

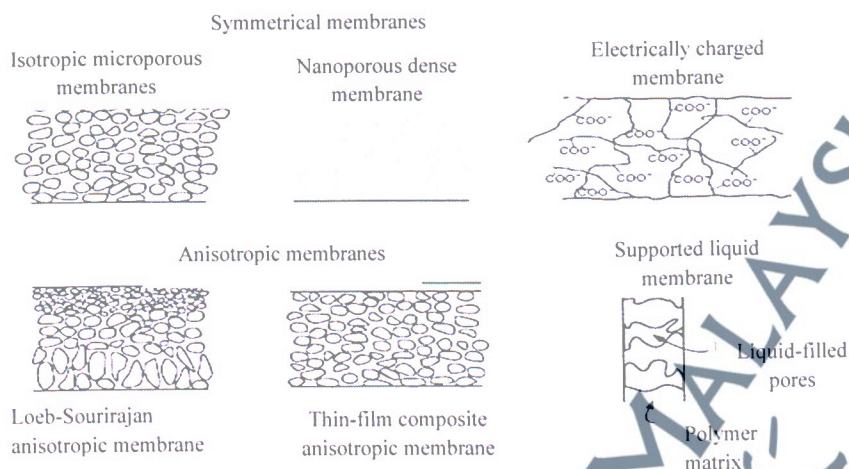
## CHAPTER II

### LITERATURE REVIEW

#### 2.1 Overview of Membrane Technology

In chemical technology, membranes have gained an important place and are used in a broad range of applications. The key properties like the ability of a membrane to control the permeation rate of chemical species through the membrane have been exploited. For example, membranes is used in controlled drug delivery where the aimed is to moderate the permeation rate of drug from a reservoir to the body. While in separation process, the main used of membranes is to allow one component of a mixture to permeate the membrane freely and hindering permeation of unwanted components. Furthermore, it is not called 'membrane' if it does not have a discrete, thin interface that moderates the permeation of chemical species in contact with. Completely uniform in composition and structure, this interface may be molecularly homogenous or it may chemically or physically heterogeneous. Figure 1 shows a diagram of different type of membrane.

**FIGURE 1:** Schematic Diagram of the Principal Types of Membranes



Amongst the membrane separation processes, microfiltration, ultrafiltration, nanofiltration and reverse osmosis commonly used in processing industries. The mode of separation in ultrafiltration and microfiltration are basically the same where the separation is molecular sieving through increasingly fine pores. However, microfiltration membranes filter macromolecules from solutions. It is a difference in reverse osmosis membranes where the membrane pores are so small, ranging between 5 to 10 Å. In reverse osmosis, usually sulfonated cross-linked polystyrene are used to develop the membrane which can be used for separation of salts and micro-solutes in solution.

Although it is not stated that nanofiltration in the four developed membrane mentioned above, nanofiltration has been widely used for removal of hardness and desalting. To fabricate nanofiltration membrane, it is generally used interfacial polymerization that employed for composite membrane separation. Nanofiltration has several advantages that give it used in large scale industrial applications due to low operating pressures, high fluxes and high retentions of multivalent salts, low investment and operation costs. Because of these advantages, nanofiltration membrane

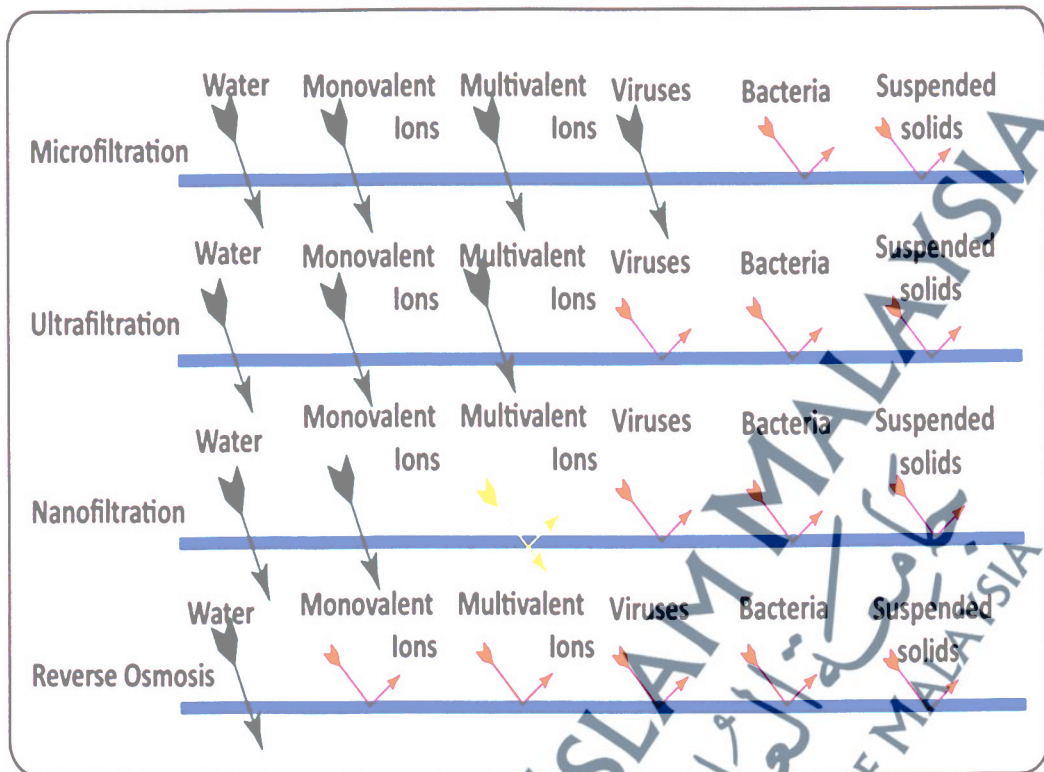
has been developed for different applications such as water softening, color removal, chemical oxygen demand (COD) and biological oxygen demand (BOD) (Baker, 2004).

## 2.2 Membrane Separation Process

To control permeation rate of different species is the most important property of membranes. There two models that used to describe the mechanism of permeation. First is solution-diffusion model. In this model, down through the concentration gradient, the permeants dissolve in the membrane materials and diffused. Due to the differences in the solubilities of the materials in the membrane and the differences in the rate, the permeants are separated which the materials diffuse through the membrane. The solution-diffusion model was used in 1940s which is to explain transport of gases through polymeric films.

Second model is called pore-flow model. For this model, permeants are transported by pressure-driven convective flow through tiny pores. Thus, in this model, the separation occurs because one of permeants is filtered from some pores in the membrane through which other permeants move. However, these two models have been used in 19<sup>th</sup> century, while pore-flow model, was early popular in 1940s because this model is related to normal physical experience (Baker, 2004). In membrane separation process, there are four type of pressure-driven membrane as shown in Figure 2 where each membrane plays a role at specific application

**FIGURE 2:** Membrane Separation Process



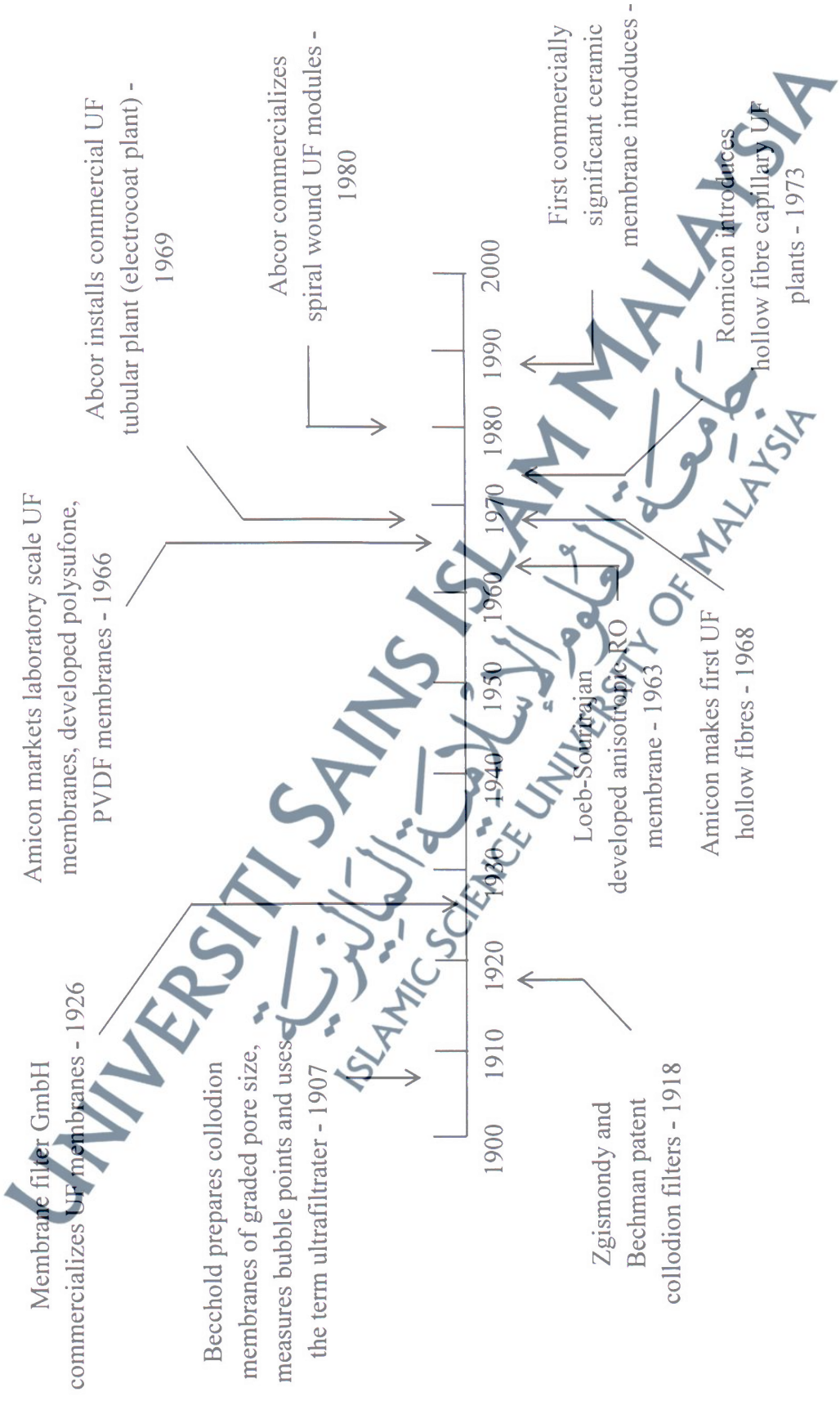
### 2.2.1 Ultrafiltration (UF)

To separate water and microsolute from macromolecules and colloids usually used a finely porous ultrafiltration (UF) membrane. The average pore diameter for UF membranes are 10-1000Å. The starting of UF membranes is prepared by Bechhold which is from collodion (nitro cellulose). Bechhold coined the term ‘ultrafilter’ and the first to measure membrane bubble points. Collodion ultrafiltration and microfiltration membranes were commercially available for laboratory use by the mid-1920s. No industrial applications of UF membrane until 1960s although it has been used as laboratory studies. Development of the anisotropic cellulose acetate membrane by Loeb-Sourirajan in 1963 has been a crucial breakthrough in membrane industry. The aim is to produce high-flux reverse osmosis membranes. UF membranes have been used widely in membrane applications. For example (Baker, 2004):

- The first commercially successful industrial UF system equipped with tubular membrane modules are installed in 1969 to recover electrocoat paint from automobile paint
- The first cheese whey UF system is installed in 1970
- In 1973, first hollow fiber membrane is sold by Romicon and spiral-wound modules, adapted to UF applications became a commercial item by 1979-1980.

