems require less nutrients due to the decline in excess sludge production (Bhattacharyya et al., 2022; Radjenović et al., 2008; Scholz & Fuchs, 2000). The microorganisms in the system reach an equilibrium state where the amount of energy provided (food) equals the microbial maintenance demand. The maintenance of biomass is preferred over the production of additional biomass. When the F/M ratio is lowered, biomass production is reduced, and the food is used for maintenance (Al-Asheh et al., 2021; Radjenović et al., 2008; Al-Malack, 2006). The low nutrient demand for biomass to treat wastewater effectively is an advantage of MBR systems over CAS since the lack of nutrients in industrial wastewater is common. In comparison, the nutrient requirement for oil biodegradation in a CAS treatment method amounts to 120 g nitrogen and 20 g phosphorus for every kg of oil, whereas MBR only needs 6.7 g nitrogen and 0.8 g phosphorus as nutrients to biodegrade 1 kg of oil (Iorhemen et al., 2016; Scholz & Fuche, 2000).

2.8.6. Effects of MLSS

MLSS concentration influences biomass growth; generally, the higher the MLSS concentration, the more biomass is in a system (Al-Asheh et al., 2021; Alsalhy et al., 2016). A high level of MLSS concentration decreases the sludge loading rate, enhances the treatment efficacy, and increases the viscosity of the mixed liquor (Hamedi et al., 2019). The mixed liquor volatile suspended solids (MLVSS) to MLSS (MLVSS/MLSS) ratio is utilized as a measure of the quantity of viable sludge in MBRs (Bhattacharyya et al., 2022;

Radjenović et al., 2008). A higher ratio of MLVSS/MLSS signifies a higher percentage of viable sludge and low inert material build-up (Vuković et al., 2006).

Alsalhy et al., 2016 studied oil refinery wastewater treatment using a membrane bioreactor (MBR). Two different MLSS concentrations (500 and 1000 mg/L) were tested for COD, BOD, and oil removal within five days at a constant temperature of 25 °C and HRT of 3 days. The COD, BOD, and oil concentrations of the system reduced from 235 mg/L to 157 mg/L, 46 mg/L to 31 mg/L, and 14 mg/L to 2.3 mg/L when using an MLSS concentration of 500 mg/L, respectively. When using an MLSS concentration of 1000 mg/L, COD, BOD, and oil decreased from 235 mg/L to 122 mg/L, 46 mg/L to 28 mg/L, and 14 mg/L to 1.3 mg/L, respectively. The findings of this study show that with an increase in the MLSS concentration, the removal of COD, BOD, and oil also increases; this can be attributed to the higher biodegradation of hydrocarbons into organic components (Bhattacharyya et al., 2022).

A study by Capodici et al., 2017 inoculated an MBR unit with a biomass concentration of 4 g/L TSS. Until Day 54, a reduction in suspended biomass was observed. This result can be attributed to the stress effect exerted by the hydrocarbons on the unacclimated biomass. Thus, to maintain biomass activity towards the toxic organic substance, from Day 54, sodium acetate was added to the influent water at a concentration of 500 mg/L. After adding the nutrients, the suspended biomass growth increased up to 7 g/L TSS, indicating favourable acclimation and an increase in biomass activity. The experiments showed that the MBR system was effective at removing COD from oily wastewater; the MBR as a whole achieved a COD removal efficiency of 88%, with the biological component contributing to 70% of the total removal efficiency. The researchers also evaluated the

removal efficiency of hydrocarbons and found that the system achieved a TPH removal efficiency of 92%, with a permeate TPH concentration below 5 ppm (Bhattacharyya et al., 2022).

Similarly, Di Bella et al., 2015 evaluated an MBR system's performance in treating shipboard slops. This study assessed hydrocarbon degradation efficiency and biomass activity under salinity variation. The MBR unit was inoculated with 3.5 g/L TSS of activated sludge from a municipal wastewater plant. Synthetic wastewater with a gradual increase in salinity was fed to the MBR system for 60 days (Phase I); after that, the unit was fed with a mixture of synthetic wastewater and shipboard slops. The percentage of shipboard slops in the wastewater was gradually increased to 50% within 30 days (Phase II). The activated sludge in the system was retained during the 30 days it was fed with increasing slop concentration, resulting in the MLSS concentration of the MBR increasing to 8 g/L TSS. This ensured biomass acclimation to salinity and hydrocarbons. The COD removal efficiency of the MBR was reported to be approximately between 57%–96%, to which organic compounds' biomass degradation contributed approximately 55%–90% in Phase I. The MBR achieved a COD removal efficiency of 65%–97%, to which 46%–85% of the COD removal was attributed to biodegradation in Phase II. The MBR unit attained a 47.5% TPH removal efficiency when the slop concentration increased to 50%. These studies show that biomass acclimation to salinity and toxic hydrocarbons is necessary for effective oily wastewater treatment. It can also be seen that biodegradation is a major component in the MBR system, accounting for the majority of the treatment efficiency (Bhattacharyya et al., 2022).

The need for a biomass acclimation period indicates that a change in biomass composition occurs with a changing environmental composition (Poursat et al., 2019; Campo et al., 2017; Mapelli et al., 2017). In the case of oily wastewater, the abundance of hydrocarbon-degrading bacteria increases while microorganisms that cannot adapt are gradually eliminated. Likewise, halotolerant and halophilic bacteria in saline wastewater increase while the non-halotolerant and non-halophilic bacteria die off (Travkin & Solyanikova, 2021). Additionally, the diversity of bacteria in activated sludge changes with treatment time (Bhattacharyya et al., 2022; Travkin & Solyanikova, 2021; Hamedi et al., 2019). Different carbon sources ensue changes in equilibrium between bacterial strains in a consortium. When a particular type of hydrocarbon is in contact with the bacteria, the strain that can metabolize it becomes dominant in the consortia; this phenomenon is called microbial succession (Poursat et al., 2019; Xu et al., 2018; Mapelli et al., 2017; Liao et al., 2016; Zdarta et al., 2016; Van der Meer et al., 1992).

2.8.7. Effects of SRT

One of the benefits of MBRs is the high sludge age attained over a long SRT compared to CAS. Long SRTs are unattainable in conventional treatment methods because of the inadequate settling capacity of sludge at high concentrations and the extraction of suspended particles with the effluent. Typically, high MLSS concentrations due to high sludge age in the MBR allow wastewaters to be treated effectively at long SRTs, which minimizes biomass yield and decrease sludge production (Radjenović et al., 2008; Sutton, 2006). High sludge age achieved through a longer SRT permits the retention of particulate, colloidal, and higher-weight organics, which provides maximum opportunity for bacteria to metabolize organic compounds and allows for the acclimation of microbes to the

biodegradable compounds. As a result, biomass adapts to wastewater without being limited to fast-growing and floc-forming microbes (Radjenović et al., 2008; Viero & Sant'Anna, 2008; Sutton, 2006; Scholz & Fuchs, 2000). The slow sludge production removes the concern for changing biomass settling characteristics (i.e., filamentous bacterial growth, bacteria dispersion, and floc densification) that disrupt treatment efficiency by worsening sludge filterability and contribute to membrane fouling (Bhattacharyya et al., 2022; Al-Asheh et al., 2021; Radjenović et al., 2008; Sutton, 2006). SRT should be chosen to prevent both the negative impacts of accumulating non-biodegradable chemicals caused by low sludge discharge and excessive sludge generation at low sludge ages. Low sludge age under a low SRT can cause foaming and sludge bulking (Bhattacharyya et al., 2022; Radjenović et al., 2008).

Kose et al., 2012 studied the effects of SRT on MBR treatment efficiencies of brackish oil and oil field-produced water. The MBR was set up as a continuous flow submerged MBR system and was operated at room temperature for 297 days. Two different SRTs, 30 days and infinite days, were used. The MBR was inoculated with sludge acquired from laboratory-scale MBR leachate. This study found that the COD removal efficiency increased from 80% to 85% due to the higher biomass concentration at a higher SRT. With an increase in sludge age, the oil and grease removal efficiency increased from 60% to 85%. At an SRT of infinity, over 99% of TPH was rejected (Bhattacharyya et al., 2022). Various other studies confirmed that longer SRT under-steady state conditions result in better COD and oil removal efficiencies (Campo et al., 2016; Iorhemen et al., 2016; Razavi & Miri, 2015; Pendashteh et al., 2012; Di Trapani et al., 2011; Le-Clech et al., 2006).

2.8.8. Effects of HRT

HRT is the amount of time that the wastewater remains in the MBR. Generally, the longer the HRT, the longer the contact time between the bacteria and the biodegradable organic compounds in the wastewater. Consequently, the removal efficiency of the organic compound and COD increase (Kuyukina et al., 2020; Pendashteh et al., 2012; Soltani et al., 2010; Viero & Sant'Anna, 2008). It is critical to emphasize that reactor performance can only be obtained when MBRs are operated under steady-state conditions. The achievement of steady-state depends not only on the length of the operating period but also on the sludge's adaptation to the wastewater components (Bhattacharyya et al., 2022; Viero & Sant'Anna, 2008).

Razavi and Miri, 2015 explored the effects of various HRTs on treating real petroleum refinery wastewater. MLSS concentration in this system was kept between 3–6.6 g/L. The three different HRTs tested were 36 h, 30 h, and 25 h. It was found that reducing HRT from 36 h to 30 h and 25 h yielded COD removal efficiencies of 81.08%, 78.92%, and 78.92%, respectively. BOD removal efficiencies were 86.1%, 87.6%, and 89%, respectively, with increasing HRTs (Bhattacharyya et al., 2022). The findings correspond with similar studies that found that complex oily industrial wastewaters need longer hydraulic retention times for effective treatment once biomass is acclimated to the harsh environment (Iorhemen et al., 2016; Shariati et al., 2013; Pendashteh et al., 2012; Soltani et al., 2010; Ren et al., 2005).

MBRs are very robust systems capable of handling oily wastewater. There are vital factors that affect the biological component of MBRs to consider when treating this type of wastewater. The first is raw water characteristics, such as composition, pH, and temperature, which affect biodegradation. With elevated levels of hydrocarbons or salinity,

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an acclimation period is needed to develop an appropriate bacterial consortium in the sludge. When treating saline oily wastewater, if MBR is inoculated with non-halotolerant bacteria, it is essential to acclimate them beforehand since the salt shock causes the dehydration and plasmolysis of bacteria, quickly killing the biomass and producing excess EPS and SMP, resulting in poor biodegradation and membrane fouling. In recent years halophilic and halotolerant bacteria known to degrade various hydrocarbons have been used to inoculate MBRs, which has proven effective, thereby eliminating the need for or reducing the duration of biomass acclimation. Then, there are operational parameters that can be controlled, including MLSS concentration; typically, the greater the MLSS, the lower the organic loading rate up to a certain point, and the better the treatment efficiency. Adequate aeration is crucial for providing the bacteria with enough oxygen to perform metabolic processes. A low F/M ratio is optimal to provide the bacteria with sufficient nutrients to maintain the biomass and aid their metabolic processes without promoting excess sludge production. SRT is another critical parameter; it should be chosen carefully to suppress the accumulation of non-biodegradable components due to low sludge discharge and excess sludge production at a low sludge age and to promote a high sludge age through long SRTs, allowing for biomass acclimation and efficient treatment. Lastly, longer HRTs are recommended for treating oily wastewater to allow biomass enough contact time with hydrocarbons to metabolize them effectively (Bhattacharyya et al., 2022).

# CHAPTER 3: MATERIALS AND METHODS

3.1. Experimental Setup and Design

3.1.1. Pilot-Scale Membrane Filtration System

The pilot-scale membrane filtration system was designed to test oil removal from oily wastewater. The supplier recommended the aeration rate (4.8 m^3/h) and membrane flux (12 L/m^2h) that were chosen. The initial oil concentration of the oily wastewater was progressively increased to determine the highest oil concentration the system could handle. The membrane filtration system ran in a closed loop where the over-flowing wastewater from the membrane section of the membrane tank spilled into the overflow section of the membrane tank and was then pumped back to the feed tank for recirculation (see Figures 3.2 (membrane filtration unit) and 3.3 (pilot-scale membrane filtration setup)).

The schematic design for the submerged membrane filtration processing unit is presented in Figure 3.2, and the lab setup schematic is shown in Figure 3.3. The 2280 mm × 914 mm × 2000 mm (L × W × H) pilot-scale unit has a membrane tank with a working volume of 340 L and houses two HF-MF polytetrafluoroethylene (PTFE) membrane modules. The Sumitomo Electric MF membrane modules (model #SPMW-11B6, Sumitomo) used in this study were surface modified using a hydrophilic polymer, decreasing its water contact angle from 146° to 58°. The Sumitomo PTFE membrane was chosen since it is known to have the broadest chemical tolerance of any polymeric membrane; it can resist and remain chemically stable in wastewaters with a pH ranging between 1 and 14 and can withstand continuous exposure to a 20% hypochlorite solution. The polymeric membrane is able to resist strong oxidants such as ozone at any significant concentration. Hydrophilic PTFE does not require alcohol treatment or frequent replacement and can remain hydrophilic after

being dried, hence is a cost-effective option (Sumitomo Electric Industries, 2021). The membrane characteristics are presented in Table 3.4.
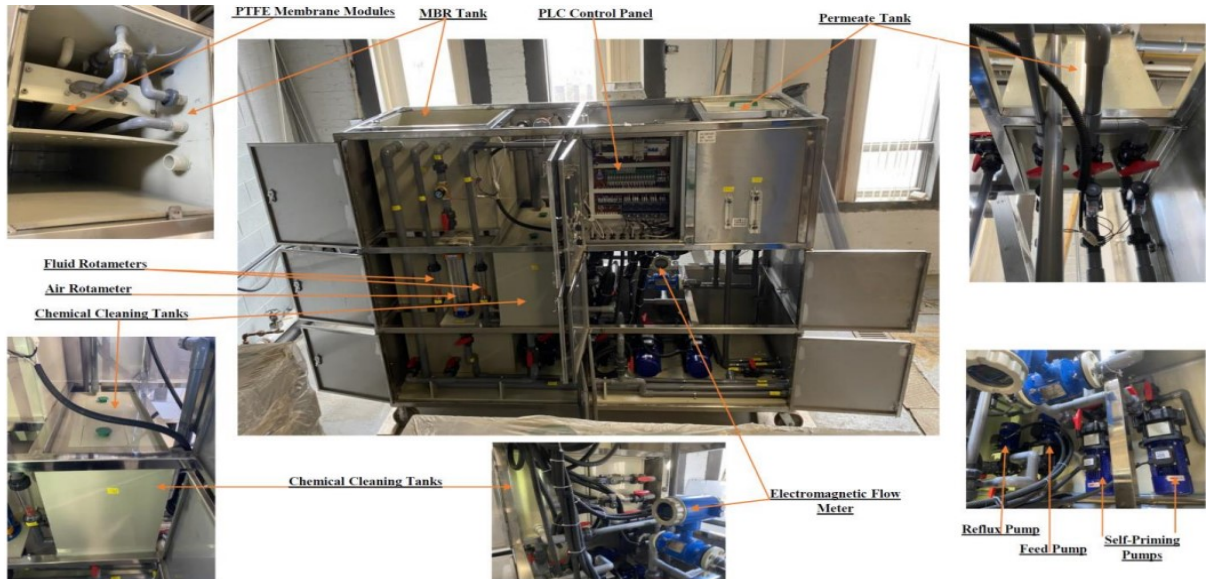
Figure 3.1. Pilot-scale membrane filtration unit
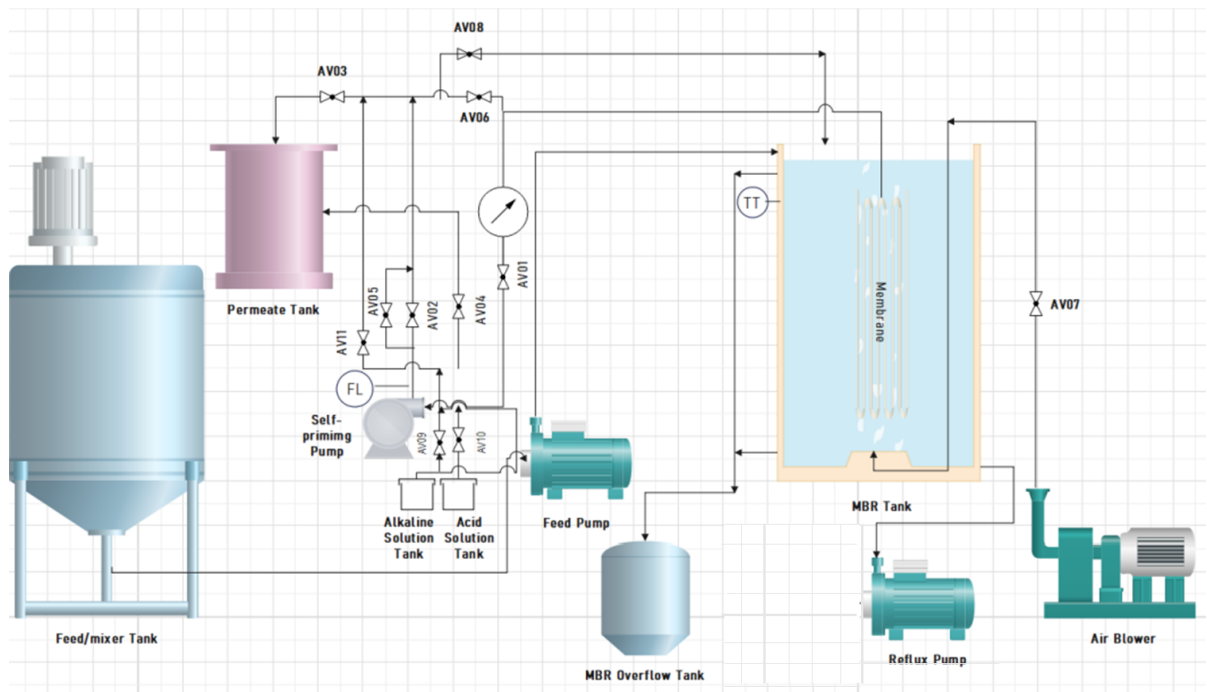
Figure 3.2. Pilot-scale membrane filtration setup

