FABRICTION OF CHITOSAN MEMBRANE: THE EFFECTS OF DIFFERENT
POLYETHYLENE GLYCOL COMPOSITIONS ON MEMBRANE
PERFORMANCE IN OILY WASTEWATER TREATMENT

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I declare that this thesis entitled "Fabrication of Chitosan Membrane: The Effects of

Different Polyethylene Glycol Composition on Membrane Performance in Oily

Wastewater Treatment" is the results of my own research except as cited in the

references. The

thesis has not been accepted for any degree and is not concurrently submitted in

candidature

of any other degree.

Signature   :   ……………………………..
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Date   :   16 MAY 2008

DEDICATION

To my beloved dad, mom and brothers, respected lecturers and
lovely friends of chemical final year student.

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ABSTRACT

A membrane is a thin layer of material that is capable of separating materials as a function of their physical and chemical properties. It can be categorized by the driving forces employed which are microfiltration, ultrafiltration, nanofiltration and reverse osmosis. Ultrafiltration is chosen to do the treatment. Membrane technology has many advantages in treating wastewater such as simple efficient separating devices to restrain oil, grease, metal, BOD and COD. Besides this technology gain low energy cost and provide clear permeate which can be re-used. By considering public health and environmental awareness, biopolymer will be focus. Chitosan is chosen as it is a basic commercialized biopolymer that is prevailingly neutral or acidic. As in membrane separation process it occur fouling problem due to it retentate that attached to the membrane surface. For that chitosan will be crosslink with other polymer which is polyethylene glycol (PEG). PEG is good water permeability and chemically stabilizes to be applying as a membrane coating. Thus improve anti-fouling properties. The performance of this chitosan membrane in oily wastewater treatment is studied by varying different composition of PEG. The membrane morphology is obtained by scanning electron microscopy (SEM). The analysis is done by swelling the membrane in oily wastewater. From the analysis the result is get by seeing the percentage of oil that can be absorbed by the membrane of sample X, sample 1, sample 2 and sample 3. As the result sample 3 which consist with 3.6 gram of PEG is the best membrane. As the conclusion, PEG enhanced the performance of Chitosan membrane.

ABSTRAK

Membran adalah satu lapisan nipis suatu bahan yang berupaya untuk memisahkan dua komponen berbeza berdasarkan sifat fizikal dan kimia komponen tersebut. Ianya boleh dikategori berdasarkan daya penggerak yang dikenakan ke atas membran. Sebahagian daripada kategori itu adalah penurasan mikro, penurasan ultra, penurasan nano dan osmosis berbalik. Penurasan ultra dipilih untuk proses rawatan ini. Teknologi membran mempunyai banyak kelebihan dalam merawat air kumbahan seperti alatan pemisahan yang efisyen dan ringkas untuk mengawal minyak, pelincir, logam, *BOD* dan *COD*. Selain itu teknologi ini memiliki kos tenaga yang rendah dan menghasilkan air jernih yang boleh diguna semula. Dengan mempertimbangkan kesihatan umum dan kesedaran alam sekitar, biopolimer digunakan. Chitosan dipilih kerana ia adalah biopolimer asas yang wujud sebagai neutral atau berasid. Dalam proses ini akan berlakunya penyumbatan oleh baki yang melekat pada permukaan membran. Oleh itu, chitosan akan digabungkan dengan polyethylene glycol (PEG). PEG mempunyai sifat yang baik terhadap air dan stabil secara kimia sebagai penyadur membran. Ini mempertingkatkan lagi sifat antipenyumbatan. Performasi membran chitosan ini dikaji berdasarkan komposisi polyethylene glycol yang berbeza-beza. Morfologi membran diperiksa menggunakan mikroskop imbasan elektron. Analisa dilakukan dengan menenggelamkan membran di dalam air sisa berminyak. Peratusan minyak yang diserap oleh membran dikaji melalui sampel X,sampel 1, sampel 2 dan sampel3. Daripada keputusan ujikaji, sampel 3 yang mengandungi 3.6 gram PEG adalah membran yang terbaik. Kesimpulannya, kehadiran PEG menambahbaik kualiti membran chitosan.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

Ws   -   Initial weight of membrane at dry condition

Wd   -   weight of membrane at wet condition at different swelling
                       time

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1   Overview

Many methods had been use to treat wastewater such as centrifuge, rotary drum vacuum filter, dissolved air flotation (DAF), slope plate clarifiers, biological treatment, evaporators, gravity separating devices and membrane technology. Centrifuge method uses large horsepower and it is effective at removing suspended solid but not for dissolved solids and heavy metal in solution. Besides overflow from centrifuge need to be treat again. For Rotary Drum Vacuum Filter, it is quite effective at removing large solids. It also needs large space to set up and it increase the capital cost. Dissolved Air Flotation (DAF) method needed large tank due to its residence time required. This cause operating cost becomes large. Slope Plate Clarifiers method is easy and cheap to use but it cannot remove colloidal materials with small mass and dissolved constituents. Using Biological Treatment requires a very skilled operator to operate it. Furthermore it can use large space to set up due to residence time for the bacteria to digest the waste. Evaporator method has very high capital costs and need lot of energy to operate. As for that, membrane technology has been chosen for it advantages of being simple efficient separating devices to restrain oil, grease, metals, BOD and COD. It also can take place while temperatures are low. This is mainly important because it enables the treatment of heat-Sensitive matter. This process also acquires low energy cost. This method provide clear permeate which can be re-used (Christie, 2003).

Membrane is simply a synthetic barrier to filter some components based on various characteristics. It can be perform in liquid, solid, homogenous or heterogeneous and can be range in thickness. Because of its multiple uses and characteristics, membrane filtration can be divided to microfiltration, ultrafiltration, nanofiltration and reverse osmosis. In this experiment, ultrafiltration had been chosen as it mostly use in wastewater treatment, protein concentration, colloidal silica concentration and for the treatment of various wastewaters in the pulp and paper industry. 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, $l/m^2 \cdot h$. Productivity is expressed as a parameter called flux, $l/m^2 \cdot h$ (http://www.lenntech.com/membrane-technology.htm).

Synthetic membranes can be divided into organic (polymeric or liquid) and inorganic (ceramic, metal) membranes. In this experiment, polymeric membrane has been chosen. Polymeric membranes were classified into two main groups according to its morphology, asymmetric and symmetric types. Asymmetric membrane has more advantages compared to symmetric due to it high selectivity of a dense membrane with high permeation rate of a very thin membrane.

From Krajewska (2005), by considering the increases of public health and environmental awareness together with increases of stricter environmental regulations on disposal, biopolymer from renewable resources had been focus as an alternative to synthetic polymer. One of it is chitosan which is produced commercially by deacetylation of chitin, which is the structural element in the exoskeleton of crustaceans such as crabs and shrimp. It is cheap and easily gets from of shellfish, the wastes of the seafood industry. Besides that it is biocompatibility, biodegradability, nontoxicity, antimicrobial properties, heavy metal ions chelation, gel forming properties, ease of chemical modification, and high affinity to proteins.