Made by Loeb-Sourirajan process, UF membranes are usually anisotropic structures. On a much more open microporous substrate, UF have finely porous surface layer or skin. Where the finely porous layer plays role in the separation, while the microporous substrate give mechanical strength. Characterized by molecular weight cut-off, the membranes discriminate between dissolved macromolecules of different sizes. Although ultrafiltration and microfiltration membranes have the same applications, however, the pore sizes make there are different. Microfiltration membranes has larger pore sizes than ultrafiltration where it has pore size in range of 0.1-10 $\mu\text{m}$ , whereas ultrafiltration is considered to be limited with pore diameters from 10-1000 $\text{\AA}$  (Baker, 2004).

**FIGURE 3:** Milestones in the Development of UF



### 2.2.2 Nanofiltration (NF)

For nanofiltration (NF) membrane, it has properties of combining size and electrical effects. Nanofiltration membrane has pore diameter typically 1nm and have fixed charges developed by dissociation of groups as sulphonated or carboxyl acids. Nanofiltration membranes can retain multivalents complex ions and transmit small uncharged solutes and low charged ions due to the properties. Also, with the small energy consumption of the process and the high fluxes make NF membranes extremely useful in fractionation and selective removal of solutes from complex process stream (Otero et. al., 2006).

Nanofiltration served several advantages such as low operations pressure, high flux, high retention of multivalent anion salts and an organic molecular above 300, relatively low investment and low operation costs. Because of these advantages, NF has been used worldwide. Back to 1970s where NF membranes is from low-pressure reverse osmosis membranes are operated. Hence, high pressure RO membranes resulted high costs in operations. By the second half of 1980s, NF had become established. Since NF is called low-pressure of RO membranes, it has been used widely in applications, especially in water treatment and pre-treatment. Where, NF membranes, can treat all kind of water including, ground, surface and wastewater (Hilal et. al., 2004).

Besides, NF membranes have two interesting features which are intermediate molecular weight cut-off (MWCO) between RO and UF membranes that have range from 200-2000 Daltons and the other is the salt rejection caused by the charge effect

due to their materials. NF membranes are effective for the production of high-quality drinking water that can be used for the removal of inorganic pollutants and organic pollutants based on the two interesting features. The of NF processes know ledged on separation performance on salts for the removal of salts in water is always important. The major effects that can explain the separation mechanism of the NF membranes process are the electrostatic and the steric-hindrance effects between the membrane and external solutions (Wang et. al., 2005).

### 2.2.3 Microfiltration (MF)

Filtration processes that use porous membranes to separate suspended particles particles are referred to microfiltration (MF) with diameters between 0.1-10 $\mu\text{m}$ . Thus, it falls between ultrafiltration membranes and conventional filters. In 1920 and 1930s, microfiltration same as ultrafiltration where it has its modern origin in the development of collodion (nitrocellulose) membranes. Membranfilter GmbH is founded and started to produce collodion microfiltration membranes commercially in 1926.

Microfiltration (MF) membranes first used at large-scale application is to culture microorganism in drinking water where this remains a significant application. As a rapid method to monitor water supply for contamination, the test for MF is developed in Germany during World War II. A number of noncellulosic materials have been used as membrane materials foe MF membranes including poly (vinylidene fluoride), polyamides, polyolefins and poly (tetraflouroethylene) have been developed over the last 40 years by Millipore and others. In other hand, the cellulose

acetate/cellulose nitrate blend membrane remains a widely used microfilter. The use of MF membranes is confined to laboratory or to very small-scale industrial application until the mid-1960s. MF became more important in biological and pharmaceutical manufacturing in 1960s and 1970s as did MF of air and water in the production of microelectronics in the 1980s.

In MF industry, the production of low-cost, single-use, disposable cartridges for pharmaceutical and electronics processes now represent a major part. In applications for which penetration of even one particle or bacterium through the membrane can be critical, MF membranes are often used. Thus, the absence of membrane defects or oversized pores as membrane integrity is important. Besides, MF membranes also have been characterized using latex challenge test and bubble point test to determine the pore size of MF membranes (Baker, 2004).

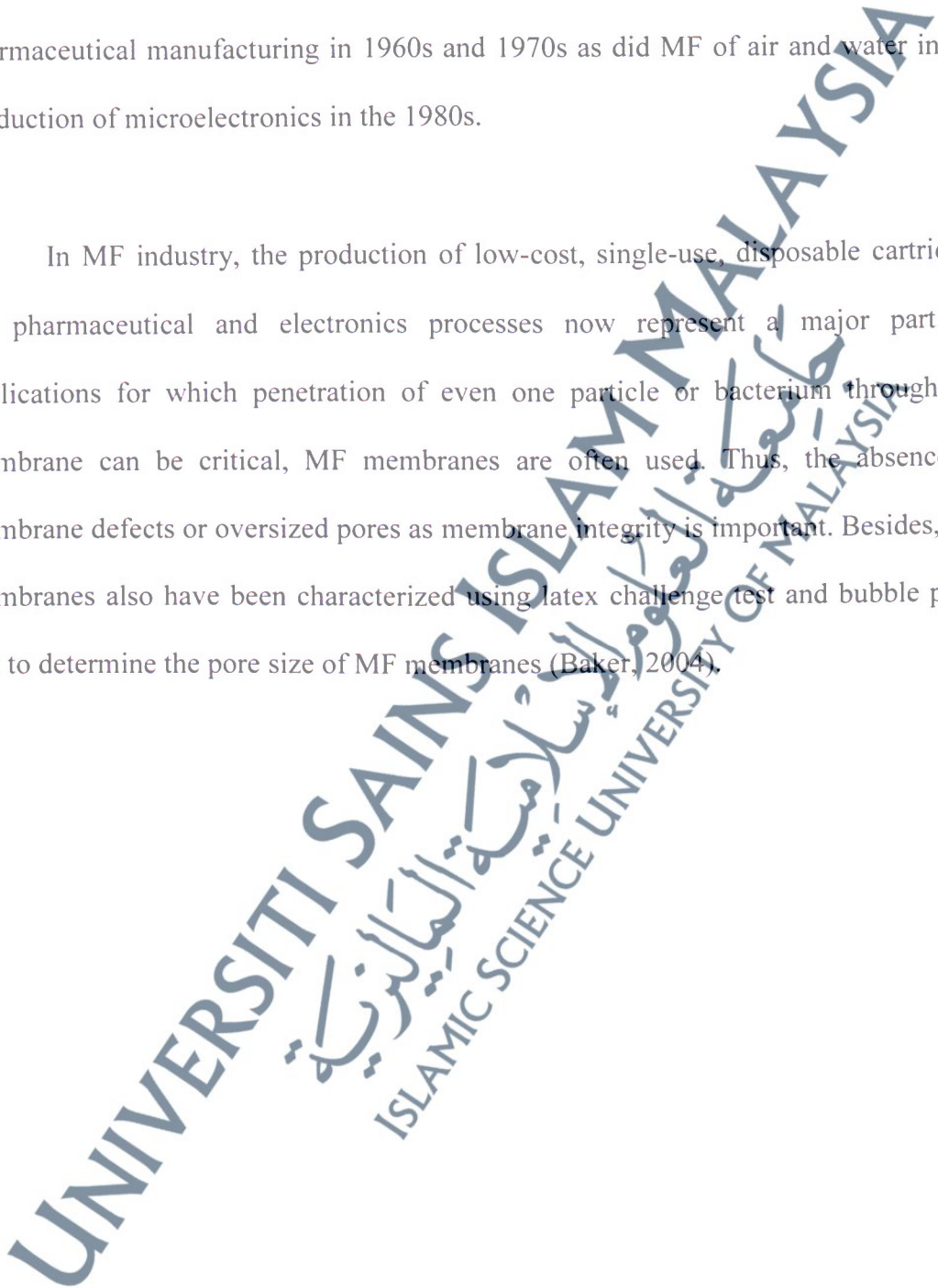
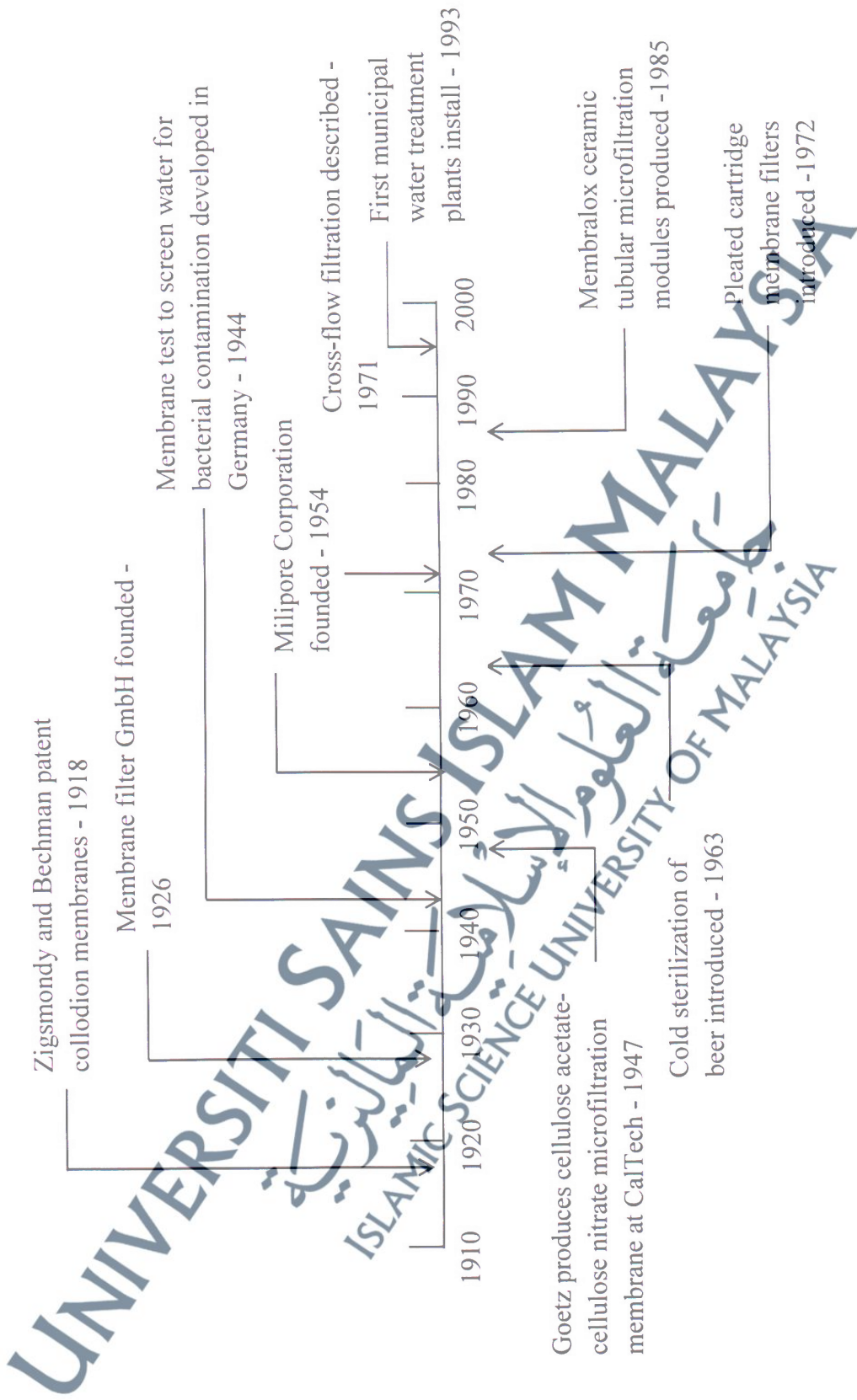


