

**EVALUATION OF THE ROLE OF POLYELECTROLYTES IN
MEMBRANE FILTRATION**

EVELYN WONG SHU LI

**A project report submitted in partial fulfilment of the
requirements for the award of Bachelor of Engineering
(Honours) Chemical Engineering**

**Lee Kong Chian Faculty of Engineering and Science
Universiti Tunku Abdul Rahman**

May 2021

DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

Signature : 

Name : Evelyn Wong Shu Li

ID No. : 15UEB05320

Date : 13th April 2021

APPROVAL FOR SUBMISSION

I certify that this project report entitled “**EVALUATION OF THE ROLE OF POLYELECTROLYTES IN MEMBRANE FILTRATION**” was prepared by **EVELYN WONG SHU LI** has met the required standard for submission in partial fulfilment of the requirements for the award of Bachelor of Engineering (Honours) Chemical Engineering at Universiti Tunku Abdul Rahman.

Approved by,

Signature : 

Supervisor : Dr. Ng Law Yong

Date : 19 April 2021

Signature : _____ -

Co-Supervisor : _____ -

Date : _____ -

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ABSTRACT

The usage of polyelectrolytes in membrane modification has gained great popularity in recent years. Some aspects relating to the polyelectrolyte-modified membranes, however, have not been evaluated in the previous works. In this paper, the roles of various types of polyelectrolytes on membrane filtration in various applications are evaluated and the characterisation results of polyelectrolyte-modified membranes to membrane filtration performance in various applications are also studied. The deposition of polyelectrolytes onto the membrane has changed the membrane's nature and properties. The modification changes have greatly benefited the micro-pollutants and foulants removal from water. Seven studies using different types of polyelectrolytes and membrane support are studied and evaluated. Furthermore, several characterisation methods such as FTIR, contact angle measurements, SEM, AFM, and XPS are characterised based on different methods. The usage of zwitterionic PMPC-co-AA has decreased the membrane fouling and has a very stable membrane performance. Next, the usage of spin-assisted LbL assembly is preferable due to its simplification operation and is timesaving. Moreover, the polyelectrolytes of CHI and ALG biopolymers are recommended as they are biocompatible, adaptable material, versatile, non-toxic, easy to obtain, and most importantly, biodegradable. Last but not least, the most used deposition method is the LbL assembly. However, an improved LbL assembly and more environmentally friendly materials usage have not been expansively investigated.

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LIST OF SYMBOLS / ABBREVIATIONS

d	lattice planar distance, nm
λ	wavelength, nm
θ	diffraction angle, °
AFM	Atomic Force Microscopy
ALG	Alginate
CHI	Chitosan
CIAPTA	[3-(acryloylamino)propyl] trimethylammonium chloride
CIVBTA	(4-vinylbenzyl) trimethylammonium chloride
EDC	N-(-3-Dimethylaminopropyl)-N-ethylcarbodiimide
EDS	Energy Dispersive Spectroscopy
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
HMPSA	[3-(methacryloylamino) propyl] dimethyl (3-sulfopropyl) ammonium hydroxide
IPF	Inorganic Polymeric Flocculants
LbL	Layer-by-layer
LLI	Liquid-liquid Interface
LPR	Liquid-phase Polymer-Based Retention
NHS	N-Hydroxysuccinimide
PAA	Poly(acrylic acid)
PAH	Poly(allyl amine) Hydrochloride
PADMAC	Poly(diallyl dimethyl ammonium chloride)
PAN	Polyacrylonitrile
PDAC	Poly (diallyl dimethyl ammonium chloride)
PDDA	Poly (diallyl dimethyl ammonium chloride)
PEI	Poly(ethyleneimine)
PES	Polyethersulfone
PEM	Polyelectrolyte Multilayer
P(HMPSA-co-	Poly[3-(methacryloylamino) propyl] dimethyl (3-

CIVBTA	sulfopropyl) ammonium hydroxide-co-(4-(vinylbenzyl) trimethylammonium chloride)]
P(HMPA-co-SSNa)	Poly[3-(methacryloylamino) propyl] dimethyl (3-sulfopropyl) ammonium hydroxideco-sodium 4-styrenesulfonate]
P(CIAPTA-co-SSNa)	Poly[3-(acryloylamino)propyl]trimethylammonium chloride-co-sodium 4-styrenesulfonate]
PMPC-co-AA	Poly(2-methacryloyloxyethyl phosphorylcholine-co-acrylic acid)
PSS	Polystyrene Sulfonate
SA-LbL	Spin-assisted LbL
SEM	Scanning Electron Microscopy
SPEs	Sulfonated Polysulfone
SSNa	Sodium Styrene Sulfonate
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
XPS	X-ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 General Introduction

Membrane technology is known to be a crucial technology in the separation process industry. It is an engineering approach to the transfer of substances across two regions with the assistance of permeable membranes. Membrane technology has been greatly used in a different type of industrial sectors such as water and wastewater treatment operations and so on.

Generally speaking, a membrane is known as a barrier in which it is used to control mass transfer. However, one or more species will selectively be allowed to pass through the membrane (Manning, 2015). Membrane filtration is one of the most favourable methods in the industrial sectors, such as the purification of the protein, as it allows high throughput and operational flexibility (Pinelo *et al.*, 2012). In addition, most of the membrane separation processes have low energy requirement, and extreme temperature and pressure are not mandatory (Pinelo *et al.*, 2012). There are 4 major filtration categories in the major filtration such as microfiltration, ultrafiltration, nanofiltration and reverse osmosis. In membrane filtration, dissolved substances and fine particles are separated via specific solutions (Muro, 2012). In a membrane separation, a driving force is mandatory to be used to transport certain particles through the membrane by accordant with the molecular or physical sizes of the dissolved substances (Muro, 2012).

There are some challenges normally encountered in the membrane filtration processes. One of the major challenges is on account of the fouling membrane interface. There will be a loss of membrane productivity with respect to time when membrane fouling is taking place (Ilyas *et al.*, 2017). In addition to that, membrane fouling will cause a dramatic flux reduction while affecting the solute selectivity and membrane operational cost, which could be explained by higher transmembrane pressure requirement and frequent membrane replacement (Pinelo *et al.*, 2012). However, membrane fouling can be minimized by optimising the operating conditions so that the membrane flux can be maximised without causing severe fouling issues during an operation. Membrane fouling management is vital as it ensures the separation process can be conducted with minimal cleaning and

membrane replacement. This will also result in lesser costs while leading to a more energy-efficient separation process (Ng *et al.*, 2014). Membrane fouling can be caused by various factors such as the quality of the feed water, type of membrane, membrane materials, and the filtration process design and operational control. The common types of membrane fouling include particle fouling, organic fouling, biofouling, and scaling (Samco Technologies, 2018). Membrane fouling will inevitably cause additional loadings on the membrane filtration in order to maintain the membrane throughput in a continuous filtration process.

Polymers, such as polyelectrolytes, play an important role in the membrane preparation and also filtration processes. Polyelectrolyte is an organic polymer that is charged and hydrolysed. They are applied in various industries, especially the water industries (Oladoja, 2016). Polyelectrolytes are categorised into two main categories, which are the cationic polyelectrolytes and anionic polyelectrolytes. In addition, the commonly used polyelectrolytes are polyacrylic acid, polymethacrylic acid, and polystyrene sulfonate, also known as polysalts (Dobrynin, 2020). Figure 1.1 displays examples of the most commonly used polyelectrolytes in different industries.

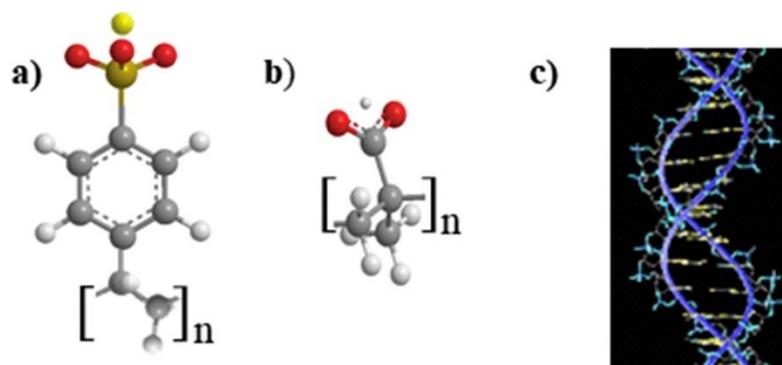


Figure 1.1: Example of polyelectrolytes (a) polystyrene sulfonate (b) polymethacrylic acid (c) DNA (Dobrynin, 2020)

By depending on the pH value, polyelectrolytes can dissociate in aqueous solutions and carry charges. The properties of polyelectrolytes are said to be indistinguishable when compared to ordinary electrolytes and polymers. This is because ordinary polyelectrolytes function the same way as electrolytes. In some cases, after the polymers are dissociated, polyampholytes are formed when the polymers contain both positively and negatively charged ions (Dobrynin, 2020). Some commonly used polyampholytes are the bovine serum (which is a protein in

the native state), gelatine (which is the denatured proteins), and synthetic copolymers (Dobrynin, 2020).

1.2 Importance of the Study

Based on the usage of polyelectrolyte on membrane filtration, various studies are working on a similar topic due to its great importance in the field. Nowadays, the utilization of membrane filtration has drastically increased, and it plays an important role in all various industrial sectors. The major advantage of membrane filtration is its effectiveness and economic approaches (Peters, 2010). Membrane processes can be used in serving different purposes. In Malaysia, the largest industry platform that requires the usage of membrane technology is water and wastewater treatment. From the previous study, daily water consumption increases 80 % since 1950, and while the population of Malaysian citizens only increases by up to 30% (Chen *et al.*, 2006). Additionally, by comparing it to the global market, a bar graph of the membrane filtration demand market is shown in Figure 1.2 below.

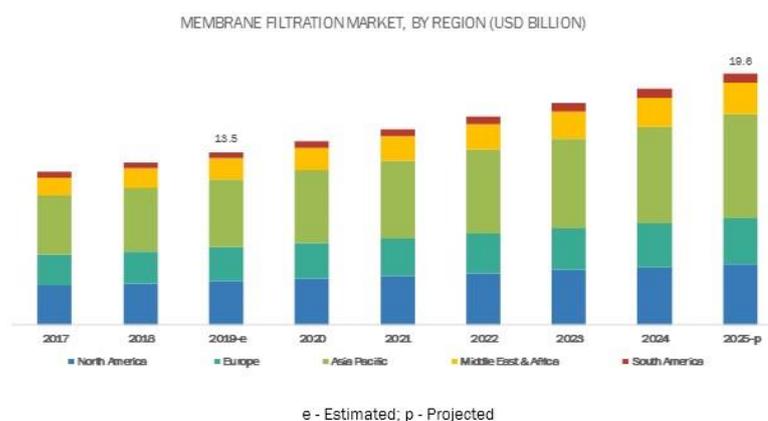


Figure 2.2: Demand for membrane filtration by region (MarketsandResearch, 2019)

Figure 1.2 clearly shows that the industry that requires the usage of membrane filtration has gradually increased from the year 2017 to 2020, and it is estimated to increase in the following years. This study emphasises the importance of membrane filtration in the current year and also its demand from time to time. Of late, polyelectrolytes have been taken into consideration in the membrane filtration process. Polyelectrolyte is able to work individually in a membrane filtration unit and also as a membrane separation unit under modification. To further explain the

statement, polyelectrolytes can be added to the water treatment process as a coagulant aid. Also, polyelectrolytes can be fabricated into a polyelectrolyte multilayer and be used for multiple applications. One of the well-known membrane modifications is the development of polyelectrolyte multilayer (PEM). PEM is widely used in industries such as water treatment, food industry, biotechnology and textile industry (Elshof *et al.*, 2020). Therefore, it is noteworthy to evaluate the role and performance of polyelectrolyte in membrane filtration.

1.3 Problem Statement

Water pollution has been a critical environmental issue that has drawn the attention of researchers worldwide. In order to solve this issue, the implementation of membrane filtration techniques in water treatment fields is favored over the last few decades. However, the major downside of the membrane filtration process is the fouling of the membrane. Membrane fouling occurs easily due to the presence of foulants in the feed stream. In order to solve this issue, the fabrication of polyelectrolyte multilayers comes into place as it has the ability of antifouling properties. Due to its anti-fouling capability, numerous researches were carried out to investigate the role of polyelectrolytes on membrane filtration. Nevertheless, the comparison between each type of deposition method on various applications is not well evaluated and limited. Besides, several characterisation methods have been implemented to evaluate the physical and chemical properties of polyelectrolyte-modified membranes. The characterization methods and results conducted on polyelectrolyte-modified membranes, however, are not well evaluated and compared in any of the previous works. Hence, this study serves to compile and evaluate the roles of various types of polyelectrolytes on membrane filtration as well as their characterisation results based on several different types of polyelectrolytes used.