Table 3.1. Sumitomo PTFE membrane characteristics

Parameters	Values
Membrane Nominal Pore Size (μm)	0.2
Membrane Area (m^2)	6
Water Contact Angle	58∘
Maximum Filtration TMP (kPa)	> -60
Maximum Backwash TMP (kPa)	< 100
Maximum Operating Temperature (℃)	50

The oily seawater emulsion is pumped from the feed tank to the membrane tank with the help of a feed pump (Dongguan Riyiguobao, MPX- 250-C-C-V-5-V38-A) and is treated by two membrane modules. The pilot-scale unit was operated continuously at a permeate flux of 12 L/m^2 h. The membrane unit operated in cycles of 9 minutes of filtration and 1 minute of relaxation. At the end of three cycles, a 15-second backwash occurred. The filtration and backwash processes were performed with the help of the bidirectional self-priming pump (Dongguan Riyiguobao, MPX-250-C-C-V-5-V38-A). The direction of the flow was controlled through automatic electromagnetic valves. The membranes were constantly aerated from the bottom of the membrane tank with the help of an air blower (HCC-301S); this helped reduce membrane fouling and promote the recirculation of liquid within the tank. The flow rate of air was adjusted using manual valves. To prevent the membrane tank from overflowing, a pipe at the bottom of the membrane tank led to a reflux pump (Dongguan Riyiguobao, MPX-250-C-C-V-5-V38-A) to recirculate water back to the feed tank. Transmembrane pressure (TMP) from the pressure gauge, filtration flow rate from the electromagnetic flow meter and temperature from a sensor in the membrane tank were recorded automatically every minute throughout each experimental run with the help of the programable logic controller (PLC). At the end of each run, the permeate and

remaining water from the membrane tank were returned to the feed tank to start the next experimental run. Once the system was reset, a run meant to test the same oil concentration as the previous run, 7 g of oil, was added to account for the oil lost in the pipes and demulsification. An additional 25g of oil was added to the wastewater to set up for a run that required an increase in oil concentration. The filtration system was tested twice for each oil concentration (e.g., runs 1 and 2 were intended to have an initial oil concentration of 25 ppm, and runs 3 and 4 were intended to have an initial oil concentration of 50 ppm, etc.). The experimental design is presented in Table 3.3.

Table 3.2. Pilot-scale membrane filtration experimental design

Run ID	Influent Oil Concentration (ppm)	Aeration Rate (m³/h)	Flux (L/m²h)
1	9.26		
2	11.34		
3	11.90		
4	12.90		
5	13.83	4.8	12
6	15.18		
7	19.60		
8	28.30		

The membrane supplier provided the membrane cleaning instruction. Chemical cleaning was performed when the TMP reached 40 kPa. Two chemical cleaning tanks with working volumes of 60 L each, one for acid and one for an alkaline solution, were built into the unit. The membrane manufacturer recommends mixing 300–3000 mg/L NaClO and 100–500 mg/ L NaOH to remove organic foulants and 300–3000 mg/L HCl for removing inorganic foulants. After injecting the chemical through the membrane into the membrane tank, it was left to soak for 2 h for each chemical solution. The membrane unit was then filled with

fresh water, ran several times to flush the chemicals from the system and drained into a wastewater collection tank before proceeding with the experiments.

3.1.2. Bench-Scale Biological Treatment and Membrane Filtration Experiments

The bench-scale experiments were designed to determine the effect of increasing initial oil concentration and HRT on an MBR system treatment efficiency.

The oily wastewater emulsions are poured into a jar tester (Standard Phipps & Bird -Fisher Scientific) along with 300ml of activated sludge obtained from an industrial wastewater treatment process (GFL Debert, Nova Scotia). GFL used the activated sludge as part of a treatment process to treat saline oily wastewater; therefore, no biological acclimation was conducted before use in this MBR study. The bench-scale experiments were conducted over four days, where the same activated sludge was reused throughout the experimental period. The oily wastewater and activated sludge mixtures were constantly stirred at a low speed to promote the aeration and mixing of the solution within the jars. After a designated HRT (3 or 6h), a portion of the solution was collected was a glass bottle and stored for later analysis (TPH, PHC, PAH, EPS, SMP, MLSS, and MLVSS). The remaining solution was filtered through a 0.2µm cellulose nitrate membrane using a filtering flask and a suction pump. The filtered solution was poured into a glass bottle and stored for later analysis (TPH, PHC, and PAH). The setup for the bench-scale experiments is shown in Figure 3.4, and the experimental design is presented in Table 3.5. The four experimental runs were run four times each, and the parameters' results were averaged. Statistical T-test analysis with a 95% confidence interval was performed for TPH and PHC results.
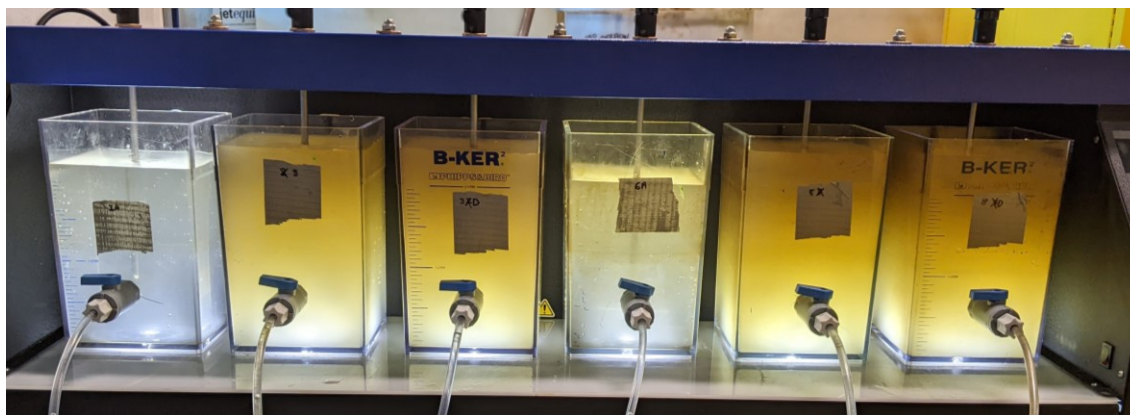
Figure 3.3. Bench-scale MBR experimental setup

Table 3.3. Bench-scale MBR experimental design

Run ID	Initial Oil Concentration (ppm)	HRT (h)
1	25	3
2		6
3	100	3
4		6

3.2. Initial Oil Concentration

The oily wastewater emulsion for the pilot-scale experiments was prepared using 25, 50, 75, and 100g of oil and 1000L of seawater in an attempt to create 25, 50, 75, and 100 ppm of oily wastewater, respectively. The experiment was run twice for each oil concentration. The intended initial oil concentrations were not attained, as seen in Figure 10. The pilot-scale filtration system ran as a closed loop, where the over-flowing wastewater from the membrane section of the membrane tank spilled into the overflow section of the membrane tank, which was then pumped back to the feed tank for recirculation (see Figures 3.2 and 3.3). As the overflow section of the membrane tank began to accumulate more wastewater, the oil would demulsify, floating to the surface and not get pumped back to the feed tank.

Additionally, at the end of each run, the wastewater from the membrane tank and the permeate from the permeate tank was emptied back into the feed tank to set up for the following experimental run. Approximately 15 cm of unrecoverable demulsified oily wastewater remained in the tank, even after draining. Oil was added to the water after resetting the experiment. To set up a run that was meant to use the same oil concentration as the previous run, 7g of oil was added to account for the oil lost in the pipes and demulsification. An additional 25g of oil was added to the wastewater to set up for a run that required an increase in oil concentration.

The oily wastewater emulsion for the bench-scale experiments was prepared using 60µl and 235µl of oil and 2L of seawater to create 25 and 100 ppm of oily wastewater, respectively. The oil concentrations reached in the bench-scale system were 27.5 and 93.1 ppm. The oil concentrations were not exact due to the oil sticking to the sides of the blender, jars, and storage bottles, thereby slightly deviating from the intended oil concentrations.

3.3. Crude Oil Characterization

Very low sulfur fuel oil (VLSFO) provided by the CCG was used to conduct experiments for this study. VLSFO was chosen since ships are encouraged by IMO 2020 regulations to switch to low sulfur fuel oil to reduce sulfur dioxide emissions. As majority of the ships have switch to low sulfur oils, this type of oil is highly likely to be seen during marine oil spill incidences (Sørheim et al., 2020). The oil was weathered to simulate the state of the oil in an oil spill event, where the oil is subject to evaporation, aqueous dissolution, sorption, oxidation, emulsification, and dispersion, all of which impact its chemical composition and physical properties (Yang et al., 2020). The weathering of the petroleum crude oil was replicated in the laboratory through air sparging to remove the volatile

chemical components (Li et al., 2009). A pre-weighed container filled with VLSFO was placed on a scale under the fume hood. One end of a pharmed tube was connected to a stainless-steel air diffuser attached to a pressurized air cylinder, and the other was placed in a container filled with crude oil. Once the setup was complete, the pressurized air tank was opened, and the air diffuser was adjusted to desired flow rate. The percentage reduction of oil mass. The percentage of oil evaporated was calculated using

$$Revap = \frac{m_i - m_t}{m_i} \times 100 \tag{1}$$

where m_i denotes the initial weight of the oil, and m_t denotes the weight of oil at time t.

VLSFO underwent a mass change of 1.5% within 48 h. The weathered oil was characterized by the following standard procedures: API gravity (ASTM D4052), density (ASTM D4052), and kinematic viscosity (ASTM D7042), as presented in Table 3.1.

<div align="center">Table 3.4. VLSFO Characteristics</div>

Density (g/cm³)	Viscosity (cPS) @20∘	API∘
0.877	10.4	29.7

3.4. Synthetic Oily Seawater Preparation

Synthetic oily seawater was prepared to simulate the decanted oily wastewater generated from a marine oil spill response operation. The simulated decanted oily wastewater was prepared by mixing the weathered oil with seawater provided by the Dalhousie University Aquatron. The Aquatron sources its seawater from the Northwest Arm of the Atlantic Ocean and treats it using four sequential sand filters followed by exposure to UV to remove suspended solids and bacteria. The seawater characteristics, such as the electrical conductivity, total dissolved solids (TDS), and salinity, were measured using a handheld conductivity meter (Ecosense EC300A). The pH of the seawater was measured using a pH

meter (ROSS Ultra, Thermo Fisher Scientific). The seawater characteristics are presented in Table 3.2.

Table 3.5. Seawater Characteristics

Parameters	Values
Conductivity (mS/cm)	39.5
Total dissolved solids-TDS (g/L)	30.5
Salinity (ppt)	31
pH	8.2

The oil droplet size of the emulsified oily wastewater solution was measured using a laser light scattering system (Mastersizer), where deionized water was applied as the dispersive phase. A laser beam passed through the emulsified oily water sample, and light scattering intensity was measured to determine the oil droplet size.

3.4.1. Pilot-Scale Emulsion Preparation

The emulsions prepared for the pilot-scale experiments used 25, 50, 75, and 100g of oil added to 1000L of seawater to generate 25, 50, 75, and 100 ppm of oily wastewater, respectively. The solution was mixed at a speed of 3515 rpm using a high-shear vertical mixer (Inoxpa) for 30 min to attain a stable emulsion before filling up the membrane tank. The mixer remained on for the length of each experimental run to ensure that the wastewater recirculating to the mixer from the membrane tank remained emulsified. The stable emulsion was created through mechanical and hydraulic shearing of the oil at high speed, in addition to the vertical suction and radial thrust, which resulted in a circulation flow within the feed tank by the Inoxpa mixer (Inoxpa, 2021).

3.4.2. Bench-Scale Emulsion Preparation

The emulsions prepared for the bench-scale experiments used 60µl and 235µl of oil added to 2L of seawater to make 25ppm and 100ppm of oily wastewater, respectively. The oil and water were placed in a blender and blended for 2 minutes at high speed.

3.5. Analytical Methods

Ultraviolet-visible (UV-Vis) spectrometry was used to measure total petroleum hydrocarbon (TPH); a 10-ml water sample was placed in a centrifuge tube, followed by 1ml of dichloromethane (DCM). The mixture was vortexed for 60s and settled until the water and DCM were completely separated. The absorbances of the separated DCM phase was measured with a UV-Vis spectrometer using wavelengths of 340nm, 370nm, and 400nm. The values from the absorbance readings were added together to calculate the TPH concentration in the samples (Song et al., 2022; Zheng et al., 2015). The percentage of TPH removed by the membrane was calculated using Eq. (2) (Radjenović et al., 2008).

$$Rrej = \frac{C_i - C_f}{C_i} \times 100 \tag{2}$$

where C_i is the initial TPH concentration of the oily wastewater emulsion, and C_f is the final TPH concentration in the permeate.

Petroleum hydrocarbon fractions (PHCs) and PAHs were evaluated by gas chromatography/mass spectrometry (GC-MS); For PHCs, a 10ml water sample was followed by 1ml of DCM used to fill a centrifuge tube. The mixture was vortexed for 60s and settled until the water and DCM were entirely separated. 100µL of the organic phase was transferred to a 150µL vial, then 10µL of internal standard was added to it. The mixture

was analyzed using Agilent 7890 A GC/MS with the help of an A30 m DB-5 ms capillary GC column, using Helium as the carrier gas. The GC oven temperature was set at 45°C for 2 min, then increased by 6°C/min up to 300°C for 20 min. The GC-detectable n-alkanes (C8-C38) representing fractions F1-F4 and PAHs were profiled and identified through specific mass/charge number (*m/z*) values using the ChemStation Software (Zheng et al., 2015).

MLSS and MLVSS were measured using Standard Method 2540 B. MLSS was measured by first drying filter papers in the oven at 105°C for 30 minutes and weighing them. 50ml of each MBR experiment jar was then filtered using the appropriate filter papers and placed in the oven for 1 hour at 105°C, then weighed to determine the MLSS concentration in the samples. Once the MLSS concentration was determined, the filter papers were folded, put in pre-weighed crucibles with lids, and placed in a 550°C furnace for an hour. After the hour, the crucibles were taken out of the furnace, cooled for 30 minutes, and weighed to determine the MLVSS concentration.