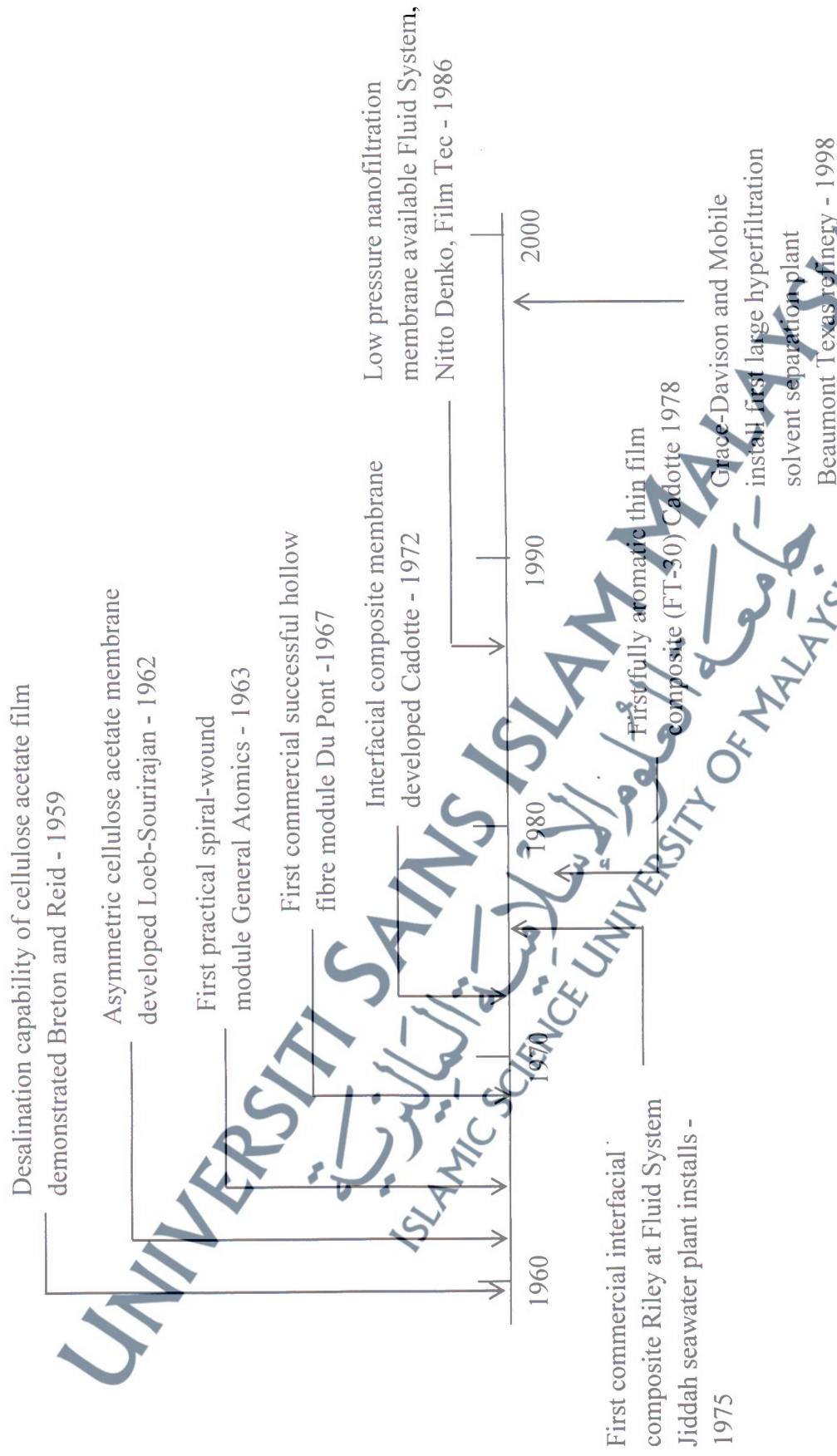
FIGURE 4: Milestone of Microfiltration (MF) membranes



### 2.2.4 Reverse Osmosis (RO)

Process for desalinating water using membranes that are permeable to water but essentially impermeable to salt is how reverse osmosis (RO) works. Water containing dissolved salts contacts the feed side of the membrane is pressurized; water depleted of salts is withdrawn as a low-pressure permeate. Early as the 1850s, Pfeffer, Traube and others has studied osmotic phenomena with ceramic membranes. The process is patented as a method of desalting water, and the term reverse osmosis in 1931. In 1959, modern interest dates from work of Reid and Brenton showed that cellulose acetate films could perform this type of separation. The development of the Loeb-Sourirajan anisotropic cellulose acetate membranes became the breakthrough discovery made by reverse osmosis a practical process. From this development, water desalination by RO membranes became a potentially practical process, and within a few years small demonstration plants are installed. Through the 1960s to the mid-1970s, anisotropic cellulose acetate membranes became the industry standard until researcher developed method on producing composite membranes through interfacial polymerization. From this method, composite membranes would have extremely high salt rejections, combined with good water fluxes. To make RO membranes, a number of membrane materials and membrane preparation technique have been used. For example, cellulosic membranes (cellulose acetate), noncellulosic polymer membranes, interfacial composite membranes and other membrane materials (polysulfone microporous support membrane is contacted first with an aqueous solution of furfuryl alcohol) (Baker, 2004).

**FIGURE 5:** Milestones in the Development of Reverse Osmosis



## 2.3 Membrane Preparation (Phase Inversion)

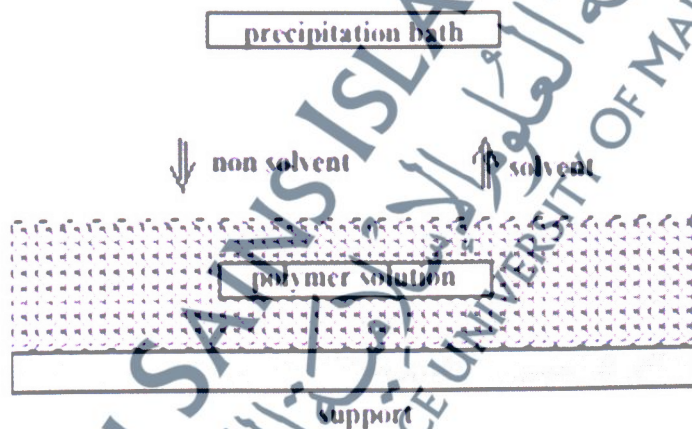
### 2.3.1 Immersion Precipitation

Polymeric membranes are widely used in industry in modern world. Microfiltration, ultrafiltration, reverse osmosis and gas separation are examples of industrial applications. In tailoring membrane to perform appropriately for specific applications, controlling the morphology of the membrane is of great importance since it is the size and distribution of pores that largely determines their function. Sintering, stretching, track-etching and phase inversion are several ways to prepare porous polymeric films. Depending on the properties of the materials and process conditions, the final morphology of the membranes obtained will vary greatly.

Phase inversion process is the most widely used. However, there are several ways that membrane formation can be induced such as thermally induced phase separation (TIPS), air-casting polymer solution, precipitation from the vapour phase and immersion precipitation. Immersion precipitation is the most efficient technique among all those techniques. In immersion precipitation technique, a polymer solution is first cast as a thin film on a support, and then is immersed into a non-solvent bath. Because the solvent in the polymer solution is exchanged for the non-solvent, precipitation will occur due to the chemical potential imbalance. After the phase separation attains a certain degree, the polymer-rich phase is then solidified in order to form the porous membrane.

Thus, in immersion precipitation technique, the process includes both liquid-liquid demixing and solidification (Wang et. al., 2008). Composition of casting solution, the harshness of precipitation bath, the precipitation temperature and the thermal treatment temperature of casting solution is parameters that affect polymer precipitation and ultimately the morphology of the formed membrane. In many application fields such as wastewater treatment or bio-medical technology, the surface properties of separation membrane are critical importance (Zhang et. al., 2008).

**FIGURE 6:** Phase Inversion Technique by Immersion Precipitation



### 2.3.2 Dry Phase

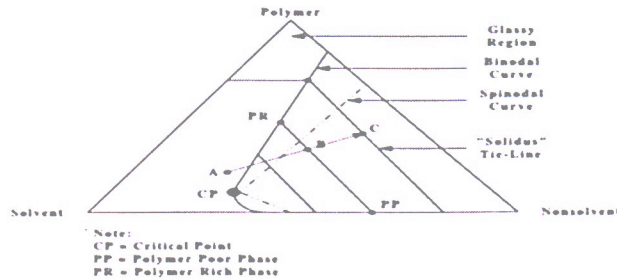
Most literature about dry phase inversion process of membrane are concerning on gas separation membrane. In membrane technology, the development of asymmetric membranes by Loeb-Sourirajan became an important breakthrough where the membranes are liable for existence of many high-flux commercial membrane separation processes. Nowadays, to have an adapting membrane to replace

conventional separation processes, the membrane industry is faced with challenge of inventing new membrane materials as well as membrane manufacturing techniques. Via “phase inversion” processes, many polymeric membranes are fabricated.

One of the several processes in phase inversion is dry-cast or complete evaporation processes which the thermodynamic state of polymer solution in the system can be altered to promote phase inversion. In dry-cast process, the evaporation of non-solvent and/or solvent from an initially homogenous single-phase polymer solution has been characterized. The evaporation takes to the formation of a cloudy two-phase solution. Then, solidification will occur where the polymer from polymer-rich phase precipitates to form a solid matrix which envelops the polymer-lean phase.

