IMPROVED OIL/WATER SEPARATION USING NANO/MICRO BUBBLE GAS FLOTATION TECHNOLOGY

by

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Abstract

This research investigated the performance of nanobubble and microbubble (NB/MB) gas flotation technology in treating oily wastewater generated after oil spill response operations. The study comprised three distinct sets of experiments. In the initial set of experiments, experiments were conducted to examine the impact of reactor configuration on the NB/MB gas flotation process. Three different reactor configurations were employed, varying in height-to-diameter ratios of 10, 20, and 30. The results indicated that reactor configuration slightly affected system performance, with gradual improvement observed as the height-to-diameter ratio increased. Following the analysis of reactor configuration, response surface methodology (RSM) was utilized to design experiments focusing on three key factors: initial oil concentration, gravity settling time and flotation time. The purpose was to analyze their impacts on oil/water separation performance and the interactions among these factors. Additionally, introducing gravity separation prior to NB/MB gas flotation aimed to assess whether allowing collected oily wastewater to settle in containers on barges would accelerate oil/water separation compared to exclusively relying on NB/MB gas flotation without gravity settling. The results from the experiment demonstrated a strong agreement between the predicted and experimental data for oil/water separation efficiency, as indicated by a high R^2 value of 0.99 and an adjusted R^2 value of 0.98. The predicted R^2 value was 0.91. Subsequently, additional single-factor experiments were conducted to determine the maximum oil/water separation efficiency. The findings revealed that an oil/water separation efficiency of 98.8% was achieved under the optimum experimental condition with the initial oil concentration of 1995 mg/L, the gravity settling time of 45 minutes and the flotation time of 38 minutes.

Likewise, a second set of separate experiments was conducted after the RSM experiments to study how different levels of oil weathering affect the oil/water separation efficiency using MB and NB gas flotation. The results indicated no significant difference in oil separation efficiency between fresh and weathered oil samples.

Furthermore, a third set of experiments was carried out at a pilot scale to scale up the technology and assess its feasibility. The experiments were conducted at a pilot scale (75 L). The results demonstrated a remarkable oil/water separation efficiency of 92% within one hour, surpassing gravity separation, which achieved only 4.62% over the same duration. Similarly, combining NB/MB gas flotation with adsorption achieved nearly 100% oil/water separation efficiency.

Thus, the result from the experiment concludes that NB/MB gas flotation is efficient in separating oily wastewater generated after oil spills. The successful implementation of NB/MB gas flotation technology in offshore oil spill response vessels offers a promising solution with exceptional separation performance and scalability, with a minimal environmental impact, as it is a chemical-free technology.

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Glossary

ANOVA	Analysis of variance
CLD	Cold Lake Dilbit
CCD	Central composite design
DAF	Dissolved air flotation
DI	Deionized
DLS	Dynamic Light Scattering
EF	Electrolytic flotation
IAF	Induced air flotation
IGF	Induced gas flotation
LD	Laser diffraction
MPRI	Multi-Partner Oil Spill Research Initiative
MBs	Microbubbles
NB	Nanobubbles
PVC	Polyvinyl chloride
RSM	Response surface methodology
R_2	Coefficient of determination
USEPA	United States Environmental Protection Agency
PPI	Parallel plate separators
CPI	corrugated plate separators
HGMS	High-gradient magnetic separation
COD	Chemical Oxygen Demand
NaCl	sodium chloride
ppm	Parts per million
CLB	Cold Lake Blend
H:D	Height: Diameter
ASTM	American Society for Testing and Materials
mg/L	Milligrams per Liters

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Chapter 1 Introduction

1.1 Background

Petroleum hydrocarbons, such as natural gas, diesel, and gasoline, are widely used as a fuel source around the world (Devan et al., 2020). It is a complex mixture of hydrocarbons and is found deep underground in the form of gases (natural gas), semisolids (bitumen), solids (wax or asphaltene) and liquids, commonly known as fossil fuel (Ossai et al., 2020; Sajna et al., 2015). These petroleum products may be released into the marine environment through exploration, transportation, drilling operations, and shipping, known as oil spills. In addition, these petroleum products are occasionally released into the marine environment during exploration, transportation, offshore drilling operations, and shipping, known as oil spills (Zhang et al., 2019). Petroleum hydrocarbons are a complex mixture of thousands of primarily hydrocarbons classified as persistent environmental pollutants due to their durable and stable nature as they tend to remain in the environment for a long time and do not readily degrade (Gennadiev et al., 2015; Abdel-Shafy and Mansour 2016). Once these petroleum hydrocarbons are released into the aquatic environment as an oil spill, various weathering processes take place, such as evaporation, dissolution, emulsification, dispersion, biodegradation, and photo-oxidation, which change the physical properties, chemical reactivity, and toxicity of the spilled oil (Tarr et al. 2016, Finch & Stubblefield, 2019, Farooq et al. 2018). In addition, the spilled oil mixes with the water due to the action of waves to form emulsified oily wastewater, which is more significant in volume than the original spilled oil (Payne, 2018). Stable emulsions consist of 60 to 80% water, resulting in a 3-5 times more significant volume of oily wastewater generation than the original volume of spilled oil (Fingas, 1995). Moreover, these emulsions may not be recoverable by traditional oil spill cleaning technologies such as gravity settling (Xie et al., 2007, Fingas & Fieldhouse, 2009).

A wide range of oil-water separation technologies and processes are available for the collection and treatment of oily wastewater generated after the oil spills, including deployment of booms, skimmers, gravity settling, in-situ burning of oil on the water surface, application of sorbents to clean up the traces of oil floating on water, application of dispersants, bioremediation (Hubbe et al. 2013, Kinner et al. 2014, Prendergast & Gschwend, 2014, Fingas, 2016; Kostka et al., 2011). However, available cleanup processes and technologies for oil spill response operations are time-consuming and ineffective because they lead to pollution (Sarbatly et al., 2016). In addition, the resource value of oil is also lost in these cleanup methods, as oil is not recovered in these cleanup methods, such as in-situ burning of oil and application of dispersants (Li et al., 2020). Additionally, these technologies do not operate on-site and require the transportation of oily wastewater to shore for treatment or disposal, which is time-consuming and expensive (Dhaka and Chattopadhyay, 2021). Also, transporting a large volume of produced oily wastewater to available waste management facilities could easily exceed the treatment capacity, leading to a great challenge for its effective management. Therefore, on-site decanting of oily waste is crucial for volume minimization, discharge to the surface, and beneficial reuse (Neff & Hagemann, 2007). Recently, NB/MB have gained more significant applications in mineral processing and wastewater treatment; however, their application has not been well in oil spill response operations.

Nanobubbles are tiny gas cavities with diameters less than 1 µm, whereas microbubbles are small gas cavities with diameters between 1 µm and 999 µm µm (Etchepare et al., 2017c; Zimmerman et al., 2011). Applications of NB/MB have recently increased due to their potential usage in mineral processing, wastewater treatment, surface cleaning, agriculture, the mining industry, medical applications, and surface cleaning (Michailidi et al., 2019; Ahmadi et al., 2014; Calgaroto et al., 2015; Cavalli et al., 2015). In addition, NB/MB-based gas flotation has been well-documented for treating wastewater (Kyzas and Matis, 2018; Xia and Hu, 2016). The application of NB/MB gas flotation has been widely studied for wastewater treatment due to its high separation efficiency, compact design, short retention time, and high loading rate when compared to conventional wastewater treatment technologies (Yu et al., 2017; Piccioli et al., 2020; Eftekhardadkhah, 2013).

1.2 Objective

The objective of this thesis is to investigate the impact of reactor configuration on NB/MB gas flotation on oil/water separation efficiency, analyze the key factors affecting oil/water separation performance using Response Surface Methodology (RSM), assess the influence of oil weathering on NB/MB gas flotation efficiency, and evaluate the performance of NB/MB gas flotation at larger volumes in a pilot-scale setup, including the integration of the adsorption process with the NB/MB gas flotation.

1.3 Thesis organization

A different set of separate experiments were conducted for this research. At first, the experiments were conducted to examine the impact of reactor configuration on the NB/MB gas flotation process. Three different reactor configurations were employed: the first reactor had an 8 cm internal diameter and an 80 cm height (height: width = 10), the second had a 5 cm internal diameter and a 100 cm height (height: width = 20), and the third had a 5 cm internal diameter and a 150 cm height (height: width = 30). Following the reactor configuration impact of NB/MB gas flotation performance, response surface methodology (RSM) was employed to design the experiment, focusing on three key factors: initial oil concentration, flotation time, and gravity settling. The purpose was to analyze their impacts on oil/water separation performance and the interaction among these factors. Subsequently, additional single-factor experiments were conducted to determine the maximum oil/water separation efficiency.

In addition to the Response Surface Methodology (RSM), a second separate set of experiments was conducted to investigate the impact of oil weathering on the performance of NB/MB gas flotation efficiency. The experiment used 1100 mg/L oil and gas flotation for 40 minutes. Both fresh and weathered oil at 2%, 5%, and 10% mass loss were used for the experiment. The objective was to study how different levels of oil weathering affect the oil separation efficiency using MB and NB gas flotation.

Lastly, a third set of separate experiments was conducted with a 75 L pilot-scale setup to evaluate the performance of NB/MB gas flotation performance at larger volumes. Our laboratory column experiments were conducted utilizing a 2-litre oil/water emulsion. Thus, the experiments were also conducted at a pilot scale to examine how the NB/MB gas flotation performs with higher oil/water volume. Moreover, the adsorption process was also integrated into the pilot-scale tests to evaluate the performance of the combined system. The flow chart below displays the thesis's experimental process.

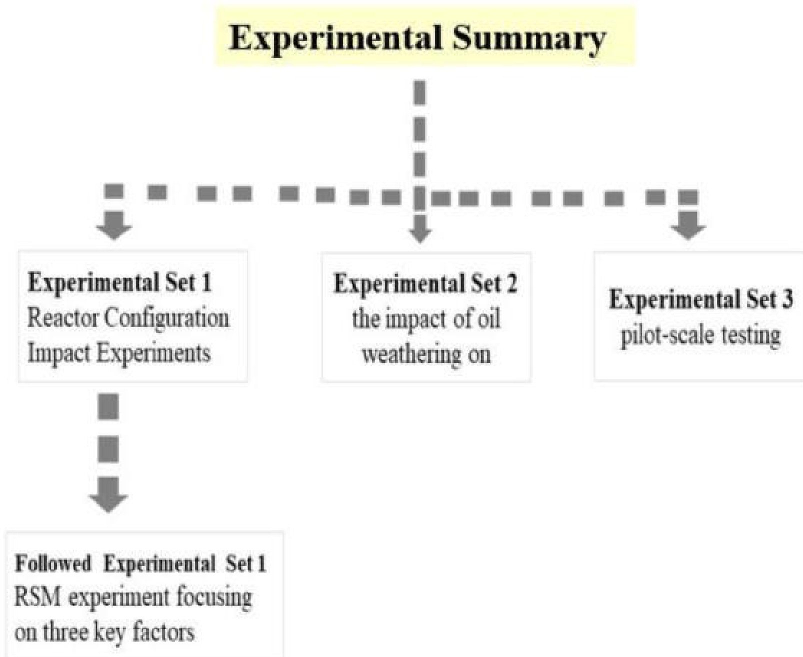


Figure 1.1 Experimental Summary

Chapter 2 Literature Review

2.1 Literature context

Approximately 71% of the Earth's surface is covered by an ocean that contains more than 97% of the planet's water and is home to over 50% of the Earth's species (Wang et al., 2020). However, the ocean's health and sustainability are often threatened by human activities, one such threat being oil spills. Petroleum products are a primary energy source worldwide, and their increased production and consumption could negatively threaten the environment (Martins et al., 2019). An oil spill could be defined as an accidental or unintentional release of liquid petroleum hydrocarbon into the environment due to human activities, such as a spill during crude oil exploration, extraction, and transportation. Despite advancements in technology, regulation, and engineering practices, the risks of oil spillage still abound (Zhang et al., 2019).

Oil spills are major environmental catastrophes with long-lasting negative impacts (Li et al., 2016). The severity of such catastrophes can be observed from The Deepwater Horizon spill disaster that occurred on April 20, 2010, which is considered the most significant volume-oil of spill in history, with an estimated release of over 200 million gallons of crude oil in the saline water, spreading across 68,000 square miles of sea surface (Ramseur, 2010; Shultz et al., 2015). Thus, preparedness and responses for such disasters are crucial for preventing, monitoring, reducing, and remediating an oil spill (Tuler et al., 2007). Also, after such undesirable disasters, rapid response using effective and efficient technology is critical for controlling the severity of a spill (White and Molloy, 2003). The world has witnessed several significant oil spill disasters, such as The Exxon Valdez spill, Northwestern Amazon Oil Spills, and Arctic Oil Spills, which have led to devastating environmental impacts (Jernelöv, 2010). The consequences of such accidents are not only economic impacts (NMFS, 2014; Hagerty, 2010), but they also cause severe environmental impacts such as effect on marine flora and fauna (Demopoulos and Strom, 2012; Lin & Mendelssohn, 2012; Mendelssohn et al., 2012), Public health impact (Landesman et al., 2013; Sabucedo et al., 2009) and social and community impacts (Gill et al., 2012; Zhang et al., 2019).

After the marine oil spill incident, collecting the spilled oil as quickly as possible is critical to minimize the danger and potential damage to people, the environment and property. Containment equipment is used to prevent the spread of spilled oil and collect it for recovery or disposal (Fingas, 2021). After the spilled oil is contained, oily wastewater is decanted. Different technologies are used to separate the oil from water. The most used technologies include differential gravity separation, membrane separation, coalescence, adsorption, electric and magnetic separation, thermal separation, and biological treatment (Medeiros et al., 2022). The oil-water mixture contains different forms of oil, such as free oil, emulsified oil and dissolved oil; therefore, a single treatment system or process does not remove all these oil forms.

Different treatment process units may be applied to achieve the desired effluent quality. The selection of the appropriate method for the oil spill cleanup is complex. It depends on factors such as Oil type, spill location, initial concentration and collected oily wastewater, weathering, and local standards and regulations (Prendergast and Gschwend, 2014).

2.2 Characteristics of oily wastewater

Various weathering process takes place immediately after a marine oil spill, including evaporation, dissolution, emulsification, dispersion, biodegradation, and photo-oxidation, which changes oil's physical properties, chemical reactivity and toxic chemical content across a wide range of time scales (Tarr et al., 2016; Finch & Stubblefield, 2019; Farooq et al., 2018). After oil spills, the fresh Petroleum hydrocarbons enter the marine water; they float on the water's surface and spread quickly because they contain many low boiling compounds that are more soluble in water and have lower viscosity fresh and promptly spread out from the source. These low-boiling hydrocarbon compounds in the oil are removed by evaporation, and the quantity of the oil that evaporates varies from roughly 10 %for heavy oils or oil products to 75% for light fuel oil, leading to the formation of more viscous oil residuals (Tarr, 2016). Similarly, the increased temperature reduces oil density and viscosity, increasing horizontal spreadability (Davidson et al., 2008). As the weathering process continues over time, spilled oil's physical and chemical properties are altered significantly, and these oil residuals can mix with the water to form emulsified oily wastewater, which can be substantially more than the original volume of spilled oil (Payne, 2018). Emulsification is the process by which oil-in-water (o/w) or water-in-oil emulsion (w/o) is generated (Fingas & Fieldhouse, 2003). A better understanding of oil/water emulsion formation because of the petroleum oil spill in the sea and its properties is essential for predicting, controlling, and mitigating the environmental impacts of petroleum hydrocarbon in marine waters (Payne, 2018). Stable emulsions comprise 60 and 80% water, resulting in 3-5 times greater wastewater than the original quantity of oil spilled. The density of the formed emulsion could be as high as 1.3 g/ml compared to the starting density of fresh oil, 0.8 g/ml (Fingas, 1995). The formation of the emulsion has a significant impact on the cleanup efforts. The volume of wastewater generated will be higher in amount; for example, emulsions with 80% water content would have wastewater volume five times greater than the original quantity of spilled oil. Most considerably, the oil's viscosity typically changes from a few hundred mPa s to about 100,000 mPa s, an expansion of 500 or more, leading to more viscous wastewater formation. In addition, the emulsion's composition changes the oil's fate in the environment since a stable emulsion reduces the evaporation rate, biodegradation, and dissolution of the soluble component, slowing the natural breakdown process of oil. Also, increased volume and viscosity complicate the cleanup process (Fingas, 2010).

