EFFECT OF VARIOUS CLEANING AGENT ON MICROFILTRATION MEMBRANE FOULED BY OIL EMULSION

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by

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LIST OF ABBREVIATION

GDP	Gross Domestic Product
POME	Palm Oil Mill Effluent
COD	Chemical Oxygen Demand
SDS	Sodium Dodecyl Sulphate
UV	Ultraviolet
DI	Deionized water
W/O	Water-in-oil-emulsion
O/W	Oil-in-water-emulsion
W/O/W	Water-in-oil-in-water
O/W/O	Oil-in-water-in-oil
DAF	Dissolved Air Floatation
TSS	Total Suspended Solid
PVDF	Polyvinylidene fluoride
Tween 80	Polysorbate 80
TMP	Transmembrane pressure
SEM	Scanning Electron Microscopy
PC	Personal Computer
FTIR	Fourier Transform Infrared Spectroscopy

KESAN PELBAGAI EGEN CUCIAN UNTUK PEMBERSIHAN MEMBRAN FILTER FOULING OLEH MINYAK EMULSI

ABSTRAK

Strategi pembersihan filter membrane yang dikotori semasa pemisahan minyak emulsi telah dipelajari dengan teliti dalam kajian tugasan ini. Terdapat pelbagai egen pencuci termasuk alkali, asid, bahan kimia surfactant dan bio surfactant dinilai mengikut kecekapan pencuci. Analisis tingkah laku fluks merujuk kemungkinan pembentukan kek ialah dominan fouling model. Model ini bersesuaian dengan efektif untuk eksperimen tingkah laku fluks. Kek yang terbentuk ini bertanggungjawab menyebabkan fouling yang teruk dan penurunan fluks membran. Kecekapan pembersihan boleh demonstrasi dengan nisbah fluks dipulihkan dan fluks pemulihan. Sodium dodecyl sulphate (SDS) mendapat nisbah fluks dipulihkan dan fluks pemulihan tertinggi masing-masing dalam 28.38% dan 24.11%. Pembersihan menggunakan SDS berjaya membuang banyak kotoran pada membran. Pengaruh kondisi operasi untuk permbersihan filter membran dilakukan seperti kepekatan, masa pembersihan, tekanan trans membrane pembersihan dan kaedah pembersihan. SDS yang mengandungi kepekatan 0.10 M telah dipilih untuk penyiasatan selanjutnya berkenaan kondisi optimum untuk medium pembersihan. SDS ditunjukkan efektif dalam permbersihan selama 30 minit dengan menggunakan teknik pembilasan ke hadapan pada tekanan trans membrane 0.1 MPa.

EFFECT OF VARIOUS CLEANING AGENT ON MICROFILTRATION MEMBRANE FOULED BY OIL EMULSION

ABSTRACT

Cleaning strategies of microfiltration membrane fouled during separation of oil emulsion have been thoroughly study in this research work. There is various cleaning medium evaluated based on their cleaning efficiencies including alkali, acid, chemical surfactant and bio surfactant rhamnolipid. Analysis of flux behaviour indicates possibly cake formation is a dominant fouling model. This model is effectively fitted to the experimental flux behaviour . The developed cake is responsible for severe fouling and decrease membrane flux. Cleaning efficiency demonstrated by determination of flux restored ratio (FRR) and flux recovery (FR). Sodium dodecyl sulphate (SDS) obtain highest flux restored recovery (FRR) of 28.38% and flux recovery (FR) of 24.11% respectively. Cleaning by SDS largely remove the foulant on the membrane. Influence of operating condition of cleaning the MF membrane were made such as concentration, cleaning time, cleaning trans membrane pressure and method of cleaning. SDS with concentration of 0.10 M SDS selected for futher investigation on the optimum condition for cleaning medium. SDS demonstrated to be effective in cleaning for 30 minutes operation of cleaning time by employing technique of forward flushing at trans membrane pressure of 0.1 MPa.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Malaysia is a fast-economic growing country for the past few decades with an advanced about 5.9% in GDP Annual Growth Rate on December 2017. However, the major consequences of these development is the increasing risks on the environment cause of rising of waste generation yearly. Oily waste water included in one of groups in First Scheduled Waste of Environment Quality under the categories of waste containing principally organic constituents (Mat et al. 2013). Due to this reason, removing oil to the environment is an important aspect for pollution control. In recent years, there are new legislation of standard discharge consent of wastewater has been implemented in some country such as Europe and United States. In 2008, Malaysia reported to has generated oil waste about 129,701.99 million tonnes and increase to 133,260.91 million tonnes in 2011 (Aja et al. 2016). Hence, it is a serious matter and requires effective planning of measures to control the oil pollution.

Sources of oily waste water generated come from various industrial sectors including petroleum refining, petrochemical, textile, metalworking, agriculture mills and oil extraction activities (Yu et al. 2017). Besides, oil spills also producing water containing oil caused from bilge pumping and tank cleaning which leading to the removal of oil by ocean going vessel (Mansor and Pourvakhshouri 2013). Composition and concentration of oil contain in waste water varies for each industry. For example, palm oil mill effluent (POME) contains about 4,000 to 6,000 mg/l of concentration which considered in the range of high oil concentration (Ahmad et al. 2005). Thus, these factors are heavily contributed on the oil pollution and become a current challenge for effectively disposed it. Wu et al. (2009) reported that, there are some problems emerging on discharging oily waste water into environment due to its high oil content and chemical oxygen demand (COD).

