EVALUATION OF ALUMINIUM OXIDE NANO-PARTICLE BASED POLYMERIC MEMBRANE FOR EMULSIFIED OIL/WATER SEPARATION

BY

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CERTIFICATION

I certify that this work "Evaluation of Aluminium Oxide Nano-Particle Based Polymeric Membrane for Emulsified Oil/Water Separation" was carried out by me, **MBAKAOGU, CHIOMA DEBORAH (20174083038)** in partial fulfilment for the requirement for the award of Masters of Engineering (M.Eng) in Petroleum Engineering Federal University of Technology, Owerri, Nigeria.

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DEDICATION

This work is dedicated God Almighty who enabled me the Wisdom and understanding all through the course of this thesis.

To my Late Father Dn. Barr. C.A Mbakaogu, this is part of your desire for me. Your support and encouragement brought me this far. Your memories lives on.This is for you.

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ABSTRACT

Crude oil emulsion formation has become a prevalent problem in oilfield and causes significant flow assurance problems during production, treatment and transportation of crude oil. When emulsions occur, they create problems which are difficult to handle and lead to numerous operational challenges such as creating high pressure drops in pipes and/or flowlines, production of off-specification crude oil damages to separation equipment. Emulsions are formed when crude oil is mixed with water as a result of factors such as high rate of shear at the production wellhead and the presence of surface active agents which naturally are present in the crude oil. Emulsions are undesirable and require demulsification to remove the dispersed water and associated inorganic salt in order to meet production and transportation specifications. Furthermore, demulsification of crude oil prevents corrosion and catalyst poisoning and ultimately increases the profitability of the crude oil. The Aluminium oxide nanoparticle membrane was prepared using support materials which are Polysulfone and polyester fabric. These membrane materials have been doped with aluminum oxide nanoparticles to enhance the separation efficiency and reduce membrane fouling. A vacuum pump was used to apply pressure at 80% stroke and 60% stroke for each of the membrane materials respectively. The result show that the aluminum oxide based polymeric membrane emulsion separation process has high separation efficiency with Polysulfone under 60% stroke pressure application having the highest efficiency of 98.5% while Polyester membrane material has the lowest separation efficiency of 96.3% under 80% stroke pressure application. Also analyses of the permeation flux reveals that polystyrene membrane material gave the highest permeation flux of 2.433 ml/cm^2-min when a pressure of 80% stroke was applied to it,while Polysulfone material gave the lowest permeation flux of0.911 ml/cm^2-min under pressure application of 80% stroke. The Polymer membrane emulsion separation process is highly suitable for separation of oil-in-water emulsions.This work presents a new approach of emulsion separation that is cheap and efficient and does not require the costly chemical additions that in most cases also impact negatively on the ecosystem.

Keywords: Emulsion, Demulsification, Flow assurance Membrane and Nanoparticle

CHAPTER ONE

INTRODUCTION

1.1 Background of the study

Crude oil production is mostly accompanied by water in petroleum production systems. This water contacts with the oil in varied proportions forming emulsions. An Emulsion can be defined as a heterogeneous liquid system composed of two immiscible liquids with one liquid dispersed intimately in the second liquid as droplets (Abdel-Raouf, 2012). Oil and water emulsion occur in many stages of petroleum operations including drilling, production, transportation and processing of crude oils. Emulsions have become a problem to petroleum engineers and thus better understanding of crude oil and water emulsion stability is crucial.

Emulsions present disposal problems especially in oily wastewaters and oil spillages into water bodies. Depending on the complexity of the emulsion, there are methods used in the treatment of emulsion. Unstable oil/water emulsions canbe easily removed by conventional separation processes, such as ultrasonic separation, coagulation/flocculation, electric field, and air flotation, chemical treatment and electrical processes (Stack *et. al.,* 2005). But they are not efficient enough for removing stable oil/ water (size ≤ 20 μm) especially when the oil droplets are finely dispersed. Furthermore, these methods are energy-intensive and require complicated machinery.

Membrane technology has gained popularity as a method of crude oil demulsification over the last few decades. Polymeric membranes with pore sizes ranging from 0.1 to 10 μm have low pressure requirements and are thus promising for simple, low-cost and effective separation of oil–water emulsions. Most membranes used for oil/water separation rely on oil-absorbent and water-repellent materials. However, hydrophobic membranes are prone to fouling and pore clogging by oil droplets, and thus have limited sustainability.

Membrane separation of oil and water emulsions is basically based on two effects, size exclusion (i.e., sieving) and selective wettability. The first effect means that the membrane allows water to pass through under an applied pressure whichblocks the oil droplets which are larger than the membrane pores (Silva, 2008). The second effect guarantees that the oil droplets do not wet and permeate the membrane through its selective wetting properties towards water and oil (e.g., hydrophilicity and underwater oleophobicity). Depending on the pore size and separation mechanism, membrane filtration can be divided into microfiltration(MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) (Langevin*et. al.,* 2004). Polymers and ceramics are generally used to fabricate filtration membranes. Polymer membranes are relatively cheap, while ceramic membranes have high mechanical strength, high resistance to harsh environments and long lifetime. Other porous materials, such as metal meshes, textile, nanofiber mats and foams can also be used for pretreatment of emulsions. Although membranes with different pore sizes and materials are commercially available, they are susceptible to fouling when used for oil/water separation. Fouling leads to continuous decline of flux over time and severely decreases the efficiency of filtration. When the membranes are badly fouled, physical cleaning (e.g., water flush and backflush) or/and chemical cleaning methods have to be performed.

Membranes can be doped with nanomaterials to prevent fouling. In this work, Aluminium oxide nanoparticle has been utilized for coating on a polymeric membranes-based material for application in the separation of oil and water emulsion at laboratory scale.

1.2 Statement of the Problem

Oil and water emulsion have resulted to varied problems in the oil and gas sector. These problems are encountered in many areas of the oil and gas business including drilling, production, transportation, processing, wastewater disposal etc. Particularly, in the Niger Delta area, increase oil spillage to water bodies have resulted to the damage of the ecosystem leading to the formation of oil and water emulsions. Emulsion treatment represents a substantial cost in the oil and gas operation and ways must be deployed to reduce the cost of crude oildemulsification. The available traditional treatment methods are not only expensive in treatment of emulsions, they are also very energy-intensive, crooked and in nature are generally not efficient in removing stable emulsions especially when the oil droplets are finely dispersed. This brings us to the use of polymeric membranes doped with Aluminium oxide nanoparticles to reduce its fouling tendencies and increase separation efficiency while reducing overall cost.

1.3 Objective of the study

The main objective of this study is to evaluate the performance of Aluminium oxide nanoparticle based polymeric membranes in separation of oil-water emulsionThe Specific objectives are

1. Preparation of oil-in-water emulsion
2. To separate oil and water from their emulsion in the laboratory using Aluminium nanoparticle based polymeric membrane
3. To investigate the effect of Aluminium oxide nanoparticle concentration on the emulsion separated.
4. To investigate the degree of demulsification using polymeric membrane process
5. To evaluate the performance of the polymeric membrane and its nanoparticle coatings

1.4 Scope/Limitation of the study

In this work, laboratory experiment was performed on stable oil-in-water. The emulsion (oil/water) was gotten from the well head in the Niger Delta (well 9L, field in Niger Delta) with wellhead conditions of pressure, 145 psi and temperature of 102^{O}F. Furthermore, distilled water was added to the field emulsion at laboratory conditions which was mixed thoroughly at room temperature and atmospheric pressure. Polystyrene, Polyester and Polysulfone polymeric membrane materials were used for the separation and were coated with Aluminium oxide nanoparticles to avoid membrane fouling and increase the efficiency of the separation process. The laboratory experiments were carried out in successive turns for each of the polymeric materials having different mesh sizes and the separation was done at different pressures for 80% stoke and 60% stroke for each of the polymeric membrane used. In each case the volume of oil and water recovered from the emulsified mixture was obtained and recorded.

The effect of various parameters on filtration characteristics like flux reduction, membrane fouling during constant temperature was observed.

1.5 Significance of study

This work will be beneficial to the oil and gas industry operators in the areas of efficient emulsion separation and management. Since oil and water emulsion is constantly encountered in the field and in process equipment. This work will present a new approach of emulsion separation that is cheap and efficient and does not require the costly chemical additions that in most cases also impact negatively on the ecosystem.

This work when published will inform the general body of knowledge, engineers, and scientist of the recent breakthroughs in oil and water demulsification using polymeric membranes. This will radically change the interest and practice of emulsion treatment in the industry.

CHAPTER TWO

LITERATURE REVIEW

2.1 Emulsions

Emulsions are defined as a heterogeneous liquid system consisting of immiscible liquids with one another where one liquid is dispersed in another in the form of drops. The emulsions are distinguished by the amount of liquid dispersed in another one. An emulsion consists basically of two phases: a continuous phase (external), where the droplets are dispersed, and a dispersed phase (internal or discontinuous), which are themselves dispersed droplets. Three conditions arenecessary for the formation of an emulsion:

1. Immiscibility between liquid of emulsion
2. Shaking to disperse one liquid in another
3. Presence of emulsifying agents (surfactants)

The characteristics of an emulsion are constantly changing since the beginning of formation until their complete resolution and vary with temperature, pressure,degree of agitation and time of formation (Saad *et. al.,* 2019). From a purely thermodynamic point of view, an emulsion is considered an unstable system due toa natural tendency of the system liquid/liquid separation and to reduce their interfacial area and thus their interfacial energy. However, most of the emulsions are stable for a period of time and have kinetic stability that is due to smaller drop sizes and the presence of an interfacial film around the drop.

2.1.1 Emulsion Formation

Emulsions can be formed during nearly all phases of oil production and processing, for example, Emulsions can be created inside oil reservoirs, in the wellbore throughout production, or in the pipelines during transportation. Emulsion formation and stability have been extensively investigated with respect to their relevance in several technological areas, such as the petroleum, coating, food, cosmetic, and pharmaceutical industries, among many others. The factors thataffect crude oil emulsions and their stabilities during emulsification have been thoroughly investigated (Roshan *et. al.,* 2018). Several studies have shown that the formation of crude oil emulsions is strongly dependent on the composition of the crude oil, which often consists of natural emulsifying agents, such as asphaltenes, acidic compounds (naphthenic acids, fatty acids, aromatic acid), and resins (Umar, 2018). The asphaltene fraction is characterized by a high percentage ofheteroatoms such as oxygen, sulfur, and nitrogen. In addition, it also contains organometallic constituents such as nickel, vanadium, and iron in crude oil. Acidic compounds like naphthenic acids are non-polar hydrocarbons, without double bonds, but including straight-chain and branched, and aromatics are formed of structures containing aromatic ring these components could be connected to all oil types. The resins contain a soluble group and interact with the aromatic constituents. This characteristic assists the natural emulsifiers in the formation of a rigid layer around the dispersed droplets that prevent coalescence from happening and make the emulsion more stable (Biniaz, *et. al.,*2016). These natural emulsifiersare abundant in heavy and extra heavy crude oils. The formation of a crude oil emulsion is initiated when there is contact between two immiscible liquids in the presence of an emulsifying agent, provided that there is adequate blending or agitating in order to disperse one liquid in the form of droplets into the other (Saad *et. al.,* 2019).

Wen *et. al.,* (2010) reported that full and partial crude oil emulsification can occur below the critical value of the water fraction and high-water fraction, respectively. The authors established that the emulsion formation *and* behavior vary from one crude oil to another. A follow-up study by Delgado-Linares *et. al.,* (2016) revealed that the natural surfactants in crude oil reduce the IFT of oil–water, leading to the formation of an interfacial film. This interfacial film, which is characterized by its mechanical strength, serves an important function in the formation and stability of the emulsion (Shehzad *et. al.,* 2018).

Studies by Ostertag *et. al.,* (2012), Bauer *et. al.,* (2010), Solansand Sole (2012) have identified the different routes by which oil droplets can be produced for the formation of emulsions. These routes include the use of devices such as dispersing machines, rotor stators, colloid mills, or high-pressure homogenizers that apply high shearing stresses; additionally emulsification can be achieved by using a membrane and applying ultrasonic waves. Chemical reactions or the nucleation of one phase in another as a result of low temperature can lead to immediate crude oil emulsification.

2.1.2 Stability of an emulsion

The stability of emulsion can be determined by the type and amount of surface-active agents or surfactants that can occur naturally in crude oil, for example, the asphaltenes. These surfactants tend to concentrate in the water/oil interface which form interfacial films stabilizing the emulsion by reducing the interfacial tension (IFT) and promotion of emulsification and dispersion of droplets. When energy is added to the system, the particles are broken down into smaller parts and with higher energy, become smaller and, consequently, greater its stability, it is more difficult to treat (Silva, 2008). Some fine solid particles present in crude oil areable to stabilize emulsions by diffusion into the oil/water interface to form rigid structures that can sterically prevent the coalescence of droplets. To act as stabilizers, the particles must be much smaller than the size of emulsion droplets. They must present themselves at the interface and be sprayed with two phases (aqueous and oily) to stabilize the emulsion. Examples of wet solids in oil are wax and asphaltenes and examples of wet solids in water are inorganic compounds such as, $CaCO_3$ and $CaSO_4$, clay and sand. The temperature can modify the physical properties of oil, water, interfacial films and the solubility of surfactants in oily and aqueous phases affecting the stability of an emulsion. When increasing the temperature, it is observed that a decrease in viscosity of emulsion is caused primarily by a decrease in oil viscosity. The temperature increases the thermal energy of droplets and, consequently, increases the frequency of droplets collisions (Saad *et. al.,* 2019). This also reduces the interfacial viscosity and results in a rate of faster drainage of the film, thus increasing the coalescence of droplets. The temperature increase leads to a gradual destabilization of interfacial films (Akbari *et. al.,* 2016). The drop size distribution affects the viscosity of emulsion, which is larger when the droplets are smaller. Usually, the emulsion with smaller droplet size is more stable and the time for separation of water must be larger. Theviscosity of emulsion will also be higher when the droplet size distribution is narrow (i.e., the droplet size is fairly constant). The pH of aqueous phase has a strong influence on the stability and the type of emulsion formed, it affects the rigidity of the interfacial film. The low pH (acid) generally produces emulsions W/O (corresponding to wettability of oil, solid films) and high pH (basic) produces emulsion O/W (corresponding to the water wettability, mobile movies). The emulsions are stabilized by films that are formed around the drops of water in water/oil interface. These films are the result of adsorption of polar molecules of high molecular weight that are interfacial active, i.e. show behavior similar to surfactants. These films increase emulsion stability by reducing the IFT and increased interfacial viscosity. Highly viscous interfacial films act as a mechanical barrier to coalescence. The characteristics of interfacial films vary depending on the type, composition and concentration of polar molecules present in crude oil, temperature and pH of the water. (Kokal, 2005).

2.1.3 Viscosity of emulsions

The viscosity of an emulsion is directly proportional to the viscosity of continuous phase and is defined as the relationship between stress and shear rate. Highly viscous oils usually form more stable emulsions. The volume fraction of the dispersed phase is the most important factor that affects the viscosity of emulsions. With increasing volume fraction of dispersed phase, the internal circulation is reduced, and the viscosity of emulsion increases (Ortiz *et. al.,* 2010). The effect of particle size distribution on the viscosity of emulsions is very important for high values of concentration of the dispersed phase. For lower concentrations, however, the effect is much smaller. When the average size of water droplets dispersed is lower, higher is the residence time of emulsion (Alsabagh *et. al.*, 2016). The shear rate influences the viscosity of emulsions only when it has characteristics of a non-Newtonian fluid. For low values of concentration of dispersed phase, the emulsion exhibits characteristics of Newtonian fluid and, consequently, the shear rate does not affect the viscosity of emulsion. For high values of concentration of dispersed phase, the emulsions exhibit features non-Newtonian (pseudoplastic fluids) and theapparent viscosity decreases significantly with an increasing shear rate (Kokal, 2005 and Silva, 2008). These oils cause emulsions difficult to treat, because they decrease the movement of droplets, retarding the coalescence.