1.4 Aims and Objectives

The following are the objectives of this study:

- To evaluate the roles of various types of polyelectrolytes on membrane filtration in various applications.
- To relate the characterisation results of polyelectrolyte-modified membranes to membrane filtration performance in various applications.

1.5 Scope and Limitation of the Study

In this research, the main priority is to evaluate the role of polyelectrolyte in each membrane filtration unit. From the previous studies, there are various applications on the role of polyelectrolytes. However, in this study, the topics to be covered only include the polyelectrolytes used in membrane filtration and for membrane modification. Polyelectrolytes used for other applications such as the amino acid separation and removal of proteins are not covered in this study.

1.6 Contribution of the Study

Throughout this research, several sources that are available for the role of polyelectrolyte in the membrane filtration unit are found in journals. The significance of the role of polyelectrolyte will be studied and evaluated by contrasting it to other sources. The study will be evaluated in terms of its role, simplicity and effectiveness. Other than that, different methods are also utilised to study the characterisations of polyelectrolyte and membrane filtration. The methods used in the membrane processes can be concluded based on the information and data obtained from the studies. In addition to that, the characterisation methods can also be used to evaluate the efficiency of each method used.

1.7 Outline of the Report

The arrangement of the thesis is summarised as follows:

Chapter 1 comprises the introduction and backgrounds of the problem. Not just that, problem statement, aims and objectives, the importance of study, limitations and contribution of the report are also included. Furthermore, Chapter 2 is the literature review, which solely focuses on the role of polyelectrolytes in different sectors of the membrane filtration unit. The ideas and researches from different authors and journals are extracted, compared and contrasted. Besides, the utilisation of various methods to determine and characterise polyelectrolyte and membrane filtration are also studied and evaluated. The most suitable approach in each membrane filtration process is also determined and evaluated. Chapter 3 is the methodology and work plan. Chapter 3 covers the extract of online data from a variety of online database. The work plan and data for the processes for each membrane filtration unit are listed out and compared. Chapter 4 encompasses results and discussion. It elaborates the data obtained and interpretation of the corresponding result to evaluate the role of

polyelectrolyte in the membrane filtration unit in terms of characterisations of polyelectrolyte and membrane filtration. Lastly, Chapter 5 is the conclusion of the study. The results from the evaluation are summarised in this section, and any recommendations for future works will be proposed.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In membrane filtration, it separates the particles existing in either liquid or gas mixtures. The membrane is semi-permeable. Thus, it allows molecules that are smaller in size to pass through the membrane. There are two types of flow filtration which is the conventional and cross-flow filtration. The most-used is cross-flow filtration. This is because the cross-flow filtration works more efficiently and results in lower and more efficient energy usage. Hence, results in lower operating cost (Synder Filtration, 2020). There all altogether four main types of membrane filtration. The type includes microfiltration, ultrafiltration, nanofiltration and reverse osmosis. In this study, the type of membrane filtration is chosen based on its aspects towards the role of polyelectrolytes in certain industries.

Polyelectrolyte serves multiple purposes. For certain specific industry, polyelectrolyte is required to be modified into selective layers to serve its purpose. One of the most conventional selective layers is the polyelectrolyte multilayer. Polyelectrolyte multilayer membrane is then used in the fabrication of the nanofiltration membrane, which is being used in several industries. In addition, a polyelectrolyte-based ultrafiltration membrane is also necessary for specific industries.

2.2 Polyelectrolyte Multilayers Deposited on Membrane

PEM is used in a various range of fields such as the water and wastewater treatment, medicine, and pharmacology field (Izumrudov, Mussabayeva and Murzagulova, 2018). It is one of the important techniques that has been used in membrane filtration applications. One of the techniques in the production of the PEM membrane is by using the layer-by-layer (LbL) method. Based on the previous study on fabricating selective layer membrane, the LbL method is considered the simplest, versatile, environmental-friendly, and low in cost method (Ilyas *et al.*, 2016). This method works by applying a coating of polyelectrolyte onto porous support (Elshof *et al.*, 2020). The polyelectrolytes used in previous work were polycation and polyanion, and they were both weak polyelectrolytes. They were selected as this pair of

polyelectrolyte can be controlled through solution pH adjustment during the coating process, which will benefit in the simplification of control over the membrane performances (Ilyas *et al.*, 2016). The negatively charged poly (acrylic acid) (PAA) and positively charged poly (allylamine hydrochloride) (PAH) were previously assembled, and the surface zeta potential of thin polymeric layers has been reported to be precisely controllable. The active separation layers of the membranes are formed when the charged polymers adsorb onto the oppositely charged surface, forming a new layer. The formation of a subsequent new layer works by releasing counter ions and reaching the entropic gain (Elshof *et al.*, 2020).

The significant asset of using a PEM membrane is due to its versatility in the layer properties. In addition, there are a few factors that affect the separation properties, which are the type of polyelectrolyte used, pH, ionic strength during coating, and the number of deposited layers used (Ilyas *et al.*, 2016). There are a few parameters that will affect the properties of polyelectrolyte, such as the ionic strength of the polymer solution used in the coating process (de Grooth *et al.*, 2015). In this case, ionic strength is vital as it is used in determining charge compensations applied to the polyelectrolytes in the multilayers. Moreover, the final layer that is adsorbed, also referred to as the terminating layer, will also affect the properties of polyelectrolyte (de Grooth *et al.*, 2015). The charges throughout the PEM membrane will constantly be in either positive or negative charge as the terminating layer is required to end with a polycation or polyanion.

Over the years, from the previous studies, they have proven a point in which PEM is the most promising way in the field of membrane surface modification. PEM has the capability of antifouling functionalities on membranes (Ilyas, English, *et al.*, 2017). The antifouling mechanism is a major upgrade on the polyelectrolyte. Thus, the PEM membrane is the most-used option in the industries.

2.3 Role of Polyelectrolyte in Membrane Filtration

There is various usage of polyelectrolytes in the membrane separation process. However, in this topic, three usages of polyelectrolyte in the industries are studied and evaluated. The industries include the forming of coagulants which aids in the water and wastewater treatment, fabrication of tunable separation layers for the removal of micro-pollutants, and lastly, the removal of antibiotics in the aquatic system.

2.3.1 Polyelectrolyte as Coagulant for Water Treatment

One of the major roles of polyelectrolyte in membrane filtration is acting as a coagulant aid in water and wastewater treatment. The most widely used process is the coagulation-flocculation process. This process is used as a pre-treatment for the wastewater treatment process, and it mainly focuses on the removal of contaminants and impurities. The coagulation and flocculation process separate all sorts of particles and thus enhances the filtration process.

In the past decades, synthetic polyelectrolytes are used in the purification of the water process. It serves as the cationic polyelectrolytes, also known as primary coagulant and binds with the large aggregates such as the non-ionic polyelectrolytes (Tzoupanos and Zouboulis, 2011). In order to improve the flocculation process, inorganic coagulants and organic polyelectrolytes are required to merge into one reagent. This is to avoid the additional addition of polyelectrolyte after adding the coagulant. Normally, polyelectrolytes are carried in a solid form, and the usage of certain equipment is required to handle the polyelectrolytes. Thus, by merging the inorganic coagulants and organic polyelectrolytes into one reagent, it will simplify the overall water treatment process. In addition, the simplification of the overall treatment will further benefit in reducing the overall cost needed for the treatment process. This is because specific equipment to handle the solid form polyelectrolytes can be avoided.

Moreover, in a water treatment plant, the use of polyelectrolytes is added to the coagulation tank for flash mixing purpose. Polyelectrolytes are added into the structure of a coagulant as a coagulate aid. The purpose of forming a coagulant aid is to destabilise the colloidal materials and agglomerate the smaller particles into larger settle-able flocs (Tzoupanos and Zouboulis, 2011). After the coagulation process, it then proceeds to the flocculant process for another slow mixing process. Furthermore, a physical separation between the solid and liquid phase is achieved by three different processes, which are decantation for sedimentation purpose, flotation, and lastly, filtration. Figure 2.1 displays the flowchart of the coagulant-flocculant process.

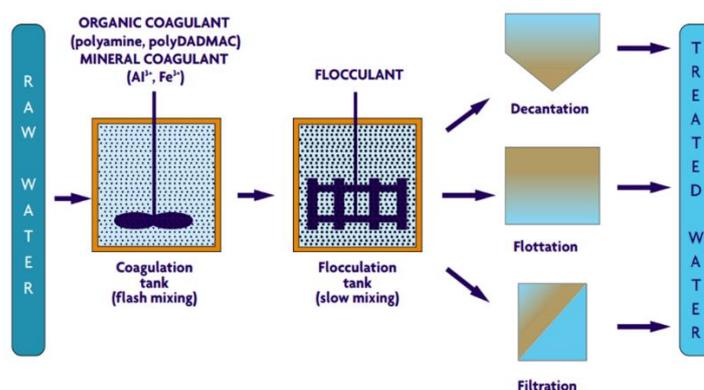


Figure 2.1: Physical-chemical process involved in the coagulation-flocculation process (Félicien Mazille, 2020).

In short, this process is essential in a treatment plant. Polyelectrolytes added as a coagulant aid into the process at the beginning. The treatment process undergoes the coagulation-flocculation process, then followed by sedimentation and filtration. For algae-existence water, flotation is required. From the separation process, the sludges obtained will have extremely high-water content, and it is required to undergo further concentration, and polyelectrolytes play a vital role in the sludge conditioning.

2.3.2 Tunable Separation Layers for Micro-pollutants Removal

Water is essentially important for drinking sources as well as aquatic life. In today's world, the occurrence of micropollutants has already massively polluted the environment. Examples of micro-pollutants included the usage of herbicides and pesticides (Chandra and Usha, 2020). In order to remove the micro-pollutants, various researches have been done for the study. The process works by incorporating the polyelectrolyte multilayers with the hollow fiber nanofiltration membranes (Ilyas, Abtahi, *et al.*, 2017).

The hollow fiber membranes are favourable as it is a promising way in all sorts of industry. The hollow fibre-based nanofiltration membrane has relatively high packing densities and is robust against backwash (Emonds, Roth and Wessling, 2020). The technique used in the formation of a hollow fibre nanofiltration membrane is interfacial polymerization. The reactant used is an aqueous solution with amine components. The microporous support structure is required to soak into

the reactant and then immersed with the second reactant of acid chloride solution (Emonds, Roth and Wessling, 2020). After contacting with the second reactant, a thin selective surface of the polyamide layer will be formed at the interface. Figure 2.2 below shows the single step of a cross-link polyelectrolyte-based nanofiltration hollow fibers.

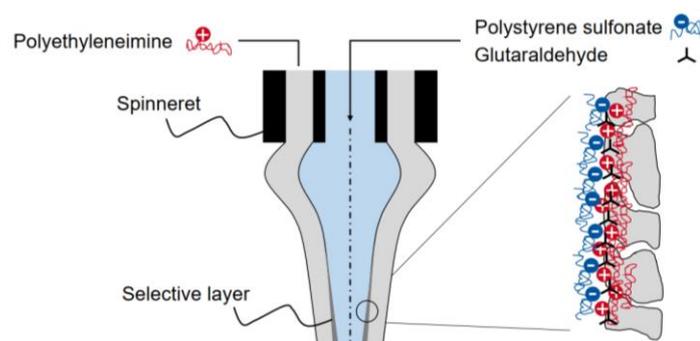


Figure 2.2: Schematic diagram of a single step cross-link polyelectrolyte-based nanofiltration hollow fibres (Emonds, Roth and Wessling, 2020).

Another way to obtain the hollow fibre nanofiltration membrane by using the LbL method, which is similar to the fabrication of polyelectrolyte multilayer membrane. It works by dip-coating the existing nanofiltration membrane with the polyelectrolytes. However, this technique is not preferable because it is time-consuming as it requires more and complicated processes (Emonds, Roth and Wessling, 2020).

The hollow fiber nanofiltration membrane is almost used in all of the water treatment industry. The hollow fiber shape is mostly used due to its design and space-saving. Due to this design, backwashing is also possible. Thus, it is favourable in the water treatment industry. One of the most used methods for the removal of micro-pollutants is through the formation of tunable separation layers using polyelectrolytes.

2.3.3 Liquid-phase Polymer-based Retention for Antibiotics Removal

Antibiotic is a type of pollutants which is harmful to the environment. Over the years, it has become a major concern to public health throughout the whole world. Among all types of antibiotics, tetracycline (TC) and ciprofloxacin are the most-used antibiotics. TC is commonly used for disease control and also the growth of animals

(Palacio *et al.*, 2020). While for ciprofloxacin, it is known as a synthetic antibacterial drug that is commonly used for anti-microbial activity (Palacio, Rivas and Urbano, 2018). Not just that, TC also possesses the capability for anti-bacterial activity, and it can be found in surfaces or underground water sources. The residuals of TC are hard to be fully eliminated using biological treatments. Hence, new technologies come in handy at this crucial moment. In the past decades, different types of materials have been used in the removal of TC from an aqueous solution, such as advanced oxidation process and electrochemical and adsorption processes. However, none of the methods achieves 100% elimination (Palacio *et al.*, 2020).