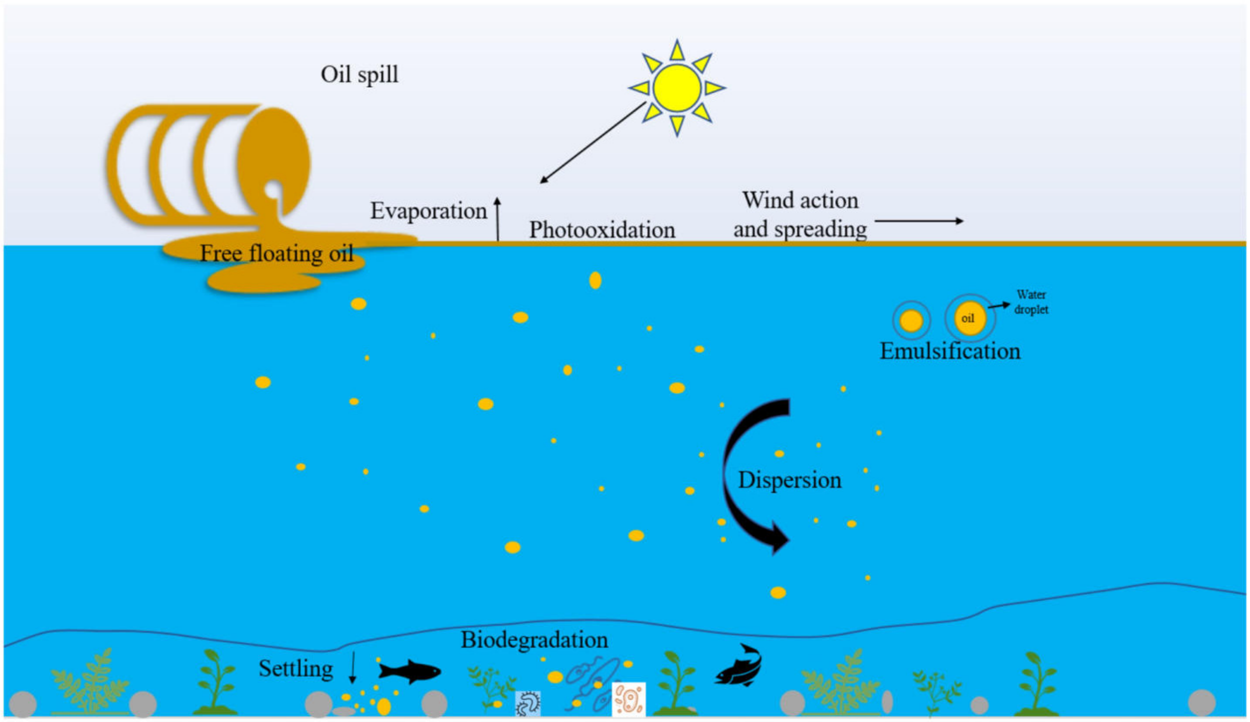


Figure 2.1 weathering of spilled oil (modified from Ward et al., 2020)

Traditional oil-spill cleaning apparatus may not recover these emulsions (Xie et al., 2007; Fingas & Fieldhouse, 2009). Moreover, a large volume of produced oily waste could easily exceed the capacity of locally available waste management facilities, leading to a great challenge for its effective management. Similarly, transporting oily residue to shore for decanting and management is complicated, time-consuming, and expensive. The existing oil cleanup method includes the deployment of booms, skimmers, and in-situ oil burning on the water surface. (Hubbe et al., 2013; Kinner et al., 2014; Prendergast & Gschwend, 2014).

However, these cleanup methods are time-consuming and ineffective as some technologies lead to pollution (Sarbatly et al., 2016). In addition, the resource value of oil is also lost in these cleanup methods. Thus, the cleanup process with efficient collection of wastewater, decanting, and energy recovery from the decanted oil and oily sludges are desired to recover energy from oily waste. Therefore, on-site collection and decanting of oily waste are crucial for volume minimization, discharge to the surface, and beneficial reuse (Neff & Hagemann, 2007). Moreover, on-site decanting improves the oil response capacity and efficiency by saving the storage space in barges and significantly saves the lengthy time and high cost of hauling decanted water to shore for disposal. Therefore, the most desirable alternative for the marine oil spill response operation is a system design that could operate at the site of disasters and continuously decant the oily waste, which could be directly released back into the ocean.

2.3 Methods for oily wastewater treatment

Various methods are available to treat oily wastewater, such as physical, chemical, mechanical, thermal, electrical, and hybrid technologies. However, it is essential to note that selecting the appropriate method depends on the characteristics of oil wastewater and its desired discharge limits. Therefore, in this literature review, different oily wastewater treatment methods have been categorized based on their working mechanisms of separation, such as gravity differential separation, filtration, coalescence/filtration, adsorption and absorption, electric and magnetic separation, and thermal separation (Medeiros et al., 2022).

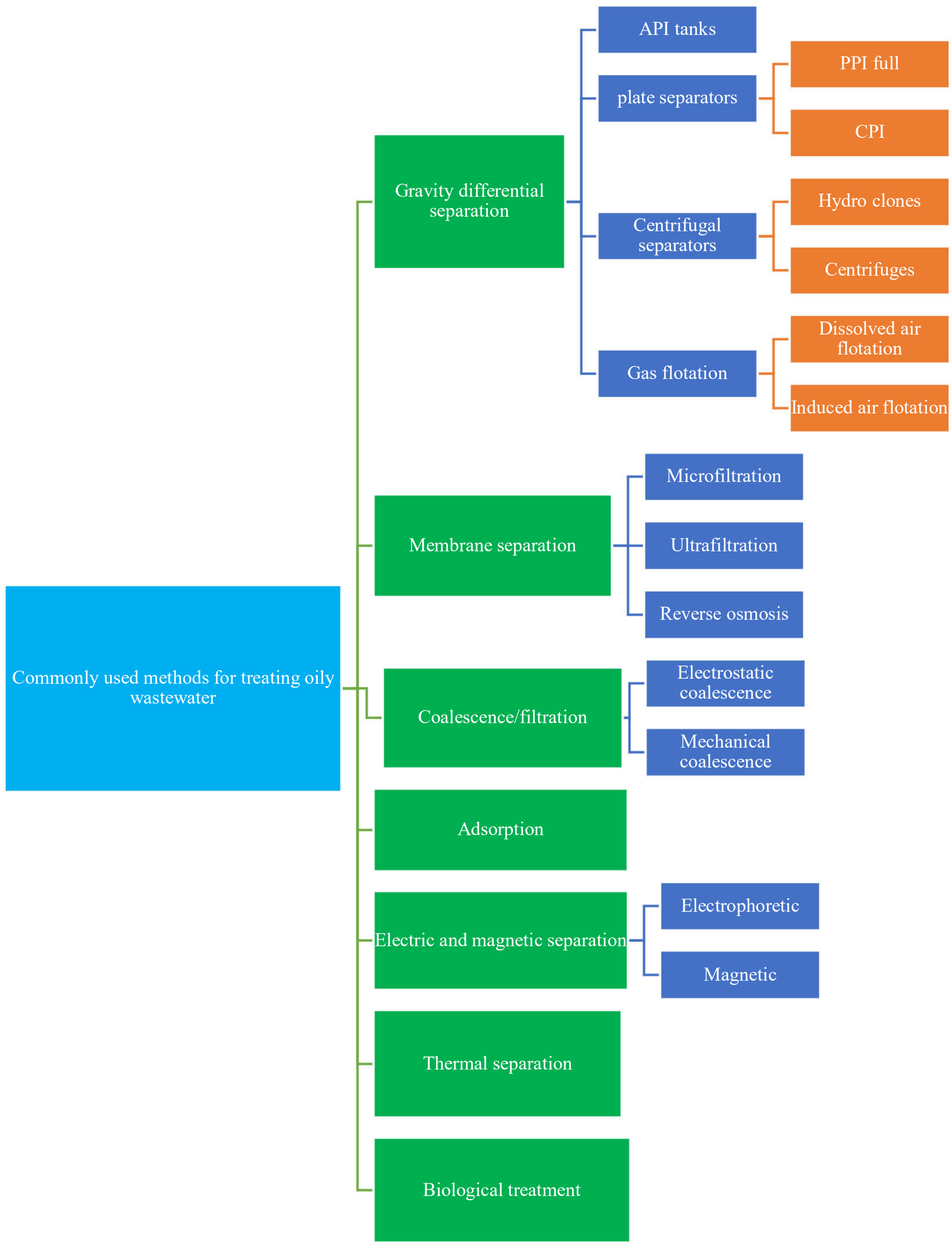


Figure 2.2: Different methods employed for oily wastewater treatment are categorized based on their working mechanisms (Modified from Medeiros et al., 2022).

Table 2.1 Table displaying different wastewater treatment methods.

Separation methods		Advantages	Disadvantages	Reference
Gravity differential separation	Gravity settling and API oil-water separator	Simple equipment with minimum operating costs	A requirement of larger footprints and inadequate removal of fine emulsion (< 150 µm)	Liu et al., 2022; Saththasivam et al., 2016
	Plate separators	Simple equipment with a higher capacity and faster separation compared to API tanks	Inefficient in the treatment of emulsified oil	Ebrahiemet al., 2022; Jaworski & Meng, 2009.
	Rotational separators	High emulsion removal efficiency, low maintenance cost, no solvent requirements and environmentally safe	Narrow optimum performance range, economically unsuitable and significantly lower size	Mao et al., 2019; Wills & Finch, 2015.

			molecules hard to settle down	
	Gas flotation	High oil/water separation efficiency and a wide range of optimum performance conditions	Complex operations and higher upfront costs	Etchepare et al., 2017; Saththasivam et al., 2016; Li et al., 2007, Hoseini et al., 2015.
Membrane Separation	Microfiltration	Efficient in removing emulsion size between 50 – 500 nm.	Membrane fouling cannot separate fine emulsions less than 50 nm.	Padaki et al., 2015; Anis et al., 2019, Cui et al., 2008.
	Ultrafiltration	Remarkably high oil/water separation efficiency, no requirements for chemical additives, can remove emulsions greater than 2 nm.	Membrane fouling, lower throughput, cannot separate ultrafine emulsion less than 2 nm, and regular maintenance is required.	He & Jiang, 2008; Tanudjaja et al., 2019; Padaki et al., 2015

	Reverse osmosis	High oil/water separation efficiency, efficient in the removal of the tiny emulsion as small as 0.3 nm	The deformable properties of emulsion also limit high initial costs, slow process, regular maintenance such as filter replacement, and separation efficiency.	Padaki et al., 2015
Coalescence/filtration	Electrostatic coalescence	High emulsion removal efficiency, low operating costs	High initial costs	Yasir et al., 2023; Ismail et al., 2020; Phalakornkule et al., 2010
	Mechanical coalescence	The better oil/water separation efficiency	High installation costs and operating energy	Sokolović et al., 2010; Zhao & Li, 2011.
Adsorption	Adsorption	Simple procedure and low processing cost, the good oil/water separation efficiency	Labour intensive	Tansel & Pascual, 2011; Abuhasel et al., 2021; Likon et al., 2013.

Electric and Magnetic separation	Electrophoretic	Easy operation and good oil/water separation efficiency	High initial costs, temperature-sensitive, regular cleaning and maintenance of electrodes, time-consuming	Kwon et al., 2010; Ismail et al., 2020
	Magnetic	Simple equipment with good oil/water separation efficiency	Regular cleaning and maintenance required	Ambashta & Sillanpää, 2010; Mirshahghassemi et al., 2017; Deng et al., 2020.
Thermal separation	Freezing and thawing	Less energy consumption, no chemicals, and less-skilled operators	Large space requirements and lengthy process	Lin et al., 2007; Sabri, 2017.
Biological Treatment	Biological Treatment	Good oil/water separation efficiency with low operating costs.	Time-consuming, sensitive to pH and temperature, larger	Jamaly et al., 2015; Nopcharoenkul et al., 2013; Srinivasan & Viraraghavan, 2010.

2.4 Gravity differential separation

Different oily wastewater treatment technologies that work based on the gravity difference between two components of oily wastewater are described below:

2.4.1 Gravity settling and API oil-water separators

Gravity settling is the oldest and most common method for oily wastewater treatment and is usually the first step in the cleaning process, which provides coarse separation, frees oil from water, and is solely driven by gravitational force. These separators and settlers were developed by the American Petroleum Institute and Rex Chain Belt Co. more than 70 years ago, and thus, these separators are referred to as API Separators. These separators are primarily intended to reduce the flow velocity of oily wastewater and provide the necessary residence time to separate oil from the mixture by gravity-driven settling. They are available in different mechanical configurations (Almorihil et al., 2021; Liu et al., 2022). Gravity-settling tanks work on the principle of Stokes' law and work based on the density difference between the wastewater and oil separated, allowing the oil in the wastewater to rise to the vessel's surface. As a result, the separated clean oil rises to the highest layer of the tank, which is suitable for energy recovery processing. Gravity separation relies on Stroke laws to separate the oil and water.

In contrast, the residual thickness of unbroken sludge emulsion lies right below the highest layer. The third layer consists of soluble components, suspended solids, and oils. Finally, the wet, oily sludge is separated at the bottom layer of the tank. API tanks are specially designed gravity separators with a minimum horizontal area, vertical cross-sectional area, and depth-to-width ratio (Pirzadeh, 2022).

Using this separation technology, a large amount of free oil and water could be separated quickly, in a few minutes to an hour, depending upon the oil's physical characteristics. Also, separation of the free water layer, in appropriate situations, increases local temporary storage capacity significantly. Moreover, the water content in oil also substantially affects the efficacy of the demulsifiers in Secondary treatment.

Stokes' law in its original form in MKS units can be expressed as follows:

$V = h/t = (D^2 g\ (\rho - \rho^{'}))/18\eta$ …………………………………… (2.1)

V = terminal velocity of the droplet (m/s), h = travel distance of droplet (m), t = time (s), D = droplet diameter (m), g = acceleration due to gravity (9.81 m/s2), r = water density (kg/m3), $\rho^{'}$ = oil density (kg/m3), η = viscosity of the continuous phase (pa·s) (Saththasivam et al. 2016).

From equation (1), we can see that the droplet diameter is squared and considerably influences the separation rate. Thus, the size of oil droplets plays a vital role in the gravity separation of free oil. Thus, it can only remove suspended free oil particles of 150 microns or larger (Liu et al., 2022; Saththasivam et al., 2016); however, it is inefficient for separating emulsified oily wastewater. It does not separate the oil droplets with fewer than 150 microns (Liu et al., 2022; Medeiros et al., 2022). Also, as smaller droplets and oil-water emulsions are not separated, further processing is required before being discharged back into the ocean or reused. Furthermore, this separation method is relatively passive in nature and time-consuming (Medeiros et al., 2022).

Gravity separation is the most common primary treatment of oily wastewater; however, treated effluent from gravity does not meet the required discharge limits. Thus, the secondary treatment steps are used to lower dissolved, emulsified, and dispersed oil levels.

2.4.2 Plate separators

Gravity settling and API tanks require larger space; therefore, the plate separators are specially designed plates to reduce the equipment size without lowering the oil-removal efficiency. Parallel plate separators (PPI) and corrugated plate separators (CPI) are the two most common plate separators. Plate separators contain underside plates, providing increased space for suspended oil droplets to coalesce to form into a larger globule. Plate separators also work on the principle of strokes law. Let us consider equation (2.1)

$V = h/t = (D^2 g\ (\rho - \rho'))/18\eta$

After the coalescence, the overall diameters of oil droplets increase and reduce the population density of smaller droplets. The above equation shows that the oil separation rate from water is directly proportional to the square of the droplet diameter. However, this separation technology may not be effective when water chemicals or suspended solids restrict or prevent oil droplets coalesce. The separation efficiency of such separators still depends upon the specific gravity between the water and the suspended oil. However, the parallel plates can enhance the degree of oil-water separation for oil droplets above 50 microns in size. Alternatively, parallel plate separators are added to the design of API Separators and require less space than a conventional API separator to achieve a similar degree of separation. The gravity separators installed with parallel plate separators can treat the water three times that of conventional units with the same treatment capacity (Ebrahiemet al., 2022). In addition to that, PPI has better separation efficiency than traditional gravity settling tanks and can remove free oil droplets with smaller diameters (Jaworski & Meng, 2009). The corrugated plate technology is the most common form of plate interceptors and is an organic mixture of gravity separation and coalescence, which is cost-effective, efficient in the termination of free oil from water and feasible to use. Thus, its popularity and use have been discussed by many researchers (Hernández, 2021; Gutteter-Grudziński & Moraczewski, 2011; Han et al., 2017). This separation method can separate the oil from the water with a diameter greater than 60 µm. Thus, making this technique more efficient than API tanks and easier in sediment handling.

2.4.3 Rotational separation (Centrifugal separation)

Centrifugal separation technology utilizes the centrifugal force to separate substances based on their densities. In wastewater treatment, they are often used to separate solids from liquids and oil from water as a primary treatment method. Both centrifuges and hydro cyclones work on the same basic centrifugal force principle; however, their operation mechanisms vary slightly. Hydro cyclones have no mechanical moving parts, and the force is applied passively (Sabbagh et al., 2015). For example, in centrifugal separators, when the wastewater having two different densities is rotated at high speed, the denser water is pushed outward from the centre of the circle, whereas the lighter oil is collected at the centre, which is obtained from the exit point (Wills & Finch, 2015; Bai & Bai, 2018).

2.4.3.1 Centrifuges

Centrifuges are a simple method for recovering oil intermixed with water using a the force of gravity, centrifugal force, and inertia to separate two or more materials without any chemical separating agents (Adeyanju & Adeosun, 2022; Eggert et al., 2017). Centrifugal separators' working mechanisms include rotating the material in a chamber at higher speed, which causes the heavier and the lighter materials to settle out separately from the lighter materials. Therefore, centrifugal separation can also be regarded as an extension of gravity separation. This is because the settling rates of particles are accelerated under the influence of centrifugal force and is a more attractive and efficient method as a primary treatment method compared to gravity settling (Mao et al., 2019; Wills & Finch, 2015).

From equation (2.1)

$V = h/t = (D^2g\ (\rho - \rho'))/18\eta$

The increase in density differences between oil and water is directly proportional to the rising velocity of the oil droplet. An experiment conducted by Mao et al., 2019 demonstrated that 92–96% oil/water separation efficiencies were obtained for all centrifugation experiments for the primary treatment of oi-water emulsion. They have suggested that secondary treatment, such as ultrafiltration using membranes with a 100 nm or lower pore diameter, would be adequate to remove most residual oil in the aqueous phase to meet the discharge limit.

2.4.3.2 Hydroclones

Hydrocyclones are simple, compact, low-weight, and low-cost centrifugal separators with a vertical pipe with a tangential inlet and two outlets, one at the top and the other near the bottom side (Liu et al., 2012). They are now widely applied in different industries to separate liquids with two different densities to support the strong centrifugal force the swirling flow creates (Zhang et al., 2021).

