HUMIC ACID REM(... LTRATION (NF)

MEMBRANE SYN ... AMINE (TEOA)

FADZILAH BINTI ABDUL LATIF

A Thesis submitted in fulfilment of

the requirements for the award of the degree of

Bachelor of Chemical Engineering

Faculty of Chemical & Natural Resources Engineering

UNIVERSITI MALAYSIA PAHANG

FEBRUARY 2013

HUMIC ACID REMOVAL BY POLYESTER NANOFILTRATION (NF) MEMBRANE SYNTHESIZED FROM TRIETHANOLAMINE (TEOA) MONOMER

ABSTRACT

Humic substances present in water sources affect the water quality causing undesirable color and taste, besides serving as food for bacterial growth in water distribution system. In order to treat this kind of natural organic matter, Nanofiltration (NF) Polyester membrane was produced by studying the effect of interfacial polymerization reaction time at constant monomer concentration. The thin film composite membranes were synthesized through interfacial polymerization with monomer concentration of 4% w/v of triethanolamine (TEOA) at different reaction time. The TEOA which was aqueous solution reacted with organic solution of trimesoylchloride (TMC) to produce new layer polyester on top of polyethersulfone (PES) microporous support. The thin film composite membrane was characterized in term of water flux, permeability and also solute rejection. The performances of NF membrane in terms of humic acid and NaCl rejection were increased as the reaction time increased. The performances in terms of flux and permeability showed that the flux and permeability were decreased as the reaction time increased. The longer reaction time had increased the layer thickness on the surface of the NF membrane which resulting the performances of the membranes.

PENYINGKIRAN HUMIK ACID MENGGUNAKAN MEMBRAN POLIESTER NANO-PENURASAN SINTESIS DARIPADA MONOMER TRIETANOLAMIN

ABSTRAK

Bahan-bahan humus yang hadir di dalam sumber air menjejaskan kuailiti air dengan menyebabkan warna dan rasa yang tidak diingini, selain digunakan sebagai makanan untuk pembesaran bakteria di dalam sistem pengagihan air. Untuk merawat bahan organic semulajadi ini,membran poliester Nano-penurasan dihasilkan dengan mengkaji kesan masa tindakbalas proses pempolimeran permukaan pada kepekatan monomer yang sama. Membran komposit filem nipis telah disintesis melalui process pempolimeran antara permukaan dengan 4%w/v kepekatan trietanolamin (TEOA) monomer pada masa tindakbalas yang berbeza. TEOA yang merupakan larutan akueus telah bertindakbalas dengan larutan organic trimesilklorida (TMC) untuk menghasilkan lapisan poliester baru di atas permukaan membran polietersulfon (PES). Membran TFC dicirikan berdasarkan fluk air, kebolehtelapan dan penyingkiran bahan larut. Kebolehan membran NF dari segi humik acid dan penyingkiran NaCl meningkat apabila masa tindakbalas bertambah. Kebolehan dari segi fluk dan kebolehtelapan menunjukkan bahawa fluk dan kebolehtelapan menurun apabila masa tindakbalas bertambah. Masa tindakbalas yang yang lebih lama telah meningkatkan ketebalan lapisan pada permukaan membran yang mengakibatkan kebolehan membran juga meningkat.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

Cp	Concentration of permeate
Cf	Concentration of feed
P_m	Permeability
J	Permeate flux
L	Liter
m	Meter
ΔP	Filtration pressure
R	Rejection
Δt	Filtration time
V	Volume

LIST OF ABBREVIATIONS

FTIR	Fourier Transform Infrared Spectroscopy
IP	Interfacial Polymerization
MF	Microfiltration
NaOH	Sodium Hydroxide
NF	Nanofiltration
NOM	Natural Organic Matter
PES	Polyethersulfone
RO	Reverse Osmosis
TEOA	Triethanolamine
TFC	Thin Film Composite
TMC	Trimesoylchloride
UF	Ultrafiltration

CHAPTER 1

INTRODUCTION

1.1 Research Background

Humic acid constitute a major class of natural organic metal (NOM) present in natural water such as lakes, groundwater and rivers. The substances affect water quality which causing undesirable color and taste, serving as food for bacterial growth in water distribution system binding with heavy metals to yield high concentration of these substances and enhance their transportation in water (Jacangelo *et al.*, 1995). It also reacts with chlorine in water treatment to produce trihalomethane which is known as human carcinogens. There are some processes developed to remove humic substances such as chemical coagulation, adsorption, and membrane separation.

