SYNTHESIS AND CHARACTERIZATION OF FORWARD OSMOSIS MEMBRANE FOR DRINKING WATER APPLICATION

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Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering

Faculty of Chemical & Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG

JANUARY 2014

ABSTRACT

As the new technology of water treatment, forward osmosis (FO) has been recognized as one of the developing membrane technologies based on separation process. Generally, forward osmosis is the transport of water across a selectively permeable membrane from a region of higher water chemical potential (feed solution) to a region of lower water chemical potential (draw solution). In order to treat water that can be suitable for drinking water application, a forward osmosis membrane was produced by studying the effect of internal concentration polarization (ICP) as the efficiency of FO membrane processes is significantly limited by it. The thin film composite membranes were synthesized through interfacial polymerization of m-phenylenediamine (MPD) series and trimesoyl chloride (TMC) series at different concentration of MPD & TMC on both series of FO membrane. The thin film composite membrane was characterized in term of water flux, permeability and also solute rejection. The longer reaction time of MPD and TMC solution during interfacial polymerization had increased the layer thickness on the surface of the FO membrane which resulting the performance of the membrane.

ABSTRAK

Sebagai teknologi baru rawatan air, forward osmosis (FO) telah diiktiraf sebagai salah satu teknologi membran yang membangun berasaskan proses penapisan. Secara amnya, FO adalah pengangkutan air melalui poros membran dari kawasan potensi kimia air yang lebih tinggi (larutan masuk) sebagai satu rantau yang lebih rendah keupayaan kimia air (larutan keluar).Dalam usaha untuk merawat air yang sesuai untuk diminum, membran FO telah dihasilkan dengan mengkaji kesan polarisasi kepekatan dalaman (ICP) sebagai kecekapan proses membran FO ketara dihalang olehnya. Filem nipis membran komposit telah disintesis melalui pempolimeran permukaan membrane menggunakan m-phenylenediamine (MPD) dan siri trimesilklorida (TMC) pada kepekatan yang berbeza pada membran FO .Filem nipis membran komposit dicirikan dari segi fluks air, keboleh telapan dan juga penyingkiran bahan larut . Masa tindakbalas yang meningkat akan meningkatkan ketebalan lapisan pada permukaan membran FO yang mengubah prestasi membrane.

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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

CP	Concentration Polymerization
DS	Draw Solution
FS	Feed Solution
FO	Forward Osmosis
IP	Interfacial Polymerization
ICP	Internal Concentration Polymerization
MF	Microfiltration
NaCl	Sodium Chloride
NF	Nanofiltration
NOM	Natural Organic Matter
PES	Polyethersulfone
RO	Reverse Osmosis
TFC	Thin Film Composite
TMC	Trimesoylchloride
UF	Ultrafiltration

INTRODUCTION

1.1   Research Background

Forward osmosis (FO) is a membrane process that has been studied in recent years as an innovative technology for treatment of a wide variety of aqueous solutions and it operates the osmotic pressure differential across a semi-permeable membrane rather than hydraulic pressure differential (for example in reverse osmosis) (Catch et al., 2009). In FO, the transport of water across a selectively permeable membrane starts from a less concentrated solution (feed solution) to a more concentrated solution (draw solution) where a less concentrated draw solution is being produced which may be further treated to extract for freshwater (Liu et al., 2008). As stated Tang et al. (2012), by using the difference of osmotic pressure across the membrane instead of hydraulic pressure or temperature as a driving force, the water and solute separation can be carried out in a much more energy efficient manner and the membrane fouling propensity is also much lower as compared to pressure-driven membrane process, such as reverse osmosis (RO). Furthermore, since no high temperature and pressure required, forward osmosis suits for sensitive applications in certain industries such as food and pharmaceutical industry.

The membrane is one of the important elements in forward osmosis technology. From what Chi et al. (2012) reviewed; the inflow of water from feed water to a draw solution through the membrane from forward osmosis membrane is not only simplified from the forward osmosis membrane but also plays an important role in maintaining a constant concentration of the draw solute and a high osmotic pressure.