In hydro clones, oily wastewater separation works based on the vortex principle in which the wastewater to be separated is injected tangentially at high speed into the upper cylindrical section, which develops a robust swivelling fluid motion. During the vortex's downward movement, more massive particles are pushed out of the vortex's centre, whereas the lighter oil particles move to the center. As a result, the treated water is collected from an exit point, whereas the separated oil is forced out through an orifice positioned in the inlet (Pal, 2017; Show & Lee, 2014). However, they are inefficient for separating the treatment of emulsified wastewater and cannot separate dispersed oil droplets within diameters less than 15 μm (Bai et al., 2011). However, attempts have been made to improve the efficiency by developing a new type of hydro cyclone, such as magnetic, direct current hydro cyclones, but these have not been applied widely for the treatment of oily wastewater due to the complexity and low reliability of the equipment (Bai et al., 2011).

Furthermore, attempts have been made to improve the separation efficiency of hydro cyclones by some researchers using air bubbles. Diesel oil with a concentration below 150 mg/l was used for the experiment, and a removal efficiency of 85% was obtained at a 16,000 Reynolds number (Bai et al., 2011). Thus, from this experiment, it can be concluded that air bubbles can improve hydro cyclones' separation efficiency. However, further research is recommended to achieve an optimal design.

2.4.4 Gas flotation

Gas flotation techniques for wastewater treatment can be regarded as a type of gravitational separation process operated by increasing density difference between continuous and dispersed phases (Painmanakul et al., 2010). The working mechanism of gas depends on the density differences between the effluent water and bubble-particle aggregate. Various gases are employed in flotation systems, with air being the most common (Saththasivam et al., 2016). After an oil spill, the collected oily wastewater contains oil-in-water emulsions as one of the primary contaminants, and these emulsified oil droplets are in order of a few micrometres in diameter. These tiny, emulsified oil-water droplets are protected from spontaneous coalescence into larger ones by electrostatic repulsion forces, making the oil separation process more complex and cannot be separated by simple gravity separation (Xiong et al., 2023). Thus, air flotation techniques are highly effective in removing these emulsified oils in such conditions. The process of gas flotation can be divided into four simple steps. The first step is the generation of air bubbles. The second step is contact between air bubbles and oil droplets, and the third step is the attachment of gas bubbles to oil droplets and the rising of air-oil combinations (Dudek et al., 2020). Air flotation techniques can remove most emulsified and free oil if the wastewater is pretreated using conventional methods, including chemical Treatment (Bennett & Shammas, 2010). Gas flotation techniques have proved efficient, practical, and reliable in separating finely dissolved oil and other contaminants from water, such as dissolved ions, fats, and suspended solids.

From equation (2.1),

$V = h/t = (D^2 g\ (\rho - \rho'))/18\eta$

From the above equation, we can observe that rate of separation is also increased if we can increase the density difference of the phases. Unlike centrifugal separation, this could be done by adding buoyant gas bubbles to the oil droplets, which reduces the density of the oil droplets.

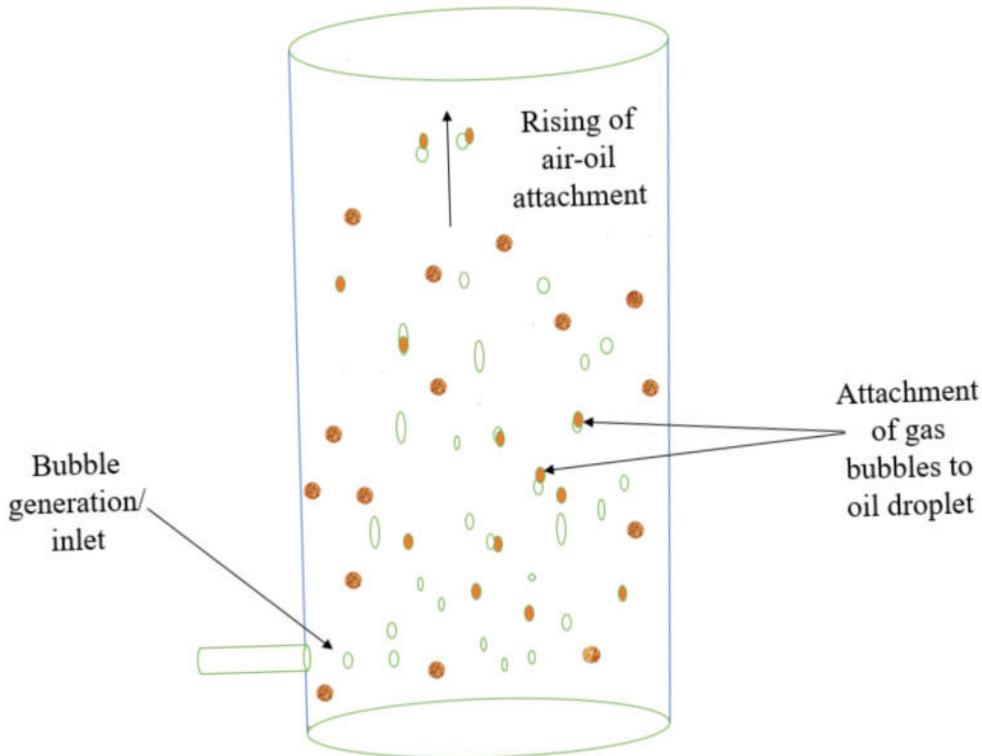


Figure 2.3 Oily droplet removal mechanisms by gas flotation

2.4.4.1 Dispersed Air

Dispersed air flotation is also known as induced gas flotation (IGF), which produces and disperses gas bubbles into the influent, which mechanical or hydraulic methods can achieve. In dispersed air flotation techniques, pressurized and supersaturated wastewater with air is reduced to atmospheric conditions in the floatation column, leading to fine bubbles in the flotation column. As these fine air bubbles rise in the flotation column, they adhere to finely dissolved oil droplets and rise to the column's surface, which can be removed by skimming (Hanafy & Nabih, 2007). For example, the study conducted by Painmanakul et al., 2010 has demonstrated that an oil/water separation efficiency of 60–80% can be achieved by using induced air flotation techniques significantly higher than those obtained with the decantation process free gravity separation (about 28%). In another study by Hoseini et al., 2015, removing total petroleum hydrocarbons from wastewater by combining coagulation and mechanically induced air flotation demonstrated 93 % removal efficiency at optimal conditions. Thus, these results confirmed that the generated bubbles interact with the oil droplets and act like "rising parachutes" for oil droplets bringing the oil droplets to the separating vessels' surface, which can be skimmed off.

2.4.4.2 Dissolved Air

Dissolve air flotation (DAF) can also be considered an accelerated gravitational separation process. In dissolved air flotation techniques, air under pressure is introduced at the bottom of the vessel containing the wastewater to be treated. As the air bubbles rise to the top of the vessel, these fine air bubbles attach themselves to the oil droplets, which decreases the specific density of oil droplets, and agglomerated material floats to the surface where it forms a scum layer which can be removed by skimming (Hanafy & Nabih, 2007). The size distribution of bubbles and the size of oil droplets play a vital role in the dissolved air flotation system's separation efficiency. Thus, smaller bubbles are preferred in the gas flotation system because their larger surface area and smaller bubbles tend to rise rapidly in the flotation column, resulting in increased separation efficiency (Santander et al., 2011; Saththasivam et al., 2016; Li et al., 2007). The study conducted by Etchepare et al., 2017 investigated the separation efficiency of emulsified oil in saline water by dissolving air flotation system using NB/MB , and their research demonstrated that oil/water separation efficiency of 99 % was obtained at optimal conditions after the separation of free oil by gravity separation methods.

Another study by Rattanapan et al., 2011 investigated that 85–95% removal efficiency was achieved during the acidification of treated biodiesel wastewater with alum in the DAF system. Similarly, the study conducted by Zouboulis & Avranas, 2000 confirmed that the DAF could be used to treat emulsified oil. The results highlighted that more than 95% efficiency is achieved when separating oil from wastewater with an initial concentration of 500 mg l^{-}. The studies also concluded that the pre-treatment of wastewater by acidification could enhance the DAF system's separation efficiency and be more economical.

2.5 Membrane separation

The free oil in oily wastewater can be easily removed by mechanical means such as gravity settling, skimming, and centrifuging. However, mechanical methods cannot remove small oily droplets less than 20 um. Therefore, filtration, such as membrane separation, has been used to treat emulsions as they are highly efficient for removing oil, do not require chemical additives, and are more economical than conventional separation techniques (Guo et al., 2020).

The working mechanisms of the membrane separation technique are simple and easy to understand. The working principles behind the membrane separation technique depend on the membrane, which acts as a semi-permeable layer between the phases to be separated and regulates the two phases' transportation. The filter allows the water to pass through the membranes, whereas it does not allow the suspended particles in the wastewater and other components to pass through the membrane (Padaki et al., 2015). The use of membrane-based separation has been increasing in recent decades due to its high oil/water separation efficiency and relatively simple operational process (Padaki et al., 2015). This method is economical and practical for separating oily wastewater with oil droplet sizes smaller than ten µm (Sang et al., 2022). In addition, membrane-based separation offers several advantages over conventional separation methods, such as high-quality permeates, straightforward automation, low footprint, no need for extraneous chemicals, and reduced waste and energy input (Szép & Kohlheb, 2010; Yang et al., 2015).

However, membrane fouling is the major problem associated with the membrane separation process, which reduces membrane filtration's productivity and operational costs (Tanudjaja et al., 2019). Improving the hydrophilicity of the membrane could help prevent membrane fouling (Li et al., 2006). The difference in the pressure-driven membrane separation process is generally categorized into microfiltration, ultrafiltration, and reverse osmosis. Conceptually, all the processes are similar except for the membranes' surface pore size, which characterizes their applications (Padaki et al., 2015).

2.5.1 Microfiltration

Microfiltration is one of the oldest pressure-driven membrane applications practiced commercially and is used in various effluents and wastewaters treatment industries, with a membrane pore size of 50-500 nm (Anis et al., 2019; Padaki et al., 2015). In this separation method, wastewater passes through the membrane, having a fixed pore size. In previous research demonstrated by Hua et al., 2007, oily wastewater was passed through a ceramic membrane with a pore size of 50 nm. Total organic carbon removal of 92.4 % was achieved in that study. Similarly, in another study conducted by Cui et al. 2008, the application of NaA zeolite microfiltration membranes on α-Al_2O_3 tube by in situ hydrothermal synthesis method having inter-particle pore sizes of 1.2 μm, 0.4 μm, and 0.2 μm demonstrated 99 % oil/water separation efficiency. Water containing less than one mg/l oil was produced after the treatment at 85 L m^{-2} h^{-1} by NaA1 at a membrane pressure of 50 kPa as an operating condition. Similarly, the study conducted in the Tehran refinery demonstrated removal efficiency higher than 95% using a tubular ceramic microfiltration system for the treatment of oily wastewater (Abadi et al., 2011)

2.5.2 Ultrafiltration

Ultrafiltration is one of the most effective techniques for separating oil from wastewater compared to traditional separation methods, as it has higher oil/water separation efficiency with no requirement for chemical additives and low energy costs (He & Jiang, 2008). In addition, it has a membrane pore size of 2-50 nm and is more helpful in separating wastewater with smaller emulsions and particles than microfiltration (Padaki et al., 2015). The comparative study of microfiltration and ultrafiltration at pilot scale for the treatment of oilfield-produced water at the North Sea demonstrated that ultrafiltration having a molecular weight cut off between 100,000 and 200,000 exhibited 96 % rejection of total hydrocarbon concentration, 54% rejection for BTX (Benzene, toluene and xylene) and 95% rejection of heavy metals like copper, zinc. Similarly, the study conducted by Yu et al., 2006 for the treatment of wastewater from an oil field using an ultrafiltration module equipped with polyvinylidene fluoride membranes modified by inorganic nano-sized alumina particles proved that ultrafiltration is very useful in the treatment of oily wastewater and their results indicated that oil concentration in the treated water was less than 1 mg/L. Likewise, Zhang et al., 2009 demonstrated that using polysulfone in ultrafiltration helps treat oily wastewater, and their results showed that separation efficiency was as high as 99.16 %. In another study (Marchese et al., 2000) investigated that the wastewater from household appliances containing emulsified oil was treated on a pilot scale having chemical oxygen demand (COD) of 1500 mg of O_2/L and a total hydrocarbon concentration (HC) of 170 mg/L as an initial oil characteristic. After the experiment, it was observed that ultrafiltration was remarkably effective for removing emulsified oil and removal efficiency as high as 90.1% and 99.7% was observed to remove COD and HC.

2.5.3 Reverse Osmosis

It has a membrane pore size of 0.3 – 0.6 nm. Reverse osmosis membranes of polymeric members offer several advantages over other membrane separation techniques. These include high efficiency in removing particles, dispersed and emulsified oils, comparatively smaller size, lower energy requirements, and relatively inexpensive compared to ceramic-based membranes (Padaki et al., 2015). The reverse osmosis application has been increasing for industrial and municipal treatment due to the growing demand for better quality drinking water and oily wastewater treatment (Aleisa et al., 2022). Although reverse osmosis is more efficient in separating oily wastes than other membrane separation techniques, one of the significant disadvantages is membrane fouling. Different researchers have conducted many studies to improve the hydrophobicity and antifouling of the membranes either by blending with hydrophilic substances or modifying their surface properties through chemical or physical alteration. Compared to other approaches, hydrophilic membranes are generally agreed upon and applied to reduce membrane fouling (Mansourizadeh & Azad, 2014; Padaki et al., 2015).

Although the membrane separation technique effectively separates oil emulsions from wastewater, their separation efficiency is limited by emulsions' deformable properties. Oil emulsions can deform under pressure, and depending on the applied force on the membrane, they can be squeezed through the pores and pollute the permeate (Shirzadi et al., 2022)

2.6 Coalescence

Coalescence can be defined as the irreversible process in which two or more droplets merge to form single larger droplets. Coalescence between droplets occurs by thinning and disrupting the thin liquid film between the droplets (Yamashita et al., 2017). The application of coalescence for treatment of emulsified wastewater treatment has attracted many researchers attention in recent years due to its convenient operation, the high oil/water separation efficiency of oil from wastewater without adding any reagent, the extended service period of coalescence materials, high value in recovered oil (Zhao & Li, 2011). Coalescence materials can be categorized into natural and artificial coalescence materials. The natural coalescence materials include anthracite, serpentine, quartz sand, silica sand, and artificial coalescence materials, including polypropylene, PVC, styrene-butadiene rubber exchange resin, fibre, modified mc nylon, abs engineering plastics, carbon steel, stainless steel, fibreglass.

The oil/water separation by coalescence works on the stroke law principle (Li, 2002; Zhao & Li, 2011).

$v = g\ (\rho_y-\rho_e)\ d^2)/(18\mu)$

Here, v is the rising velocity of oil droplets having diameter d, cm/s; g is the acceleration due to gravity, cm/s^2; μ is the fluid viscosity, g/cm/s; ρ_y is the density of water, g/cm^3; ρ_e is the density of oil, g/cm^3.

From the above expression, it can be observed that the rising velocity v is directly proportional to the square of oil size. Thus, lipophilic materials trap and absorb the oil particles when the oil passes through the coalescence bed. In this process, these oil droplets collapse and aggregate together to form larger oil droplets, increasing the diameter by 1000-fold. Hence, the corresponding rising velocity increases 1000^2-fold, easily removed from the water. Therefore, fibrous coalescence technology can effectively remove emulsified and dispersed oil with an oil droplet diameter greater than ten μm (Shibing et al., 2004; Chen et al., 2002; Li & Chen, 2007).

The experiment conducted by Li & Chen, 2007 demonstrated that using ceramics filtration ball coalescence equipment could effectively treat oilfield wastewater. Their experimental results presented that influent water has an oil concentration of 700-900 mg/l and was effectively treated with more than 90 % oil/water separation efficiency. Similarly, their results also emphasized that this equipment benefits from a more substantial pollutant removal capacity than traditional coalescence equipment.

Wastewater separation by coalescence can be broadly divided into mechanical coalescence and electrostatic coalescence.

2.6.1 Electrostatic coalescence

Historically, the electrostatic coalesce was developed for the petroleum-related industries in California. However, this separation method is widely applied to separate an aqueous phase dispersed in a dielectric oil phase with a remarkably lesser dielectric constant than the dispersed phase. In electrostatic coalescence, the presence of an electric field promotes the interaction between drops and improves the drop-drop and drop-interface coalescence, and this interaction increases the droplet size, increase the settling velocity, and reduces the separation time (Yasir et al., 2023; Ismail et al., 2020; Phalakornkule et al., 2010). Commonly, an electrostatic coalescence is constructed of a tank with electrodes, in which at least one of the electrodes is earthed, and the other one is suspended by an insulator to which an electric potential is applied (Yasir et al., 2023). In electrostatic coalescence, separation efficiency depends on the electric field's strength. The study conducted by Yang et al., 2015 demonstrated that droplet coalescence diameter increased slowly with electric field strength. However, Ismail et al., 2020 observed that the increasing electric field strength above the critical electric field strength could break the droplet into smaller droplets. Thus, the optimum electric field strength is approximately 525.6 kV m^{-1} and applying electric field strength more than this optimal value could decrease droplet diameter.

Similarly, new modified methods have been developed to combine the centrifugal force, and electrostatic coalesce to separate dispersed water/oil droplets from the continuous phase using chemical or heat treatment to reduce the viscosity of the liquid-liquid dispersion system (Shiet et al., 2023). Here, the necessity for lowering oil's viscosity is avoided by applying centrifugal force, whereas electrostatic coalescence enriches the separation of oil or water from the wastewater. Then, the emulsion is separated using a radial electric field and centrifugal force concurrently to generate a bulk interface at right angles to the direction of the electric field and centrifugal force. The applied electric field causes the emulsion to coalesce and enlarge to enough size, separated by centrifugal force without generating adequate shear force to break the emulsions. The experiment conducted by Hosseini & and Shahavi, 2012 demonstrated that the electrostatic coalescence method efficiently separates tiny oil droplets from the nanometer scale dispersed in water. Their results showed that the highest removal efficiency of 85 % was obtained at an optimal temperature of 38°C and 3000 V.

