QATAR UNIVERSITY

COLLEGE OF ENGINEERING

CROSSFLOW MICROFILTRATION OF TIGHT EMULSIONS AND SUSPENDED COLLOIDS BY CERAMIC MEMBRANES

BY

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ABSTRACT

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Title: Crossflow Microfiltration of Tight Emulsions and Suspended Colloids by Ceramic Membranes

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Produced water is known as the largest waste stream associated with the oil and gas extraction process from onshore and offshore fields; that is found in the form of either oil in water (o/w) or water in oil (o/w) emulsion. It is a very complex mixture composes of a variety of organic, and inorganic chemicals that can be found either suspended or dissolved in the water. During the oil and gas production many problems occur because of the formation of the emulsions. These emulsions can be very tight/stable and difficult to break it, and this is due to their heterogeneous composition. The presence of polar compounds such asphaltenes, surfactants and polymer used during the process and the presence of many types of fine solids such as crystallized wax, clays, and scales that participate in the formation of resistance films at the oil/water interface are known to produce unwanted stable emulsions that generate operational problems and are difficult to break. Therefore, produced water became a global concern and discharging this tremendous amount of water to the environment threatens the aquatic life and destroys the natural resources. The conventional methods in treating tight produced water emulsions and removal of suspended matters of micron size was found to have limitations, thus, there was a need to look for a robust method to solve such problems. The cross-flow ceramic microfiltration membrane is one of the promising solution for the micron-size oil droplets and colloids, yet no much work done using ceramic membrane. To this aim, a cross-flow ceramic microfiltration membrane was used to separate tight oil-in-water emulsions stabilized using Ethylene tetrakis surfactant. Diesel was used as oil source while, bentonite is used as the suspended matter source. The results showed that the cross-flow ceramic microfiltration membrane significantly removes the oil and colloidal suspended matters. It’s worthy to mention that the performance of the membrane was examined to remove the oil, bentonite, and mixture of both oil and bentonite, and it was found that the optimum pressure for the removal of both o/w emulsion-bentonite mixture, and o/w emulsion solution was at 0.5bar, where 90% of the oil content can be removed. On the other hand, the removal of suspended solids from o/w emulsion-bentonite solution was at its maximum under 0.2bar, where almost 99.97% of the suspended solids were removed. The 0.45μm ceramic membrane showed that it is a promising technology for treating any wastewater contains tight emulsions and suspended maters.

Keywords: Tight Emulsion, O/W Emulsion, Microfiltration, Ceramic Membrane, Colloids, Suspended matters, Produced water

DEDICATION

To my beloved parents, Said Abdalla and Bahira Abu-Issa,

who taught me the first lesson in this life,

To my sisters, relatives, and friends,

To the one who had given me dreams to look forward to; my husband, Ahmed El-Serty,

And, to whom is reading now.

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CHAPTER 1: INTRODUCTION

1.1.Research Overview

Despite the recent drops in oil prices, oil and gas industries still maintain their significance in the market as the major source of energy especially in Qatar and the gulf region, and it is expected to have an increase in the petroleum consumption in 2030 by 25% [1]. Nevertheless, this activity does not come without a concern–the deep drilling of the earth to extract the crude oil generates large volume of liquid waste as by-product, about 80% of which is wastewater known as produced water. Statistics have shown that the produced water volume in any crude oil extraction is three times the oil volume, which means, the water to oil ratio is 3:1 [2]. Two main sources of water are responsible of this large volume; formation and injected water. Formation water is the naturally found trapped water within the rock pores of the crude oil reservoir, while injected water is the water used to recover and enhance the productivity of the reservoir [1, 3]. That is because, with time the underground pressure will be no longer sufficient to drive the crude oil to the surface, thus, water and sometimes production chemicals are injected into a reservoir to increase and maintain the reservoir pressure and enhance the production as schematically shown in Figure 1.1[3].

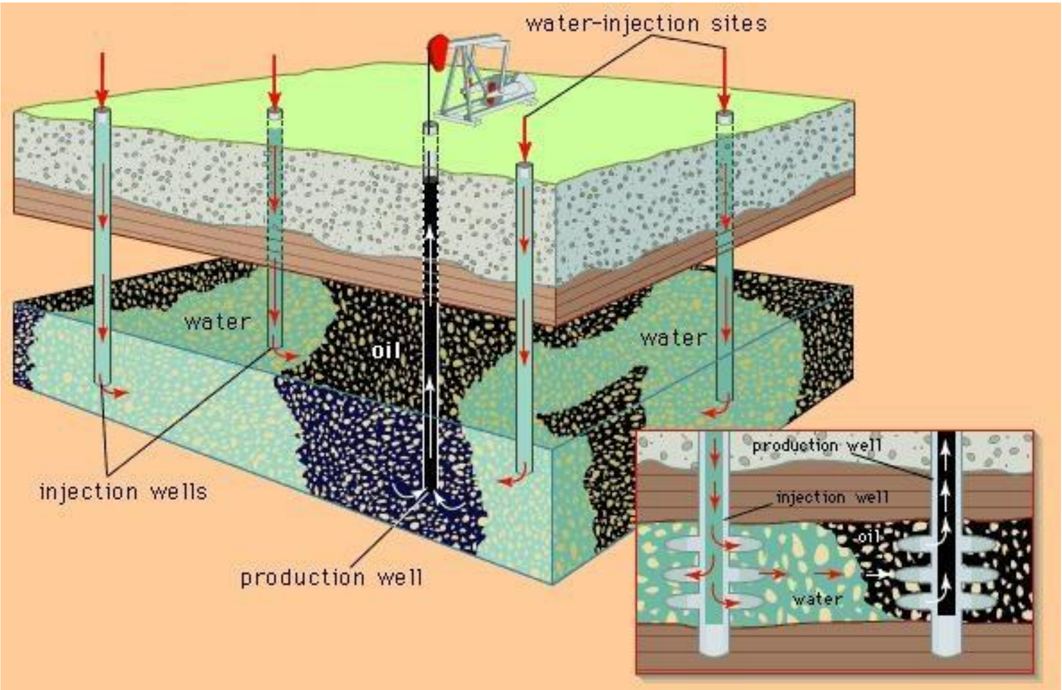


Figure 1. 1: Schematic illustration of oil and gas recovery process.

The considerably high pressure generated in the reservoir together with the shear forces, enforces the oil and water molecules to get dispersed in each other forming tight emulsions. This occurs because of the presence of some polar natural compounds such as asphaltenes, and resins, together with the presence of many types of fine solids such as crystallized wax, clays, and scales. Those compounds start to form stable film at the oil/water interface that hinders the droplets from being separated, thus hinders the phase separation between oil and water from being occurred. The formation of emulsions causes severe operational problems during processing and handling of crude oil; including corrosion and fouling of pipelines and equipment, and poisoning of catalysts during the refinery stage [4]. Discharging this tremendous amount of water to the environment threatens the aquatic life and destroys the natural resources. Thus, the removal of oil from produced water (known as demulsification or de-oiling) is of great importance and is even critical for offshore and onshore operations where meeting environmental regulations for water reinjection is a must. Such de-oiling takes place in a limited space in platforms, which makes the selection of separation methods very limited, and conventional methods in treating tight produced water emulsions and removal of suspended matters of micron size was found to be is ineffective, thus, there was a need to look for a robust method to solve such problems. The cross-flow ceramic microfiltration membrane is one of the promising solutions for the micron-size oil droplets and colloids, yet no much work done using ceramic membrane. Toward this aim, a cross-flow ceramic microfiltration membrane was used in this study to separate tight oil-in- water emulsions stabilized using Ethylene tetrakis surfactant, and diesel oil.

1.2.Tangible Objectives

The specific objectives of this study are to:

i. Study the characteristics and behavior of tight emulsions,

ii. Investigate the stability of Ethylene tetrakis as a surfactant used to stabilize tight oil-in-water emulsions using diesel as an oil source,

iii. Examine the separation of tight emulsions and suspended matters using crossflow micro filtration membrane at different trans-membrane pressure, and

iv. Investigate the membrane performance and effectiveness in removal of tight emulsions and suspended matters.

CHAPTER 2: LITERATURE REVIEW

2.1. Produced Water

Produced water is known as the largest waste stream generated during the extraction of oil and gas from onshore and offshore fields, that may account for 80% of the waste [5]. It is a very complex mixture contains a variety of organic and inorganic chemicals that can be found either suspended or in its dissolved state, and it varies in concentration from very low to very concentrated saline water. The geological location and formation of the field, the reservoir lifetime, the type of produced hydrocarbons, together with the added chemicals in the drilling and production operations are all factors affecting the volume and, chemical and physical characteristics of produced water [1, 6]. As a result, there is no two-produced water are alike, however, the chemical compositions of all produced water are qualitatively similar and can be classified into five main groups as shown below:

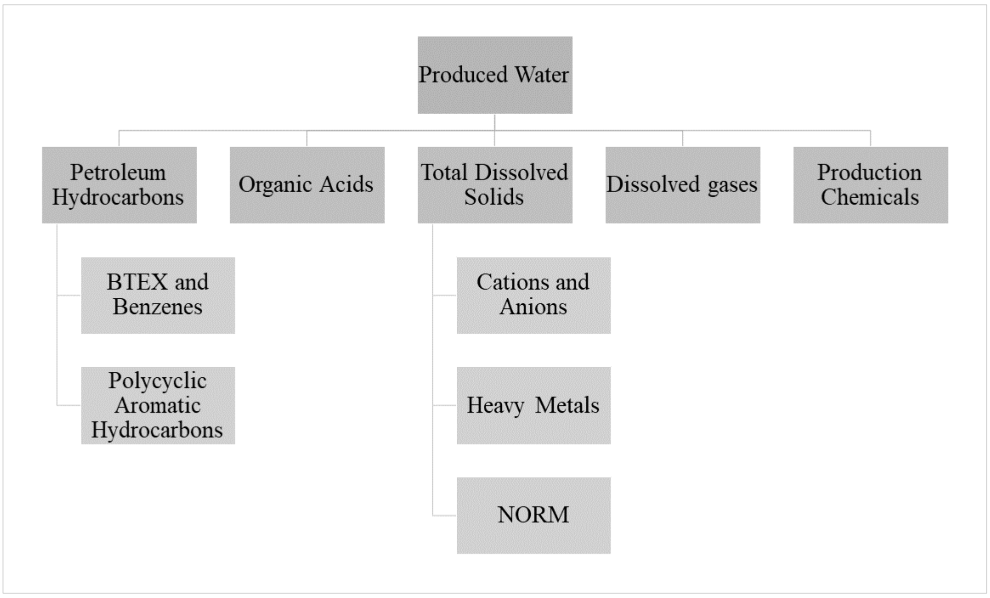


Figure 2. 1: Classification of produced water compositions

2.1.1. Petroleum Hydrocarbons

Petroleum hydrocarbons are the chemical compounds that have the greatest harmful effect in produced water to the environment. It is a mixture of organic chemicals consisting of hydrogen and carbon, and classified into two groups: saturated and aromatic hydrocarbons. These hydrocarbons can be found in both dissolved and dispersed form, and their solubility based on their polarity and molecular weight. Studies have shown that aromatic hydrocarbons are more soluble in water than saturated hydrocarbons, thus, treatment technologies other than oil/water separators are needed to effectively remove the soluble hydrocarbons from water [5-7].

2.1.1.1. BTEX and Benzenes

BTEX is an acronym for the one-ring aromatic compounds found in petroleum products and classified as dissolved oil; they are generally: Benzene, Toluene, Ethylbenzene, and Xylene. These compounds, together with the low molecular weight saturated hydrocarbons, are found in produced water at different concentrations and their concentration can reach up to 600 mg/L that can be decreased by increasing the alkylation. BTEX are highly volatile compounds, therefore, when produced water is treated using air stripping, BTEX compounds will be lost rapidly [6, 7].

2.1.1.2. Polycyclic aromatic hydrocarbons

Polycyclic aromatic hydrocarbons (PAH) are organic compounds composed of several cyclic rings formed naturally as a result of incomplete combustion of plant or animal matters, or carbon fuel such as petroleum. One of the simplest forms of PAHs is the Naphthalene, which composes of two fused aromatic rings and in most cases, it constitutes the bulk of PAH mass in produced water. PAH compounds vary in their solubility in water based on their molecular weight, ranging from average to poor soluble PAHs. Therefore, they are found in produced water as dispersed oil, and characterized as highly toxic compounds that contribute with other factors to increase the biological oxygen demand [5, 7].

2.1.2. Organic Acids

Organic acids produced as a result of the microbial degradation of hydrocarbons during the hydrocarbon bearing formation. They are mono- and di-carboxylic acids ($-$COOH) of saturated (aliphatic) and aromatic hydrocarbons. Low molecular weight carboxylic acids such as propionic, formic, and acidic acids are the commonly found types in produced water; where the bulk of the mass is usually of acetic acid. These low molecular weight organic acids account for the high TOC content in produced water, and their concentration in produced water is affected by the water alkalinity; as they decrease in concentration as the alkalinity increases [5].

2.1.3. Total Dissolved Solids

Total dissolved solids are inorganic minerals found in produced water in dissolved or micro-particulate forms. These solids can reach a concentration of 100,000 mg/L or higher based on the geological formation of the reservoir, its age and the inorganic chemicals injected during the production recovery. They are classified into three main categories; Cations and anions, Heavy metals, and Naturally Occurring Radioactive Materials (NORM). Table 2.1 shows the typical measurement for produced water minerals in an oilfield located in Qatar.

Table 2. 1: *Concentration of several elements and inorganic ions in produced water from an oilfield located in Qatar [7]*

Element/ Ion	**Produced water concentration (ppm)**
Calcium	17,240
Magnesium	3,315
Sodium	66,219
Potassium	3,370
Silica	67
Soluble iron	0.9
Total iron	1
Boron	15.4
Barium	30
Strontium	1,560
Copper	<0.01
Nickel	<0.01
Zinc	<0.01
Cobalt	<0.01
Chromium	0.02
Aluminum	<0.01
Lead	<0.01
Manganese	0.24
Cadmium	<0.01
Cyanide	<0.001
Selenium	<0.001
Arsenic	<0.001
Mercury	<0.0001
Ammoniacal nitrogen	1.2
Total phosphates as p	0.2
Chlorides	139,310
Sulphates	560
Sulphides	7
Carbonate	0
Bicarbonates	248
Free CO_2	128
Salinity as NaCl	229,860
Total oil content ppm range	$5.4\times10^4 - 39$
Total dissolved solids at 105	232,020
Total hardness as $CaCO_3$	57,530

2.1.3.1. Cations and anions

Produced water contains elevated levels of ions known as cations and anions. Usually, cations such as sodium (Na^+), calcium (Ca^{2+}), and magnesium (Mg^{2+}), and anions such as chloride (Cl^-), bicarbonate (CO_3^{2-}), and sulfate (SO_4^{2-}) are the predominant ions present in produced water. It is worth noting that both cations and anions have a significant role in affecting the chemistry of produced water in terms of its salinity, buffering capacity, scale potential and conductivity. Their concentration ratios in produced water vary depending on many factors including the oilfield depth, the origin and age of water, and the type of rocks. Researchers has found that the concentration of sodium and calcium in produced water vary from few parts per million (ppm) to about 300,000 ppm (Table 2.1) compared to about 35,000 ppm of seawater [7].

2.1.3.2. Heavy metals

The concentration of heavy metals in typical oilfield produced water varies from different formation based on the well age and its geological formation. Produced water heavy metals are usually higher in concentration than those of seawater, however since they are getting diluted in seawater their impact on marine life will be low unless their concentration is high enough to be toxic. Cadmium (Cd), barium (Ba), copper (Cu), chromium (Cr), lead (Pb), nickel (Ni), mercury (Hg), silver (Ag) and zinc (Zn) are most frequently presented in produced water in a high concentration relative to those presented in seawater [7].

2.1.3.3. NORM

Naturally occurring radioactive materials known as NORM are materials with radioactive elements that has been found naturally in environment (earth crust and rocks). During the extraction of oil and gas, produced water brought to the surface with radium226 and radium228, which are the decay of uranium and thorium. When they reach the surface, and because of the temperature difference, those NORMs precipitate in a form of sludge, and discharging them into the sea could cause severe problems in the long run. Thus, the National Pollution Discharge Elimination System (NPDES) had placed requirements for the maximum concentration of NORMs to be discharged [8, 9].

2.1.4. Dissolved Gases

Dissolved gases are normally found in oilfield brines in different concentrations based on the chemical and physical characteristics of the reservoir. In produced water, the most abundant dissolved gases are carbon dioxide, oxygen, and hydrogen sulfide. These gases are formed naturally either by the chemical reaction of the water or by the activities of the bacteria. The solubility of these gases increases with pressure and decreases with increasing salinity and temperature [1, 6].

2.1.5. Production Chemicals

During the production of oil and gas, some chemicals are added either to treat or to prevent the operational problems, these compounds are known as production chemicals. Some of the operational problems that require the addition of production chemicals are the formation of scales and corrosion, bacterial growth, presence of waxes and tight emulsion. Though, these chemicals are toxics and can threaten the aquatic life if they are discharged with water, thus, they should not exceed the maximum allowable limits [6].

2.2 Theory of Emulsions

The extraction process of crude oil is accompanied by water and other impurities resulting from the production process or from the oil reservoir geological formation. The crude oil treatment equipment is designed to separate oil and water and break emulsions by coalescing the water droplets, then by gravity separation. In order for this separation to occur, water droplets must have sufficient time to coalesce and the negative buoyant force acting on droplets must be enough to separate both phases[10, 11]. But since the product stream contains some organic and inorganic compounds such as: brine, hydrocarbons, aromatic compounds, phenols, metals and carboxylic acids, some of these components prevent the separation of oil and water. This happens when these components are absorbed at the interface between oil and water forming a stable film around the droplets and hinders them from being coalesced; this phenomenon is called emulsions. Emulsions can be defined as a heterogeneous system consists of two immiscible liquids, usually oil and aqueous, where one of the liquid phases (the disperse phase) is dispersed in the other (the continuous medium) in the form of droplets of microscopic or colloidal size (typically $\sim 1 - 10$ µm). The emulsions can be classified into two main categories depending on either the size or phase of emulsion [12]. The emulsions can be in micro or macro scale where micro scale is the most stable emulsion with a size between 1-300 nm. Whereas the macro scale is an emulsion with 1-10 µm size and in sometimes the range starts from 0.5 µm. Generally, there are three main phase types of simple emulsions, they are: water-in-oil (W/O) emulsion, oil-in-water (O/W) emulsion, and oil-in-oil (O/O) emulsion (Figure 2.2-A,B). Multiple emulsions, which is a complex emulsion system, present in the form of oil in water in oil (O/W/O) or water in oil in water (W/O/W) can also be found (Figure 2.2-C,D).

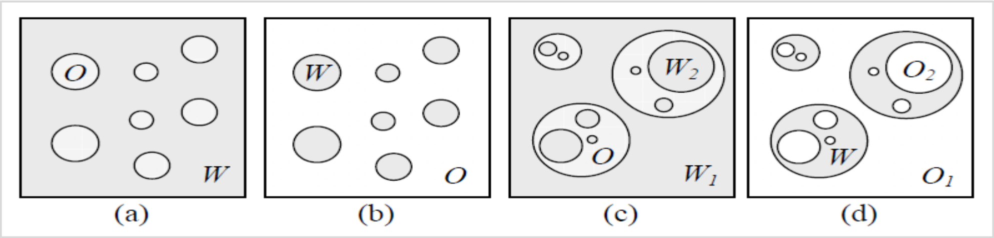


Figure 2. 2: Types of Emulsion (a) Simple O/W, (b) Simple W/O, (c) Multiple W/O/W, (d) Multiple (O/W/O) [13]

2.2.1. Water in Oil Emulsion (W/O)

When the oil content is high enough compared to water, water-in-oil emulsions exist; where the oil represents the continuous phase and water exist as droplets or dispersed phase. These emulsions are usually occurring after oil product is spilled and often called "chocolate mousse" or "mousse" because of to the presence of asphaltene and resins in high percentage. When W/O emulsions form, they cause a tremendous change in the physical properties and characteristics of oil spills; since oil and water have big differences in their characteristics. This because usually stable emulsion contains 60-80% of water in mass, and when phase inversion occurs as a result of an increase in the oil content, the volume of spilled material expands from two to five times of that the original [13, 14]. This will be followed by a change in physical properties such as densities and viscosities, where densities increase from as low as 0.80 g/ml to 1.03 g/ml or greater. Typically, viscosities change from few hundreds mPa.s to about 1000,000 mPa.s, which is an increase by a factor of 500-1000. As a result, the product state will change from liquid to a heavy/semi-solid material.

Since the emulsion properties changes with changing emulsions type, then stability is an important characteristic that need to be understood. Studies found that three different stability categories of water-in-oil emulsions formed when crude oil is mixed with water, they are: stable, meso-stable, and unstable.

Stable water-in-oil emulsions can be classified as very strong stable emulsions (known also as tight emulsions) that can remain for four weeks under laboratory conditions. With reference to the presence of asphaltene, stable emulsions are semi-solid substances with a reddish-brown color and their solid state is due to the strong viscoelastic interface. In the day of formation, they consist of 70-80% of water that will remain the same for one week. One important characteristic of stable emulsion is viscosity where it increases at least three-order of magnitude greater than the original viscosity [15].

Meso-stable water-in-oil emulsions are intermediate emulsions, where they lie in between the stable and unstable emulsions. This is due to lack of sufficient amount of asphaltene that can stabilize the water droplets, and the presences of destabilizing agents that are working on destabilizing the emulsion[16]. Meso-stable emulsions are characterized as viscous liquids with reddish-brown color. Usually, at the first day of formation they can contain up to 60-65% of water, but this percentage will drop after one week of formation to less than 30%.

Unstable water-in-oil emulsions contain only few amounts of water droplets dispersed in the oil phase, about only 40% of the system, which will make them easy to decompose into two separate phases after mixing. Only if the oil is highly viscous they can retain very few amounts of water droplets [15, 17].

2.2.2. Oil in Water Emulsion (O/W)

Transporting the heavy oil in pipelines resulted in a high pressure drop due to the high viscosity of the oil, thus it required a higher pumping energy to overcome this force. Oil-in-water emulsion is one of the feasible solutions that can reduce the viscosity of the heavy crude oil. This can be done by combining the oil with an aqueous solution comprising water, solid particles and emulsifying agent that enhances the emulsification process. In this type of emulsions, water represents the continuous phase, whereas the dispersed phase consists of the oil droplets [18]. The resulted oil-in-water emulsion will have a pH value in the range of 7.5-10.0 with a low viscosity value of about 50 mPa s [19]. Since the water viscosity, the continuous phase, is independent of temperature, thus the oil will not be affected by temperature. In other words, maintaining the lower viscosity value of the oil while transporting, will not require increasing the temperature of the mixture. Moreover, this type of emulsion will prevent the pipeline from getting fouled by the oil [20].

2.2.3. Emulsion Stability

The stability of emulsion against coalescence requires the formation of stable liquid film between the emulsion droplets. A useful theory to describe stability of emulsion is called DLVO (Dergaguin-Landua-Verwey-Overbeek) theory. DLVO states that the emulsion stability is due to the combined effect of both van-der-wall attraction force and electrostatic repulsive force arises from the electrical double layer at the particles surfaces. This means that, when the charges on droplets are the same they will repel each other maintaining stability, while if they differ an electrical attraction force destabilizes the emulsion [21]. The combination of DLVO forces resulted in three distinct energy features; the primary minimum, secondary minimum, and the maximum energy barrier as shown in Figure 2.3. The maximum energy barrier is the region where particles repel each other and stay dispersed in the continuous phase, in other words, it is the state where the emulsion could be fined as tight emulsion. The barrier height indicates the stability of the system and in order for the particles to colloid they have to overcome this barrier. But, when it is too high to overcome the maximum energy barrier, the colloidal particles will stay in the secondary minimum.

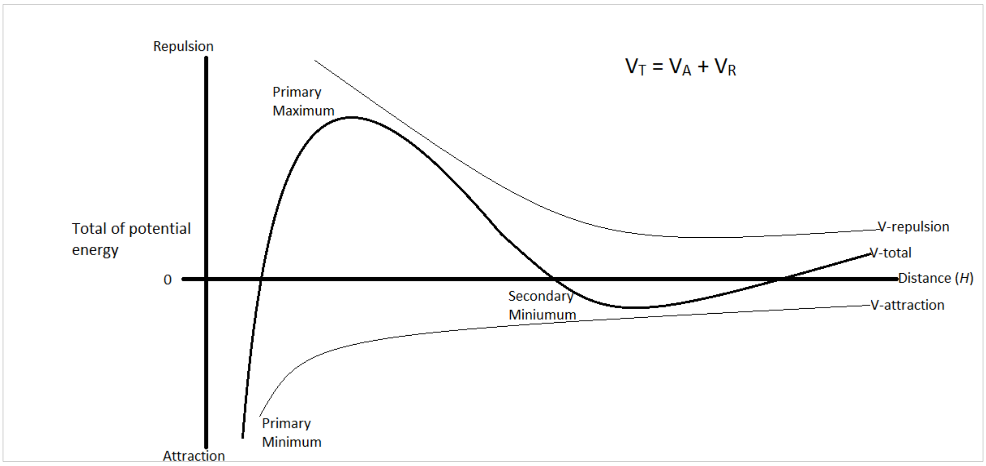


Figure 2. 3: Schematic interaction potential between two drops showing DLVO forces potentials [22].

At the primary minimum, van-der-walls attraction force dominates over the repulsive force, resulting in an aggregation of the droplets and as a result a demulsification process will take place.

2.2.3.1. Electrical Double layer

Electrical double layer is one of the most important phenomena that have a fundamental role in stabilization of emulsion/colloidal particles. This phenomenon appears when one object is exposed to another, in oil-water emulsion it could be either water or oil particles depending on the emulsion disperse phase. Once this happens and due to the different energy levels between the dispersed and continuous phase, two parallel layers of charges start to rearrange and surrounding the disperse particle forming an electrical double layer. Usually, the disperse particles carry an anionic charge and dispersed in a cationic continuous phase (water) enabling a counter charge attraction to take place [23-25]. The electrical double layer is consisting of two main layers; the stern and the diffuse layer as shown in Figure 2.4.

