FABRICATION OF CHITOSAN MEMBRANE: THE EFFECT OF EVAPORATION TIMES ON MEMBRANE PERFORMANCE IN OILY WASTE WATER TREATMENT

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JUDUL : **FABRICATION OF CHITOSAN MEMBRANE: THE EFFECT OF EVAPORATION TIMES ON MEMBRANE PERFOMANCE IN OILY WASTE WATER TREATMENT**

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WATER TREATMENT

MURUGESAN S/O PACHIAPAN

A thesis submitted in fulfillment of the requirements for the award of the degree
of Bachelor of Chemical Engineering

Faculty of Chemical & Natural Resources Engineering

University Malaysia Pahang

MARCH 2008

I declare that this thesis entitled "*Fabrication of chitosan membrane: The effect of evaporation times on membrane performance in oily waste water treatment*" is the result 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   : ....

Name of Candidate   : Murugesan S/O Pachiapan

Date   : 24 March 2008

Special dedication to my beloved mother and father, Valliama D/O Lechumanan and Pachiapan S/O Selayen Koundru, my brother and sister and all my family members that always inspire, love and stand besides me, my supervisors, my beloved friends, my fellow colleagues, and all faculty members

For all your love, care, support, and believe in me.Thank you so much.

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ABSTRACT

Fabrication of chitosan membrane and the effect of evaporation times on membrane performance in oily wastewater treatment are studied in this paper. Chitosan homogenous membranes were fabricated by casting a chitosan/acetic acid solution, and then evaporate it for different periods of time, followed by chemically cross-linking with sulfuric acid. The separation tests using the resulting membranes demonstrate that the chitosan membranes are capable of separating water–oil mixtures in wastewater. The optimized conditions for chemical cross-linking of membranes were found to be 0.5M of the cross-linking reagent (sulfuric acid) and 10 min reaction time at ambient temperature. The preparation time of chitosan membranes is the key factor to evaluate performance of separating water–oil. It was observed in orthogonal tests that the effect of membrane preparation time on the separation factor was significant. The highest separation factor was 1170 and it occurred at 120 minutes of evaporation time. The highest separation index also occurred at this period of time. The highest separation index was 1092609. These results suggested, 120 minutes is the most perfect evaporation time to produce an efficient chitosan membrane which can extract oil from waste water. As a conclusion, the present work clearly correlates the separation performance of water-oil by using the chitosan membrane resulting from the different of evaporation time.

ABSTRAK

Cara penghasilan membran chitosan dan kesan perbezaan masa pengewapan semasa menyediakan membran untuk memisahkan minyak daripada air sisa telah dikaji di dalam thesis ini. Membran daripada chitosan ini telah dihasilkan malalui pengadukan chitosan/asid asetik dan campuran itu di biarkan mengewap dengan tempoh masa yang berbeza, di ikuti proses pengenyalan membran dengan menggunakan asid sulfurik. Ujian pemisahan menggunakan membran yang dihasilkan menunjukkan membran chitosan mampu mengasingkan campuran air-minyak di dalam air sisa. Kepekatan asid sulfurik yang paling sesuai untuk membran melalui proses pengenyalan ialah 0.5M dan ia dilakukan dalam masa 10 minit pada suhu keadaan bilik. Masa pengewapan membran chitosan merupakan faktor utama untuk mengkaji kecekapan pengasingan air-minyak. Pemerhatian daripada eksperimen-ekssperimen yang telah dijalankan, masa untuk menyediakan membran mempengaruhi nilai faktor pemisahan. Nilai factor pemisah yang paling tinggi ialah 1170 dan ia berlaku selepas 120 minit masa pengewapan. Nilai indeks pemisah yang paling tinggi juga di dapati pada tempoh masa yang sama. Nilai indeks tersebut ialah 1092609. Nilai-nilai ini membuktikan, 120 minit masa pengewapan adalah tempoh masa pengewapan yang paling sesuai untuk menghasilkan membran chitosan yang mampu memisahkan minyak daripada air sisa. Kesimpulanya daripada ujikaji ini ialah, masa pengewapan yang berbeza merupakan satu factor utama untuk memisahkan minyak daripada air.

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LIST OF ABBREVIATIONS

BOD   - Biochemical oxygen demand

DAF   - Dissolved air flotation

COD   - Chemical oxygen demand

μm   - Micro meter

nm   - Nano Meter

NaCl   - Sodium chloride

RO   - Reverse osmosis

GFD   - gallons per square foot per day

HCL   -Acid hydrochloric

H_2SO_4 - Acid Sulfuric

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CHAPTER 1

INTRODUCTION

1.1   Research Background

Wastewater is sewage and water that has been used for various purposes around the community. Unless properly treated, wastewater can harm public health and the environment. Fatty organic materials from animals, vegetables, and petroleum are not quickly broken down by bacteria and can cause pollution in receiving environments. When large amounts of oils are discharged to receiving waters from community systems, they increase biochemical oxygen demand (BOD) and they may float to the surface and harden, causing aesthetically unpleasing conditions. They also can trap trash, plants, and other materials, causing foul odors, attracting flies and mosquitoes and other disease vectors. In some cases, too much oil causes septic conditions in ponds and lakes by preventing oxygen from the atmosphere from reaching the water (Mohr, 1989).

Oil and water separation covers a broad spectrum of industrial process operations. There are many techniques employed depending on the situation. This summary will address those separations, which are suited to the chitosan membrane technology. The oily wastewater application can be broken down into categories determined by the type of user and the oil-water separation desired. There is a saying: "Oil and Water don't mix". This is true, but they can exist as an emulsion. 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. Another interesting fact is that this 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. For this reason, hydrophilic membrane separations will be possible only when the oil content is less than 50 % (Zakaria, 1994).

There are several ways for separation of oil from waste water such as centrifuge, rotary drum vacuum filter, dissolved air flotation (DAF), slope plate clarifiers, biological treatment, evaporators and gravity separating devices. Below are some descriptions of the methods:

1.1.1　Centrifuge

Uses large horsepower motors and because of the number of moving parts is subject to high maintenance. While centrifuges are effective at removing suspended solids, they do not account for dissolved solids and heavy metal species in solution. The effluent from a centrifuge would need further treatment prior to disposal. Figure 1.1 shows example of centrifuge (Moulder, 1991).
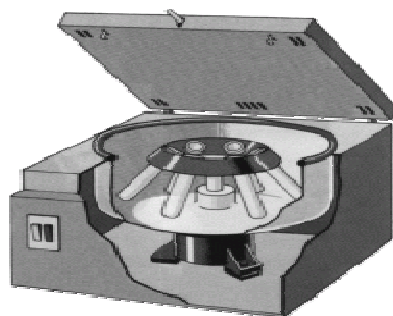
Figure 1.1: Centrifuge (Ahmad, 1994).

1.1.2 Rotary Drum Vacuum Filter

Rotary drum vacuum filter is quite effective at rejecting large solids. Sometimes filtrate must be sent back around to get all of the smaller particles. Usually employs coarse filtration. Vacuum filters require large floor areas and have high capital costs. Figure 1.2 shows example of rotary drum vacuum filter.
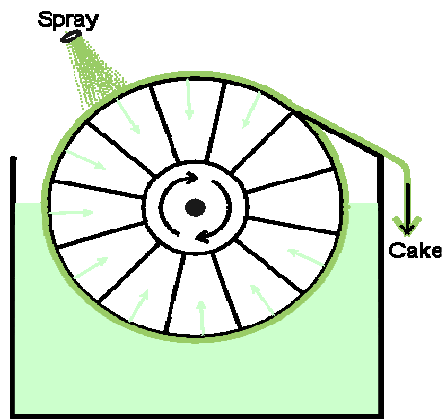
Figure 1.2: Rotary Drum Vacuum Filter (Ahmad, 1994).

1.1.3 Dissolved Air Flotation (DAF)

Large tanks where air is bubbled into the bottom and with the use of flocculants, solids are floated to the top and skimmed off. A very large tank is required due to the residence time required. Also chemical addition is a daily if not hourly process and is a significant operating cost. Figure 1.3 shows example of dissolved air flotation system.

Figure 1.3: Dissolved Air Flotation (Ahmad, 1994).

1.1.4 Slope Plate Clarifiers

The process relies on gravity to drop out heavy solids. Here again colloidal materials with small mass and dissolved constituents do not settle. Sometimes it is used in conjunction with flocculation chemicals. These chemicals have limited effect in dropping out heavy metals, BOD, and COD. Figure 1.4 shows example of slope plate clarifier.
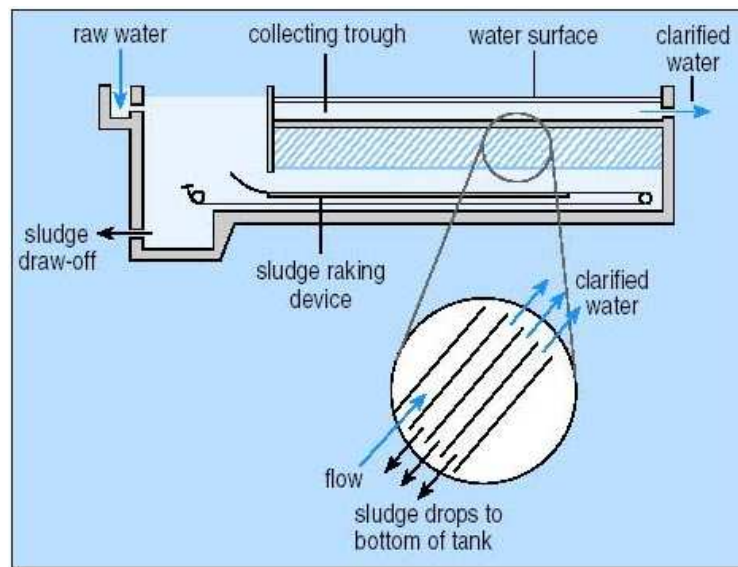
Figure 1.4: Slope Plate Clarifier (Zakaria, 1994).

1.1.5 Biological Treatment

This process relies on biological activity to digest the solids in the wastewater. The problem is that the system is extremely temperature and pH sensitive. Also loading must be done at a set rate. The operation of this kind of system usually requires a very skilled operator. It also can take up a lot of floor space due to the amount of residence time required for the bugs to digest the materials (Ahmad, 1997).

1.1.6   Evaporators

It can reduce wastewater to dry solids that can be land filled. Of course water re-use is not possible. Evaporators have very high capital costs and consume huge amounts of energy even for the most efficient models. Figure 1.5 shows example of evaporator.
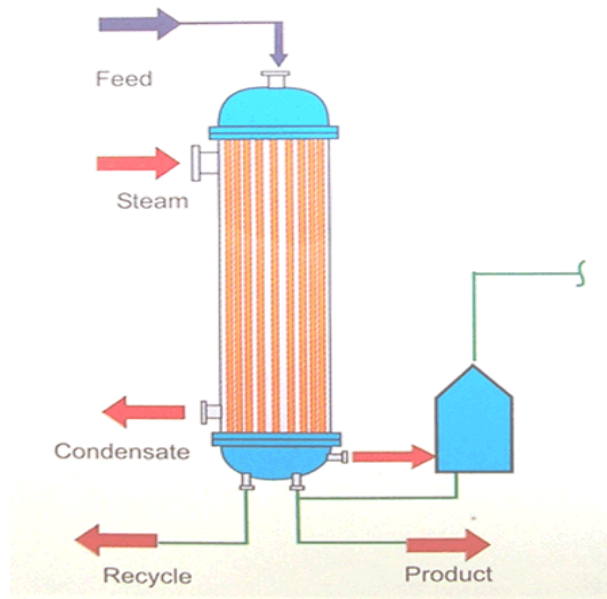
Figure 1.5: Evaporator (Zakaria, 1994).

