SYNTHESIS OF CROSSLINKED POLYVINYL ALCOHOL ULTRAFILTRATION MEMBRANE FOR TREATMENT OF LATEX WASTEWATER

NURUZAIKHA BINTI MUHAMMAD YUSUF

UNIVERSITI SAINS MALAYSIA

2013

SYNTHESIS OF CROSSLINKED POLYVINYL ALCOHOL ULTRAFILTRATION MEMBRANE FOR TREATMENT OF LATEX WASTEWATER

by

NURUZAIKHA BINTI MUHAMMAD YUSUF

Thesis submitted in fulfillment of the

requirements for the degree of

Master of Science

JUNE 2013

ACKNOWLEDGEMENTS

In the name of Allah, the Most Gracious and Most Merciful.

First and foremost, Alhamdullilah, all praise to Allah S.W.T. for the strength and blessing towards completing this dissertation in time. I would like to take this opportunity to give my sincerest gratitude to my beloved parents, Mr. Muhammad Yusuf Muda and Mrs Rafiah Shafie, and also to all my family members for their endless love, support and prayers.

I would like to grab this chance to offer my deepest gratitude to my supervisor, Prof Abdul Latif Ahmad, who has given me support throughout finishing the thesis with his excellent guidance, motivation and knowledge. Also, I would like to express gratitude to my co-supervisor, Dr. Ooi Boon Seng for his fundamental knowledge sharing and advices in this research. Special thanks also towards lecturers, technicians and staffs of Chemical Engineering School, USM for their cooperation and assistance.

To the special persons, Nuur Fahanis and Wan Khairunnisa, thank you for being there the most when I needed you. Also, not forgotten, Nurul Aini, Norhidayah Ideris, Iylia Idris and Siti Harwani for the advices and supports. Thank you friends for the wonderful moment and memories created in USM. Ukhuwwah fillah.

Last but not least. I would like to give a special thank to whom has helped and contributed either directly or indirectly in completing my research. Without a well warm cooperation from all of you I would not be successful to come out with this thesis. Thank you very much.

Nuruzaikha Muhammad Yusuf, June 2013

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATES

LIST OF SYMBOLS

		Unit
ΔP	Transmembrane pressure gradient	N/m^2
ΔC	concentration gradient	
ΔE	electrical gradient	
ΔT	temperature gradient	
η	viscosity of liquid	$N.s/m^2$
ε_m	surface porosity	
J	flux	$g/cm^2.min$
J_p	Permeate flux	$g/cm^2.min$
J_W	Water permeate flux	$g/cm^2.min$
A_m	Effective membrane surface area	cm^2
T	Temperature	˚C
t	time	min
γ	surface tension	
θ	contact angle	
r	radius of the pore	

LIST OF ABBREVIATION

ABS	Acrylbitrile Butadiene Styrene
AFM	Atomic Force Microcopy
ATR	Attenuated Total Reflectance
BOD_5	Biological Oxygen Demand
COD	Chemical Oxygen Demand
DO	Dissolve Oxygen
SBR	Styrene Butadiene Rubber
NBR	Nitrile Butadiene Rubber
PVA	Polyvinyl Alcohol
GA	Glutaraldehyde
MF	Microfiltration
RO	Reverse Osmosis
UF	Ultrafiltration
NF	Nanofiltration
3D	Three Dimensional
TSS	Total Suspended Solid
TS	Total Solid
TEM	Transmission Electron Microscopy
FTIR	Fourier Transform Infra Red Spectroscopy
SEM	Scanning Electron Microscopy
PVDF	Polyvinylidene fluoride

SINTESIS MEMBRAN PENURASAN ULTRA POLIVINIL ALKOHOL TERPAUT SILANG UNTUK RAWATAN AIR SISA LATEKS

ABSTRAK

Teknologi pemisahan membran terutamanya dalam penurasan ultra, penurasan nano dan osmosis balikan telah semakin fokus ke arah mencari penyelesaian yang sesuai untuk mengurangkan dan menyelesaikan masalah pengotoran membran tak berbalik. Pengotoran adalah satu halangan yang serius kepada pembangunan dan aplikasi sains dan teknologi membran. Penyelidikan penting juga sedang dilakukan kepada pengubahsuaian permukaan berdasarkan prinsip hidrofilik. Dengan meningkatkan sifat hidrofilik permukaan membran, ini secara amnya akan meningkatkan rintangan membran untuk berlakunya pengotoran. Tesis ini memberi tumpuan kepada penyediaan, pencirian dan penilaian prestasi membran Polyvinil Alkohol (PVA) terpaut silang ke arah proses penurasan ultra. Pembentukan membran kepingan rata telah dihasilkan dengan pengubahsuaian kepekatan polimer, suhu pautsilang dan tempoh pautsilang. PVA adalah sangat hidrofilik dan mempunyai sifat pembentukan filem dan rintangan kimia yang sangat baik. Pautsilang menggunakan bahan kimia adalah pendekatan yang paling biasa untuk menstabilkan membran PVA, yang menjadikan ia kurang mengembang di dalam air. Membran PVA tidak simetri telah disediakan dengan teknik rendaman-pemendakan dan dipaut silang dengan glutaraldehid (GA). Kajian terperinci mengenai pembentukan membran (polimer kepekatan) dan keadaan pautsilang (suhu dan tempoh) telah dijalankan. Morfologi dan cirri-ciri membran yang dihasilkan telah diperiksa dan dicirikan dari segi saiz liang dan taburan, keliangan, sudut sentuh statik, mikrostruktur permukaan dan