2.6.2 Mechanical coalescence

Another type of coalescence is mechanical coalescence, which operates by physical variation or involvement of a droplet and is influenced by physical or mechanical means (Hafsi et al., 2021). Mechanical coalescence can be sub-categorized into quiescent settlers, plate coalesces, and porous, fibrous, and granular beds. Fibrous and granular beds are most frequently used in the secondary treatment of oily wastewater among mechanical coalescence (Singh et al., 2023). In this separation technique, oil droplets are enlarged in coalescence beds due to the coalescence process, and enlarged droplets are transferred to separating columns for further treatment or removal (Li & Gu, 2005). The study conducted by Soković et al., 2010 on the separation efficiency of coalescence with different geometry, mainly vertical and horizontal configurations, demonstrated that horizontal coalescence systems had a better separation efficiency of 98.7% compared to vertical coalescence reactors having a removal efficiency of 94.6%.

Similarly, the study conducted by Chen et al., 2002 showed that oil could be effectively separated from wastewater with natural coalescence materials such as anthracite, which has lipophilic properties and can remove oil from water with an oil/water separation efficiency of 92.6 %. Also, a variety of artificial mechanical coalescence materials such as polypropylene, PVC, styrene-butadiene rubber, exchange resin, fibre, modified mc nylon, abs engineering plastics, carbon steel, stainless steel, and fibreglass are commercially available in markets that can be used to treat the oily wastewater effectively (Zhao & Li, 2011). Likewise, the experiment conducted by Yang et al. 2006 on artificial coalescence showed that Styrene-butadiene has a more inadequate oil/water separation efficiency of 71.68% than polystyrene at 86.32%.

2.7 Adsorption

Adsorption can be defined as the attachment between a sorbent and a sorbate where the sorbate molecules attach themselves to the sorbent's surface without penetrating or passing the sorbent's surface. The mechanisms of oil adsorption can be described in three steps: first, the diffusion of oil molecules occurs at the sorbent surface. After that, oil droplets are entrapped into the sorbent structure by capillary action, and finally, oil droplets accumulate within the porous and coarse surface of the sorbent (Tansel & Pascual, 2011).

Different studies have also found that oil adsorption is strongly correlated to the functional group of sorbent properties, and functional groups such as O-H, C=O, and C-O have been observed to be responsible for adsorption (Srinivasan & Viraraghavan, 2010; Said et al., 2009). In addition, some of the natural sorbents have excellent morphology for adsorption, such as kapok fibre and populous seed, which encompass hollow structures within them, which give a more significant surface area available for adsorption (Likon et al., 2013). Similarly, sorbent separation efficiency depends on different properties of sorbents, such as hydrophobicity, the functional group of oil, surface morphology, surface area, pore size and surface interaction. Higher the hydrophobicity of sorbent, the better the separation efficiency, as a lack of hydrophobicity of materials could cause a collapse in sorbent microstructure due to water adsorption (Likon et al., 2013).

Similarly, Ibrahim et al., 2009 chemically modified the barley straw, waste from the agricultural field, to study emulsified oils' removal efficiency from an aqueous solution. The study's outcomes demonstrated that removal efficiency between 15-90% was achieved. Thus, the oil/water separation efficiency using adsorption varies significantly depending upon the nature and properties of sorbent materials.

2.8 Electric and Magnetic separation

2.8.1 Electrophoretic

An electric field for separating oily wastewater has been used in the petroleum industry by applying a high electric field onto the flowing wastewater. The applied electric field promotes the flocculation and coalescence of water in oil. The electrical treatment method's basic working principle incorporates chain formation, electrophoretic, and electrophoresis, forming intermolecular bonds, dipole coalescence, and random collisions (Ismail et al., 2020). Under the influence of the electric field, droplets approach each other, leading to droplet-droplet coalescence. Kwon et al., 2010 separated water from water-in-oil emulsion using a direct current electric field demonstrated that the highest water separation efficiency of 77.2% was achieved at 75 °C under the optimal operating voltage between the range of 2 to 5 kV. Their study also presented that the separation efficiency highly depends on temperature. The separation efficiency increases with an increase in wastewater temperature as an increase in temperature is related to a decrease in viscosity, thereby decreasing residence time.

2.8.2 Magnetic

Magnetic separation of wastewater utilizes magnetism as a unique physical property that helps in water purification by influencing contaminants' physical properties in water. Besides, combining magnetism with other processes enables an improvised, efficient purification technology (Ambashta & Sillanpää, 2010). High-gradient magnetic separation (HGMS) is commonly used in magnetic separators (Deng et al., 2020). A typical HGMS device consists of a bed with magnetically susceptible wires inserted in an electromagnet interior. Thus, when the magnetic field is applied across the column, the wires create a large field gradient around the cables that attract the magnetic particles to their surfaces and trap them. The assemblage of particles varies significantly in creating these large magnetic field gradients and the size of particles and magnetic properties. To achieve a growing collection of magnetic particles by HGMS, the magnet for attracting particles in the direction of the wires must dominate the fluid drag, gravitational force, inertia, and diffusion force as the particle suspension flows across the separator (Ambashta & Sillanpää, 2010).

The study conducted by Mirshahghassemi et al., 2017 for the treatment of an oil-water mixture using magnetic nanoparticles with high gradient magnetic separation (HGMS) demonstrated approximately 85–95% oil and nanoparticle removal under all conditions. Their results also demonstrated that increasing the magnetic field strength significantly increased the oil/water separation efficiencies and assumed that HGMS is a promising oil remedy technique using PVP coated with magnetic nanoparticles. Similarly, the study conducted by Mirshahghassemi et al., 2015 to separate oil from water using a magnetite nanoparticle coated with a polyvinylpyrrolidone demonstrated that nearly 100% oil/water separation efficiency was achieved from an oil-water mixture. Moreover, their study also concluded that magnetic nanoparticles could be utilized to separate oil from oily wastewater with excellent removal efficiency under environmentally relevant conditions.

2.9 Thermal Separation

2.9.1 Freezing and thawing

In recent years, the freezing and thawing application has been reported as a practical and feasible method for treating oily wastewater (Johnson & Affam, 2019; Chen & He, 2003; Sabri, 2017). The study conducted by Lin et al., 2007 for the investigation of phase separation of oil-in-water emulsions demonstrated that the volume expansion of water turning to ice and the oil-water interface interfacial tension was the main driving force for the breaking of emulsion. The oil-water separation follows a collision mechanism and is a slower process. Due to the expansion of the volume of water, while turning into ice, the collision between an undercooled liquid droplet and a frozen droplet occurs, which leads to the coalescence of droplets, and these droplets fuse into large drops, and hence the oily wastewater can be treated (Lin et al., 2007).

The different experiments conducted by different researchers have demonstrated that freezing and thawing are reliable and efficient in treating oily wastewater. For example, the investigation carried out by Chen & He, 2003 showed that nearly 90% of water removal from w/o emulsion was obtained in their experiment. Similarly, the research conducted by Lin et al., 2007 demonstrated that the freezing in cryogenic or dry ice was best freezing method for water removal, and oil/water separation efficiency increased from 25 to 96% with the increase of water content from 30 to 65%. In addition, the oil/water separation efficiency increased significantly from 74 to 95%, increasing droplet size from 2.7 to 7.3 μm and over 85% irrespective of the emulsions' oil phase component with 60% water content.

2.10 Biological Treatment

Most hydrocarbons are considered biodegradable, and their degradation is accomplished by aiding microbial growth, which is achieved by establishing the ideal environmental conditions. Favourable conditions help microorganisms degrade the contaminants into carbon dioxide and other gases (Adedeji et al., 2022; Vamerali et al., 2010). Even though oily wastewater's biological treatment is not well developed due to microorganisms' varied nature and behaviours in different environmental circumstances. Recent studies in this field have generated remarkable oily wastewater contamination decanting efficiency (Jamaly et al., 2015; Srinivasan & Viraraghavan, 2010). For example, Nopcharoenkul et al., 2013 researched the degradation of diesel oil, crude oil, *n*-tetradecane and *n*-hexadecane using *Pseudixanthomonas* sp. RN402 demonstrated that RN402 effectively degrades around 89%, 83%, 92%, and 65% of diesel, crude, n-tetradecane, and *n*-hexadecane, respectively. Similarly, in another research by Shokrollahzadeh et al., 2008, petrochemical wastewater treatment efficiency uses 67 different types of aerobic bacteria such as pseudomonas and Comamonas Acidovorax, Flavobacterium, Cytophaga, Sphingomonas, Acinetobacter. It was seen that 89% of Chemical Oxygen Demand (COD), 99% of ethylene dichloride, 92% of vinyl chloride, and 80% of total hydrocarbon degradation were achieved efficiently. In previous studies by Santo et al., 2013 the treatment of petroleum refinery wastewater by biological treatment by activated sludge showed that high removal efficiency of COD, total organic carbon and suspended solids could be achieved using this method. Their findings indicated that the removal efficiency of 94%–95%, 85%–87%, and 98%–99% removal of COD, total organic carbon, and total suspended solids were achieved.

2.11 Summary

In summary, this comprehensive review of oil-water separation methods highlights the complex challenges of treating oily wastewater. With the continuous improvement of environmental standards for the safe discharge of treated effluent, there is still a need for better treatment methods to meet the ever-increasing standards. Although each oily wastewater treatment method presented in this literature review offers unique advantages and disadvantages, it could be observed from the literature review and past studies that NB/MB gas flotation technology has the potential to emerge as a promising innovation in this field that could significantly enhance g the efficiency and effectiveness of oil-water separation processes.

NB/MB gas flotation technology, with its remarkable high separation efficiency, compact design, short retention time, and adaptability to various conditions, presents a compelling solution for separating emulsified oily wastewater generated after oil spills. However, it is essential to note that applying NB/MB in oil spill research remains an underexplored field of study, requiring further testing and validation to integrate this technology effectively into oil spill cleanup processes. Moreover, with evolving environmental standards, there is still a need for efficient, sustainable, chemical-free and adaptable oil-water separation technology development. Thus, the rigorous study and development in the field of NB/MB gas floatation technology is crucial for addressing the challenges of treating the large volume of oily wastewater collected after the oil spill response operations. Moreover, a single NB/MB technology may not remove oil entirely from the water. Therefore, there is also a need for testing the integrated technology, such as the combination of NB/MB gas flotation technology with adsorption or absorption, to enhance the oil/water separation efficiency.

Chapter 3 Materials and Methods

3.1 Materials

All the materials used in this study were analytical-grade chemicals purchased from Sigma-Aldrich (Oakville, ON, Canada). Tetrachloroethylene purchased from the same company (≥ 99.0%, Sigma Aldrich) was used for oil extraction from the emulsion and treated water sample. Silica gel (100-200 mesh, Sigma-Aldrich) was used to clean the extract after activating at 215 °C for 24 h. Anhydrous sodium sulfate (≥ 99.0%, Sigma Aldrich) was used to separate traces of water from the extract after drying at 215 °C for 24 h. The oil phase used in the study was Cold Lake Dilbit oil, recovered from the Western Canada Sedimentary Basin (WCSB) and provided by the Multi-Partner Oil Spill Research Initiative (MPRI). The artificial seawater used in the experiment was prepared with Ultrapure water (Milli-Q ® Advantage A10) and sodium chloride ($NaCl$, ≥ 99.0%).

3.2 Oil Weathering

For the oil weathering process, 25 grams of fresh CLD (Cold Lake Dilbit) was placed in a well-ventilated chemical fume hood for five days at room temperature. After that, the weight of the container was monitored regularly until the desired weight loss was obtained. Due to the evaporation of volatile hydrocarbons resulted in a cumulative mass loss, which was recorded and plotted below in Figure 3.1. After three days, the cumulative mass loss reached 10%. The fresh oil, 2% weathered oil, 5% weathered oil and 10% weathered oil were used to prepare the emulsion to investigate the effect of oil weathering on NB/MB gas flotation performance.

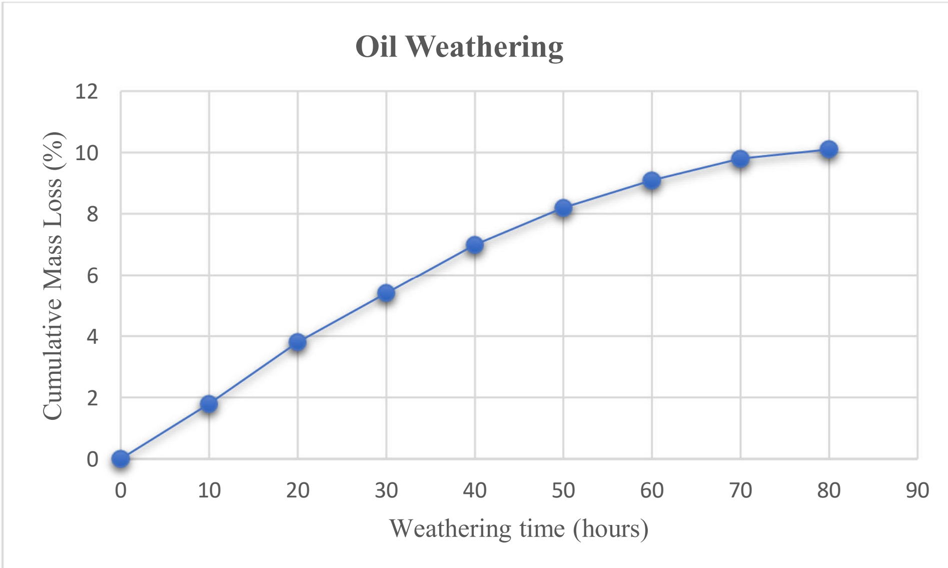


Figure 3.1 Cumulative mass loss of CLD over time

3.3 Preparation of oily wastewater (emulsion) for the experiment

At first, the saltwater required for the experiment was prepared by dissolving 35 g of NaCl in DI water to mimic the salinity of ocean water. After that, oil concentrations ranging from 200 ppm to 2000 ppm were prepared for experiments by adding the required mass of crude oil into the saltwater. After adding the oil to the salt water, the IKA mechanical homogenizer attached with its dispersing tool was used to emulsify the crude oil under the fixed mixing intensities of 8500 rpm for 35 minutes. After that, the crude oil was dispersed throughout the water phase by high shearing forces and mixing energy (Shen et al., 2022). The images of the prepared emulsion can be seen in Figure 3.2.

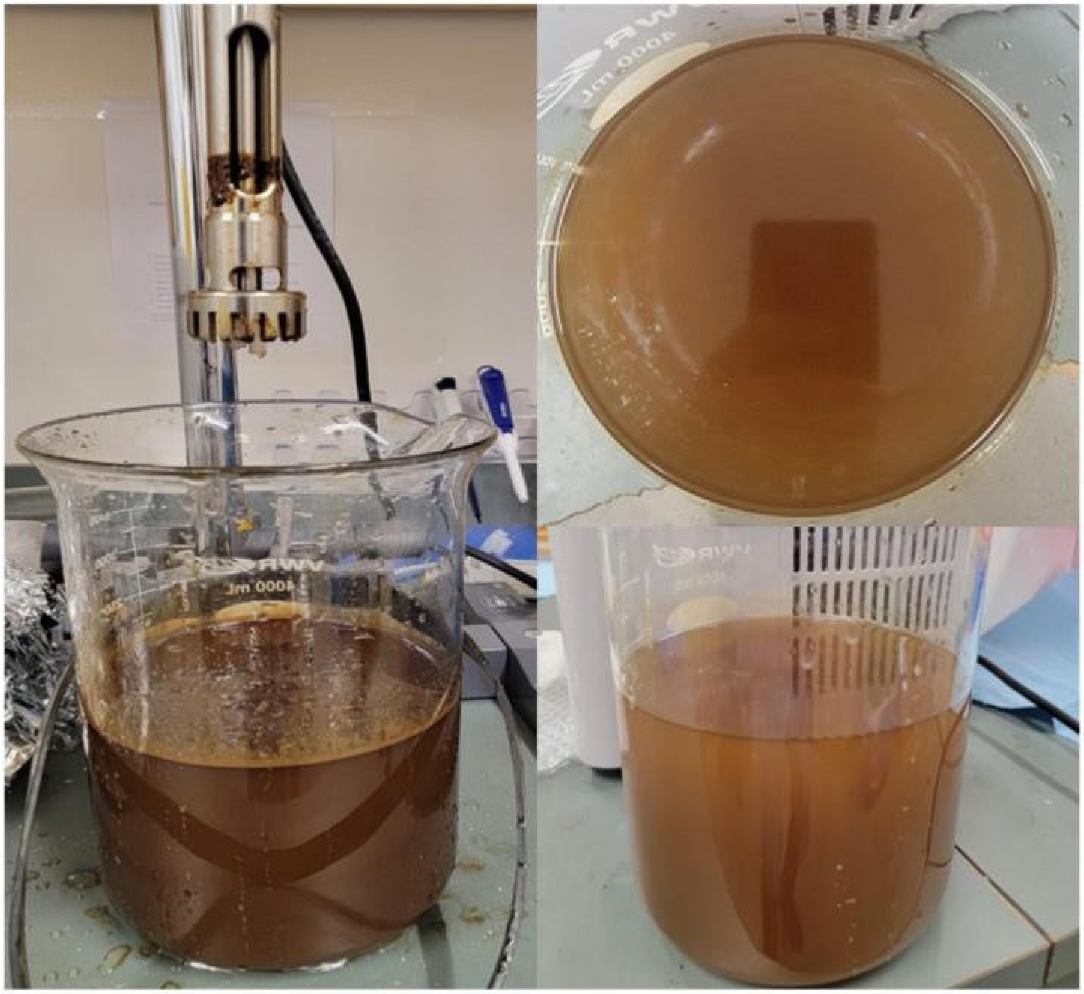


Figure 3.2 Prepared emulsion (with higher oil concentration on left and lower oil concentration on right) using IKA mechanical homogenizer.

