FABRICATION OF POLYSULFONE MEMBRANE, THE EFFECT OF ADDITIVE POLYVYNIL PYRROLIDOLE (PVP) ON MEMBRANE FLUX AND REJECTION

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“I declare that this thesis is the result of my own research except as cited references. The thesis has not been accepted for any degree and is concurrently submitted in candidature of any degree.”

Signature	:………………………….
Name of Candidate	:…………………………
Date	:…………………………

DEDICATION

Special dedication to my beloved father, mother,
brothers, sisters and all my friends……..

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Bismillahirrahmanirrahim

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ABSTRACT

In the previous research, the characteristics of microfiltration membranes showed by polysulfone membrane, the membrane was fabricated from the mixing of polysulfone (Psf) powder, n-Methyl Pyrrolidone (NMP) as the solvent and polyvinyl pyrrolidone (PVP) as an additive. The objective of that research is to find the optimum of membrane in flux and rejection by changing additive percentage. The percentage of polyvinyl pyrrolidone is the manipulative substance. The percentages of polyvinyl pyrrolidone were increased until 14 % of the solution. The phase inversion technique was used in fabrication process. The average pores size existing on the membrane surfaces are 0.25 μm, and the numbers of pores depends on the additive composition. The average of pore size will increase when the additive more than 40 % of additive.

ABSTRAK

.Dalam kajian lepas, sifat-sifat membran microfiltration ditunjukkan oleh membran polysulfone. Membran polysulfone dihasilkan daripada campuran serbuk polysulfone , n-Methyl pyrrolidone (NMP) sebagai pelarut, dan polyvynil pyrrolidone (PVP) sebagai bahan tambahan. Objektif utama kajian ini ialah untuk mencari keadaan yang optimum untuk membran bagi flux dan penyingkiran. Dengan mengubah peratusan PVP. Peratusan PVP merupakan pemboleh ubah dalam kajian ini, dan peratusan PVP akan ditingkatkan sehingga 14% daripada larutan membran polysulfone. Teknik penyongsangan fasa, merupakan proses penukaran fasa sesuatu bahan, daripada pepejal kepada cecair dan kembali semula dalam bentuk pepejal. Purata saiz liang pada permukaan membran adalah 0.25 µm dan jumlah liang bergantung kepada komposisi polyvynilpyrrolidone. Macropores (2µm) akan terbentuk pada permukaan membran, apabila larutan campuran polysulfone mengandungi lebih 40% polyvynilpyrrolidone.

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LIST OF ABBREVIATIONS

PVP	=	Polyvinyl Pyrrolidone
MUSC	=	Millipore stirred ultrafiltration cells.
Uv-vis	=	Uv-visible spectrophotometer.
T	=	Temperature
t	=	Time
P	=	Pressure
$ml/cm^2.s$	=	milliliter per (centimeter square multiple second)

Chapter 1

1.1 INTRODUCTION

Membrane is a device in separation process since 1748 and until now, we have many types of membranes, for example polymer membranes, metal membrane, ceramic membranes and in the same time, the differences of pore size of membrane will make differences classification of membranes, like microfiltration, ultrafiltration , reverses osmosis and etc. The most important property of membranes is their ability to control the rate of permeation of different species. In the membrane's separation process, we have permeate and retentate. Permeate are separated because of the differences in the solubility of the materials in the membranes and the differences in the rates at which the materials diffuse through the membranes.

1.2 OBJECTIVE

The main objective for this experimental study is, to produce polysulfone membranes and to determine the effect of polyvinyl pyrrolidone (PVP) on flux and rejection for polysulfone membranes.

1.3 SCOPE

i) To fabricate polysulfone membrane with polyvinyl pyrrolidone (PVP) as additive.

ii) To study the optimum percentage of polyvinyl pyrrolidone (PVP) on membrane performance (flux and rejection)

iii) To characterize membrane by using color solution.

CHAPTER 2

ARTICLE REVIEW

2.1 HISTORICAL DEVELOPMENT OF MEMBRANE

Systematic studies of membrane phenomena can be traced to the eighteenth Century philosopher scientists. Abbe Nolet, for example, coined the word osmosis to describe permeation of water through a diaphragm in 1748. Through the 19th and early 20th centuries, membranes had no industrial or commercial uses. But, membrane was used as laboratory tools to develop physical and chemical. For example, the measurement of solution osmotic pressure made with membranes by Traube and Pfeffer were used to the van`t Hoff in 1887 to develop his limit law, explaining the behavior of ideal dilute solutions. (Baker, 2000)