kekasaran permukaan untuk memahami sifat membran yang disintesis. Membran yang dihasilkan telah diuji menggunakan radas ujikaji penelapan membran. Tempoh pautsilang untuk membran PVA memainkan peranan penting dalam profil taburan saiz liang dan darjah pautsilang dalam struktur rangkaian polimer. Pengenalan masa pautsilang yang lebih lama boleh menyebabkan kumpulan hidroksil dari struktur rangkaian polimer untuk bertindak balas lebih dengan kumpulan aldehid GA, yang merupakan ejen pautsilang. Oleh itu, ia juga penting untuk menunjukkan bahawa terpaut silang kimia oleh kumpulan aldehid telah mengubahsuai struktur asal rangkaian PVA dan dengan itu mengurangkan dengan ketara taburan saiz liang. Hubungan di antara parameter pautsilang dan fluks penelapan telah disiasat dan dijelaskan. Dalam kajian, pembentukan membran dengan kepekatan polimer sebanyak 12% tanpa bahan tambah, ketebalan awal 100 μm dan tempoh tindakbalas pautsilang dikaji pada 0.5, 1.0, 1.5 dan 2.0 jam menghasilkan sifat hidrofilik yang tinggi. Prestasi membran dari segi fluks air tulen (J_w) dan fluks bahan larut (J_p) telah dijalankan di mana fluks bagi bahan larut adalah lebih rendah daripada fluks air tulen. Fluks air tulen mempunyai hubungan secara langsung dengan bilangan liang dan ciri-ciri permukaan sifat hidrofilik mereka.

SYNTHESIS OF CROSSLINKED POLYVINYL ALCOHOL ULTRAFILTRATION MEMBRANE FOR TREATMENT OF LATEX WASTEWATER

ABSTRACT

Membrane separation technologies particularly in the ultrafiltration, nanofiltration and reverse osmosis are progressively more focused on finding the suitable solutions for lessening and mitigating the irreversible membrane fouling. Fouling is a serious hindrance to the development and application of the membrane science and technology. Essential research is also being done on the surface modification based on the hydrophilicity principle. By increasing the membrane surface hydrophilicity, this will generally improve the membrane resistance to fouling. This thesis focuses on the preparation, characterization and the performance evaluation of crosslinked Polyvinyl Alcohol (PVA) membrane towards ultrafiltration process. Formation of the flat sheet membrane had been produced by modifying polymer concentration, crosslinking temperature and crosslinking duration. PVA is highly hydrophilic and has excellent film-forming and chemical resistance properties. Chemical crosslinking is the most common approach for stabilizing PVA membranes, which makes it less swollen in the water. Asymmetric PVA membranes were prepared by the immersion-precipitation technique and were further crosslinked with glutaraldehyde (GA). Detailed studies on membrane formulation (polymer concentration) and crosslinking condition (duration and temperature) had been carried out. The resultant membrane morphologies and properties were examined and characterized in terms of pore size

and its distribution, porosity, static contact angle, microstructure of the surface and surface roughness in order to grasp the nature of the synthesized membranes. The produced membrane was tested on the membrane permeation test apparatus. The crosslinking duration for PVA membrane plays an important role in profiling the pore size distribution and the degree of the crosslinking in the polymer network structure. Introducing a longer time of the crosslinking may cause the hydroxyl groups of the polymer network structure to react more with the aldehyde groups of GA, which was the crosslinking agent. Hence, it is also crucial to point out that the chemical crosslinked by the aldehyde group had modified the original PVA network structure, and thus significantly reducing the pore size distribution. The relationship between crosslinking parameter and permeation flux were investigated and explained. In the study, membrane formulation with polymer concentration of 12% without additive, initial thickness of 100 μm and crosslinking reaction durations studied at 0.5, 1.0, 1.5 and 2.0 hour produced high hydrophilicity. Membrane performance in terms of pure water flux (J_w) and solute flux (J_p) was carried out where the flux for solute was lower than pure water flux. Pure water flux has a direct relationship with number of pores and their surface hydrophilicity characteristics.

CHAPTER ONE

INTRODUCTION

1.0 Membrane Technology

Before 1950, membranes were developed in a small scale for laboratory applications. However, the most fundamental breakthrough in membrane technology came in late 1950s when Loeb and Sourirajan discovered very thin asymmetric membranes having a low permeation resistance for reverse osmosis (Kubota et al., 2008, Wenten, 2002). After the discovery, significant progress in various aspects on membrane related fields have been done such as automobile industry (closed system for electrodeposition paint recovery), the electronics industry (production of ultrapure water for semiconductor) and the pharmaceutical industries (concentration and purification of enzymes and antibiotics).