3.4 Experimental setup and procedure

The lab-scale gas floatation system consists of two major components: a nanobubble generator and a flotation column, as shown in Figure 3.3 below. A fine bubble generator developed by LE5S (Living Energies & Co.) was used to produce both NB/MB. The summary of nanobubble generator properties and specifications is listed in Table 3.1 below. In each experiment, 2 litres of oily wastewater were introduced into the flotation column from the top. The treated water was recycled entirely back to the bubble generator to generate the bubbles, and the bubble solution was introduced to the bottom port of the flotation column. Following the flotation process, treated water samples were collected from sampling port 1 (located at the bottom of the flotation column).

The oil/water separation mechanisms using NB/MB include electrostatic repulsion, oil-water interface adsorption, enhanced coalescence and agglomeration, buoyancy, and hydrophobic interactions. NB/MB are charged in an aqueous medium due to ions on their surfaces. The charges in the NB/MB exhibit an electrostatic repulsion, which helps prevent bubbles' coalescence and facilitates the stabilization of the dispersed gas phase in the water. These charged NB/MB migrate towards the oil and water interface due to attractive forces and attach with the oil droplets to form bubble/oil agglomeration. As this bubble/oil agglomeration has a density less than that of the aqueous phase, it rises in water, facilitating the separation of oil and water (Al-Dulaimi and Al-Yaqoobi, 2021).

Control experiments were conducted in the same experimental setup using the flotation column B (Figure 3.5) without generating MB and NB. The presence of MB could be observed from the milky appearance of the test water in a beaker in Figure 3.4 below. All the experiments were conducted at room temperature.

Table 3.1 Summary of Bubble Generator Specifications

Properties	***Values***
Outer dimensions	H360mm × W310mm × D130mm
Weight	Approx. 4.4 kg
Electric power	AC 100-110V
Power frequency	50/60 Hz
Power consumption	1.3A

Capacity	200-300 cc/min
Temperature range	0 °C to 80 °C
Viscosity max.	50 mPas
Connecting tubing size	4mm (internal diameter) and 6mm (external diameter)

For all the experiments designed by RSM, flotation column B was used, as shown in Figure 3.5. The clear polyvinyl chloride (PVC) cylindrical flotation column has a diameter of 5 cm and a height of 100 cm, with a height-to-diameter ratio of 20.

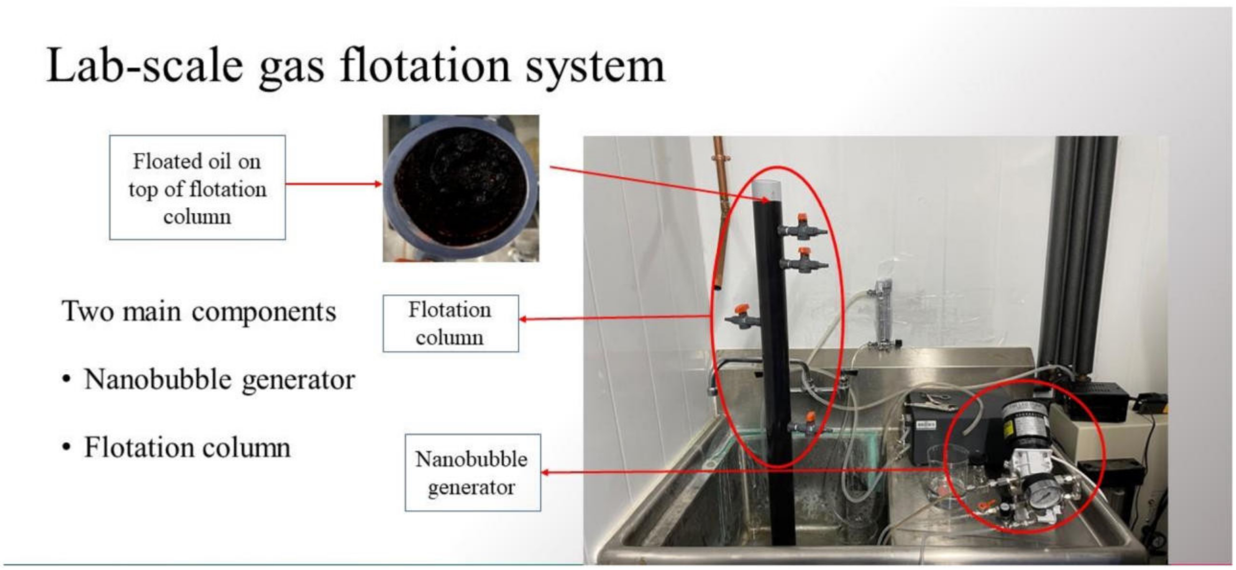


Figure 3.3 Lab scale gas flotation system showing different components.

Figure 3.4 shows the presence of NB/MB on the right and clear water without NB/MB on the left.

Description of flotation column

A: Has height of 80 cm, Internal Diameter of 8 cm and External Diameter of 8.89 cm (**Height: Diameter = 10**)

B: Has height of 100 cm, Internal Diameter of 5 cm and External Diameter of 6 cm (**Height: Diameter = 20)**

C: Has height of 150 cm, Internal Diameter of 5 cm and External Diameter of 6 cm (**Height: Diameter = 30)**

Figure 3.5 Images and specifications of the flotation column used for the experiment.

3.5 Experimental Design

The experiments were designed using Design Expert 13.0 (Stat-Ease Inc., Minneapolis, MN, USA). Response Surface Methodology (RSM) with Central Composite Design (CCD) was used to investigate the impacts of different factors, including oil concentration (ppm), weathering (weight loss %), and gravity settling time (minutes). These experimental parameters are selected based on the preliminary experiments, past studies and considering the actual oil spill response scenarios.

Oil Concentration is an essential experimental factor for this research on separating oil and water using gas flotation because it affects the efficiency of the separation process (Saththasivam et al., 2016). At low oil concentrations, the efficiency of the gas flotation process is reduced because there are fewer oil droplets to attach to the bubbles, resulting in less buoyancy and a slower separation rate. At high oil concentrations, the efficiency of the gas flotation process is increased because more oil droplets attach to the bubbles, resulting in more buoyancy and a faster separation rate (Saththasivam, Loganathan & Sarp, 2016). However, the literature has also documented that the gas NB/MB gas flotation is only suitable for treating oily wastewater with oil concentrations less than 1000 ppm (Rawlins, 2009; Wang et al., 2010; Rasouli et al., 2021). As this technology is used explicitly for marine oil spill research and the oil concentration of wastewater generated after an oil spill varies significantly, a more comprehensive range of oil concentrations has been selected. Different factors affect the typical oil concentration in wastewater after an oil spill, including oil spill response time. A longer response time can affect the concentration of collected oily wastewater because the oil can spread and disperse, resulting in a lower concentration of oily wastewater. Additionally, if the response is delayed, natural processes such as evaporation and biodegradation may occur, reducing the concentration of oily material in the collected wastewater (Guo & Wang, 2009).

Similarly, the flotation time of 0- 40 minutes has been selected based on the preliminary experiments and past studies. Most researchers have mentioned their studies' 10–30 min flotation time range (Etchepare et al., 2017a; e Silva et al., 2018). However, it was found that the optimum time for separating the Cold Lake Dilbit emulsion from the water was around 38 minutes, based on the preliminary experiment. Thus, that range has been selected for the study.

Likewise, gravity settling time enhances NB/MB gas flotation efficiency by effectively removing larger oil droplets and free oil, allowing them to float to the surface. During the actual oil spill response operations, the spilled oil with water is pumped and collected in the containers fitted inside the barges. NB/MB gas flotation technology could be applied in those containers as an on-site treatment technology instead of transporting the oily wastewater to the shore for treatment or disposal. Thus, before beginning the NB/MB gas flotation process, the gravity setting process can introduced once the containers inside the barges are filled with oily wastewater. The application of gravity settling is believed to enhance the oil/water separation process by floating the free oil to the top of the container. The floated free oil on the top of the container could be skimmed off, and the bottom oil/water emulsion could be treated with the NB/MB gas flotation. This approach aims to determine whether allowing the oily wastewater to undergo gravity separation will result in improved performance and efficiency of NB/MB technology in cleaning up oil spills.

Response surface methodology (RSM) is an effective statistical tool for optimizing various operational factors and reducing experimental runs (Bashir et al., 2015). A three-factor, three-level central composite design (CCD) was selected to design the experiment. The coded levels of the different factors and their corresponding values are listed in Table 3.2 below. To assess pure error, 17 experiments were conducted, including three replicates at the center point. The oil separation efficiency (Y) was the response variable for determining the flotation process's performance. Additionally, to assess the influence of flotation time on a broader level, single-factor experiments were conducted. Each experiment was repeated three times, and the average value was used for the analysis.

Table 3.2 Experimental design range and levels of independent variables

Independent Variables	**Coded Levels**			**Units**
	-1	**0**	**+1**	
Oil Concentration	200	1100	2000	ppm
Gravity Settling time	0	45	90	Minutes
Flotation Time	10	25	40	Minutes

Table 3.3 Experimental design table generated by CCD.

	Factor 1	**Factor 2**	**Factor 3**	**Response 1**	
Run	A: Oil concentration (*ppm*)	B: Flotation time *(Minutes)*	C: Gravity settling time *(Minutes)*	Residual oil in treated water (*ppm*)	Oil separation efficiency (%)
1	2000	25	0	240	88
2	1100	25	45	88	92

3	200	25	90	18	91
4	1100	25	45	99	91
5	1100	10	90	217.8	80.2
6	1100	40	90	14.3	98.7
7	2000	10	45	480	76
8	2000	25	90	100	95
9	1100	25	45	92.4	91.6
10	2000	40	45	44	97.8
11	1100	40	0	57.2	94.8
12	200	10	45	58.4	70.8
13	200	40	45	15.2	92.4
14	1100	10	0	407	63
15	1100	25	45	93.5	91.5
16	1100	25	45	110	90
17	200	25	0	38	81

Response 1 shows the results in two forms: the residual oil in treated water (ppm) and Oil separation efficiency (%). The oil/water separation efficiency (%) was calculated based on the difference between the emulsion's initial oil concentration and the wastewater's final oil concentration.

3.6 Pilot Scale Testing of NB/MB Performance

The shift from the 2-litre laboratory setup to the significantly larger 75-litre pilot-scale configuration targeted to mimic real-world scenarios involving larger quantities of oil/water. Furthermore, this transition from laboratory-scale to larger pilot-scale experiments serves multiple crucial purposes, including assessing processes' scalability, optimizing their performance, addressing safety and environmental considerations, and evaluating economic feasibility. This transition represents a critical stage in developing and validating novel technologies and processes. Pilot scale experiments were conducted in a larger reactor with a higher-capacity nanobubble generator. These experiments were part of the oil spill challenge project for stage 2, and further experiments are being conducted to compete for stage 3. The pilot scale system consists of a gas flotation column (135 cm in height and 30.2 cm in diameter) and an adsorption column (100 cm in height and 40 cm in diameter), as shown in Figure 3.6 below. The gas flotation column is connected to a NB generator. To enhance the concentration of NB/MB bubbles, a 5.0 GPM centrifugal pump was used between the column and the NB generator. The generator is also linked to a compressed air cylinder to facilitate gas bubble generation. The gas flotation column, manufactured from PVC materials, allows for visual observation of oil/water separation at varying depths. The NB/MB gas flotation column has a volume of 100 L, and the adsorption column has a volume of 125 L. Each column has three detachable sections to examine column configuration on oil recovery performance. All the system components are installed on a wheeled cart for easy transportation. The system can be operated in both batch and continuous modes. For continuous operation, the treatment capacity is designed to be 300 L/hr.

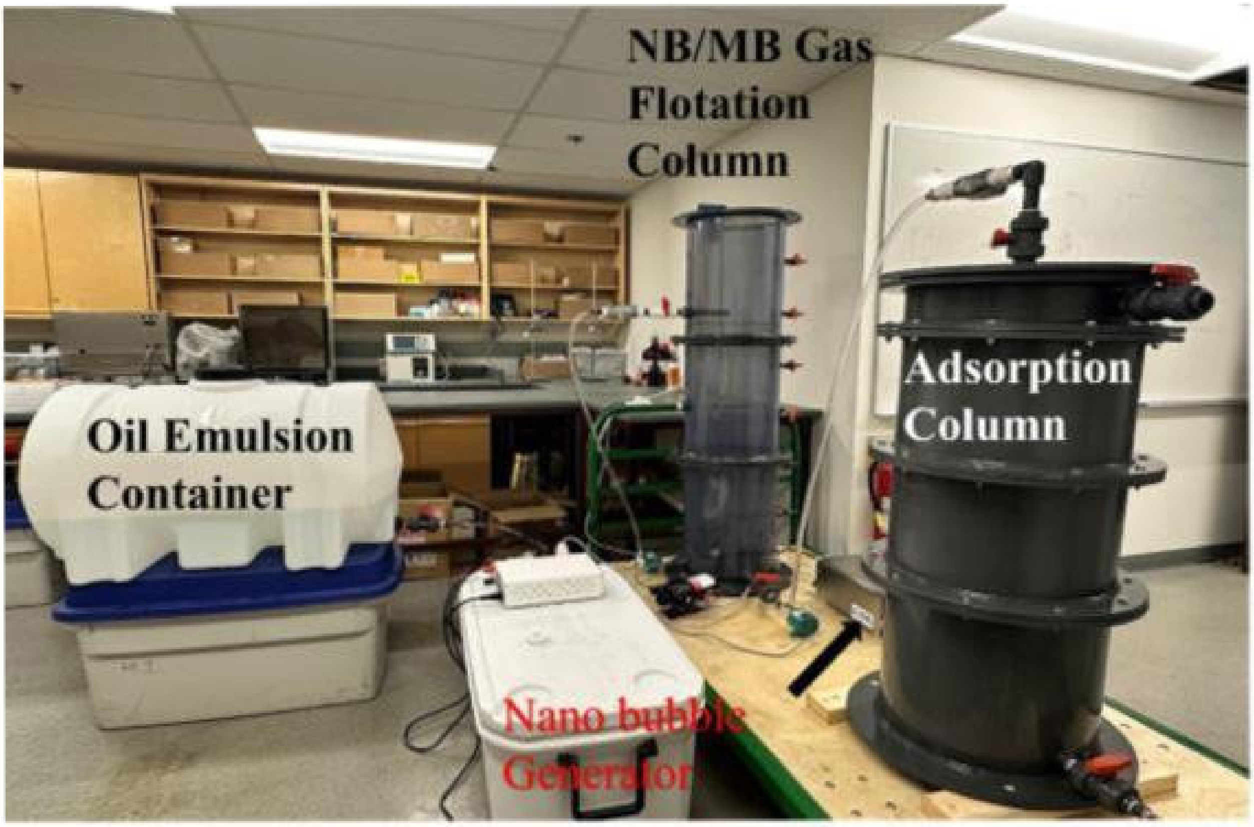
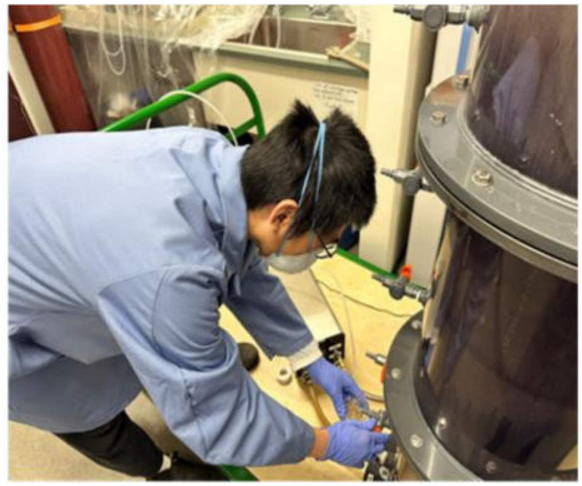


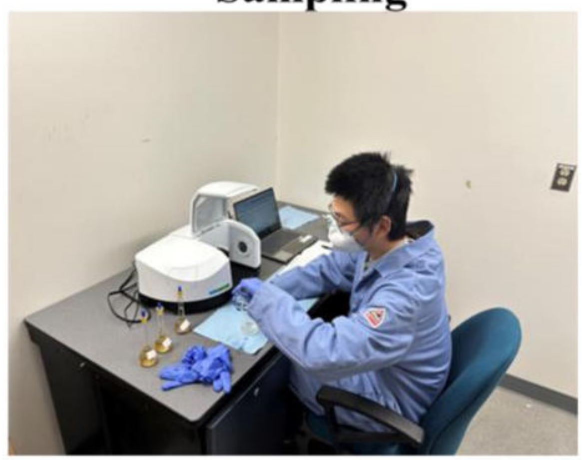
Figure 3.6 Image showing the pilot scale prototype set-up.

Assembly

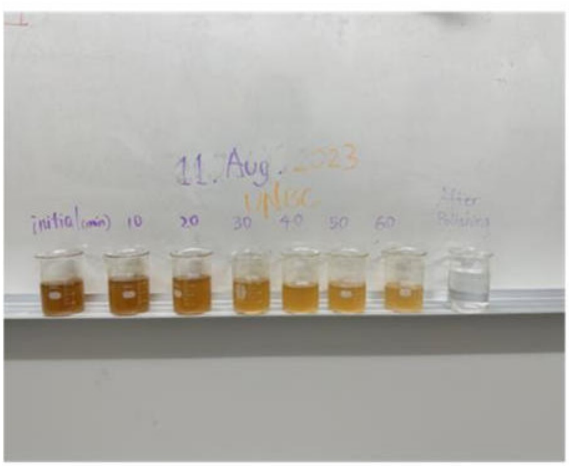


Sampling

Solvent extraction



Measurement



Visual observation

UNBC group

Figure 3.7 Image showing the different prototype testing processes and involved team members.