Extracellular polymeric substances (EPS) and soluble microbial products (SMP) proteins were measured using a modified Lowry protein assay kit (Thermo Scientific). The first step was to extract the SMP and EPS from the MLSS. Once the MLSS sample from each MBR experiment jar was collected, it was centrifuged for 5 minutes at 5000g, and the supernatant was obtained and filtered using a 1.2μm filter paper, a filtering flask, and a suction pump; this will contain the SMP of the sample. The precipitate was then resuspended using deionized water and mixed for 10 minutes. The resuspended sample was then heated for 10 minutes at 80°C and centrifuged for 10 minutes at 7000g. The supernatant was collected

and filtered using a 1.2µm filter paper, a filtering flask, and a suction pump; this contained the EPS of the sample. Once the SMP and EPS were extracted, the samples were prepared from protein readings. From the modified Lowry protein assay kit, the diluted albumin (BSA) standards, phenol reagent, and 1X Folin-Ciocalteu reagent need to be prepared according to the directions; however, instead of using deionized water as diluent seawater was used. 0.2mL of each standard and unknown sample replicate were pipetted into an appropriately labelled test tube, and 1.0mL of Modified Lowry Reagent was added to each test tube. The samples were mixed well and incubated at room temperature (RT) for exactly 10 minutes. At the end of the 10-minute incubation period, 100µL of prepared 1X Folin-Ciocalteu Reagent was added to the samples and immediately vortex to mix the contents. The samples were then covered and incubated at RT for 30 minutes. With the spectrophotometer set to 750nm, the instrument was zeroed with a cuvette filled only with seawater. Subsequently, the absorbance of all the samples was measured. The average 750nm absorbance values of the Blank standard replicates were subtracted from the 750nm absorbance values of all other individual standards, and unknown sample replicates. A standard curve (Figure 3.1) was prepared by plotting the average Blank-corrected 750nm value for each BSA standard vs. its concentration in µg/mL. The standard curve was used to determine the protein concentration of each unknown sample.
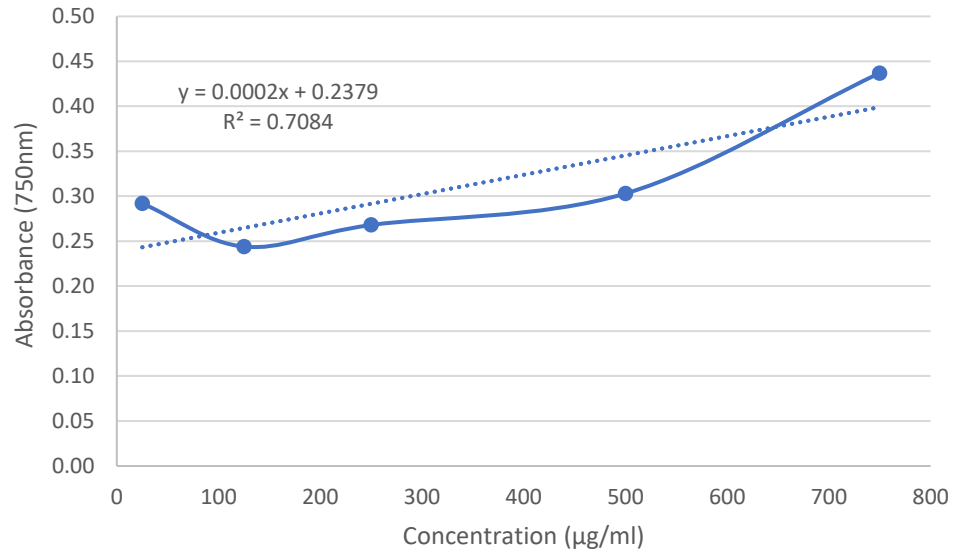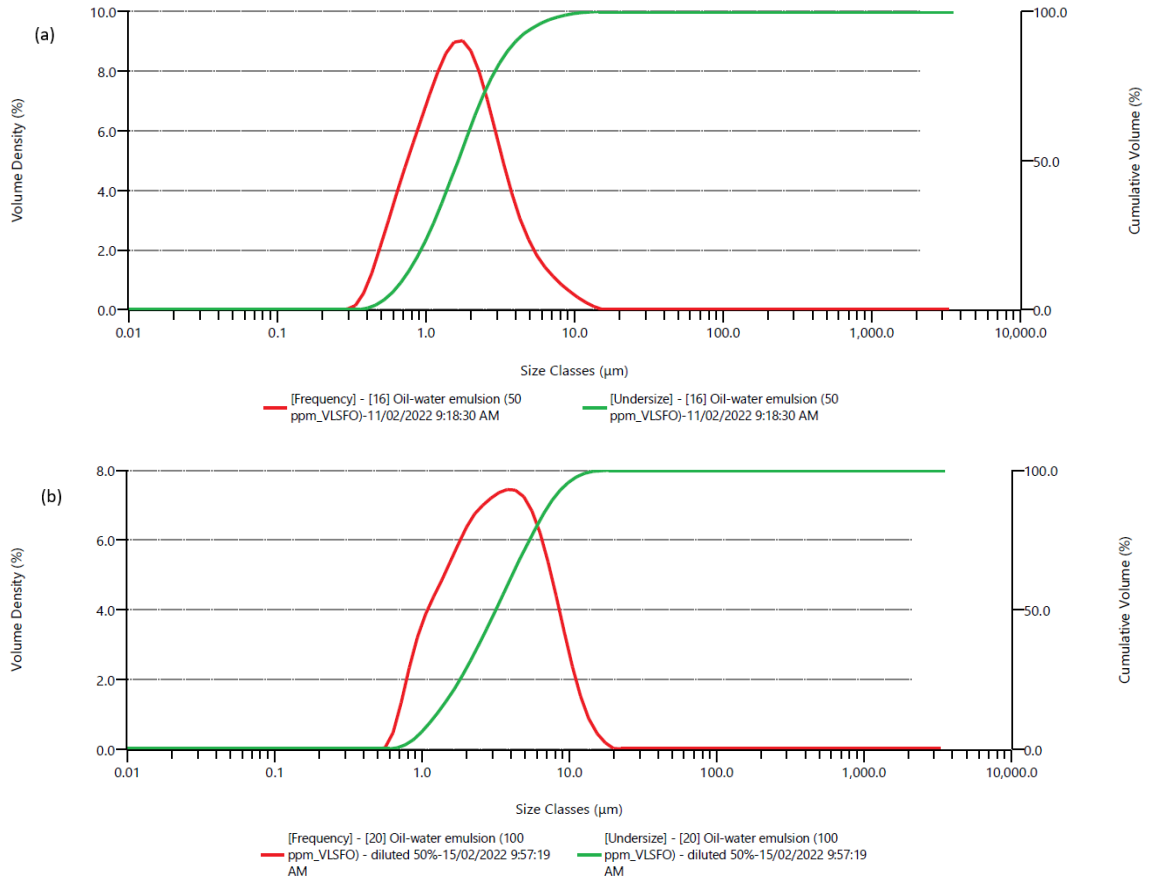
Figure 3.4. Protein standard curve used to determine EPS and SMP concentrations in bench-scale oily wastewater samples
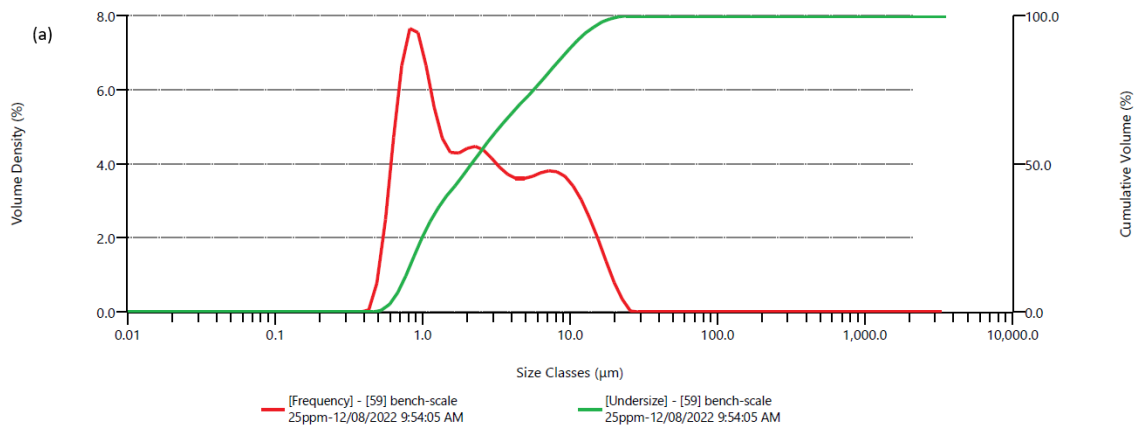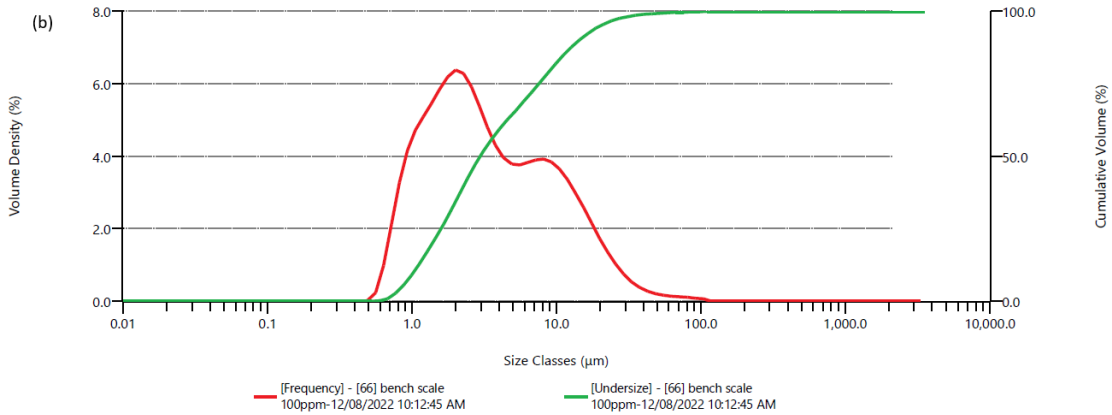
CHAPTER 4: RESULTS AND DISCUSSION

4.1. Oil Droplet Size Distribution

The targeted wastewater that the membrane filtration systesm was intended to treat for this thesis was emulsified oily wastewater. The emulsified oily wastewater that occurs after an oil spill as a result of weather conditions, which contribute to the shearing of slick surfaces and the mixing of oil with underlying water, was recreated in a lab setting (Lee et al., 2015). For the pilot-scale membrane filtration experiments, the Inoxpa high-shear vertical mixer sheared 99.4% and 95.6% of the oil in the initial solutions of Runs 4 and 8 into less than 10μm in diameter, respectively, as seen in Figure 4.1. a and b. For the MBR bench-scale experiments, a blender attained an oil droplet size of 10μm in 88.8% and 81.9% of the oil in the 25ppm and 100pm initial oil concentration solutions, respectively, as shown in Figure 4.2. a and b. The majority of the oil droplets from both sets of experiments were below 10μm in diameter. The size and distribution of emulsion droplets have a substantial influence on the stability of the emulsion. Typically, the narrower the droplet size range and the smaller the oil droplet size, the more stable the emulsion (Nie et al., 2021). The oil droplet size distribution of the pilot-scale experiments was narrower than the bench-scale experiments due to the high-shear vertical mixture being more powerful than the blender; therefore, the emulsion from the pilot-scale experiment was slightly more stable than the bench-scale emulsions.

(a)

[Frequency] - [16] Oil-water emulsion (50 ppm_VLSFO)-11/02/2022 9:18:30 AM

[Undersize] - [16] Oil-water emulsion (50 ppm_VLSFO)-11/02/2022 9:18:30 AM

(b)

[Frequency] - [20] Oil-water emulsion (100 ppm_VLSFO) - diluted 50%-15/02/2022 9:57:19 AM

[Undersize] - [20] Oil-water emulsion (100 ppm_VLSFO) - diluted 50%-15/02/2022 9:57:19 AM

Figure 4.1. Oil droplet size distribution for pilot-scale membrane filtration experiments (a) 50 ppm (b) 100 ppm

(a)

[Frequency] - [59] bench-scale 25ppm-12/08/2022 9:54:05 AM

[Undersize] - [59] bench-scale 25ppm-12/08/2022 9:54:05 AM

Figure 4.2. Oil droplet size distribution for bench-scale MBR experiments (a) 25 ppm (b) 100 ppm

4.2. Activated Sludge Acclimation and Performance in Bench-Scale MBR

Experiments

The MLSS concentration throughout the experiment had an overall increasing trend, indicating that the conditions in the bench-scale experiments were favourable for bacterial growth (Capodici et al., 2017; Razavi and Miri, 2015). Around the 51st hour, there was a dip in MLSS concentration to 0.94 g/L, possibly caused by inadequate aeration, causing some of the biomass to die off due to anaerobic conditions (Du et al., 2020; Xiaoguang et al., 2017; Wang et al., 2014; Sheng et al., 2010). The biomass quickly recovered and reached a concentration of 1.5 g/L MLSS by the end of the experiments, as presented in Figure 4.3. a. The MLVSS/MLSS ratio generally remained above 0.5 and increased up to 0.6 at the end of the experiments, as observed in Figure 4.3. b. This ratio indicated a low inert material build-up and good biomass activity throughout the study (Capodici et al., 2017; Radjenović et al., 2008). The average MLSS concentration for each run is presented in Table 4.1.

Figure 4.4. shows that with an increase in MLSS, there was an increase in SMP, indicating that a portion of the biomass struggled to adjust to wastewater conditions. SMP is typically associated with biomass decay (Capodici et al., 2017; Radjenović et al., 2008). EPS is

correlated to good biomass health since microorganisms produce EPS to interact with their environment (Radjenović et al., 2008). EPS are essential for microbial life and provide ideal environments for chemical reactions, nutrient entrapment, and protection against environmental stresses (Radjenović et al., 2008). In this study the EPS concentrations measured throughout the experiment was less than 25 μg/ml. Although EPS are useful for biodegradation, very high concentration are unwanted in an MBR as they cause membrane fouling (Radjenović et al., 2008).

The R^2 value of SMP was fairly low, 0.1058. MBR experiments generally last for long periods of time (weeks/months) with long SRTs, which allow the activated sludge to adjust to its environment and reach stable conditions to perform optimally. This study was performed within four days, which is very short in terms of MBR experiments, and there was no biomass acclimation period, which would explain the low correlation in SMP concentration with MLSS; the system was not run long enough to reach steady state condition (Radjenović et al., 2008; Viero & Sant'Anna, 2008; Sutton, 2006; Scholz & Fuches, 2000).
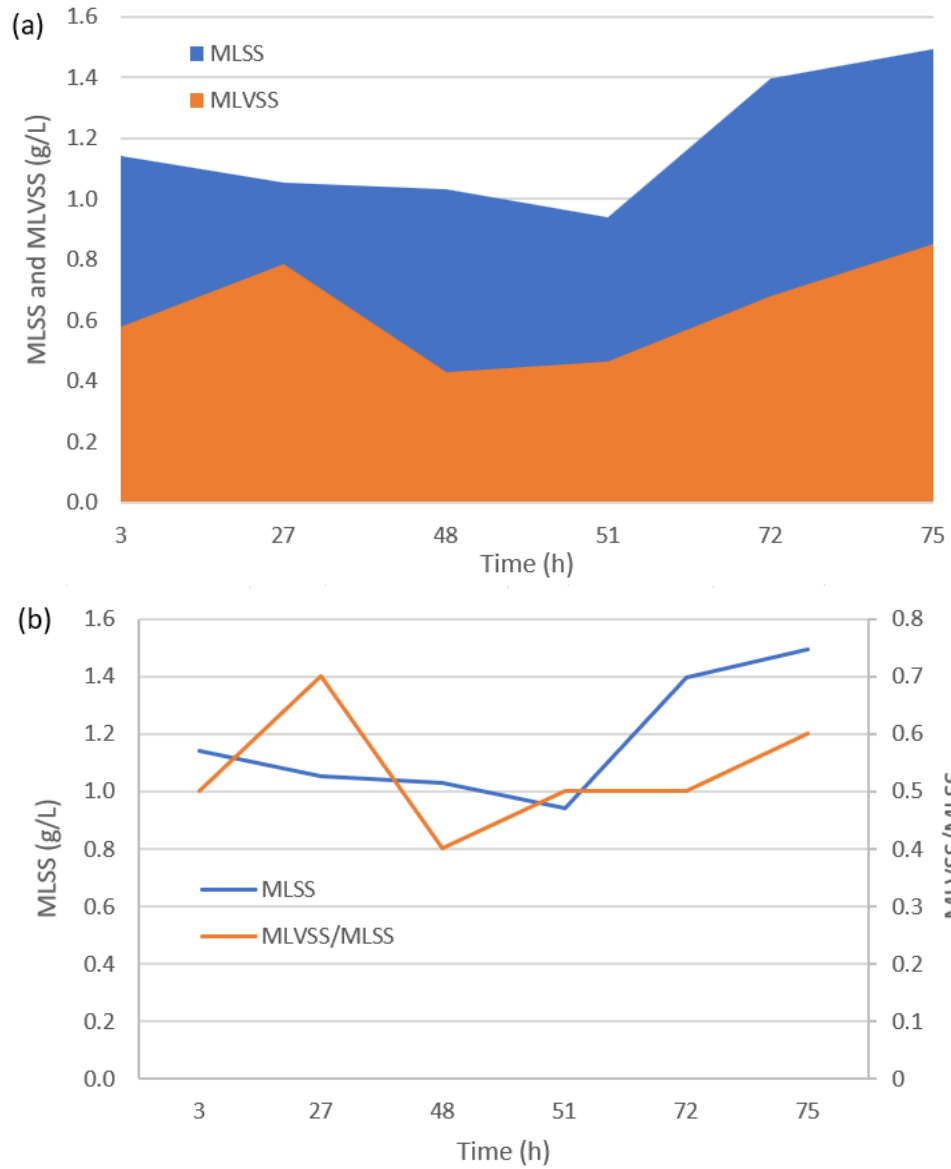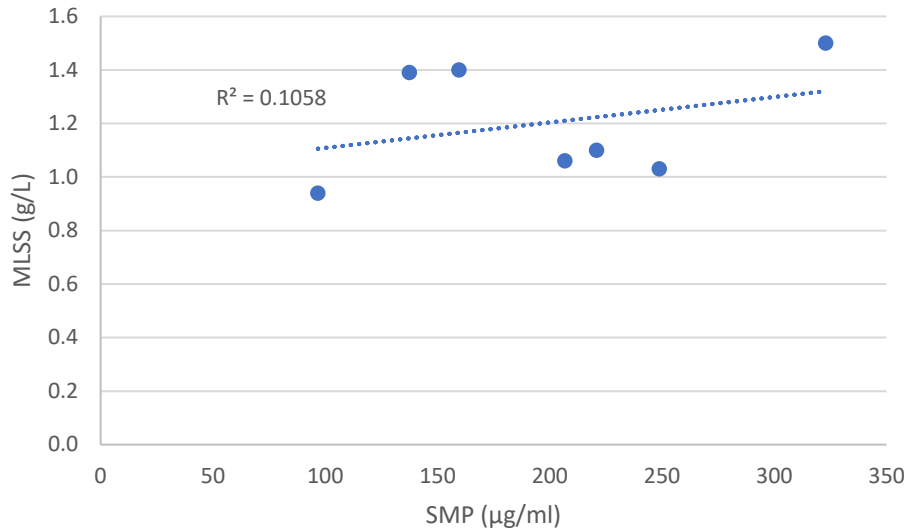
Figure 4.3. Bacteria Viability and Performance (a) MLSS and MLVSS (b) MLVSS/MLSS