Therefore, for the past few decades, there are various methods concerning for oil/water water treatment. Oily waste water usually treated by physical, chemical or/and biological treatment. There are several conventional techniques to treat oil waste previously develop such as gravity and centrifugal separations, chemical treatment, flotation, evaporation, activated carbon adsorption, biological treatment, and integrated or hybrid processes (Coca-Prados et al. 2013).

Mostly oily waste water is in the form of oil-in-water emulsion. Emulsion is dispersion in form of droplet of one liquid in another immiscible liquid. Since the particle size of oil emulsion is very small compared to free and dispersed oil, separation of oil from oily wastewater is quite difficult. Moreover, tiny oil droplets are stabilized by surfactant hence reduce the interfacial force between oil and water (Janknecht Lopes et al. 2004).

In order to meet the effluent standard, the advanced process of separation oil-water is by membrane filtration. Oil emulsion is treated by using various type of membrane filtration as the number of pores of membrane allow for filtration according to the size of droplet of oil emulsion. A study from Zaidi et al. (1992) reported, membrane extensively been used for oil and grease removal from produced water. There are two commercial petroleum applications involve which are Marathon Oil and Petro-Canada as shown in Figure 1.1. Oil and grease levels in permeate can be reduced to acceptable amounts where the performance dependent on the particular feed stream.

Table 1. 1 Commercial application of membranes for removing oil and grease from produced water in petroleum applications adapted from Zaidi et al. (1992)

	Marathon Oil	**Petro-Canada Resources**
Data Installed	Fall 1989	Fall 1990
Location	El-349B platform, Gulf of Mexico, US	Valhalla Field, Alberta, Canada
Design Capacity (m^3/day)	1000	1000
Membrane area (m^2)	45	-
Membrane pore size (µm)	0.8	0.8
Feed	Slipstream from precipitator effluent	5% from heater treater, 95% groundwater
Permeate disposal	Reinjection	Reinjection
Pre-treatment	$FeCl_3$	$FeCl_3$

Despite that, fouling is a critical factor associated to membrane technology which causing reduction of the membrane performance. Since membrane is inevitable, periodically cleaning helps remove foulant deposited in the membrane itself and restore the flux value. Cleaning agent is an essential procedure for reduce fouling effect on the membrane. The common cleaning agents available are acid/base, surfactant and enzyme. However, aggressive cleaning of membrane using too high or low pH by acid/base damage the membrane. Slow biodegradability of chemical surfactants will next become a major requirement for the development of new type of cleaning agent that will resolve these problem related acid/alkali cleaning medium (Henkel et al. 2012; Paugam et al. 2013). Concerning regarding environmental and health problems, bio surfactants is introducing for the possible cleaning agent for the future application in the industry. Among the several of bio surfactants, rhamnolipid is a most promising bio surfactants for uses of cleaning solution of membrane.

Therefore, this project aims to focus on chemical cleaning efficiency of variety cleaning agents included alkali, acid, chemical surfactant and bio surfactant rhamnolipid.

1.2 Problem Statement

Separation of water from oil emulsions becomes a current challenge for certain industries especially petroleum company to resolve this issue. There are various consequences of increasing the amount of oily waste water to the environment included quality of drinking water, endangering aquatic organism, threat for human health and pollution to atmosphere (Yu et al. 2017). The presence of oil content in water bodies cause the reduction of light penetration and photosynthesis (Jameel et al. 2011). Therefore, treating oily waste water urgently needed to solve those environmental problems.

Conventional method for oil treatment has several constraints that require other effective and advanced ways for complete separation of water from oil. This is because conventional method require higher cost and energy for separation of stabilized oil-in-water emulsion. Most conventional method not efficiently treating oil emulsion below 10 μm especially when concentration is very low and finely dispersed droplets. This technique only reduce oil concentration by no more than 1% by volume of total waste water and needs for further treatment for oil-water separation (Coca-Prados et al. , 2013)..

Development of membrane process for application of removal of oil from wastewater has been widely applied as an effective approach for treatment of oily waste water. Polymeric and ceramic membrane used in most of studied related to separation of oily waste water by using ultrafiltration and microfiltration technique (Chen et al. 1991; Safeghi et al. 2013).

Despite that, fouling phenomena is a major drawback in application of the membrane separation. Cleaning agent is introduced as low cost technique to reduce fouling. Hence, in this study will focused on different types of cleaning agent for its effectiveness to recover the flux causing from fouling phenomena caused by oil emulsion.

1.3 Research Objective

The main objectives of these study are:

1.3.1 To evaluate the performance of cleaning agent of microfiltration fouling by oil emulsion.

1.3.2 To examine the effect of operating parameters on cleaning agent of microfiltration membrane.

1.3.3 To study a fouling mechanism of oil emulsion.

1.4 Scope of Project

Study of the different cleaning agents performance on cleaning microfiltration membrane(MF) fouled by oil emulsion were conducted using DI water, acid, alkali, surfactant and rhamnolipid. Concentration of each cleaning medium were varying to obtain the highest cleaning efficiency. Preparation of oil emulsion formulate by mix diesel and Tween 80 using homogenizer according to its ratio. Cleaning evaluation is investigating accordingly start with deionized water (DI) water flux, feed line by oil emulsion, and DI water flux after cleaning. After obtaining a suitable cleaning agent, cleaning study continue to determine the optimum cleaning operating condition. Characterization study regarding contact angle measurement, Scanning Electron Microscope (SEM) and Fourier Transform Infrared spectroscopy (FTIR) analysis also included in the framework of the project.