1.2 Problem Statement

Most communities generate wastewater from both residential and nonresidential sources. Most of the Waste waters containing oily pollutants come from different industrial activities such as mining, power plants, plating facilities and electrical equipment manufacturing. All oily waste water is toxic and non-biodegradable and should be separated from waste waters.

Recently, a number of studies were carried out on low cost treatment from natural resources. The use of low cost treatment for oily wastewater derived from natural resources. Such a low cost treatment is using chitosan membrane which is a biodegradable and biocompatible polymer, produced by deacetylation of chitin. The molecular structure of chitosan is shown in Figure 1.6.
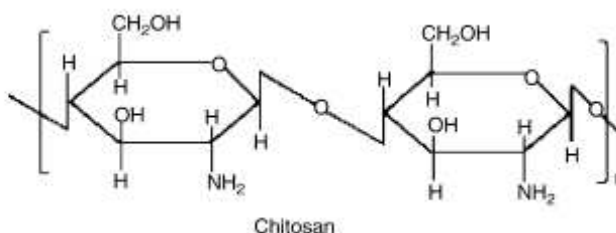
Figure 1.6: Molecular Structure of Chitosan (Younssi, 1994)

Chitin is a structural polysaccharide of crustaceans, insects and some fungi and is the most available biopolymer after cellulose. Chitosan possesses anti-microbial, anti-acid and metalion adsorbing properties which results in its utilization in many industrial applications. One of the applications of chitosan and its derivatives is for separation of oil from waste water. These studies will show that chitosan membrane can be used as a greener method for treating oily wastewater (Ahmad, 1994).

1.3   Objective

The objective for this study is to fabricate chitosan membrane and to investigate the effect of different evaporation times on membrane performance in oily waste water treatment.

1.4   Scope of Research

The scopes of this research are:

a) To fabricate chitosan membrane,

b) To Study the performance of chitosan membrane in oily waste water based on the effect of evaporation time while preparing the membrane,

c) To determine the composition of oil left in the water after treatment.

CHAPTER 2

LITERATURE REVIEW

2.1 Membranes Separation Processes

Membrane separation technology has been around for many years. Initially, the use of membranes was isolated to a laboratory scale. However, improvements over the past twenty years have made it possible to use membranes on an industrial level. A membrane is simply a synthetic barrier, which prevents the transport of certain components based on various characteristics. Membranes are very diverse in their nature with the one unifying theme to separate. Membranes can be liquid or solid, homogeneous or heterogeneous and can range in thickness. They can be manufactured to be electrically neutral, positive, negative or bipolar. These different characteristics enable membranes to perform many different separations from reverse osmosis to micro-filtration. There are four main categories of membrane filtration. These are determined by the pore size. The following tables give an overview and a classification of membrane separation processes.

Table 2.1 shows size of materials retained, driving force, and type of membrane for various membrane separation processes. Table 2.2 shows examples of applications and separation processes which compete with the respective membrane separation process.

Table 2.1: Size of materials retained, driving force, and type of membrane (Mohr, 1989).

Process	Size of materials retained	Driving force	Type of membrane
Microfiltration	0.1 - 10 µm microparticles	Pressure difference (0.5 - 2 bar)	Porous
Ultrafiltration	1 - 100 nm macromolecules	Pressure difference (1 - 10 bar)	Microporous
Nanofiltration	0.5 - 5 nm molecules	Pressure difference (10 - 70 bar)	Microporous
Reverse Osmosis	< 1 nm molecules	Pressure difference (10 - 100 bar)	Nonporous

Table 2.2: Examples of applications and alternative separation processes (Mohr, 1989).

Process	Applications	Alternative Processes
Microfiltration	Separation of bacteria and cells from solutions	Sedimentation, Centrifugation
Ultrafiltration	Separation of proteins and virus, concentration of oil-in-water emulsions	Centrifugation
Nanofiltration	Separation of dye and sugar, water softening	Distillation, Evaporation
Reverse Osmosis	Desalination of sea and brackish water, process water purification	Distillation, Evaporation, Dialysis

2.1.1 Reverse Osmosis Membranes

The first category of membranes is for Reverse Osmosis. These are the tightest membranes for separating materials. They are generally rated on the % of salts that they can remove from a feed stream. However, they can also be specified by Molecular Weight cutoff. Usually, the rejection of NaCl will be greater than 95% in order to be classed as an RO membrane. The molecular weight cutoff is shown in the table to the left. An example of their use would be for filtering seawater in order to remove the salt. They are also used to remove color, fragrance and flavor from water streams. Reverse Osmosis membranes don't have structural pores. Filtration occurs as ionic species are able to diffuse their way through the membrane itself (Mohr, 1989).

2.1.2 Nanofiltration Membranes

A great deal of recent research has led to the improvement of membranes in the range of Nanofiltration. As the name suggests, these membranes are used to separate materials on the order of nanometers. These membranes are not usually rated based on their pore size because the pores are very small and difficult to measure accurately. Instead they are rated based on the approximate molecular weight of the components that they reject or the percent of salts that they can remove from a stream. These membranes are used predominately for wastewater treatment but they are also used to concentrate material that has a wide range of particle sizes. Ultrafiltration Membranes Conventional Ultrafiltration membranes are composed of some type of polymer material with pores ranging from a little less than 0.01 μm to 0.1 μm. These membranes are used for many different separations including oily wastewater treatment, protein concentration, colloidal silica concentration and for the treatment of various wastewaters in the Pulp & Paper industry (Nunes, 2003).

2.1.3   Microfiltration Membranes

These membranes tend to be porous, with pores greater than 0.1μm. These types of membranes are used to separate larger particulate matter from a liquid phase. Some examples would be coarse minerals or paint particles, which need to be concentrated from an aqueous solution (Nunes, 2003).

2.1.4   Ultrafiltration Membranes

Ultrafiltration is a separation process that we are using in this research. It uses membranes with pore sizes in the range of 0.1 to 0.001 micron. Typically, ultrafiltration will remove high molecular-weight substances, colloidal materials, and organic and inorganic polymeric molecules. Low molecular-weight organics and ions such as sodium, calcium, magnesium chloride, and sulfate are not removed. Because only high-molecular weight species are removed, the osmotic pressure differential across the membrane surface is negligible. Low applied pressures are therefore sufficient to achieve high flux rates from an ultrafiltration membrane. Flux of a membrane is defined as the amount of permeate produced per unit area of membrane surface per unit time. Generally flux is expressed as gallons per square foot per day (GFD) or as cubic meters per square meters per day (Nunes, 2003).

Ultrafiltration membranes can have extremely high fluxes but in most practical applications the flux varies between 50 and 200 GFD at an operating pressure of about 50 psig in contrast, reverse osmosis membranes only produce between 10 to 30 GFD at 200 to 400 psig. There are some characteristic for the ultrafiltration that we should know such as:

a)   Concentration polarization

When a membrane is used for a separation, the concentration of any species being removed is higher near the membrane surface than it is in the bulk of the stream. This condition is known as concentration polarization and exists in all ultrafiltration and reverse osmosis separations. The result of concentration polarization is the formation of a boundary layer of substantially high concentration of substances being removed by the membrane. The thickness of the layer and its concentration depend on the mass of transfer conditions that exist in the membrane system. Membrane flux and feed flow velocity are both important in controlling the thickness and the concentration in the boundary layer. The boundary layer impedes the flow of water through the membrane and the high concentration of species in the boundary layer produces a permeate of inferior quality in ultrafiltration applications relatively high fluid velocities are maintained along the membrane surface to reduce the concentration polarization effect (Nunes, 2003).

b)   Recovery

Recovery of an ultrafiltration system is defined as the percentage of the feed water that is converted into permeates, or:

$$R = P/F \times 100 \qquad\qquad (2.1)$$

R = Recovery

P = Volume of permeate

F = Volume of feed

c)   Ultrafiltration   Membranes

Ultrafiltration Membrane modules come in plate-and-frame, spiral-wound, and tubular configurations. All configurations have been used successfully in different

process applications. Each configuration is specially suited for some specific applications and there are many applications where more than one configuration is appropriate. For high purity water, spiral-wound and capillary configurations are generally used. The configuration selected depends on the type and concentration of colloidal material or emulsion. For more concentrated solutions, more open configurations like plate-and-frame and tubular are used. In all configurations the optimum system design must take into consideration the flow velocity, pressure drop, power consumption, membrane fouling and module cost (Nunes, 2003).

d)   Membrane Material

A variety of materials have been used for commercial ultrafiltration membranes, but polysulfone, chitosan and cellulose acetate are the most common. Recently thin-film composite ultrafiltration membranes have been marketed. For high purity water applications the membrane module materials must be compatible with chemicals such as hydrogen peroxide used in sanitizing the membranes on a periodic basis (Nunes, 2003).

e)   Molecular-Weigh Cutoff

Pore sizes for ultrafiltration membranes range between 0.001 and 0.1 micron. However, it is more customary to categorize membranes by molecular-weight cutoff. For instance, a membrane that removes dissolved solids with molecular weights of 10,000 and higher has a molecular weight cutoff of 10,000. Obviously, different membranes even with the same molecular-weight cutoff will have different pore size distribution. In other words, different membranes may remove species of different molecular weights to different degrees. Nevertheless, molecular-weight cutoff serves as a useful guide when selecting a membrane for a particular application (Nunes, 2003).

f)   Factors Affecting the Performance of Ultrafiltration

There are several factors that can affect the performance of an ultrafiltration system. A brief discussion of these is given here (Koros, 1998).

1.   Flow across the Membrane Surface

The permeate rate increases with the flow velocity of the liquid across the membrane surface. Flow velocity if especially critical for liquids containing emulsions or suspensions. Higher flow also means higher energy consumption and larger pumps. Increasing the flow velocity also reduces the fouling of the membrane surface. Generally, an optimum flow velocity is arrived at by a compromise between the pump horsepower and increase in permeate rate (Koros, 1998).

2.   Operating Pressure

Permeate rate is directly proportional to the applied pressure across the membrane surface. However, due to increased fouling and compaction, the operating pressures rarely exceed 100 psig and are generally around 50 psig. In some of the capillary-type ultrafiltration membrane modules the operating pressures are even lower due to the physical strength limitation imposed by the membrane module (Koros, 1998).

3.   Operating Temperature.

Permeate rates increase with increasing temperature. However, temperature generally is not a controlled variable. It is important to know the effect of temperature on membrane flux in order to distinguish between drops in permeate due to a drop in temperature and the effect of other parameters (Koros, 1998).

2.2 Advantages and Disadvantages of Chitosan Membrane Technology

2.2.1 Advantages

The technologies of membrane separation have been developing to be the top of process separation. It is because there are a lot of advantages by using membrane for separation. The advantages including:

a) Save Energy

The separation of membrane is used for saving because it not needs to change phases during the process. So, in separation process, the energy can be saved and it seems to be more economical to be used by industrial (Mohr, 1989).

b) Keep the Product Quality

The separation process by using membrane can be operating in room temperature. Thus, it no needs to increase or decrease the temperature during separation process. It is suitable for separate the product which will change easily with changing temperature. From that it can keep the product quality (Mohr, 1989).

c) Easy to Operate

The separation process of membrane do not use large or complex machine which have to move from a part of plant to another part of plant. It only consist some instrument which is very easy to operate. This process can be use continuously (Mohr, 1989).

d) Direct for Scale-up

The small instrument of the separation process of membrane is direct for scaling up from laboratory to pilot plant (Mohr, 1989).

e) Environmental Friendly

This separation process of membrane is a technology which not polluted the environment. In this process, the pH will not change because it does not use any chemical matter. That's mean it will not effect the environment and some process, and separation product can be reused (Mohr, 1989).

f) Save Operation Cost and Place

There are only using small instrument in this separation in this separation process which is low cost and some place (Mohr, 1989).