However, the largest barrier to the widespread use of water purification membranes is fouling. They are the deposition of matter in a membrane's pores, internal fouling or on its surface, external fouling that leads to a change in a

membrane's flux characteristics, such as throughput and selectivity. Therefore, coating a thin, defect-free hydrophilic polymer on the surface of a porous membrane (which is usually made of a hydrophobic polymer) may provide the most effective way to eliminate internal membrane fouling while greatly reducing external fouling. Reported that the synthesis of a series of novel hydrophilic coating materials prepared by crosslinking chitosan with a bifunctional poly(ethylene glycol) macromer have been found to be satisfactory for application as a potential membrane coating for its water permeability and chemical stability. Furthermore, the molecular weight cutoff (MWCO) using polyethylene glycol feed solutions was found to be as low as 720 for these polymers, and generally varied inversely to the film's water permeability. The low MWCO indicates that high rejection can be expected for most organic contaminants, including emulsified oil droplets and most proteins. These composite membranes exhibited water flux values more than three times higher than uncoated membranes after one day of oily-water crossflow filtration, indicating that the hydrophilic polymer coating can significantly enhance anti-fouling properties (http://aiche.confex.com/aiche/2007/preliminaryprogram/abstract_88422.htm).

1.2   Problem statement

Oil or water separation covers a broad range of industrial process operations. There are many techniques employed depending on the situation. There are evaporator, centrifuge, dissolved air floatation, vacuum drum filter, biological, clarifier and membrane. Oil is not soluble in water but it can exist evenly dispersed as globules in water. The concentration of these globules is a function of mixing or stirring. If allowed to stand the emulsion will separate because oil is lighter than water, although, some amount of oil globules will remain in the water. Interesting fact is emulsion can exist two ways. If the concentration of oil is less than 50%, the water will be the suspension fluid and the oil will be the globule. A phase transition occurs if the oil content is more than 50%. When this happens, the oil is the suspension fluid and the water forms globules. Thus, in view of growing public health and environmental awareness accompanied by an increasing number of ever stricter environmental regulations on discharged wastes, oily wastewater treatment

need another alternative method that could achieve a more environmental friendly system and cheaper to be operate. As for membrane technology is suitable for this treatment where it does not require any chemical or biological processes. Chitosan is chosen for the material of the membrane and is crosslink with polyethylene glycol (PEG). The performance of this membrane is examined by ranging the composition of PEG.

1.3   Objective

The objective of this experiment is to fabricate a chitosan membrane and to study the effects of different polyethylene glycol compositions on membrane performance in oily wastewater treatment.

1.4   Scope of study

The scope of study is identified as follows:-

1. To fabricate a chitosan membrane with different poly(ethylene glycol) compositions;

2. To study the effects of different poly(ethylene glycol) composition on membrane performance in oily wastewater treatment;

3. To analyze and compare the performance fabricated membrane

CHAPTER 2

LITERATURE REVIEW

2.1 Membrane Definition

Membrane, comes from Latin word, meaning skin, is regarded generally and macroscopically as a selective barrier between two phases. The membrane is an interphase between the two bulk phases, either a homogeneous phase or a heterogeneous collection of phases (Sakai, 1994). The principle of membrane operation is shown in Figure 2.1

Phase 1   Membrane   Phase 2

Feed

Permeate

Macromolecule

Micromolecule

Driving Force

$\Delta C, \Delta P, \Delta T, \Delta E$
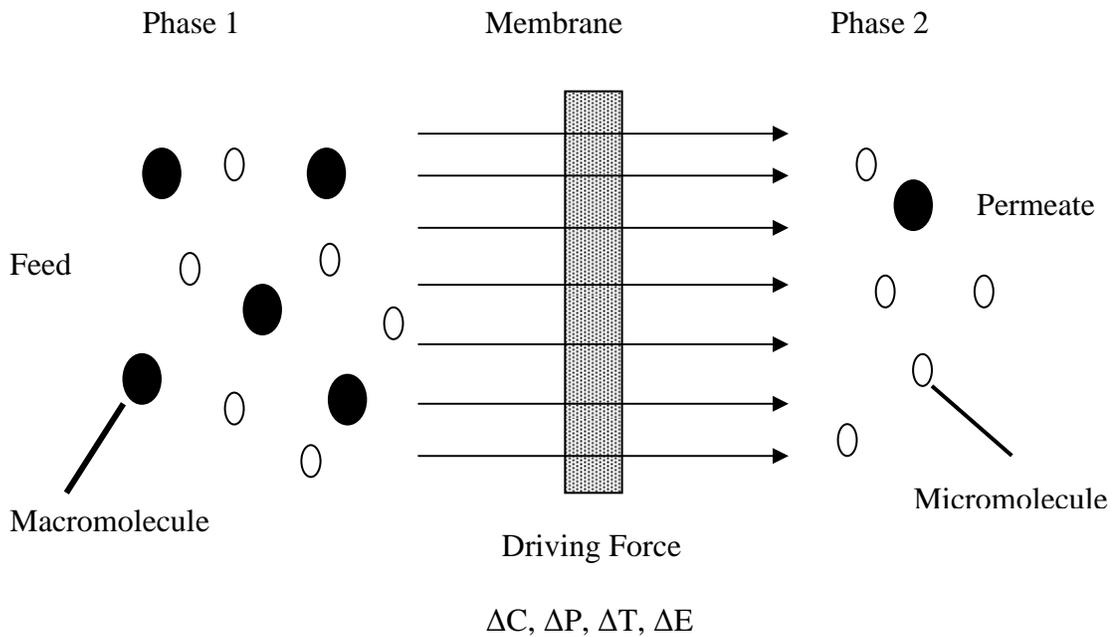
Figure 2.1: Principle of membrane operation (Richard, 2004)

A membrane process can be defined as a process where a feed stream is divided into two stream which are a permeate containing material which has passed through the membrane and retentate containing the nonpermeating species (Mallevialle, 1996).

Membrane process can be used to concentrate or to purify a solution or particle separation and to fractionate a mixture. Membrane separation gives basic advantages such as the separation process takes place at ambient temperature without phase change, which gives an energetic advantage compared to distillation. It also takes place without accumulation of products inside the membrane where the membranes are well adapted to be run continuously without any elution cycle as in chromatography. Besides the separation does not need any addition of chemical additives such as in water clarification by settlement or conventional filtration. This makes the quality of the product less pollutant waste.

Membranes can selectively separate components over a wide range of particle sizes and molecular weights, from macromolecular materials such as starch and protein to monovalents ions. Membrane separation processes can be classified into the following groups according to the driving force that causes the flow of the permeate through the membrane shown in Table 2.1.