Early membrane investigators experimented with every type of diaphragm available to them, such as bladders of pigs, cattle or fish and sausage casings made of animal gut. Bechhold devised a technique to prepare nitrocellulose membranes of graded pore size, which he determined by a bubble-test method in 1907. Other later workers, particularly Elford, Zsigmondy and Bachman, and Ferrys, improved on Bechhold’s technique. By the early 1930s micro porous collodion membranes were commercially available. During the next 20 years this early microfiltration membrane technology was expanded to other polymers, particularly cellulose acetate, and membranes found their first significant applications in the filtration of drinking water samples at the end of World War II. (Baker 2000)

European countries, especially Germany, they have many problem about water, water pollution, disease for drinking water and etc. This problem was affecting the water supplies for large communities, for drinking water and for using everyday. Us army sponsored many of capital for research in developing filters and exploited by the Millipore Company and they can produces the largest microfiltration membrane. In early of developing membrane technology, only a few and small laboratories used the membrane.

The membrane technology was developing successful in 20 years, from 1960 until 1980. The original Loeb- Sourirajan membrane technology and other process were developed for making ultra thin, high performance membrane. Interfacial and multilayer composite casting and coating was used. In that time, to make membrane with thin 0.1 pm is impossible accept a number of company.

Methods of packaging membranes into large-membrane-area spiral-wound. Hollow-fine-fiber, capillary and plate-and-frame modules were also developed, and advances were made in improving membrane stability. As a result, by 1980 microfiltration. Ultrafiltration, reverse osmosis and electrodialysis were all established processes with large plants installed around the world. The principal milestone in the 1980s was the emergence of industrial membranes gas separation processes. The first major development was the Monsanto Prism membranes for Hydrogen separation, introduced in 1980s, this information are in A I Schafer (2005).

2.2 BASIC CONCEPT OF MEMBRANE

The important things of membrane are their ability to control the rate of permeation of different species. It has two models in mechanism of permeation and Figure 2.1 (a) and 2.1 (b) show mechanism of model. One model is the solution-diffusion model, in which permeate dissolve in the membranes material and then through the membrane down a concentration gradient. The permeants are separated because of the differences in the solubilities of the materials in the membrane and the differences in the rate at which the material diffuse through the membrane. The other model is the pore flow model, in which permeants are transported by pressure-driven convective flow through tiny pores. In Leos J.Zeman said, separation occurs because one of the permeants is excluded (filtered) from some of the pores in the membrane through which other permeants move. Both models were proposed in the 19th century, but the pore flow model, because it was closed to normal physical experiences, was more popular until mid-1940s.

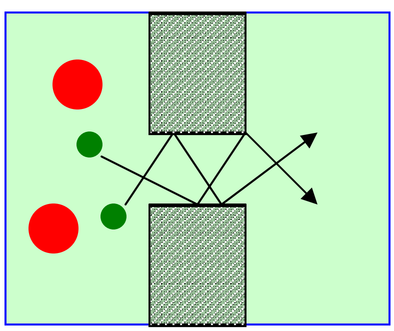

Figure 2.1 (a) Microporous membranes separation by molecular filteration

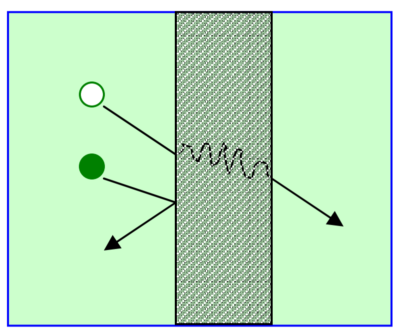

Figure 2.1 (b) Dense solution-diffusion membranes separate because of diffusion in the solubility and mobility of permeants in the membranes material

(Source: Baker 2000)

Membrane also known as selective barrier between two phases that have thin barrier that permits selective mass transport and the phase that acts as a barrier to prevent mass movement, but allows restricted and / or regulated passage of one or more species.