Nowadays, membrane technology has become a preferential alternative in separation process due to several benefits it offers. Generally, the energy consumption is low and the process can be set to be continuous process. Membrane materials can be adjusted depending on the process environment and easy to up-scale. Furthermore, the performance can be enhanced by coupling with other process (Mulder, 1996).

The pressure driven membrane processes such as microfiltration, ultrafiltration, nanofiltration and reverse osmosis show a great assurance for aqueous cleaner wastewater treatment including the isolation, concentration recycling of certain cleaning components, and possible recovery and reuse of the water stream. In particular, membrane technologies have certain properties which make them unique when compared to other separation operations. These include the ability to do continuous process, resulting in automatic and uninterrupted process operation, low energy consumption since no change in temperature and phase change during the process, modular size which is no significant size limitations, discrete membrane barrier to ensure physical separation of contaminants, less frequency of maintenance since less moving part in the system and no additional chemical required during the separation process (Wenten, 2002).

However, there is major barrier to a large-scale application of the membrane separation technology in industry which is membrane fouling (Wenten, 2002). The blockage of membrane pores during filtration process that is caused by the combination of sieving and adsorption of particulates and compounds onto the membrane surface or within the membrane pores is referred as fouling (Ma et al., 2001, Ma et al., 2007a, Ma et al., 2007b, Madaeni and Samieirad, 2010). Membrane fouling will cause the permeate flux to reduce over time, the quality of the membrane deteriorated and the life-span of the membrane itself will be shortened. Therefore, it is very crucial to know the theory of membrane fouling and the method to improve the membrane flux and the lifespan of the membrane (Kubota et al., 2008, Ri et al., 2008).

The options for fouling abatement for an installed plant has become more restricted and resolute on the physical and chemical methods summarised by (Wakeman and Williams, 2002) in Table 1.1.

Table 1.1 : Methods for reduction of flux degradation

	Physical	Chemical
Pretreatment	Prefiltration	Precipitation, Coagulation/flocculation, Use of disinfectants, Use of antiscalants, Adsorption
Design	Use of turbulence promoters, Pulsed/reversed flow, Rotating/vibrating membranes, Additional (e.g. modification electrical) fields	Choice of membrane material, Membrane surface
Operation	Limit transmembrane pressure (i.e. production rate), Maintain a high crossflow, Periodic hydraulic cleaning, Periodic mechanical cleaning	Choice of cleaning chemicals, Frequency of cleaning

1.1 Ultrafiltration for Wastewater Applications

A revolutionary water treatment process was accomplished by integrating membrane into the treatment process resulting in high effluent quality. Water treatment has become an important issue due to the scarcity of clean water sources to certain countries. A huge supply of water that covers the earth in form of ocean cannot fulfil the world water demand. Consideration for conventional desalination process must be done before it can be used as potable water.

Conventional water treatments are not capable in producing potable water that fulfilled the requirement of water quality standard that becoming more stringent nowadays. An advanced water treatment like ozonation and activated carbon can improve water quality but results in high cost and difficulty in operation. Membrane technology offers one or two simple steps to overcome it. Membrane as highly selective layer is capable to separate microorganisms' pathogen completely. Membranes are also capable of reducing hardness, controlling colour, and removing inorganic and organic compounds. Water with low quality is acceptable to be processed by membrane. In space demand, membrane processes require a smaller space compared to the conventional technology.

Every year, a massive amount of wastewater produced from various industrial sectors such as petrochemical industry, textiles industry, pharmaceutical industry and food industry which will eventually lead to severe environmental problems. Pollutants from wastewater can be eradicated to a reusable standard either by direct filtration or conventional biological wastewater treatment. The conventional methods such as gravity separation and skimming, air-flotation, coagulation, de-emulsification and flocculation could cause corrosion and re-contamination of wastewater as additional chemicals involved in the process. Several studies have been reported on the use of filtration membrane as the effective methods in separation of wastewater (Lin and Lan, 1998, Madaeni and Samieirad, 2010).

Ultrafiltration is used to separate materials in the 0.001 to 0.1 µm range (10-1000 angstroms). Basically, ultrafiltration is used to remove dissolved materials, whereas suspended solids are removed by microfiltration (Kubota et al., 2008). Ultrafiltration is a very adaptable and usually employed separation process whose nature is between reverse osmosis and microfiltration. An ultrafiltration membrane acts as selective barrier which retains species with molecular weight higher than a few thousands Dalton (macrosolutes), while freely passing small solutes (microsolutes and solvent). The separation is achieved by introducing the pressure difference in the system.

Applications of ultrafiltration (UF) membranes in water treatment have rapidly increased during these past decades. Successful operation of dead end UF processes requires meticulous experimentation and modeling in order to optimize the operating procedure. Optimum scheduling of forward and backwash cycles can play an important role in minimizing reversible fouling effects and controlling irreversible fouling (Al-Hammadi and Al-Bastaki, 2007).