Synthetic membrane can be divided into organic (polymeric) and inorganic (ceramic and metal) membranes. Organic membranes can be categorized into two main groups which are asymmetric and symmetric types. Symmetric membrane can be find either with porous or non porous having a thickness range of (10-200) µm. Decreases in membrane thickness will increases its permeation rate while the diameter of pores is almost constant. As for asymmetric membrane it consists of a very dense top layer of skin with a thickness of 0.1 to 0.5 µm. It is support by a porous sub layer with a thickness of 50 to 150 µm.

Table 2.1: Classification of membrane processes (Matsuura, 1994)

Type of driving force	Classification of the process
a) Pressure	i) Reverse Osmosis
	ii) Ultrafiltration
	iii) Microfiltration
	iv) Membrane gas and vapor separation
	v) Pervaporation
b) Temperature	i) Membrane distilation
c) Concentration	i) Dialysis
	ii) Membrane extraction
d) Electric potential	i) Electrodialysis

Asymmetric membrane has high selectivity of a dense membrane with the high permeation rate of a very thin membrane. The bottom layer will provide high mechanical strength (Dorgan, 1992). Figure 2.2 shows membrane structure for symmetric and asymmetric membrane.
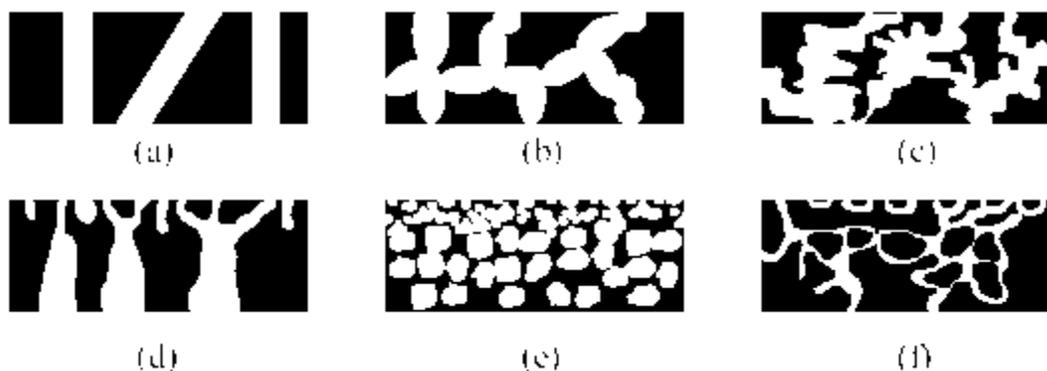
Figure 2.2: Membrane structure for symmetric membrane: a) straight pores b) foam like
c) coral like (tortuous); asymmetric membrane d) finger-like substructure
e) foam like substructure f) sintered ceramic spheres substructure.
(Scott, 1998)

## 2.2	Membrane Filtration Systems

### 2.2.1	Dead-end Filtration

In this system, all the water that enters the membrane surface is pressed through the membrane. Some component that can go through the membrane is depend on it pore size. This can cause the water hardly move through the membrane and resulting in decreasing of flux. If the flux becomes low, the membrane needs to be clean. Energy loss is less than cross-flow filtration because all energy enters the water actually passed the membrane. Dead-end filtration system is shown in Figure 2.3.

The pressure that is needed to press water through a membrane is called Trans Membrane Pressure (TMP). TMP is defined as the pressure gradient of the membrane, or the average feed pressure minus the permeate pressure. The feed pressure is often measured at the initial point of a membrane module. However, this pressure does not equal the average feed pressure, because the flow through a membrane will cause hydraulic pressure losses
(http://www.lenntech.com/membrane-systems-management.htm).

As for it cleaning process, the components are removed hydraulically, chemically or physically. After cleaning process, the membrane temporarily out of order and this system is a discontinuous process. Practically one will try to achieve the highest filtration time and lowest cleaning time. It does not have a continuous production of water if the membrane is clean with permeated and the production is low. The factor that indicates the amount of production is called recovery.
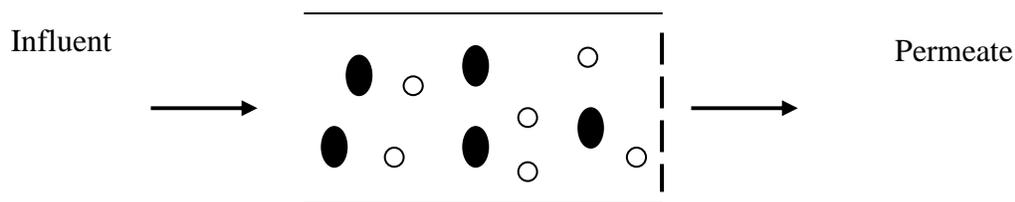
Figure 2.3: Dead-end Filtration (http://www.lenntech.com/membrane-systems-management.htm)

2.2.2 Cross-flow Filtration

In this system the feed water is recycled. During recirculation the feed water flow is parallel to the membrane. Only little of the feed water is used for permeate while the other will leave the module. Figure 2.4 shows the cross-flow filtration system. Cross-flow filtration has a high energy cost. Speed of the feed water is relatively high. The purpose of this flow is the control of the thickness of the cake. Consequentially to the flow speed of the water, flowing forces are high, which enables the suspended solids to be carried away in the water flow. This system can achieve stable fluxes but cleaning process is still needed from time to time. The cleaning process is done by using backward flushing or chemical cleaning. This system is applied for Reverse Osmosis, nanofiltration, ultrafiltration and microfiltration, depending on the pore size of the membrane (http://www.lenntech.com/membrane-systems-management.htm).
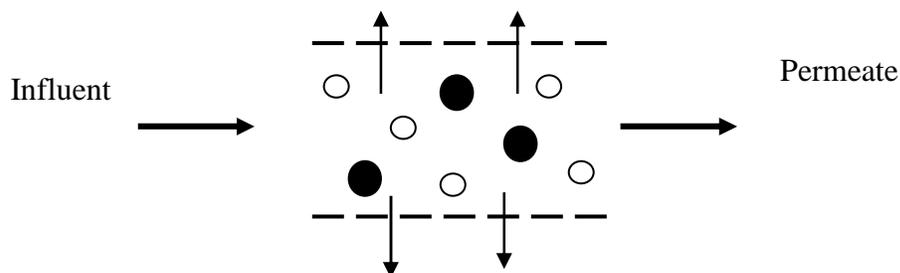
Figure 2.4: Cross-flow Filtration
(http://www.lenntech.com/membrane-systems-management.htm)

2.3   Membrane Processes

The membrane is the important element of every membrane separation process. It can be considered as a perm selective barrier of interface between two phases. Separation happens due to the ability of membrane to transfer one or more selected component from the feed mixture to permeate. These membrane processes developed separately and practiced in different industrial field. It also still in research to develop new ideas as to accomplish the recent needs. Only microfiltration, ultrafiltration, nanofiltration and reverse osmosis will be brief here.