There is no model are available to present the dry-cast process because it involves coupled heat and mass transport (Altinkaya et. al., 2005). Dry phase separation process will give amorphous polymer gas separation membranes in preparation of dry phase technique. This is because, dry phase inversion are different with wet or dry/wet process by the absence of the immersion coagulation step. It is relatively simple technique in the sense there is no exchange of non-solvent in the formation of membrane through dry phase process (Altinkaya and Ozbas, 2004).

**FIGURE 7:** Ternary Phase Diagram of Physical Events Occurring During Dry Phase Inversion



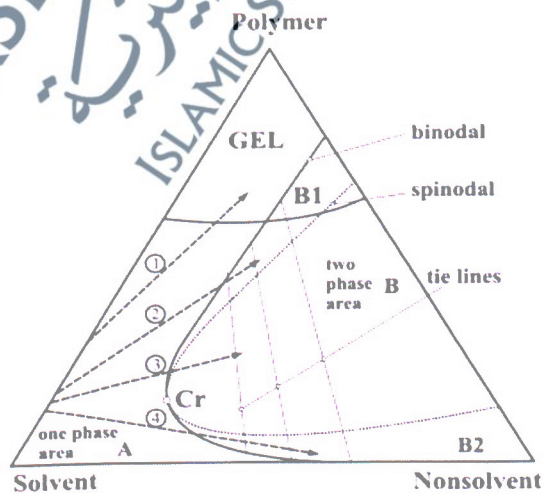
### 2.3.3 Wet Phase

Because of low cost and simple, wet phase is frequently employed during membrane formation. There is interplay between the polymer and its solvent and non-solvent in the phase inversion technique. Due to the difference in diffusion exchange between the top phase and the bottom phase of the membrane, the characteristics of the asymmetric membrane will generate (Chen et. al., 2009). According to Stropnik and Keiser (2002), they have experimental work on the formation of polymeric membrane by wet phase separation. After immersion into the coagulation bath, a thin cast layer of the polymer solution is transformed into a protomembrane which in general consists of non-solvent polymer (Stropnik and Keiser, 2002). By the demixing of a stable, homogenous polymer solution in a non-solvent precipitation baths shows how wet phase separation process can be characterized. Consists of either binary mixture of polymer and solvent or a combination of polymers, solvents and non-solvents is how the casting solution generally prepared in the wet phase process. Thus, to concentrate the outermost region of the nascent membrane rather to coagulation bath, a brief evaporation time is always used.

During the wet phase separation step, the selective skin, the transition layer supporting the skin and the open-celled substrate are formed primarily due to the results of the detailed mass transfer happening at the interface between the whole membrane and the quench bath. However, membrane produces from wet phase process have either too many defects that allow their used in application without any further treatment or rather thick selective skin. In wet phase separation process, there are four elementary processes occurred.

Based on the variety of polymeric membranes cross-section morphologies, the process is postulated which are; (i) the direct solidification, (ii) the nucleation and growth of the polymer lean phase, (iii) the spinodal composition and, (iv) the nucleation and growth of the polymer rich phase. The mechanism reasonably arranged into groups of modes of mass transport and into group of forms of the solidification during wet phase processes. Thus, in some their time-and-space combination, the arrangement is taking place in the membrane formation (Stropnik et. al., 2000).

**FIGURE 8:** Ternary Phase Occur During Wet Phase Process.



### 2.3.4 Dry/Wet Phase

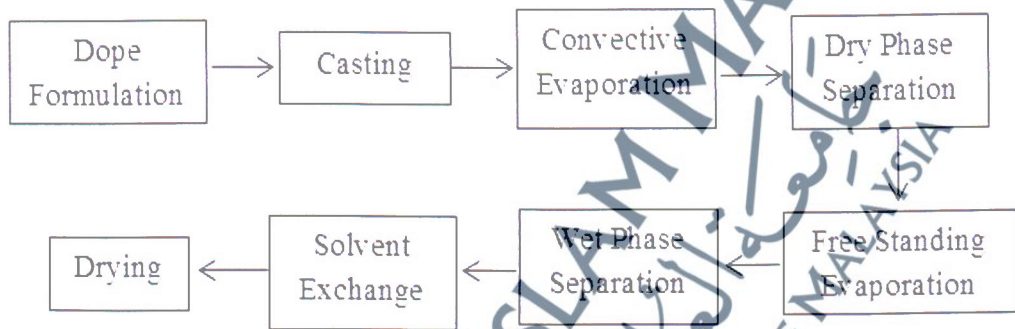
Phase inversion process is the mostly common technique in making asymmetric membrane. The asymmetric membrane has been invented by Loeb-Sourirajan in the 1960s where it gives a new future in membrane technology and industry. This asymmetric membrane is usually used in applications such as ultrafiltration, microfiltration and nanofiltration. Additional complexity is introduced in dry/wet phase process due to the presence of a non-uniform concentration profile in the film at the beginning of the quenching in the wet phase inversion process (Altinkaya, 2006).

Period for loss of a volatile solvent from a casting solution containing a carefully selected amount of a less volatile non-solvent component is required in the dry/wet phase process. Destabilization in the outermost region of the nascent membrane is because of the selective loss of volatile solvent. The almost instantaneous onset of milky in the outermost region is the result of the interfacial dry phase separation. For wet process, the nascent membrane is immersed in a non-solvent coagulant, where the bulk of the membrane structure is formed and extractions of the remaining solvents and non-solvents take place (Pesek and Koros, 1993).

Basically, in dry/wet phase process, the dope solution is exposed to the non-solvent solution (mostly water) for a time interval prior to immersion in the coagulation bath. By varying the casting solution and the formation conditions, the properties of the membrane will have a great impact with the factor of evaporation time and relative humidity (Gao et al., 2009). Besides, solvent with strong dissolving power and high volatility is needed to be chosen. A thin skin layer of solid polymer

is formed directly at the top of the cast film during the first step of desolvation by solvent evaporation due to the loss of solvent. The non-solvent diffuse into the polymer solution through the thin solid layer in the solvent-non-solvent exchange process while the solvent diffuses out (Khulbe et. al., 2002).

**FIGURE 9:** Step Involved in the Preparation of Integral-skinned Asymmetric Membranes According to the Dry/wet Phase Separation Process



#### 2.4 Membrane Formation by Phase Inversion

Phase inversion process usually is the technique in making synthetic membrane where this technique is commercially available. By means of penetrating non-solvent and/or a solvent outflow, phase inversion processes occur when homogenous polymer solution is brought to phase separation. By covering the different technique, phase inversion process will lead to specific membrane structure (Ma et. al., 2011). In preparing asymmetric porous membranes, phase inversion is the most important processes.

Examples of asymmetric membrane fabricated by phase inversion processes are microfiltration (MF), ultrafiltration (UF), reverse osmosis (RO) and support for

composite membrane. This process plays an important role in membrane's structure formation either thermodynamically and kinetically process. During the process, homogenous polymer solution will have two or more components with two-phase systems, where the solid polymer-rich phase and the liquid polymer-poor phase (Aroon et. al., 2010).

In phase process, there are four principals method which are; (i) immersion precipitation; (ii) vapour-induced phase separation; (iii) thermally-induces phase separation and (iv) dry-casting (Altinkaya and Ozbas, 2004). In the study of polyethersulfone (PES)/NMP/H<sub>2</sub>O membrane, it will discuss on immersion precipitation since this technique is commonly used in making membrane.

#### 2.4.1 PES Based Membrane

Although it usually used for ultrafiltration (UF) process, polyethersulfone (PES) also used in making asymmetric membrane for nanofiltration (NF) membrane. Besides it is commercially available, PES also has advantages such as thermally stable polymer that used in high-performance applications, good thermal resistance and chemical inertness. For important separation processes including biological, pharmaceutical and sterilization filtration, PES has been conformed as the membrane material.

However, there rare an issue with PES where it has high hydrophobicity, which severely restricts its long-term applicability and in many cases needs the use of a wetting agent prior to filtration. Important goal for PES in membrane industry is achieving the desired surface properties without modification (Rahimpour et. al.,

2010). Furthermore, PES-based membrane will have outstanding oxidative, thermal and hydrolytic stability as well as good mechanical property. Since it is prepared by phase inversion method, it always shows asymmetric structure. Composition (concentration, solvent, additive) and temperature of PES solution, the non-solvent or the mixture of non-solvents and the coagulation bath or the environment will affect the membrane final structure. Related to hydrophobicity, membrane fouling in PES-based membrane can easily occur. Adsorption of nonpolar solutes, hydrophobic or bacteria is the source for membrane fouling to occur and important problems in membrane technology.

Thus, it will result in the higher energy demand, shorter membrane lifetime and unpredictable separation performance. In biomedical fields such as artificial organs and medical devices, PES membranes are also widely used for blood purification. Since PES is not fitted to the advanced separation field such as intelligent separation, PES membrane is stable in water and is an inert membrane and acts as only a barrier in separation process (Zhao et. al., 2013).

#### 2.4.2 Polymeric Additives

In membrane separation process, most of polymeric membranes have been prepared by phase inversion process. A homogenous polymer solution is cast as a thin film or a hollow fiber shape and immersed into a non-solvent coagulant bath. Between casting solution and non-solvent, the diffusional exchange of solvent and non-solvent can make the casting solution phase-separate to form a membrane with a symmetric or

asymmetric structure. There are researchers that have been discussing on the membrane-forming mechanism during the phase inversion process.

One of the important techniques used in membrane preparation which is the addition of organic or inorganic components as a third component. Methyl cellulose, glycerine, poly (vinyl pyrrolidone) (PVP), PEG, water, LiCl and ZnCl<sub>2</sub> are types of organic and inorganic additives that have been reported can act as a pore-forming agent in enhancing permeation properties. This behaviour is explained in terms of their water-soluble character. The addition of inorganic salts on the membrane formation has been reported and it is explainable in terms of the salt effect based on activity and surface tension. However, they are not thermodynamic and kinetic factors that always used in phase inversion theory (Kim and Lee, 1998).

By common phase inversion process induced by immersion precipitation technique is not versatile in preparing the good membrane structure and properties. Usually, modification is needed to improve the properties of the membrane formation. Thus, addition of proper additive to the casting solution or the gelation media, introducing additional steps and coupling chemical reaction with phase separation process might give the right membrane properties. Table 1 show several researchers study on various type of additive they used in their study. Surfactants, polymer, mineral fillers and non-solvents are example of additives that has been used in casting solution during the preparation of polymer solution. The importance of these additives is to suppress and/or enhance the formation of macrovoids, enhance pore formation and improve pore interconnectivity and/or hydrophilicity (Rahimpour and Madaeni, 2010).