Recently, various researches have been done regarding the full elimination of TC. The new technique introduced is Liquid-phase Polymer-based Retention (LPR). This technique works similarly to ultrafiltration and microfiltration (Palacio *et al.*, 2020). The betterment of LPR is that it is able to separate and remove small molecular weight species, especially antibiotics (Huang and Feng, 2019). The LPR method works effectively on ultrafiltration membranes, and is simple to operate and also has low energy consumption (Berk, 2013).

LPR is required to incorporate with polyelectrolyte copolymers which contain quaternary ammonium and sulfonate groups. This is because they possess the ability to remove TC by electrostatic interactions (Palacio *et al.*, 2020). Their copolymers include a zwitterionic monomer, anionic monomer, and cationic monomer. To further elaborate, the zwitterionic monomer is [3-(methacryloylamino) propyl] dimethyl (3-sulfopropyl) ammonium hydroxide (HMSPA), then the anionic monomer consists of sodium styrene sulfonate (SSNa), and lastly, the cationic monomer consists of [3-(acryloylamino) propyl] trimethylammonium chloride (CIAPTA) and 4-(vinylbenzyl) trimethylammonium chloride (CIVBTA). Figure 2.3 displays the chemical structures of the polyelectrolyte copolymers.

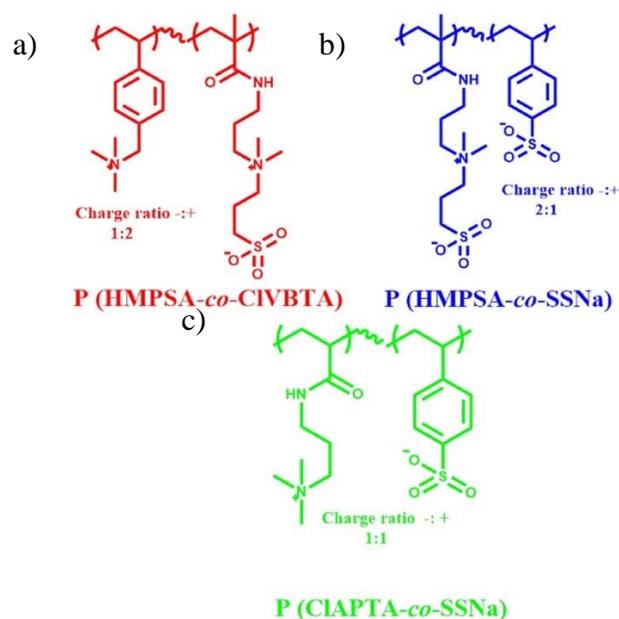


Figure 2.3: Chemical structures of polyelectrolyte copolymers a) zwitterionic monomer-co-cationic monomer b) zwitterionic monomer-co-anionic monomer c) anionic monomer-co-cationic monomer (Palacio *et al.*, 2020)

This technique then further investigates the conditions on the effects of the pH, ionic strength, polymer concentration, and desorption to obtain the data and results for the TC removal from the aqueous solution. The existence of this technique is able to remove the antibiotics in the water stream and aquatic system. In the long run, this will be a bonus in reducing the antibiotics pollutant in the environment.

2.4 Characterisation of Polyelectrolyte-Modified Membranes

To determine the characteristics of the polyelectrolyte-modified membranes, various techniques and instrumentations are used for the determination. The instrumentations include scanning electron microscopy (SEM), contact angle measurement, UV-VIS spectrophotometer, Fourier transform infrared spectrometry (FTIR), and X-ray Diffraction Analysis (XRD). For the fabrication of the PEM membrane, the (SEM), contact angle measurement, and FTIR method are used. For the evaluation of the formation of hollow fiber membrane in conjunction with PEM, a contact angle measurement technique is used. As for the polyelectrolyte as a coagulant aid, SEM, FTIR and XRD method is used. Moreover, a contact angle measurement is used to determine the properties in the removal of micro-pollutant. Lastly, a UV-VIS

spectrophotometer is used to obtain the concentration of tetracycline for antibiotics removal and also the FTIR method to determine the polyelectrolyte copolymers.

2.4.1 Scanning Electron Microscopy, SEM

SEM is an instrument that produces a series of signals over the surface of solid samples. The variety of signals is generated by a beam that works based on accelerated electrons (Susan Swapp, 2017). One of the major signals is the secondary electron which is used for the production of SEM images. Moreover, backscattered and diffracted backscattered electrons are also generated to ascertain the photons, heat, visible light, and crystallite solid samples. The incident electrons in the sample will cause an inelastic collision. The high-energy electrons will eventually drop to a low-energy state (Susan Swapp, 2017). Thus, a fixed wavelength of X-rays will be produced. Figure 2.4 displays the SEM images of the polyelectrolyte as a coagulant aid after drying at a low temperature of approximately 40 °C.

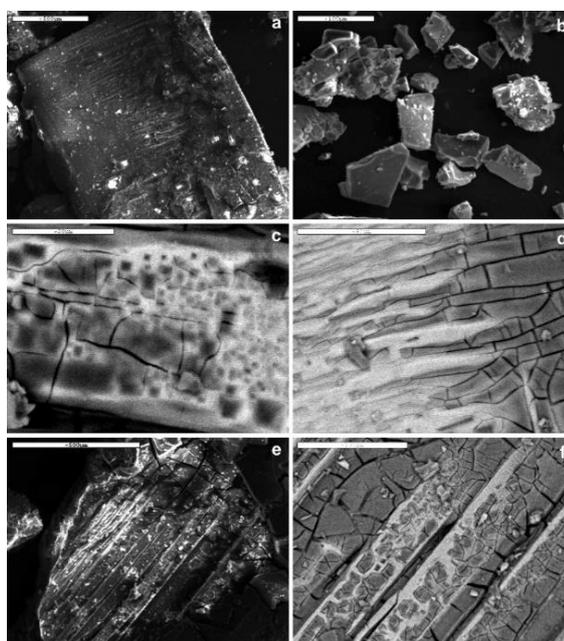


Figure 2.4: SEM images of polyelectrolyte as coagulant aid obtained after drying at low temperature (Tzoupanos and Zouboulis, 2011)

2.4.2 Contact Angle Measurement

The contact angle is the angle measured between the liquid and vapour interface to the solid surface. Contact angle measurements can be divided into static and dynamic sessile drop methods. In the static sessile drop method, it is measured by using the

optical subsystem of the goniometer. The contact angle of the interfaces is captured and analysed by high-resolution cameras and specific software of the goniometer.

In addition, the dynamic sessile drop method works quite similarly to the static method. However, the difference is the dynamic of the drop. The dynamic sessile drop method is required to add the volume of the drop dynamically instead of increasing its interfacial area. The advancing angle is the maximum possible angle, and it is obtained when the volume of the drop is maximised. Moreover, the receding angle is the smallest possible angle when the volume of the drop is minimised. The contact angle can be obtained by getting the difference between the advancing and receding angles. Figure 2.5 displays the contact angle measurements of polyelectrolyte multilayers with different terminal layers and polymer concentrations for the micro-pollutant removal.

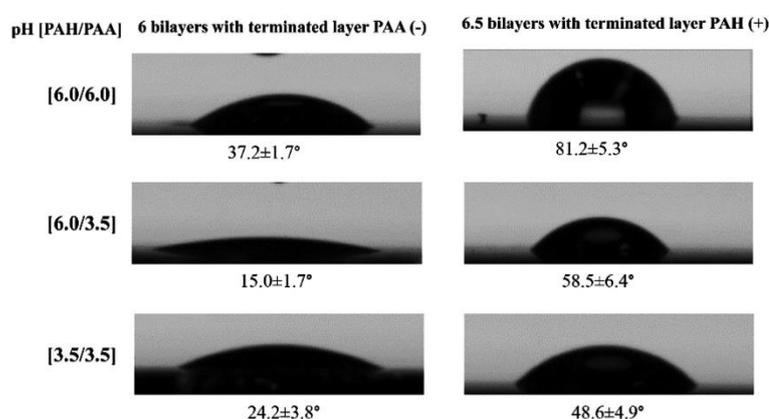


Figure 2.5: Contact angle measurements of polyelectrolyte multilayers with different terminal layers and polymer concentration for the micro-pollutants removal (Ilyas *et al.*, 2016)

2.4.3 UV-VIS Spectrophotometer

UV-VIS spectrophotometer is a technique used in determining the spectra based on the chemical compounds which will absorb ultraviolet light and visible light. The light passes through the sample will cause the ultraviolet radiation to be absorbed by the sample. The ultraviolet radiation will cause the electrons to absorb energy and jump from a ground state to an excited state. Thus, the excitation and de-excitation process will form the spectrum. Figure 2.6 displays the UV-VIS spectra of growth of CHIS/PSS multilayers in the fabrication of polyelectrolyte multilayer membranes.

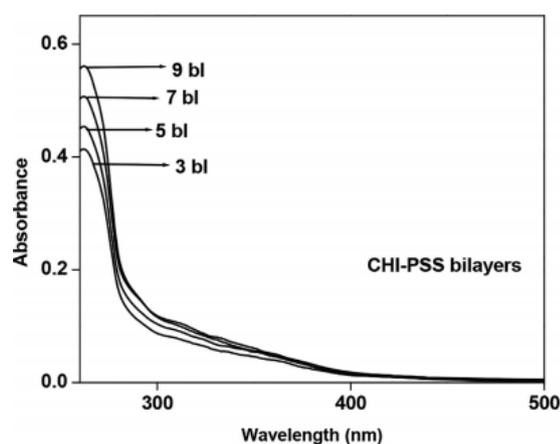


Figure 2.6: UV-VIS spectra of growth of polyelectrolyte multilayers (Chandra, Usha and Mohan, 2020)

2.4.4 Fourier Transform Infrared Spectrometry, FTIR

FTIR spectrometry is an instrument that is used to determine molecular structures based on the absorption of infrared radiation. The infrared spectrum works by the principle of vibrational and rotational energy, which causes the molecules to move from a ground state to an excited state. The molecular vibrational spectrum will be scattered across the molecules, and the molecules will absorb radiation, particularly based on the type of wavelengths. There are a few aspects of absorption peaks, such as the frequency, number, and intensity. The frequency, number, and intensity of absorption peaks are determined by the vibrational energy gap, the number of vibrational molecules, and the transition of energy levels, respectively. Figure 2.7 displays the FTIR spectra of the anionic polyelectrolytes, composite coagulants based on different polymerisation methods.

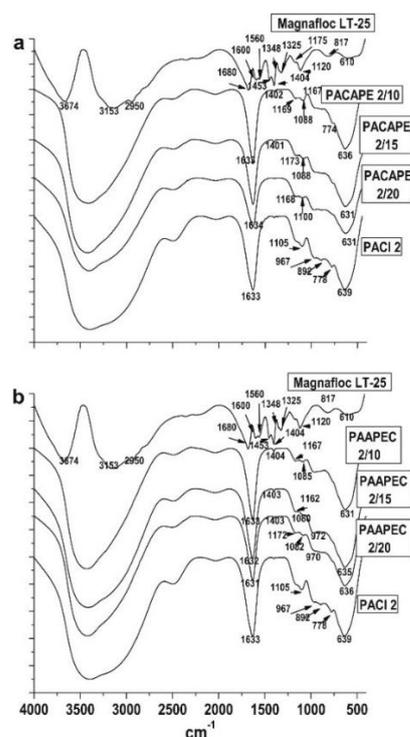


Figure 2.7: FTIR spectra of polyelectrolyte as coagulant aid (a) polymerization method (PACAPE) (b) co-polymerisation method (PAAPEC) (Tzoupanos and Zouboulis, 2011)

The advantage of using FTIR spectrometry is its accuracy in determining the wavelength, and it has a relatively short scan time with an approximate of 1 second. Besides, FTIR spectrometry has wide scan range ($1000 - 10 \text{ cm}^{-1}$) and extremely high resolutions ($0.1 - 0.005 \text{ cm}^{-1}$).

2.4.5 X-ray Diffraction Analysis, XRD

X-ray diffraction is a technique used in the characterisation of crystallite size and atomic spacing. X-ray diffraction works according to the size of the crystalline sample with constructive interference of monochromatic X-rays (Barbara L Dutrow and Christine M. Clark, 2020). Generally, X-rays work by heating the filament to produce highly concentrated electrons. X-rays are created by a cathode-ray tube, and monochromatic radiation is produced by a collimator after the X-ray is filtered. Monochromatic radiation will pass through the sample and form electrons.