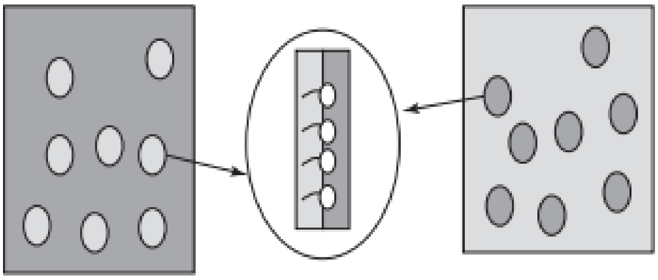
CHAPTER 2

LITERATURE REVIEW

2.1 Emulsion Oil

Oil and grease includes fats, oils, waxes, and other related constituents are found in water, generally wastewater. The concentration of oil and gases are not determined by specific compound, but the group of related compounds based on their extractability. Extractible material are non-volatile hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases, and related materials. For the characterization purpose, usually solvent used are hexane (USEPA 1999). Oil and grease are non-polar and hydrophobic compound and can exists in three forms; free, dispersed or emulsion oil (Rhee et al. 1987). These three types of oil classified based on the size of oil droplets. Free oil is characterized with droplet sizes greater than 150 mm in size, dispersed oil has a size range of 20±150 mm and emulsified oil has droplet's size typically less than 20 mm.

Emulsion defined as two immiscible liquids where in droplets of one phase encapsulated within sheets of another phase (James and Charles 1985). Three forms of emulsion are water-in-oil (W/O) emulsion, oil-in-water (O/W) emulsion and multiple emulsion. Multiple emulsion includes water-in-oil-in-water (W/O/W) emulsion and oil-in-water-in-oil emulsion (O/W/O) emulsion. W/O is formed when the water globules are an evenly dispersed throughout the oil continuous phase whereas O/W emulsion is formed when the oil globules are evenly dispersed throughout the water continuous phase. There are three conditions to produce stable emulsion; two liquids must be immiscible or mutually insoluble in each other, sufficient agitation must be applied to disperse one liquid into other and an emulsifying agent or combination of emulsifiers must be present (Li et al. 2005). Manipulating of emulsifiers, oil-water ratio, stirring speed, temperature and stirring time of emulsion show an effect on emulsion characteristics. Usually emulsion is stabilized by a surfactant as shown in Figure 2.1. Surfactant is a surface-active agent that gives kinetic stability of emulsion because of present of amphiphilic structure (Palanuwech and Coupland 2003). For example, Tween 80 is a hydrophilic surfactant and added at outer layer aqueous phase of O/W emulsion is frequently been used as emulsifiers in previous research (Jiao and Burgess 2003).



(a) (b)

Figure 2.1 Schematic diagram of emulsion structures. (a) O/W emulsion; (b) W/O emulsion. Encircled: enlarged view of a surfactant monolayer sitting at oil-water interfaces (Langevin et al. 2004)

2.2 Conventional Method of Treating Oily Wastewater

Conventional approaches for separation oil from wastewater included variety of techniques which are dissolved air floatation (DAF), gravity separation, de-emulsification, biological treatment and coagulation. Table 2.1 display the study of the oil pollution removal of oily wastewater by conventional method. Dissolved air floatation is using air to enhanced buoyancy differences of emulsified oil droplets to rising the separation of oil from wastewater (Zoubulis and Avranas 2000). Working principle of DAF is by production of air bubbles by dissolving air under pressure, where air bubble attach to droplets and raise them to the surface. DAF operated as pre-treatment process to promote coagulation and increase floc size to facilitate separation. In addition, gravity separation using low cost API separator is effective for remove oil. However, it was not success to separate smaller droplet of oil and emulsion. Hu and Scott (2008) reported that, chemical de-emulsification process also been considered as standard method for treatment of emulsion. This treatment was followed by gravity separation and require for secondary purification to meet the standard of effluent discharged. Disadvantages of de-emulsification techniques are there are higher possibility to change in influent quality, higher operating cost and increase dissolved solids in effluent.

Chemical coagulation is pre-treatment process before continues to biological treatment. These treatments conducted with aim to remove or reduce chemical oxygen demand (COD), total dissolved solid (TSS) and turbidity (Aljuboury et al. 2017). Coagulant species which usually inorganic metal salts included ferric chloride, ferrous sulphate, aluminium sulfate (alum) were added to oily wastewater influences COD removal. The investigation on COD efficiency by manipulating variables such as pH values, operating time, different types of coagulant and coagulant dosage (Yu et al. 2007).

Besides that, biological treatment is one of the conventional method in treating oily wastewater. Biochemical treatment defined as decomposition of wastewater to stable end products by using microorganism. It is based on condition of present of oxygen which categorised into anaerobic and aerobic methods. Drawback for this treatment are its produced large amount of sludge in the effluent and low efficiencies of removal COD (Jou and Huang 2003). Petroleum refinery and wastewater successfully been treated to achieve maximum removal efficiency through an advanced technology of biological treatment. Introducing a reactor immobilized microorganism and recently application of up-flow anaerobic sludge blanket and anaerobic submerged fixed-bed reactor, gives a better future in an advanced biological treatment (Zhao et al. 2006; Vendramel et al. 2015).