TABLE 1: Effect of additive on membrane

Additive (s)	Polymer	Solvent	Significant Results	References
PEG	PSF	NMP,DMaC	- PEG 6000 can be a suitable additive for making asymmetric membranes having a dense skin layer and relatively macro-void-free sponge-type support layer.	B. Chakrabarty et. al., 2008
PEG	PSF, NMP		- The effect of PEG as a pore-forming agent in the casting solution on the membrane-forming mechanism including the top-layer and macrovoid in phase inversion process	Jeong-Hoon Kim and Kew-Hoo Lee, 1998
PEG	PSF,DMF SPEEK	DMF	- The addition of PEG increase the exchange rate of additive and non-solvent, resulting in enhancement of the macrovoids formation	G. Arthanareeswaran et. al., 2010
PEG	PAN	DMSO	- PEG act as pore former which inhibit DMSO from crystallization and facilitate liquid-liquid phase separation of ternary system	Qing Yun Wu et. al., 2013
PEG, PEO	PES	DMF	- The appearance of PEO segments plays major role of fouling resistance	Yan Zhang et. al., 2011
PEG,PVP, Pluronic	PES	NMP	- PES-Plu showed the highest hydraulic permeability - PES-PEG membrane is the most hydrophilic membrane	Heru Susanto and Mathias Urbicht, 2009

TABLE 1: Continued

PVP, PMMA	PVDF	DEP	- PVDF/PMMA blend membranes showed similar surface and cross-section to those PVDF membrane	Sacid Rajabzadeh et. al., 2012
			- Addition of PVP make the outer surface became denser and spherulitic structure are eliminated	
PVP	PES	DMP	- The presence of PVP acts as preventing to some extents pore blockage due to its hydrophilic action	J. Marchese et. al., 2003
PVP, AA, HEMA	PES	DMAC	- Surface hydrophilicity of the PES membrane is enhanced by addition of AA and HEMA monomers	Ahmad Rahimpour et. al., 2010
PVP	PSF	NMP, DMAc	- Increase in MW of PVP in the membrane casting solution will make the membrane sub-layer seems to have dense structure with comparatively less macrovoids	B. Chakrabarty et. al., 2008
PVP	PES	NMP	- Thermodynamic enhancement tended to increase solvent-non-solvent demixing rate while kinetic hindrance lowered that	Mohtada Sardzadeh and Subir Bhattacharjee, 2013
PVP	PES	NMP	- The addition of additive into polymer solutions significantly alters membrane morphological structures, thus directly affecting membrane separation performances	A.F. Ismail and A.R. Hassan, 2007

TABLE 1: Continued

Acetic acid	CA	Glycol, PEG		Muhammad Zafar et. al., 2012
<b>DGDE</b>	PSF	NMP	-	The addition of DGDE decreased the exchange rate of solvent and non-solvent, resulting in the suppression of the macrovoids formation
<b>PVP</b>	PI	DME, NMP	-	The morphology change in the PI/NMP/water system is mostly due to the change in the phase separation rate
			-	The membrane morphology and the phase separation rate are significantly depend on the MW of PVP
<b>PEG, EGME, AA</b>	PPESK	NMP	-	The presence of EGME and AA as an additives could result in the change of the hollow fiber membrane structure from finger-shape structure to the sponge-like structure
<b>PEG</b>	PES	DMF	-	The presence of PEG of different molecular weights as additives exhibit significant effect on performances of PES
<b>Dextran, PVP</b>	PVA	H <sub>2</sub> O	-	Small amount of appropriate polymeric additives can change the PVA membrane structure and permeability

Ani Idris et. al., 2007

W-Y Chuang et. al., 2000

Yongqiang Yang et. al., 2006

Seong Hyun Yoa et. al., 2004

TABLE 1: Continued

<b>PVP</b>	PAN	DMSO	-	Top layer are thicker as more PVP is added and number of macrovoids like fingers gradually disappears	Bumsuk Jung et. al., 2004
<b>PEG</b>	PVDF- HFP	NMP	-	Addition of PEG promoting rapid phase demixing in the phase inversion process	Sunce Wangchitphimon et. al., 2011

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### 2.4.3 PES/NMP/H<sub>2</sub>O Blend Nanofiltration

As those present in the ultrafiltration membranes, nanofiltration membranes have properties that combine size and electrical effects with solution diffusion mechanisms, as those typically ruling transport in non-porous reverse osmosis membranes. Developed by dissociation of groups as sulphonated or carboxyl acids, the pores are typically near 1 nm in diameter and have fixed charges. Nanofiltration membranes retain multivalent complex ions and transmit small uncharged solutes and low charged ions based on those characteristics. Moreover, nanofiltration is extremely useful in fractionation and selective removal of solutes from complex process streams along with small energy consumption of the process and fluxes attained. Applied by pressure difference and by diffusion, transport uncharged solutes happen due to the concentration gradient that appears across the membrane (Otero et. al., 2006).

PES usually used as interest materials for membrane formation because PES shows outstanding oxidative, thermal and hydrolytic stability as well as good mechanical property. Besides, PES always show asymmetric structure and is prepared by a phase inversion method. Thus, the final membrane structure is influenced by the composition (concentration, solvent, additives) and temperature of PES solution, the non-solvent or the mixture of non-solvents and the coagulation bath and environment (Zhang et. al, 2013).

In preparing dope solution of PES based membrane, 1-methyl-2-pyrrolidone (NMP) is used as solvent to dissolve PES polymer where NMP is commonly used solvents in making dope of polymer solution. To determine the cloud point or the

equilibrium thermodynamic data on ternary system (polymer/solvent/non-solvent), water is used as non-solvents through turbidity titration method. Indicating that a casting solution has become thermodynamically unstable, cloud point represents an approximate transition boundary beyond which demixing (phase separation) takes place. Thus, a polymer solution is titrated with water until the cloud point is observed. Then, the amounts of non-solvent used in determine the cloud point is used for calculation of real formation of dope solution (Ismail and Hassan, 2006). Addition of additives and surfactants in the polymer solutions is to improve the performance of the membranes. Other than that, addition of additives will improve the structure and morphology of the membranes so that it can be used in the separation process.

## **2.5 Applications of Nanofiltration Membrane**

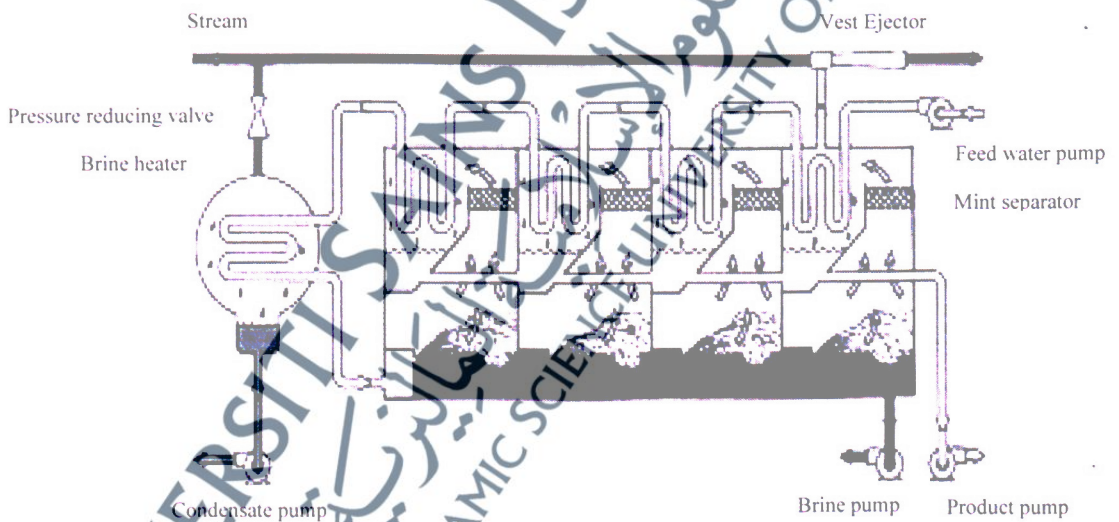
### **2.5.1 Wastewater Treatment**

In wastewater treatment, the interest in the used of membrane technology in general and nanofiltration in particular has emerged as well as drinking water and process water production during the last decade. This growth can be explained by a combination of: (i) growing demand for water with high quality; (ii) growing pressure to reuse wastewater; (iii) better reliability and integrity of the membranes; (iv) lower prices of membranes due to enhanced use and (v) more stringent standard for example in drinking water industry.

In terms of volumes, drinking water production still the largest application of nanofiltration, currently faces new challenges. Hindered by unstabilities in operation,

the potential for nanofiltration in wastewater treatment and water reuse is no worthy due to membrane fouling. In the majority of these, membrane fouling is studied as a potential problem and extension research projects in which nanofiltration is used for water reclamation have been carried out. Causes by organic fouling, scaling, biofouling and particulate fouling, industrial plants of drinking water industry might be successful. However, their successful is depends on a thorough understanding the possible interactions between the feed solution and the membrane (Bruggen et al., 2008).

**FIGURE 10:** Example of the Used Nanofiltration Membrane in Wastewater Treatment



### 2.5.2 Pharmaceutical Industry

In many respects, pharmaceutical industry is extremely complex. The factors like what to work and how intensively to invest in research and development has given influenced to the large public-sector investments in basic biomedical R&D because of

pharmaceutical has become the important industry in human health (Marron, 2006). However, any industry that related to production will have wastewater from the productions of the final product where pharmaceutical industry also included.

Thus, to treat the wastewater so that it will not harm the environment, membrane technology has taken place to solve the problems. Other potential beneficiaries of nanofiltration are in the chemical processing industry and pharmaceutical industry. By implementing membrane technology, there a huge savings could be obtained and it will give environmental benefits due to reduced energy consumption that make nanofiltration particularly attractive (Bruggen et. al., 2008).

For the production of active pharmaceutical ingredients (API) or their intermediates, the synthesis of pharmaceutical products often involves the use of reactive reagents. Thus, development of membranes has been studied to purified of API's in wastewater since it has been become the final products of the industry. Several studies are published I investigating the mechanism of rejection of nanofiltration as the pharmaceuticals are concerned. In many cases with demineralised water, these investigations are only performed on a laboratory scale. The performance of a full-scale nanofiltration treatment has been studied by a few of researchers in rejecting micropollutants such as endocrine disrupting compounds and pharmaceuticals (Radjenovic et. al., 2008).

### 2.5.3 Dyes

To meet the legislative requirement for the discharge, textile industries traditionally use a huge amount of water which is normally discharged after the wastewater treatment system to decrease the pollution load. To address these challenges, such treatment systems have been enhanced due to increasing in regulatory pressure and demand in cost reduction of water and chemicals. From a number of different textile process streams, this operation allows for the recovery of the valuable chemical components and water. Nanofiltration (NF) frequently becomes the chosen treatment process due to inefficient of conventional treatment systems.

Moreover, nanofiltration offers significant advantages such as lower osmotic pressure difference, higher permeate flux, higher retention of multivalents salts and molecular weight compounds, relatively low investment and low operation and maintenance costs. In terms of dye retention, salt rejection, permeate flux and chemical oxygen demand (COD) retention, many researchers have evaluated the performance of NF membranes. Different operating conditions of wastewater and membrane properties have become the factors that have been systematically studied for NF membranes.