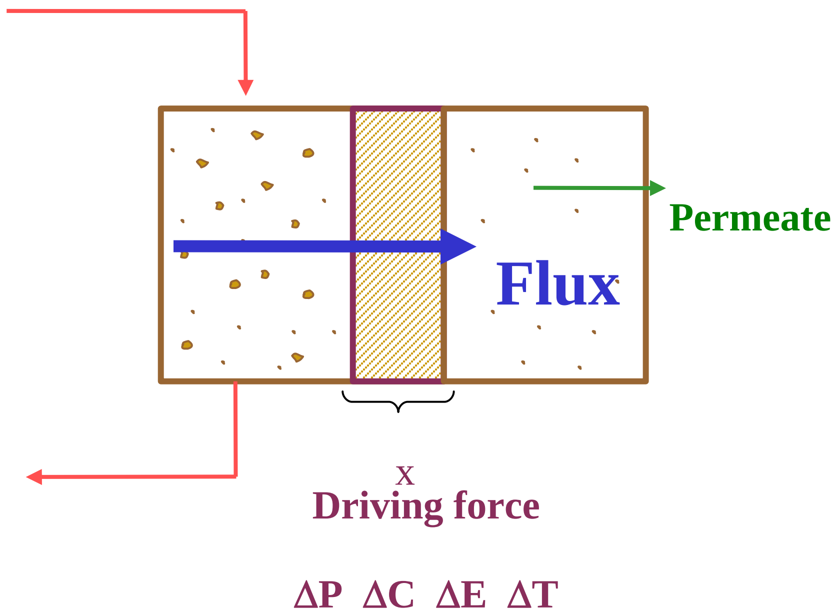

Figure 2.2 The basic membrane separation process.

(Source: Lecture note, Membrane technology, 2005)

We can see more clearly in Figure 2.2 for some basic understanding on membrane process.

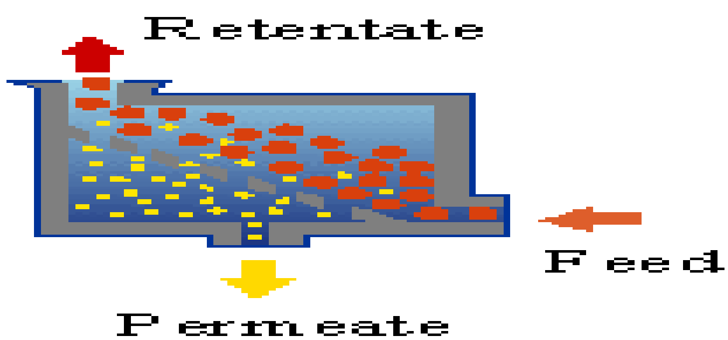

Figure 2.3: shown more clearly the membrane separation process

(Source: Lecture note, Membrane technology. 2005)

We have 4 separation processes according to their pore size diameter and there are reverse osmosis, ultrafiltration, microfiltration, and conventional filtration Membrane was be classified according to their pore size diameter refer Figure 2.3. The pore diameter size for reverse osmosis is 1A to 10A, Ultrafiltration is from 10A to 1000A, microfiltration is from 1000A to 10micrometer, and lastly is conventional filtration that is from 10micrometer to 100micrometer.

2.3 CLASSIFICATION OF FILTRATION MEMBRANE

There are some of levels for filtration membrane. Each of them has different character such as mechanisms of separation, physical morphology and chemical nature. Generally, there are 3 main classifications of filtration membrane. There are microfiltration membrane, ultrafiltration membrane, and reverse osmosis filtration membrane. Table 2.1 show the technically relevant membrane separation processes, their operating principles, and their application.

Separation Process	Membrane Type Used	Applied Driving Force	Mode of Separation	Applications
Microfiltration	symmetric porous structure, pore radius 0.05-5 μm	hydrostatic pressure 0.5-4 bar	filtration (size exclusion)	water purification, sterilization
Ultrafiltration	asymmetric porous structure, pore radius 2-10 nm	hydrostatic pressure 1-10 bar	filtration (size exclusion)	Separation & fractionation of molecular mixtures
Diafiltration	asymmetric porous structure, pore radius 2-10 nm	hydrostatic pressure 1-10 bar	filtration & dialysation (size exclusion)	purification of molecular mixtures artificial kidney
Reverse osmosis	asymmetric skin-type solution-diffusion structure	hydrostatic pressure 10-100 bar	solution-diffusion mechanism	sea & brackish water desalination
Dialysis	Symmetric porous or gel-type	concentration gradient	diffusion	artificial kidney

	structure			
Electrodialysis	symmetric ion-exchange membrane	electrical potential	migration Donnan-exclusion	water desalination
Donnan Dialysis	symmetric ion-exchange membrane	concentration gradient of individual ions	diffusion Donnan exclusion	water softening
Electrodialytic Water Dissociation	bipolar membrane	electrical potential	migration, Donnan-exclusion	acid & base production from salts
Gas Separation	homogeneous symmetric structure	vapor pressure gradient	solution-diffusion	oxygen/nitrogen separation
Pervaporation	homogeneous symmetric structure	vapor pressure gradient	solution-diffusion	separation of azeotropic mixtures
Vapor Permeation	homogeneous symmetric structure	vapor pressure gradient	solution-diffusion	recovering of organic vapors from air
Membrane Distillation	symmetric porous hydrophobic structure,	vapor pressure gradient	diffusion	liquid/solid separation
Membrane Contactores	symmetric porous structure, or liquid membrane	chemical potential gradient	diffusion solution	Solvent extraction

Table 2.1: Technically relevant membrane separation processes, their operating principles, and their application.