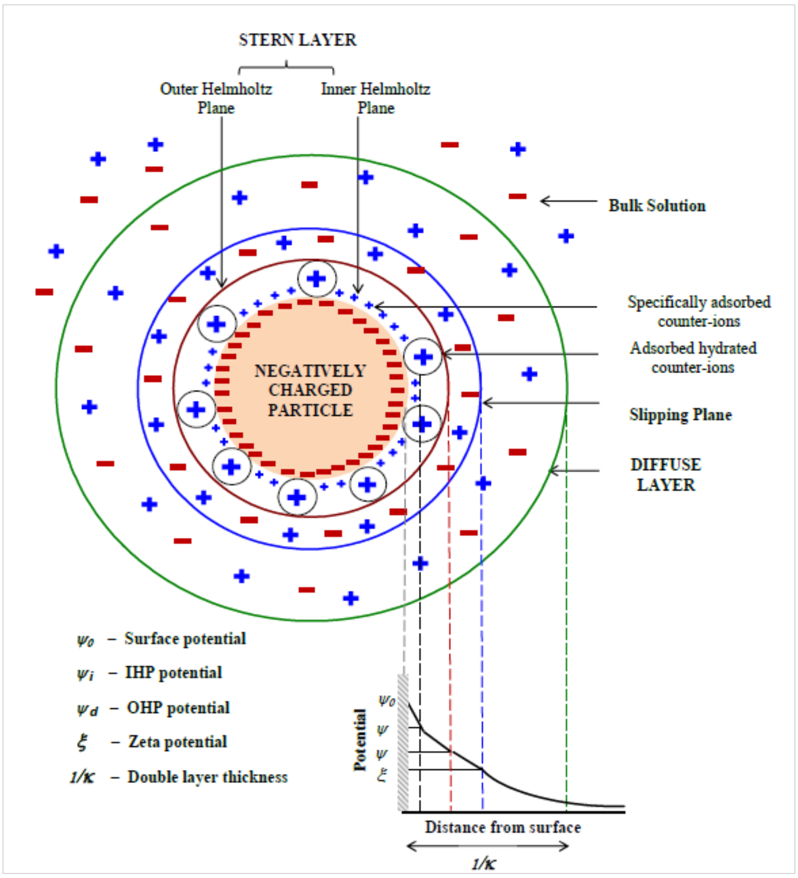


Figure 2. 4: Schematic representation of the electrical double layer phenomenon and zeta potential [26]

The stern layer is the adjacent layer to the particle surface that carries a counter charge and closely attach to it by the electrostatic force. The continuous phase surrounding the particle carries the counter-ion with a higher concentration, but they are moving around the particle under the effect of the electrostatic force. The maximum electrical potential within the electrical double layer is at the particle surface. This value will start to decrease gradually with distance until it reaches the zero potential at the electrical double layer boundaries. The electrical potential value at the stern boundary layer (slipping plane) is called the zeta potential, which is a very important parameter used to test the emulsion stability that will be discussed more in the next section [23-25].

2.2.3.2. Zeta Potential

Zeta potential is the key measure that indicates the stability of the dispersed phase in an emulsion, and it relates to the electrical double layer structure around the dispersed particle. If the thickness of the electrical double layer increase, the repulsion forces will increase causes an increase in the zeta potential value. This means, the higher the zeta potential, the more stable the droplet becomes in an emulsion. Also, the addition of suitable emulsifier is important in preparing synthetic emulsion since the type of surfactant, cationic or anionic, will affect the stern layer thickness. This is because, the type of emulsifier and other additives will either increase or decrease the layer thickness based on their properties. Another parameter that is important in z-potential values is the size of the dispersed particles, the smaller the size the higher the zeta potential and the more stable the emulsion became. In other words, when the dispersed phase consists of small particles each is surrounded with its counter electrical charge; this will increase the repulsive force and decrease the phase separation. Thus, the higher the zeta potential values, usually∓60, the more stable the system is [24].

Theoretically Henry’s equation is used to estimate the zeta potential using

$$U_{\mathrm{E}} = \frac{2\, \varepsilon\, \psi\, F(\kappa a)}{3\, \eta} \qquad \text{Eq.2.1}$$

Here, U_{E} represents the electrophoretic mobility, ε is the dielectric constant, ψ is the zeta potential to be determined, F(κa) is called Henry’s function, and η is the viscosity [27, 28].

2.2.4. Emulsion Stability Influential Parameters

Unless an emulsifying agent is added, emulsions made by agitation of the system are very weak and unstable, therefore can break rapidly resulting in a phase separation of oil and water. Thus, a surface-active material, namely surfactant, has to be added into the system to form a stable emulsion, prevent the re-coalescence of the newly formed droplets, and lower the agitation (mechanical) energy by factor of 10 or more. When surfactant is added, it gets adsorbed at the oil-water interface and it prevents the drop growth and separation of both phases. Surfactant can also be found naturally, an example of that is the asphaltenes that present in large quantities in crude oils and it helps in stabilizing the water in oil emulsions. The stability of emulsion depends on many factors including the type and amount surfactant used, difference in densities between the two phases, viscosity of the continuous phase, Temperature, pH and the particles size. In next section, the types and kinetics of emulsion are discussed in more details [13, 14]. The influence of some of these parameters is discussed in detail in this section.

2.2.4.1. Temperature

One of the most important factors that affect the emulsion stability is temperature. Changing the emulsion temperature affects its physical-chemical properties such as the density, interfacial tension and viscosity. In terms of stability, if the emulsion is heated to higher temperature this will motivate the particles leading to an increase in the coalescence kinetics. This means that increasing the temperature of an emulsion will increase the van-der-walls attraction forces over the repulsive forces, decreases the interfacial tension, and cause a phase separation. Thus, in order to maintain the emulsion stability, the temperature should be controlled [23, 29, 30].

2.2.4.2. Droplet Size Distribution

The emulsion droplet size and its distribution is a critical metric that need to be studied during the emulsion preparation. If the mean size of the dispersed phase droplets reduced, the total droplet number will increase leading to a more interface between them. Thus, the interfacial tension between them will increase, increasing the repulsive force and causing a more stable emulsion. This means that, the smaller the droplet size with fairly uniform distribution, the more stable the emulsion is [23, 29, 30].

2.2.4.3. Surfactant

Stabilizing emulsion is a process that requires a presence of certain substances with particular concentration to achieve the required stabilization, these substances are called surfactants. Surfactants consist mostly of long chain organic molecules with a polar hydrophilic head group and non-polar hydrophobic tail group, Figure 2.5. When the surfactant is added to an oil-water emulsion, the molecules will be adsorbed at the oil-water interface where they align themselves, the polar group toward aqueous phase and the non-polar towards the oil phase, Figure 2.5. This process will reduce the interfacial tension between oil and water phases and enhance the miscibility of them. Surfactants are not confined only to the commercial products, they can be found in the oil reservoir as natural substances that possess this stabilizing property and an example of that is asphaltenes. Each surfactant should have a hydrophilic-lipophilic balance (HLB) value that indicates whether the surfactant contributes in forming W/O emulsion or O/W emulsion. Lower HLB value (<10) means that the surfactant is suitable for stabilizing W/O emulsions, and when the value tends to 10 or more the surfactant can stabilize O/W emulsion [23, 29, 30].

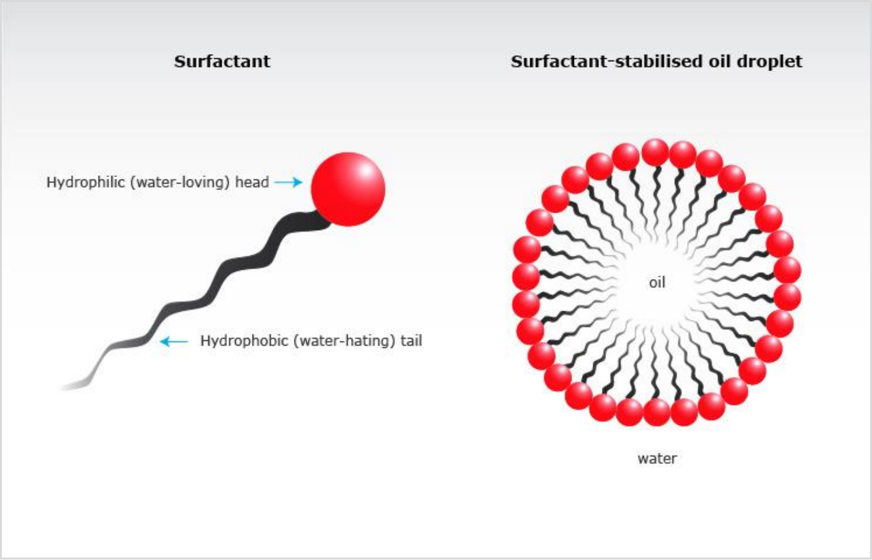


Figure 2. 5: Structure of surfactant molecule [31].

2.2.4.4. pH Value

The pH value is an important parameter that has an influence in stabilizing emulsions and it depends on the amount and composition of salts presented in the aqueous phase. Changing the pH value will change the interfacial tension between the two liquids causing either decrease in the interfacial tension and enhancing the stability, or increasing it and cause phase separation. If an emulsion is to be prepared, the pH value should be studied by adding some additives to the aqueous phase such as sodium chloride to increase the salinity and check the mixture behavior. This will give an indication of the emulsion behavior towards salinity/alkalinity, and will obtain the optimum pH range of the system. The surfactant is also affected by the pH value, where its HLB value is increases with increasing the pH. If the pH is lowered and the environment became acidic, the system tends to be W/O emulsion. Whereas increasing the pH value to a basic medium will convert the system into O/W emulsion [23, 29, 30].

2.2.5. Emulsion Instability

When liquid particles are dispersed in another immiscible liquid phase without any type of stabilizing agents, the emulsion will be very poor and the layer separating the droplets fails. Thus, particles from each phase will start to colloid and aggregate causing phase separation, or as it is called emulsion breakdown. Generally, there are three main parameters that could affect the phase separation under gravity; they are: the density of both phases, the square of the droplet radius, and the inverse viscosity of the continuous phase. Figure 2.6 is a schematic diagram of the major instability processes that emulsions undergo as discussed further below.

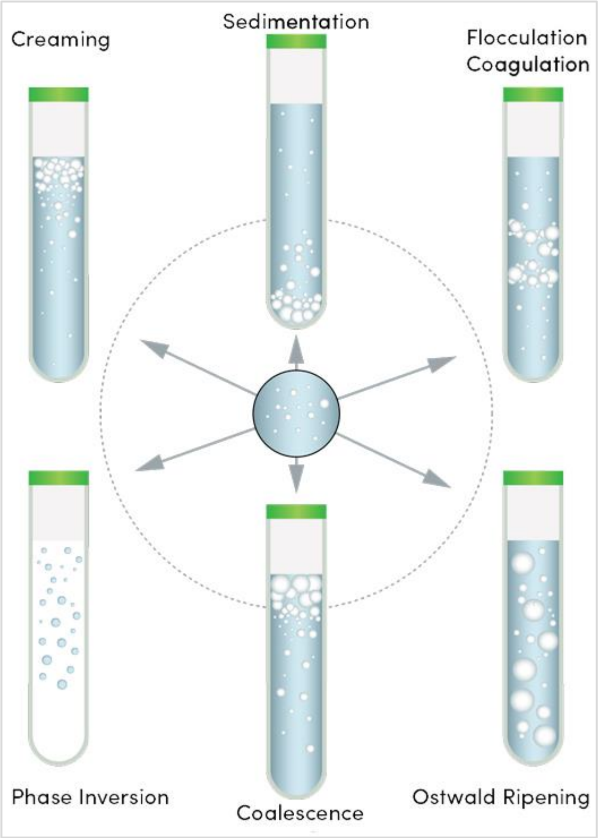


Figure 2. 6: Schematic representation of various emulsion break-down processes [16].

2.2.5.1. Flocculation

Flocculation process occurs when the electrostatic repulsive force is not enough to dominate and keep the droplets dispersed. In this case, van der walls attraction force overcomes the electrostatic repulsive force, and as a result the droplets start to aggregate without rupturing the primary droplet size as shown in Figure 2.6. Flocculation strength varies based on the magnitude of the van der wall attraction force, and its deriving forces can be classified into three main types [29, 32]:

1- Gravitational force; where the dragging force of the flocs formation is gravitational or centrifugation force in the form of creaming or sedimentation depends on the dispersed droplet size with relative to the bulk's molecules size.
2- Brownian motion; that is resulted from the collision of suspended particles with the bulk molecules.
3- Temperature gradient; may dominate the gravitational body force for very small droplets, less than 1 μm.

2.2.5.2. Creaming / Sedimentation

One of the main parameters affecting the emulsion stability is density difference between the dispersed and continuous phase, in which it is favorable for a tight emulsion to be zero or minimal. When the densities differ, either sedimentation or creaming of particles start to form; where creaming means that the lower density particles migrate under the influence of buoyant force to the top, and sedimentation occur as a result of settlement of the higher density particles under the influence of gravitational force, Figure 2.6 [29, 32].

2.2.5.3. Oswald Ripening

This phenomenon occurs when the small particles of the dispersed phase starts to diffuse through the continuous phase from smaller to larger particles as illustrated in Figure 2.6. This occurs because often immiscible liquids have an amount of solubility that cannot be neglected, so that the soluble liquid transfer from the smaller droplets to the larger ones causing it to grow in size, thus, the driving force for Ostwald ripening phenomenon is the difference in solubility between the small and large particles [29, 32]. It is also important to mention that the surface pressure increases as the radius of the droplet decreases as illustrated by Laplace equation:

$$P = 2\,\frac{\gamma}{r} \qquad \text{Eq.2.2}$$

Where P is Laplace pressure, γ is the surface tension, and r is the droplet radius.

2.2.5.4. Coalescence

Coalescence is an irreversible process in which a single large droplet forms as a result of fusion of two or more droplets. This occurs only when the interface layer that separates the droplets becomes sufficiently thin and rapturing becomes a likely possibility, Figure 2.6. Generally, coalescence process occurs in two stages: the first one is thinning the liquid film layer (film drainage), and the second one is the film rupture. The drainage stage, where thinning process takes place, depends on both film hydrodynamics and the forces acting across the film, whilst the rupturing stage depends on the film mechanical properties and thickness fluctuations. When the film reaches critical thickness (usually below 1000Å) van-der-walls forces will influence the drainage process and any significant instability will rupture the film [29, 32].

2.2.5.5. Phase Inversion/Separation

Phase inversion is said to occur when there is an exchange between disperse and continuous phase. This may happen as a result of changing the variables, such as: pressure, temperature, salinity, use of co-surfactant, or change in the proportion of oil and aqueous phase. In many cases, once phase inversion starts to take place both aqueous and oil phase will pass through a transition state whereby multiple emulsion take place [29, 32].

2.3. Challenges and Needs for Emulsion Destabilization

2.3.1. Environmental Impact

In oil and gas industries produced water is the largest volume waste stream resulted from the production and extraction activities. It has water to oil ratio of 3:1 which is a massive amount that need to be either discharged to the environment, or treated and used for industrial processes and other purposes. In the past, they relied on gravity separation before discharging the effluent to the environment with a high oil and grease concentration. But this had an inverse impact on the marine life, thus the environmental regulations became more stringent in discharging values and required an extensive treatment processes. For example, an agreement set by The Oslo Paris Convention to reduce the discharging value to 30 ppm, Australia agreed on the same value while the United States Environmental Protection Agency increased it to be 42 ppm/day of the discharged oil and grease. This was before the adoption of The EU Water Framework Directive that came with a commission to achieve zero discharge of oil and grease. This solution came to protect the aquatic life form being attacked, and will give a good alternative for providing clean water especially with the concern of ground water depletion in the area. Thus, an extensive treatment of produced water is needed, and demulsifying techniques need to be studied.

2.3.2. Needs for Emulsion Destabilization

The properties and constituents of produced water vary from site to another based on mainly the well geological formation together with the chemicals used in extraction process. Some of the natural chemicals presented in produced water act as a natural surfactant due to its high wax value that stabilize the oil in water emulsion to a very high degree, such as asphaltenes, resins, waxes, sulfur, and minerals. When produced water is subjected to a treatment unit, these chemicals start to cause several problems such as clogging, fouling, and corrosion. These technical problems can cause pressure drop, reduction in effluent flow, change in the effluent characteristics, which will lead to a decrease in the process efficiency and as a result increase in the treatment cost. Thus, the emulsified produced water need to be chemically treated first using a demulsifying agent to break down the stability and separate the phases prior being subjected to a mechanical treatment unit to prevent such problems.

2.4. Up-to-Date Literature on Technologies Used for Emulsion Demulsification

Since the objective nowadays is to achieve zero discharge of oil and grease and treat the produced water to be used for other applications, then there is a need to investigate the possible chemical, physical, biological, and mechanical solution in this area as discussed in detail in this section. Most of the known demulsification technologies will be discussed briefly, however, since the objective of this thesis is to study the behavior of microfiltration using ceramic membrane, the focus in this section will be on membrane demulsification technologies.

2.4.1. Membrane Demulsification

Membrane treatment is one of the widely spread technologies in the research area that is known to be a highly effective separation method. It is mostly suitable for treating wastewater with pollutant size of micron and submicron droplets, and it has a lower thermal energy cost compared to thermal treatment technologies. There is a wide variety of membranes being used nowadays; however, ceramic membrane became a promising method and good alternative. The main idea of the membrane technology is the separation of solutes or particles from a solution by permitting the smaller molecules to pass through the membrane while rejecting the larger ones. Membranes can be classified into four main categories based on their pore sizes; where it ranges from below 2nm to 10,000nm.

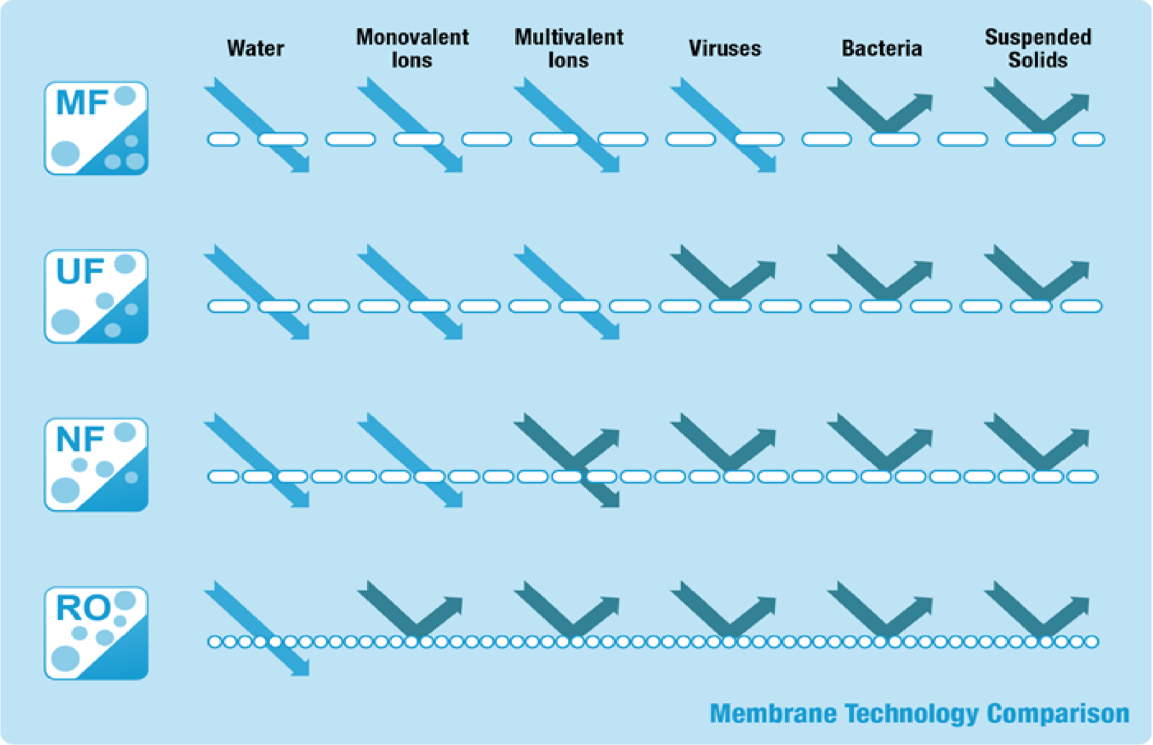


Figure 2. 7: Classification of membrane technology based on pore size [33].

The microfiltration membrane technology (MF) has the largest pore size among other membrane filtration technologies; where its pore size ranges from 0.1 to 10 microns and its molecular weight cut-off (MWCO) can reach as high as 1000,000 Daltons. It has a significant application in produced water treatment since it can be used as a pre-treatment unit to get rid of the large particles and to reduce the fouling of the next membrane treatment unit. Its pore size is large enough to reject matters such as bacteria and suspended solids, while it allows the passage of both monovalent and multivalent ions and viruses as shown in Figure 2.7. Nevertheless, it has the lowest operating pressure, as it works effectively with pressure range 0.1-2bar. Where in ultrafiltration (UF), the pore size ranges from 0.01 to 0.1 microns with a MWCO of 10,000 to 1000,000 Daltons, and the operation pressure ranges from 2-5bar. As shown in Figure 2.7, UF can retain all microbial species and some of the viruses with a moderately low pressure, however, because of the small pores, fouling issue can cause difficulties in treatment. As the filter pore size decreases, the operational pressure and removal efficiency of the membrane increases. Nanofiltration (NF) or as it is known sometimes softening membrane has a pore size of about 0.001 to 0.01 microns with a MWCO ranges from 1000 to 10,000 Daltons, and operational pressure increases to be in the range of 6-10bar. It acts as water softening membrane since it can remove the hardness of the water. However, it requires high energy to operate the system and get the water treated. Apart from all the above-mentioned types, reverse osmosis RO has the highest potential in removing all impurities from water even the dissolved ions as shown in Figure 2.7. Though, it requires a very high energy to operate the system and it is known to be prone to fouling. Its pore size is below 0.001 with a MWCO of 1000 Dalton, and it requires 10-100bar to operate the unit. The table below highlights some of the important details about membrane classification based on pore size [33].

Table 2. 2: *Summary of membrane classifications based on pore size*

Membrane type	Pore size (Mm)	MWCO	Pressure (bar)	Applications
Microfiltration (MF)	0.1-10	1,000,000	0.1-2	- Degreasing process, - Emulsion separation, - Metal separation, - Particle separation, - Pre-treatment of RO and ion exchange, and - Tertiary treatment of effluent from activated sludge process - Desalination, - Final removal of toxic components, and - Post treatment of permeate.
Ultrafiltration (UF)	0.01-0.1	10,000-1,000,000	2.0-5.0	
Nanofiltration (NF)	0.001-0.01	1,000-10,000	6.0-10	
Reverse Osmosis (RO)	<0.001	1000	10-100	

A) Membrane modules

Membrane module is the membrane body, where the fluid takes place and get treated. One of the most important parameters in selecting a membrane module in industry is the space, so that the membrane module should be selected carefully in a way to maximize the performance and minimize the functional area. Four main membrane modules were developed to match the industrial needs, they are: plate and frame, tubular, hollow fiber, and spiral wound.

1- Plate and frame

Plate and frame membrane module consists of two membrane flat sheets separated by supportive plate Figure 2.8, and to increase the productivity of the membrane the number of stacks need to be increased. Two types of configuration can be applied in this type, dead end and cross flow.

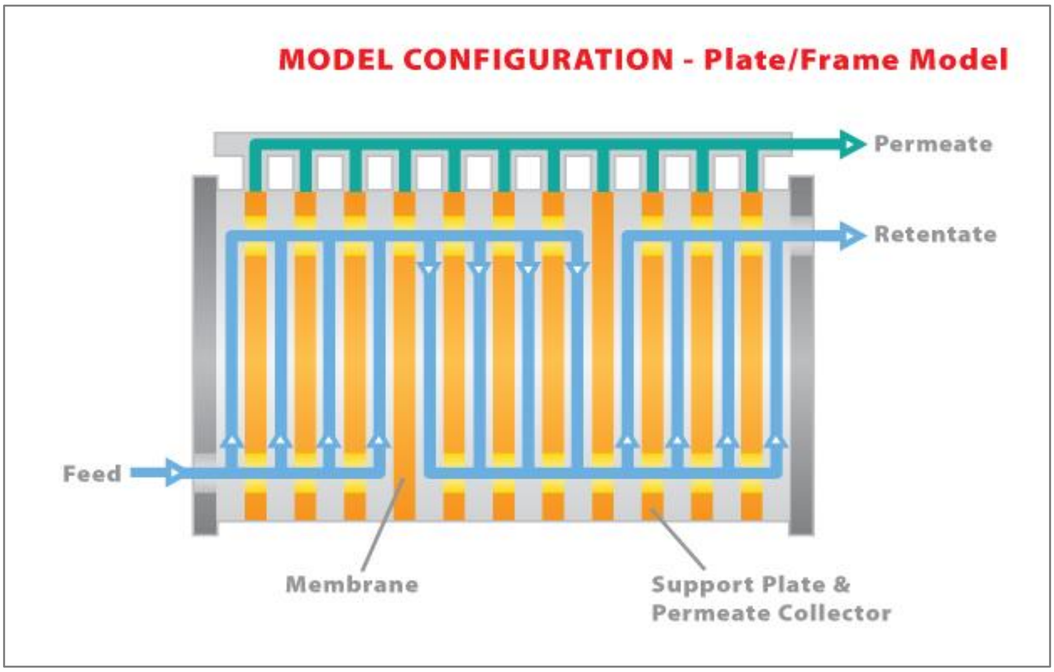


Figure 2. 8: Schematic representation of plate and frame module [34].

In dead end, the feed flows perpendicular to the membrane, where the cross flow the feed flows tangentially. Thus, the fouling in dead end configuration is higher than that of the cross flow, where in the dead end a cake layer will built up while in the cross-flow configuration the concentrate will be collected regularly. The main disadvantages of this type are the high-pressure drop, low efficiency, and the membrane can be damaged easily in the dead-end configuration because of the built-up cake layer. Though, its cleaning and maintenance is easy, and it can be lower in cost compared to other types [34, 35].

2- Tubular membrane

Tubular membrane modules consist of tubular membrane with porous surface packed inside a tubular shell. It has a cross flow configuration, where the feed flows along the tube and the concentrate collected from the other side.