3.7 Oil concentration analysis

3.7.1 Oil concentration measurement using FT-IR

The oil concentration of the emulsion and treated water was measured by FTIR (Spectrum Two, PerkinElmer, USA) by absorbance measurement (Farmaki et al., 2007). Due to its low toxicity, Tetrachloroethylene was used as an extraction solvent to extract oil from water samples (Sun et al., 2021). For each sample, a 20 mL of sample was extracted and passed through the mixture of Silica gel (1g) and Sodium Sulfate (3g) following the standard ASTM D7066-04 (2017) method. Silica gel is a solid adsorbent that removes residual water or moisture in the organic solvent or the extracted mixture. Likewise, Sodium Sulfate removes the traces of water in the organic solvent or the extracted mixture, which might be present even after passing through silica gel. A pure solvent was used as a blank, and infrared spectra were obtained between 3200-2700 cm-1 wavelengths. Crude oil consists of a complex mixture of hydrocarbons such as alkanes, alkenes, aromatics, and other functional groups containing oxygen, nitrogen, sulphur, and other elements. FT-IR measures the oil concentration in the sample by absorbance measurements. When the infrared light is passed through a sample, the molecules in the sample absorb specific wavelengths of light and vibrate upon absorbing the infrared light. Oil concentration in the sample is measured based on the intensity of vibrations by those functional groups. FTIR methods measure the absorbance of the carbon and hydrogen bonds (C–H bond), i.e. the stretching of aliphatic CH2 groups at 2930 cm–1, of CH3 groups at 2960 cm–1 and of aromatic C–H bonds at 3010– 3100 cm–1 (Farmaki et al., 2007). The oil/water separation efficiency was calculated based on the difference between the initial oil concentration in the emulsion and the final oil concentration in the wastewater by Eq. (3.1):

$$Y = (C_0 - C_r)/C_0 \times 100\% \quad (3.1)$$

Where Y is the oil separation efficiency (%), C_0 is the initial oil concentration (mg/L), and C_r is the residual oil concentration (mg/L) in the treated water.

3.7.2 Oil concentration measurement using GC-FID

Most of the samples for oil concentration measurement in the emulsion and treated water were measured using the FT-IR located in our laboratory. However, a few samples were sent to the NALS laboratory at UNBC to ensure the accuracy and reliability of the results. Gas Chromatography with Flame Ionization Detection (GC/FID) is a widely employed technique for measuring Extractable Petroleum Hydrocarbons (EPH) in water (Yang et al., 2013). The FID detects hydrocarbons based on their combustion, producing electrical signals proportional to their concentration. The concentration of EPH in the water sample can be accurately determined by comparing the resulting signals to standard calibration curves (Santos & Schug, 2017). This method offers sensitivity, selectivity, and reliability, making it an indispensable tool for environmental monitoring, pollution assessment, and regulatory compliance in various industries.

Table 3.4 Displays the oil concentration measurements obtained through FT-IR and GC analysis.

Experimental Run	*Oil concentration (mg/L) in emulsion measured by FT-IR)*	*Oil concentration (mg/L) in treated water measured by FT-IR*	*Oil concentration (mg/L) in emulsion measured by GC-FID*	*Oil concentration (mg/L) in treated water measured by GC-FID*
Run ***#10***	1100	14.3	388	44
Run ***#15***	1100	92.4	320	58
Run ***#12***	200	58.8	274	65

Thus, in this study, the oil concentrations of the three selected results, as displayed in Table 3.4, measured by FT-IR, were compared with the GC/FID to investigate any discrepancies in concentration measurements. The FT-IR is a quick and relatively inexpensive method to measure the oil concentration; however, the method's precision and reproducibility are relatively low (Mousa et al., 2022). Unlike FT-IR, the GC-FID method is relatively expensive and time-consuming, but it offers several advantages compared to FT-IR. Some advantages of using GC-FID include being more selective of hydrocarbons, having better precision and reproducibility, and providing chemical fingerprint information (Douglas et al., 2015). The measurements produced notably contrary results. The initial oil concentrations measured using FT-IR were considerably higher than those determined by GC-FID.

Nevertheless, the final TPH levels in the treated water remained relatively consistent. Some researchers have suggested that both FT-IR and GC-FID can accurately quantify TPH, regardless of the contamination levels (Paíga et al., 2012). Nonetheless, substantial discrepancies were observed in this study. Therefore, it is recommended that additional studies with more extensive sample measurements be conducted to investigate the underlying reasons for the significant measurement variations.

Chapter 4 Results and Discussion

4.1 Size distribution of NB and oil droplets in emulsion

The Nanobubbles and the emulsion samples were sent to Memorial University of Newfoundland to measure the size of nanobubbles in water and oil droplets in emulsion. The sizes of NB were determined using NanoSight NS500, a device by Malvern Instruments Ltd., which employs nanoparticle tracking analysis (NTA) technology. Although both NB/MB samples were sent to measure the size, the graph only shows the size distribution of NB, and this is because of sample holding time. NB is remarkably stable for up to three months in an aqueous solution without significantly changing bubble concentration and mean size (Michailidi et al., 2020).

Likewise, the emulsion's oil droplet size was measured using the Laser In-Situ Scattering and Transmissometry (LISST). Figure 4.1 below shows the average size of nanobubbles.

Table 4.1 Table showing the properties of Nanobubbles in samples.

Results Mean	***116 nm***
Mode	110 nm
SD	68 nm
D10	56 nm
D50	101 nm
D90	228 nm
Concentration	0.53 E8 particles/ml

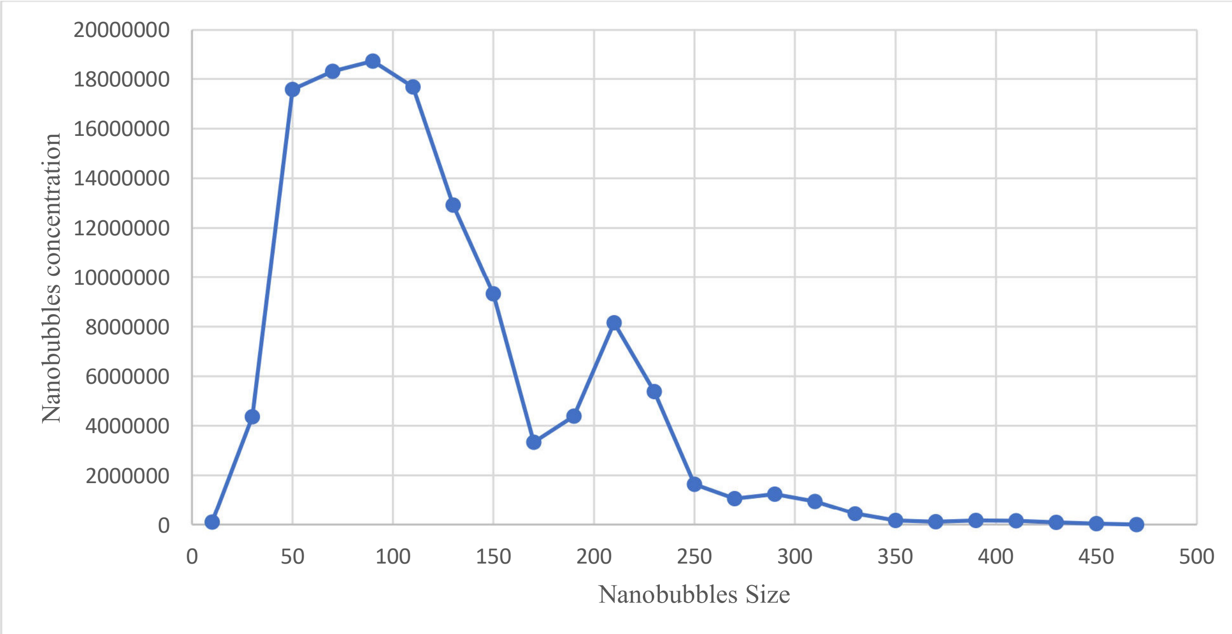


Figure 4.1 Graph displaying the size distribution of nanobubbles in the samples.

Likewise, the average oil droplet size of the emulsion was reported to be Mean: 326.25 µm with a standard deviation of 147.86.

4.2 Impact of reactor configuration NB/MB performance

Figure 4.2 displays the results showing the Impact of reactor configuration on NB/MB performance. The results indicated a slight effect of reactor configuration on system performance, with gradual improvement observed as the height-to-diameter ratio increased. However, it is worth noting that the difference in impact between the height-to-diameter ratios of 20 and 30 is very minimal. Consequently, the reactor with a height-to-diameter ratio of 20 was chosen for the remaining RSM experiments. Additionally, a reactor with a height-to-diameter ratio of 20 is more stable for fitting in barges and containers, whereas a reactor with a height-to-diameter ratio of 30 is tall and may not be stable in ocean waves.

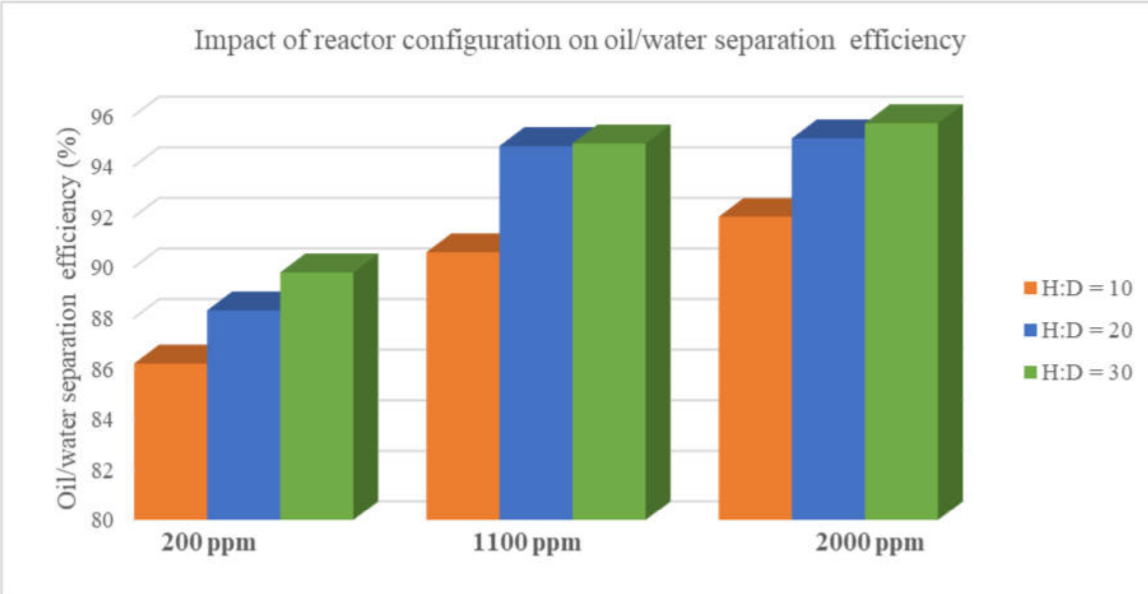


Figure 4.2 Bar graph showing the Impact of reactor configuration on NB/MB performance.

4.3 Regression model generation and statistical analysis

Table 4.2 Displays the actual and predicted values for oil/water separation.

Run Order	Actual Value	Predicted Value
1	88.00	87.44
2	92.00	91.22
3	91.00	91.56
4	91.00	91.22
5	80.20	80.55
6	98.70	98.32
7	76.00	75.19
8	95.00	95.46

9	91.60	91.22
10	97.80	97.19
11	94.80	94.45
12	70.80	69.89
13	92.40	93.21
14	63.00	64.37
15	91.50	91.22
16	90.00	91.22
17	81.00	80.54

Table 4.3 The ANOVA results of the regression model

Source	***Sum of Squares***	***Mean Square***	***F-value***	***p-value***	
Model	1545.20	171.69	115.11	< 0.0001	significant
A-Oil Concentration	58.32	58.32	39.10	0.0004	
B-Flotation time	1097.46	1097.46	735.81	< 0.0001	
C-Gravity Settling time	181.45	181.45	121.66	< 0.0001	
AB	0.0100	0.0100	0.0067	0.9370	
AC	2.25	2.25	1.51	0.2591	
BC	44.22	44.22	29.65	0.0010	
A^2	6.04	6.04	4.05	0.0841	

B^2	140.30	140.30	94.07	< 0.0001	
C^2	6.82	6.82	4.57	0.0698	
Residual	10.44	1.49			
Lack of Fit	8.07	2.69	4.55	0.0888	not significant
Pure Error	2.37	0.5920			
Cor Total	1555.64				

Table 4.4 Fit statistics

Fit Statistics			
Std. Dev.	1.22	R^2	0.9933
Mean	87.34	Adjusted R^2	0.9847
C.V. %	1.40	Predicted R^2	0.9146
		Adeq Precision	36.6591

The Predicted R^2 of 0.9146 is in reasonable agreement with the Adjusted R^2 of 0.9847; i.e. the difference is less than 0.2. Adeq Precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. The model ratio of 36.659 indicates an adequate signal. This model can be used to navigate the design space.

Oil/water separation efficiency(Y) = +91.22 + +2.70 A +11.71 B + 4.76 C + 0.0500 AC - 0.7500 – 3.32 BC - 1.20 A^2 -5.77 B^2 -1.27 C^2

Where Y is the oil separation efficiency (%), A, B, and C represent initial oil concentration (200–2000 mg/L), flotation time (10–40 min), and gravity settling time (0–90 min), respectively.

The model's significance and the impact of each parameter were validated using ANOVA, and you can find the corresponding results in Table 4.3. A low p-value of 0.0001 and a high F-value of 115.11 indicated that the created model is highly significant and effectively describes the efficiency of oil separation. Furthermore, the lack of fit was found to be insignificant, with a probability value of 0.0888, indicating that our model fits the experimental data well and is accurate enough for making predictions. Additionally, the signal-to-noise ratio (adequate precision) exceeded the desirable threshold (>4), affirming that our model possesses ample signal strength and predictive capability. Moreover, the coefficient of determination (R2) reached an impressive 0.9933, while adjusted R2 and predicted R2 were 0.9847 and 0.9146, respectively. These high and closely aligned R2 values suggest a strong fit of the regression model, indicating a high level of agreement between the experimental data and the predicted outcomes.

4.4 Analyzing the Influence of Independent Parameters on Oil Separation Efficiency

4.4.1 Impact of initial oil concentration

Figure 4.3 illustrates that increasing the initial oil concentration in the oily wastewater positively impacted oil separation efficiency. The data presented in the table supports this observation, where raising the initial oil concentration from 200 mg/L to 2000 mg/L resulted in a 7% enhancement of the oil separation efficiency from 81% to 88% (experimental runs #1 and #17). This trend was further confirmed in experimental runs #10 and #13, where increasing the oil concentration from 200 mg/L to 2000 mg/L led to an increase in 5.4% oil/water separation efficiency from 92.4% to 98.7%.

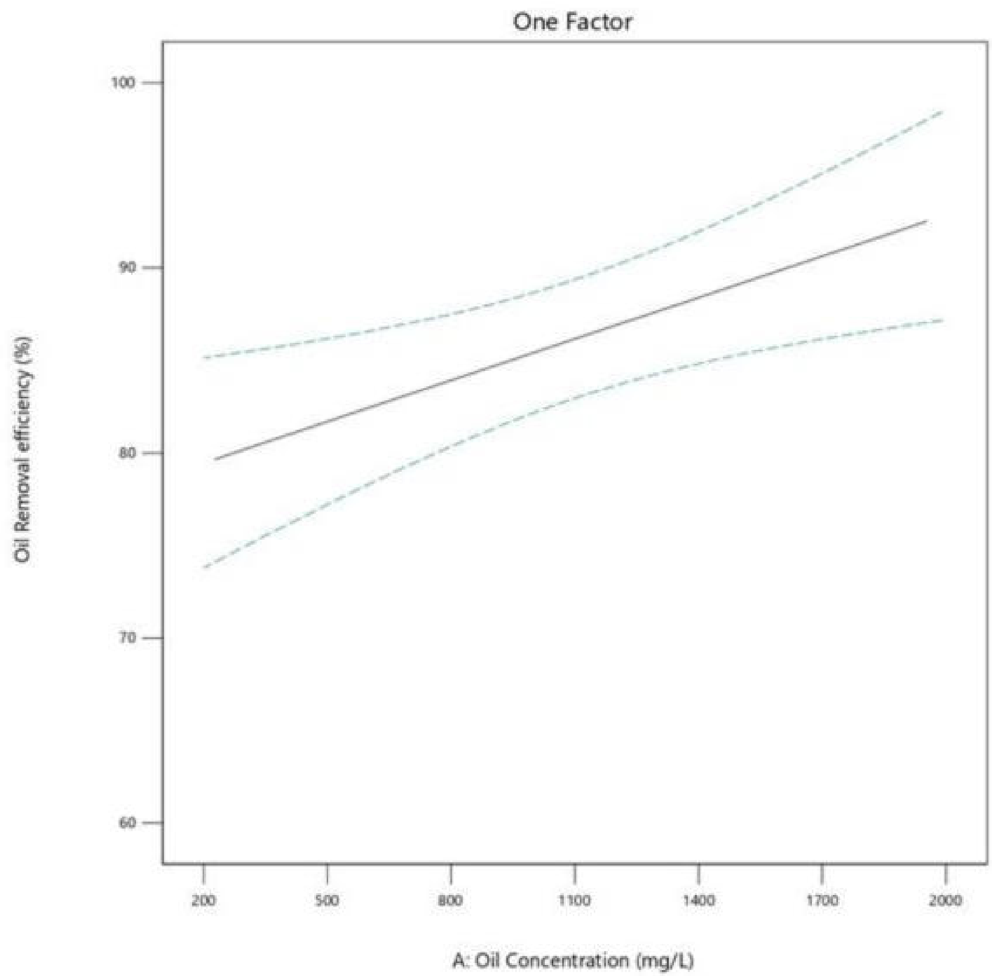


Figure 4.3 Predicted effects of oil concentration on oil/water separation efficiency.