A stable emulsion W/O consists of an aqueous phase, an oil phase and an emulsifying agent. Certain compounds and particles found in crude oil can act as emulsifying agents (surfactants) and thus promote and stabilize these emulsions. Surfactants have hydrophilic and hydrophobic regions so as to fall within the oil-water interface and stabilize emulsions (Ortiz *et. al.,* 2010). If the concentration of particles and surfactants are sufficiently high, then the coalescence of water droplets is prevented, leading to stable emulsions. Certain fractions of polar and high molecular weight exist in crude oil, natural surfactants considered, contribute to the formation of emulsions W/O (Kokal, 2005). These fractions include waxes, asphaltenes and resins and can be dissolved or particulate form (Wei *et. al.,* 2011). These compounds are seen as the main constituents of interfacial films, where they accumulate and thus stabilize the droplets and, consequently, the emulsion formed around the droplets. The accumulation of asphaltenes at the interface results in the formation of a hard film. According to Ortiz (2010) when asphaltenes adsorb onthe water/oil interface, they form an interfacial film with high elasticity. The state of asphaltenes in crude oil also has an effect on its stabilizing properties of emulsions. The asphaltenes will stabilize emulsions when they are present in colloidal form. There is strong evidence that its properties are significantly increased when stabilizers are precipitated in the oil (Antes *et. al.*, 2017). If emulsifying agents do not exist in crude oil, the instability of the system contributes to the coalescence, facilitating phase separation. If there is the presenceof an emulsifying agent, there will be a greater stability of droplets hindering the natural separation of the phases. A region not stabilized is shown with the formation of an incomplete barrier. Several studies demonstrate the importance of asphaltenes, resins and paraffins existing in crude oil in the promotion and stabilization of emulsions of water-in-oil (Bauer *et. al.,* 2010).

2.1.4 The impact of asphaltenes in oil emulsions

The formation of an emulsion W/O can be a serious obstacle for the production of oil, and some oils are particularly prone to form more emulsions than others(Muller *et. al.,* 2009). According to Ortiz *et. al.,* (2010), treatment of these emulsions W/O is still a challenge in the oil industry due to the high stability versus coalescence. Phenomenological investigations of physical and chemical properties related to the strength of emulsion are described in the literature in terms of mechanisms, properties and classes of potential compounds that stabilize emulsions. Characteristics commonly linked to w/o emulsions are the API gravity, total acidity index (TAI) and asphaltene content (Muller *et. al.,* 2009). In the petroleum industry, most of emulsions produced is of type W/O.

2.1.5 Types and Structure of Crude Oil Emulsions

Crude oil emulsions consist of complex colloidal structures, with the dispersion of fine droplets of one liquid in another liquid. The two liquid phases that constitute an emulsion are mutually immiscible. A crude oil emulsion is often produced when the oil and water phases are vigorously stirred nevertheless, once the stirring is stopped, there is an immediate break down in the emulsion (Akbarian *et. al.,* 2016). Crude oil emulsions can be classified according to the nature of the dispersed phase; thus, an O/W emulsion refers to oil droplets in water, and a W/O emulsion refers to water droplets in oil. There are also multiple emulsions, such as oil-in-water-in-oil (O/W/O) and water-in-oil-in-water (W/O/W). The composition of oil and water varies in different emulsion types, depending on the nature of the crude oil. Studies have shown that W/O emulsions have ≤ 50 % water, whereas oil-in-water emulsions contain ≥ 80% water. In some specific conditions, the water content in O/W emulsions may be ≥ 20% (Akbarian *et. al.*, 2016).

2.1.6 Demulsification Mechanism

During the demulsification process, the emulsions must go through several steps before being separated into water and oil phases. The mechanisms that are involved in this process consist of creaming and sedimentation, flocculation, Ostwald ripening, and coalescence.

Both sedimentation and creaming are caused by the difference in density between water and oil; that is, the density of water is higher than that of oil. Sedimentation is an important mechanism of crude oil demulsification and is characterized by the water droplets in an emulsion settling at the bottom of the continuous oil phase. In contrast, creaming is the rising of oil droplets to the surface of the water phase. Thus, whether sedimentation or creaming occurs is dependent on whether thedispersed phase is water or oil, respectively.

2.1.6.1 Flocculation

The water droplets in crude oil emulsions clump together during flocculation, thereby forming aggregates or flocs. The flocculation rate depends on severalfactors, such as the water content in the emulsion, temperature of the emulsion, viscosity of the oil, the density difference between the oil and the water, and the electrostatic field.

2.1.6.2 Ostwald Ripening

Ostwald ripening is another process by which crude oil is demulsified. Ostwald ripening is the process by which drops increase in size. The process takes place as soon as the dispersed phase possesses finite solubility in the continuous phase, causing drops of different sizes to migrate toward each other (Takahashi *et. al.*, 2016). Faster growth usually occurs in large volume fractions because it is easier for the drops to exchange material. For heavy oil, the solubility of oil in water or water in oil are low, which slows the drop growth process. The drop growth process via Ostwald ripening plays a crucial role in the stability of oil-in-water emulsions (Zwicker *et. al.,* 2015)

2.1.6.3 Coalescence

Coalescence is an essential step in crude oil demulsification, and it is an irreversible process whereby water droplets fuse or coalesce to form a larger one. The coalescence process often results in fewer water droplets and invariably leads to complete demulsification of the crude oil emulsion. For efficient coalescence, factors such as a high rate of flocculation, absence of mechanically strong films, high interfacial tension and water cut, low interfacial velocity, and high temperature are required.

2.1.7 Crude oil Demulsification Techniques

The techniques used in the demulsification of crude oil emulsions are given and discussed below

2.1.7.1 Chemical Demulsification

The chemical method entails the addition of demulsifiers to crude oil emulsions, and it is one of the most common methods of demulsification. The main functionof the chemical additives used for demulsification is to destabilize the emulsifying agent (Akbarian *et. al.*, 2016). A demulsifier is a surface-active compound, upon its addition to an emulsion, the demulsifier migrates to the oil–water interface and breaks the rigid film, resulting in the coalescence of water droplets. Studies have shown that the optimum disruption of crude oil emulsions by demulsifiers requires the careful selection of the chemicals for a given emulsion, the appropriate amount of the chemicals, proper mixing of the chemical in the emulsion, and sufficient retention time in the separators to allow the water droplets to settle. Also, the emulsion might be completely resolved by the addition of heat, electric grids, and coalescers. In line with this, Razi *et. al.*, (2011) studied the effect of different demulsifier formulations on the efficiency of chemical demulsification of heavy crude oil. The findings showed that the different surfactant demulsifiers varied in water separation efficiency. The best demulsifier formulation separated a water volume of about 80% in the first several minutes of the experiment. The formulated surfactant was observed to be more efficient in the demulsification of a medium crude oil emulsion compared with that of a heavy crude oil emulsion. This difference in the efficiency of the surfactant was attributed to the medium crude oil having lower asphaltene content than the heavy crude oil. In a follow-up study, Al-Sabagh *et. al.,* (2016) investigated the effect of five demulsifiers formulated from different ratios of polymers on the demulsification efficiency of W/O emulsions. The findings revealed that there was an increase in the efficiency of the water separation as the molecular weight increased.

2.1.7.2 Biological Demulsification

Based on the research output in recent publications, biological demulsification receives less research interest than chemical demulsification. The demulsification of crude oil emulsions using biological means is typically accomplished with the aid of a biodemulsifier. A biodemulsifier is a form of bio-surfactant with features that are conducive to the destabilization of a crude oil emulsion. Bio-demulsifiers are environmentally friendly, and their usage does not result in secondary pollution. Biodemulsifiers have the ability to function effectively under extreme conditions and can be used for various compositions of complex crude oil emulsions. One major merit of using a biodemulsifier is that it can be sourced from agricultural and industrial wastes. Huang *et. al.,* (2016) reported the isolation of a biodemulsifier produced by bacterial strains in an environment contaminated with petroleum. Studies have shown that the effectiveness of each isolated bacterial strain varies in different environments and is strongly dependent on factors such as temperature, soil properties, type and quantity of contaminants, and demulsification capability.

Most of the recent studies of biodemulsification have concentrated on the synergy between the effectiveness of demulsification and properties of the isolated bacteria. In line with this, Coutinho *et. al.,* (2013) investigated the demulsifying activities of Pseudomonas aeruginosa MSJ isolated from petroleum-contaminated soil for the biodemulsification of W/O and O/W emulsions. There was a strong relationship between the demulsification potential of the isolated bacterial, the cellular hydrophobicity, and the culture age. The highest biodemulsifying activity was recorded for cells and supernatants from 96 h cultures.

In a similar study by Wu *et al.,*(2018), a demulsifying Alcaligenes sp. (S-XJ-1) bacterial strain isolated from petroleum-polluted soil was used for the biodemulsification of a W/O emulsion. They achieved a demulsifying efficiency of 81.3% within 24 h using a cell concentration of 500 mg/L. The performance of the isolated bacterial strain was attributed to the highly hydrophobic cell surface and the occurrence of amphiphilic compounds in the cell walls. Although the biological demulsification of crude oil emulsions has rarely been studied, a handful of researchers have employed this technique for the demulsification of crude oil emulsions (Biniaz *et. al.,* 2016). It can be seen that organisms or their products (bacterial strains such as Alcaligenes sp., S-XJ-1, rhamnolipids, Paenibacillusalvei ARN63, and Candida sphaerica UCP 0995) isolated from different sources of petroleum-contaminated environments have been employed as demulsifying agents for the biodemulsification of crude oil emulsions. Different concentrations (ranges of 300–6000 mg/L) of cells of isolated strains have been applied in the biodemulsification process, and the resulting dewatering efficiency has rangedfrom 40% to 90%.

2.1.7.3 Mechanical Demulsification

Demulsification by mechanical means entails the disruption of physical barriers or the application of density variation between the water and the oil phases. Mechanical demulsification of crude oil emulsions can be carried out using a seriesof mechanical equipment, such as a free-water knockout drum, two-and three- phase separators (low-and high-pressure traps), desalters, and settling tanks. The presence of relatively large droplets in crude oil emulsions often results in reduced flow velocity, enabling the use of gravitational forces for the separation of oil, water, and small suspended droplets, which usually occurs within a short time in large-volume desalters or separators. The mechanism of the separator employs

flow dynamics to accumulate and concentrate the material and allows for the separation of traces of oil that can be removed from the processed crude oil. The velocity at which oil separates under gravity is one of the crucial factors for using gravity settling tanks for demulsification and is strongly dependent on the concentration of oil in the mixture. The velocity of the oil separation increases by concentrating oil traces in the separator. Usually, the oil is separated in the separator when its concentration in the mixture is very high. One piece of mechanical equipment that is rarely used for demulsification is the centrifuge since its capital cost is high and its capacity is low. In a study by Hao *et. al.,* (2016), centrifugal contactors were employed to resolve the difficulties of over-standardoil content in electric desalting wastewater. The authors investigated the effects of parameters such as rotor speed, inlet flow rate, water temperature, oil content, and crude oil density on the separation efficiency of the centrifugal contactor. They found that a decrease in the inlet flow rate increased the oil concentration and decreased the oil density, resulting in a corresponding increase in oil removal efficiency (Coutinho *et. al.,* 2013).

Unlike the rarely used centrifugal contactor, the gravity settling tank is widely applied in the industry as a mechanical demulsifier. In a gravity settling tank, emulsions sediment by gravity, thereby separating oil and water. During the sedimentation of the emulsion, the dispersed-phase droplets are brought closer together and coalesce. For efficient demulsification, a centrifugal contactor can be combined with a gravity settling tank, as reported by Akbarian *et. al.,* (2016), who investigated the kinetics of demulsification of a model O/W emulsion using a centrifugal field to mimic the force acting on emulsion droplets in O/W separators. The main focus of the study was the growth rate of the separated oil phase, as well as the variation in the mean droplet diameter of the emulsion layer, as a function of centrifugal acceleration and time. They reported a significant improvement in the demulsification of crude oil as the centrifugal acceleration and time increased, with an oil recovery efficiency of 84%.

2.1.7.4 Thermal Demulsification

Demulsification by thermal treatment refers to the separation of the oil and water phases in a crude oil emulsion by increasing the temperature of the emulsion. A heater is usually employed to raise the temperature of the crude oil emulsion before it enters a horizontal flow treater. Demulsification of crude oil at high temperature reduces the rigidity of the interface, thereby making it easier for droplets to coalesce on collision. The higher the thermal energy, the higher the rate of collision between the droplets (Akbarian *et. al.,* 2016). One major drawback of thermal demulsification is the loss of light ends from the crude oil as a result of the heating and invariable increase in the crude oil density, which has adverse effects on gravity settling. For an improved demulsification process, thermal treatment is often combined with a chemical method of demulsification because the viscosity of the emulsions can be reduced by changes in temperature. The demulsification of a crude oil emulsion by convectional and microwave heating was investigated by Akbari *et. al.,* (2016). Comparative experiments revealed that a separation efficiency of 100% was attained in a short time by microwave heatingdemulsification, whereas the separation efficiency by convectional heating was 96%. These maximum separation efficiencies by the two heating methods were obtained in optimum conditions in terms of their radiation time (3min), microwave power (360W), and demulsifier concentration (2.5vol%).

Mohammed *et. al.,* (2013) also employed microwave heating techniques for the demulsification of crude oil in a series of batch. They investigated the effects of operating variables such as irradiation power (700–900 W), water content to oil (20–80%, 30–70%, and 50–50%), and salt content (1000–3000 ppm) on the demulsification performance. The best separation efficiency was attained at 900 W of irradiation power, 50% water content, and 160 seconds of irradiation time. The effect of temperature on the demulsification of bitumen emulsions was investigated by Taylor *et. al.,* (2011) who revealed that there was gradual breaking in the bitumen emulsion as the temperature of the phase approached the cloud point. It was also observed that the bitumen–water interfacial tension decreased as the heat increased and became smaller at the cloud point temperature (Taylor, 2011).

Al-Sabagh *et. al.,* (2015) also studied the effect of heating on demulsification efficiency and showed that increasing the temperature to around 70 ◦C resulted in improved demulsification efficiency for the unbreakable asphaltenic emulsion. Martínez-Palou *et. al.,* (2013) studied microwave and oil bath heating to compare the water separation time of an oil-in-water emulsion. Microwave dielectric heating of O/W emulsions yielded better water separation in a shorter time than traditional oil bath heating.

Binner *et. al.,* (2014) conducted a comparative study on the separation of W/O emulsions by natural gravity settling and the microwave heating method. They reported that microwave heating resulted in improved water droplet coalescence in water-in-oil emulsions. It was observed that an increase in the salinity of the water phase resulted in a decrease in the settling time for untreated emulsions compared with microwave-heated emulsions.

2.1.7.5 Electrical Demulsification

Demulsification by electrical techniques entails the application of electric fields for the separation of oil and water in crude oil emulsions. Electrical demulsification techniques are more sustainable compared with other demulsification methods and have been commonly applied for more than a century. The electrical demulsification technique is gaining wide acceptance in the industry as a technological route for the demulsification of crude oil. The advantages of the technique include low sludge production, simple equipment, and a lack of chemical agents (Eow and Ghadis 2002). During electrical demulsification, an electric current is typically applied to consumable electrodes that are in contact with the crude oil emulsions, thereby resulting in an in situ coagulant dose (Zhang *et. al.*, 2018). The coagulant dose facilitates the destabilization of the repulsive charges of the surfactant molecule, which in turn enables the trapping of oil droplets and forms larger flocs that can be easily separated from the water. During electrical demulsification, the application of an electric field often causes the droplets to polarize, and drops can align in chains that are parallel to the applied field as a result of the interaction between the induced dipoles. Additionally, the electric fields promote the quick fusion of small water droplets into larger ones. Thedeformation and elongation of the droplets result in rapid coalescence. Although electrical demulsification has been deemed a substitute for thermal and chemical demulsification, the method for adapting the technique to different emulsions with varying properties is not fully understood. Several studies have reported the electrical demulsification of crude oil emulsions with an emphasis on droplet formation (Less and Vilagines, 2012).

Mousavi *et. al.,* (2014) investigated the effect of pulsatile electric fields (PEFs) on secondary droplet formation. The findings revealed that an increase in the frequency of the PEF suppressed the formation of secondary droplets in the low-frequency electric domain.

Zhang *et. al.,* (2018) examined the influence of a demulsifier on the distortion and breakup of hydrous drops in an immiscible dielectric oil under the effect of an electric source. The experimental runs were performed in a single dropmicroscopic cell under an external electric field. Their results showed that bigger drops were deformed more than smaller drops under the action of an electric field, and the interfacial tension was significantly lower in the presence of a surfactant.

In a similar study by Mhatre and Thaokar (2015), the relative merits of symmetric and asymmetric non-uniform and uniform electric fields in the electro-coalescence of three types of crude oil emulsions were investigated. They reported that electro-coalescence was affected by the non-uniformity, as well as asymmetry, of the electric field.

Wang *et. al.,* (2015) studied molecular dynamics simulations by investigating the electro-coalescence action of two loaded droplets under stable and pulsed direct current electrical sources. The application of a constant DC electric field accelerated the droplets' approach to each other before contact when encountering an attractive force.