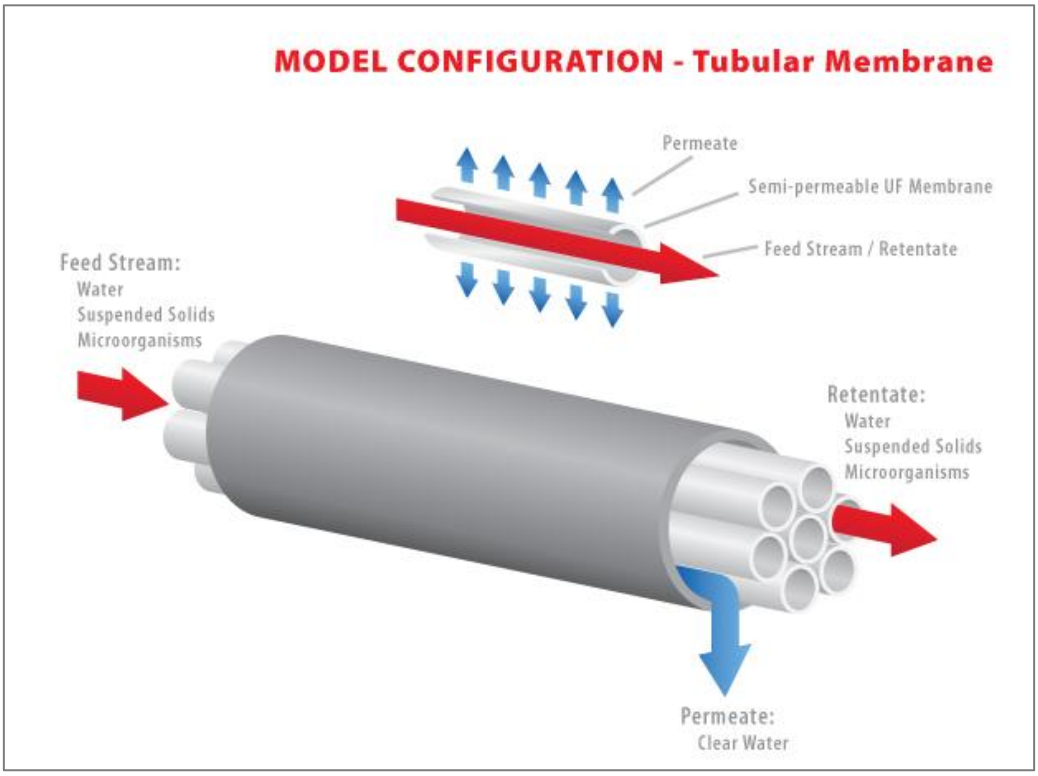


Figure 2. 9: Schematic representation of tubular membrane module [34].

The velocity of the fluid passing through the membrane decreases the concentration polarization on the wall. It is designed to be used for the treatment of difficult feed solutions, such as those with highly dissolved solutes and suspended solids. It has a low fouling factor compared to the plate and frame and can be chemically and physically cleaned, though, it is large in size and have a low packing density compared to spiral wound [34, 36].

3- Hollow fiber membrane

Same as the tubular membrane, hollow fiber membrane consists of tubular long membranes packed inside a shell, but the difference is in the material and diameter of the membrane. It is made of fiber, and have a narrow tube diameter compared to that of the tubular membrane that it makes it more flexible.

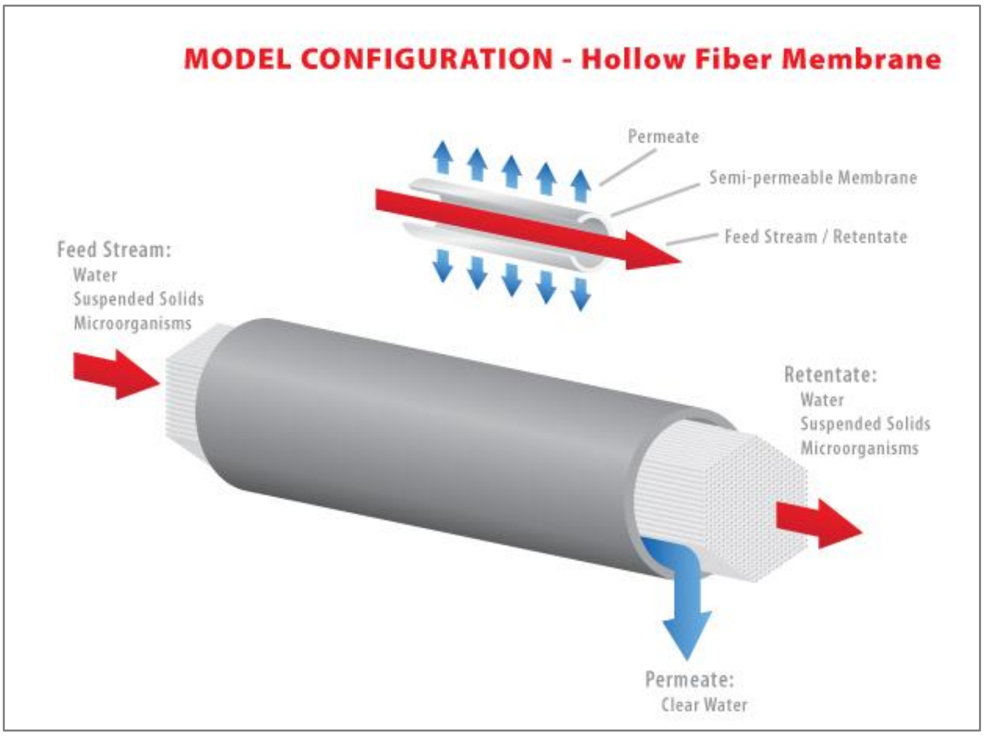


Figure 2. 10: Schematic representation of hollow fibre membrane module [34]

Packing number of membranes inside a shell means increasing the volume while utilizing smaller area. Under high pressure, and since the fiber tubes are narrow and flexible, it can be broken easily. Another disadvantage of the hollow fiber is the buildup of reverse fouling, though, because of the small diameter of each membrane, it has a high packing density [34-36].

4- Spiral wound membrane

It is basically a flat sheet membrane folded around a hollow and separated by feed separator to allow the feed to flow through the membrane forming a sandwich. The feed flows tangentially across the membrane then the permeate is being collected from the permeate channels.

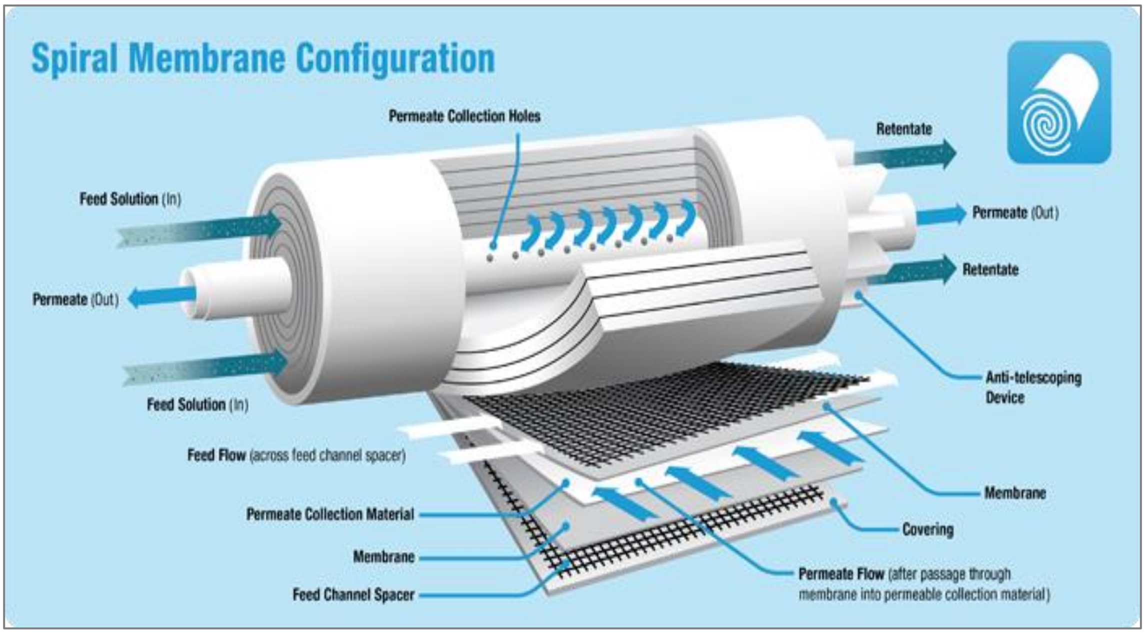


Figure 2. 11: Schematic representation of spiral wound membrane module [34].

When it comes to the packing density, it has a low packing density compared to the hollow fiber, and its fouling factor is greater than that of the tubular. Another disadvantage is that it cannot be cleaned mechanically, though, it can be cleaned in place and it fits multiple applications [34, 36].

B) Fouling problems

Membrane fouling is one of the major problems facing membrane technology. It is the deposition of particles on membrane pores and membrane surface, in which it increases the resistance through filtration, and decreasing the flux [37-39]. This resistance is classified into two main categories; resistance of the membrane itself (R_m) which is always present during the filtration process, and resistance caused by the filtration process. The filtration process resistances are:

1- **Pore blocking R_p**: Resistance occurred when the membrane pores get blocked by the particles and it depends on particle size and the structure of the membrane,

2- **Adsorption R_a**: This occurs when the particles deposit and get adsorbed in the pore walls or on top of membrane,

3- **Gel layer R_g**: The formation of cake/gel layer on top of membrane decrease the flow and hence cause flux decrease, and

4- **Concentration polarization R_{cp}**: This occurs in case where osmotic pressure takes place, where two fluids are separated by a membrane and the solutes are concentrated and deposited on one side of the membrane under the effect of the draw solution from the other side. Figure 2.12 shows the five different resistances occurs at the membrane surface and inside its pores [37-39].

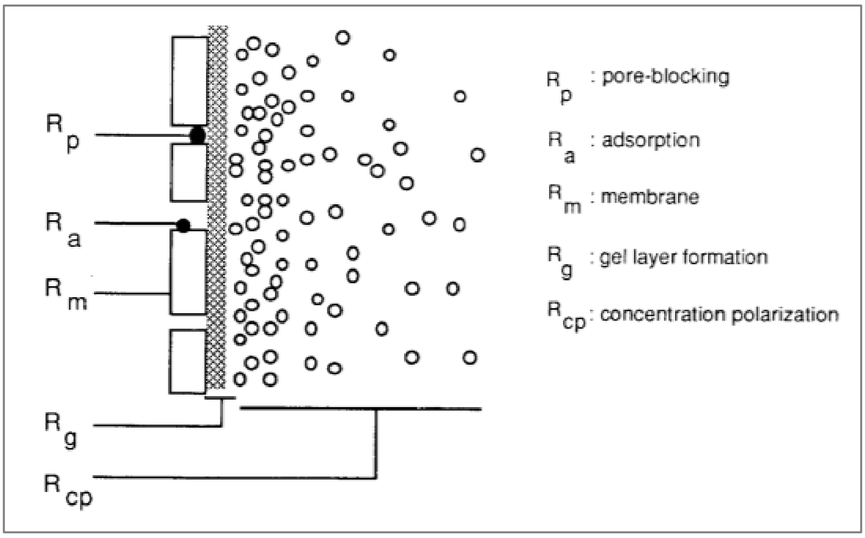


Figure 2. 12: Schematic representation of the possible resistances against flow transfer through membrane [38]

There are four main types of membrane fouling, they are: colloidal, organic, scaling, and biofouling. Colloidal fouling is cause by the natural colloids present in the water such as suspended matter, colloidal silica, aluminum, etc. These colloidal particles form a cake layer on top of the membrane that affect quantitively and qualitatively the permeate flux, and cause a hydraulic resistance to water flow. When solute is dissolved in the solution and start to stick on top of membrane surface, this is called organic foulant. Organic foulants are like oil, protein, and anti-foaming agents that built up an organic gel layer on top of the membrane and inside its pores. The main difference between organic and colloidal fouling is that the aforementioned are dissolved in the solution while the latter are particles. Scaling is called when salt is starting to precipitate on top of membrane surface forming crystals. This usually occurs in reverse osmosis technology when the salt concentration exceeds the saturation and precipitation occurs. One way to prevent scaling is to lower the pH, and recently they started to add anti-scalants. When microorganisms are the responsible of forming a layer on membrane surface, this is called biofouling. Biofouling occurs because of the reaction between the membrane material, the fluid parameter, the dissolved substances, and the microorganisms. This process is slow compared to other fouling types, though, when the biofouling occurs it starts gradually to decrease the permeate flux and affect the product. Many factors contribute in causing fouling, such as the fluid temperature, pH, pressure, hardness, composition, MWCO, and the membrane module, pore size, and material, etc. It is worth to note that fouling issue is not an immediate process, it takes time to start building up a cake layer and cause pore blockage, though, cleaning process is a must to at least preserve the membrane at its lowest performance and proof that it can work for a period of time under a certain condition [37-39].

C) Cleaning process

It is highly important to note that, cleaning process will not retain the membrane to its original performance, though, it can regenerate the membrane performance to the possible highest level. There are three main types of membrane cleaning process; physical, chemical, and biological, and the type of membrane and the fouling determines the required cleaning process. In physical cleaning process, back -flushing is the mechanical process where water with high pressure is applied from permeates side, pushing the foulants and suspended particles backward. There are many mechanical ways that can achieve this purpose, and clean the membrane. This cleaning method is widely used in industrial and it shows its advantage in cleaning the membranes. Chemical treatment method is a method where chemical substances are used in removing the foulants and regenerating the membrane. The used chemicals must be safe on membrane in a way that it will not harm it, and effective in dissolving the suspended foulants. Alkalies and acids are well known in cleaning membranes, though, other cleaning agents are being. The third cleaning method is the biological, where enzymes are being used to react and clean the membrane. They are working under mild conditions; pH, temperature, and ionic strength, and they are classified as a friendly solution for cleaning the membrane where they are safe to membrane compared with other cleaning methods [37-39].

2.4.2. Biological Demulsification

One of the best solutions to treat tight produced water emulsion problem is the use of bacteria in breaking down the emulsion. Nowadays, biological demulsification technologies are attracting researchers since it has a low toxicity and biodegradability, and can sustain its efficiency even under extreme pH, temperature and salinity conditions. In some cases, biological demulsification can take place in situ, thus eliminating the problems that could be faced during transporting. In terms of cost, its capital cost is lower compared to other technologies, but this might change in case of using hybrid system. Also, there is ability to recycle and reuse the biodemulsifier which promotes sustainability and reduce the adverse effect on environment. In this matter, there are mainly applications using different types of microorganisms that are existed already in the research sectors to be used for demulsifying tight produced water emulsion.

2.4.3. Physical Demulsification

Separation under gravitational force is one of the methods that can be used in separating oil and grease particles from produced water. A good example of this method is hydrocyclone that separates the pollutant particles based on its density with equivalent to the water density. Thus, under the influence of gravitational force and based on differences in densities and solubility, the heavy particles will settle and collected as slurry while the water is collected as the effluent. The main disadvantages of this treatment method are: the need for a pre-treatment/post-treatment processes to treat the water further and the presence of large slurry volume that need to be collected and disposed/treated.

2.4.4. Electrical Demulsification

Produced water can also be treated using electrical methods where oil-water emulsions can be break using electricity. This occurs when electrodes are places to lower the electrical double layer of the dispersed phase. The main advantage of this method is that it does not need pre-treatment using chemicals but the direct contact of the emulsion with the electrodes can cause electrochemical reaction and decrease the process efficiency. Yet, some researchers have found solution to this problem by passing the emulsion though a tube that has a low conductivity and found that it could reach a high efficiency of about 95%.

Table 2.3. shows the researchers approaches in using different technologies used to remove tight emulsion from synthetic wastewater stabilized using different surfactants. The type of surfactants and demulsifying agents, emulsion phase, the used technologies and the optimum removal of each treatment technology are summarized in the table. From these studies, it was shown that the stability of emulsion is affected by the used surfactant. In other words, different surfactants have different affinity to oil and water phases, thus, selecting the appropriate one is important in preparing the synthetic produced water. Another important parameter is the water salinity, in which it has a high influence in emulsion stabilization due to its effect on electrical double layer that will increase the electrical repulsive force and minimize coalescence hence increasing stability. It is also important to highlight that the HLB values were important in selecting the best demulsifying agents in order to achieve higher demulsifying efficiency.

Table 2. 3: *Technologies being used of separating o/w emulsions*

Application	Emulsion type	Type of oil	Stabilizing agent	Destabilizing agent	Optimum results	References
Coalescence arc plates (gravity separation)	O/W emulsion	Synthetic high salinity produced water using Catenex oil 11 (Shell)	Armac T	N/A	- The oil removal efficiency increases with increasing the arc length, since the arc length is proportional to the hydraulic retention time of the emulsion. - The optimum arc plate length for this study was found to be 14.6 cm, using a PW with an oil content of 400 mg/L flowing into the separator with flow rate of 4.0×10^{-5} m^3/s at 65°C.	[40]

Application	Emulsion type	Type of oil	Stabilizing agent	Destabilizing agent	Optimum results	References
DAF	O/W Emulsion	Catenex oil 11 (Shell, UK)	Non-ionic surfactant (Span 20)	Aluminium sulfate Ferric sulfate	- The neutral pH range was found to be the best pH condition for the destabilization process. - For rapid mixing, a velocity of 110 s^{-1} had achieved the best removal of oil. - The separation can be improved by prolonging the rapid mixing time up to 120 sec. - For a good DAF performance, an optimal flocculation time was found to be from 15 – 20 mins.	[41]

Application	Emulsion type	Type of oil	Stabilizing agent	Destabilizing agent	Optimum results	References
Alternating electric field	W/O Emulsion	Toluene (4 vol %)	Span 80 (sorbitan monooelate)	N/A	- The demulsification efficiency increases with increasing the alternating electric field up to 100 Hz - Square wave oscillation was better than the sin waves for achieving better separation, at frequencies between 10-50 Hz - Increasing the amount of organic phase, and the electric field intensity increases the rate of demulsification.	[42]

Application	Emulsion type	Type of oil	Stabilizing agent	Destabilizing agent	Optimum results	References
Continuous separation using micro-separator (Plate type)	O/W Emulsion	Shellsol D60 (Shell)	Non-ionic surfactant, Tween 80 (Aldrich)		- The structure of plate separator, consisting of hydrophobic and hydrophilic plates allows the interaction between droplets and the separator surfaces, and promotes separation. - The demulsification efficiency increases with residence time. - The device can be used for macro-equipment.	[43]

Application	Emulsion type	Type of oil	Stabilizing agent	Destabilizing agent	Optimum results	References
Comparison between PosiDaf and hybrid Coagulation— Flocculation/ DAF	O/W Emulsion	Motor oil (MO) Mobil Super 3000 5 W-40, and Metsuri chain oil (MCO).	CTAB (Acros Organics)		- The performance of PosiDAF with Poly-DADMAC and Epi-DMA was proven to be better that with CTAB - When comparing PosiDAF with Poly-DAMAC and Epi-DMA, it was shown that DAMAC has better separation with optimum dosage of 200 ppm that can reduce COD by 70% - Higher separation efficiency has achieved using PosiDAF with Poly-DAMAC over the conventional CF followed by DAF.	[44]

Application	Emulsion type	Type of oil	Stabilizing agent	Destabilizing agent	Optimum results	References
Ultrafiltration using tubular ceramic membrane	O/W Emulsion	Mixture of synthetic poly-α-olefin and tri- methylol propane trioleate ester (Spain)	Oleth-10 Brij76 CTAB (Sigma Aldrich, Germany)	N/A	- The oil permeation through membrane was negligible. - The ceramic tubular membrane was able to prevent the penetration of oil through the pores. - The COD removal/rejection by the ceramic membrane was 95% .	[45]

Application	**Emulsion type**	**Type of oil**	**Stabilizing agent**	**Destabilizing agent**	**Optimum results**	**References**
Thermal heating	O/W Emulsion	Bitumen samples obtained from production sites near Cold Lake in north-eastern Alberta	Nonylphenol Ethoxylate surfactants (Dow Surfactants)	N/A	- The heating process enhances the separation of the bitumen/water emulsion, and the interfacial tension decreases from ≈12 mN m^{-1} to a minimum value of ≈0.5 mN m^{-1} at the cloud point of 100 - 112 °C for $NP(EO)_{20}$ - Other Nonylphenol surfactants with lower degrees of Ethoxylate gives lower interfacial tension, such as $NP(EO)_{10}$ and $NP(EO)_{15}$ where the values were 0.14 and 0.79 mN m^{-1} respectively.	[46]

Application	Emulsion type	Type of oil	Stabilizing agent	Destabilizing agent	Optimum results	References
Magnetic oil-water separation for crude oil/ water Nano-emulsions	O/W Emulsion	Cyclohexane (analytical grade) Damao Chemical Reagent Co., China	Tween 60 (chemically pure) Kermel Chemical Reagent Co., China	Single-layer oleic acid-coated magnetite (Fe_3O_4@OA) nanoparticles	- The optimum demulsification efficiency was ~97% when the wettability of the magnetic nanoparticles was ~90° - The best pH range for separation process was found to in 4.0-7.5, while high pH values (8.0-11.0) exhibits lower separation efficiency. - Multiple step demulsification exhibit higher separation efficiency compared with the single-step demulsification using the same amounts of demulsifier.	[47]

Application	Emulsion type	Type of oil	Stabilizing agent	Destabilizing agent	Optimum results	References
Alternating electric field	W/O Emulsion	Mixture of organic solvent (Ethylbenzene, toluene, o-xylene, m-xylene, p-xylene, cyclohexane, and n-hexane)	Sorbitan monooleate (Span80, reagent grade)	N/A	- The square waveform electric field was more effective in separation process than the sin waveform electric field. - The demulsification rate increases with increasing the volume content of organic solvent. - Increasing the ionic strength by dissolution of electrolyte promotes demulsificatio. - This technique is effective in demulsification of water-in-oil emulsions.	[48]

Application	Emulsion type	Type of oil	Stabilizing agent	Destabilizing agent	Optimum results	References
Shirasu-porous-glass (SPG) membrane	W/O Emulsion	Kerosene	TGCR from Sakamoto Yakuhin Kogyo (Osaka, Japan)	N/A	- The demulsification efficiency decreases with increasing the surfactant concentration. - The optimum demulsification efficiency of W/O emulsion with a mean droplet diameter of 2.30 μm was found to be 91% at a transmembrane pressure of 392 kPa.	[49]

Application	**Emulsion type**	**Type of oil**	**Stabilizing agent**	**Destabilizing agent**	**Optimum results**	**References**
Hydrophilic polymer membrane	W/O Emulsion	Kerosene (Aldrich, USA)	Di-2-ethylhexyl phosphoric	n/a	- The demulsification efficiency is strongly based on membrane material and pore size, and transmembrane pressure. - Hydrophilic membrane with a pore size smaller than the emulsion droplet diameter was found to be the only possible type for demulsification among other tested types.	[50]

Application	Emulsion type	Type of oil	Stabilizing agent	Destabilizing agent	Optimum results	References
Hydrophilic Nano-sized ZrO_2 modified Al_2O_3 microfiltration membrane	O/W Emulsion	$20^{\#}$ (1g/L) Engine oil	Tween 80 and Span 80	n/a	- The modification of Al_2O_3 micro filtration with nano-sized ZrO_2 coating with thickness of about 100 nm makes the membrane more hydrophilic. - The nano-coating contribute to reducing the membrane fouling of oil droplets - The stable engine oil-water emulsion was successfully separated where the oil rejection reached above 97.8%.	[51]

Application	Emulsion type	Type of oil	Stabilizing agent	Destabilizing agent	Optimum results	References
Freeze/Thaw induced demulsification of W/O emulsion	W/O Emulsion	Chemical reagents (Petroleum ether 60-90, n-hexane, kerosene, toluene, and o-xylene)	Nonionic surfactant Span80 (sorbitan monooleate) from Tianjin Kermel Chemical Reagents	N/A	- Both cryogenic bath and dry-ice freezing methods are more effective than slow freezing methods. - In order to achieve proper rate of crystallization in emulsion, the optimal temperature of cryogenic bath should be lower than the solidification temperature. - Increasing the water content from 30% to 65% results in an increase in the demulsfication efficiency from 25% to 96%.	[52]

	- Increasing the water droplet size from 2.7 to 7.3 μm results in an increase in the demulsfication efficiency from 74% to 95%. - Regardless the type of oil phase, the demulsification efficiency can reach up to 85% with 60% water content.

Application	Emulsion type	Type of oil	Stabilizing agent	Destabilizing agent	Optimum results	References
Electrochemical Coagulation	O/W Emulsion	SAE 10W-40 motor oil (Mobil Oil)	5% Legsolve (Walter G. Legge Co.)	N/A	- The emulsion was stabilized by the addition of Legsolve surfactant, and the turbidity had a positive correlation with the oil content in the emulsion with a correlation coefficient of 1.78 FAU/(mg/L). - Sodium chloride was added to provide the needed conductivity. - The oil droplets colloid and float, then they were removed by skimming.	[53]

	- The treatment process operated with a continuous current of 2 A and duration was reduced from 4 hr to 4 min. - The effluent turbidity is below than 16 FAU which is beyond the detection limit of the spectrophotometer.

Application	Emulsion type	Type of oil	Stabilizing agent	Destabilizing agent	Optimum results	References
Gravitational settling (Using Cone-shaped centrifuge tube)	W/O Emulsion	Land Balayium crude oil (produced from Petrobel Co., Egypt)	N/A	Schiff base surfactant	- It is recommended to use demulsifying agents with high HLB value. - The separation efficiency found at its maximum when the concentration of the destabilizing agent was 100 and 250 ppm.	[54]

Application	Emulsion type	Type of oil	Stabilizing agent	Destabilizing agent	Optimum results	References
Demulsification by electrical field	O/W Emulsion	Chemical reagents (Toluene, dodecane, carbon tetrachloride, benzyl alcohol, benzyl ether)	Sodium dodecyl sulfate (SDS, ionic surfactant), and (Tween 20, nonionic surfactant) Junnsei Chemical Co. Ltd		- The electric field was sufficient to destroy the emulsion. - Destroying of electrical double layer was done by inducing the ions adsorbed on the oil droplet surface to migrate in water. - The emulsion is characterized by $\zeta = -60$ mV at 298 K and an electrical field of ∼14 V/cm was able to achieve 63% separation in 20 sec.	[55]

Application	Emulsion type	Type of oil	Stabilizing agent	Destabilizing agent	Optimum results	References
Ultrafiltration using tubular ceramic membrane	O/W Emulsions	Vegetable oil (Fuchs 165, Fuchs Lubricantes S.A.)	Anionic surfactant (Dioctyl sulfosuccinate sodium salt, 98%) and a non-ionic surfactant (Merpol OJ, an ethoxylated alcohol) Sigma Aldrich Co.	N/A	- The cross-flow velocity of 2.5 m/s was enough to minimize the concentration polarization. - The COD permeate flux was higher when the large pore size membrane was used. - The permeated phase contains less than 1000 mg/L of organic content. - Since surfactant with low CMC values are preferred, it was recommended to use 300 kDa cut-off membrane.	[56]

From the discussion made previously and the studied used applications, and reference to our objective of this study and because there is no much study in this area in the literature, we will focus in this study on the novelty of ceramic membrane in treating tight oil-in-water emulsions and suspended colloids. The literature shows that ceramic membrane is a promising technology in the field, and it can be scaled up to serve as a solution in treatment of wastewater.