2.3.1   Microfiltration (MF)

Microfiltration is a pressure-driven process that separates micron-size or sub-micron particles from the liquid or gaseous feed stream by a membrane. It have pore sizes in the range 0.1 – 10 µm and thus are usually used to retain bacteria (the purpose for which they were originally developed), biological cell fragments, colloidal materials and other particles in the micron range. The relatively large pore sizes that characterize microfiltration processes result in very high pure water fluxes up to 5×10^5 L/m^{3}h at relatively low operation pressures, typically less than 2 atm (Setford, 1995).

In industry MF is usually carried as a multistage (stages-in-series) operation in a feed-and-bleed mode of system.

2.3.2   Ultrafiltration (UF)

Ultrafiltration is a membrane separation process used to remove, concentrate, fractionate or recover macromolecules such as protein from feed solutions.   UF membrane pore diameters are in the range 10^{-3} – 10 µm.   Ultrafiltration is a pressure driven process, which freely permeable to the solvent but impermeable to the solutes to be concentrated.   The solvent molecules flow through the pores of the membrane and can be collected on the downstream side of the system.   In addition, to the concentration of macromolecular solutions, ultrafiltration processes are also used to remove low molecular weight materials from solutions, such as in the desalting of macromolecular solutions.   UF membranes are also used to fractionate different sized molecular species, by virtue of the fact that these membranes have very well defined pore diameter distributions.   UF membranes are available in a variety of configurations, the operating pressures of 2 to 10 atm are usual and its water fluxes vary widely, but can be as high as 5000 L/m^{3}h in some systems (Setford, 1995).

Ultrafiltration is used to concentrate oily wastes which including oil emulsions. The permeate can be reused and the concentrate can be incinerated without the need for supplementary fuel (Eykamp, 1975).   Feed concentrations of 1 to 5 percent oil have been successfully concentrated to 30 percent.   Permeate fluxes of 60 to 120 L/m2h are obtainable with permeate qualities of 30 to 400 mg/L of oil.   By comparison, 97 percent reduction of emulsified oil is achievable only after treatments of API separation, chemical coagulation, activated sludge, filtration, and carbon adsorption (Groves, 1976).

2.3.3   Nanofiltration (NF)

The nanofiltration membrane displays excellent rejection of divalent ions while allowing a majority of monovalent ions to pass. Organic molecules in the 200-300 Dalton molecular weight ranges are also highly rejected. The unique separation capability of NF provides the opportunity to selectively concentrate both valuable or undesirable substance from a process stream with greater effectiveness, consistency, reliability and economy (Setford, 1995).

2.3.4   Reverse Osmosis (RO)

Reverse osmosis membranes are extensively used to remove very low molecular weight solutes and ions from feed streams. The classic use of RO is in the "desalination" of sea and brackish water to yield concentrated salt solutions and drinking water. RO membrane pore diameters are typically in the range from 5×10^{-4} to 5×10^{-2} μm. Generally, the osmotic pressure of a feed solution is high and therefore, the pressure that is applied must overcome the osmotic pressure and create a sufficient driving force that ensure high solvent flow rates across the membrane. As a result, the essential property of any RO membrane is mechanical strength (Setford, 1995).

Basically for preparation of reverse osmosis membranes, Polymeric materials such as cellulose acetate and aromatic polyamide are use. High pressures of about (35-100) atm are required in order to overcome the high osmotic pressures across the membrane. Figure 2.6 shows some overview of membrane separation technology.

Size, particle diameter	1Å	10Å 0.001 μm	100Å 0.01 μm	0.1 μm	1μm
Low molecular materials	H2,O2,N2, H2O,Cl,OH N,Na	Sucrose, Egg, Albumin	Various viruses	Colloidal silica, oil emulsion	Colibacillus staphylococcus
Membrane separation method	<td colspan="5">Gas & vapor separation · Microfiltration · Ultrafiltration · PV separation · Nanofiltration · Dialysis · Electrodialysis · Reverse Osmosis</td>
Structure of separation membrane	<td colspan="5">Non-porous membrane · Nano-porous membrane · Micro-porous membrane</td>
Main applications	N2,H2, separation, organic/water separation,	Blood osmosis, Blood filtration, Water desalination and purification	Sterilization, Clarification,Waste water treatment		

Figure 2.6: An overview of membrane separation technology (Scott, 1998)

2.4   Biopolymer Membranes in Wastewater Treatment

In view of rising public health and environmental awareness accompanied by an increasing number of ever stricter environmental regulations on discharged wastes, consideration has been focused on the use of biopolymers from renewable resources as alternatives to synthetic polymers. Biopolymers are compounds that are produced in nature by living organisms and plants, participate in the natural biocycle and are eventually degraded and reabsorbed in nature.

The most widespread biopolymers are polysaccharides, cellulose, starch, chitin and lignin, whose swellability in water and viscous solution/gel-forming properties are utilized to manufacture a number of industrial and consumer products. Among the commercially available polysaccharides that are prevailingly neutral or acidic, chitin and its primary derivative chitosan are special in that they are basic. Figure 2.7 shows the structures of chitin and chitosan (Krajewska, 2005).
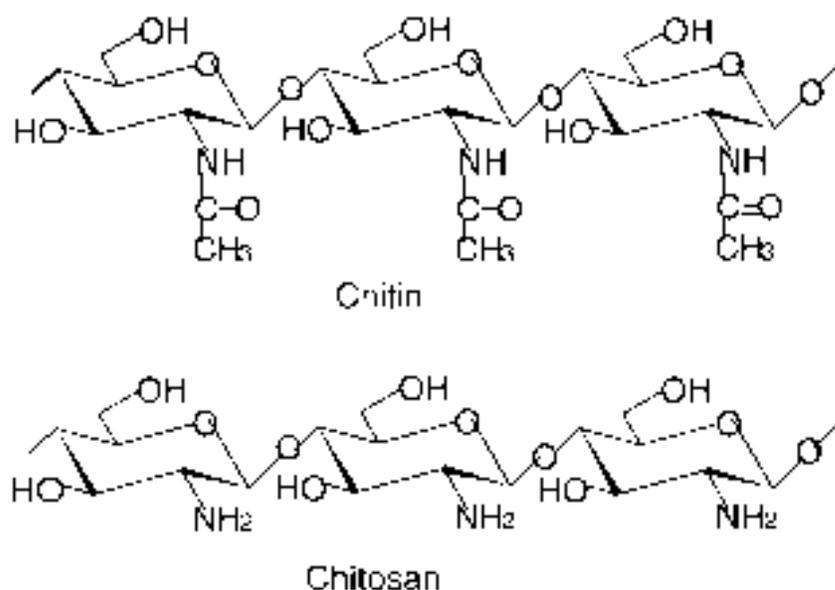
Figure 2.7: Structures of Chitin and Chitosan (Krajewska, 2005)

2.4.1   Characteristic of Chitosan

Chitosan is biopolymer from renewable resources, obtainable from shells of shellfish, the wastes of the seafood industry.   Chitosan is a linear polysaccharide composed of randomly distributed ß-(1-4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit) (Krajewska, 2005).