Various types of membrane with different specifications make it suitable for specific industrial separation demands. The membrane characteristic is partially permeable which is allows water to flow through, while catches the suspended solids and other substances when a driving force is applied across it. Nanofiltration (NF) is a membrane separation technique which is operates on the principle of diffusion and it is developed based on reverse osmosis (Petersen, 1993). As found by Van Der Bruggen & Vandecasteele (2003), NF membrane is suitable to remove the pollutants from groundwater or surface water and also applied for the combined removal of natural organic metals, micropollutants, viruses and bacteria. As in recent years, it is apparent that membrane separation processes, which are reverse osmosis and nanofiltration are becoming more popular for their ability to produce a high quality of drinking water (Taylor & Jacobs, 1996; Wilbert *et al.*, 1993).

1.2 Problem Statement

The high demand for clean potable drinking water has led to the increasing development of membrane technology. As found by Duran & Dunkelberger (1995), the drinking water has been the major application area for nanofiltration (NF) membrane and the reason is that NF membranes were essentially developed for softening. Humic substances present in natural water such as lakes, groundwater and rivers affect water quality which causing undesirable color and taste, serving as food for bacterial growth in water distribution system (Jacangelo *et al.*, 1995). Hence, it is desirable to minimize the presence of humic substances in drinking water.

1.3 Research Objectives

The objectives of this research are to produce Nanofiltration (NF) Polyester membrane for natural organic matter (NOM) removal and to study the effect of reaction time on the production of thin film composite NF and its effects on the NOM and salt (NaCl) removal performance.

1.4 Scope of Proposed Study

In order to achieve the objectives, the scope have been identified as follows:

i. Production and characterization (flux and permeability) of thin film NF composite by interfacial polymerization method using 4%w/v of triethanolamine (TEOA) as monomer at different reaction time (15, 25 and 35 min)
ii. Performance of salt removal (NaCl)
iii. Removal of NOM by the synthesized NF membrane

1.5 Significance of Proposed Study

Nowadays, nanofiltration (NF) membranes are widely known as the best technology and energy efficient processes for production of potable water. The NF process becomes more important in water treatment for domestic and industrial water supply. The membrane technology which is applicable for environmental application can be applied in cleaning technology.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction to Membrane Process

A membrane is defined as a thin layer of material which acts as a semi-permeable barrier that allows some particles to pass through it, while hindering the permeation of other components (Silva, 2007). The capability of membrane to separate the substances is due to the driving force applied across the membrane. The elements of modern membrane science had been developed since the nineteenth and early twentieth centuries. The membrane had no industrial or commercial uses, but was used as laboratory tools to develop physical and chemical theories. During period of 1960 to 1980, there were a significant change in the membrane technology include interfacial polymerization and multilayer composite casting and coating in order to produce high performance membrane (Baker, 2004).

According to Jalil (2004), the membrane process plays important role in industrial fields, such as textile, food and beverages processing, pharmaceutical, environment, paper and as well as in water wastewater treatment process.

2.1.1 Key Developments in Membrane Technology

Emerging new technologies are often characterized by key discoveries providing a breakthrough by their application and same goes to the membrane science and technology. The seminal discovery for reverse osmosis was the anisotropic concept achieved with asymmetric cellulose acetate membranes by Loeb and Sourirajan (1962). Another breakthrough in reverse osmosis membrane development was expanded by Cadotte and Petersen (1981), who made the first really efficient composite membranes. There are many more key developments that had a significant effect on the development of membrane technology such as the preparation of the first efficient ion-exchange membranes by Juda and McRae (1953) and the first tailor-made ultrafiltration membranes by Michaels and Baker in 1968. A real breakthrough in the medical application of membranes was the first successful hemodialysis treatment of patients suffering from renal failure by Kolff and Berk (1944).

2.1.2 Advantages and Limitation in Membrane Process

Membrane process offers more benefits compared to the conventional filtration. In water desalination and purification the membrane processes compete directly with the more conventional water treatment techniques. However, compared to these conventional procedures membrane processes are very energy efficient, simple to operate and yield a high quality product. The membrane processes are usually more costly but generally provide a better product water quality. Membrane process shows the simplicity of operation which is the system is relatively less complex and less sophisticated. Membrane systems consume less energy since separation does not involve phase change. Thus the system driving force is mainly pressure provided by using pump. The separation using membrane is done physically thereby undesirable by products and no side reactions and no waste generation. Membrane processes are potentially better for environment since the membrane approach require the use of relatively simple and non-harmful materials. (Mustaffar, 2004).