For the treatment of textile wastewater, the results have proven that NF membranes are suitable separation process to be employed and generally showed an acceptable rejection. It is necessary to use a suitable pre-treatment in order to prevent fouling and severe module damage to maintain the efficiency of NF membranes at a reasonable operating cost. For every kilogram source in textile refining processes, it

will produce substantial amounts of water, mineral salts and reactive dyes. Thus, from its daily operation, they generate a large amount of wastewater which contains complex contaminants (Lau and Ismail, 2009).

On the other side, containing unfixed dyes along with salts and auxiliary chemicals such as emulsifying agents, the dyeing process wastewater is a highly colored stream. Consumes large quantities of water, textile dyeing is a chemically intensive process. Difficulties in the effluent treatment arise from its non-degradable property by aerobic digestion. The alternative ways for effluent treatment of dyes wastewater is through membrane filtration processes. By reducing water consumption and minimizing effluent discharge, membrane separation process can recover reusable water from the permeate stream. The fouling of NF and RO membranes has been widely investigated throughout the recent years. Thus, modification on the membrane has been developed in order to prevent the fouling phenomena (Kim and Lee, 2006).

**FIGURE 11:** Example of NF Wastewater Treatment on Dyes at Large Scale Operations

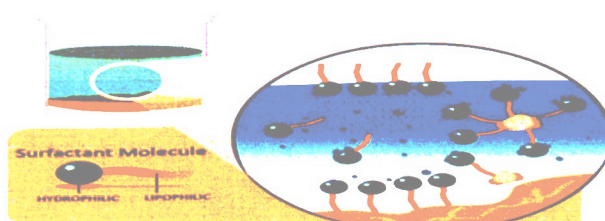


## 2.6 Surfactant

Surfactant is simplified form “surface active agent” that reduces surface and interfacial tension of liquids. Their structure composed of hydrophobic group as their tails and hydrophilic groups as their head. Thus, there are soluble in organic solvent and water. By adsorbing at the liquid gas interface, surfactants reduce the surface tension of water. Leading to minimization of the area of the surface, surface tension is defined as the free surface enthalpy/unit area and is the force acting on the surface of the liquid. On the other hands, by adsorbing at the liquid-liquid interface will reduce the interfacial tension between oil and water (Fernández et al., 2005).

Critical micelle concentration (CMC) is where concentration at which surfactants begins to form micelles. CMC will occur in water and will make the tails of surfactant to form a core that can encapsulate an oil droplet while the head will form outer shell that maintains favourable contact with water. Thus, surfactants can be function well as cleaning, wetting, dispersing, emulsifying, foaming and anti-foaming agents, modifying flow, conditioning the surface, lubrication, glossing, fabric softener and reducing static in many practical applications and products including detergents, fabric softeners, emulsions, paints, adhesives, inks, etc (Jönsson and Jönsson, (1991).

FIGURE 12: Surfactant in the Solution


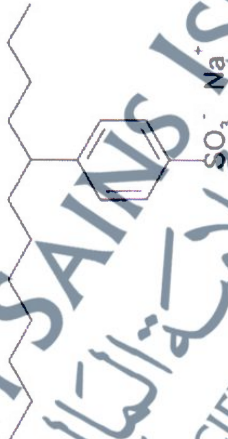



### 2.6.1 Anionic Surfactant

In United States and Europe, the used of anionic surfactants are 60% and 50% respectively. Require the addition of substances to complex calcium and magnesium ions, anionic surfactant are most high-foaming but sensitive to hard water. In particulate soil removal, they are more effective than other surfactants especially from natural fabrics. As a rule, they are easily spray-dried and thus are favoured for detergent powders (Schmitt, 1998).

In the polymerization of fluorinated monomers where the surface activity content highly fluorinated nature of micelles formed in aqueous media, anionic surfactant are useful as a emulsifier to give this unique utility. In the separation of ionic compounds from aqueous mixtures, reverse osmosis and nanofiltration were usually used (Yeom et al., 1999). Other than term “anionic”, this surfactant also used common term which is “soap” that refers to a sodium or potassium salt of fatty acid. Thus, they are commonly used surfactant and account for about 50% of the world production (Salager, 2002).

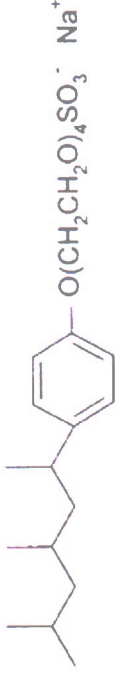
TABLE 2: Classification of Anionic Surfactant

Typical Specification	Structure	Description
<b>Alkylbenzenesulfonates (ABS)</b>	 <p>Sodium tetrapropylbenzenesulfonate (ABS)</p>	<p>- This type of anionic surfactants are only biodegradable with difficulty and generally applied to the branched-chain products</p>
<b>Linear alkylbenzenesulfonates (LAS)</b>	 <p>Sodium n-dodecylbenzenesulfonate</p>	<p>- LAS is sensitive to water hardness, has lowest cost of any surfactant and rapidly biodegradable under aerobic conditions</p>
<b>Alkyl Sulfates</b>	 <p>Sodium n-dodecyl sulfate</p>	<p>- Formed by making the sulphuric acid esters of linear alcohols which also called alcohol sulfates. It tends to be sensitive to water hardness but are very widely used in cosmetics and detergents</p>

## Ether Sulfates



Sodium *n*-dodecyltetraethoxysulfate (sodium laureth sulfate)



Sodium nonylphenol tetraethoxy sulfate

- Prepared by addition of one to four oxyethylene groups to an alcohol, this surfactants also been called as alcohol ethoxysulfates which is then sulfonated

- Oxyethelation can make the surfactants enhanced water solubility and foaming over the analogous alcohol sulfates

## $\alpha$ -Olefin Sulfonates

- Less sensitive to water hardness than most anionic and are readily biodegradable



Sodium hydroxytetradecane sulfonate



Sodium *n*-tetradecane sulfonate

TABLE 2: Continued

## Alkanesulfonates

- Also has been called as paraffin sulfonates or alkane sulfonates

Sodium 2-hexadecane sulfonate

- The commercial synthesis of this surfactants requires high capital

investment

- It has high biodegradability, low toxicity and reasonably good water solubility

- Obtained from by-products of sulfite process, widely disperse, water-soluble lignosulfonic acids with an average MW greater than 100,000

### Lignin Sulfonates

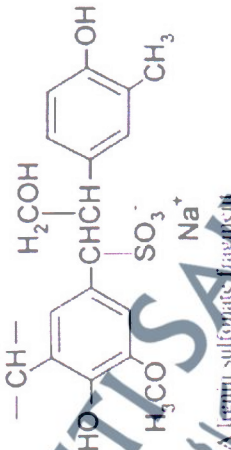


TABLE 2: Continued

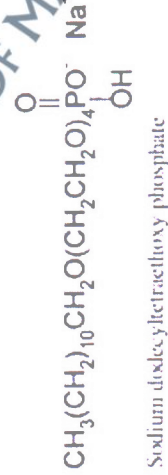
### Ester Sulfonates

- Possess good biodegradability and excellent hard-water detergency



### Phosphate Esters

- In alkaline solutions, they resist hydrolysis, they have good biodegradability and more compatible with hypochlorite



than the corresponding ethoxylated non-ionic

- The commercial products are in monoesters, diesters or the mixture of two

### Sulfosuccinate Esters

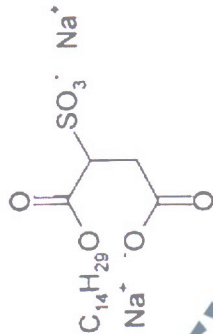


TABLE 2: Continued

### Isethionate Esters

- For synthetic bar 'soap' and cosmetic applications, it have good foaming and dispersing properties



### Acyl Taurates

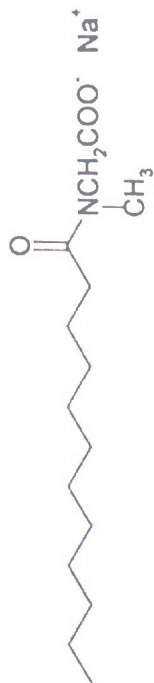
- In textile and detergent bars and shampoo applications, it have good tolerance to water hardness. However, sometimes it can be classified as amphoteric surfactant



Sodium N-methyl-N-oleoyltaurate

### N-Acylated Amino Acids

- Have been used in toothpaste, shampoo and hard cleaners as lather boosters
- It is compatible with cationic surfactants

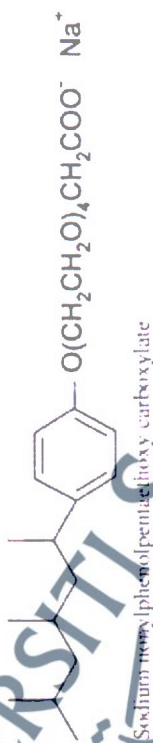


Sodium lauryl sarcosinate

TABLE 2: Continued

### Ether Carboxylates

- Sensitive to water hardness, good foamers and mild and suitable used in cosmetics



Sodium nonylphenolpolyethoxy carboxylate

### Soap

- The first synthetic surfactants are salts of fatty acids
- Potassium soaps have better solubility in nonaqueous media



Sodium stearate

## 2.6.2 Cationic Surfactant

Cationic surfactants are used in fabric softeners, corrosion inhibitors and antimicrobial agents. At neutral pH, they do not provide effective cleaning and it is not used in general purpose detergents (Schmitt, 1998). Most often of the halogen type, cationic surfactants are dissociated in water into an amphiphilic cation and an anion. Compounds such as fatty amine salts and quaternary ammoniums is a very large proportion of this class which corresponds to nitrogen with one or several long chain of the alkyl type coming from natural fatty acid. Generally, this type of surfactants is more expensive than anionics due to the high pressure hydrogenation reaction to be carried out during synthesizes. With the exception of non-quaternary nitrogenated compounds, or when a cationic complex synergetic action is sought, they are not good detergents nor foaming agents and they cannot be mixed in the formulations which contain anionic surfactants. (Salager, 2002).