Table 2.1 Pollutant removal from oily wastewater by conventional method

Type of conventional method	Type of wastewater	Percentage of pollutant removal
Coagulation by ferric chloride(Altaher et al. 2011)	Petrochemical wastewater	52% COD removal
Anaerobic submerged fixed-bed reactor (ASFBR) (Vendramel et al. 2015)	Petroleum wastewater	91% COD removal 92% TSS removal
Dissolved air floatation (Al-Shamrani et al. 2002)	Petroleum wastewater	99% Oil removal
Electrocoagulation (Oznoyar 2016)	Oil from train industry	94.5% COD removal

2.3 Membrane Technologies

Membrane separation is a promising technology after the increasing number of its application for removal of oil from oily wastewater. Membrane is a thin layer of semi-permeable material that separates substances when a driving force were applied across the membrane. It can be differentiated by size of pores and molecular weight. Application of membrane technologies in treating oily wastewater is favour due to some advantages. According to the study by Cheryan and Rajagopalan (1998), quality of the treated water from membrane separation is more uniform, a smaller foot print, have a positive barrier to rejected components and energy cost is relatively lower compare to conventional methods. Typical working system of separation of oily wastewater using membrane separation is illustrated in Figure 2.2. Also, new development for effective uses of membrane through combination with conventional method, for example flocculation and microfiltration membrane or with traditional membrane separation such as the joint separation of ultrafiltration and reverse osmosis (Zhong et al. 2003). In this section, ultrafiltration, reverse osmosis, microfiltration, ceramic and polymer membrane were reviewed.

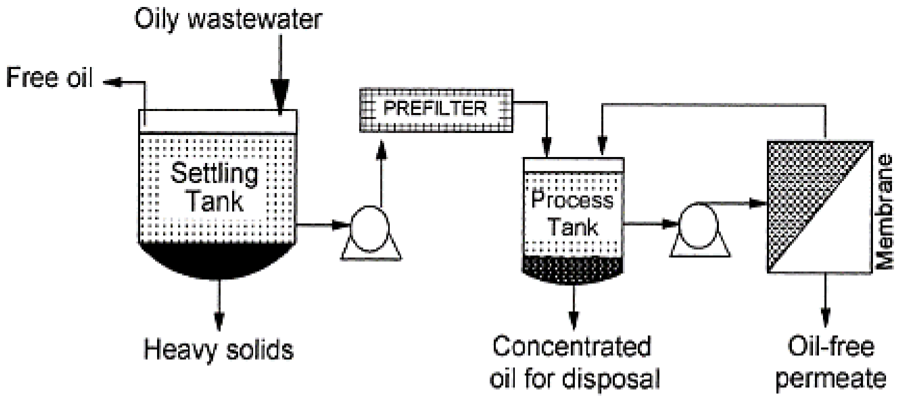


Figure 2.2 Schematic of typical membrane system of treating oily wastewater (Cheryan and Rajagoblan 1998)

Ultrafiltration in oil waste water treatment produces oily water in acceptable quality for discharge into sea. Oil phase can be incinerated then further concentrated by centrifugation. Moreover, there are study previously on the application of ultrafiltration membrane treating oil from heavy oil and metal industry which gives removal of 80% of asphaltene and 95-99% of oil (Duong et al. 1997; Marchese et al. 2000). Combination of ultrafiltration/reverse osmosis processes result on rejection of COD of 98.5% and TDS about 95.7% comparing to separation with only using an ultrafiltration membrane (Karakulski et al. 1995). These treatment efficiencies were observed by different types of membrane material using ultrafiltration method which the tubular membrane achieved highest pure water flux.

Next, membrane techniques for separation oily wastewater is reverse osmosis. Salahi et al. (2010) carried out study of efficiencies on flux performance of reverse osmosis by varies parameters such as transmembrane pressure (TMP), crossflow velocity, temperature and pH on the efficiencies of the flux performance (Salahi et al. 2010). The effluent achieved around 86.1% oil and grease content and high flux of 50 $L/m^2.h$. There is also feasibility investigation of the integrated microfiltration-reverse osmosis (MF-RO) process (Yu et al. 010). Results of combining two stages membrane process (MF-RO) gives high efficiency in the treatment of oil-containing wastewater. In MF process, the oil content in permeate was less than 12 mg/L and submitted for further treatment via RO process in order to improve the water recovery rate up to 95%.

Next is the application of microfiltration for oil emulsion separation. Koltuniewicz et al. (1995) research regarding dead end and cross flow modes of different polymeric and cellulosic MF membrane fouled by oily waste water. Their observed that after an initial phase of pore blocking, the build-up of a layer of droplets and cake filtration dominates the performance. However, because of these study uses organic membrane, some drawbacks occur due to the usage of organic membrane is sensitive to both polar and chlorinated solvents, and contain high oil fractions (Gallagher 1992).

Ceramic MF membrane also reportedly shows better separation performance in terms of higher flux, less fouling and higher oil rejection (Higgins et al. 1994). Furthermore, research on NaA zeolite MF prepared on α-Al_2O_3 tube by in-situ hydrothermal synthesis method result on 99% oil rejection (Cui et al. , 2008).. Membrane with pore size of 1.2 μm (NaA1) and 0.4 μm (NaA2) were used to treat an oil-in-water emulsion to achieved water concentration with 1 mg/L oil. Suresh and Pugazhenti (2017) does the comparison study of ceramic and composite MF membrane. Composite membrane has better flux performance and higher oil removal efficiencies of 99% while ceramic shows 93-96% of oil removal.