Most of membranes used in the FO process that were originally designed for pressure driven RO process are dense semi-permeable membranes (Tang et al., 2010). The company that is producing commercial membranes is Osmotek Inc. which is now known as Hydration Technologies Inc. (HTI). Refers to Wang et al. (2010); the HTI's patented cartridge-type FO membrane has been widely used in FO studies and is made of cellulose triacetate supported by an embedded polyester screen mesh.

Therefore, the characteristic of FO membranes should be high density of the active layer for high solute rejection; a thin membrane with minimum porosity of the support layer for low internal CP, and therefore, higher water flux; hydrophilicity for enhanced flux and reduced membrane fouling; and high Mechanical strength to sustain hydraulic pressure when used for pressure-retarded osmosis (PRO). Membranes that can achieve high flux and salt rejection, have minimal internal concentration polarization (CP), and have high mechanical strength to support high hydraulic pressures will lead to improved performance in current applications as well as development of new applications for FO (Cath et al., 2006)

Recently, high performance thin film composite (TFC) FO membranes have been testified; these membranes are typically fabricated in a two-step synthesis: where the first one is a porous substrate, formed by phase inversion with tailored features (such as thin thickness and high porosity) to enhance solute mass transfer and thus reduce internal concentration polarization (ICP) in the substrate, and a thin polyamide rejection layer is prepared by interfacial polymerization of diamine and trimesoyl chloride (TMC).

1.2   Problem Statement

The global issue of clean water is worrying due to the increasing population growth; environmental worsening and climate change is intimidating the lives of human beings all over the world (Hongwei et al., 2011). Other than reverse osmosis or nanofiltration method in water treatment process, another inventive membrane-based technology such as the forward osmosis (FO) process show great potential for seawater desalination, wastewater treatment and reclamation.(Wang et al., 2012).Nevertheless, the presence of internal concentration polarization (ICP) limits the FO flux efficiency (Tang et al., 2010). Hence, it is desirable to minimize the presence of ICP in FO membrane.

The high demand for clean drinkable 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 Forward osmosis membrane and to investigate the effect of Thin Film Composite (TFC) layer fabrication conditions on Forward Osmosis (FO) performance that is suitable for drinking water application.

1.4   Scope of Proposed Study

This research is focusing on the synthesis and characterization of forward osmosis membrane for drinking water solution. The scope of this research is as below:

- Fabrication of FO membrane using different concentration of m-phenylenediamine (MPD) (0.5 – 2.0 wt. %) at constant reaction time (30 minutes).
- Performance testing of fabricated FO membrane in term of permeability permeates flux and rejection.

1.5   Significance of Proposed Study

This study has been done in order to improve the properties of the FO membrane in terms of permeability also the structure of FO membrane. Nowadays, FO process becomes more important in water treatment for domestic and industrial water supply. This type of membrane technology is also applicable for environmental application that can be applied in cleaning technology

2   LITERATURE REVIEW

2.1   Introduction to Membrane Process

In chemical industries, membranes have grown an important place in chemical technology and are used in an expansive range of applications. The main property that is exploited is the capability of a membrane to control the permeation rate of a chemical species through the membrane (Baker, 2004). A membrane can be defined as a thin layer of material that allows some particles to pass through by acts as a semi-permeable barrier while hindering the permeation of other components (Silva, 2007).