Table 4.1. MLSS Concentration

Run ID	MLSS (g/L)
1	1.09
2	1.02
3	1.40
4	1.30

Figure 4.4. Bacteria Viability SMP Protein

4.3. TPH Removal Efficiency

4.3.1. Pilot-Scale Membrane Filtration

The oil removal efficiency of the pilot-scale membrane filtration system was over 94%, except in Run 3, which had an oil removal efficiency of only 86.6%, as presented in Figure 4.5. The decrease in TPH removal efficiency in this particular run could be attributed to a higher-than-normal reversible membrane fouling event, where the oil coalesces to form a cake layer on the surface of the membrane (Tummons et al., 2017). The highest oil removal efficiency of 98.2% was observed in Run 8, which also had the highest initial oil concentration of 28.3 ppm. It is important to note that after Run 8, the membranes experienced severe irreversible fouling, indicating that the maximum oil concentration that the Sumitomo PTFE membranes can handle without activated sludge is approximately 30ppm, which is in accordance with the maximum oil concentration information given by the Sumitomo representative.
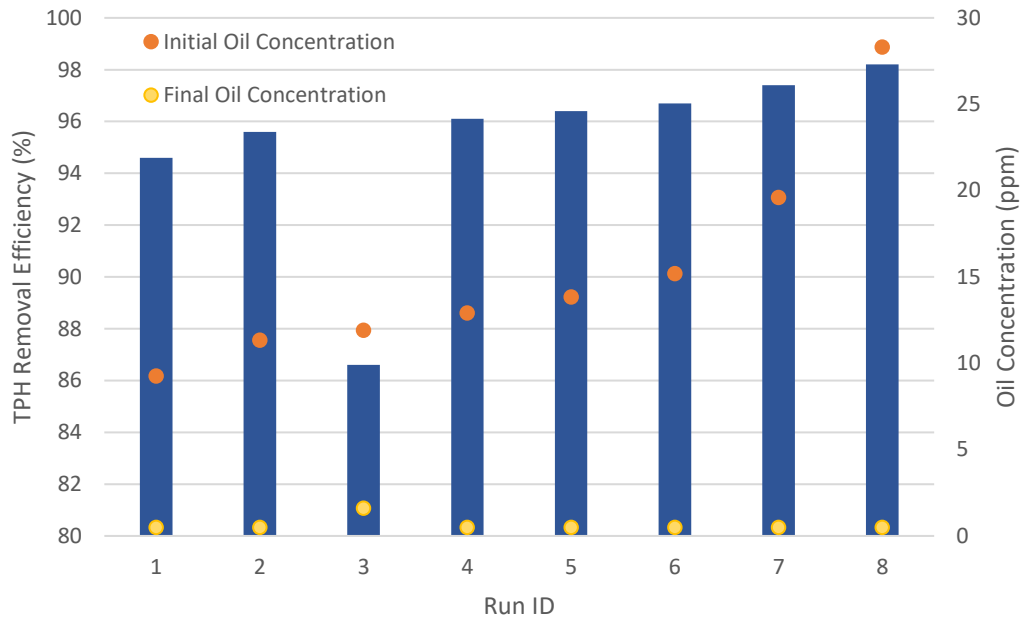
Figure 4.5. Pilot-scale membrane filtration TPH removal efficiency

4.3.2. Bench-Scale MBR

The "total" TPH removal efficiency of the bench-scale experiments was over 96%, where the activated sludge, "biological," contributed to over 92% of oil removal, as presented in Figure 4.6. The "total" and "biological" oil removal efficiency were lower in runs with a 25 ppm initial oil concentration (Runs 1 and 2) than in runs with a 100 ppm initial oil concentration (Runs 3 and 4). A study by Capodici et al., 2017, also observed similar results, where a decrease in feed TPH led to a decrease in the oil removal efficiency of the MBR. The reduction in removal efficiency can be explained by the activated sludge being acclimated to higher initial oil concentrations; with a sudden drop in TPH, the microbial community experienced nutrient depletion (specifically a carbon source), which led some of the biomass to die off. Surprisingly, the activated sludge also performed better in runs with the lower HRT of 3h (Runs 1, 3) than higher HRT of 6h (Runs 2, 4). A statistical two-tailed unpaired heteroscedastic T-test was conducted to determine the significance of

"biological" oil removal efficiency between runs with 3h HRT and 6h HRT (compared values from Runs 1 vs 2 (C_o=25ppm) and Runs 3 vs 4 (C_o=100ppm)); the p-values were less than 0.05, indicating the HRT of 3h had a better oil removal efficiency than 6h HRT. Another T-test (one-tailed, paired) was conducted to determine the significance of oil removal efficiency between "biological" and "total"; the p-values, 0.110 and 0.065, of runs 1 and 3, respectively, indicated that filtration after 3h of biological treatment made no significant impact on oil removal from the wastewater. The increased performance of activated sludge at a low HRT was caused by higher organic loading rates (OLR), consequently reducing the required reactor volume to accomplish a specific removal performance. It also stimulated EPS release from bacterial cells, causing an increase in MLSS (Iorhemen et al., 2016; Isma et al., 2014). The p-values, 0.004 and 0.001 for runs 2 and 4, revealed that even after 6h of biological treatment, membrane filtration played a significant role in removing additional oil from the wastewater samples. The highest oil removal efficiency of 99% was observed in Run 4.
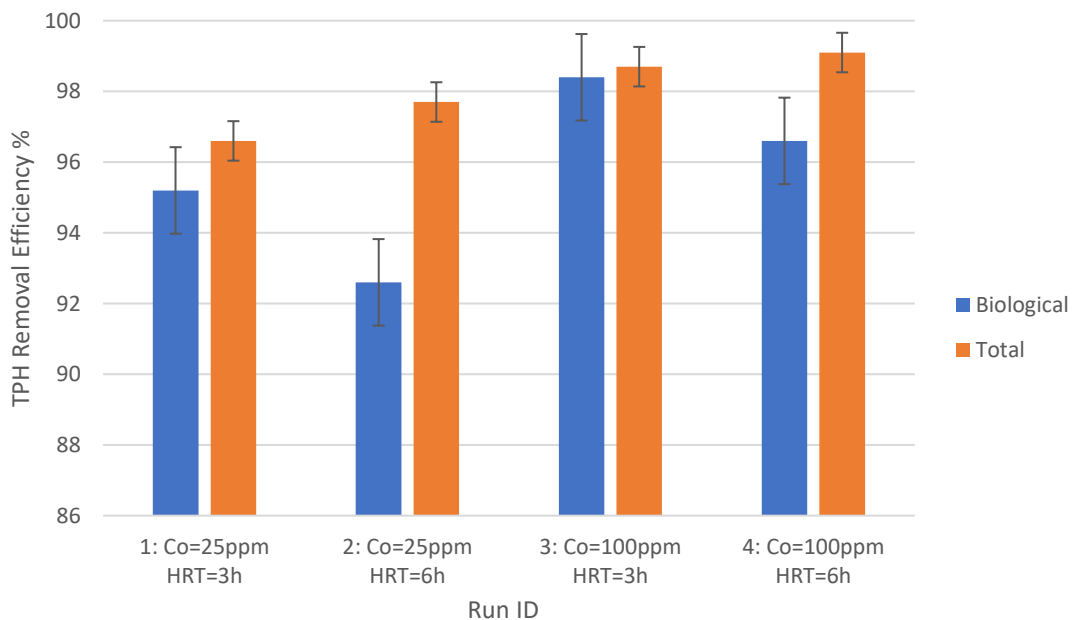
Figure 4.6. Bench-scale MBR TPH removal efficiency

4.3.3. TPH Removal Comparison Between Membrane Filtration and MBR Experiments

The permeate oil concentrations attained in both sets of experiments were significantly less than the MARPOL Annex 1 limit (<15ppm) that Canada adopted for oil discharge in emergency situations (TC, 2010). Both units had a greater than 94% oil removal efficiency. The highest initial oil concentration that the membrane filtration experiments were able to handle was 30ppm, whereas the MBR could handle much higher initial oil concentration (100ppm). The majority of the oil removal was performed by the "biological" component of the MBR. If activated sludge were to be added to the pilot scale unit, it would greatly increase the unit's capabilities.

4.4. PHC Removal Efficiency

PHCs can be divided into four categories: readily volatile decanes, F1: C6- C10; semi-volatile hexadecanes, F2: C10-C16; non-volatile tetra-triacontane, F3: C16-C34; and non-volatile pentacontane, F4: C34- C50. F1 and F2 are lighter oil fractions that are less hydrophobic than F3 and F4. The extremely hydrophobic F3 and F4 are composed of a complex mixture of aromatics, heterocyclics, aliphatics, asphaltenes, and resins (Wang, 2008).

The oil fractions detected in the VLSFO oily wastewater samples were F1-F3. The solubility of the oil fractions notably affects oil removal efficiency. A substance is considered to have low solubility if it is < 100,000 µg/L and very low solubility if it is < 1000 µg/L (ChemSafetyPro, 2021). F1 has solubilities of 430-5400 µg/L and 65,000-130,000 µg/L for aliphatics and aromatics, respectively. F2 has solubilities ranging between

0.76-34 µg/L and 5800-25,000 µg/L for aliphatics and aromatics, respectively. Lastly, F3 has solubilities of 0.00025 µg/L and 6.6-650 µg/L for aliphatics and aromatics, respectively (Maxxam, 2021).

4.4.1. Pilot-Scale Membrane Filtration

The pilot-scale membrane filtration system removed the F3 fraction the most consistently, with the removal efficiency ranging between 57 and 79% throughout all the runs. The successful F3 retention in the membrane tank can be attributed to the extremely insoluble nature of this fraction. The hydrocarbons in the F3 fraction are likely to coalesce to form larger molecules that cannot penetrate the membrane's pores (Huang et al., 2018; Tummons et al., 2017; Braak et al., 2011). Moreover, the hydrophilic nature of the PTFE membrane (water contact angle 58◦) creates a repulsive force toward the hydrophobic hydrocarbons of the F3 fraction (Zhou et al., 2009). The F2 fraction displayed good removal efficiency ranging between 23-83%. The extensive range in oil removal effectiveness could be due to the semi-volatile nature of the oil fraction. Runs 3 and 4 were detected to have an increase in the concentration of the F2 fraction in the permeate, therefore were considered outliers and taken out of consideration. The discrepancy between the initial and permeate oil concentration in runs 3 and 4 can be attributed to sampling errors or storage errors. The samples were stored in glass bottles for long periods of time until they could be shipped to Memorial University for analysis. There may have been a higher rate of oil degradation in the effluent samples than in the permeate samples while it was held in storage; there could have also been the issue of oil being stuck to the sides of the glass bottles, which led to inaccurate oil concentration readings. The F1 fraction removal efficiency in Runs 1 and 3 were 73% and 10%, respectively. The large range in F1 fraction retention can be attributed

to this fraction's volatile and highly soluble nature. Ideally, all of the F1 oil fraction should have been removed in the oil weathering process. All other Runs experienced an increase of F1 in the permeate; they were considered outliers and taken out of consideration; this can be caused by sampling or storage errors. The pilot-scale PHC removal efficiencies are presented in Figure 4.7.
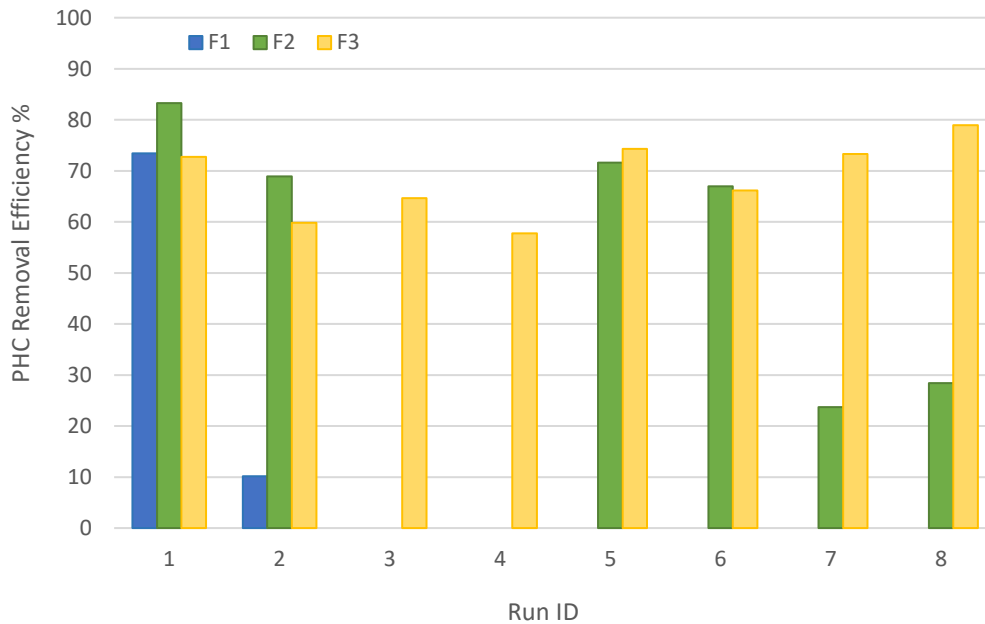
Figure 4.7. Pilot-scale membrane filtration PHC removal efficiency

4.4.2. Bench-Scale MBR

The bench-scale MBR PHC removal efficiencies are presented in Figure 4.8. Biological treatment resulted in over a 97% oil removal efficiency for all fractions; filtration contributed an additional greater than 1% removal efficiency (over 98% "total"). A two-tailed unpaired heteroscedastic T-test (compared Runs 1 vs 2 (C_o=25ppm) and 3 vs 4 (C_o=100ppm) for all oil fractions) was performed to determine the significance of HRT on oil fraction removal efficiency; it was confirmed that there was no significant impact between HRT of 3h and 6h on oil fraction removal efficiency; except for the F2 and F3 fractions with experiments that had 100 ppm initial oil concentration, which had P-values

less than 0.05. The HRT of 3 had a better oil removal efficiency than the HRT of 6 for the F2 and F3 fractions for the runs with the initial oil concentration of 100ppm.