CHAPTER 3: MATERIALS AND METHODS

In this chapter, the experimental setup is explained in detail together with the materials used and methods followed to carry out the required work.

3.1. Experimental Setup

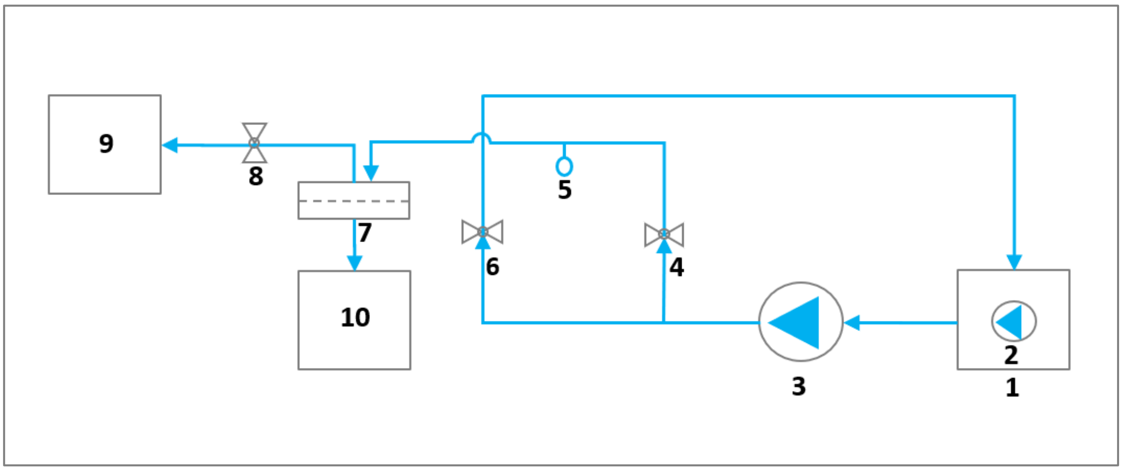


Figure 3. 1: Schematic diagram for the experimental setup

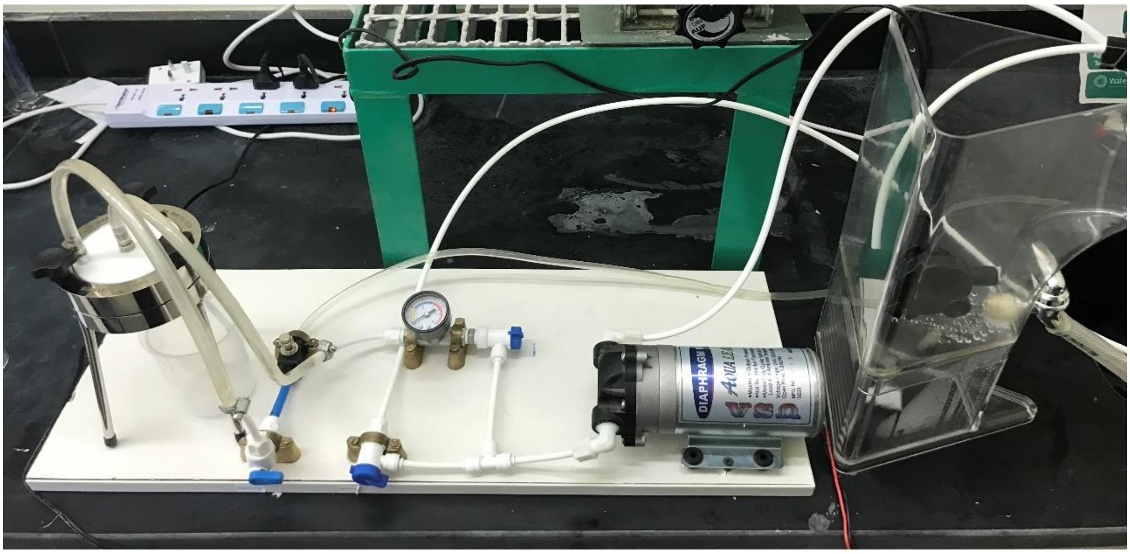


Figure 3. 2: Actual experimental setup

Table 3. 1: *Nomenclature of experimental setup*

Part #	Part Name	Part details
1	Feed tank	Three-litre tank
2	Liquid filter	220-240 V 50 Hz/ 6.6 W Flowrate: 440 LPH
3	Reverse osmosis pump	Max. pressure: 125 psi 24 VDC/0.23Amp Flowrate: 1.35 LPM
4	Feed valve	90-degree ball-valve
5	Gauge	n/a
6	Bypass valve	90-degree ball-valve
7	Ceramic membrane unit	Stainless steel disc holder
8	Retentate valve	90-degree ball-valve
9	Sink	n/a
10	Filtrate tank	250-ml beaker

In this study, bench scale micro-filtration unit was designed to meet the purpose of removing tight emulsions using ceramic membrane. The unit, as shown in Figure 3.1, consists of a reverse osmosis pump (3) connected to a three-liter feed container (1). A liquid filter (2) was installed inside the feed tank to insure a continuous homogenous medium and stabilize the emulsions during the operation. The feed pipeline was connected to a feed valve followed by bypass (6) and retentate (8) valves. The bypass valve was installed to act as a backup and to insure a continuous flow during the operation, while the retentate valve was installed to get rid of the concentrate rejected from the membrane unit through the sink. When the system is in operating mode, both feed and bypass valves should be kept open; where the feed is directed to the membrane unit to get treated while the fluid from bypass is circulated to the feed tank. When the feed flows through the ceramic membrane, the treated water known as filtrate is collected in a filtrate beaker (10), while the rejected fluid is directed to the sink. All fittings used in this setup have a diameter of 0.25 inch.

3.1.1. Ceramic membrane unit

Figure 3. 3: Ceramic membrane

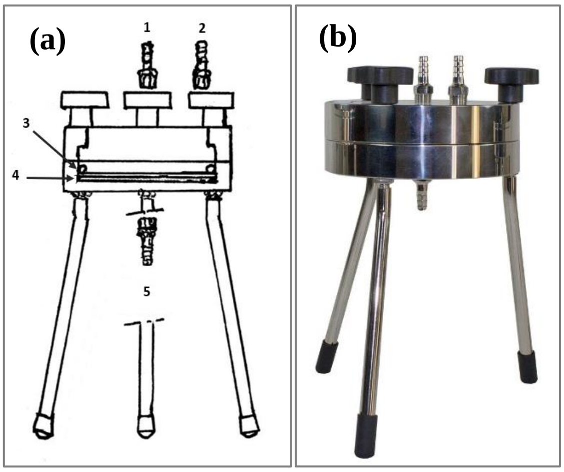


Figure 3. 4: (a) Schematic diagram for the ceramic membrane unit, (b) Actual ceramic membrane unit

Table 3. 2: *Nomenclature of ceramic membrane unit*

Part #	Part description
1	Product inlet (o/w emulsion)
2	Product outlet (concentrate)
3	O-ring
4	Evacuation spiral
5	Ceramic membrane
6	Filtrate

A cross flow microfiltration unit was supplied from SterliTech (USA) and used in this study. The microfiltration unit, as shown in Figure 3.4 (a), consists of spirlab crossflow disc holder, ceramic membrane, o-ring and evacuation spiral. The membrane disc holder is made of stainless steel, and consists of one inlet where the feed flows in, and two outlets; the concentrate and the filtrate outlet. An o-ring piece is placed between the ceramic membrane and the disc holder cover to insure a tight fit and prevent any leakage. The ceramic membrane is placed over a spiral shaped piece that forces the substance to circulate tangentially through the filtrate outlet (5). The ceramic membrane, as shown in Figure 3.3, is made of zirconium dioxide-titanium dioxide (ZrO_2-TiO_2) with a 2.5mm thickness and 90mm diameter. The membrane active layer is titania, and the active area was calculated to be 29.05 cm^2 using AutoCAD software as shown in Figure 3.5.

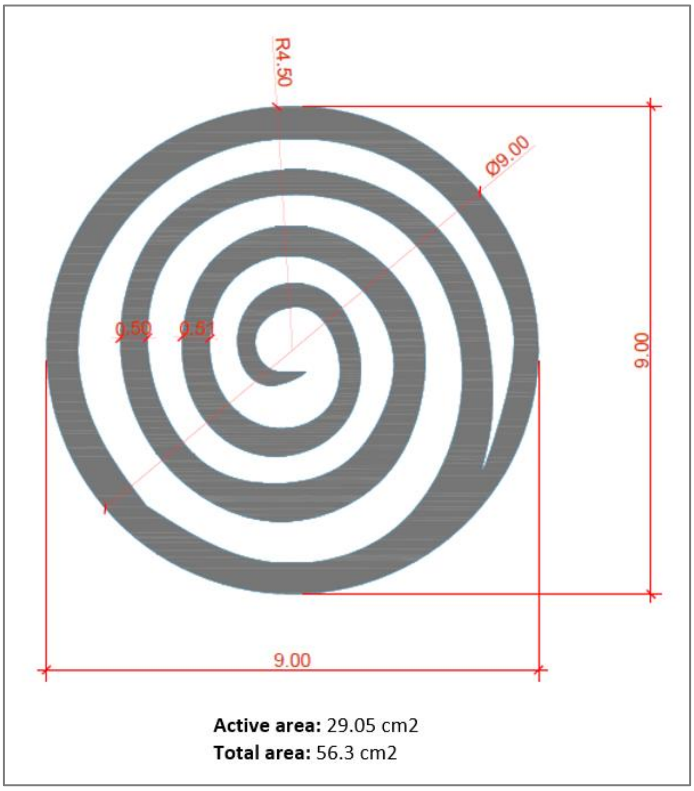


Figure 3. 5: Active filtration area of ceramic membrane obtained from AutoCAD

The characteristics of both ceramic membrane and the disc holder are summarized and tabulated in table 3.3.

Table 3. 3: *Technical specifications of ceramic membrane and disc holder*

Membrane	
Material	ZrO_2-TiO_2
Thickness	2.5 mm
Diameter	90 mm
Total area	56.3 cm^2
Active area	29.05 cm^2
Average pore diameter	3.5 μm
Cut off	0.45 μm
Maximum running pressure	4.0 bar
Operating temperature	<350° C
Ceramic Disc Holder	
Type	SpirLab
Material	Teflon and Stainless steel 316L
Diameter	90 mm
Operating pH	0-14
Operating temperature	<130° C

3.2. Materials

Oil-in-water emulsion was formulated using 10% vol. engine diesel oil obtained from Waqood petrol station (Qatar) as an oil source with a density of 0.863 g/ml, while 2% v/v of Ethylene tetrakis supplied by Sigma Al-drich, Co. (Germany) was used as a surfactant to stabilize the emulsions, with chemical formula [-CH2N[(-CH2CH2O-)x[-CH2CH(CH3)O-]yH]2]2 as shown in Figure. The density of the surfactant is 1.02 g/ml and it has a HLB value between 1-7, and a surface tension of 36 dyn/cm. Colloids were added in the second part of this study to test the ability of the microfiltration system in removal of suspended matters, thus, lab-grade bentonite clay was supplied from Sigma Al-drich Co. (Germany) and added to the emulsions mixture, chemically represented as $(Na)_{0.7}(Al_{3.3}Mg_{0.7})\ Si_8O_{20}(OH)_4.nH_2O$, and the bentonite detailed compositions are summarized in table 3.4. Other chemicals such as Sodium hydroxide NaOH and Nitric acid HNO_3, that was used in the ceramic membrane cleaning process, were obtained from BDH Chemical.

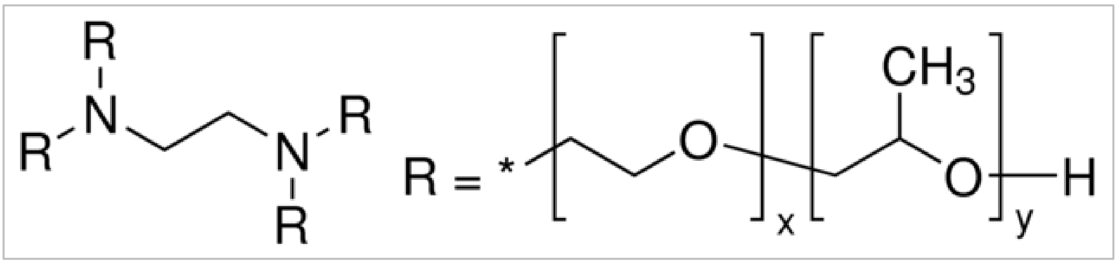


Figure 3. 6: Chemical structure of Ethylene tetrakis

Table 3. 4: *Chemical composition of Bentonite*

Composition	Weight Percent (%)
Na_2O	2.43
K_2O	0.255
Fe_2O_3	3.25
MgO	2.67
Al_2O_3	24.05
SiO_2	58.02
CaO	0.75
FeO	0.31

3.3. Methodology

In this section, the methods in preparing and analyzing the samples are described in detail.

3.3.1. Oil-in-Water Emulsions Preparation and Stability Test

At the early stages of this study, stability test of oil-in-water emulsions was desired to find the optimum surfactant concentration that can form a stable tight emulsion for a period not less than five minutes. The was prepared by mixing the surfactant with deionized water at a speed of 3500 rpm for 10-15 minutes, then the oil was added by titration to form a uniform distribution of oil droplets and to ensure a formation of tight emulsions. In order to select the optimum surfactant concentration, the stability of oil-in-water emulsions using different surfactant concentrations ranging from 0.5% vol. up to 5% vol. was investigated by monitoring the phase separation with time as shown in Figure 3.6. The chemical compositions of o/w emulsions at different surfactant concentration ranges are highlighted in table 3.5.

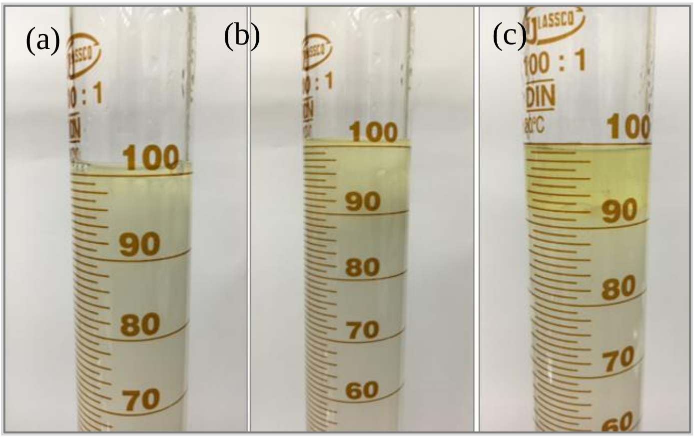


Figure 3. 7: Monitoring the phase separation with time of 2% vol. o/w emulsions (a) phase separation after 5 minutes, (b) phase separation after 30 minutes, (c) phase separation after 60 minutes.

Table 3. 5: *Chemical compositions of o/w emulsions at different surfactant concentration ranges*

Surfactant volume (ml)	**Water volume (ml)**	**Oil volume (ml)**	**Total volume (ml)**
0.25	89.75	10	100
0.5	89.5	10	100
0.75	89.25	10	100
1	89	10	100
2	88	10	100
3	87	10	100
5	85	10	100

After selecting the optimum surfactant concentration, which is 2%, all other parameters were fixed and repeated every time we run the experiment. The oil, deionized water, and surfactant percentage was 10%, 88%, and 2% respectively. Both water and surfactant were mixed every time at 3500 rpm and the oil was added by titration as shown in Figure 3.7.

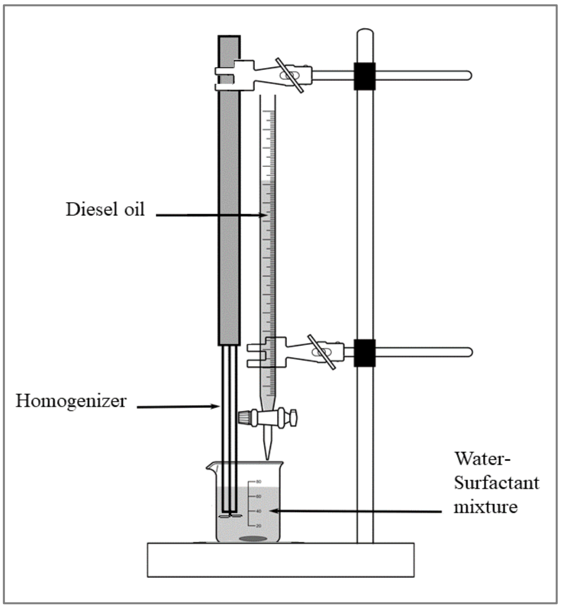


Figure 3. 8: Oil-in-water emulsions experimental setup

This procedure was also followed when deionized water was replaced with water-bentonite mixture to form oil-in-water emulsions with colloids. The water-bentonite mixture was prepared by adding 1.5g of bentonite to 1L of water and mixing to using the homogenizer at 3500 rpm for 15 minutes. The mixture is then used as a water base by taking from it 88% for preparing the oil-in-water emulsions with colloids.

3.3.2. Zeta Potential and Interfacial Tension Analysis

The stability test was followed by interfacial tension and zeta potential analysis to study the behavior of oil-in-water emulsions at different surfactant concentration ranges.

a) Interfacial Tension Analysis

The interfacial tension test was desired to check the degree of miscibility of the emulsion; where higher values indicates break of emulsion and lower values indicates a high emulsion stability. Pendant-drop method was followed in this analysis using Drop Shape Analyzer DSA100 (KRÜSS GmbH – Germany) (Figure 3.8 (b)); where diesel oil represents the bulk liquid and the water-surfactant mixture represents the liquid inside the suspended needle. To determine the interfacial tension value, the needle was submerged gradually into the bulk liquid and the software calculated the interfacial tension from the shadow image of the pendant drop as shown in Figure 3.8 (a) using Young-Laplace equation. This procedure was repeated for different surfactant concentration ranges from 0.25 vol.% to 3 vol.%, and the values were determined and studied in detail in the results and discussion chapter.

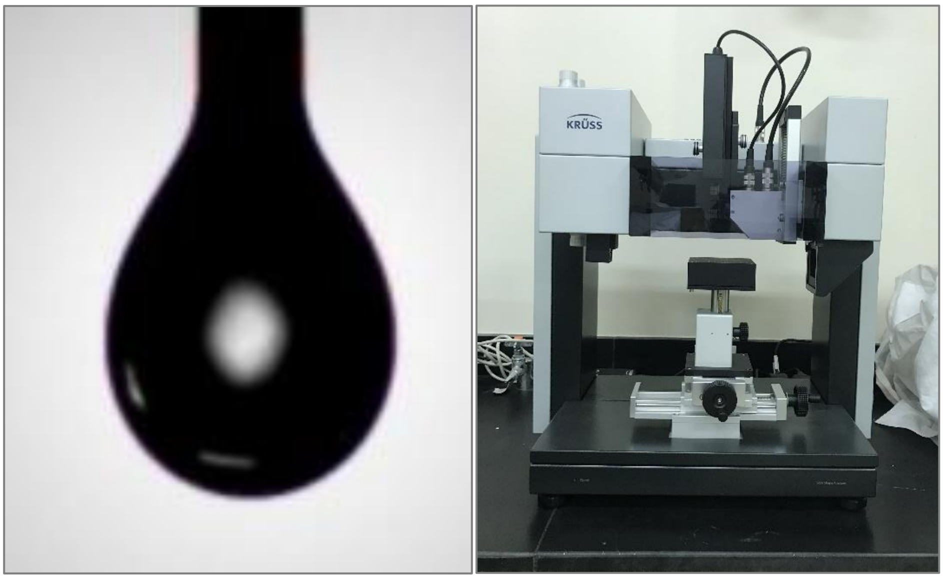


Figure 3. 9: (a) Pendant drop method image taken by the drop shape analyser DSA100, (b) Drop Shape Analyzer DSA100 device

b) Zeta-potential Analysis

The oil-in-water emulsions was prepared at different surfactant concentration ranges from 0.25 vol.% to 3 vol.% and diluted 100 times using deionized water. The zeta potential of the diluted samples was measured using Zetasizer ZEN3600 (Malvern Instruments Ltd., UK) at room temperature (Figure 3.9). Two measurement techniques are followed in Zetasizer ZEN3600, they are: Electrophoresis and Laser Doppler Velocimetry, and sometimes called Laser Doppler Electrophoresis. The method relies on determining the particle velocity and using the electrical field applied in measuring the zeta potential value. The measured value gives an indication of whether the particles are going to flocculate and break the emulsions, or the emulsions will remain stable; where high values indicates a tight stable emulsions ∓60 and low values indicates a phase separation. The diluted samples were prepared and tested, and the device was set to iterate at least 12 times to get accurate values.

Figure 3. 10: Zetasizer ZEN3600 (Malvern Instruments Ltd., UK)

3.3.3. TOC Analysis

When oil-in-water emulsions is treated using ceramic membrane, it is important to measure the total organic carbon to analyze the filtrate quality. To do so, the water samples before and after treatment were collected and diluted 1000 times prior testing them using Total Organic Carbon Analyzer TOC-L (Shimadzu, Japan) Figure 3.10. The device is designed to measure the total organic carbon by oxidizing organic compounds in the sample tube, this is done under 680°C following the combustion catalytic oxidation method. The oil-in-water emulsions was prepared at the optimum surfactant concentration, and the experiment was run at five different pressures ranging from 0.2bar to 1.4bar. The filtrate was collected over 30 minutes; in the first 10 minutes it was collected every 1 min followed by a 10 minutes interval collection, to have a total of 12 samples from each run. The samples were diluted and placed in the TOC Analyzer device, where they were oxidized and tested. A comparison of the analyzed values at the different selected pressures will be discussed in detail in the results and discussion chapter.

Figure 3. 11: Total Organic Carbon Analyzer TOC-L (Shimadzu, Japan)

3.3.4. Turbidity Analysis

For turbidity analysis, 1.5g/L of bentonite was prepared and treated using the ceramic membrane. The experiment was run at five different pressures ranging from 0.2bar to 1.4bar, and the samples were collected in an interval of 10 minutes over a period of 1 hr., to have a total of 6 filtrate samples at the end of each run. The turbidity values of both waste and treated water samples were measured using Hach 2100N bench top turbidity meter Figure 3.11. The device uses monochromatic light-emitting diode (LED) as a light source in analyzing the turbidity of the sample. The samples were collected and diluted 1000 times before and after the treatment, and the values were summarized and compared in results and discussion chapter.

Figure 3. 12: Hach 2100N bench top turbidity meter

3.3.5. Membrane Performance Test

One of the major problems in membrane technology is fouling; where solution or particles get deposited on membrane surface and the pores get blocked, hence, the membrane performance get degraded. Thus, there was a need to check the membrane permanent fouling and its minimal sustainable performance. To do so, the membrane was cleaned after each run and its performance was tested as described in detail below.

a) Membrane cleaning process

Each experiment run was followed by the cleaning process to bring the membrane to its initial status before running the next experiment, this process is called regeneration. An alkaline and acid substance were selected to be used for cleaning process as per the cleaning procedure mentioned in SterliTech manual; where sodium hydroxide was selected as the alkaline substance and nitric acid represents the acid substance. After running the experiment with emulsions, the membrane is cleaned with deionized water then submerged in a sodium hydroxide solution for 30 minutes and under 80°C. The membrane is then submerged in deionized water for 30 minutes under a room temperature before being submerged in a nitric acid solution for another 30 minutes under 80°C. After that, the membrane is submerged again in deionized water for 30 minutes under room temperature. This process was repeated after each run, and then the membrane performance was tested by running the experiment using deionized water and monitoring the filtrate flux. The filtrate flux of a virgin ceramic membrane was also measured to check the membrane fouling. The chemical compositions and conditions of the cleaning process are summarized in Table 3.6.

Table 3. 6: *Chemical compositions and conditions of membrane cleaning process*

Substance	**Amount**	**Temperature (°C)**	**Duration**
Alkaline (NaOH)	20g/L	80	30 minutes
Acid (HNO_3)	5ml/L	80	31 minutes
Deionized water	1L	Room temperature	32 minutes (two times)

b) Membrane performance test

To perform the membrane performance test, deionized water at room temperature was used through the run. When water is passed through the ceramic membrane unit and the filtrate is collected, the fouling factor can be examined, and the membrane performance can be determined. The filtrate flux was collected at each pressure ranging from 0.2bar to 1.4bar over a 1 min period. The collected filtrate flux readings after each cleaning process is tabulated and compared with those of the virgin membrane. The membrane performance and the measurements are compared and discussed in detail in results and discussion chapter.

CHAPTER 4: RESULTS AND DISCUSSION

In this chapter, the stability of Ethyene tetrakis surfactant in stabilizing oil-in-water emulsion using diesel oil was investigated. Several analyses were performed to study the emulsion stability and the optimum surfactant concentration was determined. Diesel was used oil source while, bentonite was used as the suspended matter source. A cross-flow ceramic microfiltration membrane is used to separate tight oil-in- water emulsion stabilized using Ethylene tetrakis. The performance of the membrane was tested, and the permanent permeating loss was therefore determined. The results obtained from the experimental work will be discussed in detail in the following sections.

4.1. Stability Analysis

Stability is an important parameter that needs to be achieved in preparing tight emulsion, since the actual produced water contains highly stable emulsions which cause a major concern to the environment, thus, obtaining a highly stable emulsion in this study was one of the main objectives to have reliable results. Both oil and deionized water concentration were fixed, and the surfactant concentration was changed to test its effect on the emulsion phase separation. The surfactant concentration (v/v) ranges from 0.0-5.0% as follows: 0%, 0.25%, 0.5%, 0.75%, 1.0%, 2.0%, 3.0%, and 5.0%. Figure 4.1 shows the influence of the surfactant concentration on the emulsions stability, as the surfactant concentration increase the phase separation decreases and the stability increases. When oil and water are mixed without adding surfactant, the emulsion started the separation immediately and after one minute 15% of the oil content was separated. The effect of both surfactant concentrations 0.25% and 0.75% in stability was minimal, as the emulsion start to separate immediately, and the separation keeps increasing gradually with time. The surfactant started to be effective at a concentration of 1%, as the emulsion remain stable for the first 2.5 minutes, this followed with a minimal break in emulsion with a percentage of 2% after 3 minutes. Starting from 5 to 30 minutes the emulsion breakage remains constant as the phase separation was 6% along this period. The emulsion started to be tight emulsion at a surfactant concentration 2% and more, where no change in the phase separation was noticeable.