Muto *et. al.,* (2016) investigated the effect of variables such as the type and volume fraction of an organic solvent and the ionic strength of an electrolyte in the water on the demulsification of crude oil emulsions using an alternating electric current field (square waveform and sine waveform alternating electric field). The demulsification of the crude oil emulsion was more effective under the square waveform alternating electric field than the sine waveform. Besides thisobservation, the rate of demulsification changed meaningfully when the volume fraction of the organic solvent and the ionic strength of the electrolyte were altered.The authors concluded that crude oil demulsification using an alternating electric field was very effective for W/O emulsions. The rate of demulsification of W/O emulsions in direct current fields was reported by Mohammadian *et. al.*, (2018), who showed that the rate of water separation increased with the direct current fields. The authors concluded that the demulsification of crude oil emulsions was guided by the magnitude of the applied electric field and the type of electrode. Although electrical demulsification has been successfully employed for different industrial processes, particularly in the treatment of various industry effluents frompaint manufacturing and oilfield-produced water, research efforts are stillconcentrated on improving the efficiency of the process.

2.1.7.6 Ultrasonic Demulsification

The demulsification of crude oil emulsions by the ultrasonic technique is based on the principle of condensation and the viscosity-reducing impact of ultrasound on crude oil. The ultrasound facilitates the clumping of water droplets in the crude oil, thereby facilitating the separation of the oil–water phases. The simplicity and efficiency of ultrasound demulsification applied to crude oil emulsions has attracted increasing research attention. During ultrasound demulsification, the acoustophoresis phenomenon often influences the dispersed droplets under an ultrasonic standing wave field. The variation in the density and compressibility of the dispersed droplets and the continuous phase can cause the acoustic standing wave to combine homogeneously suspended droplets. Several studies have reported the application of ultrasound energy for the demulsification of crude oil emulsions. The effect of parameters such as the irradiation input power, irradiation time, temperature, and injected water on the demulsification efficiency was investigated by Check and Mowla (2013). The interaction between the parameters resulted in the highest demulsification efficiency (99.8%) at an optimum input power of 57.7 W, irradiation time of 6.2 min, and temperature of 100 ◦C. A further investigation focused on the effects of two ultrasonic irradiations, namely, primary and secondary, for the demulsification of crude oil emulsion. The findings showed that the settling time decreased at an irradiation power of 75 W for primary irradiation and 50 W for secondary irradiation at an irradiation time of 45 s. There is a growing interest in the application of low-frequency ultrasound for the demulsification of crude oil emulsions.

Antes *et. al.,* (2015) studied the effect of low-frequency ultrasound on the demulsification of crude oil emulsions in the absence of a chemical emulsifier. They demonstrated that a demulsification efficiency of 65% was attained by low-frequency ultrasound.

Khajehesamedini *et. al.,* (2018) (also reported the use of low-frequency ultrasonic waves for the demulsification of crude oil emulsions. They attained a demulsifying efficiency of 50% at a very low frequency, low irradiation time, and high-intensity ultrasonic waves. The use of pulsed ultrasonic irradiation techniques for the demulsification of crude oil emulsions was reported by Xie *et. al.,* (2015), who observed the pulse irradiation techniques facilitated water coalescence, thereby improving the demulsification efficiency. Antes *et. al.,* (2017) used ultrasonicbaths at different frequencies for the demulsification of crude oil emulsions (Antes *et. al.,* 2017). Effective demulsification of crude oil with a 65% efficiency was achieved at a frequency range of 25–45 kHz after 15 min. At a frequency of >45 kHz, there was no evidence of crude oil demulsification.

In the work of Pedrotti *et. al.,* (2018), a demulsification efficiency of up to 93% was attained at 15 min of sonication (100% amplitude).

Pedrotti *et. al.,* (2018) proposed the use of indirect low-frequency ultrasonic energy for the demulsification of crude oil. The results showed that a higherdemulsification efficiency (up to 93%) was attained in the most intense acoustic regions compared with that positioned in the less intense acoustic field regions.

2.1.7.7 Membrane Demulsification

The use of membrane technology for the demulsification of crude oil emulsions is relatively new and receiving increasing research attention. The membrane demulsification of crude oil emulsions is based on the tendency of low pressure to move the dispersed phase, resulting in its permeation through a membrane into the continuous phase. The application of membrane technology for the demulsification of crude oil emulsions has the advantages of being an inexpensive and efficient option for the demulsification of crude oil emulsions. Recently, several studies have been published on the application of membrane technology for the demulsification of crude oil emulsions.

Wu *et. al.,* (2018) investigated the effect of membrane surface charges on crude oil demulsification and fouling resistance. Two membranes, namely, PP-g-pDMAEMA and PP-g-pOEGMA, were employed for the demulsification process. The membranes displayed positive and negative surface charges in water, respectively. A demulsification efficiency increase of 15% was obtained using PP-g-pDMAEMA compared with the use of PP-g-pOEGMA. The authors concluded that the membrane surface positive charges enhanced crude oil demulsification. Nevertheless, membrane damage after the demulsification was intensified. One major challenge faced when using membrane technology for crude oil demulsification is membrane fouling. Fouling reduces the flux and the membrane's lifespan, thereby resulting in expensive maintenance during application. The findings of Liu *et. al.,* (2007) revealed that both the surface charge and surface hydrophilicity mitigated the irreversible fouling of membranes. The use of superhydrophilic and underwater superoleophobic surfaces using high-surface-energy materials is receiving considerable attention from researchers. This is because these properties enhance the antifouling ability and separation efficiency of the existing membrane. These membranes are electro spunnanofibrous materialswith the advantages of having high porosity, high surface area, and easily tunable structures. Because of the exceptional properties of membranes with superhydrophilic and underwater superoleophobic surfaces, Chen *et. al.,* (2016) employed a silica nanosphere-coated membrane for crude oil demulsification. Application of the membrane for crude oil demulsification resulted in a high efficiency (>98%) for separating oil-in-water emulsions under the harsh influence of strong acidic and concentrated salty conditions. The authors concluded that the membrane had excellent stability since the efficiency did not visibly decrease after several uses.

In a similar study, Zhang *et. al.,* (2018) employed a thermoresponsive poly(N-isopropylacrylamide) (PNIOAAm)-modified nylon membrane for the demulsification of crude oil emulsions. The fabricated membrane has the advantages of a rough structure, appropriate pore size, and thermo-responsivewettability and is capable of separating 16 different types of stabilized O/W and W/O crude oil emulsions at different temperatures. At a temperature ofapproximately 25 ◦C, the membrane was able to separate any kind of crude oil emulsion. Conversely, at a temperature of approximately 45 ◦C, the membrane displayed high hydrophobicity and superoleophilicity, which can only be employedfor the separation of stabilized crude oil emulsions.

In a similar study, Ge *et. al.,* (2017) developed a novel superhydrophilic and underwater superoleophobic nano-fibrous membrane with a hierarchically structured skin for O/W demulsification. The membrane displayed an exceptional separation efficiency, strong antifouling properties, and an extremely high flux that was mainly driven by gravity.

2.2 Membranes

Membranes are thin semipermeable barriers that selectively separate some compounds from others (Zhao *et. al.,* 2016). This definition is necessarily broad because of the large variety of membrane materials separating an equally vast number of compounds in all phases. Separation of molecules in the feed, having different chemical potentials like pressure or concentration, is achieved by membrane processes. Some major application of membranes includes Microfiltration

1. Ultrafiltration
2. Reverse osmosis
3. Gas separation/permeation
4. Pervaporation
5. Dialysis
6. Electrodialysis
7. Liquid membranes

All membrane separations rely on a driving force across the membrane to induce the flow or flux and a separation factor which prevents some materials crossing. Pressure is the most common driving force in that case low-pressure permeate stream becomes enriched by rapidly diffusing components while the slower components are concentrated in the retentate stream. Either permeate or retentate could be the product (Zhao *et. al.*, 2016).

2.2.1 Membrane Structure

Chemical structures coupled with the subtle physical properties of a membrane influence the permeability and selectivity. The response of polymeric material to permeation is strongly influenced by polarity and steric characteristics of the barrier as well as the permeating component (Othman and Bhatia, 2009). Size and shape of the bulky groups in the main chain as well as the side chain determine certain fundamental properties like packing density and rigidity, which in turn influence its accessibility. Studies indicate that permeability and selectivity of polymeric membranes cannot be drastically improved by incorporating variationsin the basic structure of a particular polymer Kusworo *et. al.*, 2008). Such efforts only shift the compromise between permeability coefficient and selectivity, but do not constitute a concrete improvement. Therefore, the dependence of permeability on chemical structure can only be a rough approximation because the chemical structure is only one of the determinants for assessing membrane properties (Li *et. al.*, 2006). Physical structure is usually as important and therefore, has received a greater attention due to its contribution in practical applications.

The physical structure that encompasses the mechanical state of matter (density, mobility and order) has a strong bearing on gas separation properties of the membranes.

For membranes, several physical structures like microporous, dense, asymmetric and composite exist. Generally, membranes used in laboratory scale set-ups for the separation of gaseous mixtures are always homogeneous and symmetric because they are easy to cast and will directly give the intrinsic separation properties of the polymer. However, to attain commercial viability, membranes that are successful on a laboratory scale are converted to asymmetric or composite forms (Sridhar *et. al.*, 2007). These two morphologies offer the possibility of making a barrier with a thin effective separation layer, which enables high flux, while maintaining the desirable mechanical strength. Asymmetric membranes consist of a thin denselayer on top of a porous support layer of the same material. These membranes are prepared by phase inversion technique where a homogeneous polymer solution is cast as a thin film or spun as a hollow fiber and immersed in a non-solvent bath after giving it a brief evaporation time in air. The membrane is formed by the replacement of solvent by non-solvent and precipitation of the polymer (Mansourizadeh and Ismail, 2009).

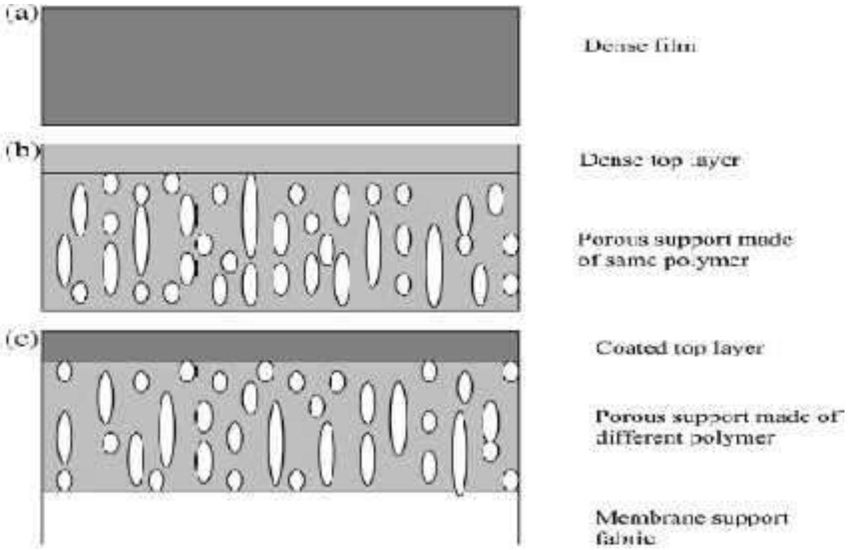

Figure 2.1: Schematic representation of three different types of membrane morphology (a) Homogeneous symmetric membrane, (b) Asymmetric membrane and (c) Composite membrane (Sridhar *et. al.,* 2007)

Asymmetric membranes consist of an extremely thin nonporous layer mounted on a much thicker and highly porous layer of the same material. This membrane porosity is more-or-less uniform throughout. An example of an asymmetric membrane is shown in Figure 2.2.

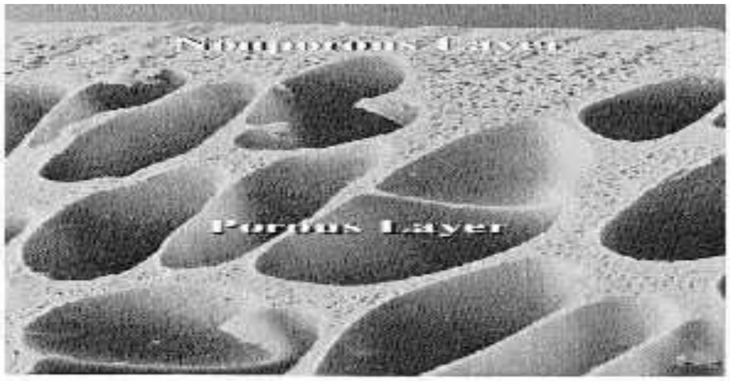

Figure 2.2: Asymmetric membrane structures (Sridhar *et. al.,* 2007)

The nonporous layer meets the requirements of the ideal membrane, that is, it is highly selective and also thin. The porous layer provides mechanical support and allows the free flow of compounds that permeate through the nonporous layer.

Although asymmetric membranes are a vast improvement on homogenous membranes, they do have one drawback. Because they are composed of only one material, they are costly to make out of exotic, highly customized polymers, which often can be produced only in small amounts (Oral, 2011).

This difficulty is overcome by producing a composite membrane, which consists of a thin selective layer made of one polymer mounted on an asymmetric membrane, which is composed of another polymer (Topuz *et al.*,2012). This composite structure allows membrane manufacturers to use readily available materials for the asymmetric portion of the membrane and specially developed polymers, which are highly optimized for the required separation, for the selective layer. An example of this structure is shown in Figure 2.3.

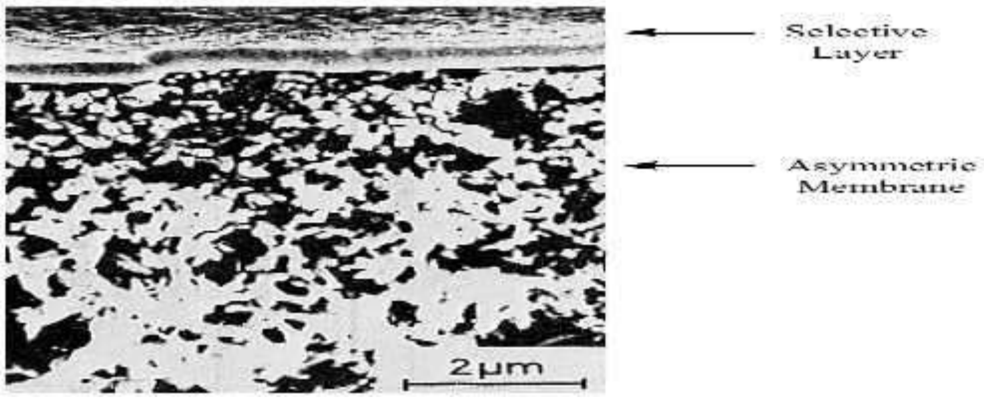

Figure 2.3: Composite membrane structures (Sridhar *et. al.*, 2007)

Composite membranes consist of a porous support layer with a thin dense skin layer coated on top of it. The top layer is made of a material different from the support layer. Utilization of composite structures minimizes the membrane cost by reducing the quantity of expensive high performance material used, if any. Composite structures are being used in most of the newer advanced CO_2 removal membranes because the properties of the selective layer can be adjusted readily without increasing membrane cost too significantly.

2.2.2 Membrane Properties

So far, most of the researches on the membrane gas absorption are largely at the stage of laboratorial scale, and the long-term stability of the membrane has seldom been considered in the literature. It is important from an economic point of view. One of the major problems in the application of porous membranes is fouling. Fortunately, in the gas absorption applications, the contactors are less sensitive to fouling since there is no convection flow through the membrane pores. However, in industrial applications, the flue gas with large content of suspended particles can cause plugging due to the small fiber diameter (Vaughn *et al.*,2012). In such a case, pre-filtration is necessary. The chemical stability of the membrane material has a considerable effect on its long-term stability. Any reaction between thesolvent and membrane material could possibly influence the membrane integrity and surface structure. Liquid absorbents with high load of acid gases are corrosive in the nature, which make the membrane material less resistance to chemical attack(Zhao *et. al.*, 2016).

Barbe (2000) examined surface morphology changes of hydrophobic Celgard 2500 and Accurel 1E-PP membranes during initial contact with water using scanning electron microscopy (SEM) and image analysis. The surfaces of both membranes showed increases in several of the following morphology parameters after 72h of contact: porosity, pore area, pore length, pore breadth, pore equivalent diameter and pore spread factor. This was attributed to non-wetting intrusion of the water meniscus into some pores with a resulting enlargement of pore entrances. Toensure the long -term stability and the maintenance of the separation efficiency, the compatibility of the membrane to the solvent needs to be investigated.