2.4 Fouling Phenomena on Membrane and Techniques for reducing the effect.

2.4.1 Membrane Fouling

Membrane fouling mainly describes as an accumulation of foulants on surface or within pores of membrane structure. The foulant may provide cake or surface deposited layer and if for microporous membrane, foulant may cause a pore plugging. Fouling affect the membrane performance by decreasing the permeate flux, permeate solute concentration increases and increasing pressure drop. Significantly, fouling will reduce the membrane's lifespan and increased the operational cost of the membrane.

2.4.2 Fouling Mechanism

Four classical filtration models are standard blocking, cake formation, intermediated blocking and completed blocking. Hermia (1982) developed the blocking filtration laws to analyse the fouling behaviour. Figure 2.3 show the interaction of oil emulsion with the membrane. Standard blocking accounts for the fouling that occurs inside the membrane pores. Complete blocking model assumes that particles arrive at the membrane and seal the membrane pores such that the particles are not superimposed upon the other. The blocked surface area is a proportional to the permeate volume. In intermediate blocking model, the assumption resembles with complete blocking except that the particles deposit on other deposited particles or directly block some membrane surface area. The cake filtration model is used to explain for the case of large particles, which cannot enter most pores, and hence, deposit forms a cake on the membrane surface.

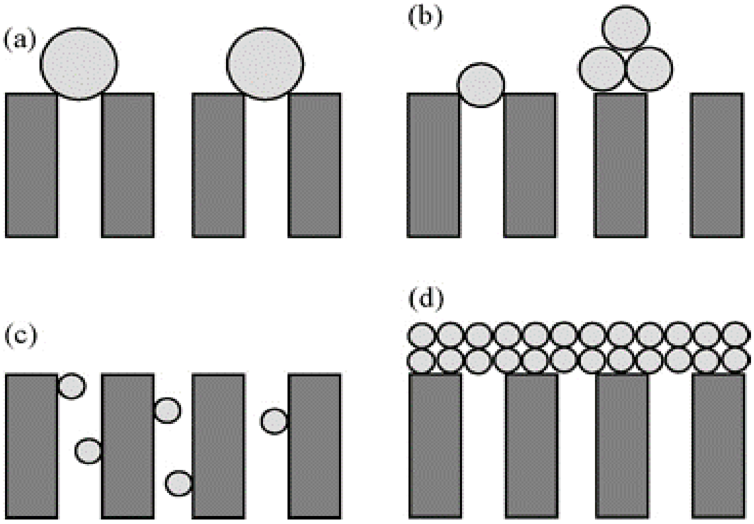


Figure 2.3 Illustration of fouling mechanism based on four models: (a) complete blocking; (b) intermediate blocking; (c) standard blocking and (d) cake layer formation.

The fouling evolutions of membranes during the treatment of oil emulsions were identified with fitting to the four fouling models. Flux decline of membrane fouled by oil emulsion calculated by regression from the model equation and corresponding correlation coefficient (R^2) and Fouling Index (K) value from the plotted graph. Fouling mechanism model formulated by Equations (2.1)-(2.4) (Vela et al. 2008).

a) Completed pore blocking

$$\ln J = \ln Jo - Kc\, t \tag{2.1}$$

b) Gradual pore blocking

$$\frac{1}{J_2^1} = \frac{1}{Jo_2^1} + Ks\; t \tag{2.2}$$

c) Intermediate blocking

$$\frac{1}{J} = \frac{1}{Jo} + Ki\; At \tag{2.3}$$

d) Cake filtration

$$\frac{1}{J2} = \frac{1}{Jo^2} + Kcf\; t \tag{2.4}$$

where Kc,Ks,Ki and Kcf = mass transfer coefficient for associated filtration laws , t = fouling period and Jo is term indicated initial water flux which depends on trans membrane pressure, membrane resistance and viscosity of filtrate.

2.4.3 Methods for reduction of fouling

As mentioned earlier, most of the study regarding oil-water separation for membrane technologies are applicable on microfiltration and ultrafiltration process. However, microfiltration has much more serious membrane fouling effects comparing to ultrafiltration. The reason because the oil droplets is easily stick onto the MF membrane surface (Suresh and Pugazhenti 2017). This cause the possible blockages of surface pores. Several ways previously attempted to solve drawbacks from fouling phenomena. Techniques involved are membrane modification (Jenkins and Tanner 1998), back-pulsing (Ma et al. 2000), effect of stabilization surfactant (Lu et al. 2015) and many more. Among all the methods, most researchers work on the modification of the membrane as it is success to recover water in the permeate line.

There are two type of membrane modification which are modification of the membrane matrix (including blending and copolymerizing) and modification of the membrane surface, where polar groups or grafting hydrophilic monomers introduced to the membrane surface (Sun et al. 2013). The hydrophilic nature of the surface is more helpful to repel oil droplets from adhering to the membrane surface that contributes to minimize the membrane fouling. The physical and chemical modifications on the membrane surface are also an effective way to improve membrane hydrophilicity and alleviate membrane fouling. Anderson et al. (1987) investigated an effect of surface modification enhance the separation of oil and water with non-anionic surfactant composed of polyethylated linear aliphatic alcohols. By using mixed ester asymmetric

MF membrane, its achieved concentration of emulsion at low value around 0.18%, v/v (Jacobs 1989).