The biological treatment in runs 3 and 4 had a higher contribution to F1 removal than in Runs 1 and 2, as shown in Figure 4.8. a. The higher biological treatment efficiency can be attributed to the high solubility of the F1 fraction and high initial oil concentration. The biomass absorbed the F1 fraction the best due to its high water solubility and was able to degrade it more easily (Radjenović et al., 2008). The p-values from the one-tailed paired T-test for runs 1, 2, and 3 were greater than 0.05, indicating that the filtration after biological treatment did not have a significant impact on oil removal efficiency; however, Run 4 had a p-value of less than 0.05, showing that membrane filtration did have a significant contribution to F1 removal.

The runs with higher initial oil concentrations had a higher oil removal efficiency of the F2 and F3 fractions than those with lower initial oil concentrations, as shown in Figures 4.8. b and 4.8. c, respectively. The biological treatment in Runs 3 and 4 had a higher contribution to F2 and F3 removal than in Runs 1 and 2. The higher biological treatment efficiency can be attributed to the high initial oil concentration. The charged EPS and SMP produced by biomass were able to absorb the extremely hydrophobic F3 fraction effectively (Lee et al., 2020; Radjenović et al., 2008). The p-values from the one-tailed paired T-test for runs 1 and 3 (HRT 3h) were greater than 0.05, indicating that the filtration after biological treatment did not have a significant impact on oil fractions F2 and F3 removal efficiency; however, Runs 2 and 4 (HRT 6h) had a p-value of less than 0.05, showing that membrane filtration did have a significant contribution to F2 and F3 removal. The insignificant contribution of the filtration components in Runs 1 and 3 can be explained by the biological

having a higher contribution to removal efficiency; therefore, it most likely began breaking down the PAH, and all the EPS and SMP were quickly saturated. The remaining smaller PAH structures were well-solubilized and could cross the membrane more easily (Xu et al., 2018; Sheng et al., 2010; Brooijmans et al., 2009).
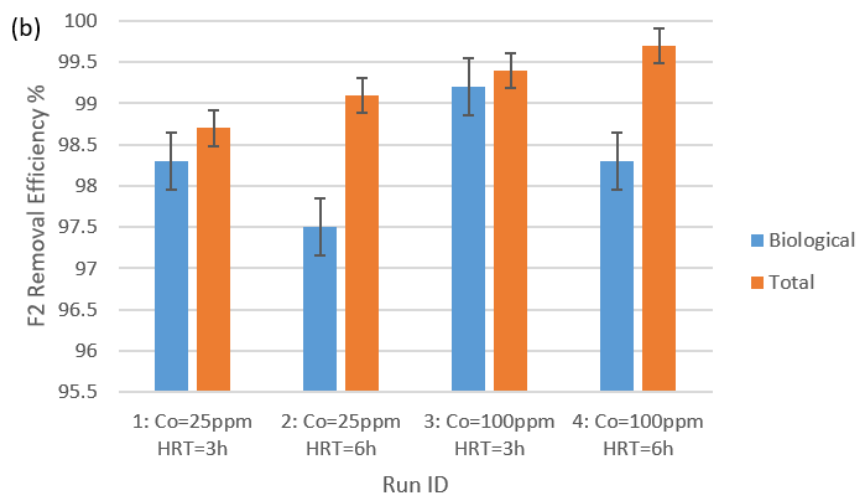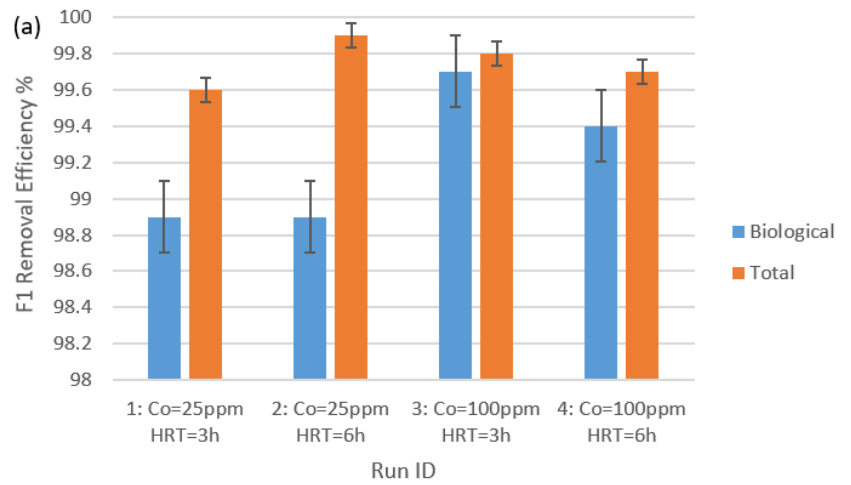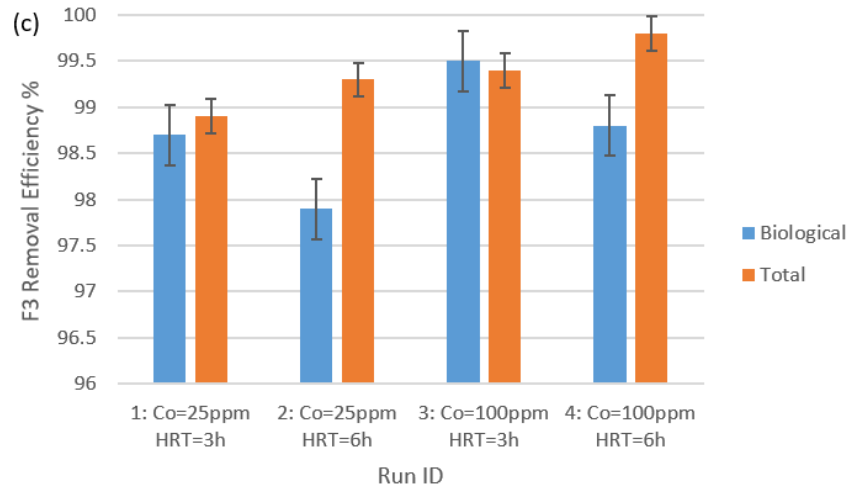
Figure 4.8. Bench-scale MBR PHC removal efficiency

4.4.3. PHC Removal Comparison Between Membrane Filtration and MBR

The oil removal efficiency of different oil fractions varied vastly in the membrane filtration experiments, and the oil removal efficiency did not exceed 83%. On the other hand, the MBR setup effectively and consistently removed all oil fractions with a greater than 98.5% removal efficiency. The higher performance of the MBR can be attributed to the biological component of the system.

Although, in general, MBR systems are conducted under steady-state conditions with long HRTs (>10 hrs) for treating oily wastewater to allow the biomass enough contact time with the hydrocarbons to metabolize them efficiently, the set of experiments conducted for this study investigated the effects of short HRT without the steady state conditions for its application to marine oil spill response (Di Bella et al., 2015; Soltani et al., 2010). The short HRT did not allow for substantial biodegradation to occur; instead, the EPS and SMP produced by the bacteria under unsteady state conditions acted as an adsorbent (Lee et al., 2020; Nouha et al., 2017; Sheng et al., 2010; Radjenović et al., 2008). The higher protein content or protein-to-carbohydrate (P/C) ratio allows for higher EPS hydrophobicity, which

correlates with the substrate provided to the microbial communities (Nouha et al., 2017). EPS hydrophobicity is notably affected by the functional groups in its protein fraction. Hydrophobicity is a key factor when EPS is intended to use in organic pollutant removal (Nouha et al., 2017; Sheng et al., 2010).

Combining activated sludge with the pilot-scale membrane filtration system would effectively remove all oil components. The EPS from the activated sludge would trap the majority of the components, especially the F1 fraction, which the pilot-scale system struggled with the most. The treated PTFE membrane would then stop the movement of the remaining components not bound by the EPS through its hydrophobic properties. Incorporating activated sludge in the pilot-scale system would enable it to treat oily wastewater with higher oil concentrations and result in a more effective operation.

4.5. PAH Removal Efficiency Compared to Canadian Water Standards for PAH

PAHs are a persistent organic subclass of PHCs that are mutagenic, carcinogenic and difficult to degrade under natural conditions. They can be hazardous if present in large quantities in surface waters, the Environmental Protection Agency (EPA) has recorded 18 "priority" PAHs contaminants to take into consideration when dealing with oily wastewater (Rutter et al., 2014). Table 4.1 presents the Canadian water quality standards for PAH and final PAH concentrations and removal efficiencies for both the pilot-scale membrane filtration and bench-scale MBR experiments. Only the runs with the highest initial oil concentrations were considered for PAH analysis for both sets of experiments to determine the extent of removal efficiencies and to evaluate the if the final PAH concentrations is below the Canadian water quality standard.

4.5.1. Pilot-Scale Membrane Filtration

100 % removal of Pyrene, Benzo(a)anthracene, and Chrysene were obtained due to their water solubilities of 135, 9.4, and 4 µg/L, indicating that they are extremely insoluble since they are less than 1000 µg/L (ChemSafetyPro, 2021; PubChem, n.d.). These PAH also have larger structures of 4 benzene rings or greater, which promote the formation of larger molecules that cannot penetrate the membrane's pores (Huang et al., 2018; Tummons et al., 2017; Braak et al., 2011). Furthermore, the hydrophilic nature of the PTFE membrane creates a repulsive force toward the hydrophobic PAH (Zhou et al., 2009).

Naphthalene, 1-Methylnaphthalene, 2-Methylnaphthalene, Fluorene, Anthracene, Phenanthrene, Acenaphthene, and Fluoranthene were the PAH with the lowest removal rate; their water solubilities of 31000, 25000, 24600, 1690, 43.4, 1100, 3900, and 200–260 µg/L, respectively, indicate that they are relatively more soluble than Pyrene, Benzo(a)anthracene, and Chrysene (ChemSafetyPro, 2021; PubChem, n.d.). Their slightly more soluble properties and smaller structures (less than or equal to 3 benzene rings) made it easier to penetrate the membrane and also experienced less repulsive force from the membrane. Acenaphthalene was detected in the membrane filtration experiment sample; however, an increase in Acenaphthalene was observed in the permeate. This can be caused by sampling or storage errors; therefore, the result was omitted.

The pilot-scale membrane filtration system effectively removed all PAH below the acceptable Canadian levels for marine and freshwater, as indicated by ECCC, except for 2-Methylnapthalene and Anthracene. The membrane filtration system exceeded the marine water limit for 2-Methylnapthalene by less than 0.2 µg/L and freshwater and marine limits for Anthracene by approximately 1 and 0.44 µg/L.

4.5.2. Bench-Scale MBR

All PAH had over 90% removal in the MBR experiments. 100% removal of Chrysene, Pyrene, Benzo(b)fluoranthene, Benzo(e)pyrene, Benzo(a)pyrene, Dibenzo(a,h)anthracene, and Benzo(g,h,i)perylene were observed. Benzo(b)fluoranthene, Benzo(e)pyrene, Benzo(a)pyrene, Dibenzo(a,h)anthracene, and Benzo(g,h,i)perylene have water solubilities of 1.5, 6.3, 1.62, 2.49, and 0.26 μg/L, respectively and are structures that are composed of greater than or equal to 5 benzene rings (PubChem, n.d.). The extremely hydrophobic PAHs were more easily trapped by the charged functional groups of EPS and SMP produced by the bacteria in the activated sludge (Nouha et al., 2017; Sheng et al., 2010). 100% of Benzo(a)anthracene was removed from Run 4 (HRT 6), whereas Run 3 (HRT 3) only had a 92.9% removal efficiency. In general, Run 4 had a higher PAH removal efficiency than Run 3, based on the TPH and PHC removal efficiencies; this can be attributed to the biomass trapping enough of the contaminants for the membrane to effectively remove the remaining PAH. In Run 3, the biological had a higher contribution to removal efficiency; therefore, it most likely began breaking down the PAH, and all the EPS and SMP were quickly saturated. The remaining smaller PAH structures were well-solubilized and could cross the membrane more easily (Xu et al., 2018; Sheng et al., 2010; Brooijmans et al., 2009).

The bench-scale MBR effectively removed all PAH below the acceptable Canadian levels for marine and freshwater as indicated by ECCC, except for Naphthalene, 2-Methylnapthalene, Fluorene, Anthracene, and Pyrene. The MBR exceeded the freshwater and marine water limit for Naphthalene by approximately less than 0.3 and 0.4 μg/L; freshwater and marine water limits for 2-Methylnapthalene by approximately less than 0.6

and 1.6 μg/L, respectively; freshwater limits for Fluorene by approximately 1.2 μg/L for Run 3; freshwater and marine water limits for Anthracene by approximately 1.3 and 0.7 μg/L for Run 3, freshwater limits for Run 4 by 0.43 μg/L; freshwater limits for Pyrene by 0.016 μg/L for Run 3.

4.5.3. PAH Removal Efficiency Comparison Between Pilot-Scale and Bench-Scale

12 "priority" PAH were detected in the pilot-scale membrane filtration experiments, whereas the 16 "priority" PAH contaminants were detected in the bench-scale MBR experiments. PAH removal efficiency ranged between 47.9% - 100% and 90.3% - 100%, depending on the PAH contaminant for membrane filtration and MBR experiments, respectively. The MBR experiments performed better in terms of overall PAH removal efficiency than the membrane filtration experiments. The higher removal efficiency of the MBR can be attributed to the activated sludge that trapped the different types of PAH with the help of EPS and SMP produced by the biomass, whereas in the membrane filtration experiments, the efficiency was solely determined by the interaction of each component with the HF membrane (Nouha et al., 2017; Sheng et al., 2010; Zhou et al., 2009).

The pilot-scale membrane filtration system effectively removed the most PAH to meet the Canadian Water Standards for fresh and marine water. The MBR met majority of the standards except for 5 of the 16 PAH. The membrane filtration system started with a very low initial oil concentration of 30ppm, contributing to the pilot-scale system's better performance; the MBR started with an initial concentration of 100ppm. The MBR marginally exceeded the limits for the previously mentioned PAH. If activated sludge were added to the pilot-scale membrane filtration unit, it could handle treating oily wastewater with a higher initial oil concentration and more effectively meet all the PAH standards. The

activated sludge would entrap majority of the PAH, and the HF-MF-PTFE membrane would create a repulsive force against the remaining "priority" PAH contaminants that are not bound to EPS and SMP, which would prevent it from crossing the membrane, resulting in a more efficacious treatment of oily wastewater from marine oil spills. The EPS and SMP produced by the biomass would act as an adsorbant (Nouha et al., 2017; Sheng et al., 2010).