(Source: Lecture note, Membrane technology. 2005)

2.3.1 Microfiltration Membrane

Microfiltration (MF) with pore size between 0.1 and 10µm ,as figure 2.4 refers to filtration processes that use porous membranes to separate suspended particles. Thus, microfiltration membranes fall between ultrafiltration membranes and conventional filters. Like ultrafiltration, microfiltration had its modern origins in the development of collodion (nitrocellulose) membranes in the 1920s and 1930s.

In 1926 Membranes filter GmbH was founded and began to produce collodion microfiltration membranes commercially. (Baker, 2000)

The water treatment activities are used microfiltration membranes. The objectives of treatment is used to culture microorganism in drinking water, this remain a significant application. The test was developed in Germany during World War II, as a rapid method to monitor the water supply to contamination.

Microfiltration membranes are often used in applications for which penetration of even one particle or bacterium through the membrane can be critical. Thus, the membrane integrity, the absence of membrane defects or oversized pores, is extremely important. From Leos J.Zeman, the characteristics of pore size for microfitration are a problem for manufactories. Most microfiltration membranes are depth filter. The average pore diameter of these membranes appears to be about 5 µm, yet the membranes are complete filters for particles or bacteria of about 0.5-µm diameter. The ability of membranes to filter bacteria from solutions depends on the pore size of the membrane, the size of the bacteria being filtered, and the number of organisms used to challenge the membrane.

Applications examples include:

- Water treatment (filtration of particulates and microorganisms).
- Clarification /Sterilization of beer and wine
- Cell recovery from broths.
- Removal of bacteria from milk and other food products.
- Removal fat and oil.
- Fractionation of proteins.
- Pharmaceutical sterilization.

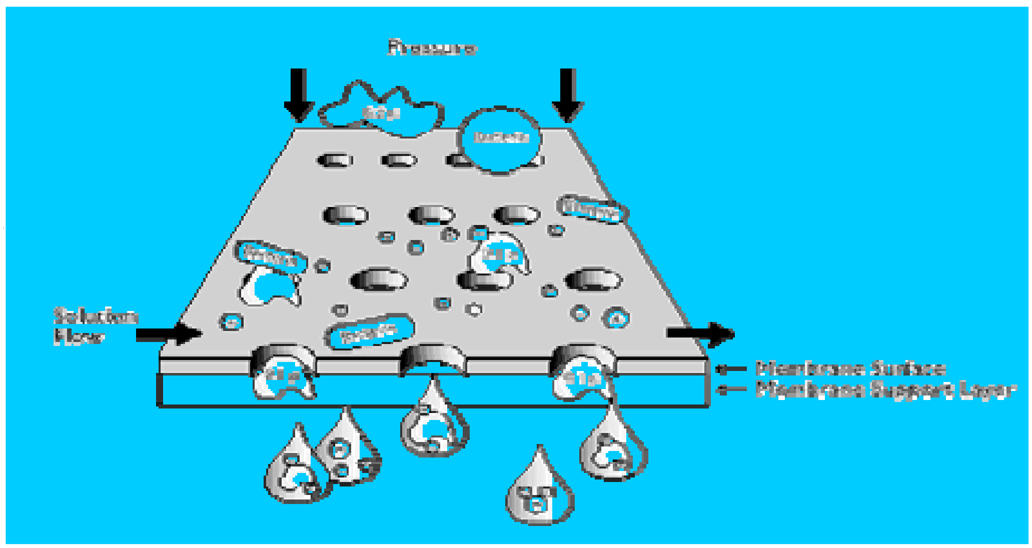

Figure 2.4: Microfiltration Processes

(Source: Lecture note, Membrane Technology, 2005)

2.3.2 Ultrafiltration Membrane

Ultrafiltration which have the average pore diameter of membranes from 10 to 1000 Å the pressure requirements are moderate at 1-10 bar as figure 2.6. Using a porous ultrafiltration membrane to separate water and microsolutes from macromolecules and colloids. The first synthetic ultrafiltration membranes were prepared by Bechhold from collodion (nitrocellulose). Bechhold was probably the first to measure membrane bubble points and he also coined the term *ultrafilter*. By the mid-1920s, collodion ultrafiltration and microfiltration membranes were commercially available for laboratory use.