2.5 Performance of Cleaning Agent

2.5.1 Cleaning agent as method of reducing fouling effect

Membrane cleaning shown an advantage on restore the initial permeate flux thus reduce the fouling effect. Cleaning techniques categorized into biological, physical, chemical and enzymatic. Chemical cleaning depends on the chemical reaction of removing foulants or impurities by cleaning agent. Adhesion forces between the foulant and membrane when foulant deposit whether on membrane the surface or pore blocking within the membrane were weaken by introducing chemical cleaning agent through the physical and chemical interactions (Tragardh 1989). The working principle of cleaning agents when remove a foulant are chemical should first loosen and dissolve the foulants, Next, keep the foulant in dispersion and solution form to avoid new fouling, and cleaning chemical should not attack the membrane. (Madaeni and Samieirad 2010).

Despite that, there are also possible effect on the interaction between fouling components and cleaning agents. Cleaning agent result on the fouling materials present on a membrane in such ways; foulants may be removed, morphology of foulants may be changed (swelling, compaction) and/or surface chemistry (Weis et al. 2003). The possible reactions between foulant and cleaning agent are hydrolysis, peptization, saponification, solubilisation, dispersion and chelation (Gun 1989). Common cleaning agents used in industry includes bases, acids, surfactant, disinfectant and enzyme. Table 2.2 illustrates details of various types and examples of cleaning agents.

Table 2.2 Basic cleaning agent categories and it examples (Gun 1989)

Bases	Acidic	Detergent/surfactant	Enzymatic	Disinfectant	Blend
NaOH	HCl	SDS	Peroxidase	H_2O_2	4Aquaclean
KOH		Alkyl sulphate		$KMnO_4$	Divos
					Triclean (triton)
					Ultrasil/Aquaclean(Ecolab)

2.5.2 Previous study on membrane cleaning

. To achieve the optimum condition of cleaning process of microfiltration membrane is difficult. Somehow, a study were done for determination of optimum condition using response surface methodology (RSM) (Jung et al. 2016). Experimental results show the cleaning efficiency of chemical (sodium hypochlorite and citric acid) are sensitive to the concentration of cleaning chemicals. Moreover, the investigation on cleaning model were perform related to the study of cleaning dynamics for a cleaning agent. Effect of cleaning agent can be effectively quantified from model calculation of the instant cleaning rate, ri and the overall cleaning effectiveness, η model developed by Zondervan and Roffel (2007). Madaeni and Samieirad (2010) demonstrated the study of different of cleaning agents and its combination between them for the cleaning efficiency. The flux recovery was observed by varies parameters such as temperature, cleaning time, velocity and cross-flow velocity.

Joshi and Brons (2013) reported that, chemical cleaning of oil refinery heat exchangers through dissolved of some constituents where the solid foulant deposited. The common method circulated the hydrocarbon streams like naphta, kerosene or gas oil to washed away foulant. However, from this report, the chemical cleaning concludes to be an ineffective because of inability to circulate high volumetric flow of solvent used for circulation.

2.5.3 Method of cleaning

Hybrid process or defined as the combination of chemical materials and physical techniques is the effective procedures to separate fouling materials from the membrane. This is because membrane cleaning is not completely achieved by usage of only chemical substance. Backwashing is one of method in hybrid process were operated by running the solution from the backside of the membrane to the surface side. There was study regarding an immersed membrane in an activated sludge mixed liquour regenerated by injection of chemicals into permeate path (Kitagawa and Hori 1997). Chemical such as hydrochloric acid (HCl) were subjected into permeate path in low pressure for a certain time. Forward and backward direction for washing the microfiltration membrane has been used in research by Jacobs (1989). Their work on the membrane for processing of microorganism were regenerated by washing with sterile water in forward and backward direction. These steps were followed by immersing washed membrane into solution of H_2O_2.

Previous investigation on different cleaning methods show that combination of chemical cleaning, followed by sonication and backwashing achieved flux recovery about 95.7 % (Lim and Bai 2003). Based on this study, DI water backwashing yield low flux recovery indicated low membrane performance Different cleaning method has each proposed cleaning principle. Combination cleaning success to an effectively clean the membrane surface. Chemical cleaning only removes cake attachment that bound with membrane surface whereas sonification and backwashing remove a cake by break bit down into smaller fragments and drives out attached particles in pores respectively. Furthermore, research regarding cleaning of polyethylene hollow fibre MF membrane were conducted for removing oil from contaminated seawater. The cleaning method is through soaking as soaking time decreased, the actual operating time/cleaning increased. The recommended of soaking time is around 8-10 hour (Al-Obedaini et al. 2008).

2.6 Alkali Cleaning Agent

Alkaline cleaning or also referred as caustic cleaning is suitable for removing adsorbed organics. Commonly alkaline cleaner used is sodium hydroxide (NaOH). Caustic cleaning show better performance in removal organic foulants comparing to acid cleaning. This is because of the presence of hydroxyl ions in alkaline solution could promote disruption of the foulant layer by increasing solubility of organic foulants, enhancing the solubility of organic foulants (Al-Amoudi and Lovitt 2007). Application of alkali in cleaning efficiency previously reported for fouling of surface water, skim milk, Bovine Serum Albumin (BSA), whey, apple juice and potable water (Zondervan and Roffel 2007).