According to Bragg's law, it correlates with the electromagnetic radiation wavelength to the diffraction angle and lattice plane distance of the crystalline sample. When the X-ray hits on the crystalline sample, it will form scattered and

unscattered beams. The unscattered beams will continue to hit on the successive planes. The successive planes are split by the interplanar distance (Barbara L Dutrow and Christine M. Clark, 2020). Thus, constructive interference will be formed. The Bragg Equation 2.1 shows how the lattice spacing, d , is measured based on the wavelength of the X-rays, λ , and angle, 2θ .

$$n\lambda = 2d \sin \theta \quad (2.1)$$

Where

λ = Wavelength, nm

d = Lattice plane distance, nm

θ = Diffraction angle, °

When the Bragg Equation is satisfied, constructive interference and peak in intensity will be formed. A detector of the setup will detect and convert the x-ray signal to a computer monitor or printer (Barbara L Dutrow and Christine M. Clark, 2020). Figure 2.8 displays the XRD patterns for the polyelectrolyte as a coagulant aid.

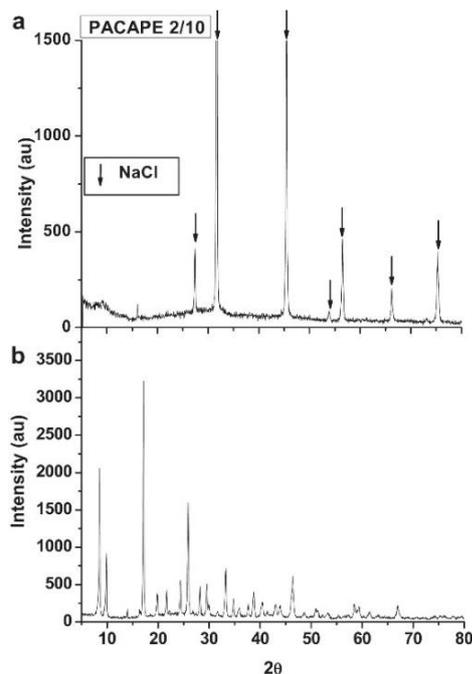


Figure 2.8: XRD patterns for the polyelectrolyte as coagulant aid (a) PACAPE sample after freeze-drying without pre-treatment (b) with the treatment of adding sulphate (Tzoupanos and Zouboulis, 2011)

2.5 Summary

Various sources for the role of polyelectrolytes on membrane filtration process are considered in this evaluation such as the formation of PEM membrane, the formation of nanofiltration membrane, polyelectrolyte as a coagulant in water treatment, the formation of hollow fiber membrane for micro-pollutant removal and removal of antibiotics in the aqua system. The formation of selective layers such as PEM is required to be fabricated in order to further extend its ability in the formation of hollow fiber membrane for the removal of micro-pollutants in water. Besides, polyelectrolytes, in conjunction with ultrafiltration membranes, are used for the removal of the antibiotic.

Characterisation of polyelectrolyte-modified membranes is also required to be carried out to determine the presence of polyelectrolytes as well as their physical and chemical properties. In order to study the properties of polyelectrolytes, instrumental analyses such as SEM, contact angle measurement, FTIR, and XRD are used as the characterisation methods.

There are several roles of polyelectrolytes on membrane filtration, such as the fabrication of PEM membranes, polyelectrolyte as coagulant aid for the water treatment, formation of hollow fiber PEM based membrane for the removal of micro-pollutants, and liquid-phase polymer-based retention for the removal of antibiotics. The methodology and characterisation methods for each specific role are studied. The methods studied for the fabrication of PEM membranes are the static layer-by-layer adsorption method and the automated dynamic layer-by-layer spraying system. For the polyelectrolyte as a coagulant aid, the methods studied are the combination of Cationic IPF and Anionic Polyelectrolyte as coagulant aid and also by using only an anionic polyacrylamide as a coagulant aid. Moreover, the method used for the micro-pollutant removal is by fabricating a tunable separation layer, and lastly, for the removal of antibiotics, the liquid-phase polymer-based retention technique is used.

CHAPTER 3

METHODOLOGY AND WORK PLAN

3.1 Introduction

The role of polyelectrolyte on membrane filtration are evaluated based on previous studies. There are several platforms used to obtain online databases such as ELSEVIER, Wiley Online Library, and SCOPUS. The online databases include journals, textbooks, and data analysis. Based on the journals, the applications and methodologies for the polyelectrolytes deposited on the membrane are compared and contrasted. For the data analysis, the SCOPUS database provides charts and graphs based on the number of journals over time.

3.2 Online databases

3.2.1 ELSEVIER

For the online database, various keywords are used for the searching of journals. Firstly, by using ELSEVIER, the keyword “role of polyelectrolyte” is used to search for the relevant journals. Journals for each type of polyelectrolyte role are extracted and reviewed. After reviewing each of the roles of polyelectrolytes, four applications of polyelectrolytes are selected. There are a few aspects in selecting the role of polyelectrolytes. The aspects are the usage of polyelectrolytes in industries, the type of polyelectrolytes used, the complexity of the design, the demand of each specific role, and the contribution to the industry and also the environment.

Furthermore, the topics that are focused on in this study is the relationship between the type of polyelectrolyte and their performance in the multilayer membrane, the capability of polyelectrolyte to work individually for the water treatment process, the relationship between a modified polyelectrolyte-based filtration membrane and their performance for the removal of micro-pollutants, and the synthesis of polyelectrolyte copolymers and their performance for the removal of antibiotics.

Moreover, for the type of polyelectrolyte and their performance in the multilayer membrane, keywords such as “polyelectrolyte multilayer membrane” are used to obtain more specific and detailed journals. In addition,

keywords such as “polyelectrolytes planted on membrane” is used in the finding of journals for their specific roles. The journals obtained with those keywords are evaluated.

3.2.2 Wiley Online Library

In Wiley Online Library, journals and textbooks are obtained for the evaluation of polyelectrolyte on membrane filtration. Similar to the usage of ELSEVIER, the keyword “role of polyelectrolyte” is used to search for the relevant journals and textbooks. Then, keywords such as “polyelectrolyte multilayer membrane” and “polyelectrolytes planted on membrane” are also used to obtain more journals.

3.2.3 SCOPUS

Journals and data analysis are obtained from SCOPUS. Similar to the usage of ELSEVIER and Online Wiley Library, certain keywords are used to search for the relevant journals. The data analysis is set within the year range of 2011 to 2020. Moreover, data analysis for the number of journals over the year is also provided. Figure 3.1 displays the data analysis for the use of polyelectrolytes based on the subject area from 2011 to 2020.

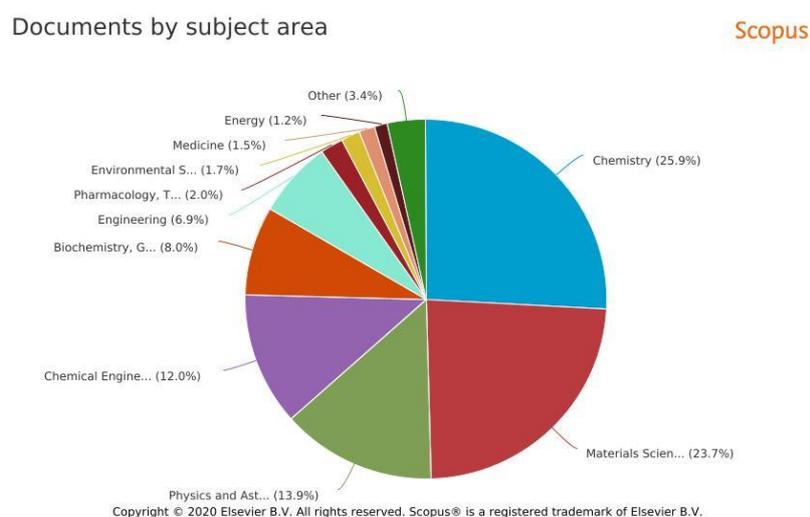


Figure 3.1: Data analysis of journals based on the subject area (SCOPUS, 2020)

Figure 3.1 shows that the role of polyelectrolytes based on the chemistry field has the highest percentage of 25.9 %. Based on the journals extracted for the chemistry field, the fabrication of polyelectrolyte multilayer membranes is chosen for this study. This is because polyelectrolyte multilayers play an important role in many industries such as water and wastewater treatment.

Furthermore, another three different applications of polyelectrolytes are selected based on environmental issues such as water pollution. Over the years, the demand for membrane filtration in the water industry has increased significantly year by year (Ilyas, English, *et al.*, 2017). The role of polyelectrolytes on membrane filtration selected is polyelectrolyte as coagulant aid for water treatment, the fabrication of hollow fibre UF membranes for the removal of pollutants, and also the removal of antibiotics using the liquid-phase polymer-based retention (LPR) method.

3.3 Data Analysis from SCOPUS

Data analysis is analysed by using the SCOPUS database. Keywords such as “Polyelectrolyte on membrane” are used to obtain the SCOPUS database. The range for analysis is set from the year 2011 to 2020. The journals for polyelectrolyte deposited on the membrane are obtained and analysed. Figure 3.2 displays the number of journals focused on the topic of polyelectrolyte deposited on membrane over the years.

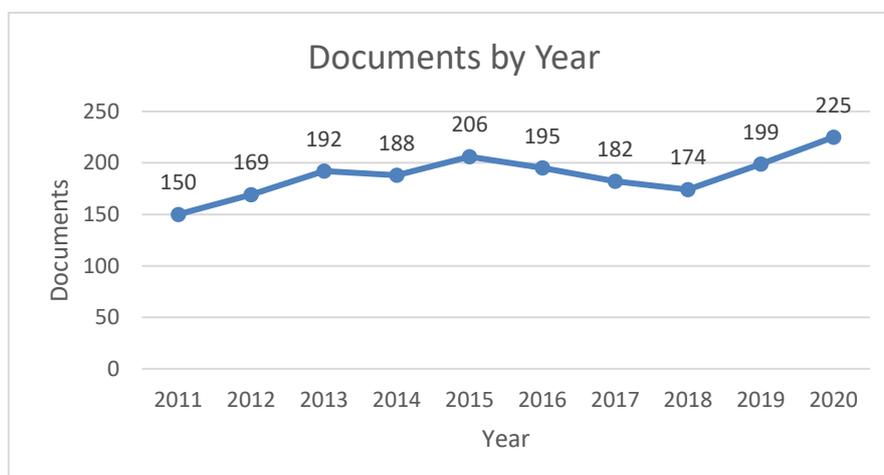


Figure 3.2: Number of journals for polyelectrolyte planted on the membrane.

3.4 Summary

The use of polyelectrolytes in membrane filtration is selected based on ELSEVIER, Wiley Online Library, and SCOPUS. The role of the polyelectrolyte selected is the fabrication of PEM membranes, polyelectrolytes as a coagulant aid, fabrication of hollow fibre UF membranes for the removal of micro-pollutants, and also the removal of antibiotics using the liquid-phase polymer-based retention (LPR) method. Certain keywords are used to obtain journals and journals with those keywords will be evaluated. Besides, the SCOPUS database is also used to obtain the data analysis. The data analysis shows the number of journals based on the use of polyelectrolytes in membrane filtration.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Introduction

In this chapter, seven materials for the deposition of polyelectrolytes on membranes are studied and evaluated. Relevant data such as different deposition methods, membrane characterisations, performances for polyelectrolyte multilayer (PEM) membranes are studied and evaluated. There are several characterisation methods used in the previous studies to characterise the deposition of polyelectrolytes on membranes, such as Scanning Electron Microscopy (SEM), Field Emission Scanning Electron Microscopy (FESEM), Fourier Transform-Infrared Spectroscopy (FTIR), UV-VIS spectroscopy, Atomic Force Microscopy (AFM), Thermogravimetric (TGA) Analysis, contact angle measurement, and zeta potential. Based on previous studies, there are multiple methods to deposit PEM on the membrane. Most of the studies involve different types of polyelectrolytes, and the material with the most significant performance will be analysed and evaluated.

4.2 Materials used to deposit polyelectrolyte multilayers on membrane

There are various materials and techniques used in the deposition of polyelectrolytes on the membrane. One of the most used techniques is the layer-by-layer (LbL) technique, as it requires lower cost and is a more straightforward method. In this research, seven different materials are studied and discussed.

4.2.1 Development of CHI/PSS membrane via LbL assembly

In today's world, the agricultural, domestic, and industrial sectors have greatly polluted the water system. With the increase of populations and industrial sectors, the presence of pollutants such as herbicides has increased tremendously, and it has greatly affected the water quality system. Hence, the first material aims to remove pollutants from the water system. This material

is carried out by using the LbL technique (Chandra, Usha and Mohan, 2020). The polyelectrolytes used in this material are Chitosan (CHI) and polystyrene sulfonate (PSS). In this study, CHI and PSS were used as they can be obtained easily, versatile, and most importantly they are environmental-friendly. Furthermore, polymeric membranes are used as they are low in cost, have high rejecting capabilities, and easy to be used. The type of polymeric membrane used for the deposition is the UltiporN66 polyamide membrane. Table 4.1 illustrates the deposition method to form the CHI/PSS layers.