Chitosan is produced commercially by deacetylation of chitin, which is the structural element in the exoskeleton of crustaceans (crabs, shrimp, etc.).   The degree of deacetylation (%DA) can be determined by NMR spectroscopy, and the %DA in commercial chitosans is in the range 60-100 %.   To afford chitosan, the obtained chitin is subjected to N-deacetylation by treatment with a 40–45% NaOH solution, followed by purification procedures.   Depending on the origin and manufacture process the obtained products may vary in composition and properties (Krajewska, 2005).

The amino group in chitosan has a pKa value of ~6.5, thus, chitosan is positively charged and soluble in acidic to neutral solution with a charge density dependent on pH and the %DA-value.   In other words, chitosan is bioadhesive and readily binds to negatively charged surfaces such as mucosal membranes.   Chitosan enhances the transport of polar drugs across epithelial surfaces, and is biocompatible and biodegradable.

2.5   Overview of Polyethylene Glycol (PEG)

Polyethylene glycol (PEG) and polyethylene oxide (PEO) are polymers composed of repeating subunits of identical structure, called monomers, and are the most commercially important polyethers.   Poly (ethylene glycol) or poly (ethylene oxide) refers to an oligomer or polymer of ethylene oxide.   The two names are

chemically synonymous, but historically PEG has tended to refer to shorter polymers, PEO to longer (Neto *et al*, 2005).

PEG and PEO are liquids or low-melting solids, depending on their molecular weights. Both are prepared by polymerization of ethylene oxide. While PEG and PEO with different molecular weights find use in different applications and have different physical properties such as viscosity due to chain length effects, their chemical properties are nearly identical. Derivatives of PEG and PEO are in common use, the most common derivative being the methyl ether (methoxypoly (ethylene glycol)), abbreviated mPEG. Their melting points vary depending on the Formula Weight of the polymer. PEG or PEO has the following structure:

$$HO\text{-}(CH_2\text{-}CH_2\text{-}O)_n\text{-}H$$
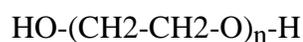
The numbers that are often included in the names of PEGs and PEOs indicate their average molecular weights. Example a PEG with n=80 would have an average molecular weight of approximately 3500 daltons and would be labeled PEG 3500. Most PEGs and PEOs include molecules with a distribution of molecular weights, i.e. they are polydisperse. The size distribution can be characterized statistically by its weight average molecular weight (Mw) and its number average molecular weight (Mn), the ratio of which is called the polydispersity index (Mw/Mn). Mw and Mn can be measured by mass spectroscopy. PEGylation is the act of covalently coupling a PEG structure to another larger molecule, for example, a therapeutic protein (which is then referred to as PEGylated). PEGylated interferon alfa-2a or -2b is a commonly used injectable treatment for Hepatitis C infection. PEG is soluble in water, methanol, benzene, dichloromethane and is insoluble in diethyl ether and hexane. It is coupled to hydrophobic molecules to produce non-ionic surfactants (http://en.wikipedia.org/wiki/polyethylene_glycol).

CHAPTER 3

METHODOLOGY

3.1   Material Use

The materials used in this research are as follow:

     1. Chitosan

     2. Polyethylene glycol

     3. Acetic acid

3.2   Membrane Preparation

Figure 3.1 shows the overall procedure to prepare the membrane. The whole procedure divided into three parts. Firstly, preparation of dope solution is the method to have the solution to be cast then. Then, membrane casting is the method to have the flat sheet membrane that will be use for testing method. Lastly, membrane testing method is where the membrane sheet will be use in Swelling Test and Scanning Electron Microscopy (SEM) Test.
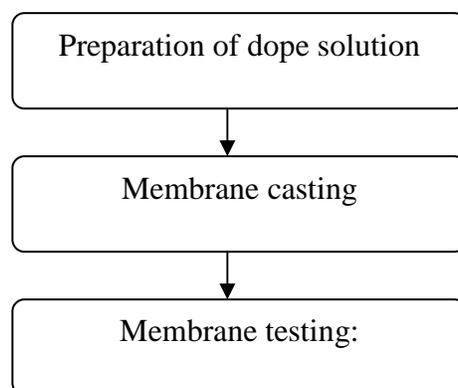
Figure 3.1: Flow chart for membrane preparation procedure

3.3   Preparation of Dope Solution

Acetic acid is poured in first, follows by chitosan. (Refer figure 3.1). The dope solution is heated to approximately $70^{o}C$. The chitosan in powder form is poured in bit by bit, to ensure that it is dissolved properly. During the whole process, the dope solution is stirred. From time to time, the PEG and distilled water is added slowly into the dope solution to avoid any agglomeration. When the entire polymer is completely dissolved, it is indicated by the clear solution appearance. It is cooled and poured into a storage bottle. Subsequently, the solution is degassed for about two hours and is kept away from sunlight to slow down its aging process. Table 3.1 shows the formation for dope solution preparation.