2.7 Acid Cleaning Agent

Acid cleaning usually used to remove precipitated salts or scalants from the surface of the membrane and pores. Possible interaction between acids as cleaning agents and foulants are hydrolysis/saponification and solubilization/chelation (Zondervan and Roffel 2007). Common acids involved in membrane cleaning are hydrochloric acid (HCl), sulphuric acid, nitric acid and phosphoric acids. Hydrochloric acid as cleaning agent display a better performance than other acids because of no oxidation ability of HCl for degradation of matters. Citric and oxalic acid on the other hand are more effective for formation and transportation of organic-metallic foulants from the membrane to the bulk solution (Porcelli and Judd 2010). Several publications studied on the application of acid in cleaning performance, however it resulted on the least efficiency by comparing with other cleaning agent even in some researches acid is not suitable for certain type of membrane fouling (Regula et al. 2014) .

2.8 Surfactant Cleaning Agent

Surfactant are widely used for cleaning membrane regarding its advantages for mild operation and maintaining membrane integrity. There are four categories of surfactant which are anionic, cationic, nonionic and amphoteric but anionic surfactant for example sodium dodecyl sulphate (SDS) were often uses for cleaning a membrane. Madaeni et al. (2010) work on the evaluation of cleaning process with different surfactant proved SDS is a best cleaner with cleaning efficiency of 99%. The mixing of surfactant with other cleaning agent increased the performance of membrane cleaning. Combination of sodium dodecyl sulfate and sodium hydroxide can be used as a cleaning material to reach the optimum recovery of the polysulfon membranes used in milk concentration industries (Mohammadi et al. 2003). Surfactant has a low surface tension contribute to the increase of significantly the wettability of the fouled membrane, which favours the contact between the chemical agents and the deposit and reduces the adhesion forces between the fouling layer and the membrane.

2.9 Rhamnolipid Cleaning Agent

Rhamnolipid is a glycolipid bio surfactant primarily a crystalline acid, is composed of β-hydroxy fatty acid connected by the carboxyl end to a rhamnose sugar molecule (Abdel-Mawgoud et al. 2010). Rhamnolipids molecules are predominantly produced by *Pseudomonas aeruginosa* and classified as: mono and di-rhamnolipids. The ratio of mono and di-rhamnolipid can also be controlled in the production method. Rhamnolipid has a property of exhibit biodegradability properties where efficiently recover the residual oil using microorganisms or their products (Bordoloi and Konwar 2008). Furthermore, with properties of low toxicity, surface active properties and microbial activities against several microbes and low critical micelle concentration (CMC).

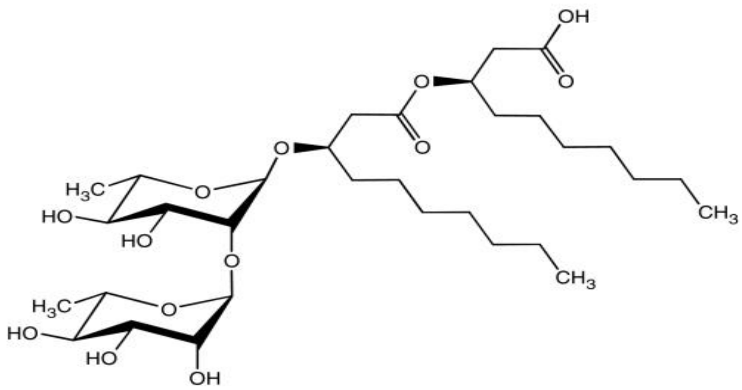


Figure 2.4 Chemical structure of the first identified rhamnolipid; simply named as *α-L*-rhamnopyranosyl-*α-L*-rhamnopyranosyl-*β*-hydroxydecanoyl-*β*-hydroxydecanoate and symbolized as Rha-Rha-C_{10}-C_{10} (Abdel-Mawgoud et al. 2010).

Rhamnolipid become a potential cleaning agent from other researches as rhamnolipid prove to remove membrane fouled by protein as it has properties of no detrimental effect if compared to current cleaning agent by surfactant and acid/alkali medium(Long et al. 2014). Rhamnolipid demonstrated to be effective in cleaning in the long-term fouling membrane. In different study, cleaning efficiencies of rhamnolipid were evaluated for cleaning of ultrafiltration membrane fouled by whey (Aghajani et al. 2018). According to this study, rhamnolipid and NaOh gives higher cleaning efficiency comparing to other types of cleaning medium.

CHAPTER 3

METHODOLOGY

3.1 Approach Research

The study was to evaluate the performance of cleaning agents of cleaning microfiltration membrane fouled by oil emulsion.

3.2 Research Plan

The overall experimental activities carried out in this study are presented in Figure 3.1. The study was to evaluate the performance of cleaning agents of cleaning microfiltration membrane fouled by oil emulsion.