2.2.2 Disadvantages

a) Membrane Fouling

In this separation process, the concentration polarization or membrane fouling will occurred. In this case, the flux will decrease and it will decrease the flow of filtration and then the performance of membrane (Mohr, 1989).

b) Short Term Used

The technology membrane can not be used for long term because the fouling will block the pore of membrane. Thus, it must be clean up in short term to avoid clog. It takes time to clean up also (Mohr, 1989).

c) Costly

The preparation of fabricate membrane is very costly process. However, it is very complicated to do so (Mohr, 1989).

2.3   Factor That Influence the Characteristic of Retentive for a Membrane

The characteristic of retentive for membrane will influence the purity and the flow rate of filtrate. However, there are some of the factors which influence the characteristic of retentive (Moulder, 1991):

2.3.1   Molecular Size

Molecular size is measured from molecular weight of molecule. If the molecular size is more than molecular weight cut-off selected membrane, the molecule will not pass through the membrane and the retention will increase (Moulder, 1991).

2.3.2   Molecular Shape

The molecule which has linear shape is easier to pass through the membrane compare to the molecule which has globular shape although both of molecules have same molecular weight (Moulder, 1991).

2.3.3   The Type of Membrane

The different types of membrane will give different characteristic of retention. It is because different types of membrane may have different molecular structure. Thus, the characteristic of retention will change with changing the types of membrane (Moulder, 1991).

2.3.4   The Configuration of Membarane

The flat membrane and the hollow fiber membrane will give the different effect of retentive respectively. Although the flat membrane and the hollow fiber membrane have same molecular weight cut-off, they have different fluxes (Moulder, 1991).

2.3.5   The Concentration of Solute

If the concentration of the species that will be blocked from pass through the membrane is high in a solution, a layer of dynamic membrane will form at the surface of membrane. The situation will cause the decreasing of the flow rate (Moulder, 1991).

2.3.6   The Effect of Environment

The effect of environment such as temperature, pH and the strength of ionic solution will influence the conformation and the shape of solute molecule for the original solution. Thus when the situation of the environment change, then it will effect on the interaction between molecules and then will effect on the flow rate (Moulder, 1991).

2.4   Phase Inversion

The phase inversion process consists of the induction of phase separation in a homogeneous polymer solution either by temperature change, by immersing the solution in a non-solvent bath (wet process) or exposing it to a non-solvent atmosphere (dry process) (Nunes, 2003).

In the thermal process, a low molecular weight component usually acts as a solvent at high temperature and as a non-solvent at low temperature. It is then removed after formation of the porous structure. Although the thermal process can be applied to a wide range of polymers, it is especially interesting for those with poor solubility, such as polypropylene, which can be hardly manufactured into a porous membrane by other phase inversion processes. An isotropic microporous structure is usually formed (Nunes, 2003).

The isothermal phase inversion is commercially more widespread. Usually the polymer solution is immersed in a non-solvent bath and a solvent-non-solvent exchanged leads to phase separation. The polymer rich phase forms the porous matrix, while the polymer poor phase gives rise to the pores. The morphology is usually asymmetric, with a selective skin on the surface, as shown in Figure 2.1 (Nunes.2003).

Basically the mechanism of phase separation depends on the crossing point the unstable region. If the solvent-non-solvent exchange brings the system first to a metastable condition (path A in Figure 2.1), the nucleation and growth mechanism is favored. A dispersed phase consisting of droplets of a polymer poor solution is formed in a concentrated matrix. If no additional non-solvent influx or temperature change in the system were induced, the composition inside the nuclei would be form the beginning that expected at the equilibrium and would, practically not change with time. If the demising path crosses the critical point, going directly into the unstable region (path B in Figure 2.1), the spinodal decomposition predominates (Nunes, 2003).
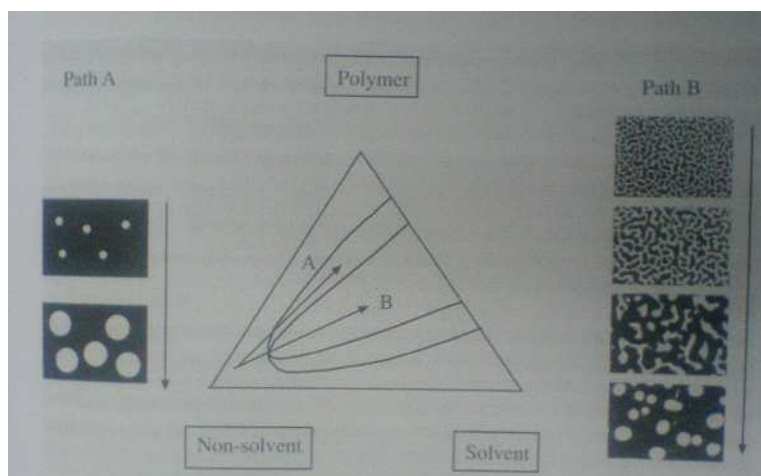
Figure 2.1 Mechanism of Phase Separation during Membrane Formation (Nunes, 2003)

2.5   Asymmetric Membrane

Dense polymer films, though providing good separation of many process streams, generally yield fluxes too low to be economical in most membrane separation applications. Most membranes have "asymmetric" structures. Integrally skinned or "simple membrane structures are typified by those constructed from cellulose acetate and aromatic polyamides in which a single membrane polymer is used for the support and thin selective layer. Polysulfone is easily formed into porous structures but is difficult to prepare with a truly pore-free skin. This obstacle is generally eliminated using a "caulking" procedure developed by Henis and Tripod of Monsanto. An interesting extension of these approaches involves the generation of "composite membrane comprising a more-or-less unskinned porous support with subsequent attachment of a second material with desirable solution-diffusion separation properties. Asymmetric and composite structures permit the preparation of nearly pore-free membranes with skin thicknesses of roughly 1000 angstroms, thus increasing flux values by more than a factor of 200 over most dense films. This represents the latest breakthrough in the drive to increase membrane productivity (Koros. 1998).

In all of these membrane types the primary separation occurs in the thin skin on these membranes. Whereas the underlying open-celled structure acts simply as a support and cushion for the skin. If the resistance to transport across the porous support layer exceeds roughly 10% of the resistance of the dense selective layer, serious loss in efficacy results. This effect places a premium on the ability to generate low-resistance open-celled porous supports (Koros, 1998).

2.6   Chitosan

Chitosan is a natural product derived from chitin, which is a polysaccharide found in the exoskeleton of shellfish or crustaceans such as crabs, shrimps, prawns, lobsters, squid, and clams. While chitosan has been in existence for years, and used for a number of purposes, it has just recently began use as a weight loss supplement (Zakaria, 1994).

Chitosan is a naturally occurring substance that is chemically similar to cellulose which is a plant fiber. Just like the plant fibers, chitosan possesses a number of properties or qualities as fiber. What sets chitosan apart from plant fiber is the fact that chitosan has the ability to significantly bind fat in the digestive tract. Hence, chitosan is often dubbed the "fat magnet" (Zakaria, 1994).

2.6.1   History of Chitosan

Chitosan (pronounced *Kite-O-San*) can be traced back to 1811 when "chitin", from which it is derived, was first discovered by Braconnot, then a professor of natural history in France. According to some research, while Braconnot was conducting research on mushrooms, he isolated what was later to be called chitin. (Koros. 1998)

Some 20 years later, there was a man who authored an article on insects in which he noted that similar substance was present in the structure of insects, as well as the structure of plants. He then called this amazing substance "chitin". Basically, the name chitin is derived from Greek, meaning "tunic" or "envelope". The concept was further known in 1843 when Lassaigne demonstrated the presence of nitrogen in chitin. (Koros. 1998)

After the discovery of chitin, the name "chitosan" emerged on the scene. It was first discovered by Rouget while experimenting with chitin. Accordingly, Rouget

observed that the compound of chitin could be manipulated through chemical and temperature treatments for it to become soluble. Then, it was in 1878 when Ledderhose identified chitin to be made of glucosamine and acetic acid. It was not actually until 1894 that Hoppe-Seyler named the tailored chitin, chitosan (Koros. 1998).

By the early 20th century, chitosan became the subject of study by most researchers. They involved sources of chitin, including crab shells and fungai. It was the work of Rammelberg in the 1930s that led to the confirmation on the identity of chitosan from these sources. It was also noted that by hydrolyzing chitin in a number of ways, it was determined by experts that chitin is a polysaccharide of glucosamine (Koros. 1998).

In the 1950s, the use of x-ray analysis had advanced the study of the occurrence of chitin or chitosan in fungai. However, it is only the most advanced technologies that proved the most reliable in identifying the presence of chitin, as well as cellulose, in the cell walls. The first book on chitosan was published 140 years after the initial observation of Braconnot, and that was in 1951 (Koros. 1998).

In the early 1960s, chitosan was investigated for its ability to bind with red blood cells. At that time also, the substance was considered as a hemostatic agent. Then, for the past three decades, chitosan has been used at water purification plants for detoxifying water. It is spread over the surface where it absorbs greases, oils, and other potential toxins (Koros. 1998).

Now, chitosan is popular as an aid for weight loss. Many people make it their dietary supplement to block fat. Chitosan is now widely marketed in many parts of Europe and Japan, and continue to spread as its popularity as a fat inhibitor continues to be known worldwide (Koros. 1998).

2.6.2 Chemical Properties of Chitosan

Chitosan has some chemical properties which include (Koros. 1998):

a)   Linear polyamine (poly-D-glucosamine)

b)   Reactive amino groups

c)   Chelates many transitional metal ions

d)   Basteriostatic and fungistatic effect

e)   Separations of protein

2.6.3 The Structural Formula and Preparation of Chitin and Chitosan

Chitin is similar to cellulose both in chemical structure and in biological function as a structural polymer. The crystalline structure of chitin has been shown to be similar to cellulose in the arrangements of inter- and intrachain hydrogen bonding (Figure 2.2). It has been proposed to define chitosan and chitin as soluble or insoluble in 0.1 M acetic acid, respectively, or by degree of deacetylation. >20% of deacetylation is the proposed definition of chitosan. Chitosan is made by alkaline N-deacetylation of chitin. The term chitosan does not refer to a uniquely defined compound, it merely refers to a family of copolymers with various fractions of acetylated units. It consists of two types of monomers, chitin-monomers and chitosan-monomers. Chitin is a linear polysaccharide consisting of (1-4)-linked 2-acetamido-2-deoxy-b-D-glucopyranose. Chitosan is a linear polysaccharide consisting of (1-4)-linked 2-amino-2-deoxy-b-D-glucopyranose (Mohr, 1989).
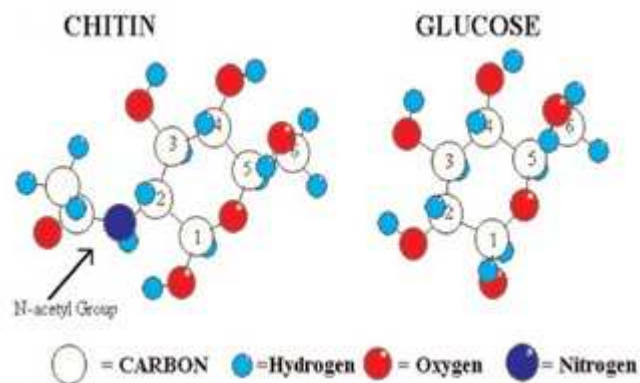
Figure 2.2: Structural formula of chitin and glucose (Ahmad, 1994).