The major disadvantage of membrane processes is that until today the long-term reliability is not completely proven. Membrane processes sometimes require excessive pretreatment due to their sensitivity to concentration polarization, chemical interaction with water constituents, and fouling. Membranes are mechanically not very robust and can easily be destroyed by a malfunction in the operating procedure. The concentration polarization and membrane fouling can reduce membrane performance, both selectivity and flux. The pH stability also is one of the membrane limitations of polymeric membrane. The pH stability of cellulosic membrane is in pH range of 4 to 8, while for polysulfone is pH 2 to 12. Membrane modules often cannot operate at much above room temperature. This is related to the fact that most membrane are polymer-based, and that a large fraction of these polymers do not maintain their physical integrity at much above 100°C.

2.2 Membrane Processes and Principle

2.2.1 Membrane separation process

Separation process is defined as a process at which a mixture of chemical is converted into two or more end-use products with respective (Soni *et al.*, 2009). There are various types of membrane separation process which are developed for specific industrial applications and they are classified according pore size and separation driving forces as shown in Table 2.1. The driven forces can be pressure, temperature, concentration, or electrical potential (Scott & Hughes, 1996).

Table 2.1 Classification of membrane processes according to their driving forces

Pressure difference	Concentration	Temperature differences	Electrical Potential Differences
Microfiltration	Gas separation	Thermo-osmosis	Electrodialysis
Ultrafiltration	Diffusion dialysis	Membrane distillation	Electro-osmosis
Nanofiltration	Pervaporation		Membrane electrolysis
Reverse Osmosis	Vapour permeation		

2.2.2 Pressure-Driven Membrane Process

Process such as Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF), and Reverse Osmosis (RO) involve pressure driving forces. These processes are appropriate to different size of molecules where the microfiltration differentiates the largest size of molecules and reverse osmosis differentiating the smallest molecules (Silva, 2007).

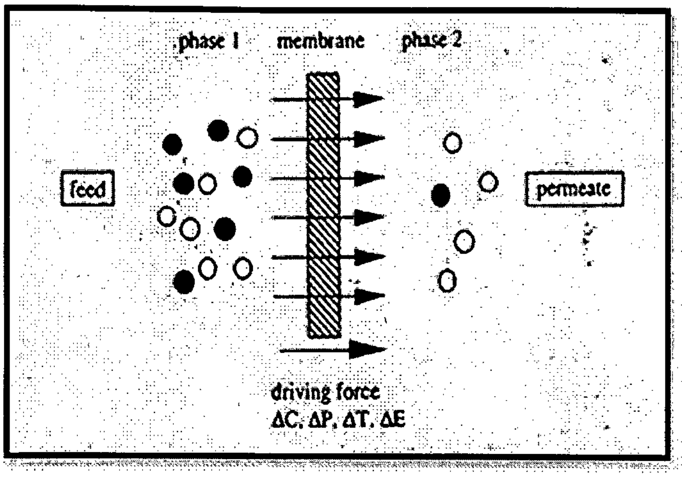

Figure 2.1 Schematic representation of a two-phase system separated by a membrane.
(Source: http://clxy.tjpu.edu.cn/mo/lljx/jj.files/image010.jpg).

Figure 2.1 represents the driving forces applied across the membrane from phase 1 to phase 2 which is separated by a semipermeable membrane. According to Mulder (2003), the membranes separation system separates an influent stream of feed into effluent streams of permeate. Permeate is the liquid which is going through the membrane. When a driving force is establish across the membrane, a flux will go through the membrane from the feed solution to the permeate side (Bier, 2007).

Membrane separation processes cover the entire size range which is from suspended solids to the mineral salts and small organics but it depends on the membrane process types. Four pressure driven membrane processes have been distinguished. MF is a membrane process with the largest pore size which is characterized by membrane pore size between 0.05μm and 2μm where the operating pressure applied is below 2bar. It can remove bacteria and "turbidity" from water treatment. UF is characterized by membrane pore size between 2nm and 0.05μm. The operating pressure is between 1bar and 10bar. It is used to remove microorganism and viruses, as well as to separate colloids like proteins from small molecules. NF is characterized by a membrane pore size between 0.5nm and 2nm and operating pressures between 5bar and 40bar. RO is characterized by a membrane pore size in the range of 0.0005microns. The operating pressure is between 7bar and 100bar. Figure 2.2 represents the pressure applied on the microfiltration, ultrafiltration, nanofiltration and reverse osmosis process and the difference permeate that pass through the membrane after the pressure is applied (Schafer, 2001).