The thermal stability of the membrane is also an important parameter in the case of gas absorption. Under high temperatures, the membrane material may not be able to resist to degradation or decomposition. The extent of membrane change depends on the glass transition temperature *T*g for morphous polymers or the melting point *T*m for crystalline polymers. Over these temperatures, the properties of the polymers change dramatically. The transition temperature of a polymer is determined largely by its chemical structure, which includes mainly the chain flexibility and chain interaction. PTFE, which has four fluoride side groups on the flexible polyvinyl chain, has a more restricted flexibility, and hence, a much higher*T* g compared to polyethylene and polypropylene. This feature contributes to its higher stability. In general, the factors that increase the *T*g/*T*m or the crystalinity ofa membrane can enhance both its chemical and thermal stability.

In conclusion, in terms of long-term stability, membrane material with suitable *T*g needs to be applied. For the H_2S off-shore removal from natural gas, membrane with moderate *T*g can be considered since the separation can be carried out at ambient temperatures. However, for the CO_2 absorption from flue gases, membrane with high *T*g (possibly over 100 ^{O}C) may need to be applied because flue gases are often emitted at high temperatures. Under such high temperatures, thermal stability of the membrane material decides the membrane performance and the economy of the operation. For such applications, fluorinated polymers are good candidates due to their high hydrophobicity and chemical stability. Polymers like Polyimide, having a *T*g as high as 300 ^{O}C could exhibit good thermal and chemical stability. Moreover, its hydrophobicity can be significantly improved by being fluorinated (Kim *et. al.*, 2000).This type of membrane can be considered to be used in the gas absorption applications.

Aluminium oxide nanoparticles can be used to improve the rheological and filtration properties of the emulsion. These results demonstrated that nanoparticle enhanced thermal stability at heightened temperature when used to dope the membrane. They impose a lower environmental impact and capital costs.

2.3 Nanoparticle and ItsTypes

We have basically two types of nanoparticle. There are:

1. Metal Oxides Nanoparticles
2. Others/Hydrophobic Nanoparticles

2.3.1 Metal Oxides Nanoparticles

With the advancement in nano-sciences, some researchers have investigated the use of some metal oxides NPs and proven their ability as membrane separation

Ogolo *et. al.*, (2012) investigated the performance of eight NPs (oxides of aluminium, zinc, magnesium, iron, zirconium, nickel, tin and silicon) and four base fluids (distilled water, brine, ethanol and diesel oil) for enhanced oil recovery. The results obtained from the experiments exhibited that Al_2O_3 nanoparticles dispersed in brine and distilled water had the tendency to improve oil recoveries through reduction of oil viscosity. Magnesium and zinc oxide in distilled water and in brine resulted in permeability problems due to their large diameter. Ragab *et. al.*, (2015) performed experiments to compare the potentials of SiO2 and Al_2O_3Nanofluid used to improve the oil recovery. They found experimentally that SiO_2 NPs with different concentrations could be used to improve the recovery actor. However, the oil recoveries of Al_2O_3 NP were not better than that of water flooding. In addition, Hendraningrat *et. al.*, (2014) investigated Al_2O_3 and TiO_2 and compared them with SiO_2. The results showed that the highest total oil recovery was achieved by using TiO_2. Then, Binshang *et. al.*, (2016) found that TiO_2 NPs in low concentration could enhance heavy oil recovery in flooding experiments on a laboratory scale.

2.3.2 Others/Hydrophobic Nanoparticles

Other commonly used nano materials are cellulose Nano crystals (CNC) and micro-gel nano-spheres. Molnes *et. al.*, (2016) investigated the injectivity of CNC in a high-permeable sandstone core, and found that CNC has potential as additivesin injection water for demulsification. Then, Heggset *et. al.*, (2017) found that

CNC has temperature stability that was stable after heating to140^{O}C for three days. Wei *et. al.*, also believed that Nano crystals are supposed to be a promisingflooding agent in the near future.

Moreover, Kanj *et. al.*, (2009) performed an experimental study on nanofluids ($BaSO_4$) core flood experiments in the ARAB-D formation of the giant Ghawar field in Saudi Arabia. Meanwhile, Wang *et. al.*, (2012) prepared a polyacrylamide micro-gel Nano-spheres and used them to enhance the recovery of Zhuangxi heavyoil in a sand-pack model. They confirmed experimentally the promising future of Nanoparticles For carbonate reservoirs.

2.3.3 Formulation of Nano-fluid and StabilityControl Mechanism.

Generally, nano particles can be prepared via chemical, biological or physical methods (Saravanan *et. al.*, 2016) although the preparation method is mainly based on the nature of the material and the associated chemical reactions, and the applications thereof. The type of nanoparticle chosen is dependent on the nature of the available dispersion fluid. Cognizance is taken while forming the Nanofluid to avoid production of Nano emulsion instead. Hence, polar nanoparticles like the metallic oxides is preferably used when the dissolution fluid is a polar solvent (e.g. fresh water, brine, ethanol etc.). Production of Nanofluid is by dissolution of the chosen Nanofluid in a given solvent. Proper agitation is very pertinent during the production process to avoid coagulation and flocculation of the nanoparticle in the fluid. Kseniya *et. al.,* (2021) worked on various gas separation; CO_2 capture; with mixed matrix membranes. An analysis of the effect of zif-8 addition on the separation properties of polysulfone at various temperatures.

CHAPTER THREE

MATERIALS AND METHODOLOGY

3.1 Introduction

This chapter gives the description of equipment, and materials. Performing several experiments related with oil-water emulsion. The equipment and materials for all the experiment are discussed collectively. Each experiment is given and discussed according to its aim.

3.1.1 Principle of Membrane Separation

A membrane is a selective barrier that permits the separation of certain species in a fluid by combination of sieving and sorption diffusion mechanism. The basic principle of membrane separation is selective permeation. Separation is achieved by selectively passing (permeating) one or more components of a stream through the membrane while retarding the passage of one or more other components.Membranes can selectively separate components over a wide range of particle sizes and molecular weights, from macromolecular materials such as starch and protein to monovalent ions.

The key properties determining membrane performance are high selectivity and fluxes, good mechanical, chemical and thermal stability under operating conditions, low fouling tendencies and good compatibility with the operating environment; and cost effective and defect-free production.

In a membrane process. The feed stream is divided into two: the retentive and the permeate. The retentive is that part of the feed that does not pass through the membrane, while the permeate is that part of the feed that does pass through the membrane.

3.1.2 Principle of membrane separation applied in Oil/water emulsion separation

Most membranes used for oil/water separation rely on oil-absorbent and water-repellent materials. Membrane separation of oil and water emulsions is basically based on two mechanisms

1. Size exclusion (i.e., sieving) and
2. Selective wettability.

Size exclusion means that the membrane allows water to pass through under an applied pressure which blocks the oil droplets which are larger than the membrane pores. However dispersed droplets (oil droplets) can deform and squeeze through pores that are smaller than. To prevent droplets of one phase from squeezing through a membrane, the surface energy of the membrane must be controlled. This problem can be solved by surface wettability. Developing Membranes with contrasting wettability have been shown to selectively filter one phase depending on whether they are hydrophilic/oleophobic or hydrophobic/oleophilic.

Selective wettability means that the membrane surface has affinity to one of the phases and repels the other phase. In oleophilic membrane separation system, the membrane surface is designed to repel water and attract oil molecules. In this system, water is preferentially driven out of the emulsion system when it comes in contact with the membrane surface under pressure application while oil adheres to the membrane surface.

In hydrophilic system, the reverse is the case, the membrane system is designed to absorb water while oil is repelled. In this system oil becomes the filtrate while water is retained.

3.2 Apparatus and material

In this section, the apparatus and materials for the experiment are Presented and discussed individually.

3.2.1 Apparatus

The apparatus used throughout the experiments performed in this work are Presented below:

1. Conical Flask
2. Beaker (several sizes: 500ml, 250ml)

3. Measuring Cylinder
4. Laboratory Oven
5. Vacuum Pump
6. pH Metre
7. Separation Funnel
8. Turbidity Meter
9. Viscometer
10. Conductivity Metre
11. Filtration Apparatus
12. Clip

3.2.2 Materials Used

1. Crude oil sample
2. Membrane Support: Porous polyester membrane (Net Fabric), polystyrene membrane, Polysulfone (non-woven material)
3. Iso-Hexane
4. Silicon Sealant
5. Aluminum oxide nanoparticle
6. Deionized water

7. Petroleum ether. 8. Silver Sulphate

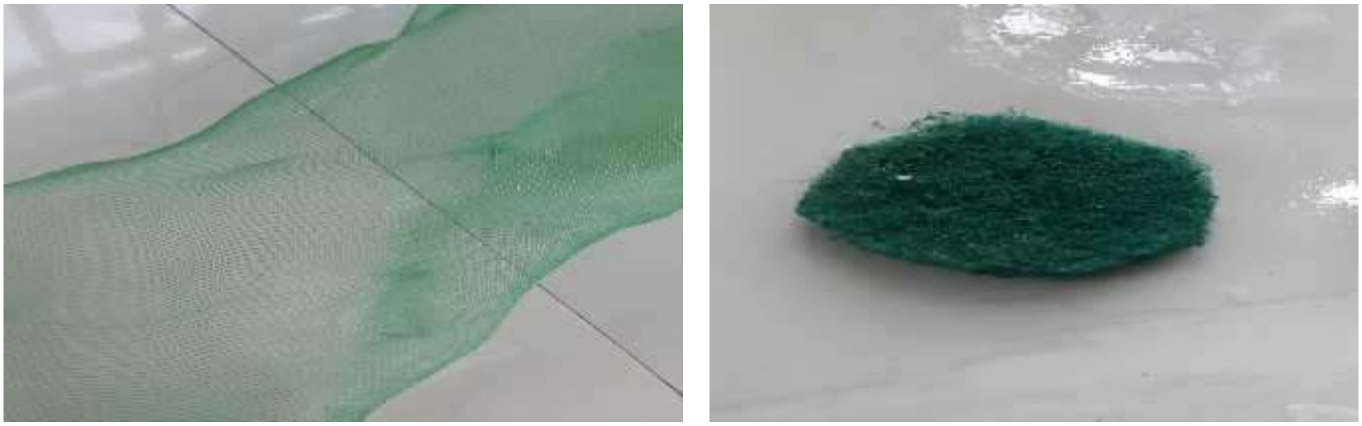
(a): Polyester (b). Polysulfone

Figure 3.1(a and b): Different Membrane support materials

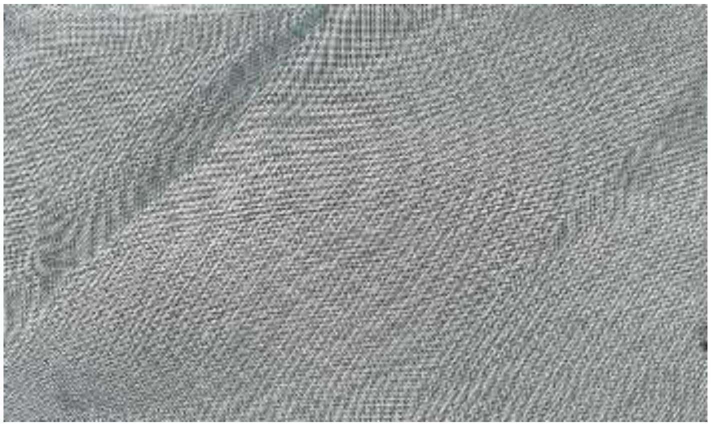

Figure 3.1c: Membrane Support material (Polystyrene)

3.3 DESRIPTION OF EXPERIMENTAL PROCEDURES

In this section, the procedures for all the experiments performed in this work are outlined sequentially. All the necessary steps taken in conducting the experiment are discussed.

3.3.1 Experiment 1: Preparation of the Aluminium oxide nanoparticle membrane

The Aluminium oxide nanoparticle membrane was prepared using the support materials which are Polysulfone and polyester fabric.

Procedure

5g of silicon sealant was dissolved in 10ml of iso-hexane.

20g of Aluminium oxide nanoparticle was put into 500ml beaker. Then 20g of the Aluminium oxide nanoparticle was added into the silicon sealant-iso-hexane solution at room temperature, this was stored for 1 minute to form a paste like slurry.The whole mixture was then stirred consistently and cast on the top of the sample membrane based support. This was also done at room temperature and then left to settle for 10 minutes. The coated membrane sample was anchored to the membrane filtration apparatus with vacuum grease and then allowed to dry in open air for about 1 hour.A thickness of 3mm was obtained.

The membrane filtration apparatus consist of the beaker, filtration apparatus and has a magnet on the bottom to fix tightly to the base. The base is connected to the stopper. In-between the base and the stopper is the nano-ultrafiltration membrane which is held tightly together with an external clip placed between the upper filtration beaker and the receiver conical flask where filtrate samples goes into.

3.3.2 Experiment 2: Preparation of Emulsified oil/water

Aim: To achieve a stable and uniform mixture of the oil and water

The apparatus used are 500g beaker and measuring cylinder.

Procedure

In preparing the oil/water emulsion: 50ml of crude was put into a beaker. 500ml of deionized water was added to the crude oil. The resulting mixture was mixed thoroughly to obtain a homogenous oil/water emulsion (0.01% w/o emulsion). The Mixture was then blended in a high speed blender at 20,000rpm (high rotational speed) for 1 minute. The oil droplet size was then measured by an optical microcopy method

Figure 3.2: The Oil-water emulsion prepared

3.3.3 Experiment 3: Characterization of the Emulsified oil-water

The oil-water emulsion was characterized using the following apparatus: pH metre, beaker

Aim: to identify the acidity of the emulsion

Procedure

A pH reading of 7 is termed neutral, a pH<5 reading indicates the water is more acidic and a pH > 9 indicates the solution is more alkaline which suggests that the quality of the solution is adversely affected due to the presence of some contaminants in it.

3.3.4 Experiment 4: Test for Oil Content

The oil content test was done because the crude oil gotten was a crude with high water content. It is necessary to determine the true volume of the oil for high efficiency of the experiment.

Aim: To determine the quantity of oil in the emulsified solution

Procedure

100ml of emulsified oil/water was measured in a conical flask**.** Then2ml of concentrated sulfuric acid was added together with 50 ml of petroleum ether. The mixture was shaken vigorously for 30 minutes and then poured into a separating funnel to demulsify the oil. The clean upper layer was then collected and poured into a pre-weighed conical flask**.** The liquid was then heated to evaporate todryness at 105^{o}C temperature**.** The product was then allowed to cool and then the conical flask was reweighed

The result was recorded

$$(W_2 - W_1) * \frac{100}{1} \quad \text{------------------------- Equation (1)}$$

Where $W_2 = Conical\ flask + dry\ extract$

$W_1 = Empty\ conical\ flask$

3.3.5: Experiment 5: Chemical Oxygen Demand (COD)

Aim:

i. To determine the amount of oxygen required for chemical oxidization such as potassium dichromate under reflux concentrations.

ii. This is an indication to measure the amount of oxygen that can be consumed by reactants in the solution.

Procedure

0.2g of silver sulphate was weighed using weighing balance. 0.25ml of potassium dichromate was prepared, then 5ml of potassium dichromate was added to 0.2g of silver. The dichromate can be known by observing yellow colour of dichromate in the flask. 2 glass bead (in the form of grain) was added to avoid bumbling (bubbles). 10ml of sample A (70%) and sample B (80%) were added to thesolution, then 15ml of concentrated tetraoxosulphate (vi) H2SO4 containing silver sulfate was added to the solution prepared above. The mixture was immediately covered to avoid escape of gas and reflux. It was binded with masking tape to beair tight. The mixture was heated for 2 hours in a water bath at 100°C.Then it was allowed to cool. Then 3 drops of Ferron indicator was added. The excess potassiumdichromate was titrated against ferrous ammonium sulphate solution (0.25M) on a scale of 50 in a burette

The burette was filled up.The cool solution was put beneath the burette which has a control valve. The initial colour of the solution was yellow. The solution was titrated until the colour changed to green. The titration was continued until the green colour disappeared. When the colour changes from bluish green colour to reddish brown colour, this indicates the end of the test. Reading was then taken from the burette and recorded. The blank was carried out in a similar manner in comparison with the main sample

Calculations

$$\text{COD}mg/l = \frac{(mlb - mls)\ x\ NFAS\ x\ 8000ml}{ml\ aliquot\ of\ sample} \quad (2)$$

Where

mlb = ml FeSO4.7H2O Required for blank

mls = ml FeSO4.7H2O Required for sample

N = Normality of FeSO4.7H2O

If aliquot = 20ml then

$\text{CODmgll} = (mlb - mls)\ x\ N\ x\ 50\ x\ 8000ml$

$|ml|NK2Cr2O7 = 8mg\ COD$

Note: Silver sulphate acts as catalyst and Mercury sulphate masks halides

3.3.6 Experiment 6: Conductivity Measurement.

The conductivity reading is used to characterize the emulsified solution and determine their maximum amount of water to maintain the solution.