1.3 Problem Statement

Membrane fouling is an exceptionally complex physicochemical phenomenon. Usually several mechanisms are involved simultaneously. Thus in case of protein-containing solutions it was suggested that it began with protein aggregates depositing on the membrane surface, thereby blocking its pores. The complexity of membrane fouling predetermines the exploiting of a variety of approaches to control this adverse process which are categorized under four main topics: pre-treatment of feed; membrane materials/surface modification; operating parameters; and cleaning procedures. However, there are not always conducive to apply to membrane operation, which will unintentionally increase costs for pre-treatment equipments and chemicals. It can also cause unscheduled downtime for cleaning procedure. Therefore, the research in membranes with antifouling properties has raised interest in recent years.

Some measures used to mitigate membrane fouling include anti-fouling membrane development. Therefore, much interest has garnered on the development of good hydrophilic UF membranes using a highly hydrophilic polymer instead of modifying the hydrophobic one. The main objective of some research works is based on the principle of increasing hydrophilicity of the membrane which in turn can generally improve the ability to resist fouling. The hydrophilic and hydrophobic properties of the membrane materials have a significant influence on the membrane flux reduction while treating solutions containing hydrophobic solutes.

In hydrophilic polymers, poly (vinyl) alcohol (PVA) is well known as a membrane material with high tensile and impact strength, good chemical and thermal stability, high water permeability and an oxygen barrier property (Chuang et al., 2000a, Chuang et al., 2000b). Being a material with good chemical stability and high water permeability, PVA appears to be an attractive material for producing membrane. PVA is highly hydrophilic, non toxic and biocompatible polymer with excellent film-forming characteristics, low fouling potential and strong pH stability (Wu et al., 2008). Because of these properties, much research work is laid on the preparation of PVA membranes and for bioseparation, while a few works has been done using PVA membranes in the treatment of oily wastewater (Wu et al., 2008).

Materials selection for the surface modification of PVA membrane is based on the enhancement of hydrophilic characteristics of the membrane. Many studies (Mukherjee, 2005, Tang et al., 2009, Pandey et al., 2003) had been done in order to increase the characteristics of the polymer membrane especially on PVA. Mukherjee (2005) did the study to increase the mechanical strength and moisture resistance and

Tang *et al* (2009) studied the membrane in order to improve hydrophilicity, reduce surface charge, smoothen membrane surface and reduce membrane permeability.

Because of its hydrophilic nature, PVA must be modified in order to minimise swelling in water when fabricated for wastewater treatment. Morphology of modified PVA membrane from the result of crosslinking PVA membrane with various crosslinking agents such as glutaraldehyde, sulfuric succinic acid, folmaldehyde and many others has been studied in order to increase chemical, thermal and mechanical stability. A review has been done for the crosslinking of PVA membranes by Bolto *et al*. (2009). In the review, Bolto et al had characterized the process of crosslinked PVA membrane and also the different approach in crosslinking process. Kim *et al*. (1993, 1994) explained the kinetics of crosslinking PVA membrane with glutaraldehyde and also the effects of the degree of crosslinking to the properties of PVA membranes.

In this study, glutaraldehyde will be used since it is the most effective crosslinking agent based on the literature for the crosslinking of PVA. Glutaraldehyde gives a less swollen product without affecting the hydrophilicity of the membranes thus can reduce fouling.

1.5 Objectives of Research

The main objectives of this research are as follows:

1) To synthesis the synthetic latex wastewater with similar properties as in industrial latex wastewater in terms of its particle size.
2) To determine the important parameters in preparing an optimum PVA membrane for latex wastewater separation.
3) To characterize the membrane produced and evaluate the final membrane performance.

1.6 Organization of the Thesis

There are five chapters in this thesis and each chapter gives the important information of this research. An introduction of membrane technology, membrane potential and its current status, poly (vinyl) alcohol membrane, problem statements, research objectives and thesis organization are outlined in chapter one.

Chapter two reviews the existing research on the topic which is latex wastewater recovery by using membrane technology. This chapter will be divided into several subchapters. First subchapter will mainly focus on highly viscous liquid wastewater. In this subchapter, the author will briefly explain the studies on several types of highly viscous liquid in wastewater including the main topic; latex wastewater. Second subchapter will elaborate the conventional methods for wastewater treatment and their limitations. Subsequent subchapters will introduce the membrane separation technology and the ultrafiltration process.

Chapter three will present the detailed methodology used to run the experiments. The details on the chemicals and instruments used, experimental procedures, analysis and characterization techniques throughout the experiment are described. In this chapter, there are three distinctive stages involved. The first one is the physical and chemical analysis on sample of industrial latex wastewater and the synthesis of synthetic latex wastewater to be used in later part of experiment. The next stage is to select a suitable method for membrane modification by using crosslinking PVA membrane with glutaraldehyde. And lastly, the liquid permeation measurement is done to determine whether the membrane is suitable for the ultrafiltration process.