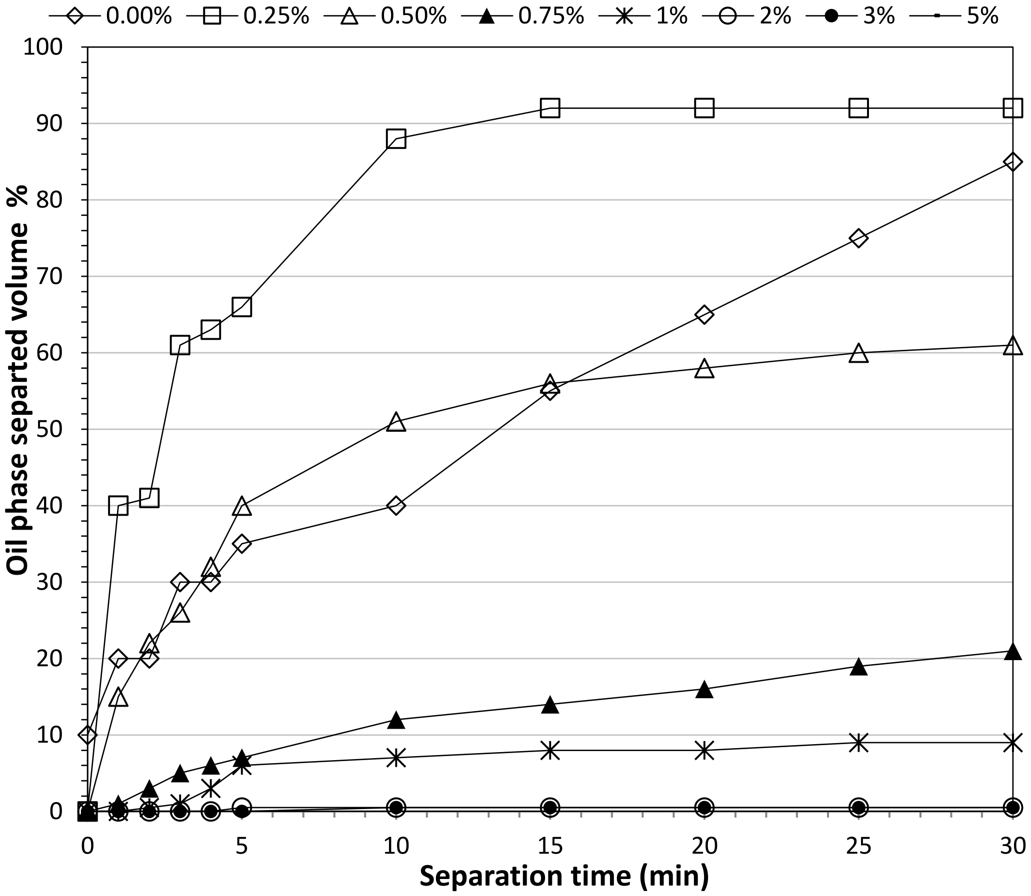


Figure 4. 1: The effect of changing the surfactant concentration in stabilizing O/W emulsion

Alternative way to describe the effect of phase separation affected by the surfactant concentration with time is shown in Figure 4.2. The graph monitored the phase separation volume after 5 minutes, 10 minutes, and 30 minutes. As it is clearly seen, when the surfactant concentration is below 2%, the emulsion was not stable. All the emulsions with surfactant concentrations below 2% had similar trend with a continuous decrease in phase separation towards the 2% surfactant concentration. This proves that, since the prepared oil-in-water emulsion of 2% surfactant concentration shows produce tight emulsion, and can last stable for at least 30 minutes, which is a sufficient time to test the membrane performance in presence of the air filter installed inside the feed tank (i.e. for mixing purpose), this concentration was selected to be the optimum surfactant concentration for all experiments.

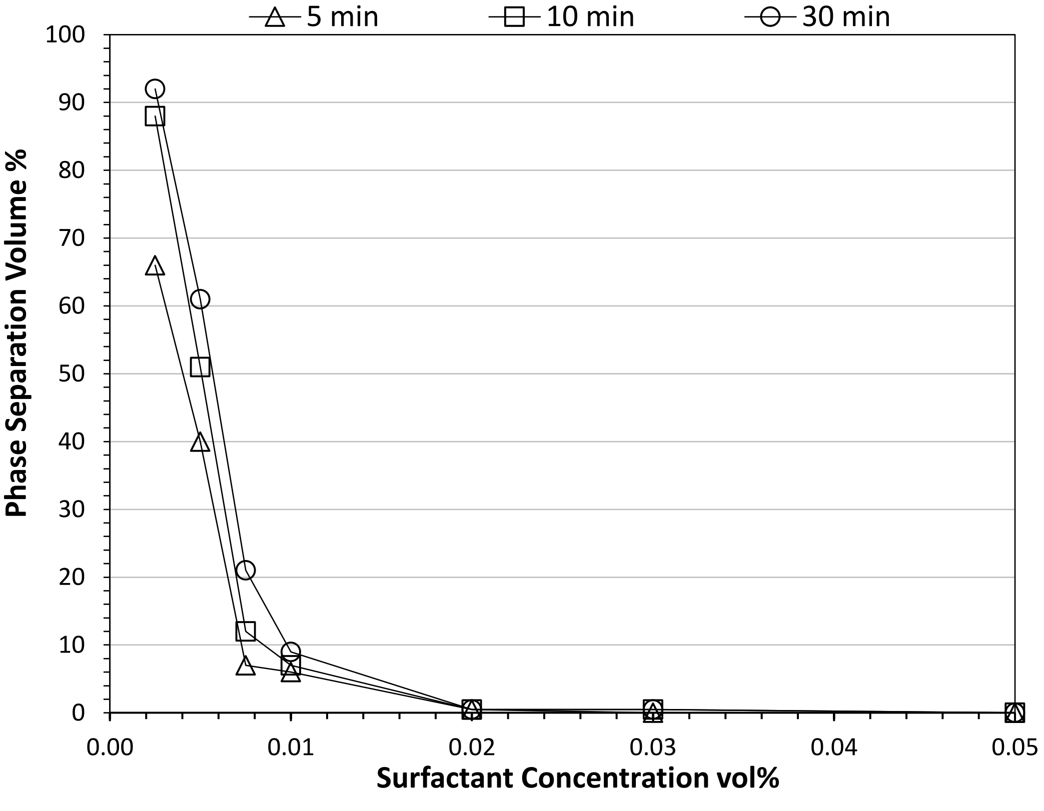


Figure 4. 2: Monitoring the O/W emulsion phase separation at three different time intervals

4.2. Zeta Potential Analysis

In this section, the zeta potential of oil-in-water emulsion in presence of different surfactant concentration ranges from 0.25-3.0% is plotted as shown in Figure 4.3. The values of zeta potential showed an increase in the magnitude from -11.8 mV in the negative direction at a surfactant concentration of 0.25% until it reaches its maximum value of -20.1 mV at a concentration of 0.75%. This value was then decreased slightly and remain almost stable (~-16 mV) with an increase in the surfactant concentration from 1-3%.

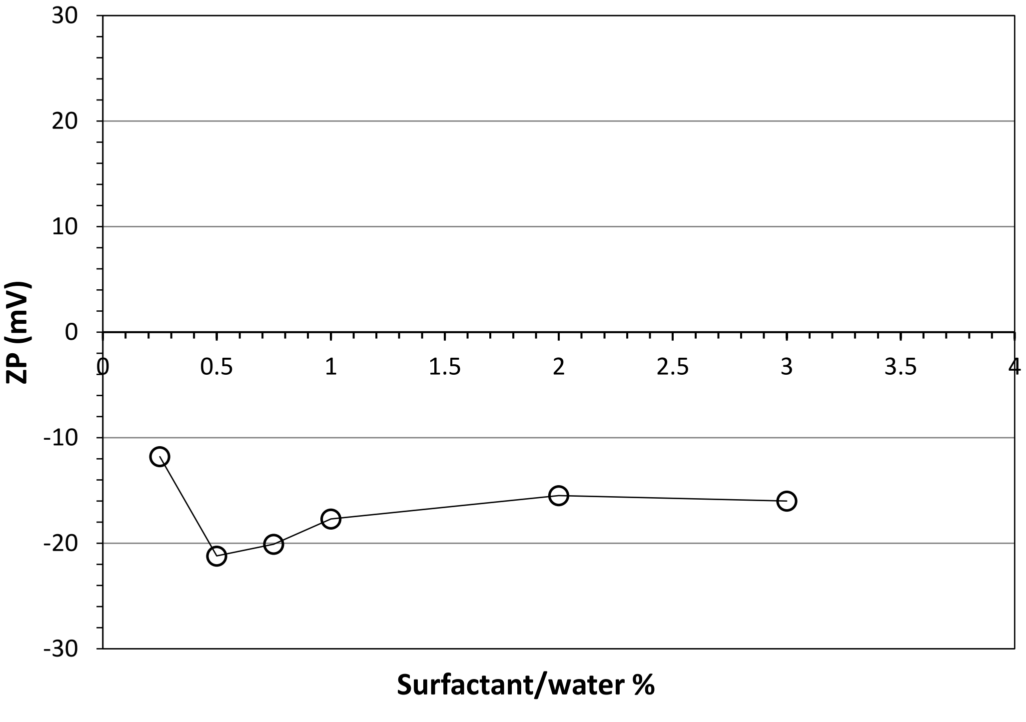


Figure 4. 3: Effect on zeta potential of O/W emulsion with increasing the surfactant concentration

The zeta potential results are in good agreement with stability analysis in this study. The results showed that the zeta potential values remained almost constant in negative value at concentration above 1 % and similarly of the phase separation results in Figure 4.3 showed that the phase separation % significantly decrease up to surfactant concentration of 1% and then almost remain constant.

The results also are in line with the literature. Jha et al. [57], used diesel oil in brine solution in presence of KCl and two different stabilizing agents; xanthan gum and aluminium stearate, the surfactant type can also influence the stability. Both surfactant worked similarly but the strength of them varies slightly; where xanthan gum showed a better stability of the emulsion with a zeta potential ranges from −78.32mV at a concentration of 0.3% and it increases in the negative direction with increasing the surfactant concentration until it reaches −168.71mV at a concentration of 0.9%. While the minimum and maximum zeta potential values obtained from using aluminium stearate surfactant were −68.28mV and −121.9mV simultaneously. This means that, the use of surfactant in preparing emulsion/synthetic produced water together with other additives have a considerable impact on the stability of the emulsion. Matos et al. [45] showed similar results, where they examined the effect of changing both the surfactant type and concentration on the oil-in-water emulsion. They used 1% of lubricant oil mixture (synthetic poly-α-olefin and tri- methylol propane trioleate ester) and different concentration of three surfactants; anionic surfactant glycolic acid ethoxylate oleyl ether (Oleth-10), nonionic surfactant olyethylene glycol octadecyl ether (Brij 76), and cationic surfactant hexadecyltrimethyl ammonium bromide (CTAB). The results showed that the cationic surfactant (CTAB) have a higher strength in stabilizing the emulsion than the other two types where the zeta potential values at different surfactant concentrations ranges from 0.25-10 (times CMC) showed an increase from +80 to +90mV. Using the anionic surfactant (Oleth-10) showed an increase in the negative direction with increasing the concentration from −45 to −50mV. However, using the nonanoic surfactant (Brji) showed a less negative zeta potential values, where the values were decreasing in the negative direction from −40 to −20mV with increasing the concentration. This means, choosing the appropriate surfactant for the used oil is important to have a tight stable synthetic emulsion, and studying the performance of each type is important as well. It also can be concluded that differences in the zeta potential values for the oil in water emulsions are due to the differences in the density and molecular weights of the used surfactant.

4.3. Interfacial Tension Analysis

Interfacial tension is an important analysis that gives an indication whether the emulsion is stable, or flocculation and phase separation will take place. As shown in Figure 4.4, it was observed that increasing the concentration of the surfactant decreases the interfacial tension (IFT) significantly. The IFT value of oil-in-water emulsion without using the surfactant was found to be 16 Nm/m, whereas by increasing the surfactant concentration from 0.25-3% the IFT values started to decrease. At a concentration of 0.25%, the IFT value was 4Nm/m before decreasing to 0.97Nm/m at a concentration of 2%. The IFT value continued in decreasing with increasing the surfactant concentration until it reaches 0.99Nm/m at 3%.

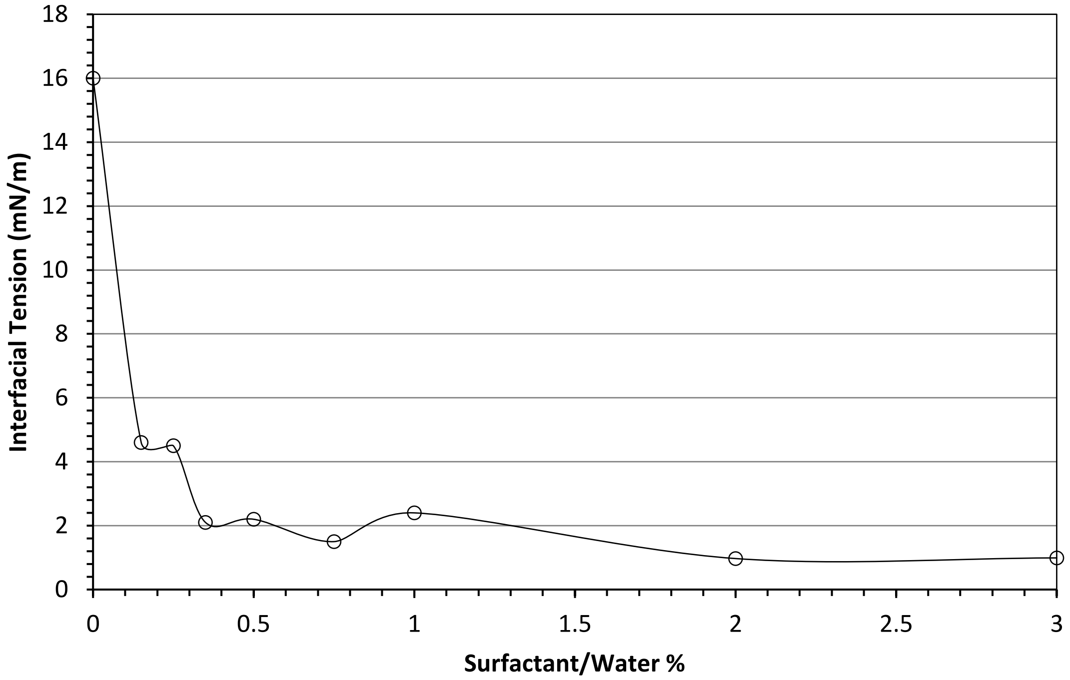


Figure 4. 4: Effect of interfacial tension in O/W emulsion with increasing the surfactant concentration

The decrease in the interfacial tension values by adding the surfactant is due to the adsorption of the surfactant at the oil-water interface which lowers the surface tension between the two immiscible liquids, hence, increasing the stability. As a result, since the interfacial tension values started to be constant in the concentration range 1-3%, and according to the former zeta potential and stability test results, the optimum surfactant concentration was selected to be at 2%. Because all stability tests prove that the higher stability was obtained at a surfactant concentration of 2% and above. According to Jha et al. results [57], the use of both Xnthan gum and Aluminium stearate showed a similar behavior of our work; where the interfacial tension of both surfactants showed a decrease in the values with increasing their concentration. Xnthan gum showed a better stability, where the lowest IFT value (11.69Nm/m) was obtained at a concentration of 0.8% while the maximum stability obtained from using Aluminium stearate was at 3% with a value of 43.29Nm/m. This proves again that each surfactant will react differently with the emulsion medium, although they all should have a similar behavior towards stabilizing the emulsion. It is worthy to mention these findings are in good agreement with zeta potential measurements. At surfactant concentration of 2%, both the values of zeta potential and interfacial tensions remain almost constant as the surfactant concentration increases.

4.4. Ceramic Membrane Performance

The performance of crossflow microfiltration ceramic membrane in treating oil-in-water emulsion was tested to investigate its effectiveness in removal of oil droplets and colloids. In the following sections, the results obtained from different experiments will be discussed in detail.

4.4.1. Oil-in-Water Emulsion: Permeate Flux

The effect of changing transmembrane pressure on permeate flux over time using 0.45μm pore size ceramic membrane, and 2% surfactant concentration of oil-in-water emulsion was investigated. Since the maximum operating pressure of the ceramic membrane disc holder is 4 bars, and it was observed that at 2 bar the system was not stable, thus, for safety purposes five different pressure readings were selected below 2 bars, starting from 0.2 to 1.4 bar. Figure 4.5 shows a steadily increase in the permeate flux with increasing the transmembrane pressure, where the initial permeate flux at the lowest pressure, 0.2 bar, was 98 L/hr.m^2 and it increased to reach 475L/hr.m^2 at 1.4 bar. At each run, the permeate flux shows a gradual decrease with time; where at 0.2 bar the flux decreases from 98 L/hr.m^2 to reach 41L/hr.m^2 at the end of the run. This is due to the effect of concentration polarization phenomena, where oil droplets start to accumulate on membrane surface and inside the pores by convection, causing a higher resistance to flow, and decreases the permeate flux. The formation of cake layer on the membrane surface, when occurs, is due to the exceedance of the membrane critical flux, which is a function of pressure, both of membrane and foulant characteristics, and resistance to mass transfer as expressed by Equation 4.1.

$$J = \frac{\mathrm{TMP}}{\mu(\mathrm{R_m}+\mathrm{R_{ads}}+\mathrm{R_{rev}}+\mathrm{R_{irrev}})} \qquad \text{Eq. 4.1.}$$

where J is the critical flux, TMP is the transmembrane pressure, μ is the fluid viscosity, $\mathrm{R_m}$ is the membrane hydraulic resistance, $\mathrm{R_{ads}}$ is the resistance due to adsorption, and both $\mathrm{R_{rev}}$ and $\mathrm{R_{irrev}}$ are the resistances due to the reversible and irreversible fouling.

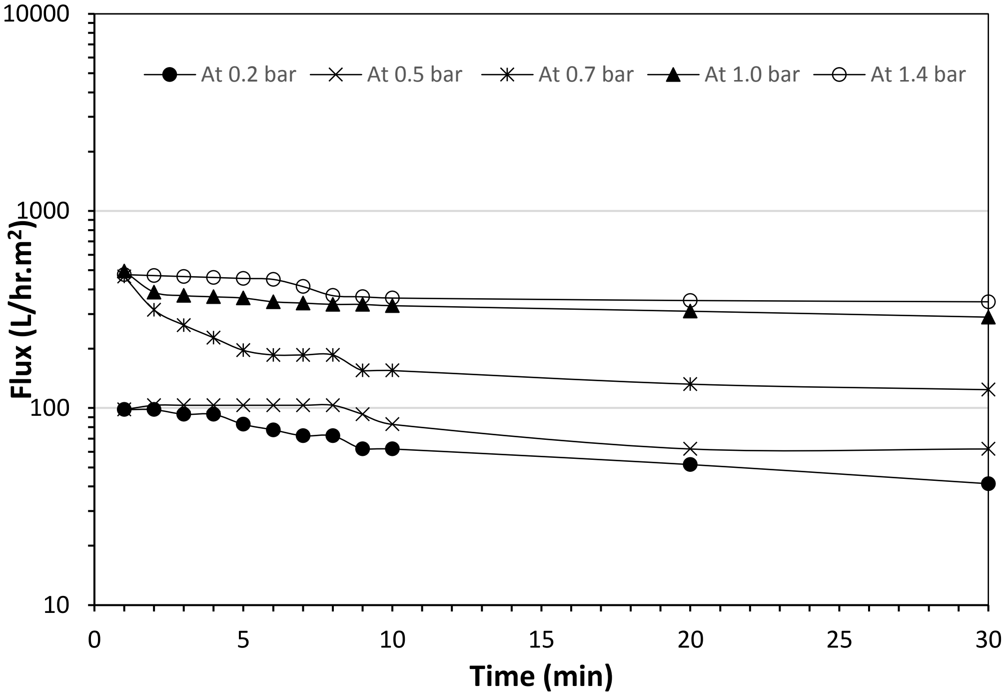


Figure 4. 5: Permeate flux at different transmembrane pressures and optimum surfactant concentration (2%) using 0.45 μm ceramic membrane

Since the transmembrane pressure and the fluid characteristics in each run are constant, then the critical flux is a function of resistance, hence, when the resistance increases the flux decreases. It is worth to mention that cleaning the ceramic membrane will never return it to its initial performance, and, it was noticed that at early stages, fouling was high compared to the last two runs. This indicates that after several runs, the membrane will sustain its performance, and the fouling factor will decrease until it reaches a point where there is no noticeable change. As shown in Figure 4.5. All runs show similar behavior, and the permeate flux decreases gradually until it reaches a steady state region between 10 and 30 minutes; the region where the change in permeate flux with time is negligible or zero.

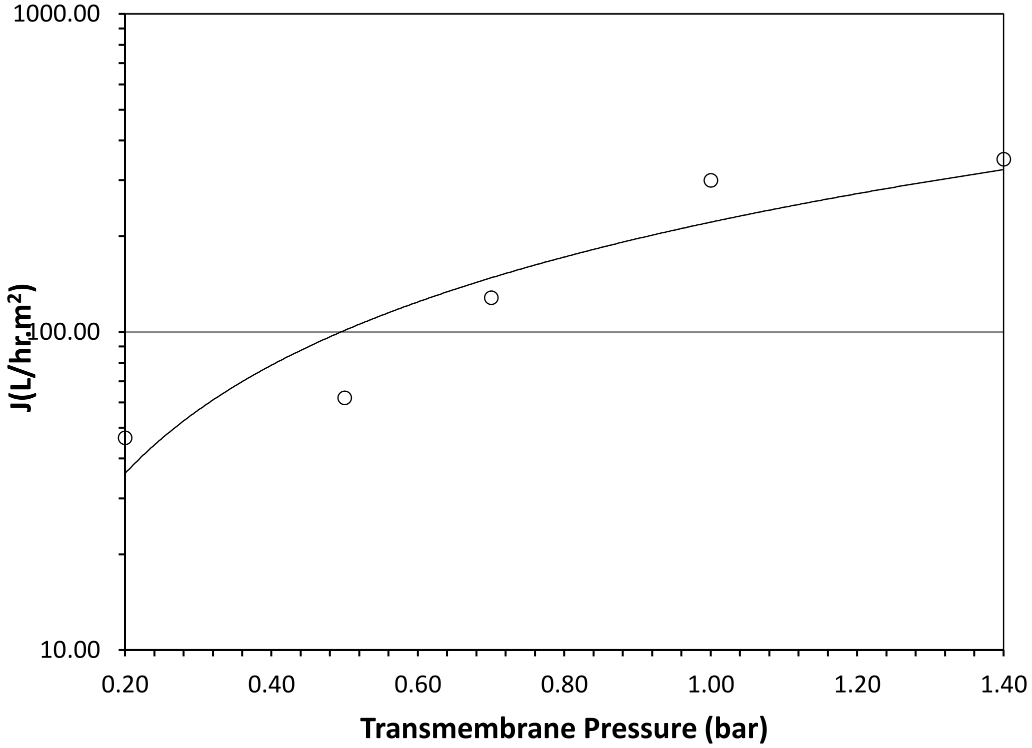


Figure 4. 6: Permeate flux at different transmembrane pressure at steady state region

Figure 4.6 shows the effect of transmembrane pressure on the steady state permeate flux of 2% oil-in-water emulsion, where it indicates a non-linear relationship between the transmembrane pressure and the flux, in which the permeate flux at steady state was 46.47L/hr.m^2 at 0.2bar before it increases to reach 348.54L/hr.m^2 at 1.4bar. This is due to the concentration polarization phenomena as described earlier.

4.4.2. Oil-in-Water Emulsion: TOC Analysis

The influence of transmembrane pressure on the removal of tight oil-in-water emulsion with 2% surfactant concentration was investigated through the TOC measurements. The obtained data from TOC analyzer indicates that the microfiltration ceramic membrane is a feasible method in treating tight emulsion, where the removal efficiency of the system reaches ∼91% as shown in Figure 4.7. The membrane performance showed similar results under the five-different transmembrane pressure, with slight decrease in the efficiency with increasing the pressure, and the lowest removal percentage was ∼79% at pressure 1.4bar. The resulted TOC removal efficiency showed a better performance compared with results found in literature; where Ebrahimi et al. [58] studied the performance of 0.1μm and 0.05μm tubular ceramic membrane as a pre-treatment process for the oil-field produced water treatment and found the TOC reduction efficiency to be 38% for the 0.1μm pore size membrane while the 0.05μm membrane was not able to reduce the TOC.

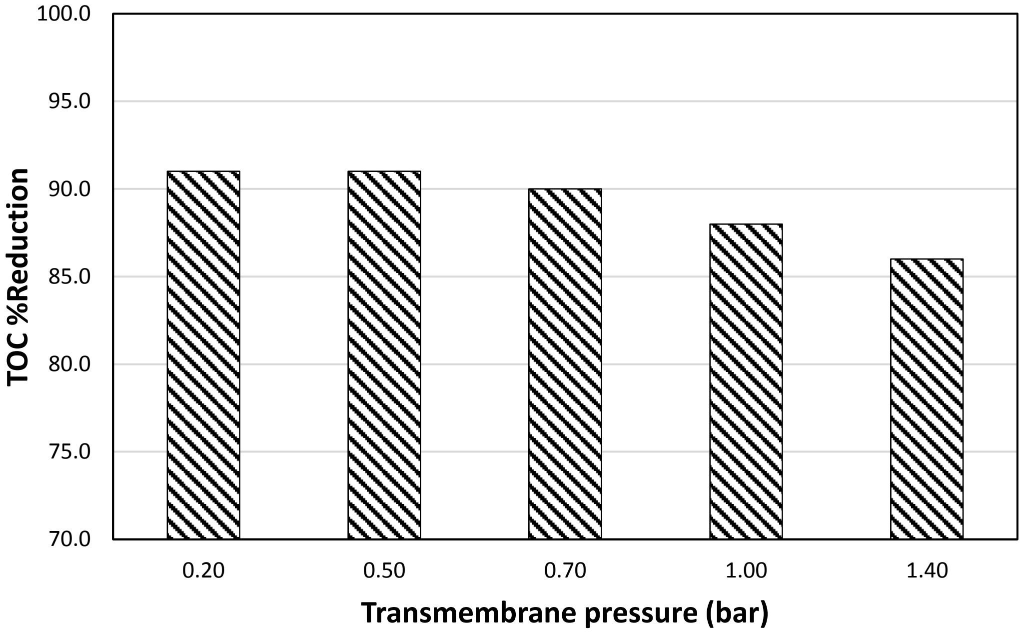


Figure 4. 7: Maximum TOC reduction from treating O/W emulsion using ceramic membrane.

4.4.3. Oil-in-Water Emulsion: Membrane Performance

Each run is followed by a cleaning process; where the system is flushed with deionized water, and the membrane is submerged in alkaline solution followed by an acid solution before being cleaned finally with deionized water. The cleaned membrane is then tested using deionized water, to examine its performance and check its sustainable lifetime, by investigating the effect of changing the transmembrane pressure in permeate flux. Figure 4.8. shows the effect of fouling in lowering the permeate flux after each run; where the minimum and maximum permeate flux of the virgin ceramic membrane was ~600L/hr.m^2 at 0.2 bar and 2168L/hr.m^2 at 1.4 bar simultaneously.