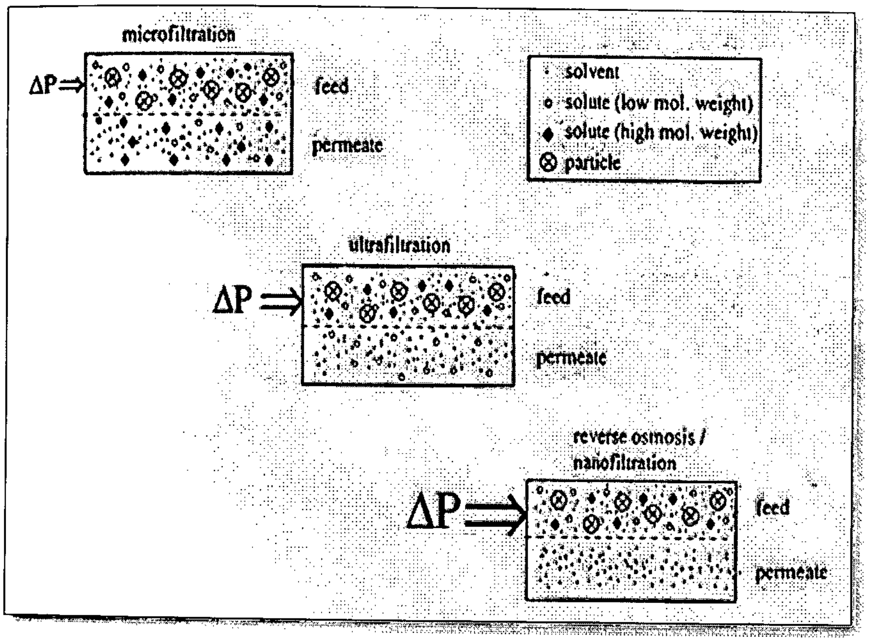

Figure 2.2 Schematic representation of microfiltration, ultrafiltration, nanofiltration and reverse osmosis
(Source: http://clxy.tjpu.edu.cn/mo/lljx/MGC.files/image048.jpg)

2.3 Nanofiltration Process

2.3.1 Nanofiltration membranes

Nanofiltration (NF) is a pressure driven membrane process which developed in the 1980s based on reverse osmosis (Zhang *et. al.*, 2003). The fundamental principle of nanofiltration membrane's technology is based on the pressure which applied across the semi-permeable membrane in order to separate soluble ions from water as shown in Figure 2.3. Although the process is similar to reverse osmosis in the way the ions were rejected, but nanofiltration membrane is more limited in size and molecular weight of the ions it does reject. It is applicable in separating dissolved components with molecular weight cut off (MWCO) of about 200-1000Da with molecular size of about 1 nm (Van Der Bruggen & Vandecasteele, 2003).

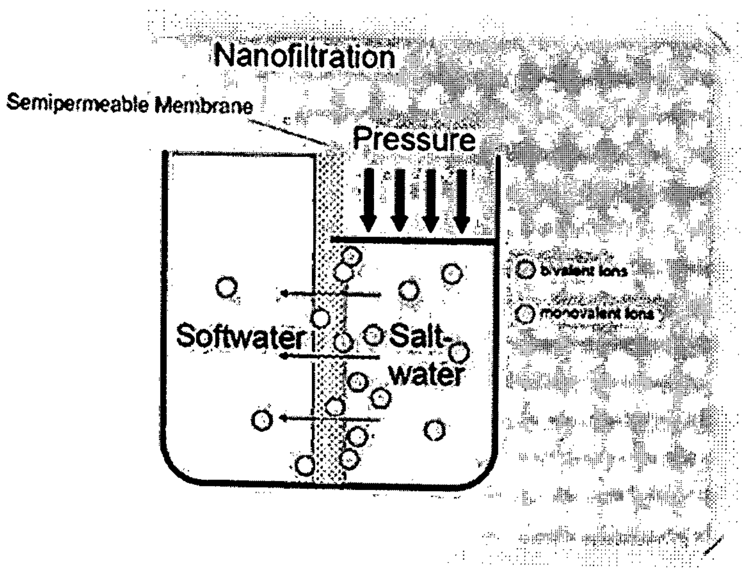

Figure 2.3 Nanofiltration membrane process through semi-permeable membrane. (Souce: http://www.fumatech.com)

2.3.2 Application of Nanofiltration Membrane

According to Raman *et al.*, (1994), nanofiltration (NF) membrane separation plays an important role in various industrial fields and its applications are increasing rapidly in chemical, biological and desalination industries, since the NF technology overcomes the operational problems that are associated with the conventional techniques. The example of applications of NF membrane process are water softening, dyes recovery, treatment of metal contained wastewaters, demineralization of whey, and antibiotics. Table 2.2 represents the examples of nanofiltration (NF) membrane applications.