Aim: To determine the salt concentration in the emulsified solution.

Procedure

250ml of emulsified solution was measured into a beaker. The conductivity meter was brought and put on. Then the conductivity metre was inserted in the emulsified solution. The reading was allowed to stabilize in order to obtain accurate readings. Then the highest reading before reduction was taken

3.3.7: Experiment 7: Viscosity test

Aim: To determine the resistance of the fluid

Procedure:

The emulsified solution was poured into a beaker at 150ml and raised to the level of the spindle. The dial reading was set at 60rpm and allowed to spin for 3 minutes. Then the reading was taken and recorded.

3.3.8: Interfacial tension test

Aim

To determine the accumulation of energy and force imbalance between the oil and water phases in the emulsion.

Procedure

A platinum ring was pulled through the surface of the water into the oil, the water adhered to the ring with an observed distance above the surface. When there was a breakage, The force was measured and the result was converted to get the interfacial surface tension.

3.3.9: Experiment 9: Contact Angle Measurement

When a drop of water is placed on a solid, it will spread on the surface based on the inter-molecular interactions between the solid and the liquid

Aim

To determine the wettability of the membrane surface

The apparatus used are: measuring cylinder, Beaker, Pipette

Procedure

The contact angle was measured using a sessile-drop technique and a contact angle device. The contact angle valve was measured 3 minutes after dropping water on the membrane surface and 3 drops were measured for each membrane sample. The average contact angle with a standard deviation of 2 were determined using the following equation

$$cos\theta = 1 - \sqrt{\frac{Bh^2}{\left(1-\frac{Bh^2}{2}\right)}} \tag{3}$$

$$B = \frac{\rho g}{2\gamma} \tag{4}$$

Where

g= gravity acceleration (980cm^2/s^2)

ρ=density of distilled water (6.9971g/cm^3)

γ =interfacial tension of distilled water (71.97g/cm^2)

h=the height of the liquid drop

3.3.10: Experiment 10: Turbidity Measurement

Turbidity metre is the instrument for measuring the turbidity of a solution

10ml of the emulsion sample was prepared and put into the turbidity device and readings were taken and recorded

3.3.11: Experiment 11: Characterization of the membrane

A three liquid mixture of isobutanol/methanol/water of ratio (15/7/25) by volume of surface tension 0.35n/m was used to partition the pore by implementing low pressure. The process used involved filling the membrane with water and displacing it from the pores with an organic phase (isobutanol saturated with water and methanol). The flux through the membrane was obtained by syringe pump to gradually increase the flux on the organic-phase side. Equilibrium pressure was measured at each cumulative stage using a pressure transducer by monitoring the applied pressure and the flux through the membrane. The radii of the opened pores at each applied pressure can be calculated using Cantor's equation:

$$r_p = \frac{2\gamma}{\Delta P} \tag{5}$$

Where

$\Delta \mathbf{P} = \textbf{Applied Pressure, bar}$

$\gamma \equiv Interfacial\ tension$

$r_p \equiv Equivalent\ pore\ radius, in$

Equation 5 determines the equivalent pore radius of the membrane as a result of applied pressure. When pressure is applied, the pore radius increases.

Separation Efficiency

$$\text{S.E} = \left(1 - \frac{C_f}{C_o}\right) x\ 100\% \tag{6}$$

Where

C_o is the oil content in the original emulsion

C_f is the oil content in the filtrate

3.3.12: Experiment 12: Emulsified oil/water separation Experiment

Two samples of Aluminium oxide nanoparticle membrane were tested.

Procedure

1. The prepared oil-water emulsion was stirred for 60minutes to achieve a homogenous mixture under ambient conditions
2. The membranes to be used were pre-wetted before used for the separation
3. The emulsion was poured into a measuring cylinder in the filtration apparatus
4. The procedure was carried out under 80% stroke and 60% strokes

Figure 3.3: Setting up the separation funnel

Figure 3.3 shows the setting up of the membrane separation funnel. The clamp must be tightly fastened to the separation funnel to be able to hold the devices throughout the experiment. This is to avoid loosening during experiment which may lead to damage of the laboratory glass wares and wastage of the fluid content in them.

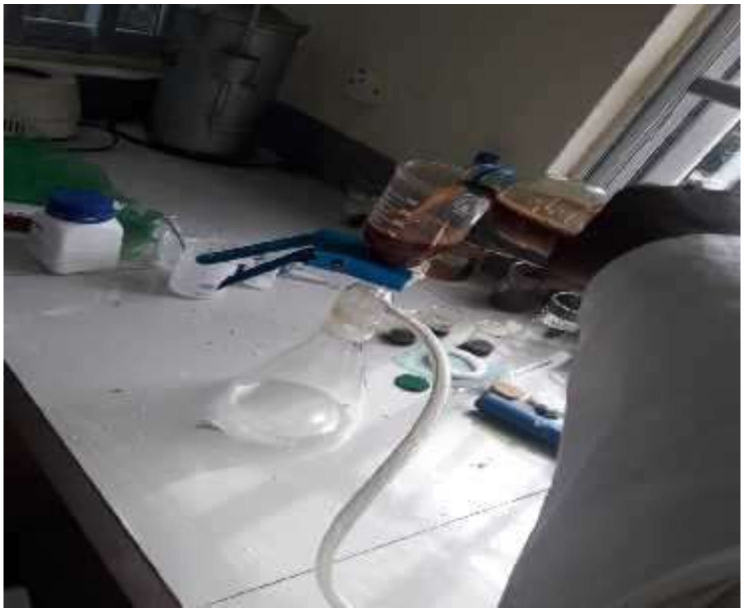

Figure 3.4: Pouring the Emulsion into the Separation Funnel set up

Figure 3.4 shows the separation funnel after being set up and the vigorously stirred emulsion sample being poured into the separating funnel prior to the separation process.

Figure 3.5: Membrane Separation Process using vacuum pump

Figure 3.5 shows the actual emulsion separation process. The separation funnel is connected to the vacuum pump via the connecting pipe. The vacuum pump supplies pressure necessary to agitate the sample and create pressure differential that will induce separation. From the figure water tends to settle at the bottom while oil floats at the top because water is denser than oil. The separation is carriedout by forcing the oily water at the bottom of the beaker in the filtration funnel to pass through the nanoparticle doped membrane substance where the oil part is retained and the water selectively allowed to pass through to the conical flaskwhere it is stored.

Figure 3.6: The Emulsified oil-water separated

Figure 3.6 shows the sample after separation. The first two black samples are oil recovered from the emulsified water after the filtration experiment while the last two samples are water that passed through the funnel as filtrate.

In the vacuum driven membrane filtration apparatus, flux was determined by calculating the volume of filtrates per unit time according to the equation given below:

Permeation flux, J

$J = \frac{V}{PAt}$ (Units in ml/cm^2-min) (7)

V= Volume of Filtrate

P = Separation Pressure

A=Area of the Membrane

t= separation time

CHAPTER FOUR

RESULT AND DISCUSSIONS

4.1 RESULTS OF EXPERIMENT

The results of the various experiments performed were summarized. See table below. Three membranes were used. Polystyrene, polyester and Polysulfone. The experiment (ultrafiltration pressure-driven membrane process) was performed for pressures of 80% stroke and 60% strokes respectively. The reason for using the pressure of 80% stroke and 60% stroke was because; an increase in pressure is required to sustain the permeation flux of the membrane to avoid caking. Also, a higher viscosity of the emulsion is needed so that the mixture can form slurry.Table 4.1 below gives the summarized result of the various experiments

Table 4.1: Summary of Experimental Results

Parameter	Raw sample	Polystyrene		Polyester		Polysulfone	
		80% stroke	60% stroke	80% stroke	60% stroke	80% stroke	60% stroke
pH	5.89	2.5	6.65	4.77	4.86	4.91	5.36
Conductivity, S/cm	33	44.95	50	34.2	23	50	44
Turbidity, NTU	15.7	49	57	10.66	16.05	11.6	18.7
Chemical Oxygen Demand (COD), mg/l	7800	1740	5520	5140	2200	1200	1200
Viscosity, mPa.s	19.9	22.33	20.75	22.77	19.83	19.41	19.34
Filtration time, min	-	7	12	8	15	18	22
Oil Content in filtrate, %	14	0.4	0.34	0.6	0.39	0.404	0.25
Volume of Filtrate, ml	-	172	176	171	175	165	170
Volume retained, ml	-	25	20	22	20	28	21
Total volume of emulsion used, ml	200	200	200	200	200	200	200

Table 4.1 above gives the summarized results for the three membrane materials used for pressures of 80% run and 60% run with the vacuum pump. A totaloil/water emulsion volume of 200ml was used in all cases considered. For Polystyrene, the filtrate volume is 172 ml and 176 ml for 80% and 60% stroke pressure application respectively. For Polyester, the filtrate volume is 171 ml and 175 ml for 80% and 60% stroke pressure application respectively. For Polysulfone,the filtrate volume is 165 ml and 170 ml respectively. Thus, Polystyrene under 60% stroke pressure application has the largest volume of filtrate, while Polysulfone under 80% stroke has the lowest volume of filtrate.

It is necessary to analyze the results for each materials used and then compare the result with the other materials in terms of performance and efficiency.

4.1.1 Results and analyses for Polystyrene membrane material

The Result for Polystyrene membrane material for 80% stroke and 60% stroke is given in table 4.2 below

Table 4.2: Result for Polystyrene membrane material for emulsion separation

Parameter	Raw sample	Polystyrene	
		80% stroke	60% stroke
pH	5.89	2.5	6.65
Conductivity, S/cm	33	44.95	50
Turbidity, NTU	15.7	49	57
Chemical Oxygen Demand (COD), mg/l	7800	1740	5520
Viscosity, mPa.s	19.9	22.33	20.75
Filtration time, min	-	7	12
Oil Content in filtrate, %	14	0.4	0.34
Volume of Filtrate, ml	-	172	176
Volume retained, ml	-	25	20
Total volume of emulsion used, ml	200	200	200
Volume absorbed by membrane	-	3	4
Volume of oil content in filtrate	-	0.69	0.60
Separation Efficiency		97.54	97.86
Permeation Flux, ml/cm^2-min		2.443	1.944
Average Filtrate Flowrate, ml/min		24.57	14.67

From table 4.2, the volume of liquid absorbed by the membrane material are 3ml and 4ml for 80% stroke and 60% stroke respectively. The volume of oil in the filtrate are 0.69ml and 0.6ml for 80% stroke and 60% stroke respectively; the separation efficiency of the separation process are 97.54% and 97.86% for 80% stroke and 60% stroke respectively; thus there is no appreciable difference in the change in pressure with the efficiency of the separation as evident from the result.

The permeation flux are 2.443 ml/cm^2-min and 1.944 ml/cm^2-min for 80% stroke and 60% stroke respectively. The average flowrate of the filtrate are 24.57ml/min and 14.67ml/min for the 80% stroke and 60% stroke respectively.

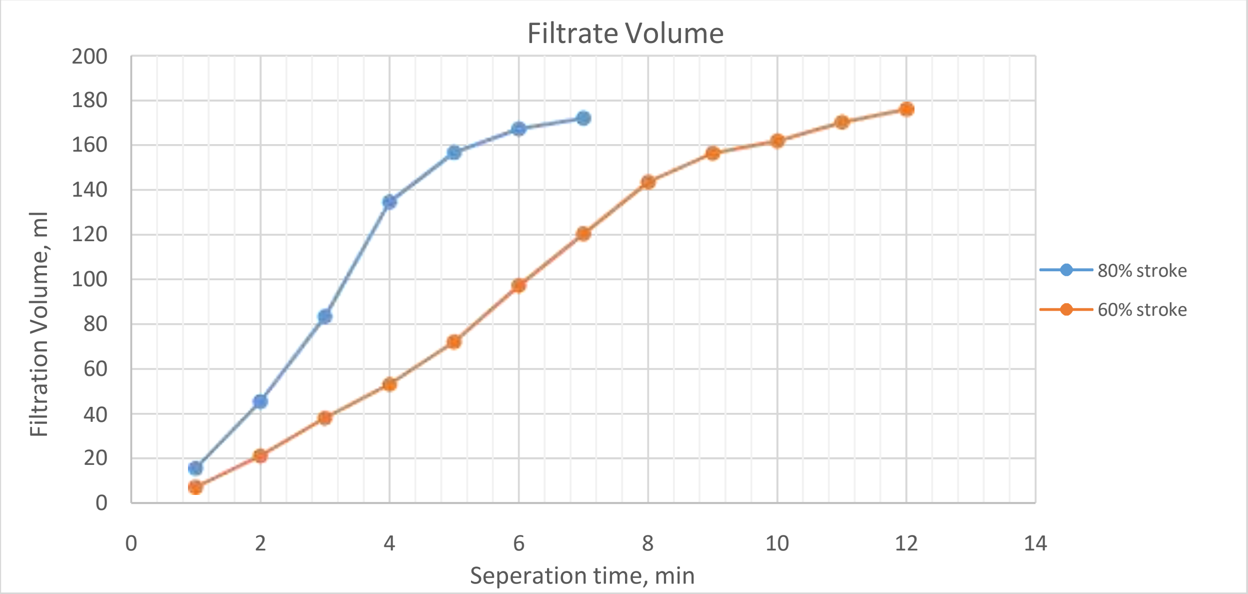

Figure 4.1: Graph of Filtrate volume and separation time for Polystyrene membrane material

From figure 4.1, it is seen that at first the 80% stroke yields more filtrate volume but it lasted for shorter time compared to 60%. The 60% stroke has less flowrate but there was more filtrate volume recovered because of the longer time it took. Thus more time was needed to achieve higher filtration volume as a result of less pressure applied. Furthermore, from figure 4.1 above, more water was removed by using a pressure of 60% than a pressure of 80% stroke. This is because higher pressure will force more emulsion to pass through the membrane unseparated.

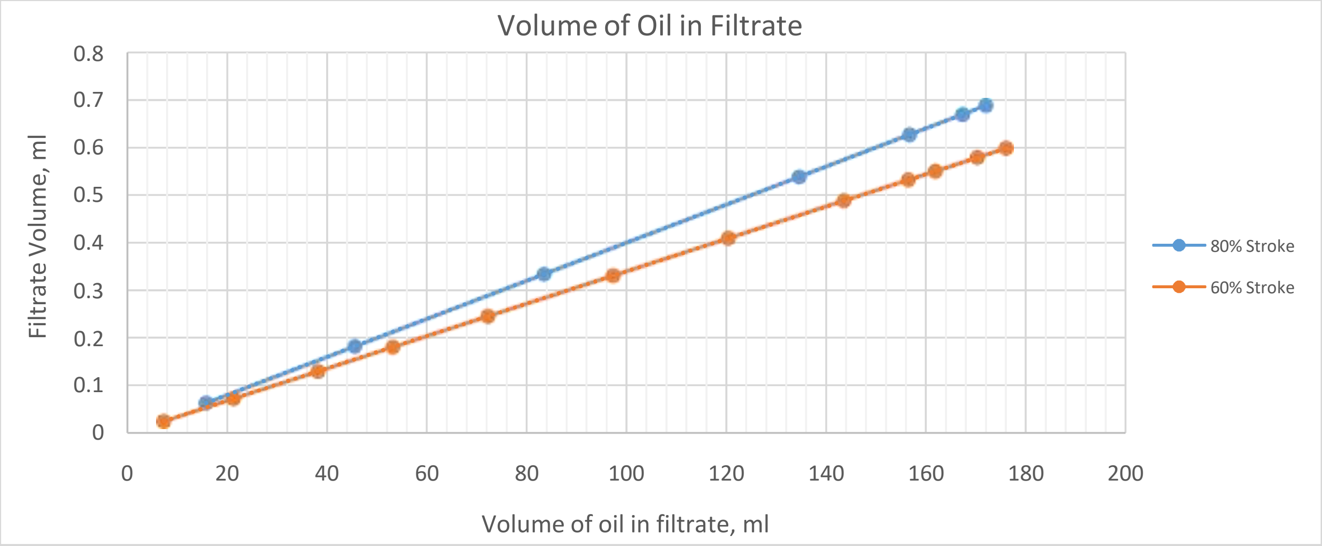

Figure 4.2: Graph of Filtrate volume and volume of oil present in filtrate for Polystyrene membrane material.

From figure 4.2, more oil was found in the filtrate volume when 80%pressure was applied than when 60% pressure was applied. This is because application of higher pressure forces the emulsion through membrane withoutproper separation.