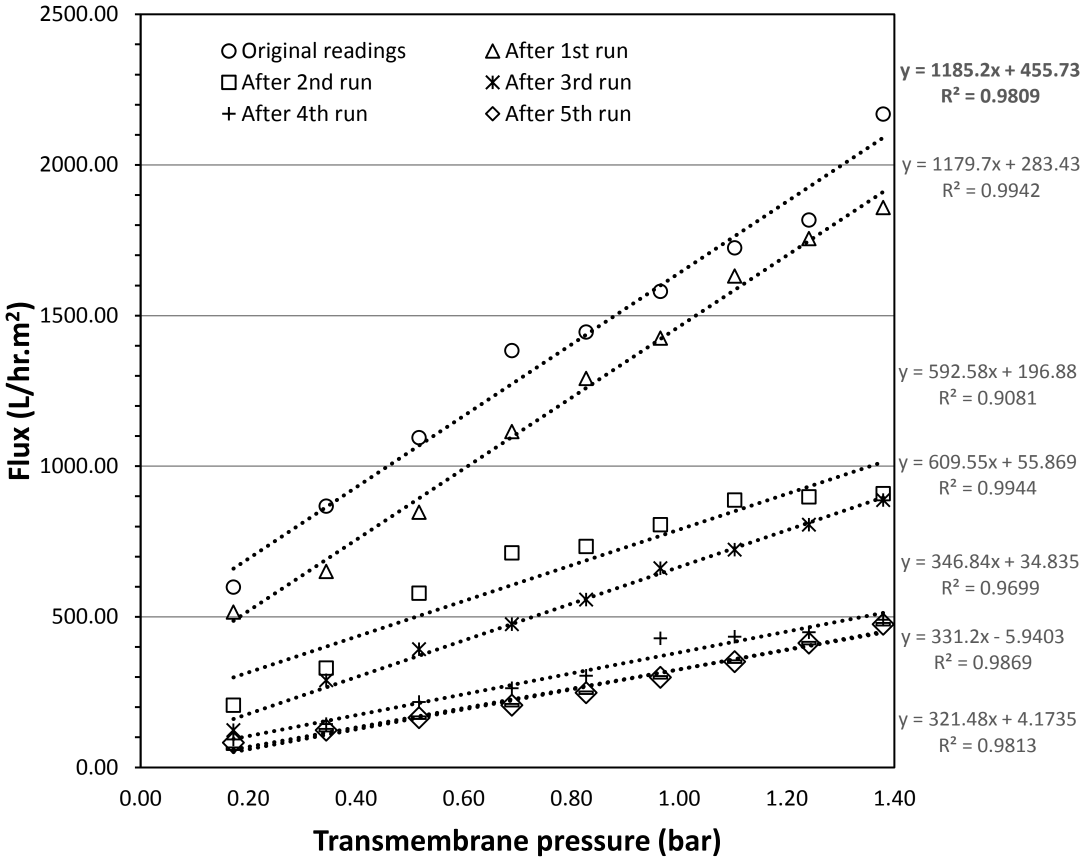


Figure 4. 8: Monitoring the ceramic membrane performance after each run of treating o/w emulsion

The flux is then decreased gradually until it reaches a point where the change was minimum, which occurs after the fourth run where the minimum permeate flux was 62L/hr.m^2, and the maximum was 475L/hr.m^2. As it is clearly shown in Figure 4.8, there was a rapid decrease in the membrane performance at the early stages, and the cleaning process did not return the membrane performance to its initial state. The amount of foulants remained inside the membrane pores explains the permanent fouling phenomena; where some of the foulants could not be removed by normal cleaning process and begins to dominate the total membrane resistance. With time, the permanent fouling value will decrease until it reaches the minimal point where no change will be noticeable beyond this point. The slope of the membrane performance plot, which is the permeate flux to pressure ratio represents the permanent permeating loss. The permanent permeating loss values were obtained from the membrane performance plot, and plotted versus the number of experimental runs (see Figure 4.9).

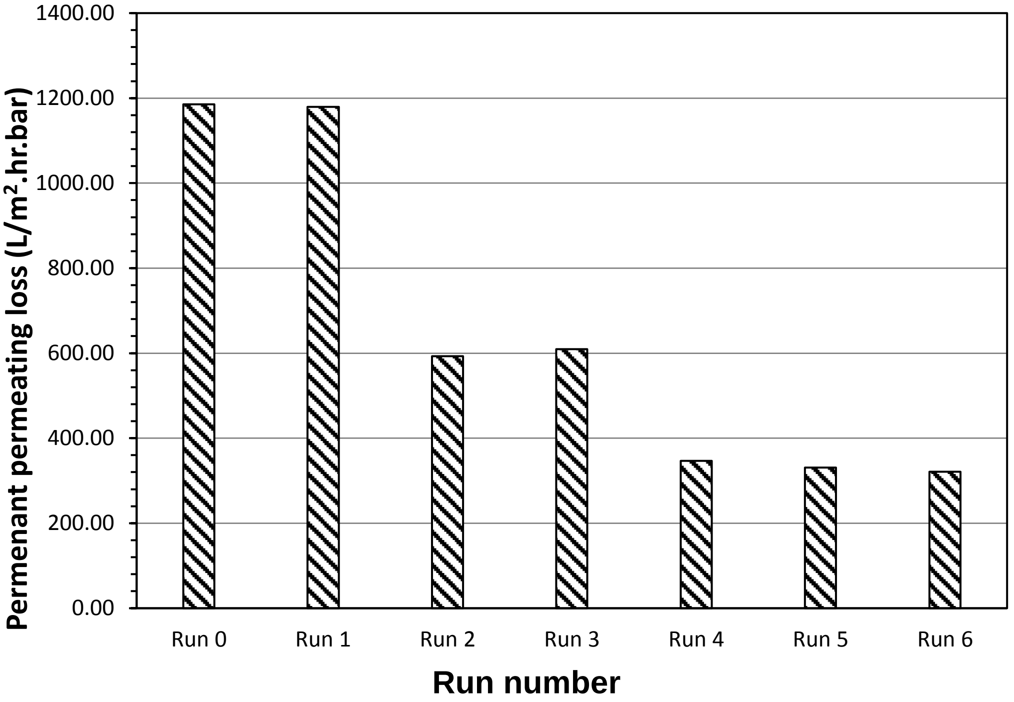


Figure 4. 9: Permanent permeating loss of regenerated membrane from treating o/w emulsion

Figure 4.9, shows the permanent permeating loss of the 0.45μm ceramic membrane; where it decreases from 1,200 bar.m^2.hr/L to ~320 bar.m^2.hr/L after 6 runs. As it is shown in the plot, the last three runs had almost the same permanent fouling values, which indicates that the maximum permanent permeating loss value of the ceramic membrane is $\sim$320 bar.m^2.hr/L, and that the lowest permeate flux that can be obtained from this ceramic membrane in treating 2% O/W emulsion is 62L/hr.m^2 under the lowest transmembrane pressure 0.2bar.

4.4.4. Colloids: Bentonite Stability Test

The performance of ceramic membrane was investigated using bentonite as a source of colloids, and the membrane removal efficiency was tested using the 0.45μm ceramic membrane. A new virgin ceramic membrane was used through the whole process, similar to what has been done in treatment of oil-in-water emulsion. To do so, it was important to select the optimum pH value that will provide a suitable medium for the bentonite to stay suspended. The effect of changing pH on turbidity, and zeta potential was investigated using 1.5g/L of bentonite. Figure 4.10 indicates that increasing the alkalinity of the mixture promotes the suspension which can be clearly seen from the turbidity and zeta potential values.

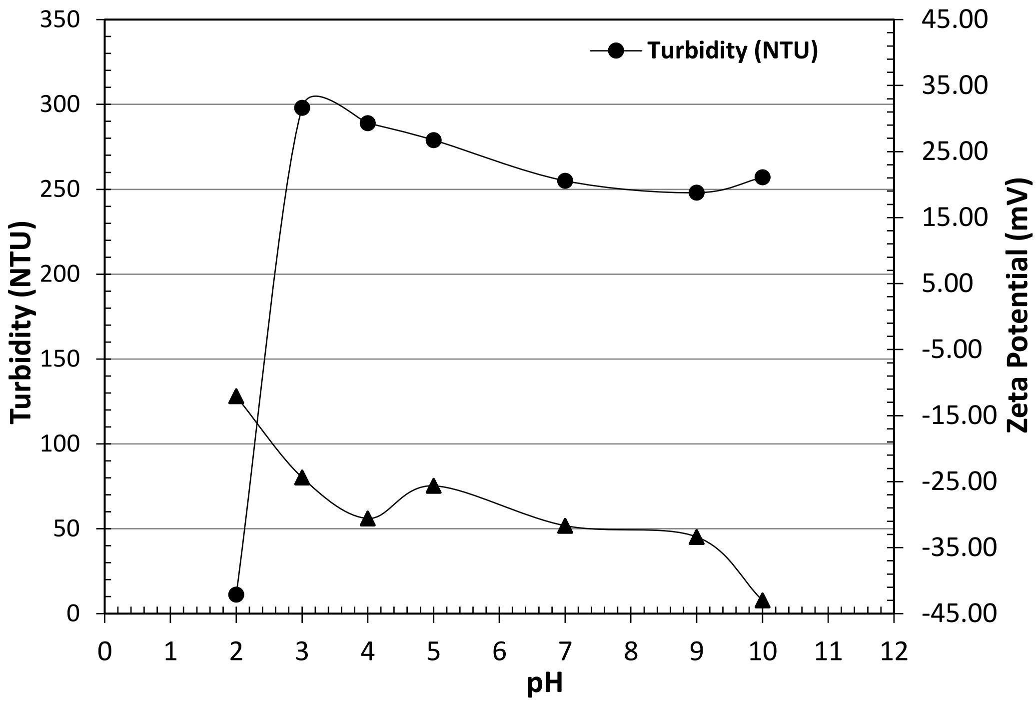


Figure 4. 10: The effect of changing pH on both turbidity and zeta potential values of the bentonite mixture

It is observed that under acidic conditions the zeta potential tends to decrease, in other words, the colloids tend to aggregate forming sediments in the beaker. This was emphasized by the turbidity readings, where the turbidity was at its lowest values in the in the acidic region. Thus, increasing the alkalinity of the mixture, drags the mixture behavior towards the suspension, where it is clearly seen at a pH value of 9.0 the zeta potential value reaches −35mV (i.e highly stable) and the turbidity was 250 NTU.

4.4.5. Permeate Flux of Stable Colloid Suspensions

The bentonite mixture was treated using new virgin ceramic membrane to investigate its performance and study different parameters similar to the former discussion in the o/w emulsion part. Thus, the effect of changing the applied transmembrane pressure on the permeate flux of the bentonite mixture was studied as illustrated in Figure 4.11.

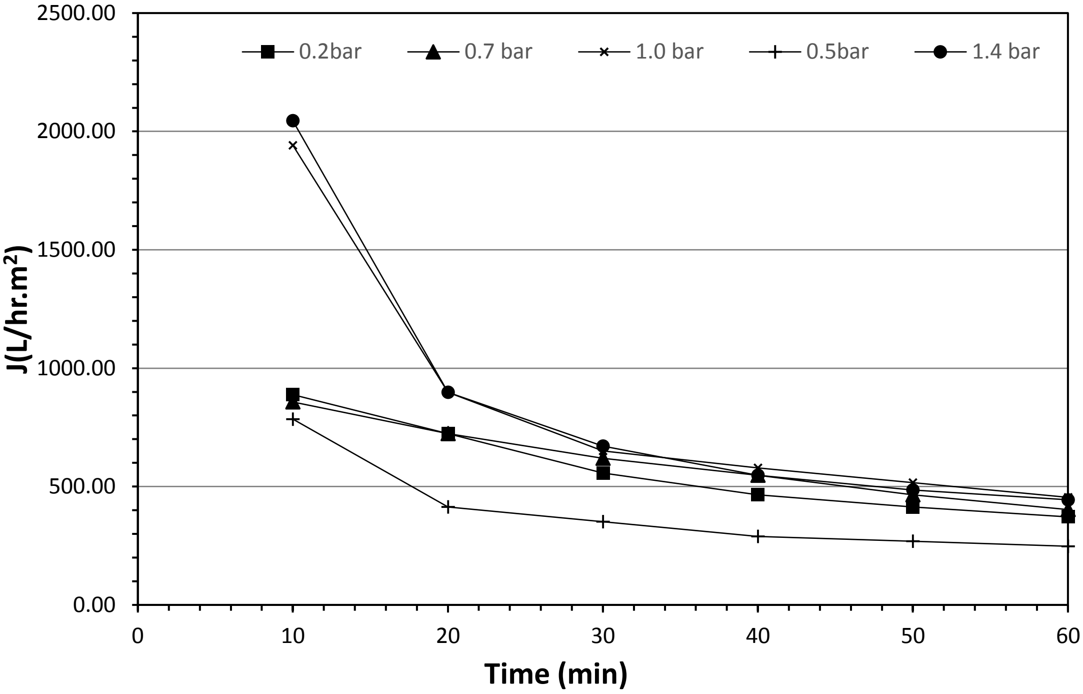


Figure 4. 11: Permeate flux at different transmembrane pressures as a function of time for stable bentonite dispersions using 0.45mm ceramic membrane

As it is shown in the plot, each run last for one hour, and represent a pressure value ranging from 0.2-1.4bar. It is noticed that increasing the pressure increases the permeate flux, which was discussed earlier in the o/w emulsion permeate flux part. Nevertheless, the minimum and maximum flux obtained at 1.4bar was 444L/m^2.hr and 2,044L/m^2.hr simultaneously, which is higher than those obtained from the treatment of o/w emulsion. In other words, the reduction of suspended solids by the ceramic membrane is higher than the reduction of oil particles. This is mainly due to the membrane pore size and type, since the microfiltration membranes are known to be able to remove all suspended solids, but partially remove oil particles. Accordingly, the permeate flux value obtained from treating the bentonite mixture at steady state region, which is between 30-60 minutes, are higher compared to those of the o/w emulsion as shown in Figure 4.12.

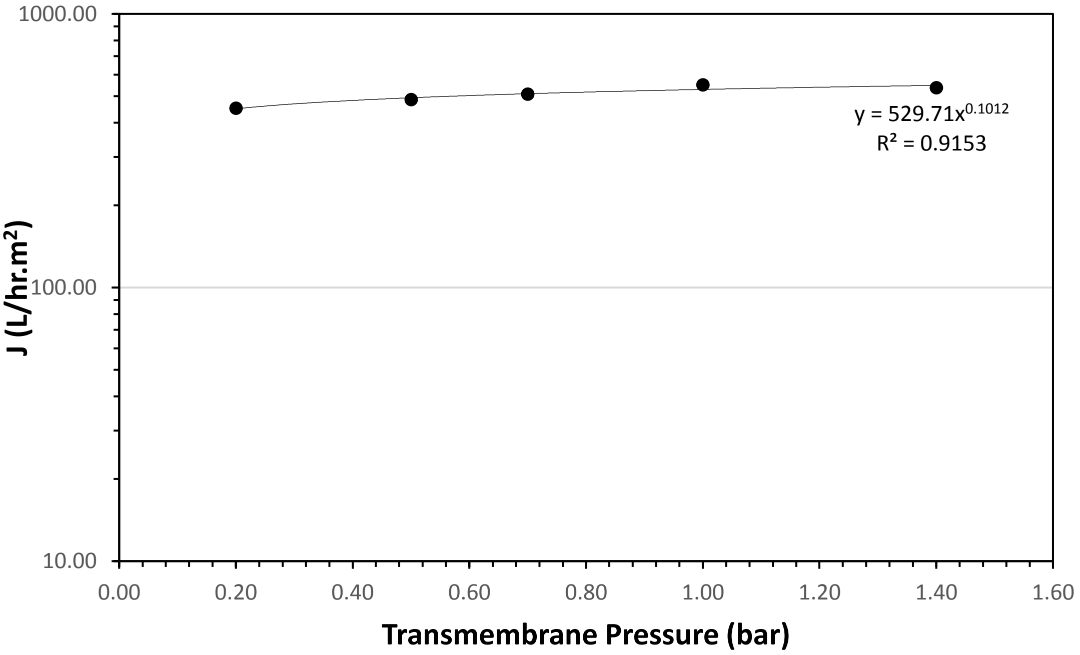


Figure 4. 12: Permeate flux as a function of transmembrane pressure at steady state region

Figure 4.12 illustrates that the flux change with pressure at steady state is non-linear, though; the trend shows a gradual increase in flux. This means that the occurred concentration polarization was not significant compared to what has been found in the o/w emulsion treatment, which can be proved by the minimum and maximum flux at steady state where the flux increased from 452L/hr.m^2 to 537L/hr.m^2.

4.4.6. Turbidity Analysis for Suspended Colloids.

To investigate the membrane efficiency in rejection of suspended solids, turbidity analysis was conducted for all the collected samples, together with the initial bentonite mixture before treatment. A bentonite mixture of 1.5g/L was prepared, and pH was kept at 9, and the turbidity value of the feed was found to be 260 NTU. This mixture was treated using 0.45μm ceramic membrane under different pressure values ranging 0.2-1.4bar. It was shown that at all pressure, the rejection of suspended solids was significant and reached almost ~99.9%, having permeate turbidity of 0.78-1.3 NTU under all pressure ranges. The resulted rejection efficiency was better than what is found in literature; according to Zsirai et al. [59] where they investigated the effectiveness of SiC and TiO_2 membrane in turbidity rejection at four different membrane sizes, 50 kDa, 0.04μm, 0.5μm, and 2μm. It has been found that the rejection efficiency ranges from 83-95%, where the higher efficiency owed to the lower pore size membranes which are the ultrafiltration membrane, while the lower efficiency was obtained from the microfiltration membranes. The membrane module, its characteristics and the fluid characteristics, the pressure and the flow rate all are influencing the efficiency of removal, though; it is worth to mention that the 0.45μm ceramic membrane can effectively remove the suspended solids with very minor permeation.

4.4.7. Membrane Performance for Suspended Colloids

In order to check the membrane performance in treating and removal of suspended solids, the cleaning process was implemented after each run. The membrane permeate flux is then measured with time using deionized water and under different pressures from 0.2-1.4bar. Figure 4.13 shows how the membrane performed after each run using virgin ceramic membrane, which indicates that in the first three runs the membrane was fouled and a concentration polarization takes place, before reaching the dead point where the drop in the flux was negligible.

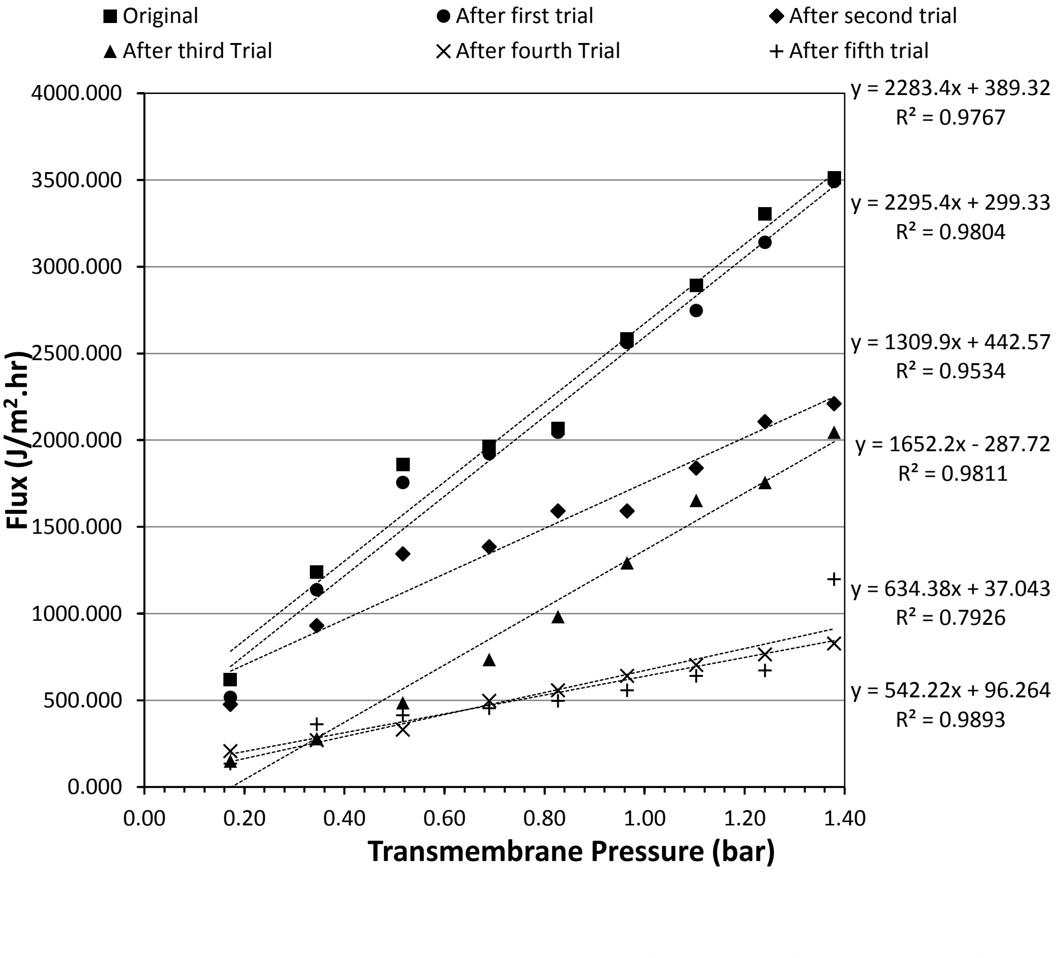


Figure 4. 13: Monitoring the ceramic membrane performance after each run of treating bentonite mixture

In comparison with the previous discussion of the membrane performance after treating the o/w emulsion, it was found that treating suspended colloids shows a better performance. As the maximum flux obtained from regenerating the fouled membrane with oil droplets was 475L/m^2.hr, where 1198L/m^2.hr was obtained from regenerating the fouled membrane with colloids. This is due to the nature of foulants, where oil droplets together with the surfactant posse a sticky viscus nature that may need not only chemical cleaning, but also mechanical cleaning to get rid of the deposited particles on surface and in membrane pores. On other hand, the colloidal particles are solid state particles, and with chemical treatment the membrane was able to sustain a better performance compared with the one used in o/w emulsion. Figure 4.14 shows the permanent permeating loss resulted from using the membrane for several treatments.

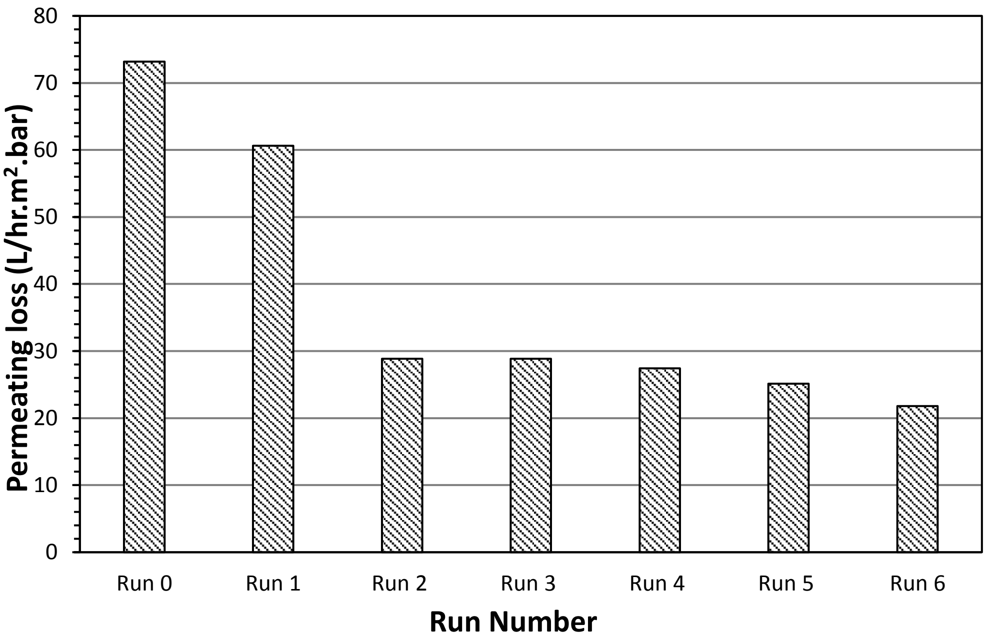


Figure 4. 14: Permanent fouling of regenerated membrane from treating stable bentonite-water mixture

The plot shows the effect of fouling on membrane; in the first run it indicates that the concentration polarization phenomena did not take place, and cleaning the membrane regenerate its performance to its virgin condition. This was followed by a sharp decrease in the performance, which means that more foulants were deposited and cause drop in flux. when the membrane was cleaned again, it removed a good portion of the foulant, which can be clearly seen in the third run. The permanent fouling kept in increasing until it reaches a point where the change was minimal.

4.4.8 Mixture of O/W Emulsion and Suspended Bentonite mixture: Permeate Flux

According to the first two experimental setups, where the permeate flux was investigated using two different solutions; o/w emulsion, and bentonite solution. The third experimental setup consist of preparing the o/w emulsion using bentonite mixture instead of deionized water. The solution was prepared and the same procedure in investigating the permeate flux was followed, and the obtained results are summarized in Figure 4.15.