Commercial chitin and chitosan consists of both types of monomers. Chitosan is found in nature, to a lesser extent than chitin, in the cell walls of fungi. Chitin is believed to be the second most abundant biomaterial after cellulose. The annual biosynthesis of chitin has been estimated to 109 to 1011 tons. Chitin is widely distributed in nature. Among several sources, the exoskeleton of crustaceans consists of 15% to 20 % chitin of dry weight. Chitin found in nature is a renewable bioresource. Chitin and chitosan are both prepared using the common process illustrated and described in Figure 2.3 (Mohr, 1989).
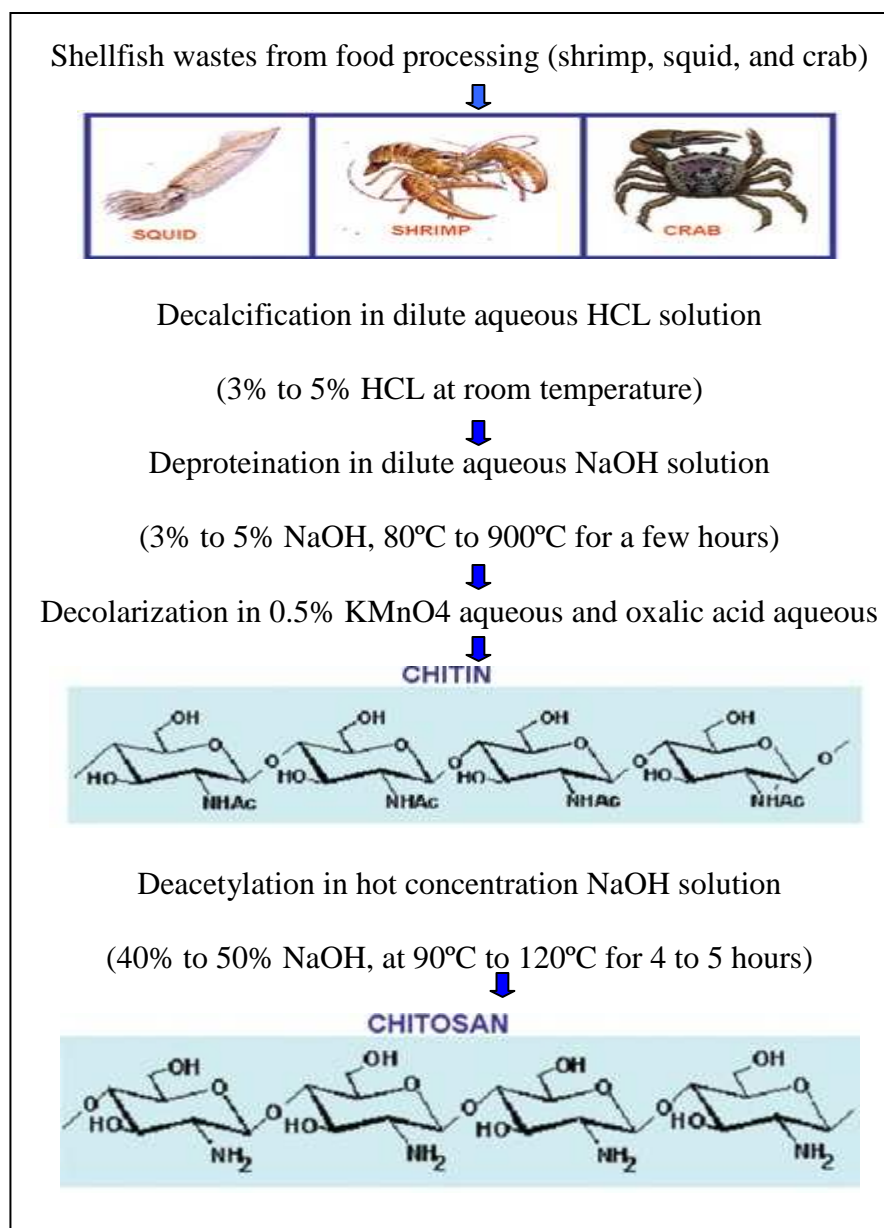
Figure 2.3: Preparation of chitin and chitosan (Ahmad, 1994)

2.6.4   The Amino Group in Chitosan

According to some chitosan chemistry studies, chitosan contains an amino group which has a pKa value of ~6.5. This means that chitosan is positively charged and soluble in acidic to neutral solution, with a charge density dependent on pH as well as %DA-value. With this information, it is concluded that chitosan is bio-adhesive and readily binds to negatively charged surfaces like the mucus membranes. Furthermore, chitosan has the ability to enhance the transport of polar drugs across the epithelial surfaces. With that, chitosan is found biocompatible and biodegradable (Younssi, 1994).

2.6.5   Multitude of Chitosan applications

Chitosan is a biological product with cationic (positive electrical charge) properties. It is of great interest, all the more so because most polysaccharides of the same types are neutral or negatively charged. By controlling the molecular weight, the degree of deacetylation and purity, it is possible to produce a broad range of chitosans and derivatives that can be used for industrial, dietary, cosmetic and biomedical purposes. Together these properties have led to the development of hundreds of applications so far. There are plethora of literature, books and conference proceedings that documented the multiple uses of the chitosan4. It is out of the scope of this article to describe extensively every applications of chitosan. We will concentrate on the major uses of chitosan and the most promising future applications. Applications of chitosan can be classified mainly in 3 categories according to the requirement on the purity of the chitosan:

1.   Technical grade for agriculture and water treatment,

2.   Pure grade for the food and cosmetics industries,

3.	Ultra-pure grade for biopharmaceutical uses (Mohr, 1989).

2.6.5.1   In Agriculture

Chitosan offers a natural alternative to the use of chemical products that are sometimes harmful to humans and their environment. Chitosan triggers the defensive mechanisms in plants (acting much like a vaccine in humans), stimulates growth and induces certain enzymes (synthesis of phytoalexins, chitinases, pectinases, glucanases, and lignin). This new organic control approach offers promise as a biocontrol tool. In addition to the growth-stimulation properties and fungi, chitosans are used for:

1.	Seed-coating,

2.	Frost protection,

3.	Bloom and fruit-setting stimulation,

4.	Timed release of product into the soil (fertilizers, organic control agents, nutrients),

5.	Protective coating for fruits and vegetables (Mohr, 1989).

2.6.5.2   For Water Treatment

At the present time, physicochemical-type treatment is widely used at potable and wastewater treatment plants. The major disadvantage of using synthetic chemical products is the risk of resulting environmental pollution. Treating wastewater using "greener" methods has become an ecological necessity. Chitosan, due to its natural origin and being biodegradable, has proven to be a most interesting alternative from several points of view (Mohr, 1989).

Integrating a natural polymer made of crustacean residue into an existing system achieves a two-fold purpose: it improves the effectiveness of water treatment while reducing or even eliminating synthetic chemical products such as aluminum sulphate and synthetic polymers. Here are a few characteristics of chitosan that offer an ecological solution:

1. Natural and biodegradable,

2. A powerful competitor for synthetic chemical products,

3. Potentially reduces the use of alum by up to 60% and eliminates 100 % of the polymers from the treated water,

4. Improves system performance (suspended solids and chemical oxygen demand),

5. Significantly reduces odor (Mohr, 1989).

2.6.5.3 Food Industry

Chitosan is already used as a food ingredient in Japan, in Europe and in the United States as a lipid trap, an important dietetic breakthrough. Since chitosan is not digested by the human body, it acts as a fiber, a crucial diet component. It has the unique property of being able to bind lipids arriving in the intestine, thereby reducing by 20 to 30% the amount of cholesterol absorbed by the human body. This raises the question: is chitosan really a "Fat Magnet"?

In solutions, chitosan has thickening and stabilizing properties, both essential to the preparation of sauces and other culinary dishes that hold their consistency well. Finally, as a flocculating agent, it is used to clarify beverages. Because of its phytosanitary properties, it can be sprayed in dilute form on foods such as fruits and

vegetables, creating a protective, antibacterial, fungi static film. In Japan, a dilute solution of chitosan is commonly sprayed on apples and oranges as a protective measure. There are many other applications in the areas of nutraceutical and nutritional supplements, particularly for the broad range of chitosans that have been chemically or enzymatically modified. Principal commercial applications include:

1.   Preservatives,

2.   Food stabilizers,

3.   Animal feed additives,

4.   Anti-cholesterol additives (Mohr, 1989)

2.6.5.4   In Cosmetics

Chitosan forms a protective, moisturizing, elastic film on the surface of the skin that has the ability to bind other ingredients that act on the skin. In this way, chitosan can be used in formulating moisturizing agents such as sunscreens, organic acids, etc. to enhance their bioactivity and effectiveness. Today, chitosan is an essential component in skin-care creams, shampoos, and hairsprays due to its antibacterial properties. Many patents have been registered and new applications are just beginning to appear including the most highly prized moisturizing and antibacterial properties. Applications include:

1.   Maintain skin moisture,

2.   Treat acne,

3.   Tone skin,

4.   Protect the epidermis,

5.   Reduce static electricity in hair,

6.   Fight dandruff,

7.   Make hair softer (Mohr, 1989).

2.6.5.5   Biopharmaceutical Uses

It is in the field of health that the many properties of chitosan (bacteriostatic, immunologic, antitumoral, cicatrizant, hemostatic and anticoagulant) are of interest. For example, because of its biocompatibility with human tissue, chitosan's cicatrizant properties have proven its effectiveness as a component, notably, in all types of dressings (artificial skin, corneal dressings, etc.), surgical sutures, dental implants, and in rebuilding bones and gums. Applications currently being developed include artificial skin, surgical sutures that are absorbed naturally after an operation, and corneal contact lenses. Finally, chitosan delivers and time-releases drugs used to treat animals and humans. There are many potential chitosan applications in the health field but their development calls for the use of components that comply with strict pharmaceutical-grade requirements. Possible applications include:

1.   Ointments for wounds,

2.   Surgical sutures,

3.   Ophthalmology,

4.   Orthopedics,

5.   Pharmaceutical products (delivery agent),

6.   Contact lenses (Mohr, 1989).

CHAPTER 3

METHODOLOGY

3.1   Chemicals

The main chemical (shown as Figure 3.1) used to fabricate the chitosan membrane is chitin. Chitin is a most important chemical in fabrication of chitosan membrane. Another chemical is acetic acid which is used to increase the number of pore for membrane. Both of these chemicals will be mixed together to become a solution named chitosan solution. This solution will let to be evaporated for different period time and at the end of the process a thin layer of chitosan membrane appear. This membrane will be soaked into H_2SO_4 for 10 minutes. H_2SO_4 act as a cross linking agent which will strengthen the membrane structure.

Figure 3.1: Chitin

3.2   Equipments

3.2.1   Glass Rod

This glass rod is used as a casting knife in fabricating the chitosan membrane. Firstly, coat the masking tape at both end of the rod constantly until the thickness of masking tape achieved 0.05cm. It uses to flatten the chitosan solution on surface of flat glass. Membrane's thickness can be adjusted by adjusting the thickness of masking tape. Figure 3.2 shows example of glass rod.

Figure 3.2: Glass rod

3.2.1   Aluminium Foil

Aluminum foil is use to cover the beaker which contain a solution of chitin. It is because there will be a lot of bubbles forms during mixing of solution and the bubbles take time to come out from solution. Aluminum foil is use to avoid the solution influenced by environment because the solution will act with the water from air to become chitosan membrane. Figure 3.3 shows example of aluminium foil.

Figure 3.3: Aluminium foil

3.2.3 Pressure Supply

Pure nitrogen (99.98% pure) is use to increase the pressure in the equipment of filtration. Operation pressure can be adjusted from 100 until 500 kNm-2 (14.5 to 72.5psi). Nitrogen with no oxygen is connected to the membrane testing unit. Figure 3.4 shows example of pressure supply.