These findings demonstrate that elevating the initial oil concentration generally leads to higher oil separation efficiency. This is because, at higher oil concentrations, the oil droplets become denser and more uniformly distributed, making it easier for the bubble-oil aggregates to capture more oil droplets. Consequently, the overall separation efficiency is significantly enhanced.

4.4.2 Impact of Gravity Settling Time

Figure 4.4 demonstrates that allowing wastewater to undergo gravity settling before gas flotation significantly enhances oil-water separation efficiency. For instance, in experimental runs #1 and

#8, when the oily wastewater is treated directly with NB/MB gas flotation (without gravity settling time), the oil/water separation efficiency is 88%. However, when the same wastewater is allowed to settle by gravity for 90 minutes before gas flotation, the efficiency increases to 95%. Similarly, in runs #11 and #6, increasing the gravity settling time from 0 to 90 minutes improves efficiency from 94.8% to 97.8%. These findings conclude that gravity settling time is crucial in enhancing gas flotation efficiency by removing larger and denser particles from the water before flotation.

In summary, the data indicate that incorporating gravity settling before gas flotation helps achieve a more effective separation process by eliminating larger and denser particles, improving overall oil-water separation efficiency.

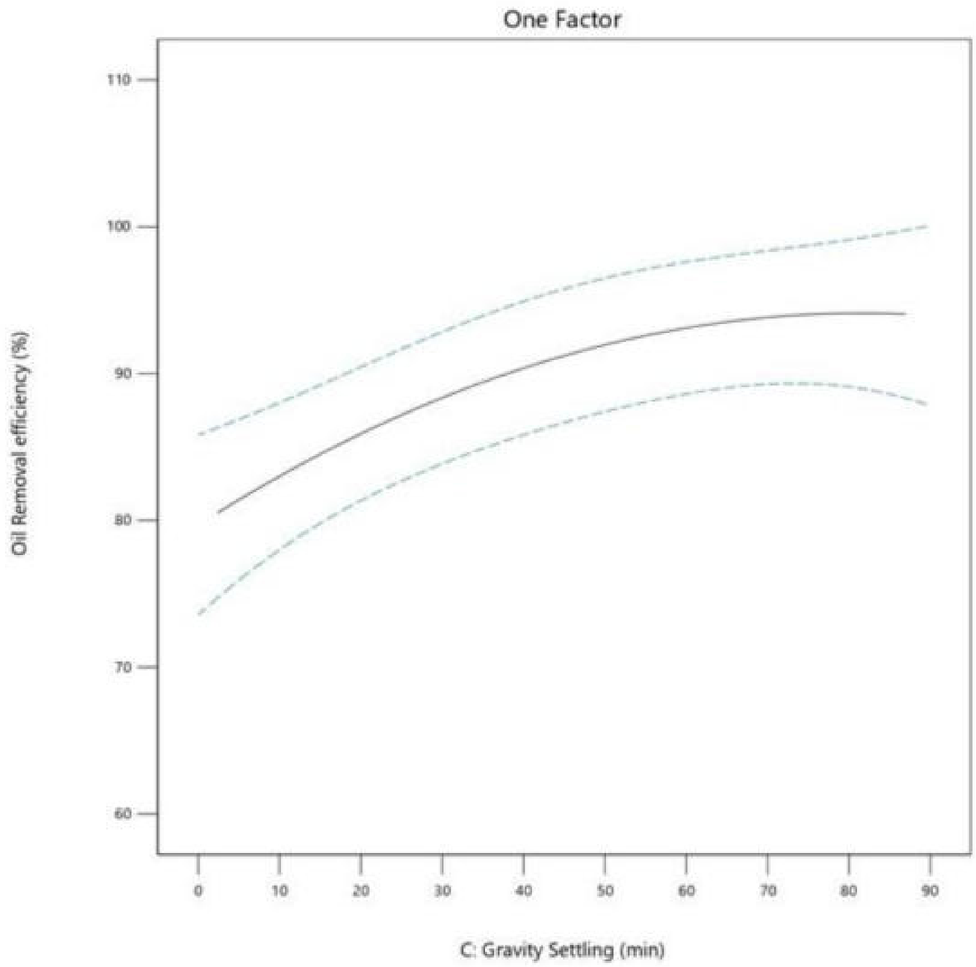


Figure 4.4 Predicted effects of gravity settling time on oil/water separation efficiency.

4.4.3 Impact of Flotation Time

The flotation time was the most critical parameter affecting oil-water separation efficiency in the experiment. Increasing the flotation time led to a significant improvement in oil-water separation efficiency. This can be observed in the single-factor graph, where increasing the flotation time from 10 minutes to 40 minutes (Experimental Run #11 and #14) resulted in a remarkable increase in oil/water separation efficiency of 31.8% from 63% to 94.8%. Consequently, the residual oil concentration in treated water decreased substantially from 407 mg/L to 60.5 mg/L.

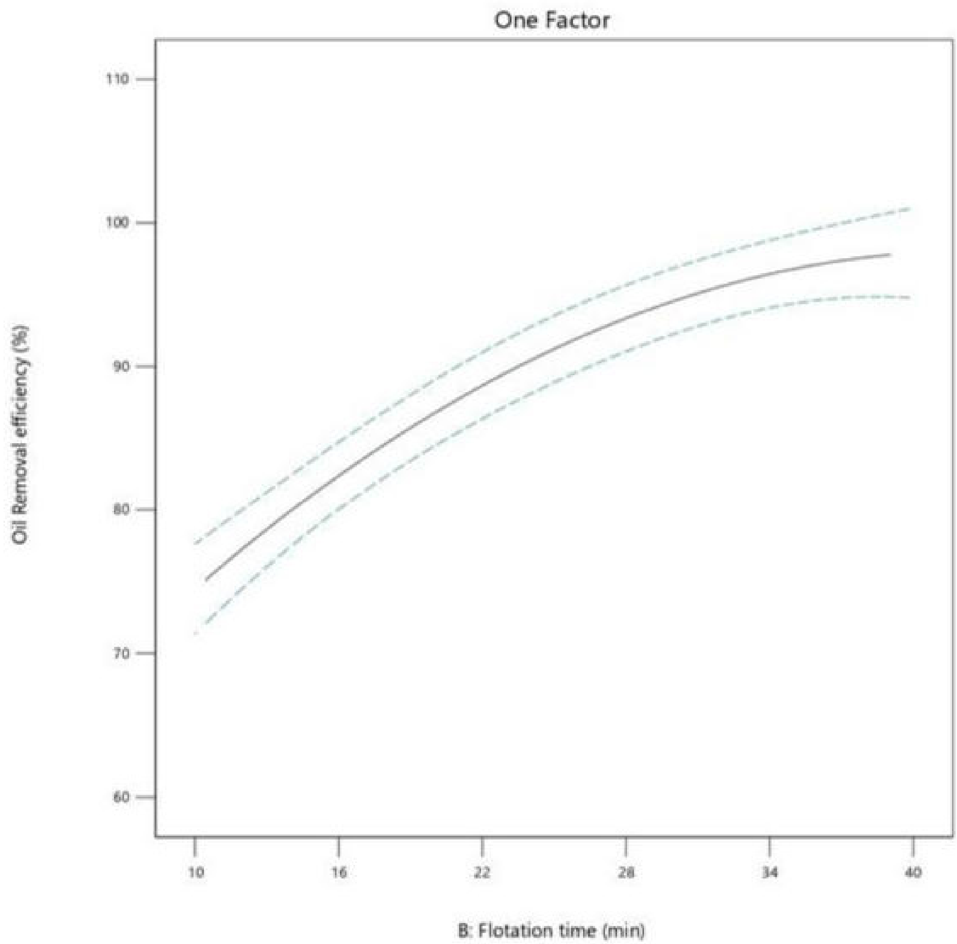


Figure 4.5 Predicted effects of flotation time on oil/water separation efficiency.

Additional single-factor experiments were conducted to investigate further the impact of flotation time over a broader range. These experiments were conducted using an oil concentration of 1100 mg/L, a gravity settling time of 0 minutes, and the flotation time varied from 0 to 60 minutes.

Samples were collected at 10-minute intervals, and the oil concentration in the treated water was measured. The results indicated that the increase in flotation time positively affected oil-water separation efficiency for up to 20 minutes, beyond which the separation rate was significantly reduced. This trend is depicted in the graph below. Interestingly, after the 20-minute mark, the oil/water separation efficiency continued to increase with flotation time until reaching 35 minutes; however, the oil/water separation efficiency rate was much slower. Beyond 35 minutes, there was no significant improvement in oil-water separation efficiency, indicating that extending the flotation time beyond this point would not significantly increase oil/water separation efficiency.

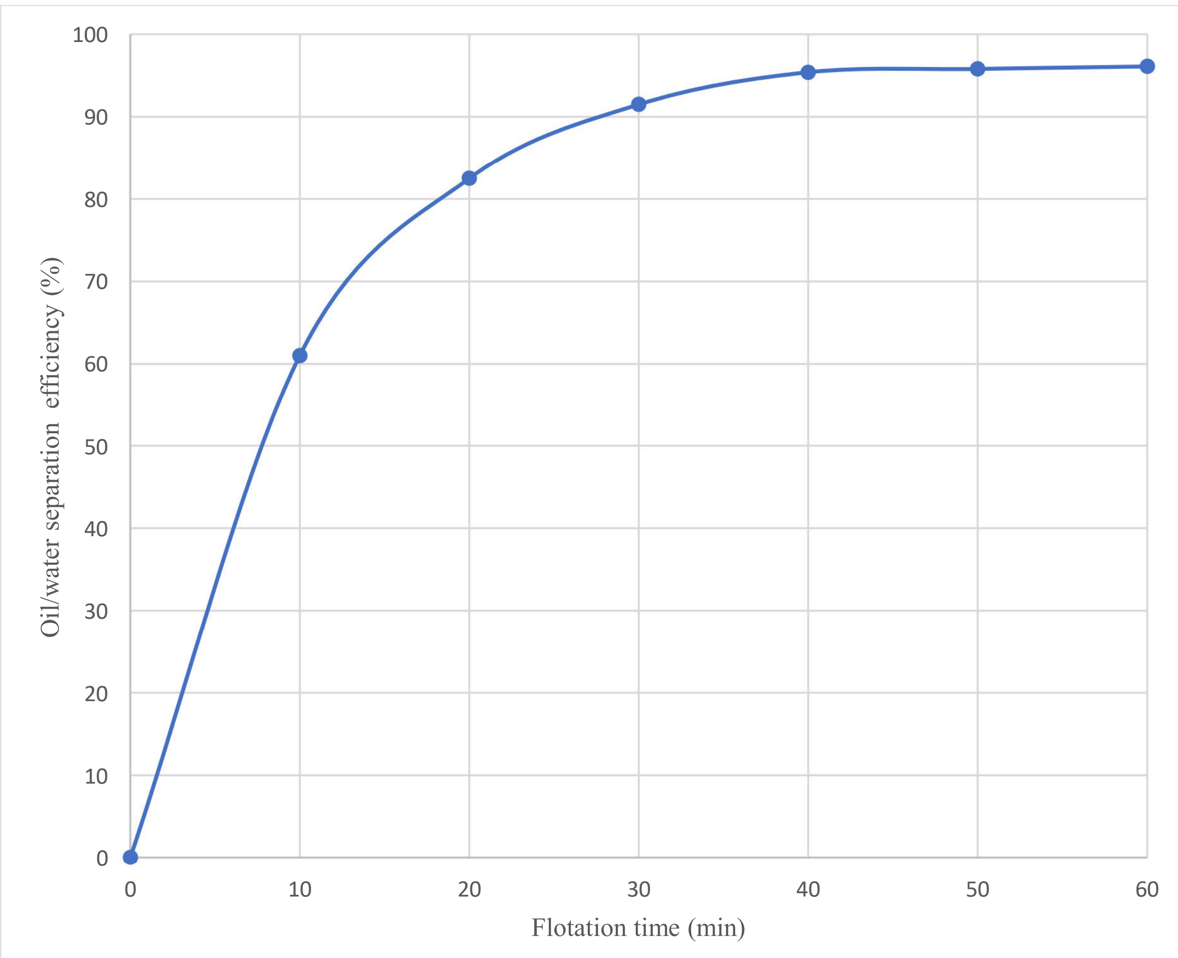


Figure 4.6 Graph showing the impact of flotation time on oil/water separation efficiency.

4.5 Interaction of parameters

The study investigated the interaction effects of experimental factors on the efficiency of gas flotation using NB/MB. Figure 4.7 shows the interaction between flotation time and oil concentration, and it can be observed from the graph that increasing the flotation time led to improved oil separation efficiency. The oil/water separation efficiency gradually increases with the oil concentration and flotation time. This could be because the greater flotation time allows gas bubbles and oil droplets to attach and float to the surface. Additionally, when the emulsion is prepared with a low oil concentration, it generates stable small oil droplets that are finely dispersed. These small droplets pose a more significant challenge for separation using NB/MB compared to emulsions prepared with higher oil concentrations. In contrast, emulsions with higher oil concentrations have relatively larger and unstable oil droplets, making them easier to separate through the gas flotation (Dickhout et al., 2017). However, with the lower oil concentration in the emulsion, the individual oil droplets are relatively small and finely dispersed throughout the water, resulting in slower and less efficient separation of oil from water.

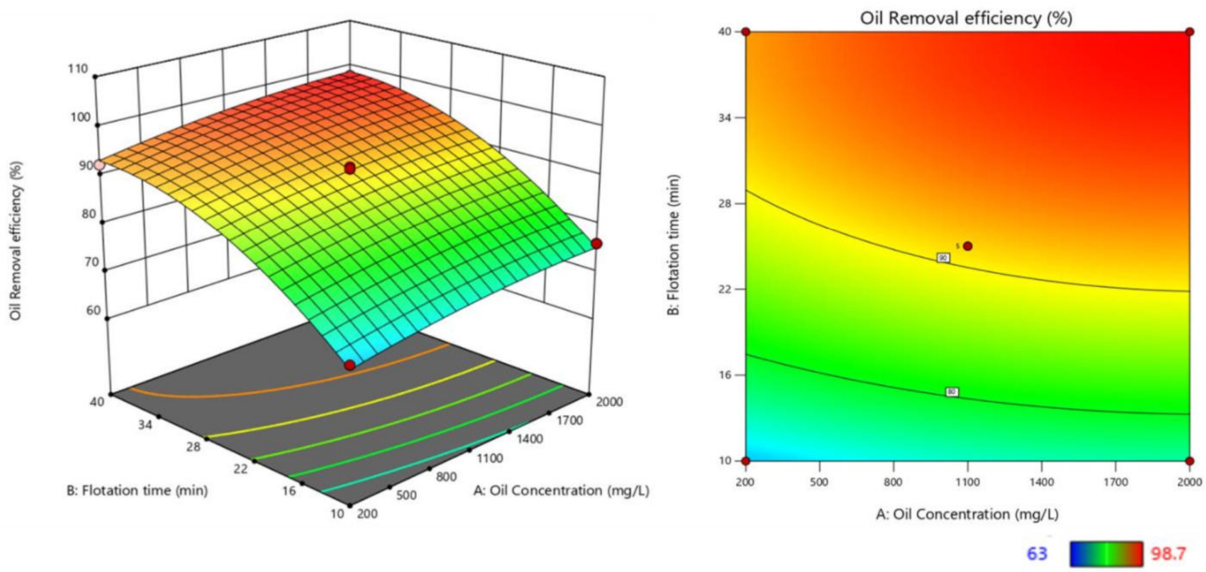


Figure 4.7 response surface graph showing the interaction between oil concentration and flotation time.

Figure 4.8 shows the interactive relationship between gravity settling time and flotation time, explicitly focusing on oil/water separation efficiency. Increasing flotation time and gravity settling time significantly increased the oil/water separation efficiency. However, approximately after 40 minutes of gravity settling and 35 minutes of flotation time, oil/water separation efficiency levels off, showing slight improvement with further increases in gravity settling and flotation time. Furthermore, with more extended gravity settling time, even a relatively short flotation time of 20 minutes is sufficient to achieve higher oil/water separation efficiency of over 90%. On the other hand, with shorter gravity settling durations, longer flotation times are required to observe similar results (Liu et al., 2021).

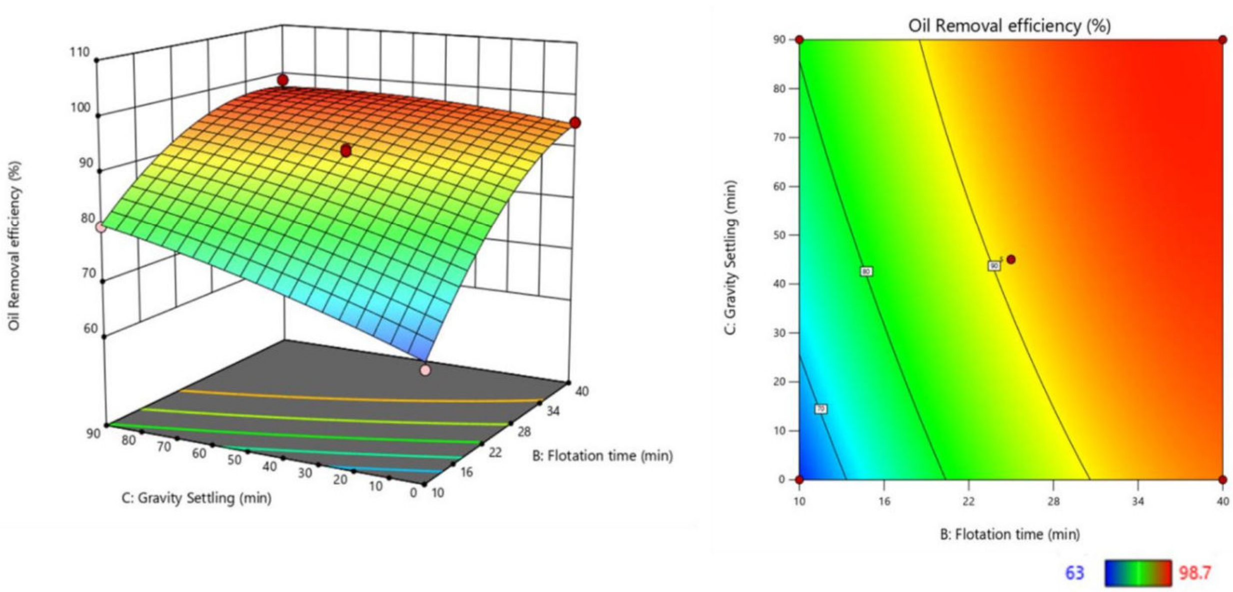


Figure 4.8 response surface graph shows the interaction between flotation and gravity settling time.