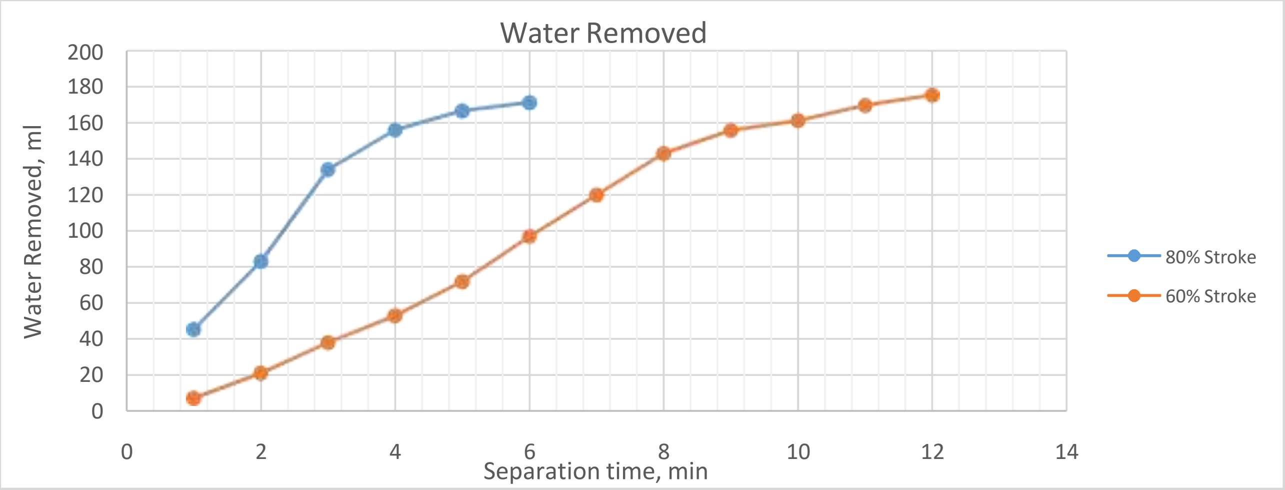

Figure 4.3: Water removed from the Polystyrene Membrane material at different pressures

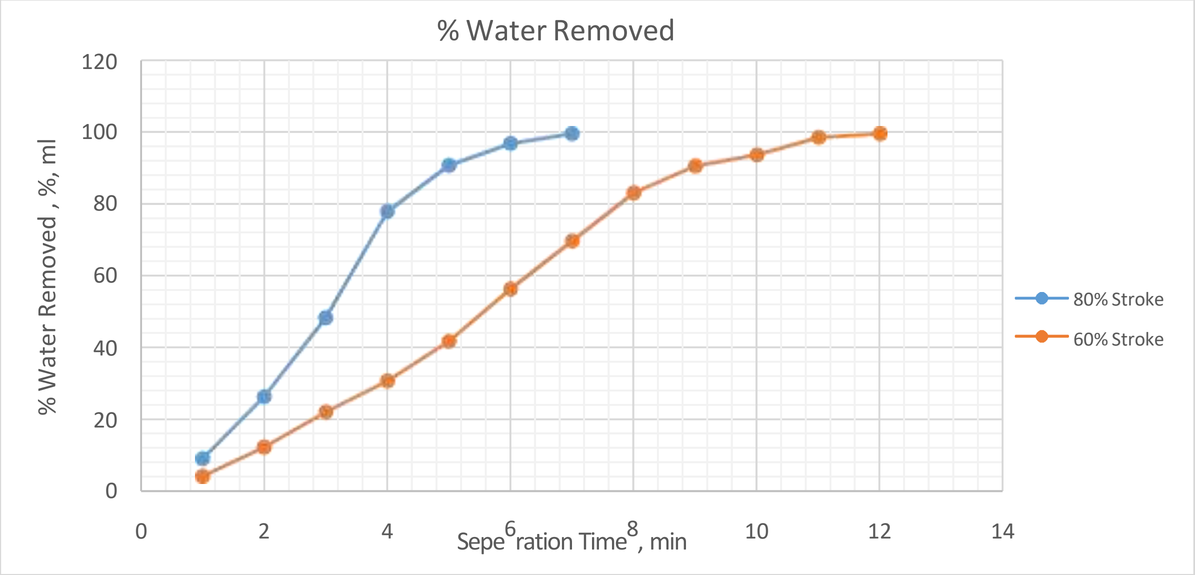

Figure 4.4: Graph of Percentage water removal from the Polystyrene membrane material

From figure 4.4. The percentage water removed from 60% stroke is more than that for 80% stroke at the end of the separation test. But initially due to higher average flow-rate as a result of higher pressure, more water per time was separated from the 80% stroke but it only endured for less time compared to that of 60% stroke.

4.1.2 Results and analyses for Polyester membrane material

The Result for Polyester membrane material for 80% stroke and 60% stroke is given in table 4.3 below

Table 4.3: Result for Polyester membrane material for emulsion separation

Parameter	Raw sample	Polyester	
		80% stroke	60% stroke
pH	5.89	4.77	4.86
Conductivity, S/cm	33	34.2	23
Turbidity, NTU	15.7	10.66	16.05
Chemical Oxygen Demand (COD), mg/l	7800	5140	2200
Viscosity, mPa.s	19.9	22.77	19.83
Filtration time, min	-	8	12
Oil Content in filtrate, %	14	0.6	0.39
Volume of Filtrate, ml	-	171	175
Volume retained, ml	-	22	20
Total volume of emulsion used, ml	200	200	200
Volume absorbed by membrane		7	5
Volume of oil content in filtrate		1.03	0.68
Separation Efficiency		96.3	97.57
Permeation Flux, ml/cm^2-min		2.125	1.933
Filtrate Flowrate, ml/min		21.375	14.583

From table 4.3, the volume of liquid absorbed by the membrane material are 7ml and 5ml for 80% stroke and 60% stroke respectively. The volume of oil in the filtrate are 1.03ml and 0.68ml for 80% stroke and 60% stroke respectively; the separation efficiency of the separation process are 96.3% and 97.57% for 80%

stroke and 60% stroke respectively; thus there is no appreciable difference in the change in pressure with the efficiency of the separation as evident from the result. The permeation flux are 2.125 ml/cm^2-min and 1.933 ml/cm^2-min for 80% stroke and 60% stroke respectively. The average flowrate of the filtrate are 21.38ml/min and 14.58ml/min for the 80% stroke and 60% stroke respectively.

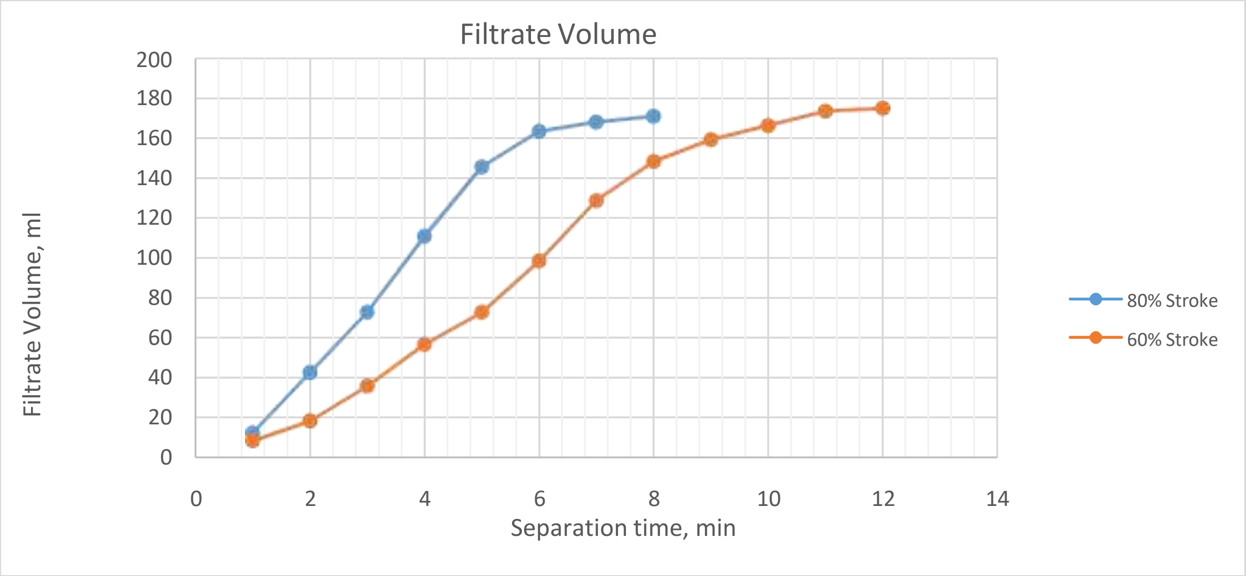

Figure 4.5: Graph of Filtrate volume and separation time for Polyester membrane material

From figure 4.5, more filtrate volume was recovered from 60% stroke than 80% stroke for the Polyester membrane material use. But on the contrary, more filtrate flowrate is for 80% stroke than 60% stroke but the 60% stroke took longer separation time and hence the longer period of time yielded more filtrate volume. Furthermore, from the figure 4.5 above, more water was removed by using a pressure of 60% than a pressure of 80% stroke. This is because higher pressure will force more emulsion to pass through the membrane unseparated

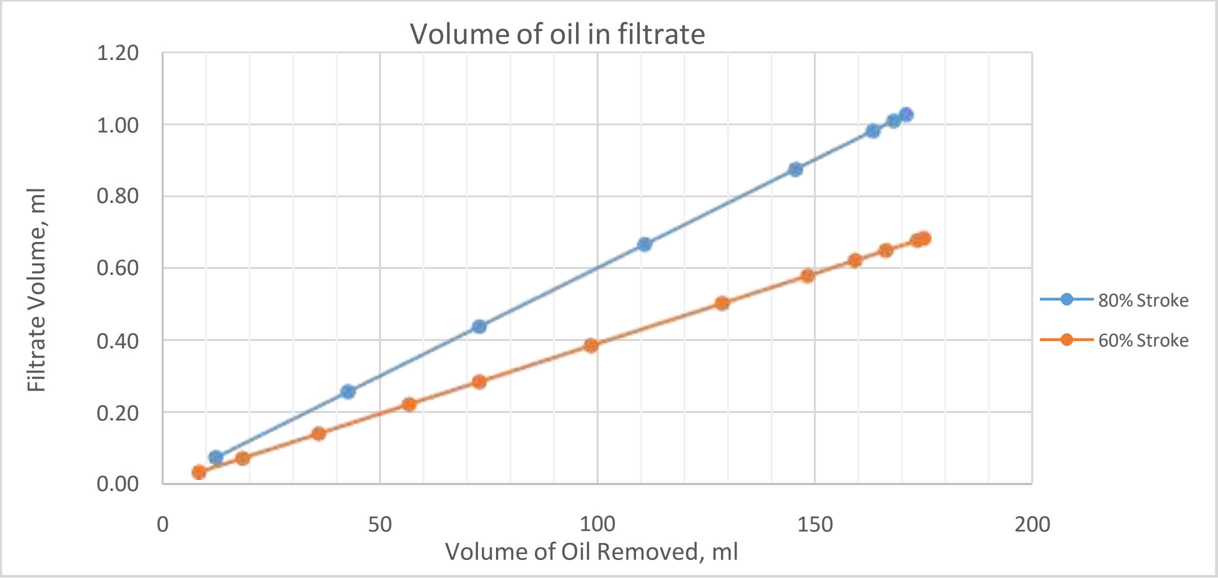

Figure 4.6: Graph of Filtrate volume and volume of oil present in filtrate for Polyester membrane material

Applying higher pressure results to higher volume of oil in the filtrate volume recovered. This is evident from figure 4.6 where 80% stroke gives more oil in the filtrate volume than 60% stroke. More pressure leads to greater emulsion agitation which may forcefully find its way unseparated to the filtrate volume thereby weakening the membrane pores.

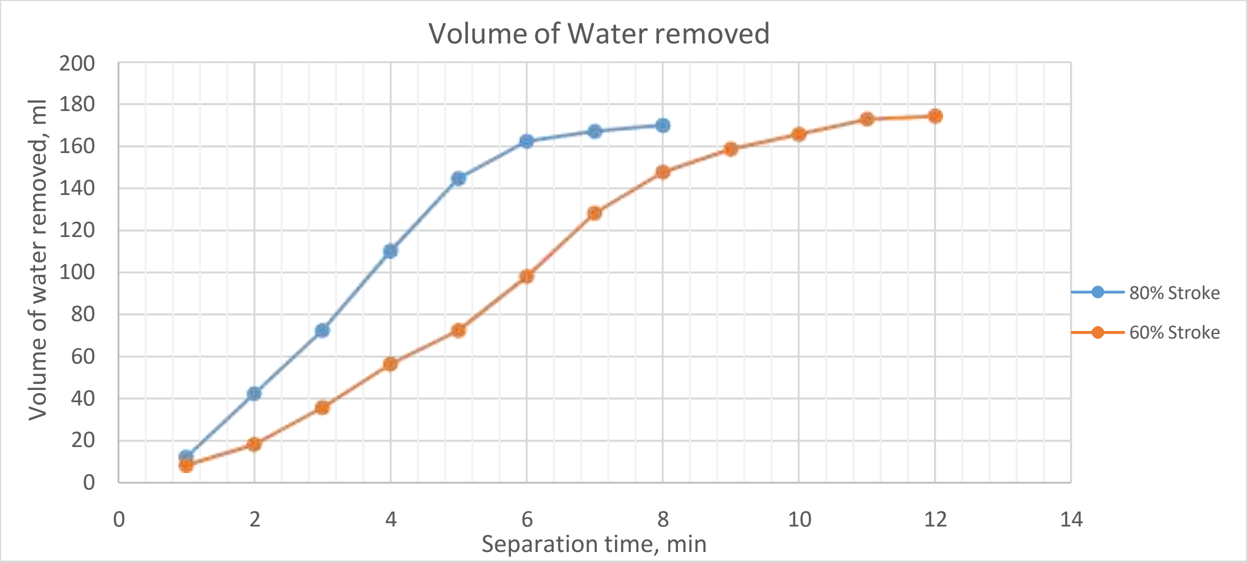

Figure 4.7: Water removed from the Polyester Membrane material at different pressures

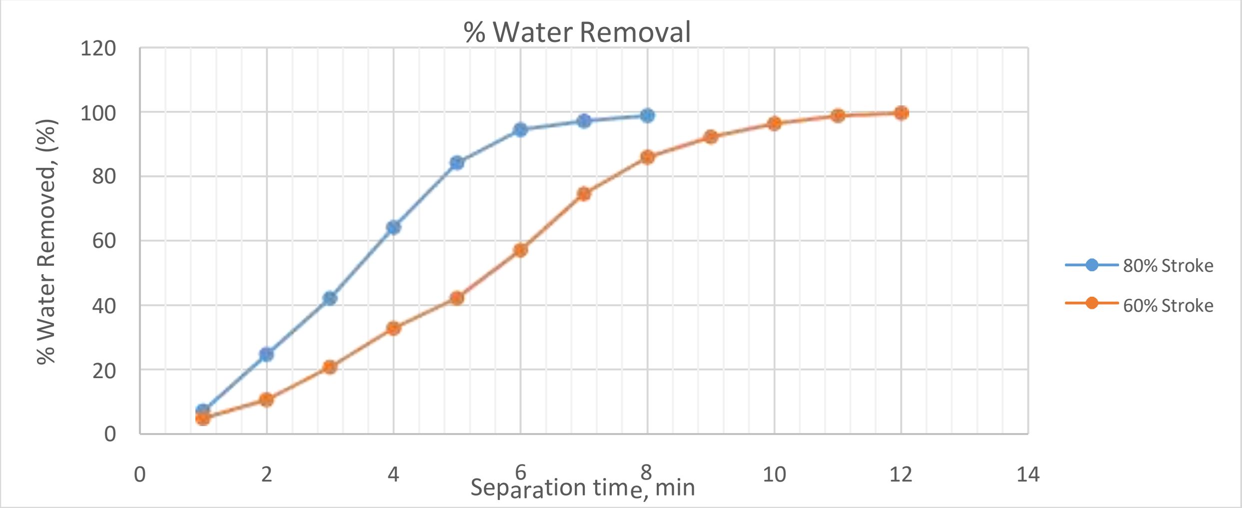

Figure 4.8: Graph of Percentage water removal from the Polyester membrane material

From figure 4.8. The percentage water removed from 60% stroke is more than that for 80% stroke at the end of the separation test. The graph line for 60% stroke (the red line) is longer than that of the 80% stroke (the blue line). But the blue line is above the red line signifying that the 80% stroke yields more initial average flow-rate of filtrate than the 60% stroke. But eventually more water was recovered from the 60% stroke due to longer period of separation.