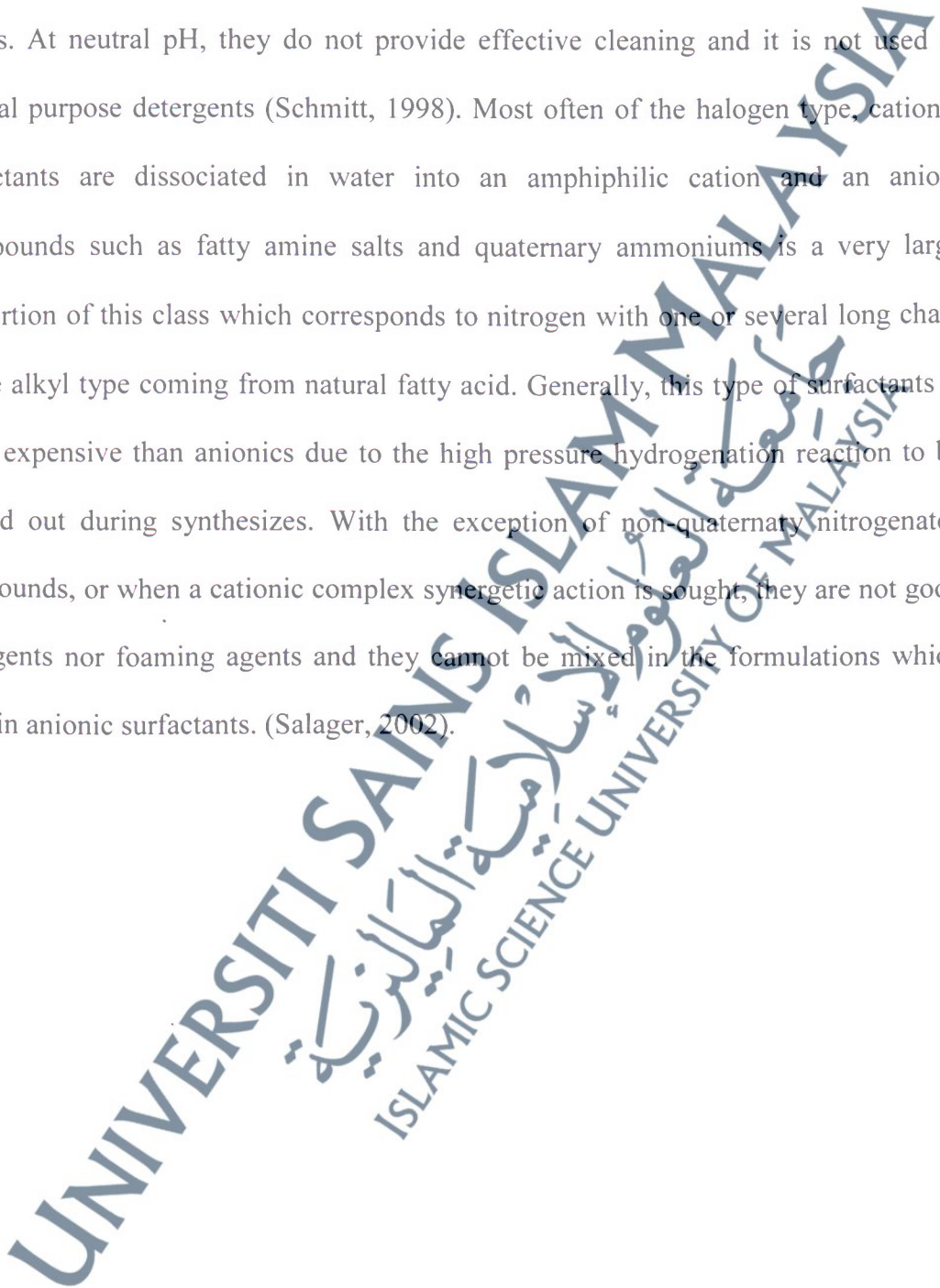


TABLE 3: Classification of cationic surfactant

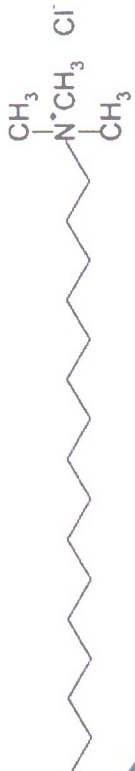
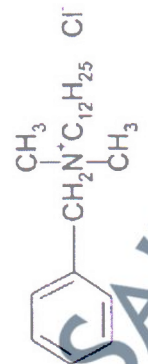

Typical Specification	Structure	Description
Alkyl Quaternary Ammonium Salts	 <p> <math display="block">\text{C}_{15}\text{H}_{31}\text{N}^+\text{Cl}^-</math> </p>	<ul style="list-style-type: none"> <li>- Made from naturally occurring fatty acids</li> </ul>
Benzylalkylammonium Salts	 <p> <math display="block">\text{C}_{12}\text{H}_{25}\text{N}^+\text{Cl}^-</math> </p>	<ul style="list-style-type: none"> <li>- Widely used in pharmaceuticals and also called benzalkonium salts</li> </ul>
Amidoamine Quaternaries	 <p> <math display="block">\text{C}_{15}\text{H}_{31}\text{N}^+\text{Cl}^-</math> </p>	<ul style="list-style-type: none"> <li>- The most common products are prepared from tallow fatty acids and diethylenetriamine</li> </ul>

TABLE 3: Continued

<p><b>Quaternary Compounds</b></p>		<p>- Quaternization greatly stabilise the imidazoline structure. It is also used as fabric softeners and antistatic agents</p>
<p><b>Ester Quats</b></p>	<p>A di-C<sub>16</sub> quaternary imidazolium methyl sulfate</p>	<p>- Quaternized with dimethyl sulfate or methyl chloride, the most common used is fatty acids esters if triethanolamine</p>

### 2.6.3 Non-ionic Surfactant

Non-ionic accounts for roughly 40% of worldwide surfactant use. Which makes the requirements for “builders” in laundry detergent less demanding, non-ionic are generally more tolerant than anionic of water hardness. Thus, for removal of oily soil from synthetic fabrics, they tend to be more effective than other surfactant. Non-ionic surfactant has characteristics of low-foaming products, have good cold water solubility and have low critical micelle concentration that make them effective at low concentration. Non-ionic surfactant also is more common in industrial applications than anionic (Schmitt, 1998).

Almost 45% from the overall industrial production non-ionic surfactant comes. Due to their hydrophilic group is of a non-dissociable type, they do not ionize in aqueous solution such as alcohol, phenol, ester, ether or amide. By the presence of a polyethylene glycol chain, a large proportions of non-ionic surfactant are made hydrophilic which obtained by the polycondensation of ethylene oxide. As found in many commercial products, non-ionic surfactant compatible with other types and are excellent candidates to enter complex mixtures. Besides, non-ionic surfactants are good detergents, wetting agents and emulsifiers. However, some of them have good foaming properties and others exhibit a very low toxicity level. Nowadays, non-ionic surfactant has been used widely in domestic and industrial products such as powdered or liquid formulations (Salager, 2002).

TABLE 4: Classification of non-ionic surfactant


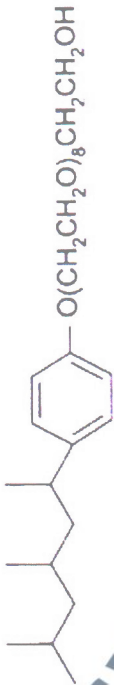


Typical Specification	Structure	Description
<b>Ethoxylated Alcohols</b>	 <p>Dodecanol 9-mole ethoxylate</p>	<ul style="list-style-type: none"> <li>- Largest used of this compounds is in detergents</li> </ul>
<b>Ethoxylated Alkylphenols</b>	 <p>Cumylphenol 9-mole ethoxylate</p>	<ul style="list-style-type: none"> <li>- Slowly reach complete biodegradation upon release to the environment</li> </ul>
<b>Ethoxylated Esters (PEG Esters)</b>	 <p>Dodecanic acid nonaethylene glycol ester</p>	<ul style="list-style-type: none"> <li>- Can be considered to be esters of fatty acids and polyethylene glycol</li> </ul>
<b>Fatty Acid Alkonalamides</b>	 <p>Dodecanic acid N-cosanolamide</p>	<ul style="list-style-type: none"> <li>- In increasing the viscosity and liquid performances, it is very effective. It is also sensitive to water hardness in the absence of other surfactants</li> </ul>

TABLE 4: Continued

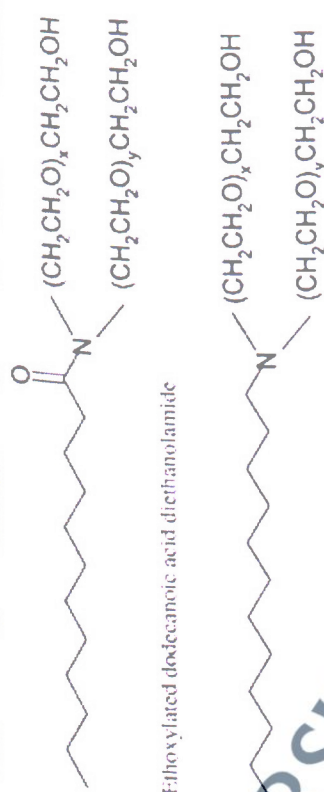

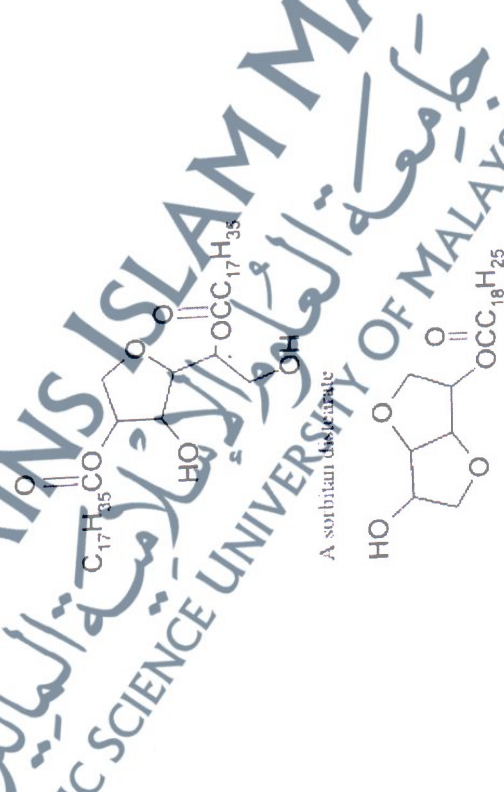
<b>Ethoxylated Alkanalamides</b>	 <p style="text-align: center;">Ethoxylated dodecanoic acid diethanolamide</p>	- It is produced by addition of ethylene oxide to hydroxyl group of the alkanolamide
<b>Ethoxylated Amines</b>	 <p style="text-align: center;">Ethoxylated dodecylamine</p>	- These are made by ethoxylation of amines that are prepared from naturally occurring fatty acids

TABLE 4: Continued

<b>Esters of Polyhydroxy Compounds</b>	 <p style="text-align: center;">A sorbitan distearate</p> <p style="text-align: center;">A disorbitan monostearate</p>	- Consists of fatty acid esters of glycerine, sorbitol and similar polyfunctional alcohols that is broad class of food emulsifiers
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### Ethoxylated Esters

- Ethylene oxide is added to the unesterified hydroxyl functional groups which is widely used as emulsifiers in food and cosmetics also in specialty applications

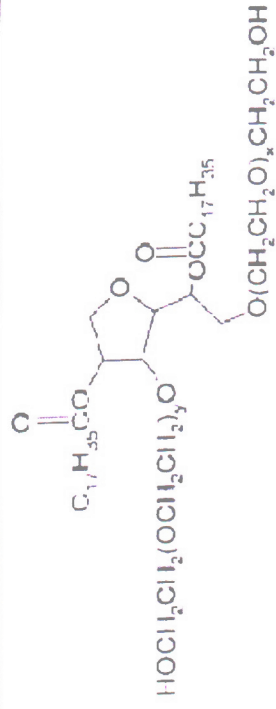
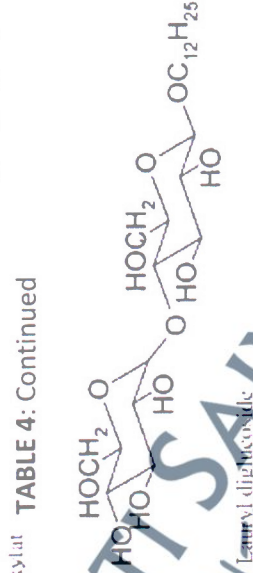


TABLE 4: Continued



Lauryl diglycoside  
Copolymer of the polyoxamer type

### Ethylene Oxides

- Generally made by KOH-catalysed polymerisation of propylene oxide to form hydrophobic base poly(propylene glycol) groups
- Usually with hydrogen oxide, it is made by oxidation of tertiary amines.