Table 4.2. Canadian water quality standards for PAH and final PAH concentrations and removal efficiencies

PAH	Canadian Water Standards (µg/L) from ECCC (L. Britton)	Membrane Filtration Final PAH Concentration (µg/L) for Run 8	Membrane Filtration PAH Removal Efficiency % for Run 8	MBR Final PAH Concentration (µg/L) for Runs 3 & 4 "total"	MBR PAH Removal Efficiency % for Runs 3 & 4 "total"
Naphthalene	*Freshwater*: 1.1 *Marine*: 1.2	1.092	59.2	*Run 3*: 1.493 *Run 4*: 1.241	*Run 3*: 91.7 *Run 4*: 93.1
1-Methylnaphthalene	*Freshwater*: 2 *Marine*: N/A	1.684	47.9	*Run 3*: 1.754 *Run 4*: 1.382	*Run 3*: 90.3 *Run 4*: 92.4
2-Methylnaphthalene	*Freshwater*: 2 *Marine*: 1	1.175	76.2	*Run 3*: 2.581 *Run 4*: 1.987	*Run 3*: 92.2 *Run 4*: 94.0
Acenaphthalene	*Freshwater*: 4840 *Marine*: N/A	N/A	N/A	N/A	N/A
Acenaphthene	*Freshwater*: 23 *Marine*: 9.7	0.100	70.1	*Run 3*: 0.223 *Run 4*: 0.162	*Run 3*: 92.3 *Run 4*: 94.4
Fluorene	*Freshwater*: 0.2 *Marine*: N/A	0.203	66.2	*Run 3*: 0.322 *Run 4*: 0.178	*Run 3*: 95.2 *Run 4*: 97.4
Anthracene	*Freshwater*: 0.035 *Marine*: 0.6	1.042	69.5	*Run 3*: 1.326 *Run 4*: 0.474	*Run 3*: 97.2 *Run 4*: 99.0
Phenanthrene	*Freshwater*: 6.3 *Marine*: 4.6	0.079	76.5	*Run 3*: 0.068 *Run 4*: 0.009	*Run 3*: 98.9 *Run 4*: 99.9
Pyrene	*Freshwater*: 0.025 *Marine*: N/A	0	100	*Run 3*: 0.041 *Run 4*: 0	*Run 3*: 99.0 *Run 4*: 100
Fluoranthene	*Freshwater*: 4 *Marine*: 1.6	0.788	49.4	*Run 3*: 0.245 *Run 4*: 0.021	*Run 3*: 99.0 *Run 4*: 99.9
Benzo(a)anthracene	*Freshwater*: N/A *Marine*: N/A	0	100	*Run 3*: 0.097 *Run 4*: 0	*Run 3*: 92.9 *Run 4*: 100
Chrysene	*Freshwater*: 0.0001 Marine: 0.1	0	100	*Runs 3 & 4*: 0	*Runs 3 & 4*: 100
Benzo(b)fluoranthene	*Freshwater*: 0.03 *Marine*: N/A	N/A	N/A	*Runs 3 & 4*: 0	*Runs 3 & 4*: 100
Benzo(e)pyrene	*Freshwater*: N/A *Marine*: N/A	N/A	N/A	*Runs 3 & 4*: 0	*Runs 3 & 4*: 100
Benzo(a)pyrene	*Freshwater*: 0.0014 *Marine*: N/A	N/A	N/A	*Runs 3 & 4*: 0	*Runs 3 & 4*: 100
Dibenzo(a,h)anthracene	*Freshwater*: 0.002 *Marine*: N/A	N/A	N/A	*Runs 3 & 4*: 0	*Runs 3 & 4*: 100
Benzo(g,h,i)perylene	*Freshwater*: 0.0002 *Marine*: N/A	N/A	N/A	*Runs 3 & 4*: 0	*Runs 3 & 4*: 100

CHAPTER 5: CONCLUSION

5.1. Summary and Conclusion

The high tanker traffic through Canada's EEZ elevates the risk of oil spill accidents, endangering marine life, human health, destroying the coastline, and the local economy; therefore, it is vital to mitigate the damage resulting from oil spill incidents. Under current regulation, it is illegal to discharge any oily wastewater collected from oil spill response operations, even though up to 60% of the collected fluids constitute of seawater, due to the concern of releasing harmful "priority" contaminants into the aquatic environment. The zero-discharge policy significantly hinders response operations as it limits temporary storage space on barges and requires multiple cycles of trips to shore to transfer the wastewater to an intermediate storage facility. The lack of response capacity does not permit for quick and effective recovery of the spilled oil, instead allows for its propagation further into the ocean or shorelines, causing compounding environmental damage. One of the research areas that has recently received attention is onsite decanting to ensure quick and efficient clean-up operations. As part of this thesis, one of the tasks was to design a system that can effectively treat decanted oily wastewater onsite and discharge the excess seawater back into the ocean to increase the oil spill response capacity. This thesis explores the possibility of installing a membrane bioreactor filtrations system on board as part of a treatment train to treat decanted oily seawater. The membrane filtration would be the last polishing step of the treatment system that would ensure that the water discharged back into the ocean has a very low oil concentration (below 15 ppm) and, most importantly, filter out the "priority" PAH contaminants of concern from the wastewater. Removing "priority"

PAH would render the decanted water that is dicharged back to the ocean as non-deleterious to maine life.

This thesis compared the treatment efficiency and capacity of a submerged PTFE-MF-HF membrane filtration system vs. an MF-MBR system. The MBR system had an overall better performance than the membrane filtration system for TPH, PHC, and PAH removal. The MBR system shows very good potential to be part of an onsite treatment system for decanted oily seawater generated from oil spill response operations.

The pilot-scale membrane filtration system performed well in terms of oil removal efficiency as long as the initial oil concentration remained below 30ppm. It effectively removed most PAH in the wastewater to an acceptable level for Canadian surface waters. When analyzing the removal efficiency of different oil fractions, the membrane filtration struggled to remove F1 fractions and had a wide removal efficiency range when it came to F2 fractions.

On the other hand, the bench-scale MBR experiments proved to be able to treat a much higher oil concentration (100ppm). The MBR system effectively removed all three oil fractions at a higher rate than the membrane filtration unit. The MBR system met the water quality standards for all PAH, apart from Naphthalene, 2-Methylnapthalene, Fluorene, Anthracene, and Pyrene, where the concentration in the permeate in some of the runs were marginally higher than the standard set out by ECCC. Moreover, it was determined that the activated sludge in the MBR system played a major role in the successful treatment of saline oily wastewater, achieving 98.4% "biological" removal efficiency at an HRT of 3h and an initial oil concentration of 100ppm. It was determined that an HRT of 3h had a

significantly higher oil removal efficiency than an HRT of 6h; however, the runs with an HRT of 3h had no significant oil removal contribution from the membrane. The enhanced performance of activated sludge at a low HRT was instigated by higher OLR due to the small reactor volume, which triggered a higher rate of EPS release from the bacterial cell.

Longer HRTs (>10 hrs) are typically recommended for treating oily wastewater to allow biomass enough contact time with hydrocarbons to metabolize them effectively; however, since the MBR system is intended to be used for oil spill response, short HRTs (3 and 6h) were tested. The MBR was very effective at removing PAH and reducing oil concentration at low HRTs, because of the EPS and SMP produced by the bacteria in the activated sludge acted as an adsorbent. Hence, although short HRT times are not enough to biodegrade the oil components, the flocs created by the microorganisms are effective in trapping the oil and removing it from the wastewater. Additionally, the low MLSS concentration contributed to the high OLR that, in turn, triggered the bacteria to produce excess EPS and SMP, which helped the treatment efficiency. The insignificant contribution of the filtration components in Runs with HRT of 3h can be caused by the biological having a higher contribution to removal efficiency; therefore, it most likely began breaking down the PAH, and all the EPS and SMP were quickly saturated. The remaining smaller PAH structures were well-solubilized and could cross the membrane more easily, reducing the membrane's effectiveness.

5.2. Recommendations for Future Studies

Future experiments should investigate the effects of adding activated sludge to the pilot-scale membrane filtration system to determine if the Sumitomo membranes can handle high oil concentration (>30 ppm) and still effectively remove oil and the "priority" PAH to meet

Canadian water quality standards. Optimal parameters such as sludge concentration and aeration rate should also be determined for this unit. Another consideration to take into account is to test different types of crude oil on the pilot-scale MBR system.

References

Abuhasel, K.; Kchaou, M.; Alquraish, M.; Munusamy, Y.; Jeng, Y. T. (2021). Oily wastewater treatment: Overview of conventional and modern methods, challenges, and future opportunities. *Water (Switzerland)*, *13*(7). https://doi.org/10.3390/w13070980

Adams, J.; Charbonneau, K.; Tuori, D.; Brown, R. S.; Hodson, P. V. (2017). *Canadian Science Advisory Secretariat (CSAS) Review of Methods for Measuring the Toxicity to Aquatic Organisms of the Water Accommodated Fraction (WAF) and Chemically-Enhanced Water Accommodated Fraction (CEWAF) of petroleum*. http://www.dfo-mpo.gc.ca/csas-sccs/

Adetunji, A. I.; Olaniran, A. O. (2021). Treatment of industrial oily wastewater by advanced technologies: a review. *Applied Water Science*, *11*(6). https://doi.org/10.1007/s13201-021-01430-4

Afzal, M.; Rehman, K.; Shabir, G.; Tahseen, R.; Ijaz, A.; Hashmat, A. J.; Brix, H. (2019). Large-scale remediation of oil-contaminated water using floating treatment wetlands. *Npj Clean Water*, *2*(1). https://doi.org/10.1038/s41545-018-0025-7

Ahmed, Y.; Yaakob, Z.; Akhtar, P.; Sopian, K. (2015). Production of Biogas and Performance Evaluation of Existing Treatment Processesin Palm Oil Mill Effluent (POME).Renew. Sustain. Energy Review. 42, 1260–1278.

Akhondi, E.; Zamani, F.; Tng, K. H.; Leslie, G.; Krantz, W. B.; Fane, A. G.; Chew, J. W. (2017). The performance and fouling control of submerged hollow fiber (HF) systems: A review. *Applied Sciences (Switzerland)*, 7(8). MDPI. AG. https://doi.org/10.3390/app7080765

Al-Asheh, S.; Bagheri, M.; Aidan, A. (2021). Membrane bioreactor for wastewater treatment: A review. In *Case Studies in Chemical and Environmental Engineering*. 4. Elsevier Ltd. https://doi.org/10.1016/j.cscee.2021.100109

Al-Hawash, A. B.; Dragh, M. A.; Li, S.; Alhujaily A.; Abbood, H. A.; Zhang, X.; Ma, F. (2018). Principles of microbial degradation of petroleum hydrocarbons in the environment. In *Egyptian Journal of Aquatic Research*, 44 (2), 71–76. National Institute of Oceanography and Fisheries. https://doi.org/10.1016/j.ejar.2018.06.001

Al-Malack, M. H. (2006). Determination of biokinetic coefficients of an immersed membrane bioreactor. *Journal of Membrane Science*, *271*(1–2), 47–58. https://doi.org/10.1016/j.memsci.2005.07.008

Alsalhy, Q. F.; Almukhtar, R. S.; Alani, H. A. (2016). Oil Refinery Wastewater Treatment by Using Membrane Bioreactor (MBR). *Arabian Journal for Science and Engineering*, *41*(7), 2439–2452. https://doi.org/10.1007/s13369-015-1881-9

Altinbas, M.; Ozturk, H.; İren, E. (2021). Full Scale Sanitary Landfill Leachate Treatment by MBR: Flat Sheet vs. Hollow Fiber Membrane. Journal of Membrane Science and Research, 7(2), 118–124. https://doi.org/10.22079/jmsr.2020.123563.1358

Atlas, R. M. (1985). *Effects of Hydrocarbons on Microorganisms and Petroleum Biodegradation in Arctic Ecosystems*.

Atlas, R. M. (1991). Microbial hydrocarbon degradation—bioremediation of oil spills. *Journal of Chemical Technology & Biotechnology*, *52*(2), 149–156. https://doi.org/10.1002/jctb.280520202

Author/Compiled by Eawag (Swiss Federal Institute of Aquatic Science and Technology) Dorothee Spuhler (seecon international gmbh). (2019, June 3). Activated sludge. SSWM. Retrieved December 6, 2022, from https://sswm.info/factsheet/activated-sludge

Baig, N.; Salhi, B.; Sajid, M.; Aljundi, I.H. (2021). Recent Progress in Microfiltration/Ultrafiltration Membranes for Separation of Oil andWater Emulsions.*Chem. Rec.*2021,22, e202100320.

Barani, M.; Bazgir, S.; Keyvan Hosseini, M.; Keyvan Hosseini, P. (2021). Eco-Facile Application of Electrospun Nanofibers to the Oil-WaterEmulsion Separation via Coalescing Filtration in Pilot- Scale and Beyond. *Process Saf. Environ. Prot*.148, 342–357.

Bassin, J. P.; Dezotti, M.; Sant'Anna, G. L. (2011). Nitrification of industrial and domestic saline wastewaters in moving bed biofilm reactor and sequencing batch reactor. *Journal of Hazardous Materials*, *185*(1), 242–248. https://doi.org/10.1016/j.jhazmat.2010.09.024

Bérubé, P.R.; Lei, E. (2006). The Effect of Hydrodynamic Conditions and System Configurations on the Permeate Flux in a Submerged Hollow Fiber Membrane System. *J. Membr. Sci*. 271, 29–37.

Bhattacharyya, A.; Liu, L.; Lee, K.; Miao, J. (2022). Review of Biological Processes in a Membrane Bioreactor (MBR): Effects ofWastewater Characteristics and Operational Parameters on Biodegradation Efficiency When Treating Industrial Oily Wastewater. *J. Mar. Sci. Eng*. 10, 1229. https://doi.org/10.3390/jmse10091229.

Bouhabila, E. (2005). Fouling Characterisation in Membrane Bioreactors. *Sep. Purif. Technol.* 51, 95–103.

Braak, E., Alliet, M., Schetrite, S., Albasi, C. (2011). Aeration and hydrodynamics in submerged membrane bioreactors. *J. Membr. Sci.* 379 (1–2), 1–18. https://doi.org/10.1016/j.memsci.2011.06.004.

Branch, L. S. (2022, October 28). Consolidated federal laws of Canada, Canadian Environmental Protection Act, 1999. Canadian Environmental Protection Act, 1999. Retrieved September 8, 2022, from https://laws-lois.justice.gc.ca/eng/acts/c-15.31/

Brooijmans, R. J. W.; Pastink, M. I.; Siezen, R. J. (2009). Hydrocarbon-degrading bacteria: The oil-spill clean-up crew. In *Microbial Biotechnology*. 2(6) 587–594. https://doi.org/10.1111/j.1751-7915.2009.00151.x

Brookes, A. Immersed Membrane Bioreactors for Produced Water Treatment .Ph.D. Thesis, Cranfield University School of Water Sciences, Cranfield, UK, 2005.

Brzeszcz, J.; Kaszycki, P. (2018). Aerobic bacteria degrading both n-alkanes and aromatic hydrocarbons: an undervalued strategy for metabolic diversity and flexibility. *Biodegradation*. 29, 359-407. https://doi.org/10.1007/s10532-018-9837-x

Cabassud, C.; Laborie, S.; Durand-Bourlier, L.; Lainé, J.M. (2001). Air Sparging in Ultrafiltration Hollow Fibers: Relationship betweenFlux Enhancement, Cake Characteristics and Hydrodynamic Parameters. *J. Membr. Sci*. 181, 57–69

Campo, R.; Di Prima, N.; Freni, G.; Giustra, M. G.; Di Bella, G. (2016). Start-up of two moving bed membrane bioreactors treating saline wastewater contaminated by hydrocarbons. *Water Science and Technology*, *73*(4), 716–724. https://doi.org/10.2166/wst.2015.512

Campo, R.; Giustra, M. G.; De Marchis, M.; Freni, G.; Di Bella, G. (2017). Characterization and treatment proposals of shipboard slop wastewater contaminated by hydrocarbons. *Water (Switzerland)*, *9*(8). https://doi.org/10.3390/w9080581

Canada, E. and C. C. (2022, February 23). Government of Canada. Canada.ca. Retrieved September 19, 2022, from https://www.canada.ca/en/environment-climate-change/services/managing-pollution/fisheries-act-registry/frequently-asked-questions.html

Cao, K.; Zhi, R.; Zhang, G. (2020). Photosynthetic bacteria wastewater treatment with the production of value-added products: A review. *Bioresource Technology*. 299. Elsevier Ltd. https://doi.org/10.1016/j.biortech.2019.122648

Capodici, M.; Cosenza, A.; Di Bella, G.; Di Trapani, D.; Viviani, G.; Mannina, G. (2020). High salinity wastewater treatment by membrane bioreactors. In *Current Developments in Biotechnology and Bioengineering: Advanced Membrane Separation Processes for Sustainable Water and Wastewater Management - Case Studies and Sustainability Analysis*. 177–204. Elsevier. https://doi.org/10.1016/B978-0-12-819854-4.00008-3

Capodici, M.; Cosenza, A.; Di Trapani, D.; Mannina, G.; Torregrossa, M.; Viviani, G. (2017). Treatment of oily wastewater with membrane bioreactor systems. *Water (Switzerland)*, *9*(6). https://doi.org/10.3390/w9060412

Cappello, S.; Volta, A.; Santisi, S.; Morici, C.; Mancini, G.; Quatrini, P.; Genovese, M.; Yakimov, M.M.; Torregrossa, M. (2016). Oil-degrading bacteria from a membrane sbioreactor (BF-MBR) system for treatment of saline oily waste: Isolation, identification and characterization of the biotechnological potential. *Int. Biodeterior. Biodegrad.* 110, 235–244. https://doi.org/10.1016/j.ibiod.2015.12.028.

Chanunpanich, N.; Hongsik, B.; Inn-Kyu, K. Membrane Morphology: Phase Inversion to Electrospinning. (2005). *Membr. J.* 15, 85–104.

ChemSafetyPro. 2021. "Water Solubility." https://www.chemsafetypro.com/Topic s/CRA/Water_Solubility.html. Conmy, R., Barron, M., SantoDomingo, J., Deshpande, R., 2017. Characterization and Behavior of Cold Lake Blend and Western Canadian Select Diluted Bitumen Products. EPA/600/R-17/273. United States Environmental Protection Agency, Washington, DC.

Cosenza, A.; Di Trapani, D.; Mannina, G.; Nicosia, S.; Torregrossa, M.; Viviani, G. (2017). Comparison between two MBR pilot plants treating synthetic shipboard slops: the effect of salinity increase on biological performance, biomass activity and fouling tendency. *Desalination and Water Treatment.* *61*, 240–249. https://doi.org/10.5004/dwt.2017.11123

Das, N.; Chandran, P. (2011). Microbial Degradation of Petroleum Hydrocarbon Contaminants: An Overview. *Biotechnology Research International.* 1–13. https://doi.org/10.4061/2011/941810

DeTemmerman, L.; Maere, T.; Temmink, H.; Zwijnenburg, A.; Nopens, I. (2014). Salt stress in a membrane bioreactor:Dynamics of sludge properties, membrane fouling and remediation through powdered activated carbon dosing. *Water Res*. 63, 112–124. https://doi.org/10.1016/j.watres.2014.06.017.