Table 3.1: Formation of dope solution preparation

| Sample	Chitosan, gram	Water, gram	Acetic Acid, gram	Polyethylene Glycol, gram
X	3	35	80	-
1	3	35	80	13.3
2	3	35	80	5.7
3	3	35	80	3.6
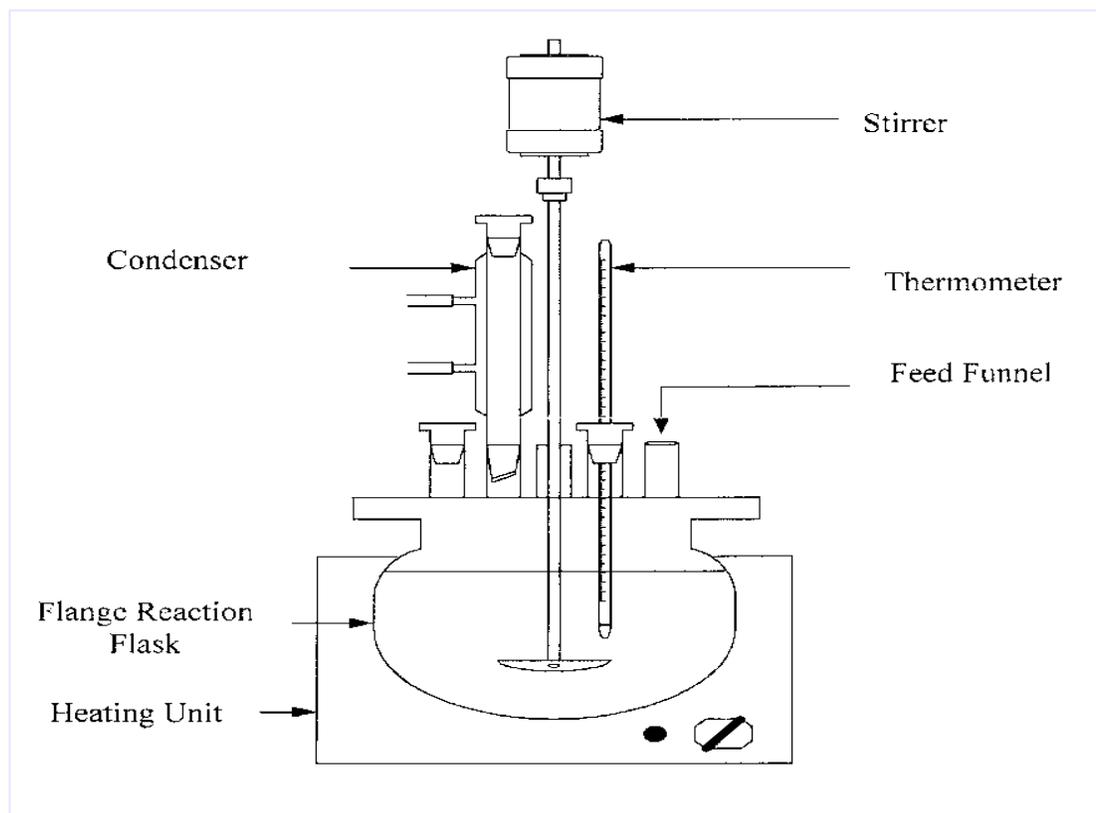
Figure 3.2: Schematic representation of a reaction vessel (Ani, 2001)

3.4   Membrane Casting

The membrane is casted using a casting knife on a glass plate. Figure 3.3 below shows the conventional method using casting knife for flat sheet membrane casting, which is similar in concept to the casting machine. Firstly, A suitable amount of the solution is poured onto the center well of the casting blade, which is placed on the glass plane. Then, the flat sheet membrane is formed with the entire membrane thickness of 200 µm. Next, the membrane is let to be evaporated in the air for couple of days before it is immersed into a water bath to complete the phase separation. The membrane is then transferred to another container containing Sodium Hydroxide (NaOH) for post-treatment to remove the excess acetic acid from the membrane. Eventually, the

membrane was transferred to another container containing distillated water until it was used for experimental testing.
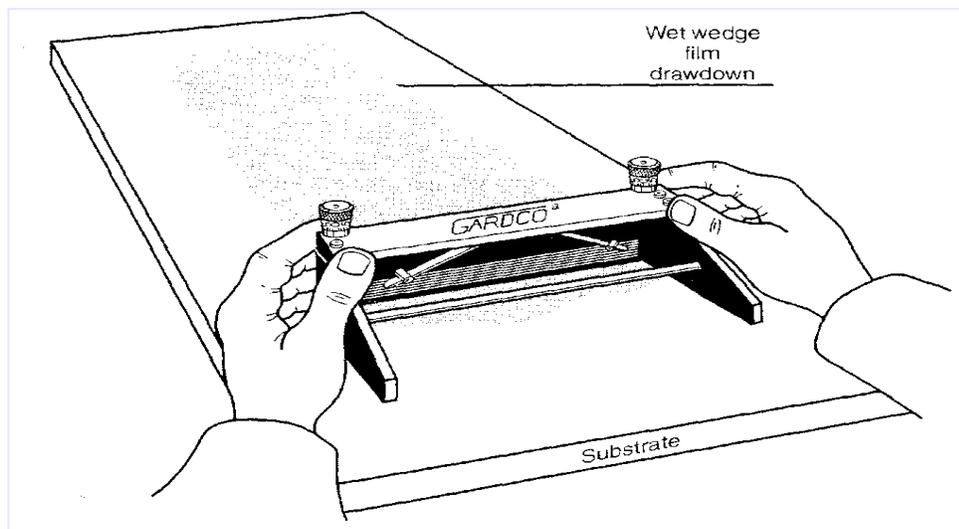
Figure 3.3: Casting flat sheet membrane using casting knife (Ani, 2001)

3.5   Membrane Testing

3.5.1   Scanning Electron Microscopy (SEM) Test

The membranes will be snap under liquid nitrogen, which gave a generally consistent and clean break. The membrane is then sputter coated with thin film of gold. The membrane will be mounting on a brass plate using double sided adhesion tapes in a lateral position. The cross section of the chitosan membranes were being viewed with SEM to characterize the membranes fabricated. Figure 3.4 shows the Scanning Electron Microscopy (SEM) equipment.

Figure 3.4: Scanning Electron Microscopy (SEM)

3.5.2   Swelling Test

The swelling properties (SR) of samples were studied by immersing the membranes in a solution and at different periods of time at room temperature. The membranes were cut into small part. At predetermined time intervals, the disks were taken out from the solution, gently wiped with filter paper to remove the surface solution weighed and returned to the same container until equilibrium.

The swelling ratios (SR) of these samples were calculated by using the Eq. (3.1)

Swelling ratio, %=[(Ws–Wd)/Wd]* 100   (3.1)

where Ws is the weight of swollen membrane and Wd is the weight of dry membrane at different swelling time.

CHAPTER 4

RESULTS AND DISCUSSION

4.1   Introduction

Polyethylene glycol (PEG) had been chosen as the copolymer that wants to add to chitosan. The purpose is to see the performance of the chitosan membrane by adding PEG in different compositions. PEG been chosen because of its water permeability and chemical stability was satisfied for application as a potential membrane coating. This hydrophilic polymer coating also can significantly enhance anti-fouling properties. Table 4.1 shows the properties of fabricated membranes while Figure 4.1 shows some of the membrane sheets that have been made.