Chapter four which is the results obtained from the experiment outlined from the previous chapter will be presented. This chapter is divided into three distinctive sub chapters. The first sub chapter deals with the results obtained from the nitrile butadiene rubber (NBR) latex wastewater characterization and the pore size distribution of synthetic latex wastewater to be used throughout the experiments. The second sub chapter focuses on discussing the preparation and characterization of PVA membrane on the basis of several formulation parameters such as polymer concentration and crosslinking conditions. Lastly, the final subchapter will discuss the performance evaluation of optimum conditions for PVA membranes based on the flux test.

The last chapter concludes the findings in the current work with several recommendations to improve the research in future works.

CHAPTER TWO

LITERATURE REVIEW

2.0 Introduction

Wastewater industry has faced many challenges since last few decades concerning on achieving efficient and economic treatment methods. Membrane technology has become one of the major focuses in treating the wastewater and choice of membrane selection, pre-treatment methods, processing and operational parameters are crucial in determining the efficiency of the separation process. They are very promising techniques because their ability to remove particles including microorganisms, organic pollutant and to achieve biologically stable water to diminish the growth of microbial in the distribution system.

Wastewater treatment is a process in which the wastes in wastewater are partially removed and partially changed by breaking down the complex organic solid. In most processes, primary and secondary treatments remove the majority of biological oxygen demand (BOD) and suspended solids in the wastewaters. Nonetheless, these treatments have been proven to be insufficient for fully treating the industrial wastewater. Therefore, further treatment stages have been included into wastewater treatment plants for additional organic and solids removals and removal of nutrients and toxic materials. There have been several new developments in the water treatment field in the last few years (Lin and Lan, 1998, O'Reilly, 2000, Li et al., 2005, Mousa and Al-Hitmi, 2007).

Advanced wastewater treatments have become an area of global focus as individuals, communities, industries and nations attempt for ways to keep essential resources available and suitable for use. Advanced wastewater treatment technology, coupled with wastewater reduction and water recycling initiatives, urge expectation of slowing, and perhaps halting, the inevitable loss of usable water. Membrane technologies are well suited to the recycling and reuse of wastewater. Membranes can selectively separate components over a wide range of particle sizes and molecular weights. Membrane technology has become a distinguished separation technology over the past decades. The major reason of membrane technology being the most reliable process in wastewater treatment is that it does not require additional chemical for the process, with relatively low energy use and easy and systematic process separation (Owen et al., 1995, Sonune and Ghate, 2004).

2.1 Highly Viscous Liquid Wastewater

2.1.1 Overview of High Viscous Liquid

Different liquids have different properties. One of these properties is viscosity, the liquid's resistance to flowing. Water, milk, and fruit juice are comparatively thin and flow more easily than thicker, more viscous liquids such as honey, corn syrup, shampoo or liquid soap. In food industrial sector, frequently viscous liquid are encountered in various industrial membrane processes, e.g. concentration by reverse osmosis of fruit juices and white egg, ultrafiltration for producing clarified fruit juice directly from puree, microfiltration for separating fungal cells and purifying the polysaccharide produced, and microfiltration for dewatering feeds containing fine particle matter. The variations in permeate flux with respect to operating conditions reveal unusual effects: the shear rate exponent in laminar flow for non-Newtonian fluids give unusual values, and the fall in permeate flux is not proportional to the logarithm of the bulk concentration, which is obtained for Newtonian fluids and predicted by the concentration polarization model with a constant mass transfer coefficient (Charcosset and Choplin, 1996).

2.1.2 Oil-water Emulsions

Oil-water emulsions are one of the main pollutants emitted into water by industry and domestic sewage. The particularly stable emulsions are generated during several mechanical operations such as grinding, rolling, alkaline degreasing and transportation. Another source of very fine emulsions is condensate from compressed air stations. The common industrial practice to collect sewage from various sources in common storage tanks usually multiply the problems (Koltuniewicz and Field, 1996, Chakrabarty et al., 2008).

Oil and grease in wastewater can be existed in several forms; emulsified, free and dispersion which can be distinguished by different size particles (Cheryan and Rajagopalan, 1998, Chakrabarty et al., 2008). In an oil-water mixture, if the droplet size is greater than 150 µm in size, it is most probably be free oil. For dispersed oil, the droplet size will have the size in a range of 20 – 150 µm however for emulsified oil; the droplet size is typically lower than 20 µm.

2.1.3 Textile Industries

Textiles industries utilize thousands of tons of various chemicals for wet and dry processing. For wet processing of textiles, large water and dyes consumption are unavoidable. To remove dirt, grit, oils, and waxes, detergents and caustic are used. Bleach is used to improve whiteness and brightness. Dyes, fixing agents, and many in-organics are used to provide the brilliant array of colours the market demands. Sizing agents are added to improve weaving. Oils are added to improve spinning and knitting. Latex and glues are used as binders. A wide variety of specialty chemicals are used such as softeners, stain release agents, and wetting agents. A lot of these chemicals will be constituent in the final product where others will be eliminated in the waste streams.