Di Bella, G.; Di Prima, N.; Di Trapani, D.; Freni, G.; Giustra, M. G.; Torregrossa, M.; Viviani, G. (2015). Performance of membrane bioreactor (MBR) systems for the treatment of shipboard slops: Assessment of hydrocarbon biodegradation and biomass activity under salinity variation. *Journal of Hazardous Materials.* *300*, 765–778. https://doi.org/10.1016/j.jhazmat.2015.08.021

Di Bella, G.; Di Trapani, D.; Torregrossa, M.; Viviani, G. (2013). Performance of a MBR pilot plant treating high strength wastewater subject to salinity increase: Analysis of biomass activity and fouling behaviour. *Bioresource Technology.* *147*, 614–618. https://doi.org/10.1016/j.biortech.2013.08.025

Di Trapani, D.; Capodici, M.; Cosenza, A.; Di Bella, G.; Mannina, G.; Torregrossa, M.; Viviani, G. (2011). Evaluation of biomass activity and wastewater characterization in a UCT-MBR pilot plant by means of respirometric techniques. *Desalination.* *269* (1–3), 190–197. https://doi.org/10.1016/j.desal.2010.10.061

Di Trapani, D.; Di Bella, G.; Mannina, G.; Torregrossa, M.; Viviani, G. (2014). Comparison between moving bed-membrane bioreactor (MB-MBR) and membrane bioreactor (MBR) systems: Influence of wastewater salinity variation. *Bioresource Technology. 162*, 60–69. https://doi.org/10.1016/j.biortech.2014.03.126

Dickhout, J. M.; Moreno, J.; Biesheuvel, P. M.; Boels, L.; Lammertink, R. G. H.; De Vos, W. M. (2017). Produced water treatment by membranes: A review from a colloidal perspective. *Journal of Colloid and Interface Science*. 487, 523–534. Academic Press Inc. https://doi.org/10.1016/j.jcis.2016.10.013

Du, X.; Shi, Y.; Jegatheesan, V.; Ul Haq, I. (2020). A review on the mechanism, impacts and control methods of membrane fouling in MBR system. *Membranes. 10*(2). MDPI AG. https://doi.org/10.3390/membranes10020024

Environmental Climate Change Canada. Lee Britton. Personal communication. Shared Database of Guidelines for Priority Contaminants.

EMSA. (2010, October). European Maritime Safety Agency-Pollution Preparedness and Response Activities. Retrieved 9 15, 2022.

Ferrer-Polonio, E.; García-Quijano, N. T.; Mendoza-Roca, J. A.; Iborra-Clar, A.; Pastor-Alcañiz, L. (2016). Effect of alternating anaerobic and aerobic phases on the performance of a SBR treating effluents with high salinity and phenols concentration. *Biochemical Engineering Journal. 113*, 57–65. https://doi.org/10.1016/j.bej.2016.05.010

Floris, R.; Rizzo, C.; Giudice, A.L. (2018). Biosurfactants from Marine Microorganisms. *Metabolomics—New Insights into Biology and Medic*ine; IntechOpen:London, UK. https://doi.org/10.5772/intechopen.80493.

Frederickson, K.C. (2005). The Application of a Membrane Bioreactor for Wastewater Treatment on a Northern Manitoban Aboriginal Community; University of Manitoba: Winnipeg, MB, Canada.

Gao, Y.; Zhang, Y.; Dudek, M.; Qin, J.; Oye, G.; Osterhus, S. W. (2021). A multivariate study of backpulsing for membrane fouling mitigation in produced water treatment. *Journal of Environmental Chemical Engineering. 9*(2). https://doi.org/10.1016/j.jece.2020.104839

Ghimire, N.; Wang, S. (2019). Biological Treatment of Petrochemical Wastewater. In *Petroleum Chemicals - Recent Insight*. IntechOpen. https://doi.org/10.5772/intechopen.79655

Godfrin, M. P.; Sihlabela, M.; Bose, A.; Tripathi, A. (2018). Behavior of Marine Bacteria in Clean Environment and Oil Spill Conditions. *Langmuir. 34*(30), 9047–9053. https://doi.org/10.1021/acs.langmuir.8b01319

Guibert, D.; Aim, R.B.; Rabie, H.; Côté, P. (2002). Aeration Performance of Immersed Hollow-Fiber Membranes in a Bentonite Suspension. *Desalination*. 148, 395–400.

Guidelines for decanting settled out water. Spillcontrol. (2022). Retrieved September 15, 2022, from https://spillcontrol.org/2015/03/02/guidelines-for-decanting-settled-out-water/

Guo, W.; Ngo, H. H.; Li, J. (2012). A mini-review on membrane fouling. *Bioresource Technology*. *122*, 27–34. https://doi.org/10.1016/j.biortech.2012.04.089

Hamedi, H.; Ehteshami, M.; Mirbagheri, S. A.; Rasouli, S. A.; Zendehboudi, S. (2019). Current Status and Future Prospects of Membrane Bioreactors (MBRs) and Fouling Phenomena: A Systematic Review. *Canadian Journal of Chemical Engineering*. *97(1),* 32–58. Wiley-Liss Inc. https://doi.org/10.1002/cjce.23345

Han, M.; Zhang, J.; Chu, W.; Chen, J.; Zhou, G. (2019). Research Progress and prospects of marine Oily wastewater treatment: A review. *Water (Switzerland). 11(12)*. MDPI AG. https://doi.org/10.3390/w11122517

Home. Ship-source Oil Pollution Fund. (n.d.). Retrieved September 9, 2022, from https://sopf.gc.ca/?page_id=109

Hosseinipooya, S. A.; Hu, G.; Lee, K.; Li, J.; Ng, K. T. W.; Vu, H. L. (2022). A System Dynamics Modeling Approach for Estimation of Oily Waste Generation From Marine Oil Spill Response: A Case Study of an Oil Spill in Central Coast of British Columbia. *Frontiers in Environmental Science*. *10*, 801. https://doi.org/10.3389/FENVS.2022.902229/BIBTEX

Huang, S.; Ras, R.H.A.; Tian, X. (2018). Antifouling Membranes for Oily Wastewater Treatment: Interplay between Wetting and Membrane Fouling. *Curr. Opin. Colloid Interface Sci*. 36, 90–109

IPIECA/OGP (2013). The use of decanting during offshore oil spill recovery operations. OGP Final Report. London, UK.

Inoxpa. 2021. "ME1100 Vertical Mixer." https://www.inoxpa.com/products/mixing/high-shear-mixers/vertical-mixer.

Islam, S. (2007). Investigation of Oil Adsorption Capacity of Granular Organoclay Media and the Kinetics of Oil Removal from Oil-in-Water Emulsions; Texas A&M University: College Station, TX, USA.

Isma, M.I.A.; Idris, A.; Omar, R.; Razreena, A.R.P. (2014). Effects of SRT and HRT on treatment performance of MBRand membrane fouling. *Int. J. Chem. Mol. Nucl. Mater. Metall. Eng*. 8, 485–489.

Ismail, N.H.; Salleh, W.N.W.; Ismail, A.F.; Hasbullah, H.; Yusof, N.; Aziz, F.; Jaafar, J. (2020). Hydrophilic polymer-based membrane for oily wastewater treatment: a review. *Sep. Purif. Technol*. 233, 116007. https://doi.org/10.1016/j.seppur.2019.116007.

Iorhemen, O. T.; Hamza, R. A.; Tay, J. H. (2016). Membrane bioreactor (MBR) technology for wastewater treatment and reclamation: Membrane fouling. In *Membranes*. 6(2). MDPI AG. https://doi.org/10.3390/membranes6020033

Ji, L.; Zhou, J. (2006). Influence of aeration on microbial polymers and membrane fouling in submerged membrane bioreactors. *Journal of Membrane Science*. *276*(1–2), 168–177. https://doi.org/10.1016/j.memsci.2005.09.045

Judd, S. (2010). The MBR Book: Principles and Applications of Membrane Bioreactors for Water and Wastewater Treatment. Elsevier:Amsterdam, The Netherlands, 2010.

Judd, S.; Judd, C. (2006). The MBR Book: Principles and Applications of Membrane Bioreactors in Water and Wastewater Treatment, 1sted.; Elsevier: Oxford, UK.

Kang, Y.; Xia, Y.; Wang, H.; Zhang, X. (2019). 2D Laminar Membranes for Selective Water and Ion Transport. *Adv. Funct. Mater*. 29. 1902014.https://doi.org/10.1002/adfm.201902014.

Karlapudi, A.P.; Venkateswarulu, T.C.;Tammineedi, J.;Kanumuri, L.;Ravuru, B.K.; Dirisala, V.R.; Kodali, V.P. (2018). Role of biosurfactants in bioremediation of oil pollution—A review. *Petroleum*. 4, 241–249. https://doi.org/10.1016/j.petlm.2018.03.007.

Kose, B.; Ozgun, H.; Ersahin, M.E.; Dizge, N.; Koseoglu-Imer, D.Y.;Atay, B.; Kaya, R.; Altınbas, M.; Sayılı, S.; Hoshan, P. (2012). Performance Evaluation of a Submerged Membrane Bioreactor for the Treatment of Brackish Oil and Natural Gas Field Produced Water. *Desalination*. 285, 295–300. https://doi.org/10.1016/j.desal.2011.10.016.

Kundu, P.; Mishra, I.M. (2018). Treatment and Reclamation of Hydrocarbon-Bearing Oily Wastewater as a Hazardous Pollutant by Different Processes and Technologies:A State-of-the-Art Review. *Rev. Chem. Eng*. 35, 73–108. https://doi.org/10.22079/jmsr.2016.19154.

Kuyukina, M. S.; Krivoruchko, A. V.; Ivshina, I. B. (2020). Advanced bioreactor treatments of hydrocarbon-containing wastewater. *Applied Sciences (Switzerland)*. 10(3). MDPI AG. https://doi.org/10.3390/app10030831

Le-Clech, P.; Chen, V.; Fane, T. A. G. (2006). Fouling in membrane bioreactors used in wastewater treatment. In *Journal of Membrane Science*. 284 (1-2), pp. 17–53. https://doi.org/10.1016/j.memsci.2006.08.019

Lee, J.; Ahn, W.-Y.; Lee, C.-H. (2001). Comparison of the filtration characteristics between attached and suspended growth microorganisms in submerged membrane bioreactor. *Wat. Res.* 35(10).

Lee, K., Boufadel, M., Chen, B., Foght, J., Hodson, P., Swanson, S., & Venosa, A. (2015). Royal Society of Canada Expert Panel Report: The Behaviour and Environmental Impacts of Crude Oil Released into Aqueous Environments. Royal Society of Canada. http://deslibris.ca/ID/10049082

Lefebvre, O.; Moletta, R. (2006). Treatment of organic pollution in industrial saline wastewater: A literature review. *Water Research.* 40(20), 3671–3682. Elsevier Ltd. https://doi.org/10.1016/j.watres.2006.08.027

Li, L.-J.; Qi, P.-S.; Liu, Y.-Z.; Qi, Z.; Zhao, J.-J. (2009). Poly Ferric Silicate Sulphate (PFSiS): Characterization, Coagulation Behavior and Applications in Oily Wastewater Treatment. In Proceedings of the 2009 3rd International Conference on Bioinformatics and Biomedical Engineering, Beijing, China, 11–13 June 2009; pp. 1–4.

Li, S.; Hu, S.; Shi, S.; Ren, L.; Yan, W.; Zhao, H. (2019). Microbial diversity and metaproteomic analysis of activated sludge responses to naphthalene and anthracene exposure. *RSC Advances*. 9(40), 22841–22852. https://doi.org/10.1039/c9ra04674g

Liao, X.; Li, B.; Zou, R.; Xie, S.; Yuan, B. (2016). Antibiotic sulfanilamide biodegradation by acclimated microbial populations . *Appl. Microbiol. Biotechnol*. 100, 2439–2447.https://doi.org/10.1007/s00253-015-7133-9.

Liu, B.; Chen, B.; Ling, J.; Matchinski, E.J.; Dong, G.; Ye, X.; Wu, F.; Shen, W.; Liu, L.; Lee, K. (2022). Development of AdvancedOil/Water Separation Technologies to Enhance the Effectiveness of Mechanical Oil Recovery Operations at Sea: Potential and Challenges. *J. Hazard. Mater*. 437, 129340

Maneerat, S. (2005). Biosurfactants from marine microorganisms. *J. Sci. Technol*. 27, 1263–1272.

Mannina, G.; Cosenza, A.; Di Trapani, D.; Capodici, M.; Viviani, G. (2016). Membrane bioreactors for treatment of saline wastewater contaminated by hydrocarbons (diesel fuel): An experimental pilot plant case study. *Chemical Engineering Journal*. 291, 269–278. https://doi.org/10.1016/j.cej.2016.01.107

Mansir, N.; Jones, M. (2012). Environment Impacts of Marine Oil Spill; A Case Study of Deep Water Horizon Oil Spill at the Gulf of Mexico United States of America 2010 (A Review). *Chemsearch Journal*. 3(2): 64 – 70.

Mapelli, F.; Scoma, A.; Michoud, G.; Aulenta, F.; Boon, N.; Borin, S.; Kalogerakis, N.; Daffonchio, D. (2017). Biotechnologies for Marine Oil Spill Cleanup: Indissoluble Ties with Microorganisms. In *Trends in Biotechnology.* 35(9), 860–870. Elsevier Ltd. https://doi.org/10.1016/j.tibtech.2017.04.003

Maxxam. 2021. "Evaluation of the rationale behind new regulation 153 groundwater standards for F3 and F4 petroleum hydrocarbons." https://kodiak.clientszone.net/wp-content/uploads/2021/01/Solubility-for-F3-F4.pdf.

Mohammadi, L.; Rahdar, A.; Bazrafshan, E.; Dahmardeh, H.; Susan, M.A.B.H.; Kyzas, G.Z. (2020). Petroleum Hydrocarbon Removal from Wastewaters: A Review. *Processes.* 8, 447. https://doi.org/10.3390/pr8040447.

Mutamim, N.S.A.; Noor, Z.Z.; Hassan, M.A.A.; Olsson, G. (2012). Application of Membrane Bioreactor Technology in Treating High Strength Industrial Wastewater: A Performance Review. *Desalination.* 305, 1–11.

Net Environmental Benefit Analysis Neba. Home. (n.d.). Retrieved September 11, 2022, from http://www.oilspillprevention.org/oil-spill-cleanup/oil-spill-cleanup-toolkit/net-environmental-benefit-analysis-neba

Nie, C.; Han, G.; Ni, J.; Guan, S.; Du, H.; Zhang, Y.; Wang, H. (2021). Stability Dynamic Characteristic of Oil-in-Water Emulsion from Alkali–Surfactant–Polymer Flooding. *ACS Omega.* 6(29), 19058–19066. https://doi.org/10.1021/acsomega.1c02367

Nieuwenhuis, E.; Post, J.; Duinmeijer, A.; Langeveld, J.; Clemens, F. (2018). Statistical Modelling of Fat, Oil and Grease (FOG) Deposits in Wastewater Pump *Sumps.Water Res.* 135, 155–167. https://doi.org/10.1016/j.watres.2018.02.026.

Nouha, K.; Kumar, R.S.; Balasubramanian, S; Tyag, R.D. (2017). Critical review of EPS production, synthesis and composition for sludge flocculation. *Journal of Environmental Science.* http://dx.doi.org/10.1016/j.jes.2017.05.020

Obotey Ezugbe, E.; Rathilal, S. (2020). Membrane Technologies in Wastewater Treatment: A Review. *Membranes.* 10 (89).