Table 2.2 Examples of nanofiltration (NF) membrane applications
(Source: http://www.pure-aqua.com/nanofiltration-systems.html)

Application	Permeate	Concentrate	Benefits of NF
Whey permeate	Salty wastewater	Desalted whey concentrate	Allows recovery of lactose and whey protein concentrate with reduced salt content
Textile	Dyes	Water, salts, BOD, COD, and color	NF is used to desalt dyes resulting in a higher value product
Caustic cleaning solutions	Caustic cleaning solution	BOD, COD, suspended solids, caustic cleaner	Allows caustic cleaning solution to be recycled resulting in reduced cleaning chemical costs
Water	Softened water	Hard water	Potable water production. Softened water reduces scaling on equipment and heat exchange surfaces

2.4 Interfacial Polymerization

2.4.1 Description of Process

Most of nanofiltration membranes are thin-film composites fabricated by the interfacial polymerization technique in purpose to overcome the limitations and problems faced by asymmetric membrane formed by the phase inversion method (Rao *et al.,* 1997). The higher molecular weight polymer is produced in the interfacial process compared to the usual polymerization. This is due to the monomers diffusing to the interface will react only with polymer chain ends. The reaction rates which are so high make the monomers molecules react with the growing polymer chain ends before they can penetrate through the polymer film to start the growth of new chains.

According to Mulder (2003), the advantage of this technique is that the reaction is self-inhibiting through passage of limited supply of reactants through the already form layer, resulting in an extremely thin film of thickness within 50nm range. The thin layer produced by this technique generally will control the efficiency of the membrane process (Abu Seman *et al.,* 2010).

In this process, the ultra-thin selective layer with a dense property is produced separately onto porous support having good mechanical properties (Tang *et al.*, 2008). A polymerization reaction between two reactive monomers will occurs at the interface of two immiscible solvents. This is shown schematically in Figure 2.4. The support layer is generally an ultrafiltration or microfiltration membrane. It is immersed into aqueous solution containing reactive monomer which usually is amine-type. Then, it is immersed in organic solution containing water-immiscible solvent in which the reactive monomer is usually an acid chloride. These two reactive monomers will react with each other to form a dense polymeric top layer (Mulder, 2003).

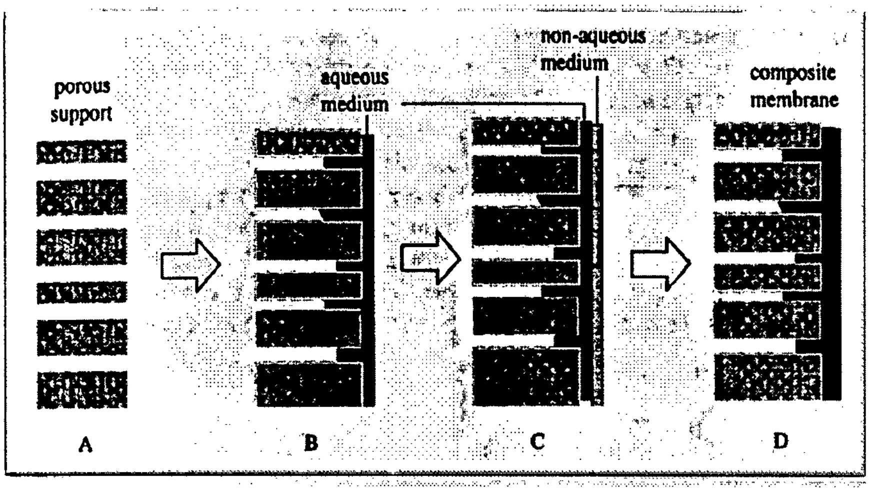

Figure 2.4 Schematic drawing of the formation of a composite membrane via interfacial polymerization (Source: Mulder, 2003).

2.4.2 Triethanolamine (TEOA) as Monomers

In recent years, studies have been focused on choosing or synthesizing the new monomers with special functional group to prepare the TFC membrane. According to Tang *et al.,* (2008), it is natural to seek an inexpensive monomer to manufacture a new membrane whose property spectrum has the optimum cost-performance balance for application. It is found that triethanolamine (TEOA) is an active monomer which is environment-friendly, economical and easy to be obtained.