Textile industries are able to generate an enormous volume of wastewater with high in Biological Demand Oxygen (BOD), Chemical Oxygen Demand (COD), Total Dissolved Solids (TDS) and colour (Cheremisinoff, 1998).

2.1.4 Latex Waste/Emulsion

Hevea brasilliensis is commercially used for the production of natural rubber that is used industrially for various finished products. With the increasing of the world rubber demand, the production of industrial sector which involving concentrated latex and skim crepe rapidly increase to cater the inadequate world demand. This situation led to serious environmental problems of pollutants and bad odor from the wastewater treatment plant of the concentrated latex and skim crepe industries. For long, the conventional treatment for any type of wastewater will be introduced in order to eliminate and reduce the problem. As research been done by Thonglimp et al. (2005), to study the effect of food to microorganism ratio (F/M ratio), hydraulic retention time (HRT), sulfate, and calcium concentration on activated sludge treatment of concentrated latex industrial wastewater. The activated sludge (AS) system is one of the biological wastewater treatment process which will be further discussed on the next topic on conventional approach towards wastewater treatment.

Vijayaraghavan *et al.* (2008) mentioned in their study, the conventional means of rubber wastewater treatment are based on the following treatment system, namely: an anaerobic-cum-facultative lagoon system; anaerobic-cum-aerated lagoon system; aerated lagoon system (with extended aeration); and oxidation ditch system. The wastewater generated from the latex processing unit in Malaysia in most cases had the following characteristics: pH 4.2–4.8; COD 2,000–6,000 mg/L; BOD_5 1,000–3,500 mg/L; suspended solids 250–400 mg/L and TKN 250–700 mg/L. Vijayaraghavan *et al*. research on latex wastewater were more focusing on using electrolytic treatment using hypochlorous acid. The results from their investigation showed that at the end of a 90-min electrolysis period for the optimum operating condition, the treated wastewater had the following characteristics: pH 7.3, COD 78 mg/L, BOD5 55 mg/L, TOC 45 mg/L, residual total chlorine 136 mg/L, turbidity 17 NTU and temperature 54^{o}C. During the electrochemical oxidation process, the latex wastewater undergoes in-situ disinfection due to the generated hypochlorous acid which can contribute to the excess chlorine concentration.

Same with Vijayaraghavan, Ersu *et al.* (2004) also has study on latex wastewater using alternative treatment. However the difference is that Ersu *et al*. has used ultrafiltration process as the approach of treatment. Membrane filtration could become a method for separating useable product from latex wastewater and discharging negligible amount of effluent, hence latex processing becoming green process. Ersu et al. study the feasibility of flat-sheet cellulose material membrane to filter latex waste and to present the possibility of concentrating the wastewater and recycling permeate for reclaim in the manufacturing process or to safely discharge permeate into the ecosystem. The study by Ersu et al showed that it could concentrate latex wastewater from a Total Solid (TS) concentration of 3.8% to a TS concentration of 20% and could produced permeates that looked clear to the naked eye with turbidities ranging from 0.13 to 0.4 NTU. It is likely that latex wastewater can be concentrated and recycled while the permeate can be reused for rinsing purposes due to its relatively low TS concentration.

Long before Ersu *et al.* did their research on ultrafiltration on latex wastewater, Konieczny and Bodzek (1996) has done study on ultrafiltration on spent latex wastewater. The study was essentially not restricted to pollution control purposes only but also to recover the valuable by-products produced from the wastewater. From the study, they found that Polyacrylonitrile (PAN) and polysulfone (PSf) membranes are suitable for the UF of latex wastewaters containing styrene-methacrylane butadiene latex as it was the aim of of these investigations to determine the suitability of tubular polyacrylonitrile and polysulfone membranes for ultrafiltration of latex wastewaters.

2.2 Conventional Wastewater Treatment and Limitations

Industrial wastewater contains much higher concentration of pollutants even though it is lower in volume. High viscous liquids, oil and grease are common pollutant in industrial wastewater. Industries involved in the emission of oil and grease pollutant effluents are steel, aluminium, food, textile, leather, petrochemical, latex and metal finishing. The term of oil and grease are literally broad, it could include animal and vegetable source oils, fatty acids, petroleum hydrocarbons, surfactants, phenol-based compounds, naphthenic acids, etc.

Conventional water and wastewater treatment processes have been long established in removing many chemical and microbial contaminants of concern to public health and the environment. However, the effectiveness of these processes has become limited over the last two decades because of three new challenges. First, increased knowledge about the consequences from water pollution and secondly, the public desire for better quality water have promoted the implementation of much stricter regulations by expanding the scope of regulated contaminants and lowering their maximum contaminant levels.

General terms used to describe different degrees of treatment, in order of increasing treatment level, are preliminary, primary, secondary, and tertiary and/or advanced wastewater treatment. The conventional technologies in treatment of high viscous wastewater are:

- Physical Treatments (e.g. filtration, sedimentation, adsorption, and membrane etc)

- Chemical Treatment (e.g. neutralization, oxidation, reduction, catalytic oxidation, ion exchange etc).
- Biological Treatments (e.g. aerobic/ anaerobic digestion, plant absorption, bio-scrubbers, bio-filtration etc.).