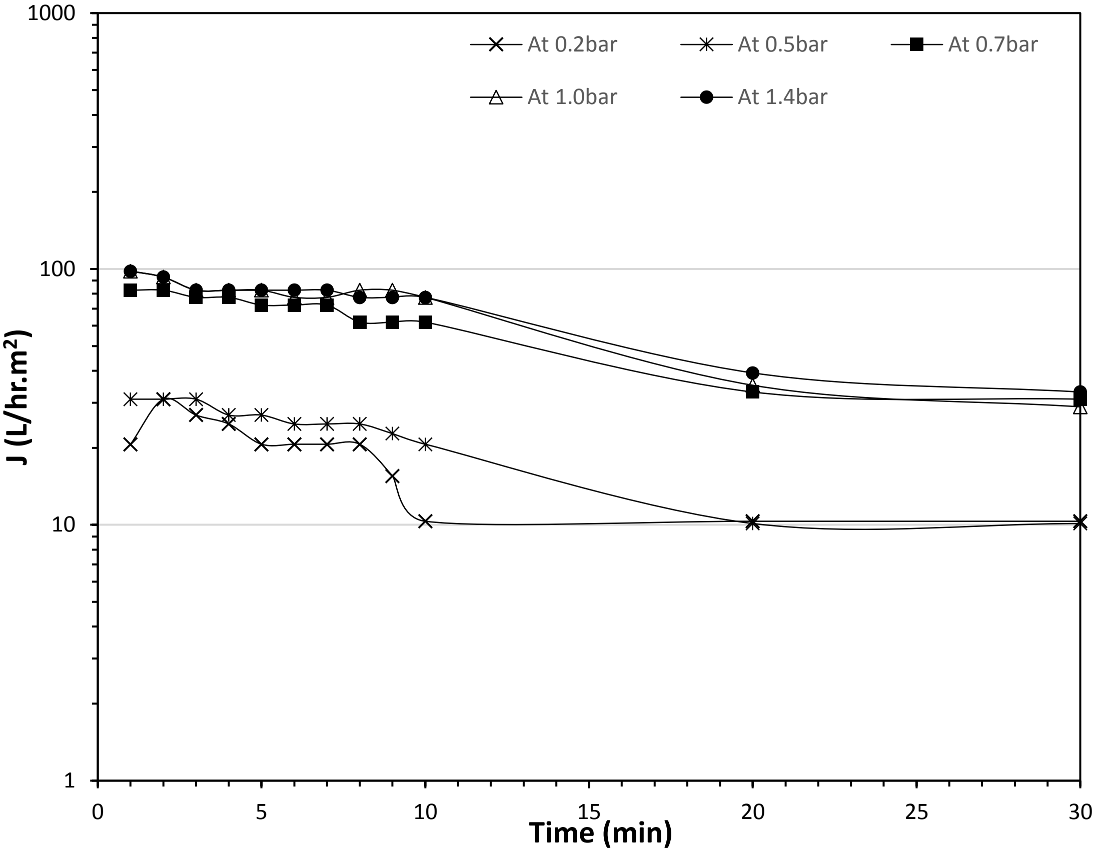


Figure 4. 15: Permeate flux at different transmembrane pressures of treating mixture of o/w emulsion and bentonite mixture using 0.45μm ceramic membrane

As it is shown in Figure 4.15, the permeate flux has a similar trend to the former discussion in sections 4.4.1, and 4.4.5, where the flux increases with increasing the pressure, and at each run it decreases gradually with time. When both solutions were mixed and treated using the ceramic membrane, the permeate flux showed a much lower performance compared to the prior treatments of o/w emulsion and turbid water contains suspended bentonite separately. This is mainly due to the adsorption of oil particles by bentonites [60]; where bentonite act as an adsorbent, and the oil droplets together with the bentonite started to form flocs. These flocs might be bigger in size than the membrane pore size, and immediately block the membrane pores and with time it starts to form cake layer on top of the membrane surface, which justified the observed low permeate flux. Figure 4.15 indicates that the maximum permeate flux obtained from operating the system with the o/w emulsion and bentonite mixture was 98L/m^2.hr which is 20 times less than the higher flux obtained from treating the turbid water contains suspended bentonite, and 5 times less than that of the o/w emulsion. Though, the membrane had a similar trend, where the flux started to decline gradually with time, until it reaches the steady state region where the change in flux with time is zero or minimum. This started to occur after 10 minute, and last for 20 minutes which is the run total duration as shown in Figure 4.16.

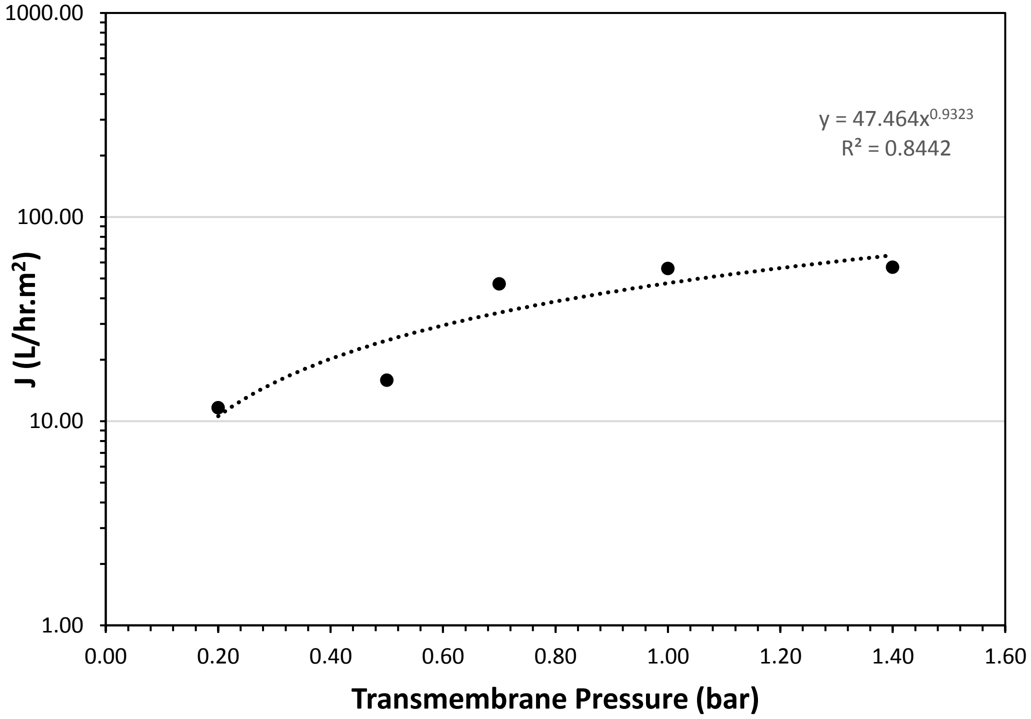


Figure 4. 16: Permeate flux at different transmembrane pressure at steady state region

A gradual increase in the flux with changing the transmembrane pressure is observed from Figure 4.16. Where 12L/m^2.hr was permeated from the membrane at 0.2bar, and increasing the pressure lead to an increase in the flux until it reaches ~60L/m^2.hr at 1.4bar.

4.4.9 Mixture of O/W Emulsion and Bentonite: Turbidity Analysis

The turbidity analysis from treating o/w emulsion-bentonite mixture using 0.45µm membrane was performed before and after the treatments to check the percentage removal of suspend solids (Bentonite). The initial value of suspended solids was 85115 NTU, and the microfiltration membrane was able to remove ~92-99.7% of the solid particles, where the higher removal was obtained at 0.2bar and as the pressure increases the removal decreases slightly.

4.4.10 Mixture O/W Emulsion and Suspended Bentonite: TOC Analysis

The TOC rejection analysis was performed as well and the oil content of the samples before and after the treatment process were tested. It was found that, the microfiltration ceramic membrane was able to remove the oil content by ~43-99% where the higher removal efficiency was obtained at the first four minutes of the run, under low pressures (0.5 and 0.7bar).

4.4.11. Mixture of O/W Emulsion and Suspended Bentonite: Membrane Performance

The ceramic membrane used in removal of the o/w emulsion-bentonite mixture, was a new virgin membrane. The cleaning process was performed, and a membrane test was carried out using deionized water. Figure 4.17 shows the membrane behavior before and after the treatment.

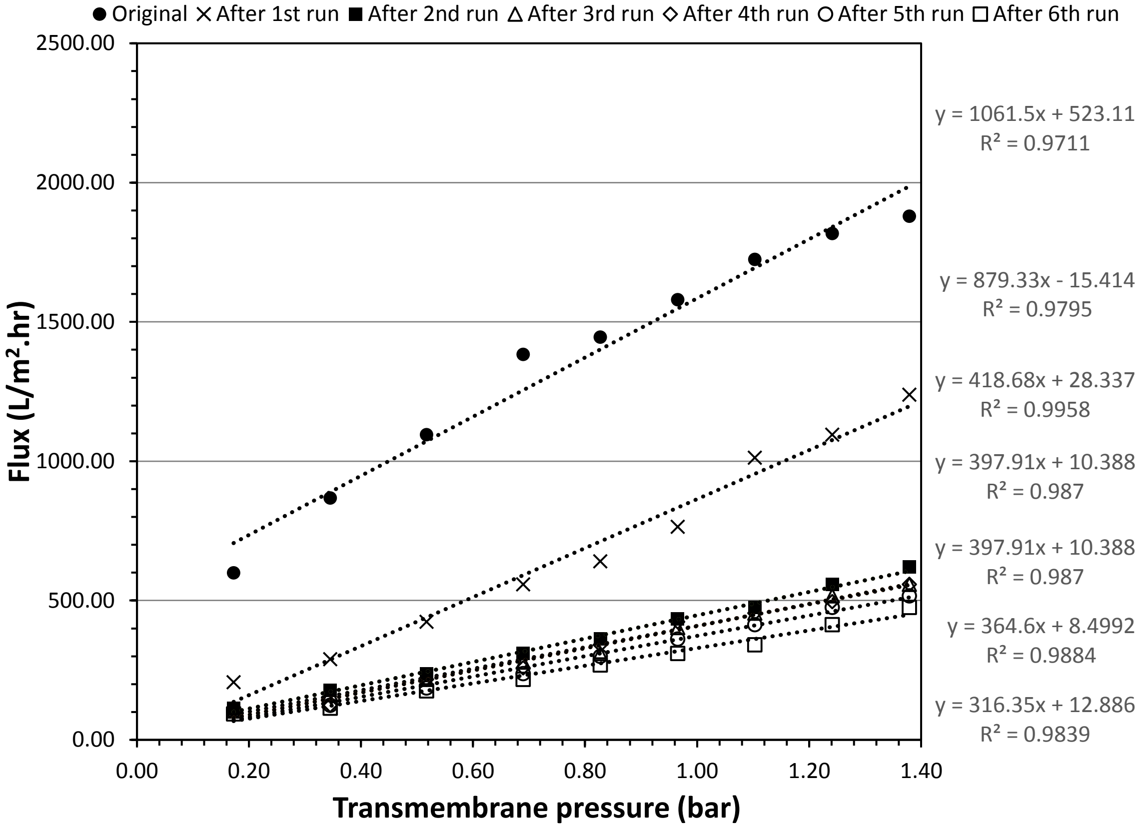


Figure 4. 17: Monitoring the ceramic membrane performance after each run of treating o/w emulsion-bentonite mixture

Figure 4.17 indicates that the virgin membrane was able to carry out $\sim 600 - 1900$L/m^2.hr as a minimum and maximum permeate flux. The first run resulted in a steadily decline in the flux, which proves that the blockage occurred immediately after the first run. This decline followed by a graduate decrease in the flux obtained from the following runs. The flux decreased slowly after the second run from 113-620L/m^2.hr as minimum and maximum permeate flux to 103-516 L/m^2.hr after the sixth run, which indicates a lower concentration polarization factor compared to the previous runs.

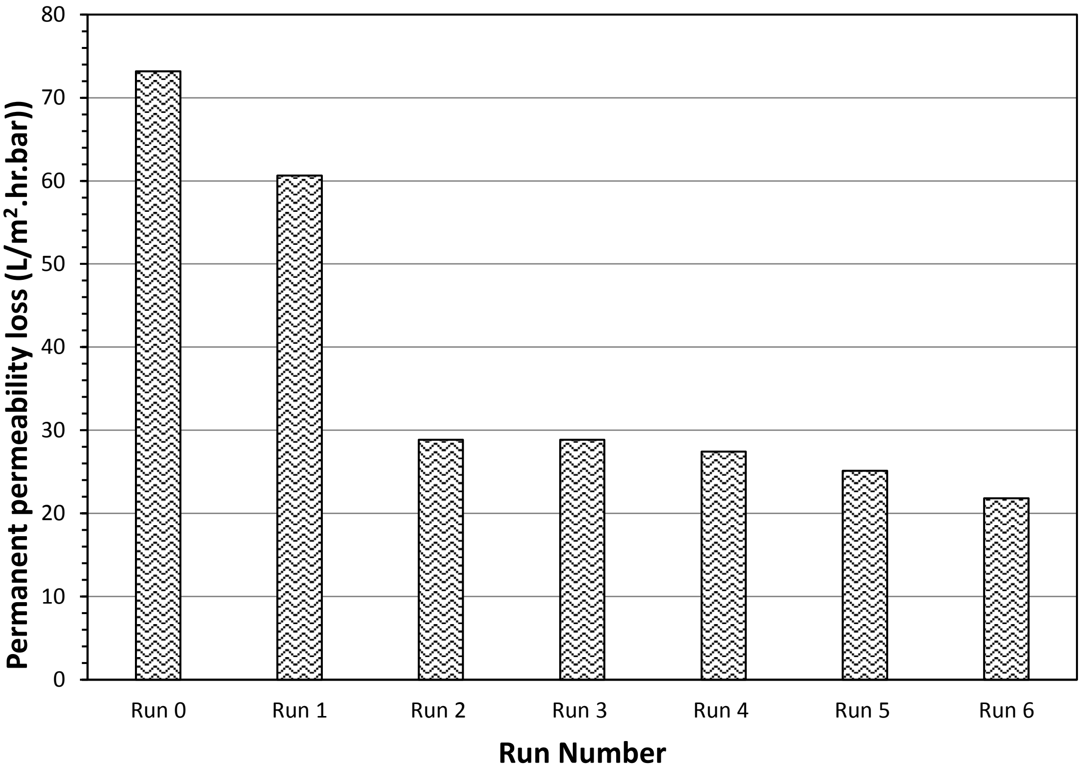
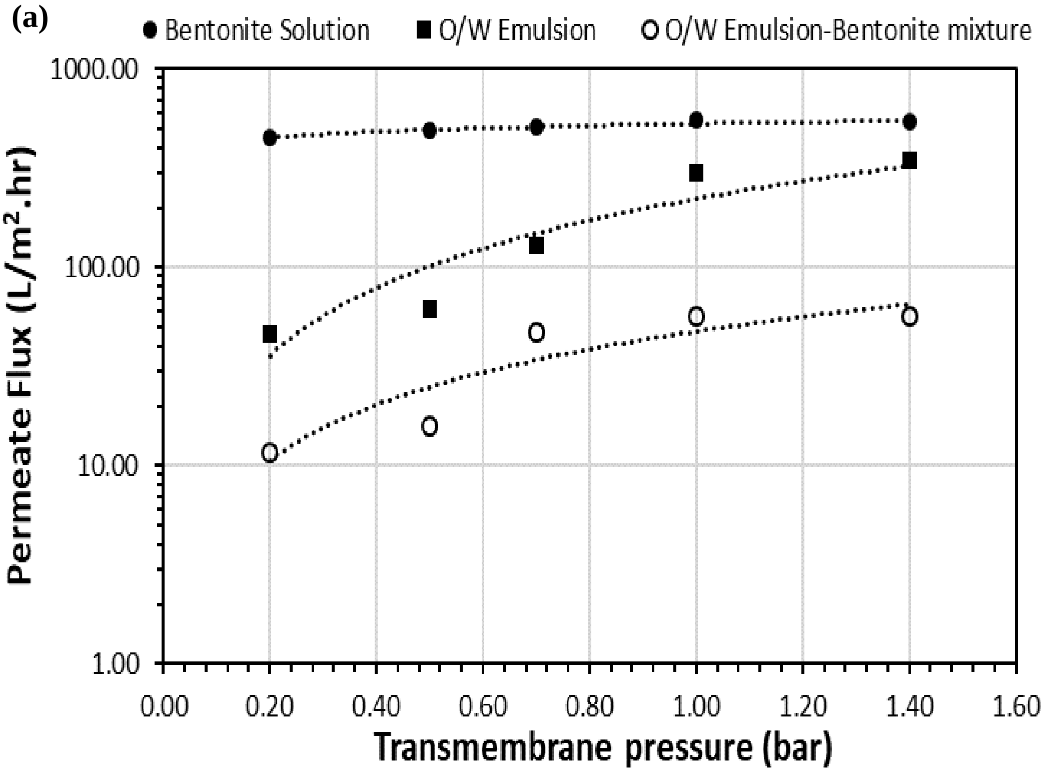
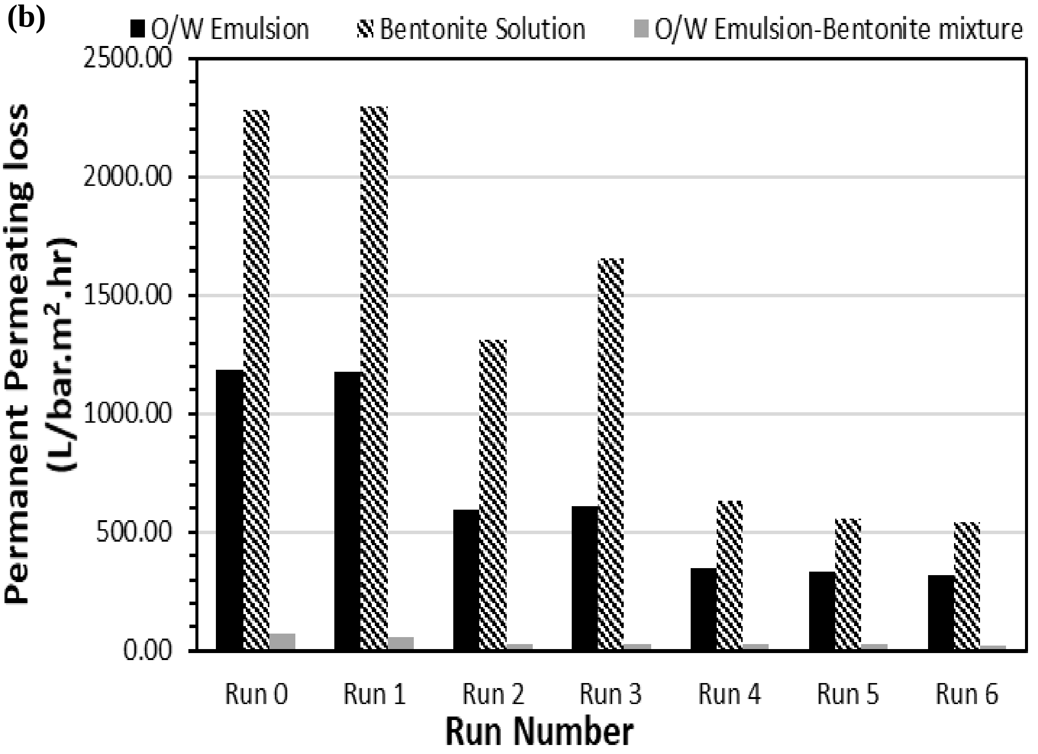


Figure 4. 18: Permanent permeability loss of regenerated membrane from treating o/w emulsion-bentonite mixture

The decline in the flux permeation is explained in Figure 4.18, where it shows an immediate drop in the flux at the early stage, followed by a graduate decline, which is reasonable since the cleaning process will never return the membrane to its initial performance.

4.5. Over All Comparisons





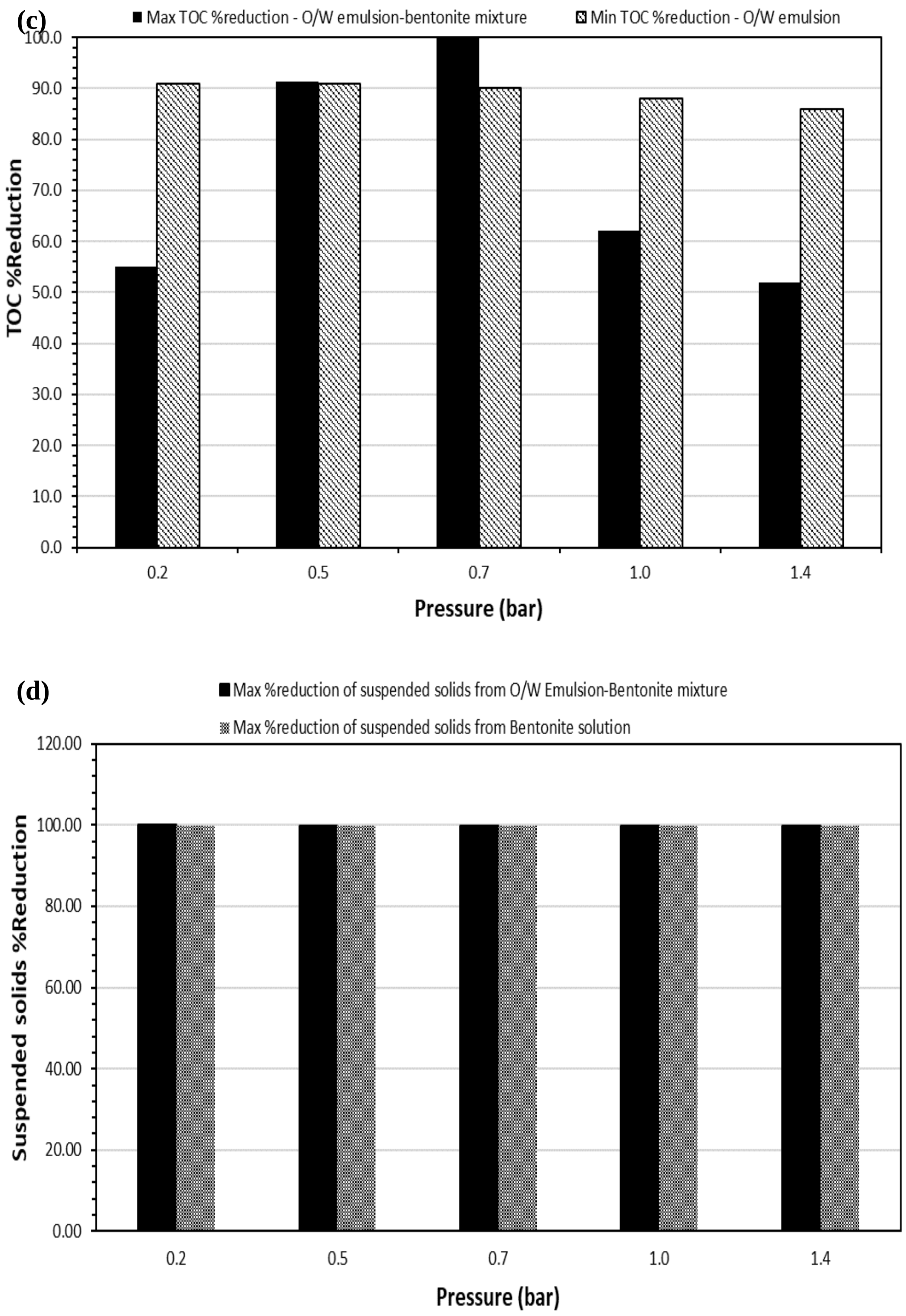


Figure 4. 19: Summary of results from using 0.45μm ceramic membrane for treating three different solutions

Figure 4.19 summarizes the main findings of the experimental part using 0.45μm ceramic membrane to treat oil-in-water emulsion and suspended colloids. Three different solutions were treated using three new ceramic membranes having the same characteristics, to study the effect of each solution on the new ceramic membranes. The solutions are: o/w emulsion, bentonite solution, and mixture of both o/w emulsion and bentonite solution. Figure 4.19 (a) shows the permeate flux obtained from operating the membrane using the three different solutions. It indicates that the ceramic membrane best performance was in removal of suspended solids. This can be clearly seen from the permeate flux trend, where the higher permeate flux was obtained using the bentonite solution, while the mixture of both o/w emulsion and bentonite solution resulted in a higher fouling factor that decreases the permeate flux. It is also worth to mention that the performance of ceramic membrane in treating bentonite solution, and under different pressures, shows much lower fouling factor than operating the system using the other two solutions. This can be clearly seen from the permeate flux range under all transmembrane pressures for the different solutions, where the change in the permeated flux of bentonite solution was slight compared to the other two solutions. Another indication of the fouling effect on the membrane performance is the permanent permeating loss, which is described in Figure 4.19(b). The ceramic membrane shows a good performance in treating o/w emulsion, and a better performance in removal of suspended solids, which is reasonable since the microfiltration systems have an excellent removal of suspended solids, and good removal of oil. Both TOC and turbidity measurements were summarized and compared in Figure 4.19(c) and (d), which indicates the maximum removal of both pollutants using the ceramic membrane. The optimum pressure for the removal of both o/w emulsion-bentonite mixture, and o/w emulsion solution was at 0.5bar, where 90% of the oil content can be removed. On the other hand, the removal of suspended solids from o/w emulsion-bentonite solution was at its maximum under 0.2bar, where almost 99.97% of the suspended solids were removed.

CHAPTER 5: CONCLUSIONS AND FUTURE PEROSPECTS

The main objective of this study is to investigate the effect of Ethylene tetrakis as a surfactant in stabilizing tight oil-in-water emulsion using diesel as an oil source, and to study the performance of ceramic membrane in treating tight oil-in-water emulsion as a promising technology for wastewater treatment. The study of stabilizing bentonite as colloidal particles in deionized water, and in oil-in-water emulsion was one of the objectives as well.

The phase separation, zeta potential, and interfacial tension analysis were performed to understand the stability mechanisms, and select the optimum surfactant concentration that can tightly stabilize oil-in-water emulsion. The higher surfactant concentrations, at 1% and above, showed good results in stability based on the undertaken analysis, where the emulsion preserved its stability for 30 minutes when the surfactant concentration was 2%. Thus, the 2% concentration was selected to be the optimum concentration used in stabilizing the emulsion.

On the other hand, the stability of bentonite was investigated by monitoring the effect of changing pH values on turbidity and zeta potential measurements. Results have shown that at pH value of 9, the colloids suspension was stable, which means that the stability increases with increasing the alkalinity of the solution. The effect of mixing both bentonite and oil-in-water emulsion, and treating it using ceramic membrane was performed as well.

The ceramic membrane performance was investigated using deionized water, after cleaning the membrane chemically after each run. The membrane showed similar results obtained from running the experiment using the three different solutions, though, there was a noticeable difference in the readings between the solutions. This was mainly because of the solution characteristics, where the treatment of bentonite solution showed the better results, and proves that microfiltration membranes works effectively with suspended solids. The maximum reduction obtained from treating oil-in-water emulsion, and bentonite solution were 90% and 99.9% simultaneously. Where the mixture of both o/w emulsion and bentonite solution showed a reduction percentage of both TOC and suspended solids of 90 and 99.97%. Thus, the ceramic membrane showed its viability and effectiveness in removal of oil and suspended solids, and it is found to be a promising technology for the treatment of produced water, and any other type of wastewater.

The results indicated that, high treatment efficiency can be obtained from using the ceramic membrane in treating o/w emulsion, and suspended solids. The removal of suspended solids was higher than of the oil droplets, due to the ability of micromembrane to highly remove suspended solids. One of the main constraints was the permeation flux, which is affected by fouling phenomena that increases the permanent permeating loss.