The transport rate of a component through a membrane is determined by the structure of the membrane, by the size of the permeating component, by the chemical nature and electrical charge of the membrane material and permeating components and by driving force, i.e. concentration, pressure or electrical potential gradient across the membrane (Strathmannet.al., 2006).Jalil (2004) stated that the membrane process are beneficial 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 Advantage and Limitation in Membrane Process

In various applications, such as water desalination and purification, the membrane processes is competing greatly with other water treatment techniques. However, compared to these conventional procedures membrane processes benefits in energy efficient, simpler to operate and produce a higher quality product. It goes the same for the separation, concentration, and purification of drugs and food products or in medical and pharmaceutical applications. These membrane processes also have in addition to easy up and down scaling the advantage of operating at ambient temperature avoiding any change or degradation of products. In water desalination reverse osmosis or electrodialysis can be used. Depending on local conditions, including water quality,

energy cost and the required capacity of the desalination plant, either electro dialysis or reverse osmosis can be the more efficient process. For very large capacity units and in case a power plant can be coupled with the desalination unit, distillation is generally considered to be more economical. For surface water purification and waste-water treatment membrane processes, micro- and ultrafiltration are competing with flocculation, sand bed filtration, carbon adsorption, ion-exchange and biological treatment. In these applications the membrane processes are usually more costly but generally provide a better product water quality. Very often a combination of conventional water treatment procedures with membrane processes results in reliable and cost-effective treatment combined with high product water quality (Strathmann et.al., 2006).

Despite the advantages mentioned in the previous paragraph, Strathmann et.al.,(2006) also clarify that the disadvantage of membrane processes is that in many applications, especially in the chemical and petrochemical industry, their durable reliability is not yet established. Besides, sometimes it is require for membrane processes to excessive pretreatment due to their sensitivity to concentration polarization and membrane fouling due to chemical interaction with water constituents. Moreover, mechanically membranes are not very robust and can be damaged by a malfunction in the operating procedure.

2.2   Membrane Processes and Principle

2.2.1 Membrane separation process

A separation process is a process where given mixture of chemicals being transform into two or more compositionally distinct end-use products (Soni*et al*., 2009).According to Scott & Hughes (1996), various types of membrane separation process are technologically advanced for specific industrial applications and they are categorized according to pore size and separation driving force as shown in Table 2.1. The driving force of membrane process can be pressure, temperature, concentration or electrical potential.

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

Membrane processes such as Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF) and Reverse Osmosis (RO) involve pressure driving forces (Jelen 1992). These processes are suitable to different size of molecules where the microfiltration separates the largest size of molecules and reverse osmosis separating the smallest molecules (Silva, 2007).
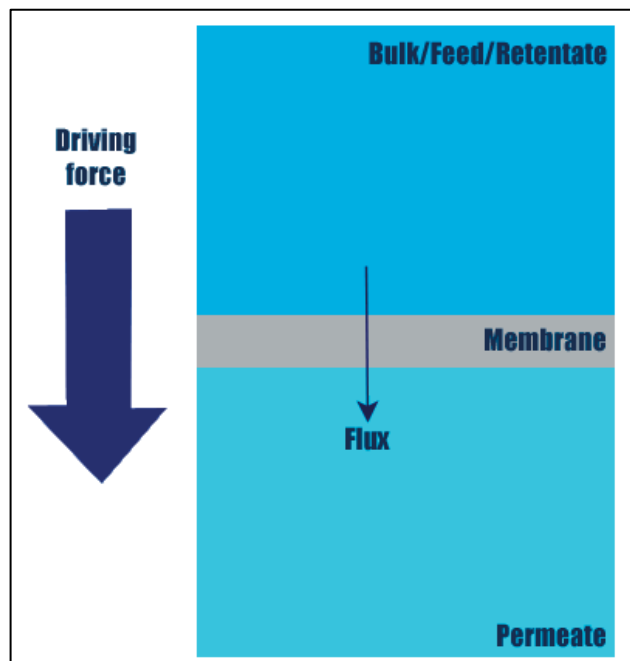

Figure 2.1: Sketch of a membrane process. The core is the membrane itself, through which a driving force induces a flux from the bulk to the permeate side. (Source: Pressure Driven Membrane Processes 2nd edition, Saren 2007)

From Figure 2.2 the feed side is denoted as the bulk solution. The retained components in the bulk solution that has been in contact with the membrane can also be referred as retentate. A flux will go through the membrane from the bulk solution to the permeate side when a driving force is established across the membrane. The flux will be nominated as letter "J" and is often given in the units of $L/(m^2 \cdot h)$. The liquid that are going through the membrane is called permeate.