Collodion membranes were widely used in laboratory studied, no industrial application existed until 1960s. (Baker, 2000)

From Loeb-Souriranjan process with anisotropic structures is the concept in Ultrafiltration. They have a finely porous surface layer or skin supported on a much more open microporous substrate. The finely porous surface layer performs the separation; the microporous substrate provides mechanical strength. The membranes discriminate between dissolved macromolecules of differences sizes and are usually characterized by their molecular weight of the globular protein molecule that is 90 percent rejected by the membranes.

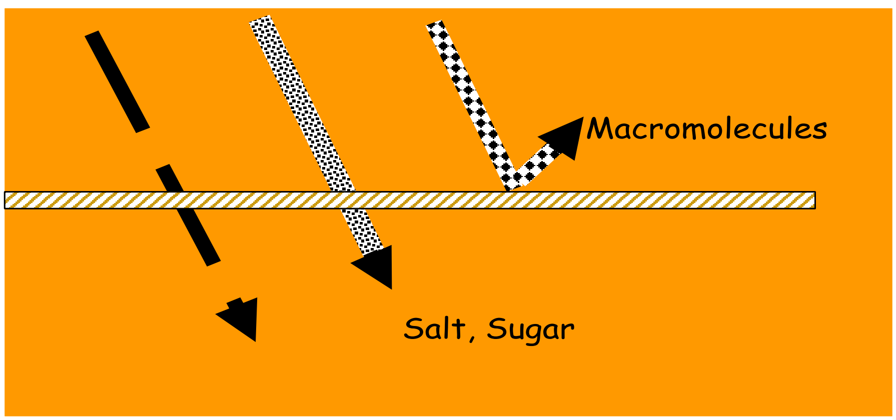

Figure 2.5: Ultrafiltration Membrane Process

(Source: Lecture note, Membrane Technology, 2005)

2.3.3 Reverse Osmosis Filtration Membrane

Many company of drinking water in our country used the concept of Reverse Osmosis (RO). Reverse Osmosis (RO) is a process for desalting water that uses membranes that are permeable to water but essentially impermeable to salt. Pressurized water containing dissolved salts contacts the feed side of the membrane; water depleted of salt is withdrawn as a low-pressure permeates. The ability of membranes to separate small solutes from water has been known for a very long time. Pfeffer, Traube and other studied osmoric phenomena with ceramic membranes as early as the 1950s. (Leos J.Zeman)

In 1931the process was patented as a method of desalting water and the term reverse osmosis was coined. This Reverse Osmosis has the smallest pores 0.0001- 0.001 microns and has the highest-pressure requirement 10-100 bar. Figure 2.6 show the process of reverse Osmosis Membrane.

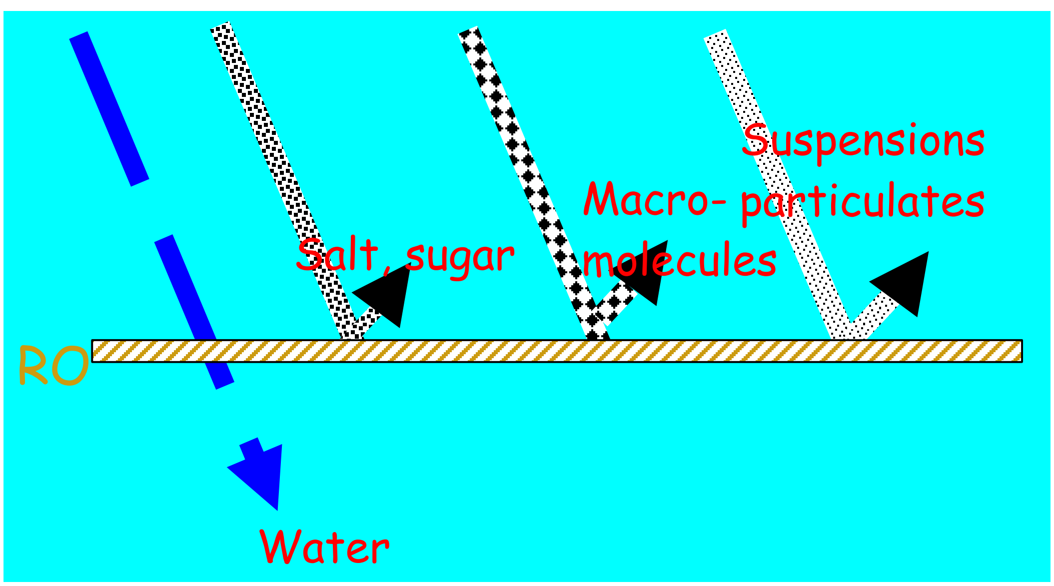

Figure 2.6: Reverse Osmosis Filtration membrane Process.

(Lecture note, Membrane Technology. 2005)