Figure 4.1: Deposition Method for CHI/PSS Layers.

Before the deposition, the Ultipor N66 membrane is required to be stored in distillation water for up to 24 hours and was immersed into the polycation solution containing CHI. After immersing for 15 minutes, the membrane containing CHI was washed continuously to rinse off excess CHI. Then, the process is repeated by immersing into a polyanion solution containing PSS. A single layer of CHI/PSS will be formed. The process is recycled several times to form polyelectrolyte multilayers.

After obtaining the desired CHI/PSS multilayer membranes, the membranes are being studied. There are four instruments and analyses needed to characterise the CHI/PSS multilayer membranes. Firstly, an FTIR analysis is required to characterise the CHI/PSS multilayer membranes build up. After characterising the membrane build up, UV-VIS spectroscopy is used to obtain the absorption spectra data of a bare membrane ranging from 200 to 900 nm to be used as a reference. The following characterisation method is AFM, which is used to characterise the surface membrane as the structure of the membrane is modified after adding salt. The last analysis is the TGA analysis. Different

salt concentrations on the membrane will affect thermal behaviour. Thus, TGA analysis is required to analyse the characteristics of thermal behaviour on the membrane (Chandra, Usha and Mohan, 2020).

4.2.2 Fabrication of PAH/PSS membrane with zwitterionic as the final layer

The second material is the fabrication of polyelectrolyte multilayer with zwitterionic as the final layer. Similar to Material 1, Material 2 uses the LbL technique to remove contaminants such as humic acids, alginates, silica nanoparticles, and charged proteins from the drinking water. The foulants used in this study are Alginic acid sodium salt, Bovine Serum Albumin, LUDOX®, lysozymes, and humic acids. In Material 2, the type of polyelectrolytes used is poly (allylamine hydrochloride) (PAH) and poly (sodium 4-styrene sulfonate) (PSS), while the membrane applied is the sulfonated polysulfone (SPEs) hollow fiber membrane (Virga, Žvab and de Vos, 2021). The process is similar to Material 1, as shown in Figure 4.2 below. Figure 4.2 displays the PAH/PSS layers.

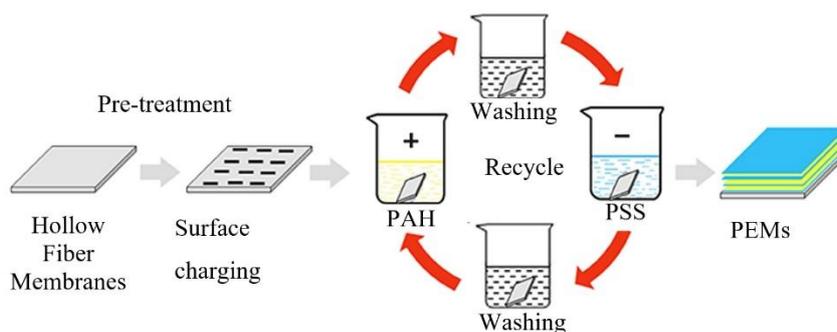


Figure 4.2: Deposition Method for PAH/PSS Layers.

For the pre-treatment, the SPEs hollow fiber membranes are kept in fresh water and dipped in NaCl solution at room temperature. Subsequently, the polyelectrolytes prepared were dissolved in a NaCl solution. Then, the membrane was dipped into the NaCl solution containing the PAH for 15 minutes. The membrane is then rinsed with NaCl aqueous solution for another 15 minutes to wash off excess polyelectrolytes. The steps are repeated after dipping into the NaCl solution containing PSS polyelectrolytes. The whole process is repeated until the desired multilayers are obtained. Moreover, to

obtain the zwitterionic as the top layer, PMPC-co-AA are required to deposit on the membrane surface containing PAH/PSS. In order to obtain the top layers containing PAH/PSS, the membrane surfaces were dipped in glutaraldehyde for 5 hours. In contrast, to obtain a top layer of zwitterionic layers, the membrane surfaces are required to dip in N-Hydroxysuccinimide (NHS) and N-(3-Dimethylaminopropyl)-N-ethylcarbodiimide (EDC) solution for 1 hour. In this material, ion chromatography is used to analyse the water permeability, ion, and salt retention capabilities (Virga, Žvab and de Vos, 2021).

4.2.3 Synthesis of PDAC/PSS membrane by spin-assisted LbL

The third material is the synthesis of polyelectrolyte multilayer by using the spin-assisted LbL technique. Traditionally, in the past few years, dip-LbL is the most used deposition method. However, Material 3 has successfully developed an improved assembly which is the spin-assisted LbL (SA-LbL) assembly. SA-LbL has been proven that is a more time-saving process and can produce smoother surfaces and a highly ordered internal layer as compared to the dip-LbL method (Fadhillah *et al.*, 2021). Figure 4.3 displays both the dip-LbL and SA-LbL assembly.

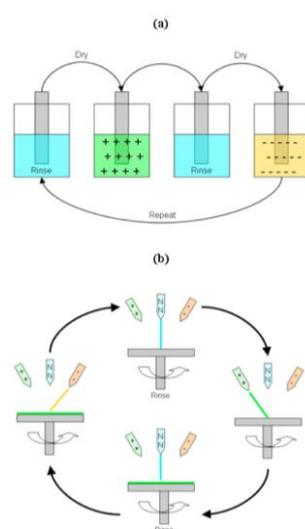


Figure 4.3: LbL assembly using different techniques (a) the deposition of films using dip-LbL assembly, (b) the deposition of films using SA-LbL assembly (Vojar *et al.*, 2009).

In this study, Material 3 has been tested out to investigate the possibilities of divalent salts removal from the polyelectrolyte multilayer nanofiltration membranes fabricated using the SA-LbL technique. The types of polyelectrolytes used are poly (diallyl dimethyl ammonium chloride) (PDAC) and poly (sodium 4-styrene sulfonate) (PSS). As this material is carried out in saline water, PDAC and PSS are the best selection as they have strong stability towards saline water. The membrane used is the Polyether sulfone (PES) membrane.

Firstly, the PES membrane is required to be pre-treated by using a plasma cleaner to introduce a polar group with oxygen onto the surface. The purpose of this process is to enhance the membrane to be more hydrophilic, clean, and more highly negatively charged. The PES membrane is then inserted onto the spin coater. NaCl solutions containing PDAC and PSS each are then deposited onto the PES surface alternately. After the deposition of the PDAC solution, the PES film is spin-dried for 20 seconds and then deionised water is used to wash off the excess PDAC molecules. An additional 40 seconds of spin-drying is used to dry off the excess deionised water. The steps are repeated by depositing the PSS solutions. The process is repeated until the desired number of bilayers is obtained (Fadhilah *et al.*, 2021).

There are two characterisation methods involved in this study to characterise the membrane. Atomic force microscopy (AFM) is used to study the surface morphologies of the polyelectrolyte multilayers formed by using the SA-LbL assembly. Furthermore, contact angle measurement is also used to investigate membrane hydrophilicity. After the membrane characterisation, a permeation test was carried out to examine the membrane fouling.

4.2.4 Fabrication of CHI/ALG based hydrogel membrane

Other than the removal of pollutants and contaminants, polyelectrolyte multilayers are also used in fields such as biomedical science. In this material, the LbL technique is used to study the surface properties of cell response. The polyelectrolytes used in this material are chitosan (CHI) and alginate (ALG), which are extracted from algae. Both CHI and ALG are biodegradable. The membrane used is a hydrogel membrane. Two polyelectrolyte multilayers are formed in this study. The multilayers are AC_1C_2 and AC_2C_1 . C_1 is the higher

degree of deacetylation, while C_2 is the lower degree of deacetylation (Zheng *et al.*, 2019). In the preparation of AC_1C_2 , the alginate solution was deposited on the dry up glass slide and soaked in $CaCl_2$ solution for 30 minutes to form calcium alginate gels. Then, the hydrogel membrane formed is immersed into the NaCl solution containing C_1 to form the AC_1 membrane. The membrane formed is being rinsed with NaCl solution to rinse off excess C_1 molecules. Subsequently, the AC_1 membrane is then dipped into the NaCl solution containing C_2 . The AC_1C_2 membrane will be formed after 45 minutes. In contrast, to form the AC_2C_1 membrane, a similar method is used except for the immerse sequence of C_1 and C_2 .

Several characterisation methods being used in this method. Scanning electron microscopy (SEM) was used to study on the morphology of the membrane surface. Furthermore, contact angle measurements were carried out to measure the contact angles of the polyelectrolyte multilayers. Lastly, X-ray photoelectron spectroscopy (XPS) was performed to obtain the composition and of both membranes (Zheng *et al.*, 2019).

4.2.5 Development of PEI/PSS membrane as an LLI support

In this material, an electrified liquid-liquid interface (LLI) is used with respect to the normal LbL assembly. The type of polyelectrolytes used is poly(ethyleneimine) (PEI) and polystyrene sulfonate (PSS). This material deposits the polyelectrolytes onto the fiberglass membrane and is used as a base support for the electrified LLI. Figure 4.4 displays the electrified LLI process.

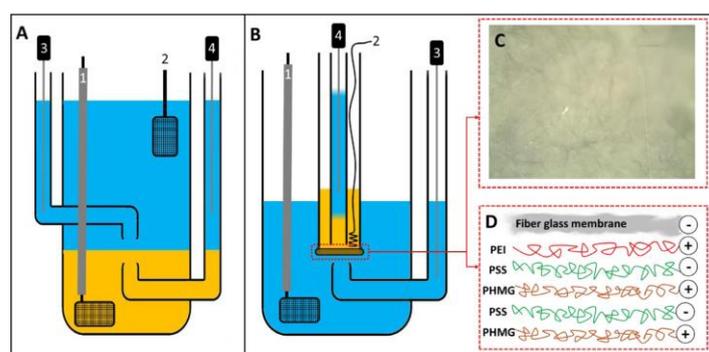


Figure 4.4: A) Electrochemical cells used to sustain macroscopic LLI B) Electrochemical cells used to investigate the modified and unmodified

membrane C) Optical microscopy photo of the unmodified membrane D) schematic photo of the modified membrane (Borgul *et al.*, 2020).

Four electrodes present in the electrochemical experiment are used to polarise the LLI. Two electrodes are platinum wires, while the other two electrodes are Ag/AgCl wires. There are three characterisation methods used in this material. Firstly, infra-red spectroscopy is used to obtain the absorption spectra of the modified fiberglass membrane. Subsequently, SEM is used to obtain the unmodified and modified fiberglass membranes. The last characterisation method is by using the AFM. AFM is used to characterise the surface morphology of the fiberglass membrane (Borgul *et al.*, 2020).

4.2.6 Fabrication of PDDA/PAA membrane via counterion exchange

Material 6 is the fabrication of polyelectrolyte multilayers through counterion exchange. This material focuses solely to separate and purify the organic solvent. By doing so, a hydrophobic polyelectrolyte multilayer membrane is fabricated through the counterion exchange technique. Similar to the previous material, Material 6 uses the LbL method. The type of polyelectrolytes used is poly (diallyl dimethyl ammonium chloride) (PDDA) and polyacrylic acid (PAA) while the membrane applied is the polyacrylonitrile (PAN-50) ultrafiltration membrane. Figure 4.5 displays the process of the fabrication of hydrophobic polyelectrolyte multilayer.

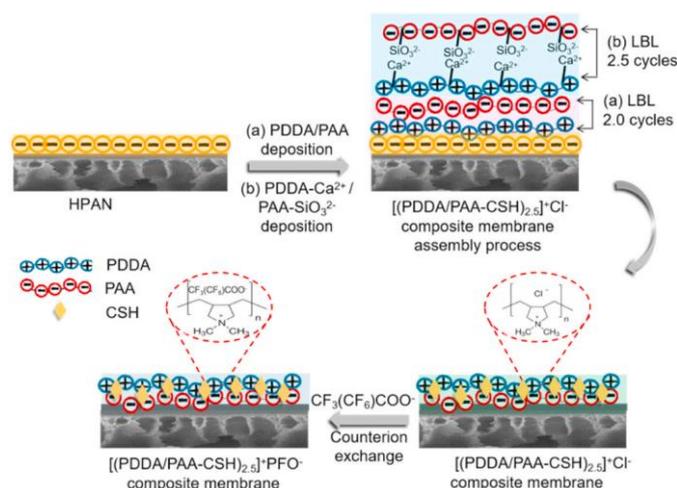


Figure 4.5: Schematic diagram of the fabrication process of PDDA/PAA layers (Lu *et al.*, 2021).