2.2.1 Physical Treatment

Physical methods include processes where there are no gross chemical or biological changes are carried out and strictly physical phenomena are used to improve or treat the wastewater.

Examples would be coarse screening to remove larger entrained objects and sedimentation (or clarification). In the process of sedimentation, physical phenomena relating to the settling of solids by gravity are allowed to operate. Usually this consists of merely keeping wastewater for a short period of time in a tank under inert conditions, allowing the heavier solids to settle, and removing the "clarified" effluent. One of the most common physical treatment processes that are used to accomplish the treatment is sedimentation. Sedimentation for solids separation is a very common process operation and is routinely employed at the beginning and end of wastewater treatment operations. Another physical treatment process consists of aeration which is, physically adding air in order to provide oxygen to the wastewater. Still another physical occurrence used in wastewater treatment consists of filtration. The concept of filtration is that wastewater passes through a filter medium to separate solids. An example would be the use of sand filters to further remove entrained solids from a treated wastewater. Certain phenomena will occur during the sedimentation process and can be advantageously used to further improve water quality. Permitting greases or oils, for example, to float to the surface and skimming or physically removing them from the wastewaters is often carried out as part of the overall treatment process.

Physical methods for breaking emulsions include heating, centrifugation, precoat filtration, fibre beds, ultrafiltration and reverse osmosis, and electrochemical methods. Centrifugation is normally applied to oily sludge though it might be employed for small volumes of dilute oil waste in special cases. Precoat filtration and coalescers have also been successfully employed for breaking oil emulsions.

Gravitational sedimentation has a wide range of applications, such as the removal of solids from liquid sewage wastes, the settling of crystals from liquor, the separation of a liquid–liquid mixture in solvent extraction, the settling of solid food particles from a liquid food, and the settling of a slurry from a soybean leaching process. The dispersed phase can be solid particles or liquid drops, and the continuous phase can be a liquid or a gas at rest or in motion. The separation efficiency of gravitational sedimentation greatly depends on the size and density of the dispersed drops relative to those of the continuous phase (Eow et al., 2002).

2.2.2 Chemical Treatment

Chemical treatment consists of using some chemical reaction or reactions to improve the water quality. Probably the most commonly used chemical process is chlorination. Chlorine, a strong oxidizing chemical, is used to kill bacteria and to slow down the rate of decomposition of the wastewater. Bacterial kill is achieved when vital biological processes are affected by the chlorine. A chemical process commonly used in many industrial wastewater treatment operations is neutralization. Neutralization consists of the addition of acid or base to adjust pH levels back to neutrality. Since lime is a base it is sometimes used in the neutralization of acid wastes.

Coagulation consists of the addition of a chemical that, through a chemical reaction, forms an insoluble end product that serves to remove substances from the wastewater. Polyvalent metals are commonly used as coagulating chemicals in wastewater treatment and typical coagulants would include lime (that can also be used in neutralization), certain iron containing compounds (such as ferric chloride or ferric sulfate) and alum (aluminum sulfate).

The standard method for treatment of emulsified oily wastes is chemical de-emulsification followed by secondary clarification. The systems require the use of a variety of chemicals including sulphuric acid, iron and alumina sulphates and proprietary chemicals such as polymers, waste pickle acid, etc. The water phase from chemical treatment needs secondary purification to meet quality requirements for discharge systems. The equally difficult problems also concern the multi-component sludge from decanters. This is often burned with coal emitting an additional pollutant to the air. The competitive thermal process of oil removal requires large amounts of energy.

2.2.3 Biological Treatment

Effluents from the industrial sources satisfy high quality consent limits before being discharged to the environment. In order to meet the required limits, biological treatments are usually preferred since they are relatively inexpensive and simple to operate. Several new effective methods relating to the biological treatment have been recently developed to solve the problem of oily wastes. Biotechnology offers a new approach based on biodegradation and biotransformation of fats and oily wastes (Koltuniewicz and Field, 1996). Application of biological is mainly to eliminate other components that are dissolved in the water and tiny oil drops are harmful to the environment and difficult to treat. If the waste water is to be released as surface water, it must be treated to remove not only floating oil and SS, but also virtually all of the dissolved components that contribute to the high COD of the water.

Biological treatment is an effective and economical way that can be used in oil de-emulsification and waste water treatment. In application for waste water produced from oilfield, crude oil degrading microorganisms, namely bacteria, yeast and fungi, which can grow using crude oil as carbon source, have been reported as oil degraders. Biodegradation of crude oil by these indigenous microorganisms is one of the primary mechanisms by which petroleum and other hydrocarbons are eliminated from the environment.

The activated sludge (AS) system is one of the biological wastewater treatment process which the organic substances in the wastewater are digested by the aerotrope microorganism suspended in the aeration pond which was aerated by mechanical aerators or air diffuser. The well treated wastewater from aeration pond was flow to the sedimentation tank, clear water was overflow at the upper part of the tank and the concentrated microorganism at the bottom called sludge was return to the aeration pond in order to control the microorganism concentration in this pond at the designed value. The excess sludge was dried in the sand drying bed or further digested in a sludge digester.