### Amine Oxides



Lauryl dimethylamine oxide

## 2.7 Nanofiltration Surfactant Membrane

Literally means by active at a surface, surfactant is an abbreviation for surface active agent. Show a tendency to adsorb at liquid/solid, liquid/liquid and air/liquid interfaces, surface active agents are compounds having a hydrophobic and a hydrophilic group. Classified according its hydrophilic group in anionic, cationic, non-ionic and amphoteric surfactants, they are mainly used in aqueous solutions.

Surfactants are strongly adsorbed at an interface or they form colloid aggregates in solution at very low concentration and lowering the interfacial tension due to their chemical structure. Used as detergency, wetting, cleaning, emulsification, foam control and lubricity in industrial systems, surfactants have found many industrial applications. Several studies on microfiltration (MF) and ultrafiltration of surfactants can be found in the literature since membrane separation techniques are often used. To improve permeate flux and reduce fouling, some of the research are concerned with surfactant pre-treatment of UF membrane. Because of their effect upon flux and rejection, in all cases, interactions between surfactant and membrane have been investigated.

Besides, because of the important role of the hydrophobic/hydrophilic surface interactions, most of the main research is carried out using organic membranes (Fernández et. al., 2005). Nanofiltration membrane has several advantages include flux enhancement, heat recovery, high temperature cleaning and pasteurization; it has become an interested separation process in wastewater treatment and pre-treatment. Can be used in the treatment of various hot fluid streams, nanofiltration membrane

tend to be at high temperature become the advantages without strict temperature control. Which further saves operating cost, the enhanced flux due to high temperature may allow certain reduction of operating pressure of the systems (Wu et. al., 2009).

Thus, addition of surfactant on nanofiltration membrane polymer solution will give significance different in the performance and morphological structure of the membrane. The differences on morphological structure will lead to the different performances of the membrane. It has been investigated that addition of surfactant will enhanced the permeation flux of nanofiltration membrane and give high performance on the separation process of the nanofiltration membrane. Moreover, different types of surfactants will give different morphological structure on the membrane. For example, if Span-80 surfactant is added to the polymer solution, it will suppress the macrovoids of the membranes. This will lead to the high performance of the membrane itself. Another example is, if Tween-80 is added on the small amount, it will increase the formation of macrovoids and finger-like in the sub-layer of the membranes (Amirilargani et. al., 2009). Thus, it will give significance different in performance of the membrane since it has lot of finger-like structure that will help in separation process.

## 2.8 Dyes

Absorb part of the visible light, dyes are unsaturated organic substances. They should have an affinity to substrate such as textiles, paper, etc. In the late 19<sup>th</sup> century, the introduction of synthetic dyes from petroleum sources has ended the market for natural dyes from plant origin, which has been used since 3500 B.C. For commercial

purpose, more than 100,000 different dye structures have been synthesized and it is estimated that more than 3600 individual dyes are being produced. According to their chemical structures, organic dyes can be classified such as azo compounds (60%-70%), anthraquinones (15%), triarylmethanes (3%), phthalocyanines (2%), etc with the values within parenthesis indicating % of total volume.

According to applications, dyes can be classified as acid (16%), disperse dyes (18%), direct dyes (16%), and reactive dyes (13%). One class of dye may be used for different applications (Tehrani-Bagha and Holmberg, 2013). Besides, many dyes are difficult to be decolorized and decomposed biologically due to their complex structure and synthetic origin. Giving the great impacts towards environment, dye will released to the mainstream. Thus, many researchers try to find an effective and economical way of dye-containing wastewater treatment for protecting the environment and to meet the stringent government law (Ahmad et. al., 2002).

**TABLE 5:** Advantage of physical and chemical methods of dye removal from industrial effluent

Physical/chemical method	Advantages	Disadvantages
<b>Fentous reagent</b>	Effective decolorisation of both soluble and insoluble dyes	Sludge generation
<b>Ozonation</b>	Applied in gaseous state: no alteration of volume	Short half-life (20 mins)
<b>Photochemical NaOCl</b>	No sludge production, initiate and accelerate azo-bond cleavage	Formation of by-products, release of aromatic amine
<b>Cucurbituril</b>	Good sorption capacity for various dyes	High cost
<b>Electrochemical destruction</b>	Breakdown compounds are non-hazardous	High cost of electricity
<b>Activated carbon</b>	Good removal of variety	Very expensive

<b>Peat</b>	of dyes Good adsorbent due to cellular structure	Specific surface area for adsorption are lower than activated carbon
<b>Wood chips</b>	Good sorption capacity for acid dyes	Requires long retention times
<b>Silica gel</b>	Effective for Basic dye removal	Concentrated sludge production
<b>Ion exchange</b>	Regeneration: adsorbent loss	no Not effective for all dyes
<b>Irradiation</b>	Effective oxidation at lab scale	Requires a lot of dissolved O <sub>2</sub>
<b>Electrokinetic coagulation</b>	Economically feasible	High sludge production

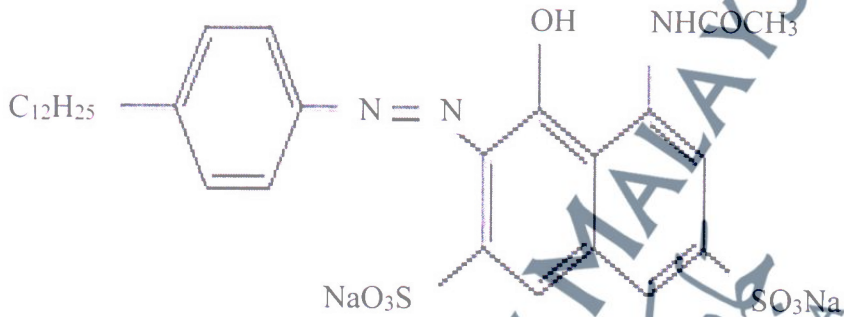
### 2.8.1 Anionic Dye

The water soluble dyes carry a charged group which may be anionic or cationic. Containing sulfonate and carboxylate substituent is structures of anionic dyes. A dye with a sulfonate groups remains anionic over the entire pH range since sulfonic acid is very acidic. On the other hand, carboxylic acid contents are weak and relatively high in pH is needed for a carboxylate-containing dye to be anionic and water soluble. In certain polymeric fibers, wool and silk, anionic dyes are suitable for colouration (Tehrani-Bagha and Holmberg, 2013).

From the most varied classes of dyes, anionic dyes includes many compounds which exhibit characteristics differences in structure but possess common feature, water-solubilizing and ionic substituent. From the chemical standpoint, anionic dyes also include direct dyes and it includes a large proportion of the reactive dyes. Using different adsorbents, many researchers have studied the adsorption of anionic dyes using ammonium-functionalized MCM-41. However, adsorption of anionic dyes

such as mango seed, soy meal, bagasse and bamboo has been an alternative due to the low-cost and available adsorbents (Salleh et. al., 2011).

**FIGURE 13:** Example of Anionic Dyes Structure



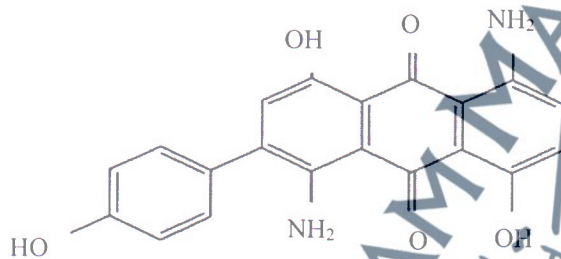
### 2.8.2 Cationic Dye

Cationic dyes are widely used in acrylic, wool, nylon and silk dyeing. Based on substituted aromatic group, these dyes include different chemical structures. Thus, this group of dyes is considered as toxic colorants and can cause harmful effects such as allergic dermatitis, skin irritation, mutations and cancer. Which are generally contains hydrochloride and zinc chloride complexes, these dyes are also called basic dyes and depends on a positive ion. Furthermore, cationic dyes is water soluble which carry a positive charge in their molecule and yield colored cations in solution.

Cationic functions is found in various types of dyes, mainly in cationic azo dyes and methane dyes , also in anthraquinone, di- and tri-arylcarbenium, phthalocyanine dyes, various polycarboxylic and solvent dyes. Crystal violet is used as model in dye adsorption for cationic dyes (Salleh et. al., 2011). Due to several characteristics such as moderate substantivity, relative economical, high tinctorial strength, wide shade range and shows good brightness, cationic dyes is exclusively

used for coloration of acrylic fibers. However, cationic also have their own limitations which are high acid contents, colored backwaters, poor shade stability and preferential dyeing that can cause harm towards body when has direct contacts with it (Kolorjet Chemicals PVT. LTD., 2014).

**FIGURE 14:** Example Structure of Cationic Dyes



### 2.8.3 Non-ionic Dye

Contains no charges is how non-ionic dyes defined. It is widely used in synthetic hydrophobic fibers from aqueous dispersions (Ali et. al., 2005). In non-ionic dyes includes disperse, vat and sulphur dyes. Like  $\text{NO}_2$ , disperse dyes are small and planar with polar substituents. Dyes color affected by the polar group influences the UV adsorption by the dyes. The non-ionic dyes are basically applied in aqueous solution at high temperature ( $120^\circ\text{C}$ - $130^\circ\text{C}$ ).

With this high temperature, the thermal supplied causes the polymer's structure become looser and less crystalline and open the gaps for the dye entrance. Vat and sulphur dyes, are two other water-insoluble dyes. The common blue dye is indigo. They are often used for dark colors, such as black and brown and they are always in complex mixtures (Tehrani-Bagha and Holmberg, 2013).

#### 2.8.4 Ionic Dyes

Ionic dyes tend to aggregate in diluted solutions and this will lead to the formation of dimer and higher order aggregates. The ionic dyes behaviour may changes due to the aggregation in general. Increasing the dye concentration or ionic strength may increase the aggregation and may decrease with increasing temperature. The additions of organic solvents also lead to decline of aggregation dyes and also may rise and decline with additions of sulphonate groups to the dye structure. This may cause higher hydrophobic interaction in solution. In order to analyse the ionic dyes, color absorption using UV-Vis spectrophotometer is the most suitable method quantitative analysis (Antonov et. al., 1999).