A total of 3 membranes are fabricated in this study. The first multilayer is the PDDA/PAA multilayer. Then, the next multilayer fabricated is the [(PDDA/PAA-CSH)_{2.5}]⁺Cl⁻ composite membrane, and lastly, is the [(PDDA/PAA-CSH)_{2.5}]⁺PFO⁻ composite membrane. To fabricate a hydrophobic polyelectrolyte multilayer membrane, a pre-treatment is required. The PDDA and PAA are required to be stored in deionised water until it turns transparent. The duration takes up to around 2 hours. Subsequently, the PAN membrane is required to be hydrolysed by immersing in the NaOH solution for 30 minutes and wash off with deionised water. Then, the hydrolysed PAN membrane is dipped into the PDDA solution. The excess PDDA molecules are rinsed off with deionised water. The process is then repeated with a PAN solution. To fabricate the [(PDDA/PAA-CSH)_{2.5}]⁺Cl⁻ membrane, the PDDA, and PAA solutions are required to be added into the calcium acetate solution first before the LbL process takes place. Then, the [(PDDA/PAA-CSH)_{2.5}]⁺Cl⁻ membrane is added into a sodium perfluorooctanoic acid solution to produce the [(PDDA/PAA-CSH)_{2.5}]⁺PFO⁻ membrane (Lu *et al.*, 2021).

There are several techniques used in this study to characterise the membrane. SEM is used to observe the samples. Then, an energy dispersive spectroscopy (EDS) is used alongside SEM to analyse the elemental composition of the membrane. An ATR-FTIR is used to measure the chemical groups found in the membrane. Next, an X-ray photoelectron spectroscopy (XPS) is used to obtain the composition and chemical bonds in the membrane surface. Subsequently, water contact angle measurement is used to determine the wettability of the membrane surface. The next characterisation method used is the AFM. AFM is used to determine the surface roughness of the membrane. Lastly, a zeta potential of the membranes was characterised.

4.2.7 Development of weak PAH/PAA tunable separation layers

The following material aims to solve the environmental issues. Material 7 is the development of weak tunable separation layers, and it is used to remove the micro-pollutants present in aquatic and marine life. Micro-pollutants are normally present in a very small concentration. However, after a long period, the micro-pollutants tend to grow rapidly and the unfettered accumulation and

build-up will affect the surface and groundwater and thus, degrading the quality of the water. Hence, this research is carried out to provide assistant to the wastewater treatment industry for micro-pollutant removal. In this material, the type of polyelectrolytes used is Poly (allylamine hydrochloride) (PAH) and Poly (acrylic acid) (PAA). The type of micro-pollutants used is the chloride salts, such as NaCl, CaCl₂ and Na₂SO₄. Figure 4.6 illustrates the schematic diagram of the fabrication of PAH/PAA layers using the LbL method.

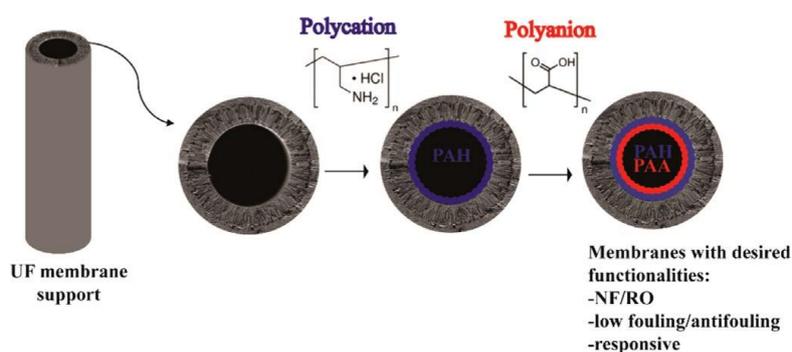


Figure 4.6: Schematic diagram of the fabrication of PAH/PAA layers (Ilyas, Abtahi, *et al.*, 2017).

Similar to any LbL deposition process, this material deposits weak polyelectrolytes onto a UF membrane. The membrane is immersed into the PAH solution and the excess PAH molecules are rinsed off by the deionised water. Subsequently, the membrane containing the PAH molecules is immersed into the PAA solution and the excess is washed off by deionised water. Then, the process is repeated until the desired number of layers is obtained.

In this study, reflectometry and contact angle measurement is used for the characterisation of the multilayers. The reflectometry is used to examine the adsorption alteration of the polyelectrolyte that has been deposited on the membrane. Next, the contact angle measurement is used to characterise their water contact angle of the polyelectrolyte multilayers.

4.3 Methods used for membrane characterisation

Several instruments or analyses are commonly used to characterise the polyelectrolyte multilayer membranes. Functional groups on the polyelectrolyte multi-layered surfaces can be analysed by Fourier Transform Infrared Spectroscopy (FTIR). Scanning electron microscopy (SEM) can be carried out to obtain the data on surface morphology, nanostructure, and particle size of the membrane. Besides that, UV-VIS absorption spectra can also be used to check the optical behaviour of polyelectrolyte multi-layered membranes while Atomic Force Microscopy (AFM) is used to study the surface topography of the modified membranes.

4.3.1 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR analysis has been used to determine the functional groups of the polyelectrolyte multi-layered surfaces. In Material 1, the CHI/PSS membrane surface is characterised using the FTIR. Figure 4.7 displays the spectrum of the CHI/PSS layers based on the number of bilayers.

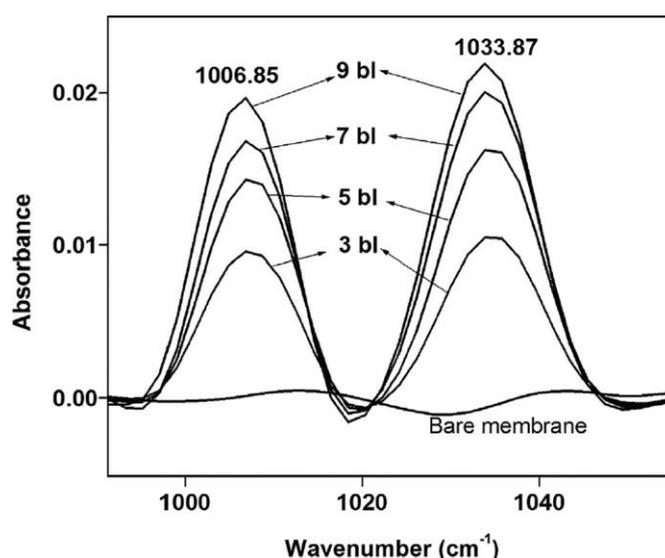


Figure 4.7: ATR-FTIR Spectrum of CHI/PSS based on the number of bilayers (Chandra, Usha and Mohan, 2020).

From Figure 4.7, four bilayers are being characterised. The membranes consist of 3 bilayers, 5 bilayers, 7 bilayers, and 9 bilayers. The reference was set using the sulfonate and aromatic ring peaks of the number of bilayers.

There is an inplane vibration of PSS aromatic rings at the peak of 1006.85 cm^{-1} . Based on the IR Spectrum table obtained from Sigma Aldrich, there is no absorption at this region of the UF membrane. Then, uniform growth of peaks can be seen at the peak at 1033.84 cm^{-1} . Results indicated that the spectrum of the sulfonate group at the peak of 1033.84 cm^{-1} attributed to CO-O-CO groups stretching vibration (Chandra, Usha and Mohan, 2020).

Next, in Material 6, the chemical groups on the hydrophobic polyelectrolyte multilayer membranes fabricated by the counterion exchange method are also characterised by FTIR. Figure 4.8 displays the spectrum of the PDDA/PAA layers formed.

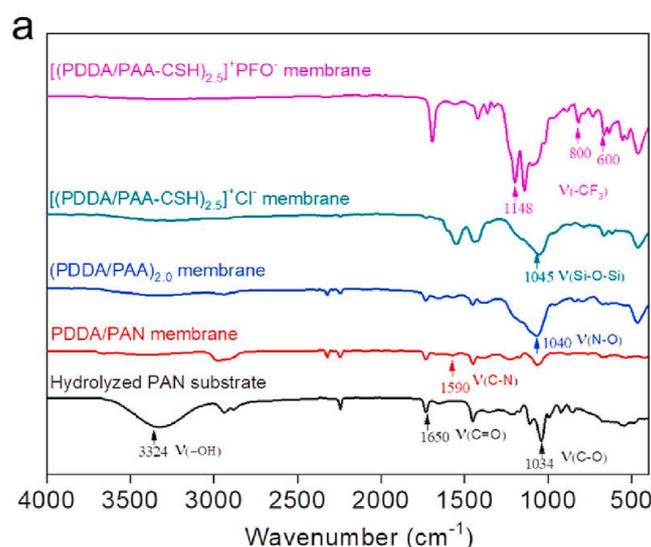


Figure 4.8: PDDA/PAA FTIR spectrum based on different membranes (Lu *et al.*, 2021).

Figure 4.8 shows that the peak of the hydrolysed PAN membrane is at 1650 cm^{-1} which is attributed to the COO^- groups. Then, a single layer of PDDA/PAN bilayer added on the PAN substrate has the peak at 1590 cm^{-1} which is attributed to the C-N bond. Results indicated that PDDA had been assembled onto the PAN membrane through electrostatic attraction. With the addition of two PDDA/PAN layers, the membrane has a peak at 1040 cm^{-1} which indicates that it has attributed to the N-O groups stretching vibration. Next, by assembling PDDA- CA^{2+} and PAA- SIO^{2-} onto to PAN substrate, the absorption peak was found at 1045 cm^{-1} which is attributed to the Si-O groups

stretching vibration. Lastly, by the counterion exchange of PFO^- , the $[(\text{PDDA}/\text{PAA}-\text{CSH})_{2.5}]^+\text{PFO}^-$ has three vibration peaks at 1148 cm^{-1} , 800 cm^{-1} , and 600 cm^{-1} . These characteristic peaks have been attributed to the C-F bond in $\text{C}-\text{F}^3$ groups. The asymmetric peaks have proved that the Cl^- ions have been exchanged with the PFO^- ions (Lu *et al.*, 2021). From the results, it has been proven that the desired molecules and particles are obtained based on the functional group found on the surface.

4.3.2 Contact Angle Measurement

The contact angle measurements have been employed previously to study the hydrophilicity of the membranes. Material 4 has implemented the usage of contact angle measurement to characterise the wettability of the membrane surfaces. There are two CHI/ALG membranes formed, which are AC_1C_2 and AC_2C_1 membrane. Both contact angles of the membranes are measured using water. Figure 4.9 displays the water contact angle measurements of the CHI/ALG membranes.

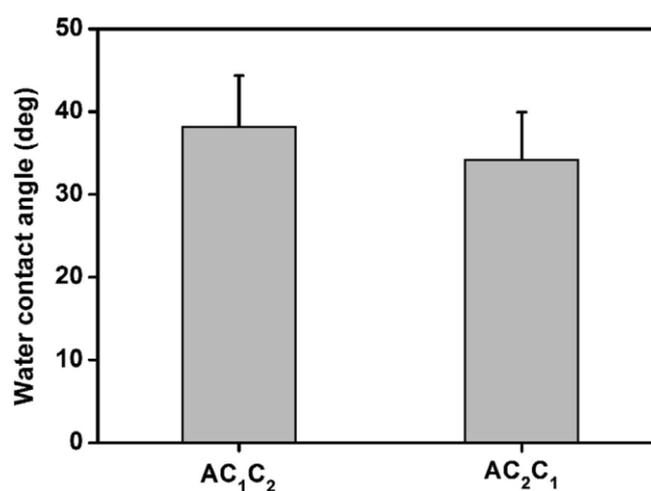


Figure 4.9: Water contact angle measurements of CHI/ALG membranes (Zheng *et al.*, 2019).

Figure 4.9 has shown that both membranes do not have a big difference. The contact angle for both AC_1C_2 and AC_2C_1 membrane are approximately 40° . This has indicated that both membranes with different deposition sequences have similar surface chemical compositions (Zheng *et al.*, 2019). Furthermore, in Material 7, the wettability of the polyelectrolytes at

different pH combinations was characterised. Figure 4.10 illustrates the water contact angle measurements of the multilayers at different pH combinations.