Figure 3.4: Pressure supplier

3.2.4   Beaker Amicon

The Figure 3.5 shows the filtration apparatus, Amicon (model 8200) is used in this experiment. It has volume capacity of 200m1 and can place a piece of chitosan membrane with diameter of 62mm and area of 28.7cm^2. The maximum pressure of this equipment is 517 kNm^{-2} (75psi). This equipment is shape in cylinder which can hold the membrane, has a small tube for solution to flow out, stir magnet inside the equipment. The stir magnet is design to be close with the surface of membrane which uses to stir the solution to avoid polar concentrate when it is passing through the membrane.

During the operation, the membrane is put between the metal porous (to avoid the membrane from damage when giving pressure on it) and gasket bangle-O. Then it place inside the Amicon. Infuse the solution of red color solution into the Amicon. Close the cover of Amicon. Set the rate of stir magnet and let the solution about 10 minutes to make sure it is stable before experiment. Set the operation pressure with on the button on the cylinder of nitrogen.

Figure 3.5: Amicon beaker

3.2.5 Magnet Stirrer

A magnetic stirrer which from HANNA instruments, model HI 303N, United Kingdom is used during solution preparation and solution separation. It is use as stirrer inside the Beaker Amicon to reduce the occurred adjustment for temperature and an adjustment for speed during mixing. The equipment is shown in Figure 3.6.

Figure 3.6: Magnetic stirrer

3.3 Fabrication of Chitosan Membrane

Preparation of membrane proceeded using two gram of chitosan dissolved in 100ml water with 3ml acetic acid. Chitosan solution was stirred for 2 hours and left over night. The solution stirred again for about 20 minute and filtrated through cloth to remove undissolve chitosan and debris. The solution of chitosan and silica complex was cast into a Petri dish and left in oven with 333K heating temperature.

This solution will let to be evaporated for different period of time and as a result of that, a thin dense chitosan-silica membrane was produced. The Petri dish should be

put on horizontal place to make the uniform thickness across the area. The dried membrane was then gauge out by a small thin picker.

After the evaporation process, the thin dense chitosan-silica membrane soaked into 0.5 M H_2SO_2 for cross linking purposes. Cross linking process is a must because it will strengthen the structure of the membrane. Without cross linking process, the membrane will easily tear. The whole chitosan fabrication process is summarized in Figure 3.7.

```
┌─────────────────────────────────────────────────────────────┐
│                   Preparation of Chitosan                    │
└─────────────────────────────────────────────────────────────┘
                              │
                              ▼
┌─────────────────────────────────────────────────────────────┐
│          2 g Chitosan + 100 ml water + 3ml Acetic Acid       │
└─────────────────────────────────────────────────────────────┘
                              │
                              ▼
┌─────────────────────────────────────────────────────────────┐
│          Stirred for 2 hours and left it over a night        │
└─────────────────────────────────────────────────────────────┘
                              │
                              ▼
┌─────────────────────────────────────────────────────────────┐
│     Stirred again for 20 minutes and filtrate it through cloth│
└─────────────────────────────────────────────────────────────┘
                              │
                              ▼
┌─────────────────────────────────────────────────────────────┐
│  Cast the solution in petri dish and left it in oven with 333(K) temperature │
│                   (Different evaporation time)               │
└─────────────────────────────────────────────────────────────┘
                              │
                              ▼
┌─────────────────────────────────────────────────────────────┐
│ Membrane removed from the Petri Dish, soaked it in $H_2SO_4$ for 10 mins │
└─────────────────────────────────────────────────────────────┘
                              │
                              ▼
┌─────────────────────────────────────────────────────────────┐
│          Thin dense chitosan silica membrane produced        │
│                   (Membrane ready to use)                    │
└─────────────────────────────────────────────────────────────┘
```
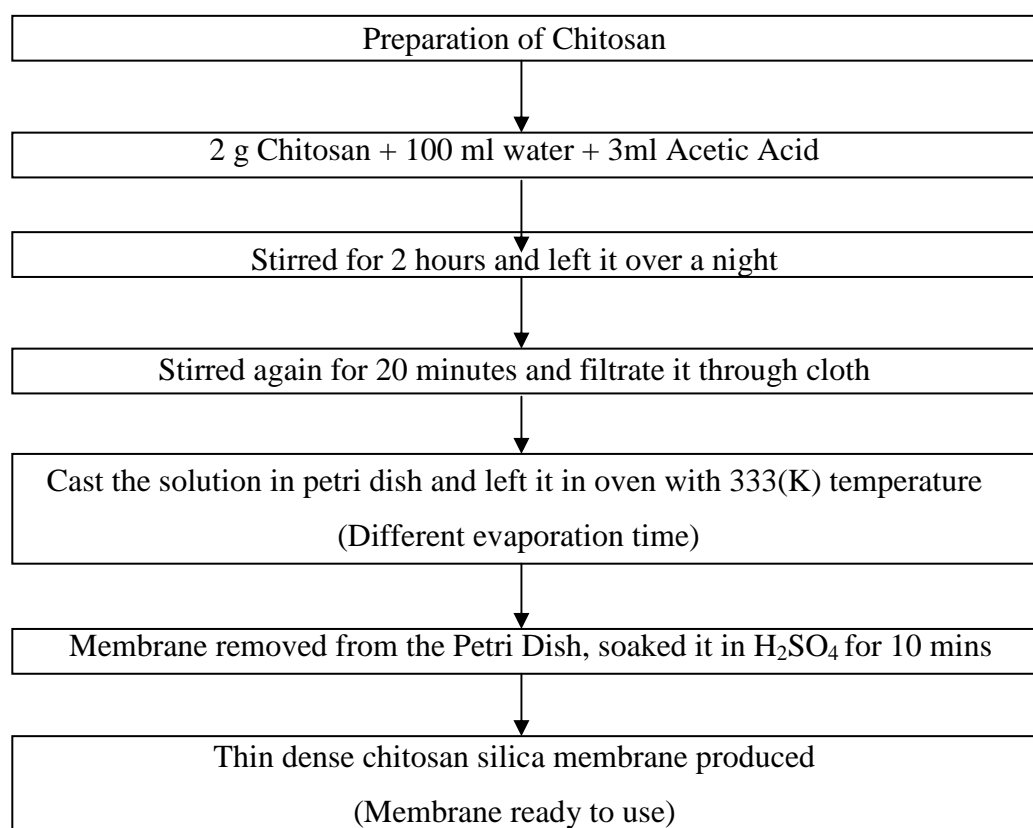
Figure 3.7: Flow chart fabrication of chitosan membrane

The effects of the fabrication conditions, such as concentration of H_2SO_4, chitosan concentrations of cast solutions and heating temperature also are also discussed in this part. In order to examine the effects of these three conditions on the separation factor of the chitosan membranes, an orthogonal experiment test was designed. From doing these experiment we can choose the best condition where evaporation time can be measured. Three different values of each element were taken so that nine experiments were carried out for this study. Nine chitosan membranes were prepared for the orthogonal test and evaluated by separation of oil–water. The procedure to run this orthogonal experiment shown in Figure 3.8, Figure 3.9 and Figure 3.10.

```
┌─────────────────────────────────────────────────────────────┐
│       2 g Chitosan + 100 ml water + 3ml Acetic Acid          │
└─────────────────────────────────────────────────────────────┘
                              │
                              ▼
┌─────────────────────────────────────────────────────────────┐
│         Stirred for 2 hours and left it over a night          │
└─────────────────────────────────────────────────────────────┘
                              │
                              ▼
┌─────────────────────────────────────────────────────────────┐
│      Stirred again for 20 minutes and filtrate it through cloth │
└─────────────────────────────────────────────────────────────┘
                              │
                              ▼
┌─────────────────────────────────────────────────────────────┐
│ Cast the solution in petri dish and left it in oven with 333(K) temperature │
└─────────────────────────────────────────────────────────────┘
                              │
                              ▼
┌─────────────────────────────────────────────────────────────┐
│      Membrane removed from the Petri Dish and soaked in        │
│        (0.5M, 1.0M, 2.0M) $H_2SO_4$ for 10 minutes            │
└─────────────────────────────────────────────────────────────┘
                              │
                              ▼
┌─────────────────────────────────────────────────────────────┐
│       Thin dense chitosan silica membrane produced            │
│                (Membrane ready to use)                         │
└─────────────────────────────────────────────────────────────┘
```

Figure 3.8: Flow chart fabrication of chitosan membrane

(different concentration of H_2SO_4)

(1 g, 2g, 3g) Chitosan + 100 ml water + 3ml Acetic Acid

↓

Stirred for 2 hours and left it over a night

↓

Stirred again for 20 minutes and filtrate it through cloth

↓

Cast the solution in petri dish and left it in oven with 333(K) temperature

↓

Membrane removed from the Petri Dish and soaked in 0.5M H_2SO_4 for 10 minutes

↓

Thin dense chitosan silica membrane produced (Membrane ready to use)
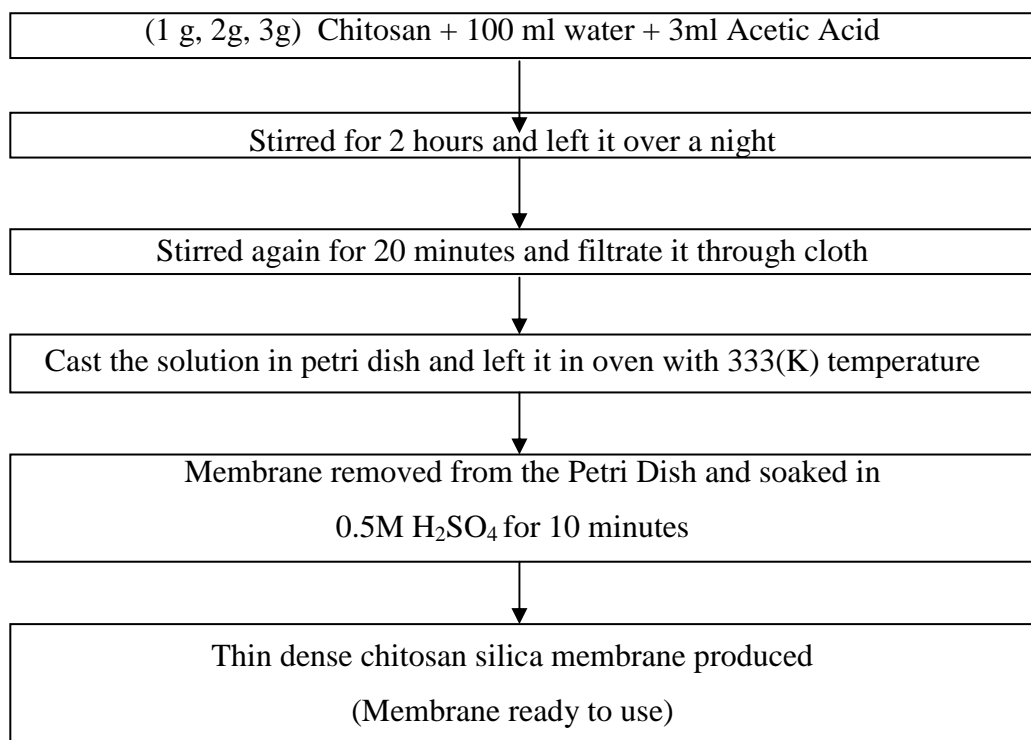
Figure 3.9: Flow chart fabrication of chitosan membrane