**Table 4.1:** Properties of fabricated membranes

| Sample	Weight,g	Diameter,cm
X	0.1753	7
1	0.1954	7
2	0.1535	7
3	0.1377	7

Figure 4.1: Membrane sheets

4.2 Scannning Electron Microscopy (SEM) Test

In this test only 2 membrane sheets that had been done which are sample 3 and sample X. Sample 1 and sample 2 cannot be done because it is less thick for the SEM machine to detect the morphology of the membrane. Figure 4.2 shows the cross section image of sample X while Figure 4.3 shows the cross section image of sample 3. SEM image for X seems do not have any pores or only slightly. This is because there is no PEG added in its dope solution preparation. The absence of PEG in the membrane promotes a dense spongy non-void structure. Seong *et al.* (2004) also showed that the absence of hydrophilic agents in certain polymer/solvent system would give similar structure and result. Shieh *et. al* (2001) state that PEG is known as pore forming agent. From sample 3, it shows that there is some pores exist but it appearance is not good enough. Composition of acid is too many than water composition as that may made the pore structure is uneven. As stated by Torrestiana *et. al* (1999) and Sang *et. al* (2005), by adding water which is as hydrophilic non solvent in the casting solution enhance the solute permeability of the membrane which it increase the skin porosity thus allow the solute to pass through the membrane easily. Water did not affect the water clearance but it effect the morphology of the membrane produced.
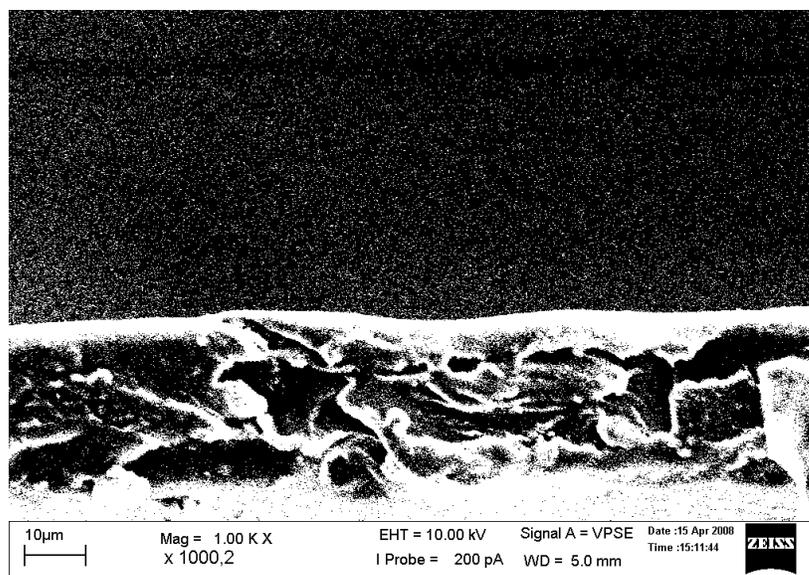
Figure 4.2: Cross section image of sample X
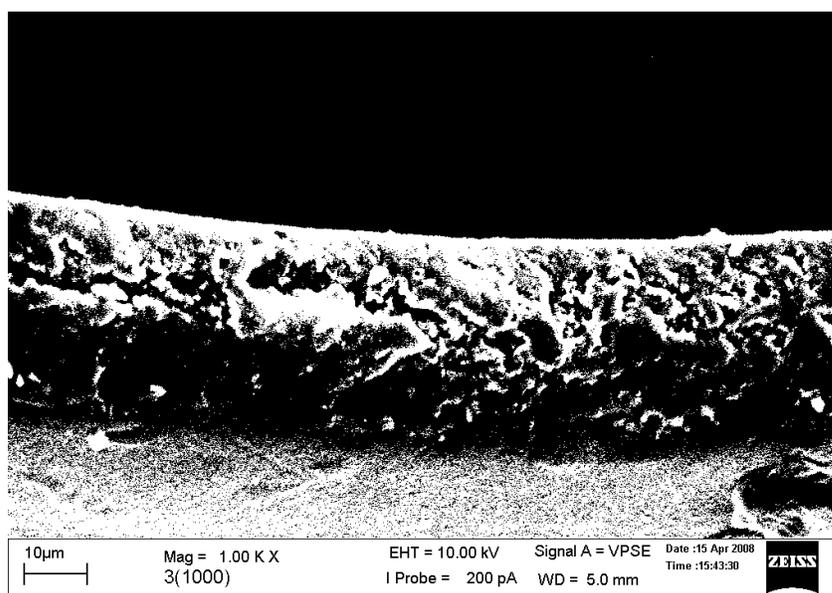
Figure 4.3: Cross section image of sample 3
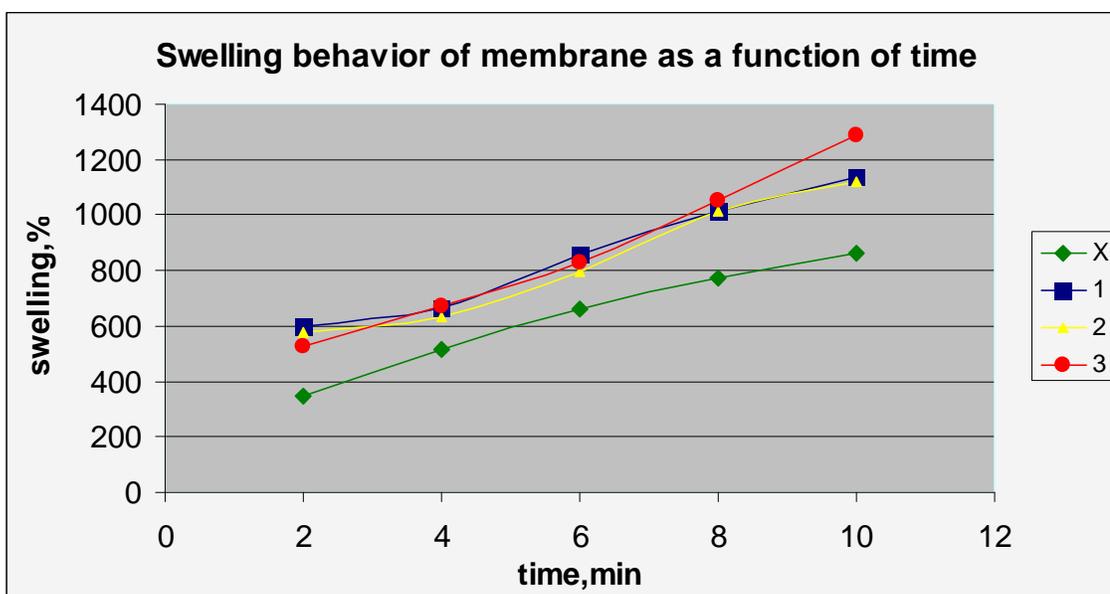
4.3   Swelling Test

Table 4.2 show the degree of swelling on each membrane. From the table, as the time increases the swelling percentage also increases. The lowest degree of swelling is for sample X which does not contain any PEG for the control. This shows that although only a small of PEG amounts is required, its absence will give a negative impact, which reduces the performance of the membrane. This result showed that additional of hydrophilic agent in the dope formulation improves the membrane performance and this seems to be in agreement with many authors (Hayama *et al.,* 2004; Kim and Lee, 2004; Seong *et al.*, 2004). The highest degree of swelling is for sample 3 which contain 3.6 gram of PEG. Too high amount of additives produced high viscosity dope solutions, which is difficult to cast. Han and Nam (2002) also revealed that the viscosity of dope solution would significantly increase when the amount of additives added beyond 10 %wt and the flux decreased drastically. This state is adjacent to the results for sample 1 and sample 2 where both results start increase rapidly then suddenly it slow down nearly to be constant.