Figure 4.9 shows the interaction between the oil concentration and the gravity separation. Increasing oil concentration and gravity separation increases the efficiency of oil/water separation. This could be because when the emulsion contains a high oil concentration, the oil droplets are larger and more numerous, leading to increased coalescence and the formation of bigger oil masses that could be separated with a longer duration of gravity separation. These larger oil droplets rise more quickly during gravity separation, resulting in faster and more effective separation and higher oil/water separation efficiency. However, When the oil concentration in the emulsion is low, the individual oil droplets are relatively small and finely dispersed throughout the water, which takes a relatively longer time to rise to the water's surface and leads to less efficient oil separation from water.

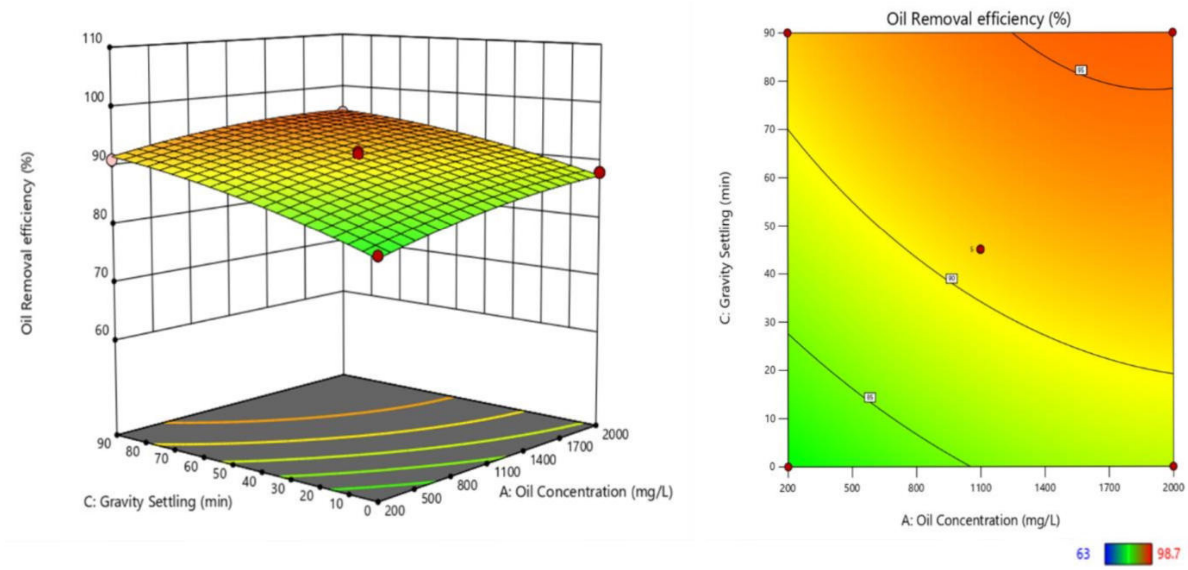


Figure 4.9 Response surface graph showing the interaction between oil concentration and gravity settling time.

4.6 Optimization and validation of optimized results

To optimize the operational conditions for the RSM experiments, Design Expert software version 13 was selected. Two experimental runs with the highest and second highest oil separation efficiency were selected to identify the optimum operational conditions while keeping three independent variables within a predefined range. Using an empirical model, it was found that the maximum oil separation efficiency of 98.8% was achieved by maintaining an initial oil concentration of 1995 mg/L, a flotation time of 38 minutes, and a gravity settling time of 45 minutes. Under these specific conditions, the model's desirability index reached 1. Three verification experiments were conducted under the projected optimal conditions to authenticate the reliability of the empirical model and the outcomes of our optimization efforts. Table 4.5 shows the average oil separation efficiency of 97.4%, exhibiting a narrow standard deviation of 1.2. This outcome closely reflected the projected value of 98.7%, establishing a solid agreement.

Table 4.5 Validation results with the actual and the predicted efficiency

Run	Actual Efficiency (%)	Predicted Efficiency (%)	Error (%)
1	97.2	98.7	-1.5
2	96.7	98.7	-2
3	98.2	98.7	-0.5
Mean Efficiency	97.4	Standard deviation	1.2

4.7 Control experiments

The control experiments aimed to examine the impact of oil droplet buoyancy on oil separation efficiency in prepared oily wastewater. Three separate control experiments were conducted under specific optimal conditions obtained through RSM. These experiments allowed the prepared oily wastewater to undergo gravity separation in the flotation column without any flotation process. The duration of gravity separation was also extended from 40 to 130 minutes. Throughout these control experiments, the initial oil concentration was kept constant. It can be observed from Figure 4.9 below that after 40 minutes of gravity separation, the oil separation efficiency was 37.4%, and the oil separation efficiency reached 74.3% after 130 Minutes of gravity separation. However, after 40 min of gas flotation, the oil separation efficiency was significantly increased to 98.7%, indicating that applying MBs and NB can significantly assist the separation of Cold Lake Dilbit in the flotation system.

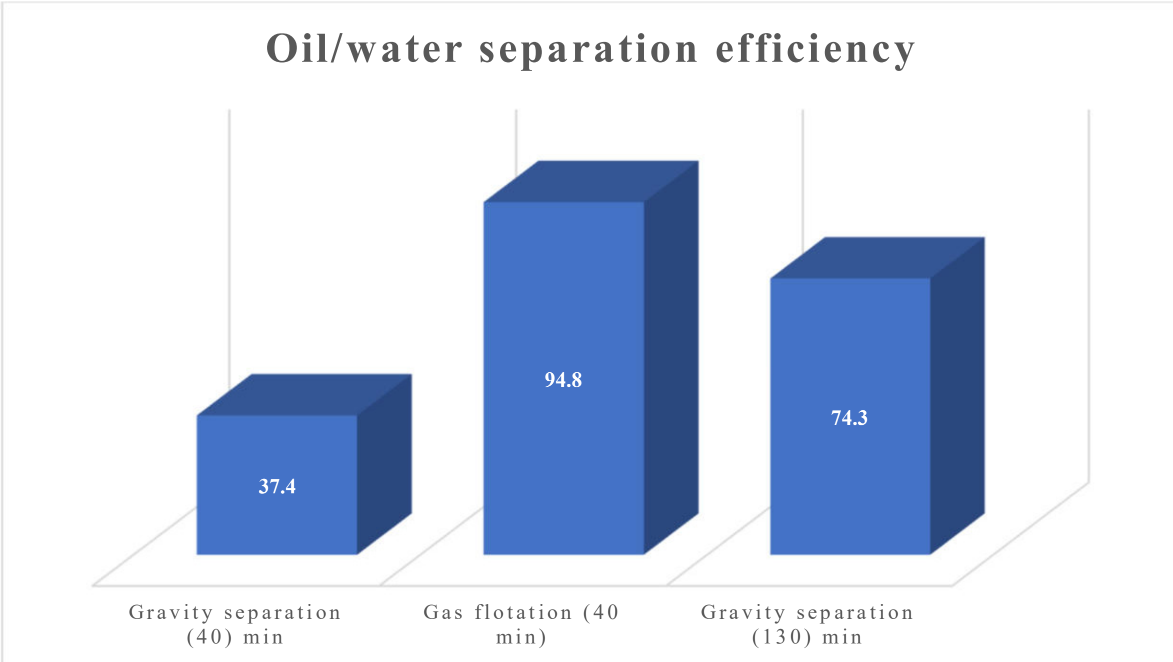


Figure 4.10 Comparison of gravity separation with gas flotation methods.

4.8 Effect of oil condition on oil separation efficiency

In addition to the Response Surface Methodology (RSM), a separate set of experiments was conducted to investigate the impact of oil weathering on the performance of NB/MB gas flotation efficiency. The experiment involved using 1100 mg/L oil and gas flotation for 40 minutes. Both fresh and weathered oil at 2%, 5%, and 10% mass loss were used for the experiment. The objective was to study how different levels of oil weathering affect the oil separation efficiency using MB and NB gas flotation. The results in Figure 4.11 indicate no significant difference in oil separation efficiency between the oily wastewater prepared with fresh oil and those prepared with weathered oil.

After 40 minutes of gas flotation, the oil separation efficiency for fresh oil-contaminated wastewater was 94.8%. In comparison, the oil separation efficiency reached 95.8% for the wastewater containing weathered oil after the exact duration of gas flotation. These findings suggest that gas flotation with MBs and NB effectively separated fresh and weathered crude oil.

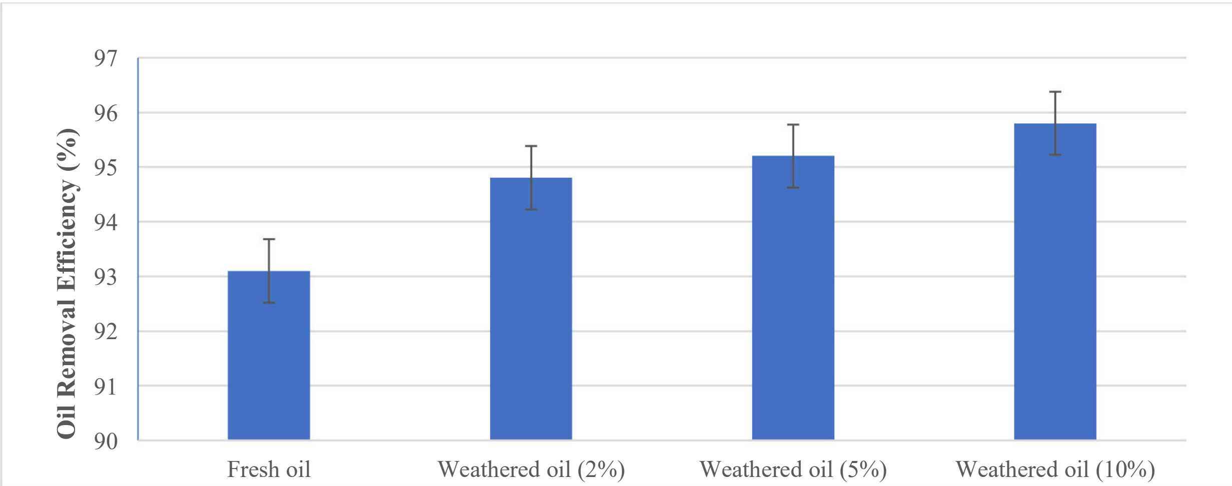


Figure 4.11 Graph showing the impact of oil weathering on NB/MB performance.

4.9 Pilot Scale Testing of NB/MB Performance

These pilot-scale experiments validate the effectiveness of the lab-scale NB/MB system, showcasing its ability to rapidly and efficiently separate oil from oil/water emulsions while minimizing environmental impacts. In our laboratory column experiments utilizing a 2-litre oil/water emulsion, we observed an oil/water separation efficiency of 98.7% following 1 hour of NB/MB flotation treatment. Likewise, when a similar experiment was conducted at the pilot scale, NB/MB gas flotation exhibited a remarkable oil/water separation efficiency of 92% within one hour of separation. Compared to the baseline technology, gravity separation only achieved a separation efficiency of 4.62% over 1 hour. Similarly, when combining NB/MB gas flotation and adsorption, nearly 100% oil/water separation was achieved, whereas gravity separation yielded a mere 4.62%. Thus, the results from this pilot-scale testing demonstrate a substantial performance improvement compared to the baseline and offer a timely on-site oil/water separation, ultimately reducing the costs of transporting oil/water emulsions back to shore for processing/treatment.

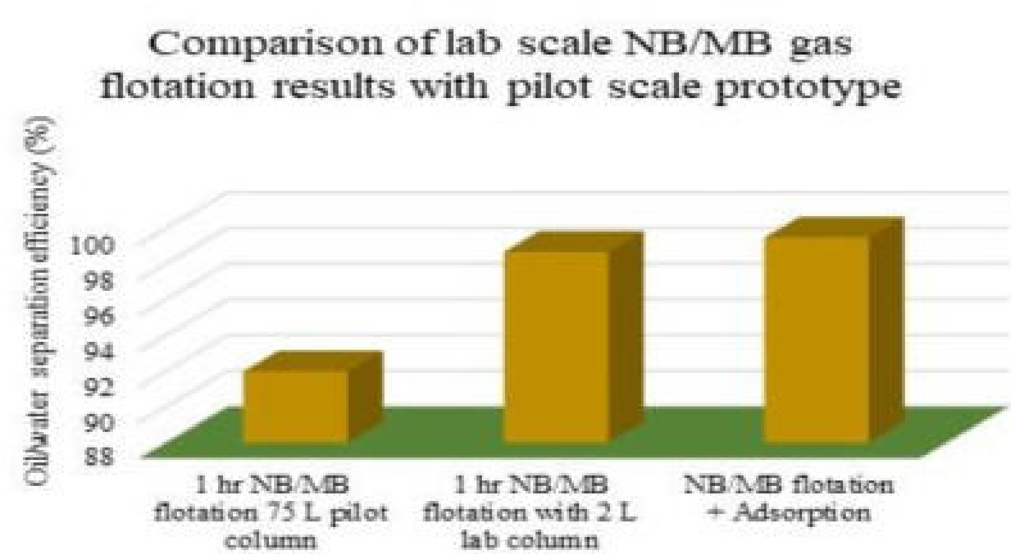


Figure 4.12 Comparison of lab results with pilot scale prototype.

Chapter 5 Conclusions

5.1 Research summary

This study experimented on the effectiveness of MB and NB gas flotation in separating dispersed crude oil droplets from oily wastewater. The RSM design examined different independent variables, such as initial oil concentrations, flotation times, and gravity settling time, to explore their effects on oil separation. Likewise, different sets of experiments were also conducted to investigate the impact of reactor configuration and oil weathering on the MB/NB gas flotation performance. Moreover, pilot-scale experiments were also conducted to validate the effectiveness of the lab-scale NB/MB gas flotation system. The significant findings of this study are as follows:

(1) All three tested parameters were positively correlated with oil separation efficiency, and the influential effects were ranked as initial oil concentration (A) > flotation time (B) > gravity settling (C). A higher oil concentration in the wastewater leads to increased oil/water separation efficiency. This could be attributed to increased collision probability between oil droplets and gas bubbles. Likewise, the increased flotation time also significantly improved the system's effectiveness in separating the oil from the water. Moreover, it was also found from this study that gravity settling of oily wastewater before the gas flotation enhanced the oil separation efficiency. This could be because the gravity setting helped the larger particles to float to the surface and improved overall oil-water separation efficiency.

(2) The highest oil/water separation efficiency was observed under specific conditions of oil concentration of 1995 mg/L, a flotation time of 38 minutes, and 45 minutes of gravity separation. The results indicate that as the oil concentration, flotation time and gravity settling time increase, there is a gradual improvement in oil separation efficiency. This enhancement is linked to a more substantial difference between the initial oil concentration in the emulsion and the final oil

concentration when higher oil concentrations are used, leading to a higher oil separation. However, even with lower oil concentrations, although the percentage of oil separation is relatively lower, the treated water still exhibits a significantly reduced oil concentration, as shown in Table 3.3.

(3) NB/MB gas flotation outstandingly improved oil separation efficiency compared to gravity separation. After 40 minutes of gravity separation, the oil separation efficiency was 37.4%; however, with 40 minutes of gas flotation, separation efficiency was significantly increased to 98.7%.

(4) MBs/NB gas flotation effectively separates fresh and weathered crude oil from oily wastewater, and the separation efficiency differences between fresh and weathered oil were negligible. Thus, it can be used to treat both fresh and weathered oil spills.

(5) The pilot-scale experiments validated the effectiveness of using gas flotation with NB/MB µm for treating oily wastewater on a larger scale. Combining this technology with other methods, such as adsorption, is highly recommended, as it efficiently removes nearly all the oil from water.

5.2 Limitations and future research

This research explored a laboratory-scale gas flotation system employing NB/MB gas flotation to effectively remove oil droplets from oily wastewater. While our laboratory experiments yielded promising results, it is crucial to validate the practicality of this method on a larger scale. Few experiments were conducted at the pilot scale to validate the lab results. However, the industrial trial is recommended to test the technology's effectiveness and practical application. The following are recommendations for potential future research stemming from this study:

1) In future research, exploring different types of oil is advisable, as this study focused on Cold Lake Dilbit (CLD) and Heavy Conventional Crude Oil (HCCO).

2) Future studies should investigate the impact of NB/MB size distribution on performance, as this aspect was not explored in this study due to equipment limitations.
3) It is recommended to widen the scope of experimentation by testing the system in freshwater environments in addition to the marine conditions explored in this thesis.
4) Future studies should consider conducting continuous instead of batch mode experiments to accommodate larger reactor column volumes and gain a more comprehensive understanding of the system's performance.
5) Similarly, this study generated nanobubbles/microbubbles (NB/MB) using air gas. However, it is highly recommended that alternative gas sources, such as nitrogen or ozone, be explored in future research to investigate their impact on oil/water separation efficiency.

Chapter 6 References

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