(different chitosan concentration)

```
┌─────────────────────────────────────────────────────────────┐
│          2g Chitosan + 100 ml water + 3ml Acetic Acid         │
└─────────────────────────────────────────────────────────────┘
                              │
                              ▼
┌─────────────────────────────────────────────────────────────┐
│          Stirred for 2 hours and left it over a night         │
└─────────────────────────────────────────────────────────────┘
                              │
                              ▼
┌─────────────────────────────────────────────────────────────┐
│      Stirred again for 20 minutes and filtrate it through cloth│
└─────────────────────────────────────────────────────────────┘
                              │
                              ▼
┌─────────────────────────────────────────────────────────────┐
│      Cast the solution into petri dish and left it in oven with│
│              (303K, 333K, 353 K) temperature                  │
└─────────────────────────────────────────────────────────────┘
                              │
                              ▼
┌─────────────────────────────────────────────────────────────┐
│      Membrane removed from the Petri Dish and soaked in       │
│              0.5M H₂SO₄ for 10 minutes                        │
└─────────────────────────────────────────────────────────────┘
                              │
                              ▼
┌─────────────────────────────────────────────────────────────┐
│          Thin dense chitosan silica membrane produced         │
│              (Membrane ready to use)                          │
└─────────────────────────────────────────────────────────────┘
```
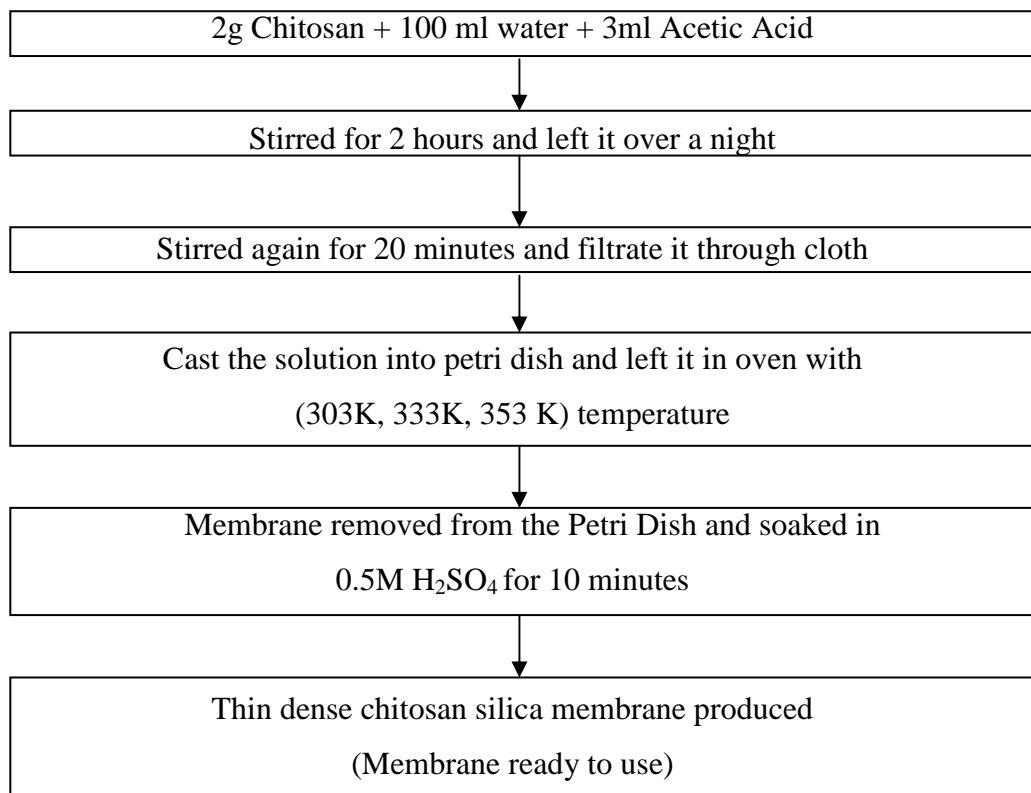
Figure 3.10: Flow chart fabrication of chitosan membrane

(different heating temperature)

3.4   Filtration

The next step after the preparation of chitosan membrane is filtration process. Before we start the filtration process, the membrane must be cut into round shape so that it can fit into the filtration chamber. The effective area of the membrane was 0.00283m2. After cut the membrane into around shape, place it in membrane cell in amicon beaker. 200 ml oily wastewater filled onto the membrane and let it filtrate. Set the effective pressure around 5bar to let the oily wastewater to pass through the membrane. The flux will come out and the sample will be tested with refractometer. The compositions of permeate and feed solutions were determined at 303K by using a refractometer.
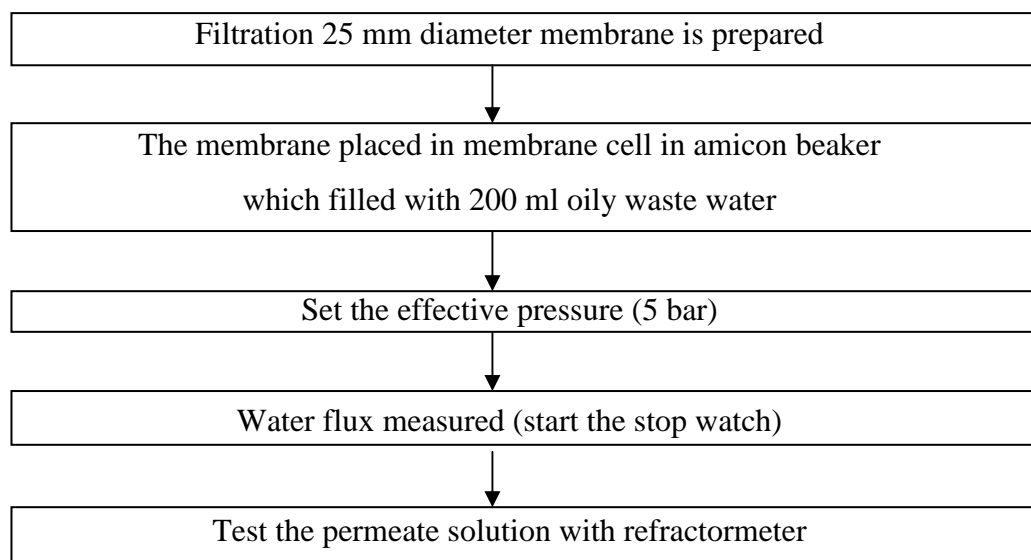
Filtration 25 mm diameter membrane is prepared

↓

The membrane placed in membrane cell in amicon beaker which filled with 200 ml oily waste water

↓

Set the effective pressure (5 bar)

↓

Water flux measured (start the stop watch)

↓

Test the permeate solution with refractormeter

Figure 3.11: Flow chart of filtration process (Nakatsuka, 1992).

The evaluation of separation performance was carried out by using two parameters, flux and separation selectivity. The flux (J) was calculated from the following expression (Nakatsuka, 1992):

$$J = \frac{W}{A \times t} \qquad\qquad (3.1)$$

Where W is the mass of permeate (g), A is the area of the membrane (m2), and t is the evaluation time (h). The separation factor (α) was obtained by (Nakatsuka, 1992):

$$\alpha = \frac{c_{1p}/c_{2p}}{c_{1f}/c_{2f}} \qquad\qquad (3.2)$$

Where C_{1p} and C_{1f} (iD1, 2) are the concentrations of component i in permeate and feed, and the subscripts 1 and 2 refer to water and ethanol, respectively. The pervaporation separation index (PSI) was calculated by (Nakatsuka, 1992):

$$PSI = J \times \alpha \qquad (3.3)$$

CHAPTER 4

RESULT AND DISCUSSION

4.1   Effect of the Degree of Cross-Linking

H_2SO_4 is one of the most effective cross-linking agents for chitosan. However, high concentrations of H_2SO_4 would cause a problem, particularly in the washing step of the fabrication process. In order to optimize the concentration of H_2SO_4, the experiments were carried out by using a concentration at 0.5M, 1.0M and 2.0 M of H_2SO_4. The chitosan membranes were prepared by a two-step process, casting and evaporate it at room temperature, followed by cross-linking with a H_2SO_4 solution for 10 minutes. The resulting membranes were tested for evaporation performance. The results of this experiment are summarized in Table 3 in appendix.
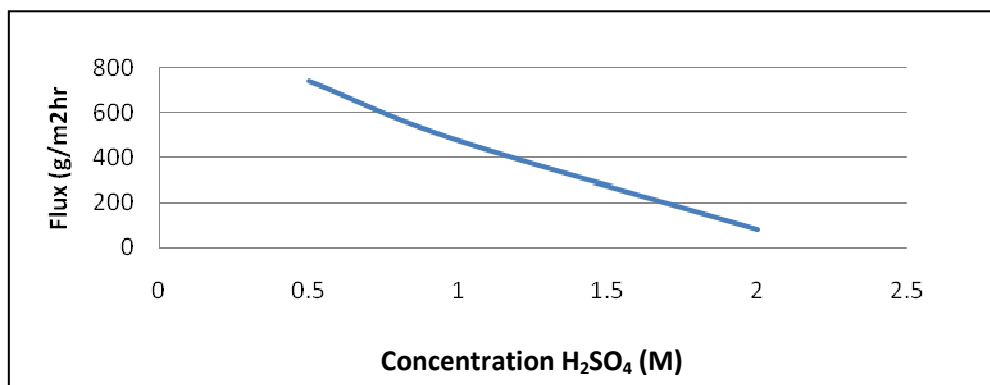
Figure 4.1: Flux versus concentration H_2SO_4
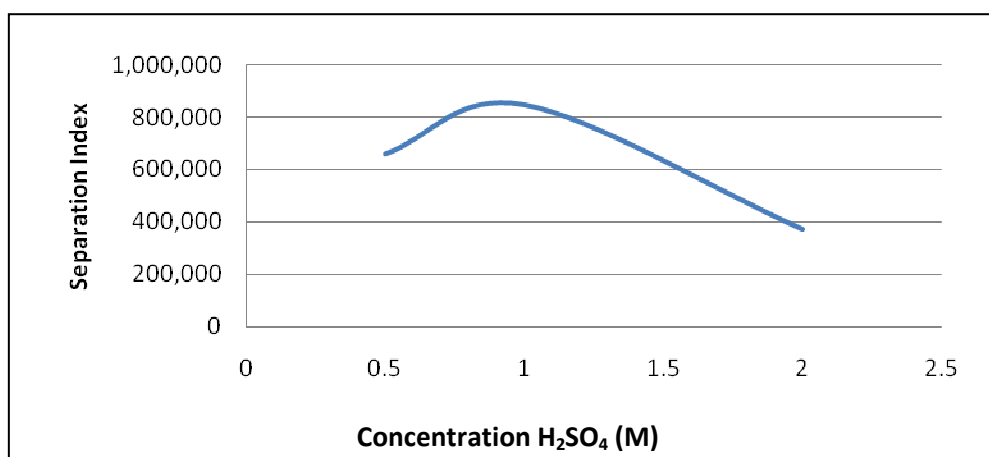
Figure 4.2: Separation index versus concentration H_2SO_4

It can be seen in Figure 4.1and Figure 4.2 that an increase in concentration of H_2SO_4 leads to a decrease in flux. At the other point, by increasing the concentration of H_2SO_4, the separation flux also increase at the beginning but it start to decrease when using higher than 1M. This is due to the fact that a higher concentration of the cross-linking reagent leads to a higher degree of cross-linking. H_2SO_4 with 0.5M concentration produce 739 g/m^2h flux and it was the highest value compare to other concentration. The highest separation index is 845352 and it obtained when the concentration of H_2SO_4 is 1.0 M. This indicates that the separation index is related to the degree of cross-linking. As good performance evaporation membranes, both good separation indexes and high fluxes are essential. A high flux and a separation index mean good separation productivity for evaporation membranes (Nakatsuka, 1992). The highest flux and a good separation index are obtained by using 0.5M H_2SO_4. Therefore, 0.5 M concentration is of H_2SO_4 optimum for cross-linking.