2.3 Forward Osmosis

2.3.1 Forward Osmosis Process

Forward osmosis (FO) is a concentration-driven membrane process, which consumes the difference of osmotic pressure across a selectively permeable membrane as the driving force for the transport of water through the membrane (Wang, 2010). Han et.al., (2012) stated that in the FO process, water flows across the semi-permeable membrane from a low-osmotic-pressure feed solution to a high osmotic-pressure draw solution driven by the osmotic pressure difference, during which no external hydraulic pressure is applied. Table 2.3 below shows the differences between Reverse Osmosis and Forward Osmosis.

Table2.3: The Comparisons Between RO and FO (Source: Han et.al., 2012)

Sort	Reverse Osmosis	Forward Osmosis
Driven Pressure	High hydraulic pressure	Osmosis pressure difference
Water Recovery	30%-50%	At least 75%
Environment Effect	Harmfully	Friendly
Membrane Fouling	Seriously	Hardly
Modules	Compression resistance	Without particular desire
Application	Normal separation system	Temperature sensitive system; Pressure-sensitive system; Renew energy; Controlled Released of drug
Energy Consumption	High energy expenditure	Low energy demand
Equipments	High-pressure pumps; Energy recovery unit; Resistant high-pressure pipelines; High investment in equipments	Low investment in equipment
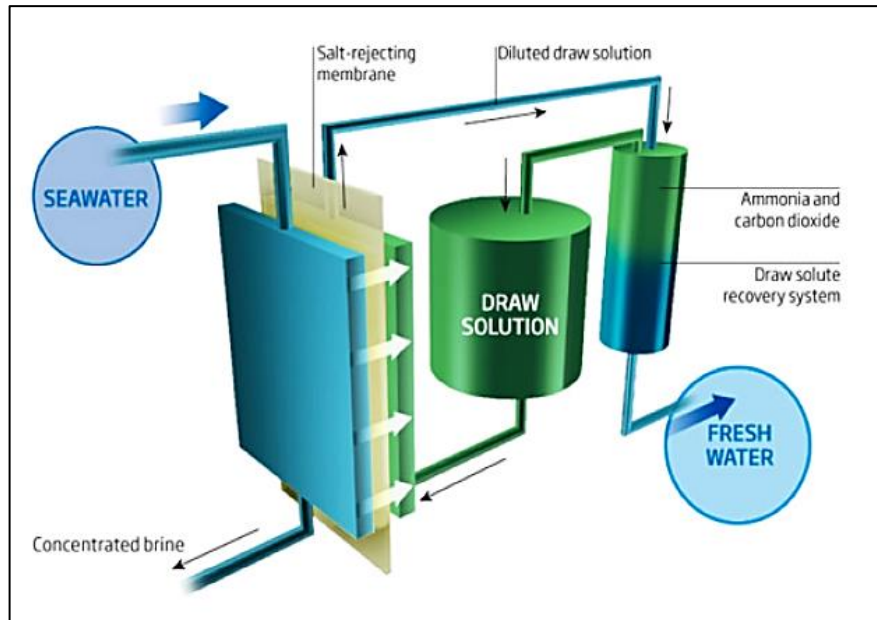
Figure 2.2: An Illustraion of Forward Osmosis Desalination

(source: www.mdpi.com)

2.3.2 Forward Osmosis Membrane

A FO membrane is significantly different from an RO membrane in terms of the characteristic of the porous sub-layer and the compression resistance of the whole membrane (Liu et.al., 2009). FO membranes also tend to have low fouling tendency even though there were complicated mechanisms involved. In FO, the priority research areas consist of the improvement high performance FO membranes in addition to the search for suitable draw solutions. Due to internal concentration polarization (ICP) water flux in FO processes tends to be limited, which refers to the buildup of solutes in the porous membrane support when the active rejection layer faces the draw solution membrane orientation) or the dilution of the draw solution inside the support layer when the active layer faces the feed solution (Saren et.al., 2011)