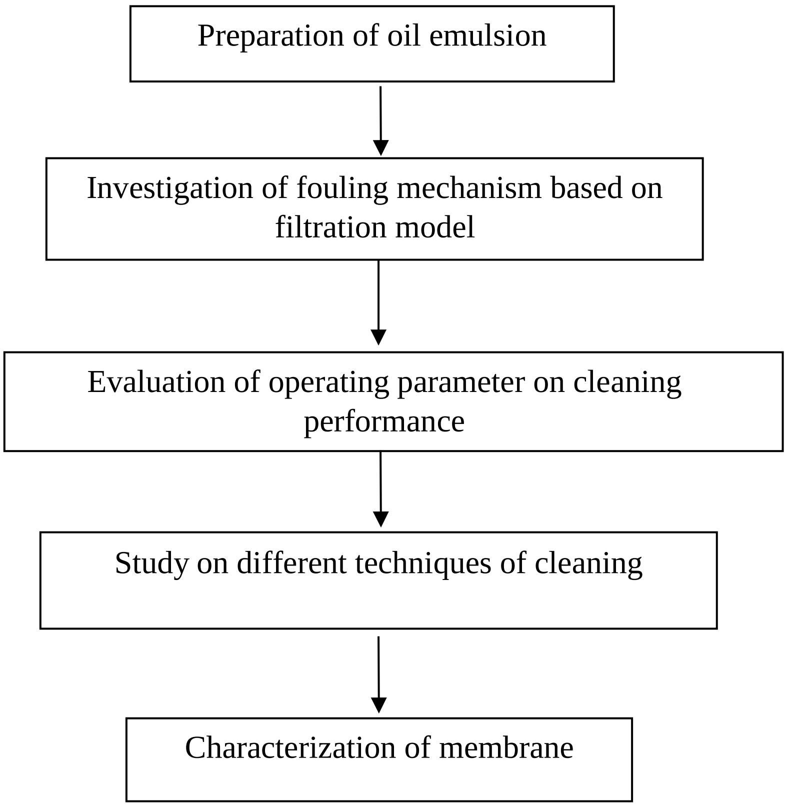


Figure 3.1 Flowchart activities throughout the project

3.3 Experimental Overview

The experiments were carried out to determine the suitable cleaning agents of membrane fouling by oil emulsion. Along with this, the effect of concentration of cleaning agents on cleaning efficiency that represented in form of flux recovery (FR) and flux restored ratio (FRR) were observed. This term reflect the accurate extent on the removal of foulant via taking account of water flux; initial (J_w), after fouling (J_f) and after cleaning (J_c). Cleaning agents are each vary in three concentrations under constant cleaning conditions for time taken 30 min, TMP of 0.5 bar and using method of cleaning by forward flushing. According to the results, the best cleaning agent selected based on the highest cleaning performance. Next, cleaning study of the best cleaning agent were conducted regarding the effect of operating parameters such as varies on time cleaning, cleaning method and TMP. The suitable condition for cleaning SDS for microfiltration membrane fouled by oil emulsion were identified. Furthermore, a fouling mechanism were investigated prior to the four fouling models to determine the best fitted line. Characterization study also included.

3.4 Materials

In this project, rhamnolipid was supplied from School of Biological Sciences of Universiti Sains Malaysia, Penang. Table 3.1 is data provided from research group who responsible for production of cell-culture rhamnolipid. Also attached is Table 3.2 listed chemical with its usage.

Table 3.1 Properties of Rhamnolipid from research group of School of Biological Sciences of USM

Properties	Description
Concentration of Rhamnolipid	2.64 g/L
Critical Micelle Concentration	0.2 mg/L
Cell life span	12 weeks
Condition for storage	Fridge's Temperature

Table 3.2 List of chemicals used with its usage

Materials	Chemical formula	Supplier	Usage
Hydrochoric acid	HCl	J.T. Baker Chemical	Cleaning performance purpose
De-ionized(DI) water	-		Cleaning performance purpose, for preparation of oil emulsion
37% purity of Sodium hydroxide	NaOH	QReC	Cleaning performance purpose
Sodium dodecyl sulphate(SDS)	$NaC_{12}H_{23}SO_4$	Friendeman Schmidt Chemical	Cleaning performance purpose
Tween 80	$C_{64}H_{124}O_{26}$	J.T. Baker Chemical	For preparation of oil emulsion
Diesel	$C_{12}H_{24}$	Petronas station	For preparation of oil emulsion

3.5 Equipment and Instrumentation

All equipment used in this research are listed in Table 3.3. This equipment used for instrumentation and analysis throughout the experiment.

Table 3.3 List of equipment, model and its usage

Equipment	Model	Usage
Scanning Electron Microscopy (SEM)	Quanta Feg. 450	To characterize a surface membrane
UV-Visible Spectrometer	DR-5000	To determine absorptivity
Homogenizer	Ultra Turrax T50	Mixing purpose of preparation of oil emulsion
pH meter	MARTINI	To determine pH of sample
Weighing Balance	HR-250A2	To identify weight of sample
Weighing Balance	FX-3000i	To identify weight of permeate sample

3.6 Membrane module

Study on the membrane fouling and cleaning performance completed by using polyvinylidene fluoride (PVDF) hydrophilic microfiltration membrane with 0.22µm purchase from Merck Millipore. Table 3.4 is the list of performance characteristics of the membrane.

Table 3.4 Performance of characteristics of hydrophilic PVDF membrane obtained from Merck Millipore

Membrane name	Hydrophilic PVDF
Pore size	0.22 µm
Membrane Material	Modified PVDF
Average bubble point	57 psi
Biocompatibility	Biological test for plastics, Class VI
Average Thickness	125 µm
Flow rate (at 13.5 psi)	7.2 mL/min/cm^2
Membrane Code	GVPP

3.7 Cross-flow microfiltration membrane

The experimental rig for crossflow microfiltration is shown in Figure 3.2 and list of equipment summarize in Table 3.5. The emulsion was delivered from feed tank by means