4.2   Effect of Membrane Preparation Conditions

The effects of the fabrication conditions, such as chitosan concentrations of cast solutions and heating temperature also will give effect to the separation process. In order to examine the effects of these two conditions on the separation factor of the chitosan membranes, an orthogonal experiment test was designed. From doing these experiment we can choose the best condition where evaporation time can be measured. Two different values of each element were taken so that six experiments were carried out for this study (Table 4 and Table 6 in appendix). Six chitosan membranes were prepared for the orthogonal test and evaluated by separation of oil–water. The separation experiments of these chitosan membranes were carried out at room temperature.
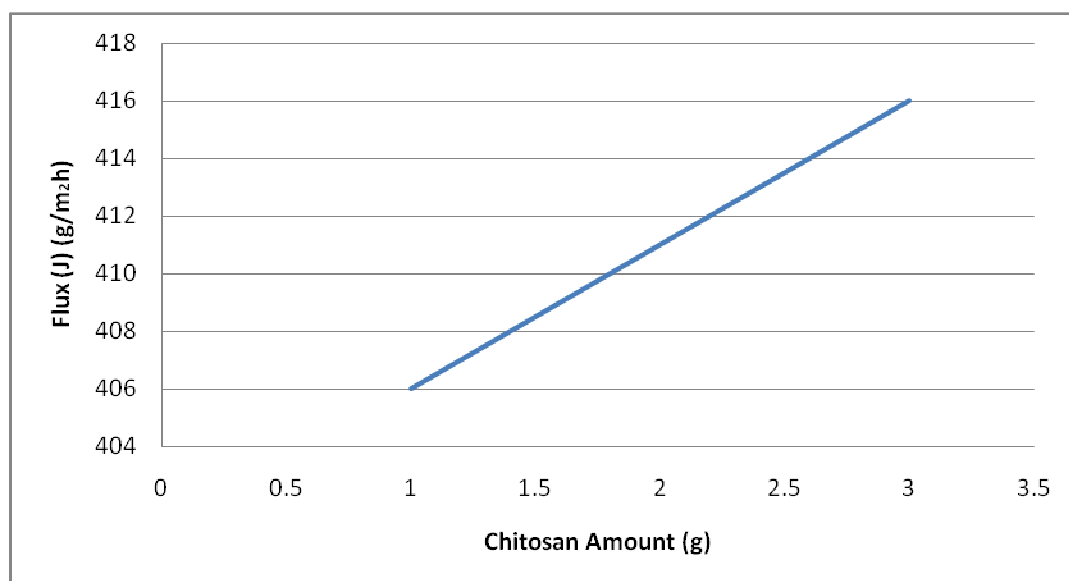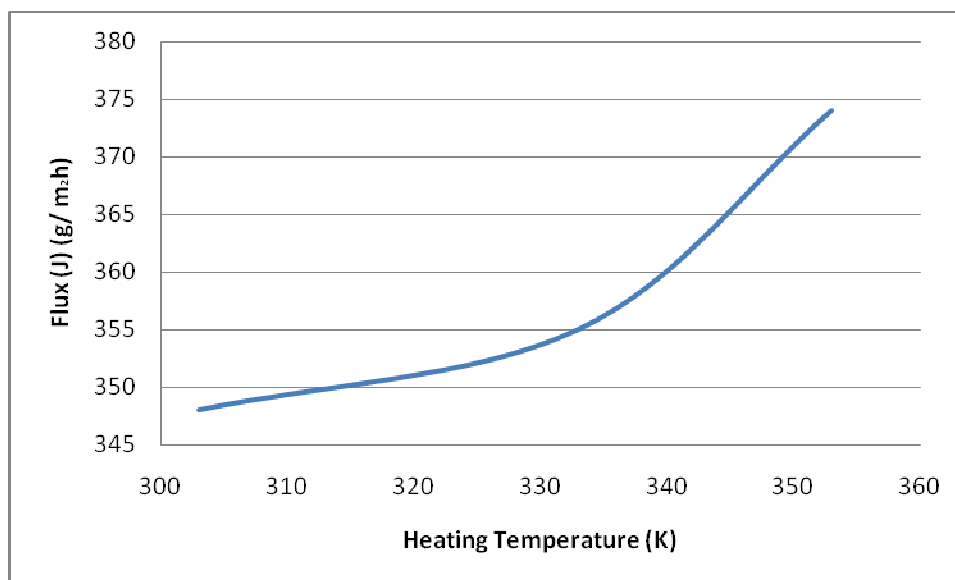

Figure 4.3: Flux versus chitosan amount

Figure 4.4: Flux versus heating temperature

It can be seen from Figure 4.3, increasing amount of chitosan will increase the flux. The highest flux using different amount of chitosan was 416 g/m^2h and the lowest flux was 406 g/m^2h. The percentage different between highest and lowest amount of chitosan is 2.46 % and it suggest that amount of chitosan while fabricate the membrane did not give much effect to the flux. Same goes to different heating temperature while preparing chitosan membrane. Figure 4.4 shows by that, increase in heating temperature will increase the flux. According to the result, the highest flux using different heating temperature is 374 g/m^2h and the lowest flux is 348 g/m^2h. The percentage different between these two values is just 7.47%. The result indicates that the flux of chitosan membrane with different concentration of chitosan and heating temperature are almost the same for each factor. As a conclusion, the results suggest that flux is slightly affected by the concentration of chitosan and heating temperature. Therefore, we take the average heating temperature (333K) and average concentration of chitosan membrane (2g) taken to study the effect of evaporation time while preparing chitosan membrane in separating water-oil.

4.3   Effects of Evaporation Time on Separation Performance

A series of chitosan membranes were prepared by evaporate the chitosan membranes at different time (30, 60, 90,120, 150,180 and 210 minutes) with the same heating temperature (333K) and same chitosan concentrations (2g) of cast solutions. Conditions of the cross-linking reactions were kept identical 0.5M H_2SO_4, 10 min. The experiments using the chitosan membranes were carried out at room temperature and the effect of evaporation time was examined by measuring the separation index of the chitosan membranes. The results are given in Table 8 in appendix.

Figure 4.5 and Figure 4.6 shows the effects of evaporation time on flux and the separation factor. The highest flux was 2549 g/m^2h at 30minutes of evaporation time and the lowest flux is 321 g/m^2h at 210 minutes of evaporation time. It can be seen in Figure 4.5 that the flux decreases as the evaporation time increases. In figure 4.4, the highest separation factor is 1170 at 120 minutes of evaporation time and the lowest separation factor is 120 at 30 minutes of evaporation time. From here, we can obtain that 120 minutes of evaporation time give the best separation factor in fabricating chitosan membrane. According to the dissolution–diffusion mechanism, the separation factor depends on the selective dissolution and selective diffusion. From the previous study, reported that the separation factor more strongly depended on selective dissolution than on selective diffusion (Nakatsuka, 1992). From the point of view of surface science, a change in the structure of materials causes a change in selective dissolution. It is known that the diffusion rates depend on the degree of density of the membrane. The low flux and high separation factor seem to suggest a significant change in the membrane structure. The structure at 120 minutes of evaporation time is the perfect structure for separating water-oil mixture because at this time, it gives the highest separation factor.
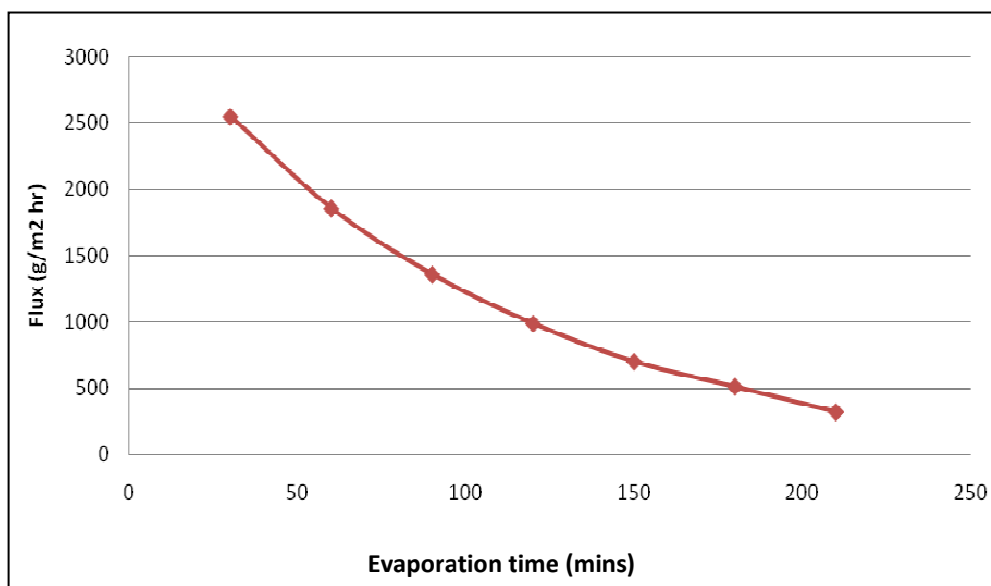
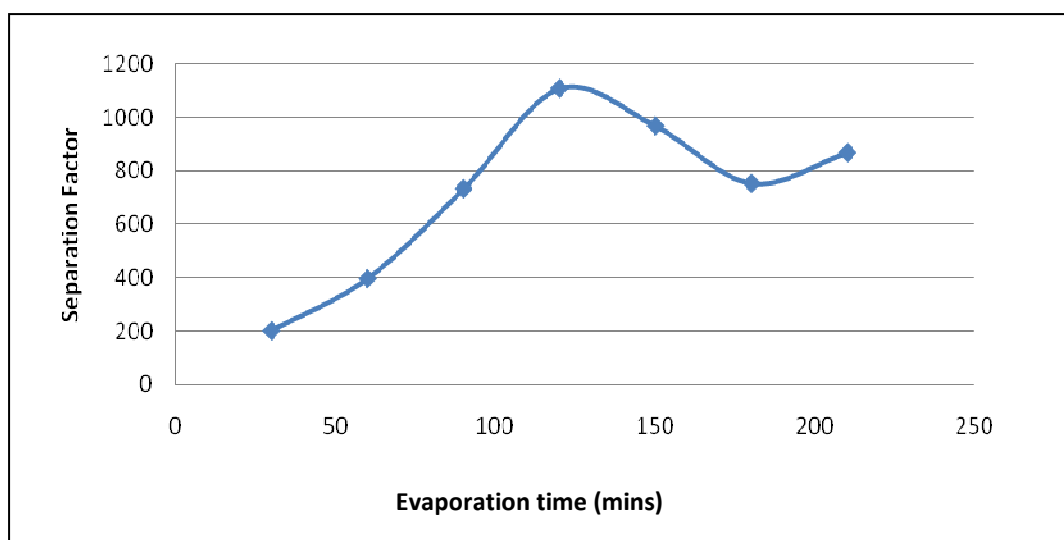Figure 4.5: Graph flux versus evaporation time