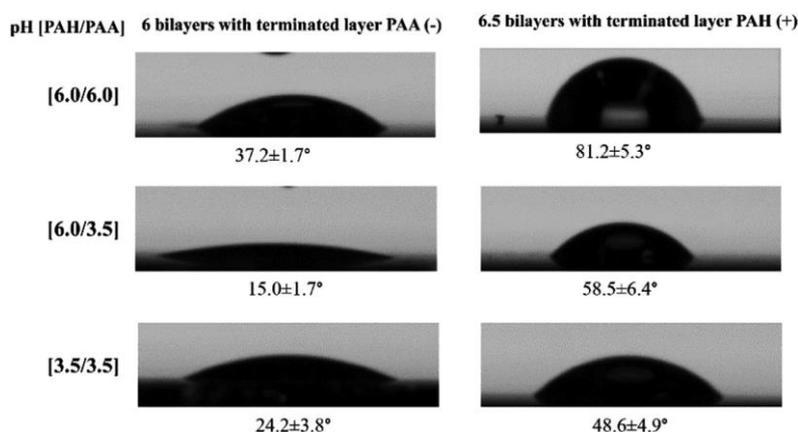


Figure 4.10: Water contact angle measurements of multilayers are different pH combinations (Ilyas, Abtahi, *et al.*, 2017).

Figure 4.10 shows that the terminating layers have affected the hydrophilicity of the membrane. The positive terminating layers of PAH have a higher contact angle than the negative terminated layers of PAA. Moreover, the pH combinations have also affected the wettability of the membrane surface. The [6.0/6.0] layers have greater contact angles of 37° at PAA terminating layers and 81° at PAH terminating layers. Results indicated that higher pH combinations cause more hydrophobic layers. This is because higher pH causes a higher level of intrinsic charge compensations and denser structure layers. Then, for the PAA terminating layers, the contact angle measurements for [6.0/3.5] and [3.5/3.5] are 15° and 24°, respectively. While for the PAH terminating layers, the contact angle measurements are 59° and 49°. Results indicated that PAA terminating layers has more hydrophilic properties as compared to the PAH terminating layers (Ilyas, Abtahi, *et al.*, 2017). The results have proven that polyanion layers with higher pH have a higher contact angle as they consist of more hydrophobic layers.

4.3.3 Scanning Electron Microscopy

The following characterisation method is by using SEM to study the surface morphology of the membranes. In Material 5, SEM is used to determine the surface characteristics of both the bare membrane and the modified

polyelectrolyte multi-layered fiberglass membrane. Figure 4.11 displays the SEM images of the fiberglass membrane before and after modification.

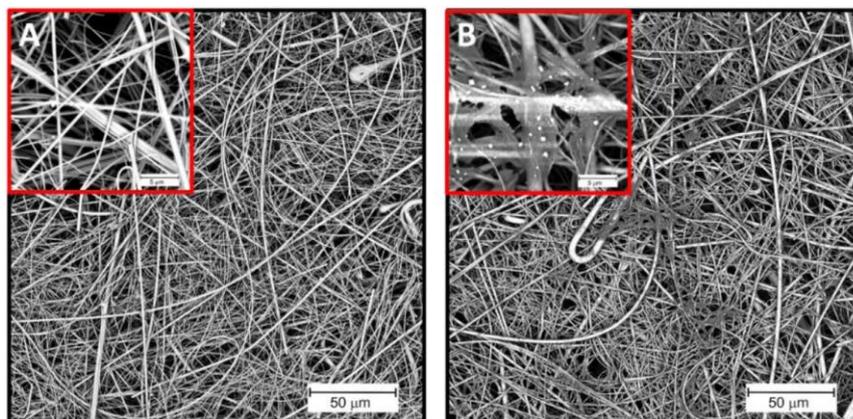


Figure 4.11: SEM images of (A) fiberglass membrane before modification (B) fiberglass membrane after the deposition of PEI/PSS multilayers (Borgul *et al.*, 2020).

Figure 4.11 has clearly shown the surface characteristics between the modified and the unmodified membrane through microscopic images. Figure 4.11 (B) shows that there are visible thin films found between the single glass fibers. Results showed that the thin films are the polyelectrolyte multilayers formed after the modification process. A more detailed topological change on the surface is then characterised by using AFM. Another material using SEM is Material 6. SEM in Material 6 is used to characterise the surface morphologies of the hydrolysed PAN membrane, $[(\text{PDDA}/\text{PAA}-\text{CSH})_{2.5}]^+\text{Cl}^-$ membrane, and $[(\text{PDDA}/\text{PAA}-\text{CSH})_{2.5}]^+\text{PFO}^-$ membrane. Figure 4.12 displays the SEM images of the PDDA/PAA membranes.

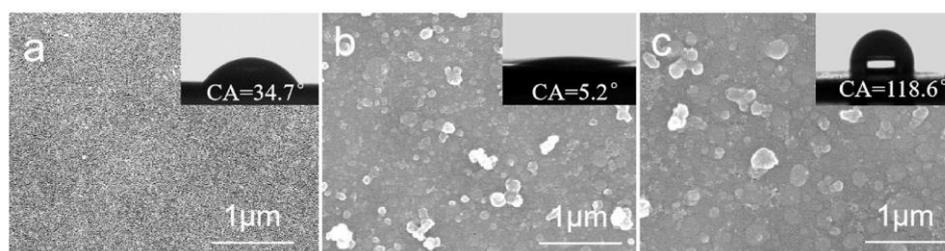


Figure 4.12: SEM microscopic images of a) hydrolysed PAN membrane b) $[(\text{PDDA}/\text{PAA}-\text{CSH})_{2.5}]^+\text{Cl}^-$ membrane c) $[(\text{PDDA}/\text{PAA}-\text{CSH})_{2.5}]^+\text{PFO}^-$ membrane (Lu *et al.*, 2021).

From Figure 4.12 (a), it can be seen that in the hydrolysed PAN substrate, there are a large number of nanopores in the membrane. Subsequently, after fabricating the $[(\text{PDDA}/\text{PAA}-\text{CSH})_{2.5}]^+\text{Cl}^-$ membrane, the growth of CSH has causes a large number of nanoparticles to form in the membrane which can be seen in Figure 4.12 (b). For the $[(\text{PDDA}/\text{PAA}-\text{CSH})_{2.5}]^+\text{PFO}^-$ membrane, there are no obvious changes between the surface morphology of $[(\text{PDDA}/\text{PAA}-\text{CSH})_{2.5}]^+\text{Cl}^-$ and $[(\text{PDDA}/\text{PAA}-\text{CSH})_{2.5}]^+\text{PFO}^-$ membrane. However, there is a huge increase in the water contact angle measurement of 118.6° as shown in Figure 4.12 (c). By comparing the three membranes, $[(\text{PDDA}/\text{PAA}-\text{CSH})_{2.5}]^+\text{PFO}^-$ membrane is clearly on the upper hand as it has a thinner membrane and more hydrophobic property (Lu *et al.*, 2021). The results obtained have clearly shown the structures of the membrane surface after the modification process. This has been proven that the modification process has successfully modified the membrane into a polyelectrolyte multilayer. The polyelectrolytes added have greatly increased the separation efficiency of the membrane.

4.3.4 Atomic Force Microscopy (AFM)

The following method is by using the AFM characterisation method. Material 1 uses the AFM to study the characterisation of the surface topography of bare and modified membranes. Figure 4.12 illustrates the AFM images of the bare membrane and CHI/PSS multi-layered membranes.

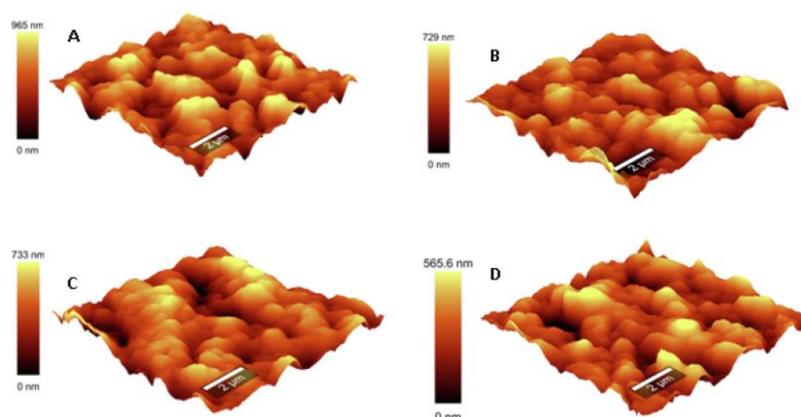


Figure 4.13: AFM images of (A) bare CHI/PSS membrane, (B) CHI soaked in 1 M NaCl solution/ PSS membrane, (C) CHI/ PSS soaked in 1 M NaCl

solution membrane, and (D) Both CHI/PSS soaked in 1 M NaCl solution membrane (Chandra, Usha and Mohan, 2020).

From Figure 4.13, the darker regions indicate the membrane pores, and the lighter regions indicate the highest points of the membrane. The highest peak is found in the bare membrane, which is 965 nm, while the lowest peak is found in both CHI/PSS soaked in NaCl solution membrane. Since the bare membrane has the highest peak, it has a higher affinity for the pores to occur at the base of the membrane. From Figure 4.13 (B) to Figure 4.13 (D), the bilayers with salt concentrations have shown that they possess a smaller pore size and smoother membrane surface due to the salt addition (Chandra, Usha and Mohan, 2020).

Subsequently, based on previous studies, Material 3 uses AFM to characterise the surface morphologies of the films assembled by the SA-LbL technique. Figure 4.14 shows the surface morphologies of PDAC/PSS membranes prepared with the presence and also the absence of salt.

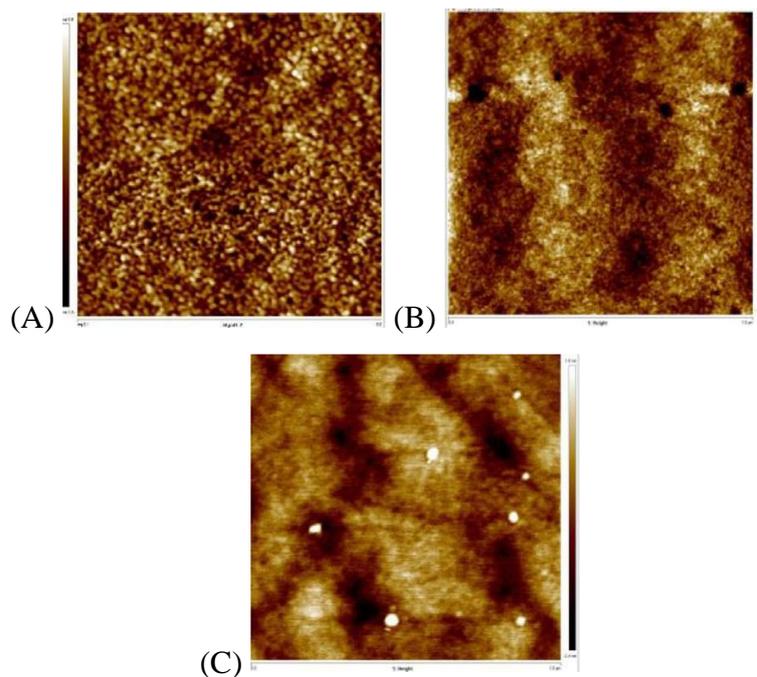


Figure 4.14: AFM images of (A) bare PES UF membrane, (B) PDAC/PSS layers, and (C) PDAC/PSS layers with salt addition (Fadhillah *et al.*, 2021).

By comparing Figure 4.14 (A) with Figure 4.14(B), the membrane deposited with polyelectrolyte has a much smoother surface as compared to the bare membrane. In addition, by comparing Figure 4.14 (B) with Figure 4.14 (C), by adding salt, the surface morphology changes drastically. The PDAC/PSS layers with salt have produced a smoother surface. Both Material 1 and 3 have proven a point that the addition of polyelectrolyte has smoothed the surface. Moreover, the addition of salt will smoothen the surface even more (Fadhillah *et al.*, 2021). The smoothness of the membrane will also affect the efficiency of the membrane.

4.3.5 X-ray Photoelectron Spectroscopy (XPS)

Another characterisation method used in the fabrication of polyelectrolyte multilayers is the XPS technique. Material 4 uses the XPS to analyse the amino groups found on the AC₁C₂ and AC₂C₁ membranes surface. Figure 4.15 illustrates the XPS spectrum of the AC₁C₂ and AC₂C₁ membranes.

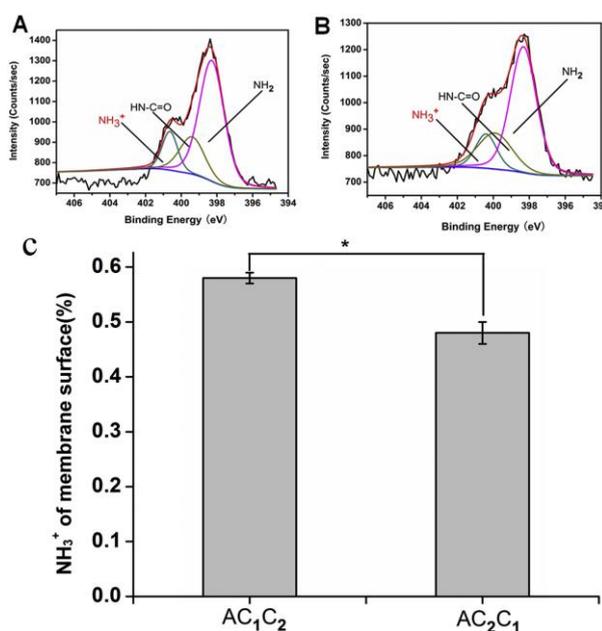


Figure 4.15: XPS spectrum of (A) AC₁C₂ membrane, (B) AC₂C₁ membrane, and (C) Surface positive charges on the membranes (Zheng *et al.*, 2019).