Table 4.2: Degree of swelling on each membrane

| Sample	Time,min				
	2	4	6	8	10
	Swelling %				
X	350	512.5	659.4	773.3	861.3
1	600	667.6	857	1012.7	1137.7
2	576.5	634.8	797.3	1012	1119.8
3	525	674.3	830.6	1054.5	1285.5

Figure 4.4 show that PEG gives the significant effect to the membrane performance. Graph for sample X shows that within every two minutes the increases of it become slow down. As for graph sample 1 and sample 2 it increases for a while then decrease back. For sample 1 which contains 13.3 gram of PEG start to slow at sixth

minute. For sample 2 which contains 5.7 gram of PEG start to slow at eighth minute. As for sample 3 the graph shows that it is still increase even until tenth minute. Membranes which contain high amounts of PEG, seem to generate fine nanopores which do not seem to encourage wastewater clearance. The results seem to be in agreement with Kessler and Klein (1992), who revealed that higher amount of PEG, which contain more than 10 %wt PEG, reduced or readjust the dissolving power of the solvent for the polymer and induces the formation of numerous porous polymer network entities with a finite size.

Figure 4.4: Swelling percentage of membrane as a function of time

Final results for swelling test are concluding in Figure 4.5 where it shows the performance of the membranes in oil swelling. The lowest performance is sample X with value of 861. 3% degree of swelling. The highest performance is sample 3 with value of 1285.5 % degree of swelling.
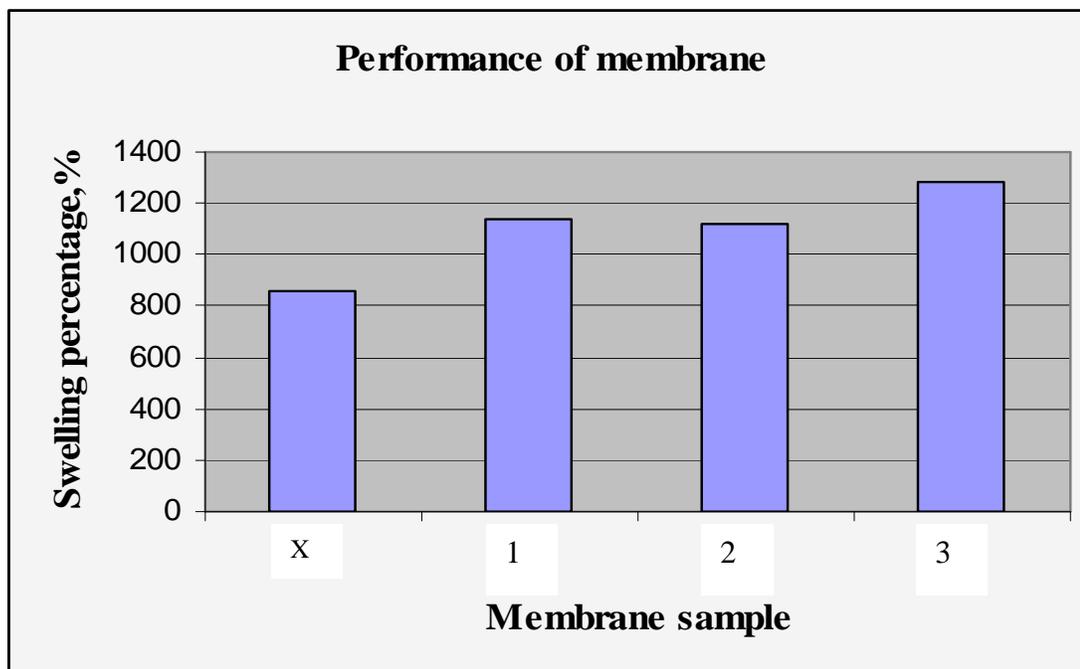
Figure 4.5: Performance of membrane in oil swelling

CHAPTER 5

CONCLUSION

5.1   Conclusion

Membrane is one of the practical wastewater treatments that can be develop more in the future. Furthermore to reduce the cost on wastewater management, Chitosan had been chose as the material for preparing the membrane. Chitosan is easy to get, biodegradability and biocompatibility. Membrane that only consists of Chitosan is not strong enough to do treatment. So to solve this matter, PEG had been chose as it crosslinking agent to increase the membrane strength and also to improve the membrane's permeability.

As the conclusion; sample 3 which consist of 3.6 gram of Polyethylene glycol gives the best performance for Chitosan/PEG membrane. This is proved in the swelling test where it adsorbed the most oil content from POME solution as the time increases. It proved that lower amount of Polyethylene Glycol present in membrane exhibits significant effect on performance of Chitosan membrane than Chitosan membrane without PEG. This observation is in agreement with the study done by Torrestiana *et al*. (1999). As cited by Shieh *et. al*, (2001) some researchers reported that PEG was used to improve membrane selectivity where it is hydrophilic in character and as pore forming agent Although adding PEG is like catalyst for this membrane to perform better in filtrating the oil from the wastewater, PEG composition which is more than 10 wt% can decrease the performance of the

membrane. The results seem to be in agreement with Kessler and Klein (1992), who revealed that higher amount of PEG, which contain more than 10 %wt PEG, reduced or readjust the dissolving power of the solvent for the polymer and induces the formation of numerous porous polymer network entities with a finite size. Frommer and Massalem (1973) also revealed that the presence of higher amount of modifying agents, PEG in this case reduce the rate of precipitation and favor a more dense sponge structure.

5.2   Recommendations

Based on result and discussion, some adjustment or improvement can be done to increase the quality of this membrane to be applied in wastewater treatment. Here are some recommendations that can be done to upgrade the future studies in this topic:

- Beside cross linking Polyethylene glycol to Chitosan membrane, one or more polymer should be added to increase membrane strength. Other polymers such as Polyethersulfone, Polydimethylsiloxane, Poly (vinyl Alcohol) or poly (vinyl pyrrolidone).

- The membrane should be thicker to do the Scanning Electron Microscopy (SEM) method. Besides using Scanning Electron Microscopy (SEM), Atomic force microscopy (AFM) also can be used.

- To see the performance of the membrane in oily wastewater treatment, oil-water solution can be used instead of using POME because in POME solution it is not only contain of water and oil but other particles and elements.

- More study should be done on membrane application in Wastewater treatment especially for biopolymer membrane.

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APPENDIX

A   Data from swelling testing

Sample	Time,min					
	0	2	4	6	8	10
	Mass,gram					
X	0.1753	0.7874	1.0718	1.3289	1.5282	1.6852
1	0.0488	0.3415	0.3746	0.467	0.543	0.604
2	0.0566	0.3829	0.4159	0.5079	0.6294	0.6904
3	0.1377	0.8605	1.0662	1.2815	1.5898	1.9078

Swelling ratio, $\% = [(W_s - W_d)/W_d] * 100$

where;

W_d is initial weight of membrane at dry condition

W_s is weight of membrane at wet condition at different swelling time