Figure 4.6: Graph separation factor versus evaporation time

As can be seen from Figure 4.7, the separation index for the feed solutions reaches the maximum value when the evaporation time is 120 minutes. The separation index value at 120 minutes is 1092609. These experimental results clearly demonstrate that the optimum evaporation time for the best performance of chitosan membrane is at 120 minutes. When the evaporation time is higher than 120 minutes, the separation factor slightly decreases. This is because the structure of the membrane becomes slightly looser when the evaporation time is higher than 120 minutes. Based on the results obtained below, it can be concluded that the evaporation time at 120 minutes leads to the densest structure of chitosan membranes.
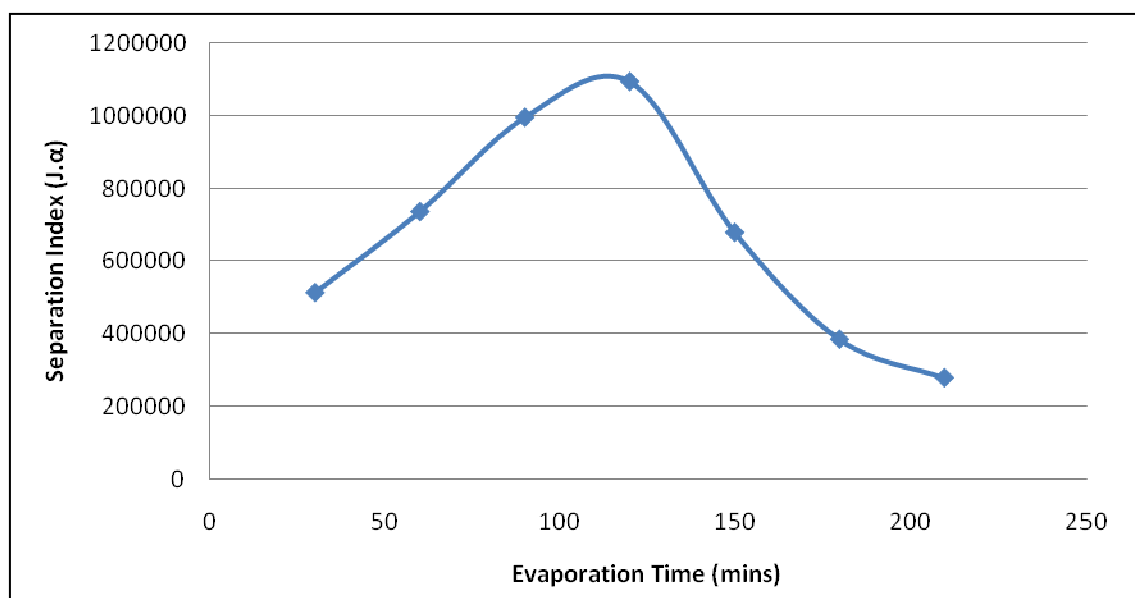

Figure 4.7: Graph separation index versus evaporation time

4.4 Problems Encountered While Doing Experiment

There are a lot of problems occur while doing this experiment. The main problem that affects the experiment was the lack of chemicals in the lab. Tetraethoxysilane is the best cross linking agent to make the membrane become stronger and elastic. Because of the delay in delivering the tetraethoxysilane, the whole chitosan membrane preparation process had to be changed. The process have been done by using H_2SO_4 as the cross linking agent. The consequence of changing the cross linking agent, the membrane had lost it flexibility and elasticity. We have to handle the membrane very carefully because it would easily tear. Figure 4.8 shows example of chitosan membrane after soaked in H_2SO_4.

Figure 4.8: Chitosan Membrane

The thickness of the membrane solution while pouring it in Petri dish also gives a big problem. A series of test for the solution thickness had been done as shown in Figure 4.9. The figures show the different thickness of the chitosan solutions before letting the solution to evaporate to become chitosan membrane. At the end of the evaporation process, Solution with 2cm thickness had been selected because the perfect quality of the membrane required to do the filtration of water-oil is achieved with 2cm thickness.

Figure 4.9: Test for Thickness of Chitosan Solution

Letting the evaporation process of chitosan solution in the oven is one of the main process that should be handled carefully. The temperature in the oven must be monitored frequently. The optimum temperature for the evaporation process is 333K. The solution heated by using higher temperature, the membrane will stick strongly with the Petri dish and it s very hard to separate them. Using high temperature also will cause big holes in the membrane surface which will affect the filtration process. Figure 4.10 shows the overheated chitosan membrane.

Figure 4.10: Over Heated Chitosan Membrane

The stirring process while preparing the chitosan solution using magnetic stirrer was not effective because the solution of the chitosan has high viscosity. Magnetic stirrer had been changed to paddle stirrer (Figure 4.11). The stock of chitosan flake in

the lab contains some other materials and it reduced the efficiency of the membrane to separate the water-oil mixture. Pouring the chitosan solution straight away on the Petri dish caused problem while taking it out. As the solution, we must wrap the Petri dish with aluminum foil before pouring the solution into it (Figure 4.12). So that, it will be easy to take off the membrane after evaporation process and it will be easy to cut them into the shape we want.
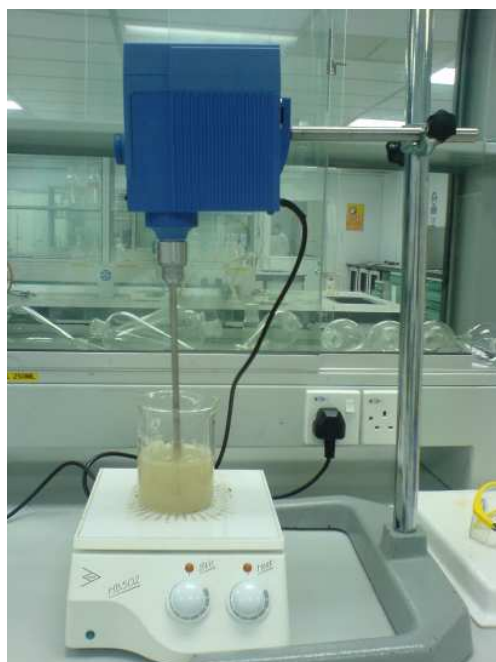

Figure 4.11: Paddle Stirrer

Figure 4.12: Petri Dish Covered with Aluminum Foil

CHAPTER 5

CONCLUSION

The present study clearly demonstrated the effect of evaporation times while preparing chitosan membranes. The perfect evaporation period while fabricating chitosan membrane is obtain at 120 minutes of evaporation time. Evaporation at this period if time gives the highest separation index and highest separation factor which is 1092609 for separation index and 407 for separation factor. From these values we can conclude that the perfect structure of the chitosan membrane to separate oil from wastewater is obtained at 120 minutes of evaporation time. Manufacturing plants' as well as the oil waste hauling industries' efforts to meet environmental regulations if they utilize of membrane filtration combined with chitosan membrane. The availability of new membrane material and technology make it possible to treat the more difficult streams with very successful and economic results.

It is recommended for the future researcher to do a detail analysis in choosing the perfect heating temperature, concentration of H_2SO_4 and concentration of chitosan. These entire factors must be tested using more samples with different values so that we could identify the perfect condition while fabricating the chitosan membrane. Other than that, it is also recommended to conducting a research on the structure of the membrane after fabricate the membrane. By doing this we can identify the best pore size of the membrane n separating water-oil mixtures.

REFERENCES

Ahmad Faiz. (1986). Chromatography of phosphorylases on *N*-acylchitosan gels, Journal of Membrane Technology.86(3):781.

Koros,P.(1984), Chitin, Chitosan and Related Enzymes, Academic Press, New York,

Miya,M. Iwamoto,R. Yoshikawa,S. and Mima, S.(1982). Feasibility of Chitosan Membrane for Ultrafiltration, Kobunshi, Ronbunshu. 39(2):649.

Mohr,C.(1986). Chitin in Nature and Technology, Plenum Press, New York,

Moulder,Y. (1991). Pervaporation dehydration of isopropanol with chitosan membranes. Journal of Membrane Science.53 (1):124.

Nakatsuka,S. and Andrady,A. (1992), Permeability of vitamin B-12 in chitosan membranes. Effect of crosslinking and blend with poly(vinyl alcohol) on permeability, Journal of Polymer science.44(1):17.

Nunes,T. and Ohsumi,Y.(2003), Studies on syntheses and permeabilities of special polymer membranes. 35. Preparation and permeation characteristics of chitin membranes, Journal of Polymer 22(3): 1155.

Younssi, Y. (1994).Alkaline phosphate and pepsin immobilized in gels, Journal of Biotechnology. 21(1): 711.

Zulia Zakaria.(1994).Chitosan membranes for reverse osmosis application.
Journal of Food Science. 49(1): 91.

Zhang,s. and Drioli,E, (1995). Pervaporation Membranes. Journal of Separation
Science.30 (1):1.

APPENDICES

Appendix A- Example Calculation

A.1   Flux

$$J = \frac{W}{A \times t}$$

$= $ 4.81 g / (0.00283m2 x 2 h)

$= $ 739 g / m^2 h

A.2   Separation Factor

$$\alpha = \frac{c_{1p}/c_{2p}}{c_{1f}/c_{2f}}$$

$= $ (17.45 / 5.2)/ (0.31/82.3)

$= $ 891

A.3   Separation Index

$$PSI = J \times \alpha$$

$= $ 739 g/ m^{2}h x 891

$= $ 658,849 g/m^{2}h

Appendix B – Table of Result

Table 1: The Result of Effect for Different H_2SO_4 Concentration

Concentration of H_2SO_4 (M)	Mass of Permeate (g)
0.5	4.18
1.0	2.67
2.0	0.45

Table 2: The Result of Effect for Different H_2SO_4 Concentration

Concentration of H_2SO_4 (M)	C_{1P} (mg/L)	C_{2P} (mg/L)	C_{1F} (mg/L)	C_{2F} (mg/L)
0.5	17.45	5.2	0.31	82.3
1.0	24.96	3.7	0.31	82.3
2.0	37.42	2.1	0.31	82.3

Table 3: Effect of concentration of H_2SO_4 on performance of chitosan membranes

Concentration of H_2SO_4 (M)	Flux (J) (g/m^{2}h)	Separation Factor (α)	Separation index (PSI) (J. α)
0.5	739	891	658,849
1.0	472	1791	845,352
2.0	79	4731	373,749

Table 3: Result of Effect for Different Chitosan Concentration

Amount of Chitosan (g)	Mass of Permeate (g)
1	2.30
2	2.33
3	2.36

Table 4: Effect of Chitosan Concentration in membrane Fabrication

Amount of Chitosan (g)	Flux (J) (g/m^{2}h)
1	406
2	411
3	416

Table 5: Result of Effect for Different Heating Temperature

Heating Temperature	Mass of Permeate (g)
303	1.97.
333	2.01
353	2.12

Table 6: Effect of heating temperature in membrane Fabrication

Heating Temperature	Flux (J) (g/m^2h)
303	348
333	355
353	374

Table 7: Result of Effect for Different Evaporation Time

Evaporation time (minutes)	Mass of Permeate (g)	C_{1P} (mg/L)	C_{2P} (mg/L)	C_{1F} (mg/L)	C_{2F} (mg/L)
30	14.43	6.10	7.9	0.32	83.3
60	10.50	10.80	7.1	0.32	83.3
90	7.69	17.70	6.3	0.32	83.3
120	5.59	22.10	5.2	0.32	83.3
150	3.97	18.57	5.0	0.32	83.3
180	2.89	12.12	4.2	0.32	83.3
210	1.82	12.98	3.9	0.32	83.3

Table 8: Effect of evaporation times on performance of chitosan membranes

Evaporation time (minutes)	Flux (J) (g/m^{2}h)	Separation Factor (α)	Separation index (PSI) (J. α)
30	2549	201	512349
60	1856	396	734976
90	1358	732	994056
120	987	1107	1092609
150	701	967	677867
180	511	752	384272
210	321	867	278307

Appendix C – Physical Properties

C.1 – Physical Properties of Sulfuric Acid (H_2SO_4)

Properties of Sulfuric acid	
Molecular formula	H_2SO_4
Molar mass	98.078 g/mol
Appearance	clear, colorless, odorless liquid
Density	1.84 g cm^{-3}, liquid
Melting point	10 °C, 283 K, 50 °F
Boiling point	290 °C, 563 K, 554 °F (bp of pure acid. 98% solution boils at 338°C)
Solubility in water	fully miscible (exothermic)
Viscosity	26.7 cP at 20°C

C.2 – Physical Properties of Acetic Acid

Properties of Acetic acid	
Molecular formula	CH_3COOH
Molar mass	60.05 g/mol
Appearance	Colourless liquid or crystals
Density	1.049 g·cm^{-3} (l) 1.266 g·cm^{-3} (s)
Melting point	16.5 °C (289.6 K, 61.6 °F)
Boiling point	118.1 °C (391.2 K, 244.5 °F)
Solubility in water	Fully miscible
Acidity (pK_a)	4.76 at 25 °C