2.2.4 Dissolved Air Flotation

Dissolved air flotation (DAF) uses air to increase the buoyancy of smaller oil droplets and enhance separation. Emulsified oil in the DAF influent is removed by de-emulsification with chemicals, thermal energy or both. DAF units typically employ chemicals to promote coagulation and increase floc size to facilitate separation (Cheryan and Rajagopalan, 1998). Dissolved air flotation is a process for removing suspended particles from liquid by bringing the particles to the surface of the liquid. Air is dissolved at high pressure in a saturator, and microbubbles are formed when water is released in the flotation cell at atmospheric pressure. The microbubbles become attached to the particles increasing their buoyancy and allowing them to rise to the surface (Al-Shamrani et al., 2002). The bubble formation process is a two step process, first nucleation and the growth. The first step commences spontaneously after the pressure reduction at the nozzle and the bubble nuclei are produced in the super-saturated water. After the excess air in the saturated water is transferred from the dissolved to the gas phase, the second step of bubble growth begins. During this step, the total air volume remains constant but bubbles grow due to coalescence and the decrease in the hydrostatic pressure as they rise through the flotation tank. Al-Shamrani et al. (2002) has done work to optimise the operation parameters to enhance the efficiency of DAF in separation of oil droplets from a synthetic wastewater and to improve the understanding of separation mechanism in terms of zeta potential measurements. In the study, the synthetic wastewater was prepared by stabilising oil droplets using a non-ionic surfactant and the aluminium sulphate and four different polyelectrolytes were used as destabilising agents.

2.2.5 Limitations of Conventional Treatments

Cheryan and Rajagopalan (1998) has listed the drawbacks of using traditional treatment towards oil in water separation. Gravity separation is the most common primary treatment of oily wastewater. If the resulting effluent does not meet required discharge limits, secondary treatment steps are used to lower the levels of dissolved emulsified and dispersed oils. Breaking of emulsions with chemicals, followed by DAF or sedimentation, is then used to remove additional oil. Chemical emulsion breaking is effective if properly applied, but it suffers from several shortcomings: such as conventional process is highly susceptible to changes in influent quality and requires customization at every site to determine the type and quantity of chemicals required. The conventional approach also requires close control and skilled operators to achieve optimal operation depending on the application, and the equipment has a large footprint area which eventually leads to the increasing of operating costs. The production of large volumes of sludge could not be avoided hence creating another problem to be solved.

2.3 Membranes Technology Overview

Membrane technology has become a dignified separation technology over the past decades. The main force of membrane technology is the fact that it works without the addition of chemicals, with a relatively low energy use and easy as well as well-arranged process conductions. Membrane technology is an emerging technology which can be used in most separation processes because of its multidisciplinary character (Caetano et al., 1995). There are numerous benefits when using membrane such as the systems are easy to operate and maintain since there are minimum moving parts involved in the operation, membrane properties are variable and can be adjusted, the compact design makes it easy for scale-up and less space consuming ; and no chemical additives are required for the operation.

Membrane technology is a generic term for a number of different, very characteristic separation processes. These processes are of the same kind, because in each of them a membrane is used. Membranes are used more and more often for the creation of process water from groundwater, surface water or wastewater. Membranes are now competitive for conventional techniques. The membrane separation process is based on the presence of semi permeable membranes. Currently, membrane application has broaden over various industries such as metal recovery, pollution control, food and biotechnology, leather and textile industries and many more. Waste treatment has been part of the application on membrane process since last three decades.

The principle is quite simple: the membrane acts as a very specific filter that will let water flow through, while it catches suspended solids and other substances. There are various methods to enable substances to penetrate the membrane. Examples of these methods are the applications of high pressure, the maintenance of a concentration gradient on both sides of the membrane and the introduction of an electric potential (Mulder, 1996).

Membranes act as a selective separation wall. Certain substances can pass through the membrane, while other substances are retained on its surface. Membrane filtration can be used as an alternative for flocculation, sediment purification techniques, adsorption (sand filters and active carbon filters, ion exchangers), extraction and distillation. There are two factors that determine the affectivity of a membrane filtration process; selectivity and productivity. Selectivity is expressed as a parameter called retention or separation factor (expressed by the unit $L/m^2 \cdot h$). Productivity is expressed as a parameter called flux (expressed by the unit $L/m^2 \cdot h$). Selectivity and productivity are membrane-dependent.

2.3.1 Membrane transport mechanism

The word membrane derives from a Latin word ‘membrana’ which means skin. Word ‘membrane’ today has been extended to describe a thin flexible sheet or film. This film acts as a selective boundary between two different phases because of its semi permeable properties. Membrane could be in a liquid or solid form which functions as a separation agent that is based on the difference of pressure, diffusivity coefficient, electric current or solubility. Membrane is defined as a barrier which