2.4   *Nanofiltration*

2.4.1 *Nanofiltration Membrane*

The nanofiltration (NF) membranes are mostly defined as having rejection characteristics that range from "loose" RO to "tight" ultrafiltration where they have the capability to selectively reject different dissolved salts with high rejection of low molecular weight and dissolve component compare to other membranes (Craig. et al., 2007). In a general filtration of liquid containing trapped particles, the liquid mixture is forced (by gravity or applied pressure) through a filter medium that has pores or passages of a size that allows the liquid and small particles to pass through, but prevents the passage of larger particles. Figure 2.3 provides a graphical represent the Nanofiltration membrane process.
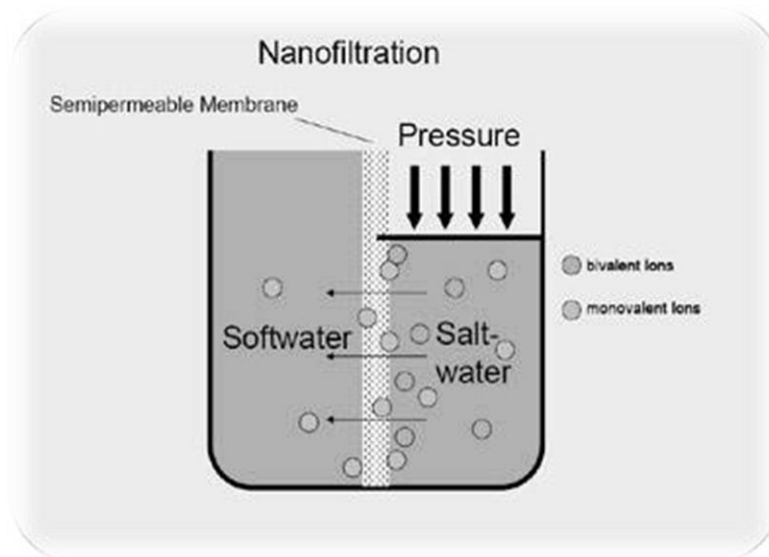

Figure 2.3 Nanofiltration membrane process through semi-permeable membrane.

(Souce: http://www.fumatech.com)

2.4.2 Application of Nanofiltration Membrane

From Craig et al., 2007 point of view, normally, nanofiltration membranes are mainly used to partially soften potable water, permitting some minerals to pass into the product water and thus increase the stability of the water and prevent it from being aggressive to distribution piping material. Moreover, NF membranes are finding increasing use for purifying industrial effluents and minimizing waste discharge.

Table 2.4 Overview of possible applications of nanofiltration in various industries.

Industry	Application
Food	Demineralisation of whey
	Demineralisation of sugar solutions
	Recycle of nutrients in fermentation processes
	Separation of sunflower oil from solvent
	Recovery of Cleaning-In-Place solutions
	Recovery of regeneration liquid from decolouring resins in sugar industry
	Effluent treatment
Textile	Purification of organic acids
	Separation of amino acids
	Removal of dyes from waste water
Clothing and leather	Recovery of water and salts from waste water
Paper and graphical	Recovery and reuse of chromium(III) and chromium(II)
	Recovery of water from waste water or waste water treatment effluent
Chemical	Recovery of bleaching solution
	Sulfate removal preceding chlorine and NaOH production
	CO_2-removal from process gasses
	Preparation of bromide
	Recovery of caustic solutions in cellulose and viscose production
	$CaSO_4$ precipitation
Metal plating and	Separation of heavy metals from acid solutions

product/electronic and optical	Removal of metal sulfates from waste water
	Cleaning of machine rinsing solutions
	Removal of Nickel
	Recovery of Cu-ions from ore extraction liquids
	Al^{3+} removal from canning industry waste water
Water production	Recovery of LiOH during treatment of battery waste
	Removal of degreasing agents from water
	Removal of precursors of disinfection byproducts
	Hardness removal
	Removal of natural organic matter (a.o.colour)
	Removal of pesticides
	Removal of heavy metals (As, Pb), Fe, Cu, Zn and silica
	Treatment of brackish water
Landfills	Removal of phosphate, sulphate, nitrate and fluoride
Agriculture	Removal of algal toxins
	Purification of landfill leachate
	Removal of selenium from drainage water