4.1.3 Results and analyses for Polysulfone membrane material

The Result for Polysulfone membrane material for 80% stroke and 60% stroke is given in table 4.4 below

Table 4.4: Result for Polysulfone membrane material for emulsion separation

		Polysulfone	
Parameter	Raw sample	80% stroke	60% stroke
pH	5.89	4.91	5.36
Conductivity, S/cm	33	50	44
Turbidity, NTU	15.7	11.6	18.7
Chemical Oxygen Demand (COD), mg/l	7800	1200	1200
Viscosity, mPa.s	19.9	19.41	19.34
Filtration time, min	-	18	22
Oil Content in filtrate, %	14	0.404	0.25
Volume of Filtrate, ml	-	165	170
Volume retained, ml	-	28	21
Total volume of emulsion used, ml	200	200	200
Volume absorbed by membrane	-	7	9
Volume of oil content in filtrate	-	0.67	0.43
Separation Efficiency	-	97.6	98.5
Permeation Flux, ml/cm^2-min	-	0.911	1.024
Filtrate Flowrate, ml/min	-	9.17	7.73

From table 4.4, the volume of liquid absorbed by the membrane material are 7ml and 9ml for 80% stroke and 60% stroke respectively. The volumes of oil in the filtrate are 0.67ml and 0.43ml for 80% stroke and 60% stroke respectively; the separation efficiency of the separation process are 97.6% and 98.5% for 80% stroke and 60% stroke respectively. The permeation flux are 0.911 ml/cm^2-min and 1.024 ml/cm^2-min for 80% stroke and 60% stroke respectively. The average flowrate of the filtrate are 9.17ml/min and 7.73ml/min for the 80% stroke and 60% stroke respectively.

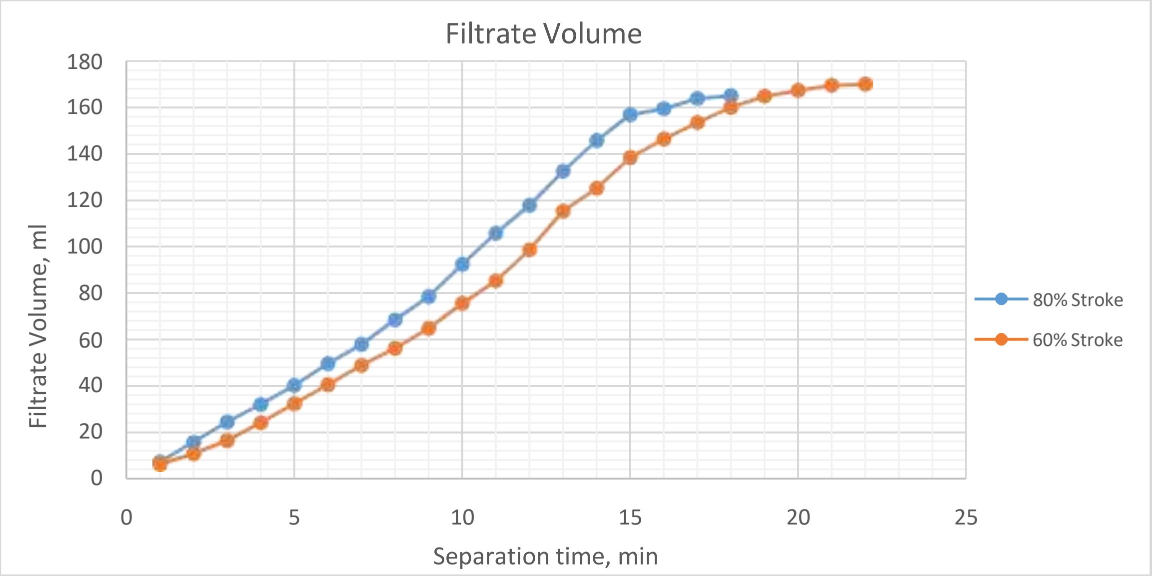

Figure 4.9: Graph of Filtrate volume and separation time for Polysulfone membrane material

Analyzing the filtrate volume with time for Polysulfone membrane reveals that the 60% stroke yields more volume of filtrate than the 80% stroke, although by considering the closeness of the red and the blue line the difference is not profound meaning that the influence of pressure does not have appreciable effect on the filtrate volume for Polysulfone membrane material. Furthermore, from figure 4.9, more percentage water removal is realized from 60% stroke than 80% for the Polysulfone membrane material. The percentage water removal for 80% stroke is 95.5% while that of the 60% stroke is 98.6%.

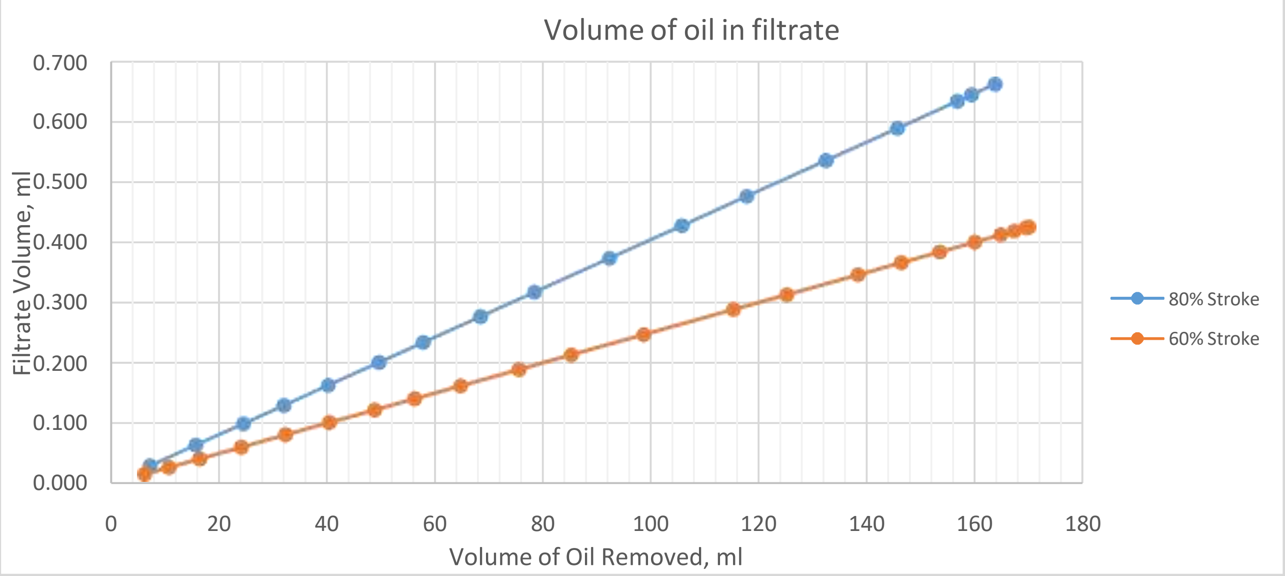

Figure 4.10: Graph of Filtrate volume and volume of oil present in filtrate for Polysulfone membrane material

More oil is present in the filtrate volume for 80% stroke application than 60% stroke as seen in figure 4.10. This is because of increase in fluid velocity due to increase in pressure which forces the emulsion to pass through the pores without proper separation. This signifies that too high pressure is not good for membrane selectivity and separation as it damages the membrane surfaces and forces the sample down without proper separation.

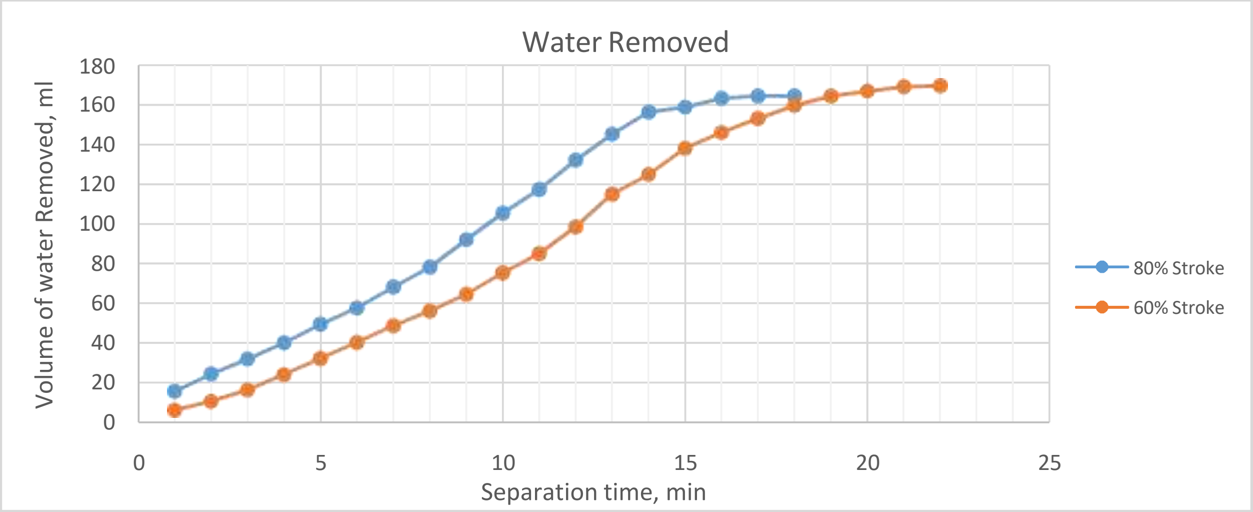

Figure 4.11: Graph of water removal from the Polysulfone membrane material

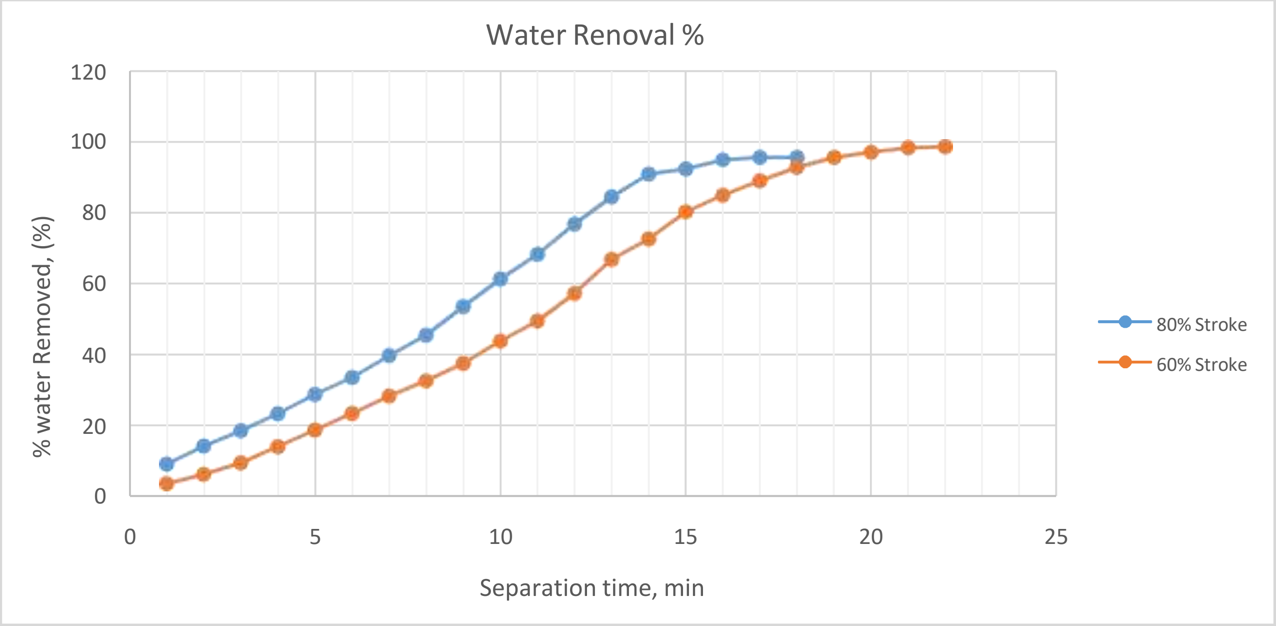

Figure 4.12: Graph of Percentage water removal from the Polysulfone membrane material

The 60% stroke pressure application on the Polysulfone membrane material gave higher percentage of filtrate water from the emulsion solution than the 80% stroke pressure application.

4.2: Comparison of Performance of the Membrane materials

The different Membrane material are analyzed in terms of volume of oil left in filtrate and the percentage water removed with respect to separation time

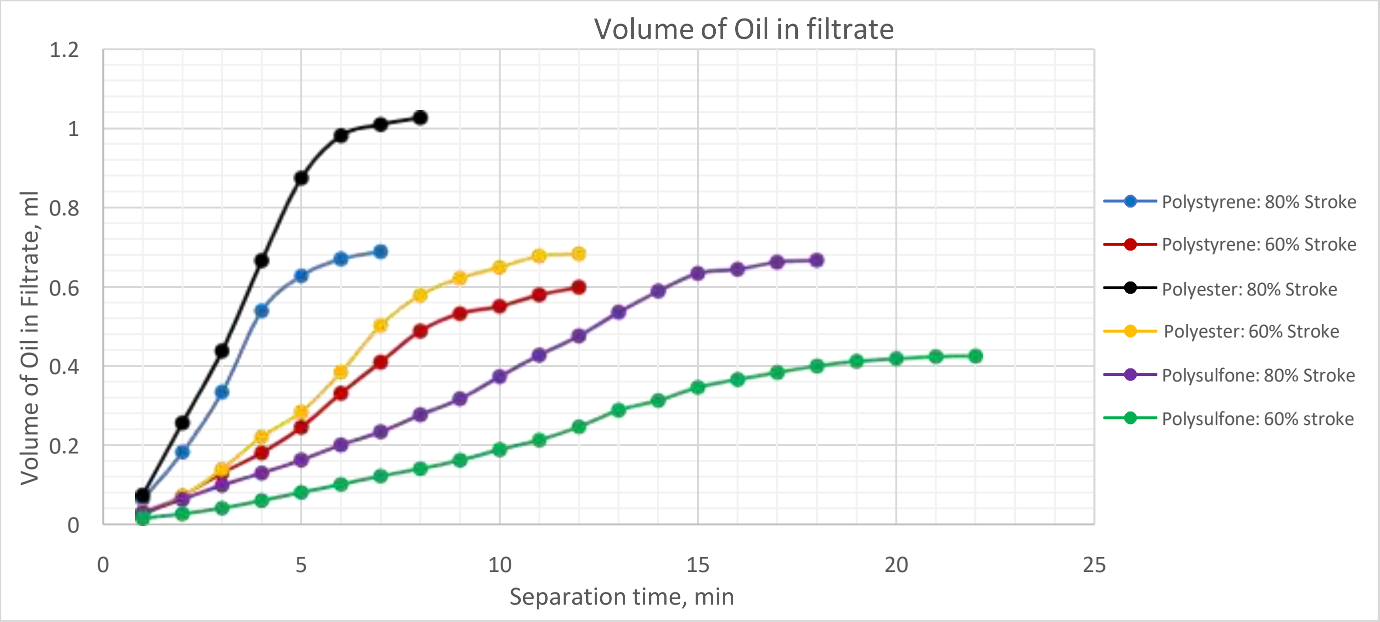

Figure 4.13: Graph of volume of oil in filtrate with separation time for all Membrane materials used at different pressures

From figure 4.13, Polyester membrane material on application of pressure of 80% stroke has the highest volume of oil in filtrate. Conversely, Polysulfone with 60% stroke pressure application has the lowest volume of oil in filtrate volume.

Generally both for 80% stroke and 60% stroke pressure application, Polysulfone material showed lowest volumes of oil in filtrate volumes. This makes Polysulfone the best material for the membrane separation.