To improve this work, and overcome the current problems, combining two or more ceramic membranes in series need to be studied, since it can reduce the fouling problem and act as pretreatment unit. It is also important to study the effect of changing salinity, pH, and surfactant on stability of oil-in-water emulsion. Another factor that needs to be studied is the ceramic membrane performance in treating actual produced water, and the effect of using demulsifier as a pretreatment of the ceramic membrane unit.

REFERENCES

1. Igunnu, E.T. and G.Z. Chen, Produced water treatment technologies. International Journal of Low-Carbon Technologies, 2014. **9**(3): p. 157-177.
2. Challenges in reusing produced water 2011, Society of Petroleum Engineers
3. Li, G., B. Bai, and K.H. Carlson, Characterization of solids in produced water from wells fractured with recycled and fresh water. Journal of Petroleum Science and Engineering, 2016. **144**(Supplement C): p. 91-98.
4. Clark, C. and J. Veil, Produced water volumes and management practices in the United States. 2009, Argonne National Laboratory (ANL).
5. Lee, K. and J. Neff, Produced water: environmental risks and advances in mitigation technologies. 2011: Springer.
6. El-Naas, M. and D. Moussa, Electrochemical technologies for produced water treatment. Materials Research Foundations. **16**.
7. Ahan, J.A., CHARACTERIZATION OF PRODUCED WATER FROM TWO OFFSHORE OIL FIELDS IN QATAR. 2014.
8. Fakhru'l-Razi, A., et al., Review of technologies for oil and gas produced water treatment. Journal of Hazardous Materials, 2009. **170**(2): p. 530-551.
9. Veil, J.A., et al., A white paper describing produced water from production of crude oil, natural gas, and coal bed methane. 2004, Argonne National Lab., IL (US).
10. Chakrabarty, B., A.K. Ghoshal, and M.K. Purkait, Ultrafiltration of stable oil-in-water emulsion by polysulfone membrane. Journal of Membrane Science, 2008. **325**(1): p. 427-437.

11. Dezhi, S., et al., Demulsification of water-in-oil emulsion by wetting coalescence materials in stirred- and packed-columns. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 1999. **150**(1): p. 69-75.
12. Elektorowicz, M., S. Habibi, and R. Chifrina, Effect of electrical potential on the electro-demulsification of oily sludge. Journal of Colloid and Interface Science, 2006. **295**(2): p. 535-541.
13. Finster, M., et al., Geothermal produced fluids: Characteristics, treatment technologies, and management options. Renewable and Sustainable Energy Reviews, 2015. **50**: p. 952-966.
14. Hlavacek, M., Break-up of oil-in-water emulsions induced by permeation through a microfiltration membrane. Journal of membrane science, 1995. **102**: p. 1-7.
15. Fingas, M., B. Fieldhouse, and J. Mullin, Water-in-oil emulsions results of formation studies and applicability to oil spill modelling. Spill Science & Technology Bulletin, 1999. **5**(1): p. 81-91.
16. Kang, W., et al., Influence of demulsifier on interfacial film between oil and water. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2006. **272**(1–2): p. 27-31.
17. Fingas, M.F., Water-in-oil emulsions: formation and prediction. Journal of Petroleum Science Research, 2014.
18. Kim, Y.-H., D. Wasan, and P. Breen, A study of dynamic interfacial mechanisms for demulsification of water-in-oil emulsions. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 1995. **95**(2-3): p. 235-247.

19. Dos Santos, R.G., et al., Physico-chemical properties of heavy crude oil-in-water emulsions stabilized by mixtures of ionic and non-ionic ethoxylated nonylphenol surfactants and medium chain alcohols. Chemical Engineering Research and Design, 2011. **89**(7): p. 957-967.

20. Fink, J., Petroleum engineer's guide to oil field chemicals and fluids. 2015: Gulf Professional Publishing.

21. TO, S.O.M.L., Emulsion Stability and Testing. 2011.

22. Campbell, L. Studentfolio. DLVO Theory [cited 2017 November]; Available from: https://folio.brighton.ac.uk/user/lc355/dlvo-theory.

23. Albers, W. and J.T.G. Overbeek, Stability of emulsions of water in oil: I. The correlation between electrokinetic potential and stability. Journal of Colloid Science, 1959. **14**(5): p. 501-509.

24. Bhattacharjee, S., DLS and zeta potential–What they are and what they are not? Journal of Controlled Release, 2016. **235**: p. 337-351.

25. Verwey, E., Theory of the electric double layer of stabilized emulsion. Proc. Konink. Nederland. Akad. Wetenschap, 1950. **53**: p. 375.

26. Shaikh, S.M.R., et al., Influence of polyelectrolytes and other polymer complexes on the flocculation and rheological behaviors of clay minerals: A comprehensive review. Separation and Purification Technology, 2017. **187**(Supplement C): p. 137-161.

27. Kaszuba, M., et al., High-concentration zeta potential measurements using light-scattering techniques. Philosophical Transactions of the Royal Society of London A: Mathematical, Physical and Engineering Sciences, 2010. **368**(1927): p. 4439-4451.

28. Baszkin, A. and W. Norde, Physical chemistry of biological interfaces. 1999: CRC Press.

29. Abdel-Raouf, M.E.-S., Factors affecting the stability of crude oil emulsions, in Crude oil emulsions-Composition stability and characterization. 2012, InTech.

30. Zolfaghari, R., et al., Demulsification techniques of water-in-oil and oil-in-water emulsions in petroleum industry. Separation and Purification Technology, 2016. **170**: p. 377-407.

31. Science learning hub. Surfactants 2017; Available from: https://www.sciencelearn.org.nz/images/1291-surfactants.

32. Adams, F., et al., Modern aspects of emulsion science. 2007: Royal Society of Chemistry.

33. KOCH membrane systems Membrane Technologies 2017 [cited 2017 November]; Available from: https://www.google.com/url?sa=i&rct=j&q=&esrc=s&source=images&cd=&ved=0ahUKEwjR4OWUyczXAhXFPRQKHTyUAt8QjhwIBQ&url=http%3A%2F%2Fwww.kochmembrane.com%2FLearning-Center%2FTechnologies.aspx&psig=AOvVaw0CNWaVh6PwClTj1Lfo4opT&ust=1511247330238475.

34. Module Configureations & Process 2017 [cited 2017 Oct]; Available from: http://synderfiltration.com/learning-center/articles/module-configurations-process/.

35. Balster, J., Plate and Frame Membrane Module, in Encyclopedia of Membranes. 2013, Springer. p. 1-3.

36. De, S., Membrane based separation processes. Novel Separation Processes. Indian Institute of Technology, Kharagpur, 2012.

37. Abdelrasoul, A., H. Doan, and A. Lohi, Fouling in membrane filtration and remediation methods, in Mass transfer-advances in sustainable energy and environment oriented numerical modeling. 2013, InTech.
38. Franken, A., Prevention and control of membrane fouling: practical implications and examining recent innovations. Membraan Applicatie Centrum Twente bv, 2009.
39. Yan-jun, Z., et al., Fouling and cleaning of membrane–a literature review. Environmental Science, 2000. **12**(2): p. 241-251.
40. Almarouf, H.S., et al., Demulsification of stable emulsions from produced water using a phase separator with inclined parallel arc coalescing plates. Journal of Petroleum Science and Engineering, 2015. **135**: p. 16-21.
41. Al-Shamrani, A., A. James, and H. Xiao, Destabilisation of oil–water emulsions and separation by dissolved air flotation. Water Research, 2002. **36**(6): p. 1503-1512.
42. Muto, A., T. Matsumoto, and H. Tokumoto, Continuous flow demulsification of a water-in-toluene emulsion by an alternating electric field. Separation and Purification Technology, 2015. **156**: p. 175-182.
43. Roques-Carmes, T., et al., Influence of the plate-type continuous micro-separator dimensions on the efficiency of demulsification of oil-in-water emulsion. Chemical Engineering Research and Design, 2014. **92**(11): p. 2758-2769.
44. Karhu, M., T. Leiviskä, and J. Tanskanen, Enhanced DAF in breaking up oil-in-water emulsions. Separation and purification technology, 2014. **122**: p. 231-241.

45. Matos, M., et al., Surfactant effect on the ultrafiltration of oil-in-water emulsions using ceramic membranes. Journal of Membrane Science, 2016. **520**: p. 749-759.

46. Taylor, S.E., Thermal destabilisation of bitumen-in-water emulsions–A spinning drop tensiometry study. Fuel, 2011. **90**(10): p. 3028-3039.

47. Liang, J., et al., Magnetic demulsification of diluted crude oil-in-water nanoemulsions using oleic acid-coated magnetite nanoparticles. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2015. **466**: p. 197-202.

48. Muto, A., et al., Effects of organic solvent and ionic strength on continuous demulsification using an alternating electric field. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2016. **506**: p. 228-233.

49. Kukizaki, M. and M. Goto, Demulsification of water-in-oil emulsions by permeation through Shirasu-porous-glass (SPG) membranes. Journal of Membrane Science, 2008. **322**(1): p. 196-203.

50. Kocherginsky, N., C.L. Tan, and W.F. Lu, Demulsification of water-in-oil emulsions via filtration through a hydrophilic polymer membrane. Journal of membrane science, 2003. **220**(1): p. 117-128.

51. Zhou, J.-e., et al., Separation of stable oil–water emulsion by the hydrophilic nano-sized ZrO 2 modified Al 2 O 3 microfiltration membrane. Separation and Purification Technology, 2010. **75**(3): p. 243-248.

52. Lin, C., et al., Freeze/thaw induced demulsification of water-in-oil emulsions with loosely packed droplets. Separation and purification technology, 2007. **56**(2): p. 175-183.

53. Yang, C.-L., Electrochemical coagulation for oily water demulsification. Separation and Purification Technology, 2007. **54**(3): p. 388-395.

54. Atta, A.M., H.A. Allohedan, and G.A. El-Mahdy, Dewatering of petroleum crude oil emulsions using modified Schiff base polymeric surfactants. Journal of Petroleum Science and Engineering, 2014. **122**: p. 719-728.

55. Ichikawa, T., Electrical demulsification of oil-in-water emulsion. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2007. **302**(1): p. 581-586.

56. Lobo, A., et al., Ultrafiltration of oil-in-water emulsions with ceramic membranes: Influence of pH and crossflow velocity. Journal of Membrane Science, 2006. **278**(1): p. 328-334.

57. Jha, P., V. Mahto, and V. Saxena, Study the Effects of Xanthan Gum and Aluminium Stearate on the Properties of Oil-in-Water Emulsion Drilling Fluids. Arabian Journal for Science & Engineering (Springer Science & Business Media BV), 2016. **41**(1).

58. Ebrahimi, M., et al., Investigations on the use of different ceramic membranes for efficient oil-field produced water treatment. Desalination, 2010. **250**(3): p. 991-996.

59. Zsirai, T., et al., Ceramic membrane filtration of produced water: Impact of membrane module. Separation and Purification Technology, 2016. **165**: p. 214-221.

60. Okiel, K., M. El-Sayed, and M.Y. El-Kady, Treatment of oil–water emulsions by adsorption onto activated carbon, bentonite and deposited carbon. Egyptian journal of petroleum, 2011. **20**(2): p. 9-15.

APPENDICES

APPENDIX A: STABILIY ANALYSIS

Table A. 1: *Phase separation volume% of oil with time*

	Phase Separation volume % of oil							
Time (min)	**0.00%**	**0.25%**	**0.50%**	**0.75%**	**1%**	**2%**	**3%**	**5%**
0	10	0	0	0	0	0	0	0
1	20	40	15	1	0	0	0	0
2	20	41	22	3	0.5	0	0	0
3	30	61	26	5	1	0	0	0
4	30	63	32	6	3	0	0	0
5	35	66	40	7	6	0.5	0	0
10	40	88	51	12	7	0.5	0.5	0
15	55	92	56	14	8	0.5	0.5	0
20	65	92	58	16	8	0.5	0.5	0
25	75	92	60	19	9	0.5	0.5	0
30	85	92	61	21	9	0.5	0.5	0

APPENDIX B: INTERFACIAL TENSION ANALYSIS

Table B. 1: *Interfacial tensions analysis for different surfactant concentrations*

Interfacial Tension (mN/m)	
% Surf/W	**New Surfactant**
0	16
0.15	4.6
0.25	4.5
0.35	2.1
0.5	2.2
0.75	1.5
1	2.4
2	0.97
3	0.99

APPENDIX C: ZETA POTENTIAL ANALYSIS

Table C. 1: *Zeta potential analysis for different surfactant concentrations*

Zeta potential	
% of s/w	ZP (mV)
0	
0.25	-11.8
0.5	-21.2
0.75	-20.1
1	-17.7
2	-15.5
3	-16

APPENDIX D: OIL-IN-WATER EMULSION RESULTS

A) Permeate Flux

Table D. 1: *Effect of transmembrane pressure on permeate flux*

Time (min)	**Filtrate Flux (L/hr.m2)**				
	At 0.2bar	At 0.5bar	At 0.7bar	At 1.0 bar	At 1.4bar
1	98.11	98.11	464.72	495.70	475.04
2	98.11	103.27	314.97	387.26	469.88
3	92.94	103.27	263.34	371.77	464.72
4	92.94	103.27	227.19	366.61	459.55
5	82.62	103.27	196.21	361.45	454.39
6	77.45	103.27	185.89	345.96	449.23
7	72.29	103.27	185.89	340.79	413.08
8	72.29	103.27	185.89	335.63	371.77
9	61.96	92.94	154.91	335.63	366.61
10	61.96	82.62	154.91	330.46	361.45
20	51.64	61.96	132.16	309.81	351.12
30	41.31	61.96	123.92	289.16	345.96

Table D. 2: *Membrane permeate flux at steady state*

At steady state, 600 ml/min feed flow rate	
P (bar)	**Flux (L/hr.m2)**
0.20	46.47
0.50	61.96
0.70	128.06
1.00	299.48
1.40	348.54

B) TOC Analysis

Table D. 3: *TOC analysis results obtained from TOC Analyzer*

SN	Timing (min)	Pressure (bar)	TOC (mg/L)	%Removal
0	0.00	0.00	111500.00	0.00
1	1.00	0.20	10169.82	90.88
2	2.00	0.20	11158.83	89.99
3	3.00	0.20	12917.07	88.42
4	4.00	0.20	14635.35	86.87
5	5.00	0.20	15524.46	86.08
6	6.00	0.20	13006.98	88.33
7	7.00	0.20	12287.70	88.98
8	8.00	0.20	18001.98	83.85
9	9.00	0.20	18981.00	82.98
10	10.00	0.20	19690.29	82.34
11	20.00	0.20	16023.96	85.63
12	30.00	0.20	13596.39	87.81
13	1.00	0.50	13396.59	87.99
14	2.00	0.50	13156.83	88.20
15	3.00	0.50	14885.10	86.65
16	4.00	0.50	14155.83	87.30
17	5.00	0.50	10249.74	90.81
18	6.00	0.50	13376.61	88.00
19	7.00	0.50	13476.51	87.91
20	8.00	0.50	14055.93	87.39
21	9.00	0.50	13536.45	87.86
22	10.00	0.50	13006.98	88.33
23	20.00	0.50	14025.96	87.42
24	30.00	0.50	14565.42	86.94
25	1.00	0.70	11238.75	89.92
26	2.00	0.70	14135.85	87.32
27	3.00	0.70	14575.41	86.93
28	4.00	0.70	15974.01	85.67
29	5.00	0.70	15324.66	86.26
30	6.00	0.70	17792.19	84.04

31	7.00	0.70	17802.18	84.03
32	8.00	0.70	19230.75	82.75
33	9.00	0.70	16683.30	85.04
34	10.00	0.70	15924.06	85.72
35	20.00	0.70	19490.49	82.52
36	30.00	0.70	15524.46	86.08
37	1.00	1.00	13376.61	88.00
38	2.00	1.00	15254.73	86.32
39	3.00	1.00	15564.42	86.04
40	4.00	1.00	14855.13	86.68
41	5.00	1.00	15204.78	86.36
42	6.00	1.00	15174.81	86.39
43	7.00	1.00	14155.83	87.30
44	8.00	1.00	14185.80	87.28
45	9.00	1.00	17502.48	84.30
46	10.00	1.00	16613.37	85.10
47	20.00	1.00	17282.70	84.50
48	30.00	1.00	14575.41	86.93
49	1.00	1.40	23376.60	79.03
50	2.00	1.40	20829.15	81.32
51	3.00	1.40	18041.94	83.82
52	4.00	1.40	18031.95	83.83
53	5.00	1.40	18571.41	83.34
54	6.00	1.40	19720.26	82.31
55	7.00	1.40	16443.54	85.25
56	8.00	1.40	17842.14	84.00
57	9.00	1.40	15624.36	85.99
58	10.00	1.40	16823.16	84.91
59	20.00	1.40	22377.60	79.93
60	30.00	1.40	16433.55	85.26

C) Membrane Performance

Table D. 4: *Permeate flux readings using deionized water after cleaning process*

Transmembrane pressure (bar)	**Flux (L/m^2.hr)**						
	Original	**After 1st run**	**After 2nd run**	**After 3rd run**	**After 4th run**	**After 5th run**	**After 6th run**
0.2	598.97	516.35	206.54	123.92	92.94	82.62	61.96
0.3	867.47	650.60	330.46	289.16	144.58	123.92	123.92
0.5	1094.66	846.82	578.31	392.43	216.87	165.23	165.23
0.7	1383.82	1115.32	712.56	475.04	263.34	206.54	206.54
0.8	1445.78	1290.88	733.22	557.66	304.65	247.85	247.85
1.0	1580.03	1425.13	805.51	660.93	428.57	299.48	299.48
1.1	1724.61	1631.67	888.12	722.89	433.73	351.12	351.12
1.2	1817.56	1755.59	898.45	805.51	449.23	413.08	413.08
1.4	2168.67	1858.86	908.78	888.12	490.53	475.04	475.04

Table D. 5: *Permanent permeate loss resulted after each run*

Run#	**Permanent Permeate Loss (bar.hr.m2/L)**
Run 0	1185.20
Run 1	1179.70
Run 2	592.58
Run 3	609.55
Run 4	346.84
Run 5	331.20
Run 6	321.48

APPENDIX E: COLLOIDS RESULTS

A) Permeate Flux

Table E. 1: *Effect of transmembrane pressure on permeate flux*

Time (min)	Filtrate Flux (L/hr.m2)					
	0.2bar	0.3bar	0.5bar	0.7bar	1.0 bar	1.4bar
10	888.12	3304.65	784.85	857.14	1941.48	2044.75
20	722.89	2065.40	413.08	722.89	898.45	898.45
30	557.66	1858.86	351.12	619.62	650.60	671.26
40	464.72	1755.59	289.16	547.33	578.31	547.33
50	413.08	1672.98	268.50	464.72	516.35	485.37
60	371.77	1672.98	247.85	402.75	454.39	444.06

Table E. 2: *Membrane permeate flux at steady state*

At steady state, 600 ml/min feed flow rate	
P (bar)	**Flux (L/hr.m2)**
0.20	451.81
0.50	485.89
0.70	508.61
1.00	549.91
1.40	537.01

B) Turbidity Analysis

Table E. 3: *Turbidity analysis results obtained from turbidity meter*

Feed turbidity (NTU)	**260**				
	Turbidity (NTU)				
Time (min)/Pressure (bar)	**0.2 bar**	**0.5 bar**	**0.7 bar**	**1.0 bar**	**1.4 bar**
10	1.1	0.32	0.454	0.62	0.575
20	1.18	0.33	0.509	0.59	0.402
30	1.05	0.4	0.415	0.56	0.351
40	1.03	0.292	0.577	0.567	0.507
50	0.968	0.18	0.51	0.54	0.38
60	0.9	0.385	0.41	0.523	0.36

C) Membrane Performance

Table E. 4: *Permeate flux readings using deionized water after cleaning process*

Transmembrane pressure (bar)	**Flux (L/m2.hr)**						
	Original	**After 1st run**	**After 2nd run**	**After 3rd run**	**After 4th run**	**After 5th run**	**After 6th run**
0.2	619.62	516.35	475.04	149.74	206.54	134.25	113.60
0.3	1239.24	1135.97	929.43	278.83	268.50	361.45	330.46
0.5	1858.86	1755.59	1342.51	485.37	330.46	413.08	382.10
0.7	1962.13	1920.83	1383.82	733.22	495.70	454.39	413.08
0.8	2065.40	2044.75	1590.36	981.07	557.66	495.70	454.39
1.0	2581.76	2561.10	1590.36	1290.88	640.28	557.66	516.35
1.1	2891.57	2746.99	1838.21	1652.32	702.24	640.28	619.62
1.2	3304.65	3139.41	2106.71	1755.59	764.20	671.26	722.89
1.4	3511.19	3490.53	2209.98	2044.75	826.16	1197.93	929.43

APPENDIX F: O/W EMULSION IN BENTONITE MIXTURE RESULTS

A) Permeate Flux

Table F. 1: *Effect of transmembrane pressure on permeate flux*

Time (min)	**Filtrate Flux (L/hr.m2)**				
	At 0.2bar	**At 0.5bar**	**At 0.7bar**	**At 1.0 bar**	**At 1.4bar**
1	20.65	30.98	82.62	98.11	98.11
2	30.98	30.98	82.62	92.94	92.94
3	26.85	30.98	77.45	82.62	82.62
4	24.78	26.85	77.45	82.62	82.62
5	20.65	26.85	72.29	82.62	82.62
6	20.65	24.78	72.29	77.45	82.62
7	20.65	24.78	72.29	77.45	82.62
8	20.65	24.78	61.96	82.62	77.45
9	15.49	22.72	61.96	82.62	77.45
10	10.33	20.65	61.96	77.45	77.45
20	10.33	10.12	33.05	35.11	39.24
30	10.33	10.12	30.98	28.92	33.05

Table F. 2: *Membrane permeate flux at steady state*

At steady state, 600 ml/min feed flow rate	
P (bar)	**Flux (L/hr.m2)**
0.20	11.62
0.50	15.90
0.70	46.99
1.00	56.02
1.40	56.80

B) Turbidity Analysis

Table F. 3: *Turbidity analysis results obtained from turbidity meter*

Feed turbidity				**85114.8**	**NTU**
Pressure (bar)/Time (min)	**0.2**	**0.5**	**0.7**	**1**	**1.4**
1	208.79	108.89	87.91	137.86	7042.95
2	132.87	109.89	78.92	314.69	3446.55
3	104.90	121.88	88.91	699.30	3676.32
4	152.85	254.92	95.90	2027.97	6593.40
5	24.98	332.89	116.88	3076.92	5694.30
6	60.94	335.89	149.85	4325.67	4055.94
7	92.91	353.88	186.81	4375.62	1578.42
8	51.95	374.88	198.80	4485.51	1998.00
9	89.91	374.88	244.76	4845.15	1138.86
10	129.87	389.87	298.70	4835.16	2777.22
20	143.86	389.87	377.62	5884.11	2637.36
30	34.97	395.87	453.55	4235.76	2427.57

C) TOC Analysis

Table F. 4: *TOC analysis results obtained from TOC Analyzer*

	Feed TOC		162737.1	mg/L
SN	**Time (min)**	**Pressure (bar)**	**TOC (mg/L)**	**TOC Removal%**
1	1	0.2	73056.87	55.11
2	2	0.2	78940.98	51.49
3	3	0.2	84805.11	47.89
4	4	0.2	74875.05	53.99
5	5	0.2	74585.34	54.17
6	6	0.2	80919.00	50.28
7	7	0.2	81248.67	50.07
8	8	0.2	87702.21	46.11
9	9	0.2	85734.18	47.32
10	10	0.2	80119.80	50.77
11	20	0.2	74395.53	54.28
12	30	0.2	78191.73	51.95
13	1	0.5	14115.87	91.33
14	2	0.5	21408.57	86.84
15	3	0.5	23406.57	85.62
16	4	0.5	30039.93	81.54
17	5	0.5	36503.46	77.57
18	6	0.5	40988.97	74.81
19	7	0.5	48201.75	70.38
20	8	0.5	69000.93	57.60
21	9	0.5	74895.03	53.98
22	10	0.5	88461.45	45.64
23	20	0.5	88891.02	45.38
24	30	0.5	92897.01	42.92
25	1	0.7	379.32	99.77
26	2	0.7	4739.26	97.09
27	3	0.7	22417.56	86.22
28	4	0.7	34435.53	78.84
29	5	0.7	48941.01	69.93
30	6	0.7	57192.75	64.86
31	7	0.7	53366.58	67.21

32	8	0.7	70249.68	56.83
33	9	0.7	69190.74	57.48
34	10	0.7	60069.87	63.09
35	20	0.7	82817.10	49.11
36	30	0.7	93866.04	42.32
37	1	1	61668.27	62.11
38	2	1	71778.15	55.89
39	3	1	73626.30	54.76
40	4	1	79880.04	50.91
41	5	1	81658.26	49.82
42	6	1	86383.53	46.92
43	7	1	84815.10	47.88
44	8	1	83146.77	48.91
45	9	1	86513.40	46.84
46	10	1	87522.39	46.22
47	20	1	79680.24	51.04
48	30	1	86693.22	46.73
49	1	1.4	83496.42	48.69
50	2	1.4	78311.61	51.88
51	3	1.4	82996.92	49.00
52	4	1.4	87712.20	46.10
53	5	1.4	81178.74	50.12
54	6	1.4	83486.43	48.70
55	7	1.4	82097.82	49.55
56	8	1.4	82457.46	49.33
57	9	1.4	81358.56	50.01
58	10	1.4	79070.85	51.41
59	20	1.4	83526.39	48.67
60	30	1.4	82996.92	49.00

D) Membrane Performance

Table F. 5: *Permeate flux readings using deionized water after cleaning process*

Pressure (bar)	**Flux (L/m2.hr)**						
	Original	**After 1st run**	**After 2nd run**	**After 3rd run**	**After 4th run**	**After 5th run**	**After 6th run**
0.2	598.97	206.54	113.60	92.94	103.27	103.27	103.27
0.3	867.47	289.16	177.62	113.60	165.23	123.92	123.92
0.5	1094.66	423.41	237.52	175.56	216.87	216.87	185.89
0.7	1383.82	557.66	309.81	216.87	278.83	258.18	237.52
0.8	1445.78	640.28	361.45	268.50	309.81	340.79	299.48
1	1580.03	764.20	433.73	309.81	402.75	423.41	361.45
1.1	1724.61	1012.05	475.04	340.79	454.39	454.39	413.08
1.2	1817.56	1094.66	557.66	413.08	516.35	495.70	475.04
1.4	1879.52	1239.24	619.62	475.04	557.66	557.66	516.35

Table F. 6: *Permanent permeate loss resulted after each run*

Run Name	**Permanent Permeating loss (bar.hr.m2/L)**
Run 0	73.185
Run 1	60.628
Run 2	28.867
Run 3	28.867
Run 4	27.435
Run 5	25.138
Run 6	21.812