3   METHODOLOGY

3.1   Chemicals

The chemical used are Trimesoyl Chloride (TMC), and m-phenylenediamine (MPD) purchased from Sigma- Aldrich.Co.(UK), Sodium Hydroxide (NaOH) and n-Hexane as solvent for organic solution were purchased from Merck KGaA (Germany) and NF membrane obtained from Faculty of Chemical Engineering laboratory.

3.2   Equipment

3.2.1   Peristaltic Pump

Peristaltic pump (model BT100-1L) was used for the membrane performance test. The flux of the membrane at different concentration of MPD and TMC reaction time was measured by using this Peristaltic pump. Figure 3.1 showed the pump used.

Figure 3.1 Peristaltic pump (model BT100-1L)

3.2.2 Acrylic Crossflow Cells

The NF membrane was placed in an acrylic cross flow cells for filtration process. The feed solution that enters the membrane will flow tangentially across the membrane surface. The plate will be connected to peristaltic pump so the feed solution can flow across the membrane surface.

Figure 3.2 Acrylic Crossflow Cells

3.2.3 Ultrasonic Water Bath

The (Crest) ultrasonic water bath as shown in Figure 3.3 was used to make the pore structure more compact and stable before interfacial polymerization process were done.

Figure 3.3 Ultrasonic Water Bath

3.2.4 UV-Vis Spectrophotometer

UV-Vis Spectrophotometer (U-1800, HITACHI) as shown in Figure 3.4 was used to determine the absorbance of humic acid solution in the feed, retentate and permeate aqueous solutions. The Ultra-pure water was used for the blank sample before the samples of humic acid solution were tested.

Figure 3.4 UV-Vis Spectrophotometer

3.2.5 Conductivity Meter

The conductivity meter (HI8733, Hanna) was used to determine the conductivity of feed, retentate and permeate solution of NaCl and humic acid solution. The conductivity readings were measured in mili Siemens/cm (mS/cm) or micro Siemens/cm (μ/cm).

3.3   Preparation of Thin Film Composite (TFC) FO Membranes

3.3.1 Interfacial Polymerization

The rejection layer of composite FO membrane can be form from interfacial polymerization process of MPD and TMC solutions. For MPD series, the aqueous solutions were prepared with concentration starting from 0.5 wt/v %, 1.0 wt/v % and 2.0 wt/v %. For TMC series, the TMC concentration was held constant at 0.5 wt./v %, in n-hexane solution.

Firstly, before interfacial polymerization, the NF membrane support substrates were heated in a 70 °C water bath for 2 min and then reduced in a 23 °C water bath. This was to make the pore structure more compact and stable. The substrates were then soaked in an MPD solution for 30 min. After removing the excess MPD solution on the substrate surface with compressed air, a TMC solution was gently poured onto the substrate surface. TMC was allowed to react with MPD for 60 seconds to form the polyamide rejection layer, followed by draining off the excess TMC solution from the membrane surface. The nascent composite membrane was washed with fresh tap water and stored