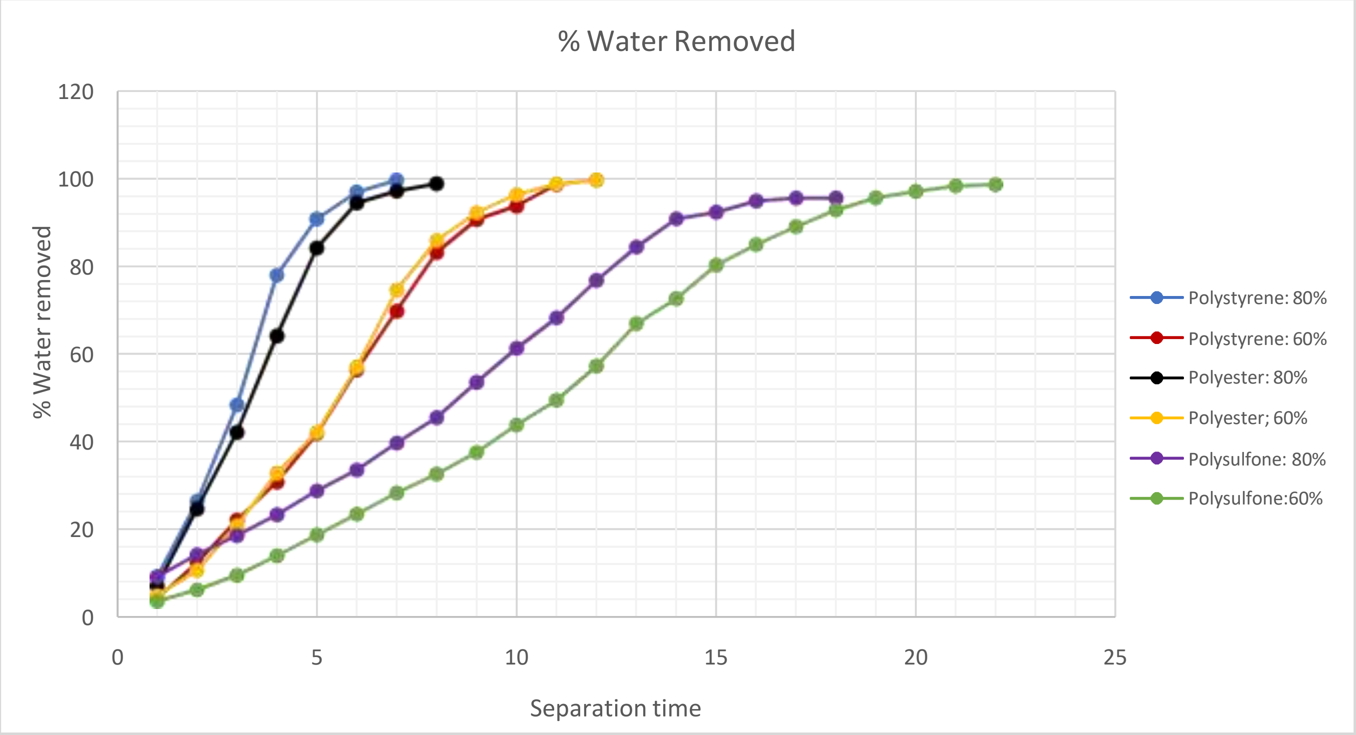

Figure 4.14: Graph of % water removed and separation time for all membrane materials used at different pressure applications.

Figure 4.14 shows the percentage water removed from each of the membrane material at pressure application of 80% stroke and 60% stroke. From the figure, Polysulfone membrane material at 60% stroke has the largest percentage volume of water removed from the emulsion solution, followed by Polysulfone membrane material at 80% stroke pressure application. The least percentage water removed was obtained using polystyrene with 80% pressure application. Polystyrene and Polyester showed almost identical percentage volume of water removed from the figure as seen by the red and yellow line in figure 4.14.

Table 4.5: General performance indices for all the membrane materials

Parametres	Polystyrene		Polyester		Polysulfone	
	80% Stroke	60% Stroke	80% Stroke	60% Stroke	80% Stroke	60% Stroke
Separation Efficiency	97.54	97.86	96.3	97.57	97.6	98.5
Volume absorbed by membrane	3	4	7	5	7	9
Volume of oil content in filtrate	0.69	0.6	1.03	0.68	0.67	0.43
Permeation Flux, ml/cm^2-min	2.443	1.944	2.125	1.933	0.911	1.024
Average Filtrate Flowrate, ml/min	24.57	14.67	21.375	14.583	9.17	7.73
Filtration time, min	7	12	8	12	18	22

The table 4.5 above gives the general performance results for all the membrane materials used and for the different pressure applications.

Table 4.6: Comparison of results for works done on Membrane use for oil/water emulsion separation

S/N	**AUTHORS**	**SEPARATION MATERIALS**	**EFFICIENCY OF SEPERATION (OIL REJECTION)**
1	Saki and Uzal, 2018	Polysulfone and Polyethersulfone membrane coated with CaCO3 nanoparticle	98%
2	Sustrisna*et al.*,2012		91.70%
3	Saththasivam*et al.*,2019	Ti3C2Tx (Mxene) nanoparticle coated on print paper	99%
4	Zhu*et al.*,2014	Single walled Carbon nanotube membrane (SWCNT)	99.95%
5	Li *et al.*,2014	Solid supported metallic membrane doped with Layer-by-Layer self-assembly of silicon Oxide (SiO2) nanoparticle	99.40%
6	Xu *et al.*,2011	Polyacrylamide hydrogel coated SSM membrane	99%
7	Kota*et al.*,2012	Fluorodecyl Polyhedral Oligomeric silsesquioxane (POSS) and Polyethylene glycol diacrylate (x-PEGDA) coated on SSM membrane	99%
8	Feng *et al.*,2016	PFDAE grafted Zinc Oxide (ZnO) PTFE Membrane	99.50%
9	Hu*et al.*,, 2015	Double coating of Polydopamine coated single walled CNTs (SWCNTs) with porous cellulose ester substrate	99.99%
10	Matsuyama and Yoshioka, 2019	Porous Polyketone membrane coated with silica nanoparticle	99.90%
11	Liu *et al.*,2019	PVDF-HFP coated with Cu(CH3COO)2	99.70%
12	Chioma*et al.*,.2020	Polysulfone membrane coated with Aluminium oxide nanoparticle	98.59%

From table 4.6, it can be seen that the use of membranes for oil/ water emulsion separation gives very high efficiency. The efficiency of separation gotten from the use of Polysulfone membrane material coated with Aluminium oxide nanoparticle which is 98.5% is within the range of accuracy of membranes coated with nanoparticles as can be observe from table 4.6 above

4.3 Discussions

Discussions of the results of the experiment is given in details below

4.3.1. Separation Efficiency

Separation efficiency tells us the how effective each of the membrane material is able to achieve separation of the water from the oil. The separation efficiency describes the relative volume of oil in the filtrate sample compared to the volume of oil in the emulsion solution before separation. Analyzing table 4.5, the membrane material that gave the highest separation efficiency is Polysulfone witha separation efficiency of 98.5% when a pressure application of 60% stroke was applied to it. Conversely, the membrane material that gave the lowest separation efficiency is Polyester with a separation efficiency of 96.3% when a pressure of 80% stroke was applied to it. From the table it is seen that higher pressure reduces the separation efficiency. This is because higher pressure leads to agitation which may enlarge the pores of the membrane substance causing membrane fouling and allowing much of the emulsion fluid sample to pass through.

4.3.2. Permeation Flux

The permeation flux describes the movement of the fluid species across the membrane material. Permeation flux describes how easily the membrane allows materials to pass through it. Note that permeation flux could be decrease due to fouling of the membrane material.

From table 4.5, polystyrene membrane material gave the highest permeation flux when a pressure of 80% stroke was applied to it, the permeation flux was 2.433 ml/cm^2-min. The lowest permeation flux was realized when Polysulfone was used under pressure application of 80% stroke, this lowest permeation flux as given by the Polysulfone is 0.911 ml/cm^2-min.

4.3.3. Volume of Oil in Filtrate

Investigating the residual oil in filtrate after separation gives an indication of the success of the separation using the membrane material. Some membranes may achieve higher volume of filtrate but at the expense of higher oil content byvolume leading to lower separation efficiency.

from table 4.5, Polyester gave the highest volume of oil in filtrate which is 1.03ml, this occurred under a pressure application of 80% stroke while Polysulfone membrane material under 60% stroke pressure application gave the least volume of oil in filtrate which is 0.43ml.

4.3.4. Volume of fluid absorbed by Membrane material

During the experiment, there were some volumes lost due to absorbent on the membrane material. This explains the reason why the initial volume of the emulsion before the separation process and the final volume (filtrate volume and residue volume) are not equal. This difference in volume is accounted for thatbeing absorbed by the membrane material if all things being equal and there are no spillage or wastages during the experiment.

From table 4.5, Polysulfone had the highest fluid absorbent volume (i.e. 9ml) when a pressure of 60% stroke was applied to it while polystyrene had the lowest volume of fluid absorbed (i.e. 3ml) when a pressure of 80% stroke was applied to it. Thus, Polysulfone retained more of the fluid which is counted as wastage because of this, Polysulfone is most susceptible to fouling than all the other membrane materials used.

4.3.5 Membrane Fouling

Membrane fouling occurs due to the accumulation of the solutes in the oil on the membrane surfaces. The fouling is as a result of the oil left behind on the membrane surface. The solutes form pollutants that block the pore spaces of the membrane reducing its quality and performance. The accumulation of this solutes makes the membrane to bulge and sag. The extent of the membrane fouling was more noticeable with longer time. The fouling reduces the permeation flux and generation reduces the volume of filtrate.

Fouling processing leads to pore blocking, solute aggregation that leads to cake formation or gel layers on the membrane surface, or adsorption that is caused by concentration polarization and convective forces to and trough the membrane. Membrane fouling decreases system productivity, and increases the amount of energy needed for the separation process. Hence to achieve reduction in overall process cost, decision must be made whether to clean up the membrane or change it entirely depending on the degree of the fouling process.

Generally, membrane substances with higher oil retention has greater tendencies for fouling, from the three membranes, Polysulfone has more oil retention on the membrane surface due to its smaller pore microstructure and hence more tendency for fouling

The picture for the fouled membrane is given in appendix D, the Polysulfone membrane material fouled after a long time of repeated usage. The brown layer is the hard cake formed due to accumulation of the solutes in the oil retained in the membrane surface reacting with the Aluminium oxide nanoparticle and the membrane material.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

Crude oil emulsion separation process has been conducted using Aluminium oxide based polymeric membrane system to separate oil-in-water emulsion. The inclusion of the Aluminum oxide nanoparticles enhanced the polymeric membrane separation process and reduced the rate of membrane fouling. Three membrane substance materials were analyzed, they are Polystyrene, Polyester, Polysulfone membrane materials under 80% stroke and 60% stroke pressure application. During the emulsion separation process using the membrane, the parametres analyzed were separation efficiency, volume of oil retained in filtrate volume, membrane permeation flux, filtrate volume and volume of liquid absorbed bymembrane material.

According to the results from this study, Polysulfone membrane material shows best performance under the relevance factors analyzed, it gave the highest separation efficiency of 98.5% under 60% stroke pressure application and gave the least volume of oil in filtrate volume. This means that only very minimal oilcontent is left in the water after separation of the oil from the water. Furthermore, Polyester membrane material gave the lowest separation efficiency of 96.3% and the highest volume of oil in filtrate volume when the three membrane materials are analyzed. Nonetheless, all the membrane materials used gave very high separation efficiencies and are candidate for used in crude oil demulsification.

Membrane fouling occurs after repeated use of the membrane for crude oil demulsification. Aluminium oxide nanoparticles were incorporated into membranes support materials to improve oil-adsorption resistant ability. Even though the aluminum oxide nanoparticle delayed the membrane fouling process, fouling still occur at longer time periods. The fouling was as a result of theaccumulation of solute on the membrane surface which leads to substantial reduction of permeate flux. This work will present a new approach of emulsion separation that is cheap and efficient and does not require the costly chemical additions that in most cases also impact negatively on the ecosystem.

5.2 Recommendation

Nanoparticle based membrane separation method of crude oil demulsification is hereby recommended as a solution to emulsion crude oil emulsion problems prevalent in oil and gas operations. The polymer membrane system is chosen because of its high separation efficiency, lower cost, ease of separation and general environmental friendliness. The polymer membrane should be properly padded with the nanoparticle to ensure efficient separation efficiency and lower rate of membrane fouling. The polymer membrane emulsion separation alternative is recommended for oil-in-water emulsion separation in oil and gas operations especially in the Niger Delta region of Nigeria.

5.3 Contribution to Knowledge

The contribution of this research work to scientific and engineering knowledge are

1. The development of a highly efficient separation system for separation of crude oil and water emulsion which has been a peculiar problem in oil and gas operation
2. The determination of the relationship between various membrane materials and their efficiency of emulsion separation.
3. The development of a more effective membrane polymer membrane architecture through proper design and impregnation with Aluminum oxide nanoparticle material
4. The reduction in membrane fouling time which is a peculiar in use ofpolymer membranes by doping membrane materials with Aluminium oxide nanoparticle.
5. Deployment of easy to use, non-hazardous separation system for oil water emulsion with less complicated designs and more environmental friendliness

Membrane Fouling

Figure D: Fouled Membrane

Figure D shows the Fouled Polysulfone membrane when used and left for a longer period of time

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APPENDIX

Appendix A: Polystyrene Membrane Material

Table A: Result for general indices and performance of Polystyrene membrane material

	Filtrate Volume		Volume of oil in filtrate		Water Removed		% Water Removed	
Separation Time, min	80% Stroke	60% Stroke	80% Stroke	60% Stroke	80% Stroke	60% Stroke	80% Stroke	60% Stroke
1	15.8	7.3	0.06	0.02	15.74	7.28	9.15	4.23
2	45.6	21.3	0.18	0.07	45.42	21.23	26.41	12.34
3	83.5	38.2	0.33	0.13	83.17	38.07	48.35	22.13
4	134.6	53.2	0.54	0.18	134.06	53.02	77.94	30.83
5	156.7	72.2	0.63	0.25	156.07	71.95	90.74	41.83
6	167.3	97.3	0.67	0.33	166.63	96.97	96.88	56.38
7	172	120.4	0.69	0.41	171.31	119.99	99.60	69.76
8		143.5		0.49		143.01		83.15
9		156.4		0.53		155.87		90.62
10		161.8		0.55		161.25		93.75
11		170.2		0.58		169.62		98.62
12		176		0.60		175.40		99.8

Appendix B: Polyester Membrane Material

Table B: Result for general indices and performance of Polyester membrane material

Separation time	Filtrate Volume, ml		volume of oil in filtrate, ml		Volume of water removed, ml		% water removal	
	80% Stroke	60% Stroke	80% Stroke	60% Stroke	80% Stroke	60% Stroke	80% Stroke	60% Stroke
1	12.3	8.4	0.07	0.033	12.226	8.367	7.108	4.865
2	42.7	18.4	0.26	0.072	42.444	18.328	24.677	10.656
3	72.9	35.9	0.44	0.140	72.463	35.760	42.129	20.791
4	110.9	56.7	0.67	0.221	110.235	56.479	64.090	32.837
5	145.6	72.8	0.87	0.284	144.726	72.516	84.143	42.161
6	163.4	98.5	0.98	0.384	162.420	98.116	94.430	57.044
7	168.1	128.7	1.01	0.502	167.091	128.198	97.146	74.534
8	171	148.3	1.03	0.578	169.974	147.722	98.822	85.885
9		159.2		0.621		158.579		92.197
10		166.3		0.649		165.651		96.309
11		173.5		0.677		172.823		98.756
12		175		0.683		174.318		99.610

Appendix C: Polysulfone Membrane Material

Table C: Result for general indices and performance of Polysulfone membrane material

	Filtrate Volume, ml		volume of oil in filtrate, ml		Volume of water removed, ml		% water removal	
Separation time	80% Stroke	60% Stroke	80% Stroke	60% Stroke	80% Stroke	60% Stroke	80% Stroke	60% Stroke
1	7.3	6.3	0.029	0.016	15.771	6.284	9.169	3.654
2	15.8	10.8	0.064	0.027	24.536	10.773	14.265	6.263
3	24.6	16.5	0.099	0.041	32.001	16.459	18.605	9.569
4	32.1	24.2	0.130	0.061	40.170	24.140	23.355	14.035
5	40.3	32.4	0.163	0.081	49.537	32.319	28.801	18.790
6	49.7	40.5	0.201	0.101	57.699	40.399	33.546	23.488
7	57.9	48.9	0.234	0.122	68.266	48.778	39.690	28.359
8	68.5	56.3	0.277	0.141	78.223	56.159	45.479	32.651
9	78.5	64.8	0.317	0.162	92.083	64.638	53.537	37.580
10	92.4	75.6	0.373	0.189	105.427	75.411	61.295	43.844
11	105.8	85.3	0.427	0.213	117.373	85.087	68.240	49.469
12	117.8	98.7	0.476	0.247	132.024	98.453	76.758	57.240
13	132.5	115.3	0.535	0.288	145.165	115.012	84.398	66.867
14	145.7	125.2	0.589	0.313	156.211	124.887	90.821	72.609
15	156.8	138.4	0.633	0.346	158.767	138.054	92.306	80.264
16	159.4	146.4	0.644	0.366	163.156	146.034	94.858	84.903
17	163.8	153.5	0.662	0.384	164.338	153.116	95.545	89.021
18	165	160	0.667	0.400	164.333	159.600	95.543	92.791
19	-	164.8	-	0.412	-	164.388	-	95.574
20	-	167.3	-	0.418	-	166.882	-	97.024
21	-	169.5	-	0.424	-	169.076	-	98.300
22	-	170	-	0.425	-	169.575	-	98.590