Oil spills. National Oceanic and Atmospheric Administration. (2020). Retrieved October 3, 2022, from https://www.noaa.gov/education/resource-collections/ocean-coasts/oil-spills

Ojagh, S. M. A.; Fallah, N.; Nasernejad, B. (2020). Biological treatment of organic compounds in produced water with use of halotolerant bacteria. *Journal of Environmental Chemical Engineering.* 8(6). https://doi.org/10.1016/j.jece.2020.104412

Pendashteh, A. R.; Abdullah, L. C.; Fakhru'L-Razi, A.; Madaeni, S. S.; Zainal Abidin, Z.; Awang Biak, D. R. (2012). Evaluation of membrane bioreactor for hypersaline oily wastewater treatment. *Process Safety and Environmental Protection.* 90(1), 45–55. https://doi.org/10.1016/j.psep.2011.07.006

Pourbozorg, M.; Li, T.; Law, A.W.-K. (2017). Fouling of Submerged Hollow Fiber Membrane Filtration in Turbulence: Statistical Dependence and Cost-Benefit Analysis. *J. Membr. Sci.* 521, 43–52

Poursat, B. A. J.; Van Spanning, R. J. M.; De Voogt, P.; Parsons, J. R. (2019). Implications of microbial adaptation for the assessment of environmental persistence of chemicals. *Critical Reviews in Environmental Science and Technology*. *49*(23), 2220–2255. https://doi.org/10.1080/10643389.2019.1607687

Prince William Sound Regional Citizens' Advisory Council. Prince William Sound. (2022, October 5). Retrieved September 11, 2022, from https://www.pwsrcac.org/

Prince, R.; Atlas, R. M. (2014). *BIOREMEDIATION OF MARINE OIL SPILLS*.

PubChem (no date) National Center for Biotechnology Information. PubChem Compound Database. U.S. National Library of Medicine. Available at: https://pubchem.ncbi.nlm.nih.gov/ (Accessed: November 10, 2022).

Radjenović, J.; Matošić, M.; Mijatović, I.; Petrović, M.; Barceló, D. (2008). Membrane bioreactor (MBR) as an advanced wastewater treatment technology. *Handbook of Environmental Chemistry.* Volume 5: Water Pollution, 5 S2, 37–101. https://doi.org/10.1007/698_5_093

Razavi, S. M. R.; Miri, T. (2015). A real petroleum refinery wastewater treatment using hollow fiber membrane bioreactor (HF-MBR). *Journal of Water Process Engineering*. *8*, 136–141. https://doi.org/10.1016/j.jwpe.2015.09.011

Research spotlight: Dr. Kenneth Lee, expert in oil spill response technologies. Clear Seas. (2020, September 26). Retrieved September 10, 2022, from https://clearseas.org/en/blog/research-spotlight-dr-kenneth-lee/

Reid, E.; Liu, X.; Judd, S. J. (2006). Effect of high salinity on activated sludge characteristics and membrane permeability in an immersed membrane bioreactor. *Journal of Membrane Science*. *283*(1–2), 164–171. https://doi.org/10.1016/j.memsci.2006.06.021

Ren, N.; Chen, Z.; Wang, A.; Hu, D. (2005). Removal of organic pollutants and analysis of MLSS-COD removal relationship at different HRTs in a submerged membrane bioreactor. *Int. Biodeterior. Biodegrad*. 55, 279–284.

Responding to oil spills in Canadian waters. Clear Seas. (2020, December 9). Retrieved September 8, 2022, from https://clearseas.org/en/responding-to-oil-spills/

Rojo, F. (2009). Degradation of alkanes by bacteria: Minireview. *Environmental Microbiology.* 11(10), 2477–2490. Blackwell Publishing Ltd. https://doi.org/10.1111/j.1462-2920.2009.01948.x

Rutter, A.; Zeeb, B.; Matovic. D. (2014). Sustainable Remediat. Pet. Hydrocarb. Using phyto technologies. https://www.eralberta.ca/wp-content/uploads/ 2017/06/CCEMC-Sustainable-Remediation-Final-Report.pdf.

Salahi, A.; Mohammadi, T.; Behbahani, R.M.; Hemmati, M. (2015). Experimental Investigation and Modeling of Industrial Oily Wastewater Treatment Using Modified Polyethersulfone Ultrafiltration Hollow Fiber Membranes. *Korean J. Chem. Eng*. 32,1101–1118.

Saththasivam, J.; Loganathan, K.; Sarp, S. (2016). An Overview of Oil–Water Separation Using Gas Flotation Systems. *Chemosphere*. 144, 671–680. https://doi.org/10.1016/j.chemosphere.2015.08.087.

Scholz, W.; Fuchs, W. (2000). Treatment of oil contaminated wastewater in a membrane bioreactor. www.elsevier.com/locate/watres

Sharghi, E. A.; Bonakdarpour, B.; Roustazade, P.; Amoozegar, M. A.; Rabbani, A. R. (2013). The biological treatment of high salinity synthetic oilfield produced water in a submerged membrane bioreactor using a halophilic bacterial consortium. *Journal of Chemical Technology and Biotechnology*. 88(11), 2016–2026. https://doi.org/10.1002/jctb.4061

Shariati, F.P.; Mehrnia, M.R.; Sarrafzadeh, M.H.; Rezaee, S.; Grasmick, A.; Heran, M. (2013). Fouling in a Novel Air-lift Oxidation Ditch Membrane Bioreactor (AOXMBR) at Different High Organic Loading Rate. *Sep. Purif. Technol*. 105, 69–78. https://doi.org/10.1016/j.seppur.2012.12.008.

Sheng, G. P.; Yu, H. Q.; Li, X. Y. (2010). Extracellular polymeric substances (EPS) of microbial aggregates in biological wastewater treatment systems: A review. *Biotechnology Advances*. 28(6), 882–894). https://doi.org/10.1016/j.biotechadv.2010.08.001

SL Ross. (2005). Transfer of decanting technology research to oil spill response organizations and regulators. 63. Available online: https://www.bsee.gov/sites/bsee.gov/files/osrr-oil-spill-response-research/512aa.pdf (accessed on 10 December 2021).

Soltani, S.; Mowla, D.; Vossoughi, M.; & Hesampour, M. (2010). Experimental investigation of oily water treatment by membrane bioreactor. *Desalination*. 250(2), 598–600. https://doi.org/10.1016/j.desal.2009.09.031

Song, X.; Chen, B.; Liu, B.; Lye, L.M.; Ye, X.; Nyantekyi-Kwakye, B.; Zhang, B. (2022). Impacts of frazil ice on the effectiveness of oil dispersion and migration of dispersed oil. *Environ. Sci. Technol*. https://doi.org/10.1021/acs.est.1c04014.

Sørheim, K. R., Daling, P. S., Cooper, D., Buist, I., Faksness, L.-G., Altin, D., Pettersen, T.-A., & Bakken, O. M. (2020, July 10). Characterization of low sulfur fuel marine fuel oils (LSFO) - A new generation of marine fuel oils. Retrieved December 6, 2022, from https://sintef.brage.unit.no/sintef-xmlui/bitstream/handle/11250/2675579/Summary+Report_Low+sulphur+fuel+oils.pdf?sequence=2

Stewart, M.; Arnold, K. (2009). Produced Water Treating Systems. In *Emulsions and Oil Treating Equipment.* pp. 107–211. Elsevier. https://doi.org/10.1016/b978-0-7506-8970-0.00003-7

Sumitomo Electric Industries. 2021. "POREFLON Microfiltration/Ultrafiltration Membrane Module."https://sumitomoelectric.com/products/poreflon-microfiltration-ultrafiltration-membrane-module.

Sutton, P. M. (2006). Membrane bioreactors for industrial wastewater treatment: Applicability and selection of optimal system configuration.

Tan, X.; Acquah, I.; Liu, H.; Li, W.; Tan, S. (2019). A critical review on saline wastewater treatment by membrane bioreactor (MBR) from a microbial perspective. *Chemosphere.* 220, 1150–1162. Elsevier Ltd. https://doi.org/10.1016/j.chemosphere.2019.01.027

Tang, Y.; Lin, Y.; Ford, D.M.; Qian, X.; Cervellere, M.R.; Millett, P.C.; Wang, X. A. (2021). Review on Models and Simulations of Membrane Formation via Phase Inversion Processes. *J. Membr*. Sci. 640, 119810.

Tanudjaja, H. J.; Hejase, C. A.; Tarabara, V. V.; Fane, A. G.; Chew, J. W. (2019). Membrane-based separation for oily wastewater: A practical perspective. In *Water Research.* 156, 347–365. Elsevier Ltd. https://doi.org/10.1016/j.watres.2019.03.021

Transport Canada. (2010, January 19). 2. marine acts and regulations. Transport Canada. Retrieved September 12, 2022, from https://tc.canada.ca/en/marine-transportation/marine-safety/2-marine-acts-regulations

Transport Canada. (2019, February 5). National Oil Spill Preparedness and Response Regime. Transport Canada. Retrieved September 13, 2022, from https://tc.canada.ca/en/marine-transportation/marine-safety/national-oil-spill-preparedness-response-regime-0

Transport Canada. (2020, April 9). Ship-source oil spill response and preparedness regime report to Parliament, 2011-2016 – TP 15418E (2019). Transport Canada. Retrieved October 3, 2022, from https://tc.canada.ca/en/marine-transportation/marine-pollution-environmental-response/ship-source-oil-spill-response-preparedness-regime-report-parliament-2011-2016-tp-15418e-2019

Travkin, V. M.; Solyanikova, I. P. (2021). Salicylate or phthalate: The main intermediates in the bacterial degradation of naphthalene. *Processes.* 9(11). MDPI. https://doi.org/10.3390/pr9111862

Tripathi, L.; Irorere, V.U.; Marchant, R.; Banat, I.M. (2018). Marine derived biosurfactants: A vast potential future resource. *Biotechnol. Lett*. 40, 1441–1457.https://doi.org/10.1007/s10529-018-2602-8.

Tummons, E.N.; Chew, J.W.; Fane, A.G.; Tarabara, V.; (2017). Ultrafiltration of saline oil- in-water emulsions stabilized by an anionic surfactant_ Effect of surfactant concentration and divalent counterions. *J. Membr. Sci*. 12. https://doi.org/10.1016/j.memsci.2017.05.012.

Ubani, O.; Atagana, I. H.; Thantsha, S. M. (2013). Biological degradation of oil sludge: A review of the current state of development. *African Journal of Biotechnology*. *12*(47), 6544–6567. https://doi.org/10.5897/ajb11.1139

Ueda, T.; Hata, K.; Kikuoka, Y. (1996) Treatment of Domestic Sewage from Rural Settlements by a Membrane Bioreactor.*Water Sci. Technol*. 34, 189–196.

Van der Meer, J.R.; DeVos, W.M.; Harayama, S.; Zehnder, A.J. (1992). Molecular mechanisms of genetic adaptation to xenobiotic compounds. *Microbiol. Rev*. 56, 677–694.

Viero, A. F.; Sant'Anna, G. L. (2008). Is hydraulic retention time an essential parameter for MBR performance? In *Journal of Hazardous Materials*. 150(1), 185–186. Elsevier. https://doi.org/10.1016/j.jhazmat.2007.09.090

Vuković, M.; Briški, F.; Matošić, M.; Mijatović, I. (2006). Analysis of the activated sludge process in an MBR under starvation conditions. *Chemical Engineering and Technology*. *29*(3), 357–363. https://doi.org/10.1002/ceat.200500314

Wan, C. F.; Yang, T.; Lipscomb, G. G.; Stookey, D. J.; Chung, T.S. (2017). Design and fabrication of hollow fiber membrane modules. *Journal of Membrane Science*. 538, 96–107. https://doi.org/10.1016/j.memsci.2017.05.047

Wang, W. (2008). Toxicity Assessment of PAHs and Metals to Bacteria and the Roles of Soil Bacteria in Phytoremediation of Petroleum Hydrocarbons. https://uwspace.uwaterloo.ca/handle/10012/4068

Wang, H.; Wang, B.; Dong, W.; Hu, X. (2016). Co-acclimation of bacterial communities under stresses of hydrocarbons with different structures. *Scientific Reports*. *6*. https://doi.org/10.1038/srep34588

Wang, W.; Wang, L.; Shao, Z. (2018). Polycyclic aromatic hydrocarbon (PAH) degradation pathways of the obligate marine PAH degrader Cycloclasticus sp. strain P1. *Applied and Environmental Microbiology*. *84*(21). https://doi.org/10.1128/AEM.01261-18

Wang, Z.; Ma, J.; Tang, C. Y.; Kimura, K.; Wang, Q.; Han, X. (2014). Membrane cleaning in membrane bioreactors: A review. In *Journal of Membrane Science*. 468 276–307). Elsevier. https://doi.org/10.1016/j.memsci.2014.05.060

Webb CE, C. C. (2005). *Chapter 25 Bioremediation of Marine Oil Spills*.

Wen, S.; Liu, H.; He, H.; Luo, L.; Li, X.; Zeng, G.; Zhou, Z.; Lou, W.; Yang, C. (2016). Treatment of anaerobically digested swine wastewater by Rhodobacter blasticus and Rhodobacter capsulatus. *Bioresource Technology*. 222, 33–38. https://doi.org/10.1016/j.biortech.2016.09.102

Wibisono, Y.; Cornelissen, E.R.; Kemperman, A.J.B.; Van der Meer, W.G.J.; Nijmeijer, K. (2014). Two-Phase Flow in Membrane Processes:A Technology with a Future. *J. Membr. Sci*. 453, 566–602.

Xiaoguang, C.; Gang, L.; Haibo, L.; Yuling, L.; Yanxue, M.; Ruobin, D.; Jiqiang, Z. (2017). Operation performance and membrane fouling of a spiral symmetry stream anaerobic membrane bioreactor supplemented with biogas aeration. *Journal of Membrane Science*. 539, 206–212. https://doi.org/10.1016/j.memsci.2017.05.076

Xu, X.; Liu, W.; Tian, S.; Wang, W.; Qi, Q.; Jiang, P.; Gao, X.; Li, F.; Li, H.; Yu, H. (2018). Petroleum Hydrocarbon-Degrading Bacteria for the Remediation of Oil Pollution Under Aerobic Conditions: A Perspective Analysis. In *Frontiers in Microbiology*. 9. Frontiers Media S.A. https://doi.org/10.3389/fmicb.2018.02885

Yang, M.; Hadi, P.; Yin, X.; Yu, J.; Huang, X.; Ma, H.; Walker, H.; Hsiao, B.S. (2021). Antifouling Nanocellulose Membranes: How Subtle Adjustment of Surface Charge Lead to Self-Cleaning Property. *J. Membr. Sci*. 618, 118739

Yang, S. Z.; Jin, H. J.; Wei, Z.; He, R. X.; Ji, Y. J.; Li, X. M.; Yu, S. P. (2009). Bioremediation of Oil Spills in Cold Environments: A Review. *Pedosphere*. *19*(3), 371–381. https://doi.org/10.1016/S1002-0160(09)60128-4

Yu, L.; Han, M.; He, F. (2017). A review of treating oily wastewater. *Arabian Journal of Chemistry*. 10, S1913–S1922). Elsevier B.V. https://doi.org/10.1016/j.arabjc.2013.07.020

Zdarta, A.; Smułek, W.; Pietraszak, E.; Kaczorek, E.; Olszanowski, A. (2016). Hydrocarbons biodegradation by activated sludge bacteria in the presence of natural and synthetic surfactants. *Journal of Environmental Science and Health - Part A Toxic/Hazardous Substances and Environmental Engineering*. *51*(14), 1262–1268. https://doi.org/10.1080/10934529.2016.1215194

Zhao, C.; Zhou, J.; Yan, Y.; Yang, L.; Xing, G.; Li, H.; Wu, P.; Wang, M.; Zheng, H. (2020). Application of coagulation/flocculation in oily wastewater treatment: A review. *Sci. Total Environ*. 765, 142795.

Zheng, J.; Liu, B.; Ping, J.; Chen, B.; Wu, H.; Zhang, B. (2015). Vortex- and shaker-assisted liquid–liquid microextraction (VSA-LLME) coupled with gas chromatography and mass spectrometry (GC-MS) for analysis of 16 polycyclic aromatic hydrocarbons (PAHs) in offshore produced water. *Water Air. Soil Pollut*. 226 (9), 318. https://doi. org/10.1007/s11270-015-2575-3.

Zhidong, L.; Na, L.; Honglin, Z.; Dan, L. (2009). Study of an A/O submerged membrane bioreactor for oil refinery wastewater treatment. *Petroleum Science and Technology*. *27*(12), 1274–1285. https://doi.org/10.1080/10916460802455228

Zhou, Y.; Yu, S.; Gao, C.; Feng, X. (2009). Surface Modification of Thin Film Composite Polyamide Membranes by Electrostatic SelfDeposition of Polycations for Improved Fouling Resistance. *Sep. Purif. Technol*. 66, 287–294

Zulkefli, N.F.; Alias, N.H.; Jamaluddin, N.S.; Abdullah, N.; Abdul Manaf, S.F.; Othman, N.H.; Marpani, F.; Mat-Shayuti, M.S.; Kusworo, T.D. (2021). Recent Mitigation Strategies on Membrane Fouling for Oily Wastewater Treatment. *Membranes*. 12, 26.