in ultrapure water before further use. The flow of the interfacial polymerization process to produce polyamide rejection layer is summarized in Figure 3.5.
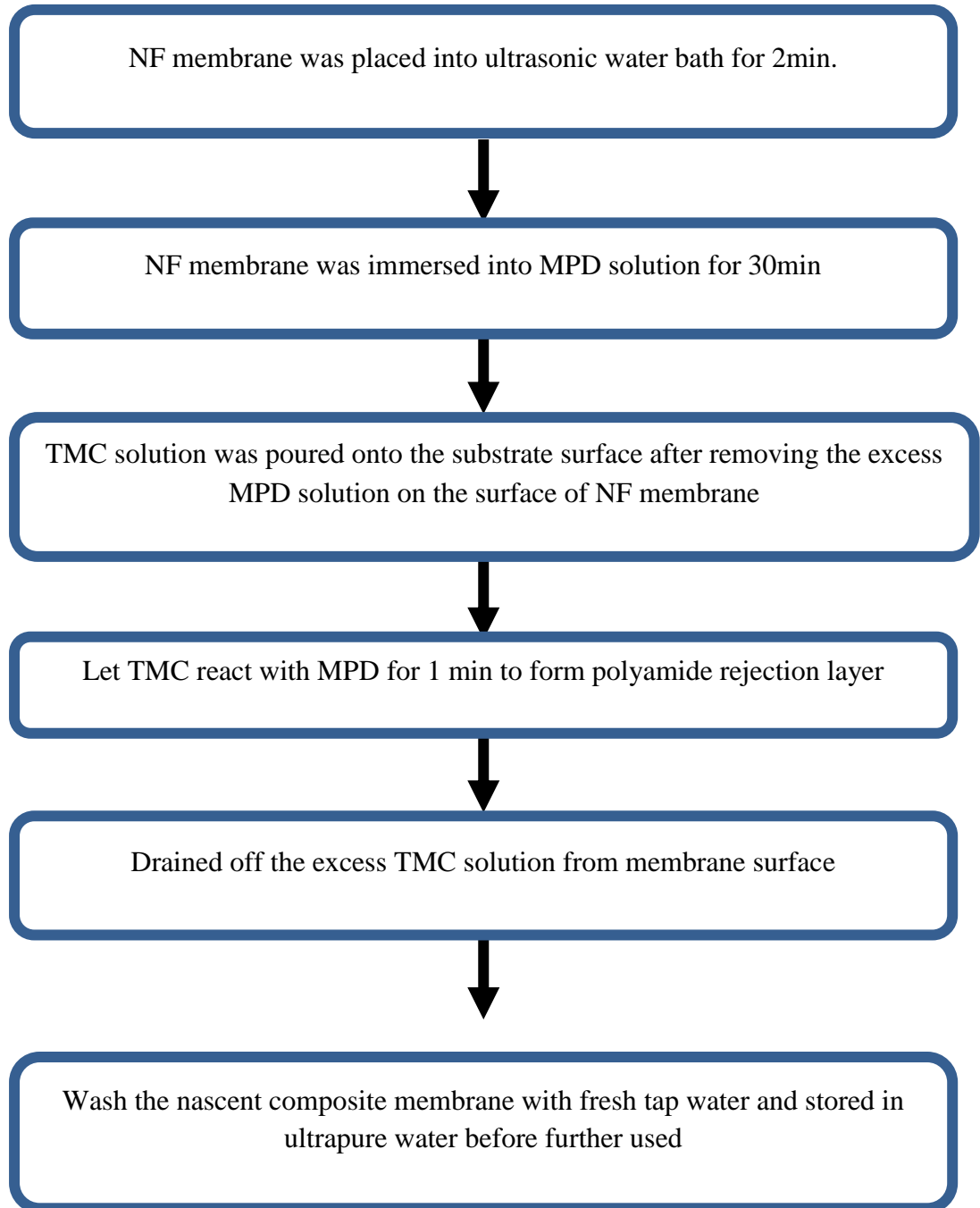
NF membrane was placed into ultrasonic water bath for 2min.

↓

NF membrane was immersed into MPD solution for 30min

↓

TMC solution was poured onto the substrate surface after removing the excess MPD solution on the surface of NF membrane

↓

Let TMC react with MPD for 1 min to form polyamide rejection layer

↓

Drained off the excess TMC solution from membrane surface

↓

Wash the nascent composite membrane with fresh tap water and stored in ultrapure water before further used

Figure 3.5 Preparation polyamide rejection layer membranes through interfacial polymerization