Figure 4.15 has shown that the 339 eV binding energy is attributed to the NH₂ group, while the peak of binding energy is at 399.7 eV. The peak was attributed to N-C=O chemical bonding. Lastly, when the binding energy is at

401.4 eV, the peak was assigned to amino groups in the ammonium form. Furthermore, the XPS data is required to undergo an analysis of the positively charged amino groups on the membrane surface to qualitatively analyse the inherent binding on the surface. Figure 4.15 (C) shows that the positively charged amino groups dispersed on the AC₁C₂ membrane are higher than the AC₂C₁ membrane. Theoretically, a higher number of positively charged amino groups will cause greater adhesion of cells. However, in this study, the cell adhesion of the AC₁C₂ membrane decreases drastically as compared to the AC₂C₁ membrane. Thus, this theory can not be applied (Zheng *et al.*, 2019).

Moreover, in the next material, Material 6 uses XPS to determine the presence of CSH and PFO⁻ ions in the [(PDDA/PAA-CSH)_{2.5}]⁺PFO⁻ membrane. Figure 4.16 illustrates the XPS spectrum of hydrolysed PAN membrane and [(PDDA/PAA-CSH)_{2.5}]⁺PFO⁻ membrane based on different kinds of elemental on the membrane.

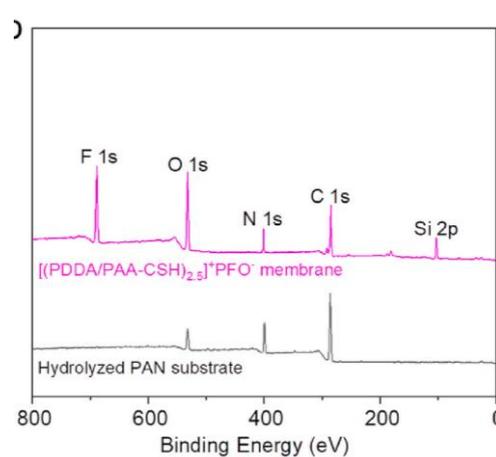


Figure 4.16: XPS spectrum of hydrolysed PAN membrane and [(PDDA/PAA-CSH)_{2.5}]⁺PFO⁻ membrane (Lu *et al.*, 2021).

By comparing the peaks in Figure 4.16, the high resolution of the C1s spectrum for the membranes are fitted. Figure 4.17 illustrates the high-resolution C1s XPS spectrum for the hydrolysed PAN membrane and [(PDDA/PAA-CSH)_{2.5}]⁺PFO⁻ membrane based on the C1s elements.

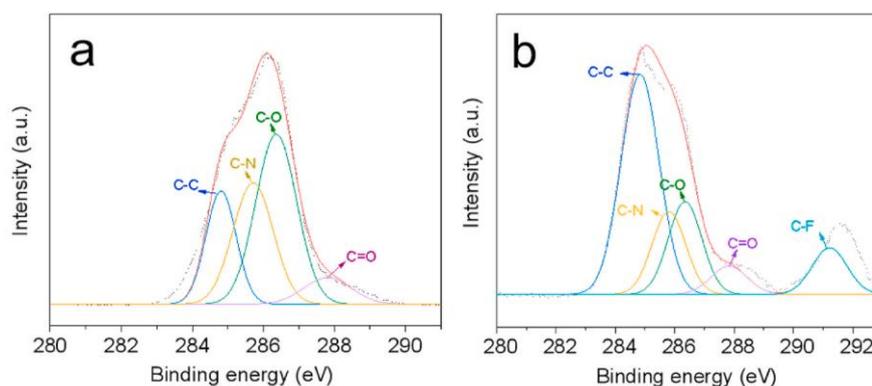


Figure 4.17: C1s XPS spectrum of (a) hydrolysed PAN membrane and (b) [(PDDA/PAA-CSH)_{2.5}]⁺PFO⁻ membrane (Lu *et al.*, 2021).

Figure 4.17 shows that there are four peaks found in the high-resolution C1s XPS spectrum. From Figure 4.17(a), the four peaks indicated the characteristic of C, C-C, C-O, C=O, and C-N binding on the PAN membrane. Nevertheless, Figure 4.17(b) indicates that after the counterion exchange, the peak at 290.87 eV was attributed to the C-F bond. Results indicated that the PFO⁻ has managed to exchange onto the membrane surface through the counterion exchange (Lu *et al.*, 2021). The results have shown the atomic composition present on the membrane surface. The atomic composition found on each stage proved that the polyelectrolyte has been successfully deposited on the membrane.

4.4 Summary on all different deposition methods

Table 4.1 summarises a list of polyelectrolytes used, the type of pollutants involved, applications of PEM, and its performances that have been reported based on the latest studies. Most of the studies have used the simple LbL method, which is easy to conduct and more versatile.

Table 4.1 Fabrication of PEM membranes using various types of polyelectrolytes, different types of pollutants, applications and their performances.

Type of Polyelectrolytes	Types of Membranes	Types of Pollutants	Application	Performances	References
MATERIAL 1:					
Chitosan (CHI), Polystyrene sulfonate (PSS)	Ultipor N66 Polyamide Membrane	Herbicides	Removal of herbicides by ion-exchange	Rejection rate: - Stability rate: 96.36 % Flux recovery: -	(Chandra, Usha and Mohan, 2020)
MATERIAL 2:					
Poly (allylamine hydrochloride) (PAH), Poly (sodium 4-styrene sulfonate) (PSS)	SPEs Hollow Fiber Membrane	Humic Acids, Alginates, Silica Nanoparticles, negatively and positively charged Proteins	Removal of foulants by Na ⁺ , Ca ²⁺ and Mg ²⁺ rejection	Rejection rate: ~ 70 % Stability rate: - Flux recovery: 5.45 L/m ² ·h·bar	(Virga, Žvab and de Vos, 2021)

MATERIAL 3:

Poly (diallyl dimethyl ammonium chloride) (PDAC), Poly (sodium 4-styrene sulfonate) (PSS)	PES membrane	Sodium Chloride	Removal of organic foulants by ion-exchange	Rejection rate: 94.58 % Stability rate: - Flux recovery: 3.32 L/m ² ·h·bar	(Fadhillah <i>et al.</i> , 2021)
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MATERIAL 4:

Chitosan (CHI) and Alginate (ALG)	Hydrogel membrane	Mouse fibroblast cell	Adhesion of cells by sequential usage of higher degree and lower degree of deacetylation of CHI	Rejection rate: - Stability rate: measures by elasticity modulus AC ₁ C ₂ : 11.5 ± 0.23 kPa AC ₂ C ₁ : 3.3 ± 0.08 kPa Flux recovery: -	(Zheng <i>et al.</i> , 2019)
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MATERIAL 5:

Poly(ethyleneimine) (PEI) and Polystyrene sulfonate (PSS)	Fiberglass membrane	Chloride salts	Permeation of modified membranes through an electrified liquid-liquid interface by ions exchange	Rejection rate: measures by hydrodynamic radius (r) from Einstein-Stokes equation $r = 0.38\text{nm}$ (nonpermeable for molecules with $r > 0.38\text{ nm}$) Stability rate: - Flux recovery: -	(Borgul <i>et al.</i> , 2020)
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MATERIAL 6:

Poly (diallyl dimethyl ammonium chloride) (PDDA) and Polyacrylic acid (PAA)	Polyacrylonitril e (PAN-50) ultrafiltration membrane	Humic acids	Improved hydrophobic membrane for the separation of dyes from ethanol through counterion exchange	Rejection rate: 99.1 % Stability rate: - Flux recovery: 53.5 L/m ² ·h·MPa	(Lu <i>et al.</i> , 2021)
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MATERIAL 7:

Poly (allylamine hydrochloride) (PAH) and Poly (acrylic acid) (PAA)	Hollow fiber UF membrane	Chloride salts	Removal of micro-pollutants by using different pH of the coating solution	Rejection rate: 40 % - 80 % Stability rate: - Flux recovery: pH condition [6.0/6.0] $3.0 \pm 0.5 \text{ L/m}^2 \cdot \text{h} \cdot \text{bar}$ [6.0/3.5] $1.5 \pm 0.8 \text{ L/m}^2 \cdot \text{h} \cdot \text{bar}$ [3.5/3.5] $7.2 \pm 0.48 \text{ L/m}^2 \cdot \text{h} \cdot \text{bar}$	(Ilyas, Abtahi, <i>et al.</i> , 2017)
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4.5 Summary

In this study, a total of 7 materials are studied and evaluated. The characterisation methods are also evaluated based on each material. The type of polyelectrolyte pairs used in each material is different. For the deposition method, all 7 materials discussed uses the LbL assembly for the deposition of polyelectrolytes on the membrane. Moreover, Material 3 uses an improved LbL technique which is the spin-assisted assembly. There are 5 characterisation methods discussed in this study such as FTIR, contact angle measurement, SEM, AFM, and XPS. The results obtained from FTIR have shown the functional groups found on the membrane surface. The functional groups obtained indicate the presence of the polyelectrolyte molecules found on the modified membrane. Next, the results obtained from contact angle measurement has indicated the hydrophilicity of the membrane. The results have successfully proven that polyanion layers with higher pH exhibit higher contact angles as they consist of more hydrophobic layers. Subsequently, the results obtained from SEM have shown the structural layers of the bare membrane and the modified polyelectrolyte multilayers. There are visible changes before and after the deposition process. Furthermore, the results obtained from AFM have shown the surface morphology of the membranes. The addition of polyelectrolyte has smoothened the membrane surface drastically and by adding salt, it will smoothen the membrane surface even more. Lastly, the results obtained from XPS have indicated the atomic composition found on the membrane surface and this indicates that the membrane has been successfully modified.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Overall, this research introduces the recent progress in the study of polyelectrolyte multilayer fabrication as well as their applications. There are several applications reviewed previously. The applications of polyelectrolyte multilayers include polyelectrolyte as coagulant aid for the water and wastewater treatment, development of tunable separation layers for the micro-pollutant removal, and fabrication of liquid-phase polymer-based retention for antibiotics removal found in aquatic or water resources. Subsequently, there are multiple characterisation methods used to characterise the membrane, such as SEM, contact angle measurement, UV-VIS spectrophotometer, FTIR, and XRD.

Moreover, this study is conducted due to a high number of researches carried out every year. For the past decades, the number of researches on the polyelectrolytes multilayers has an average of 191 research papers per year. Among all the research papers, seven materials for the depositions of polyelectrolytes are studied. For Material 1, CHI and PSS are deposited on the Ultipor N66 polyamide membrane to remove herbicides from the water through ion exchange. Next, Material 2 uses PAH/PSS SPEs hollow fiber membrane to remove humic acids, alginates, silica nanoparticles, negatively and positively charged proteins by Na^+ , Ca^{2+} and Mg^{2+} rejection. Similar to Material 3, deposits PDAC and PSS onto the PES membrane to remove sodium chloride from water through ion exchange. Subsequently, Material 4 uses CHI/ALG hydrogel membrane to increase the adhesion of cells for special tissue engineering usage. Then, Material 5 deposits PEI and PSS onto the fiberglass membrane to increase the permeation through an electrified liquid-liquid interface by ions exchange. The following material uses PDDA and PAA as the dipping polyelectrolytes and polyacrylonitrile (PAN-50) ultrafiltration membrane as the membrane support. The improved hydrophobic membrane has improved the separation of dyes from ethanol through counterion exchange. Lastly, Material 7 uses PAH/PAA hollow fiber UF membranes to remove chloride salts by using different pH of the coating solution.

By comparing and contrasting the seven materials previously, Material 6 is the most optimum deposition method as the polyelectrolyte multilayer formed has the highest rejection rate of 99.1 & 53.5 L/m²·h·MPa flux recovery.

5.2 Recommendations for future work

The LbL method has been used worldwide for decades. Despite the impressive and significant results of the LbL method, continuous research is needed to improve on the LbL assembly. There are a few impressive findings found on previous research and the findings are listed below:

- (i) Material 2 added the zwitterionic PMPC-co-AA with the polyelectrolytes used. The addition of the zwitterionic has reduced the percentage of membrane fouling and has a stable membrane performance.
- (ii) Material 3 uses the spin-assisted LbL assembly. This technique is very easy to use and is timesaving.
- (iii) The polyelectrolytes used in Material 4 are CHI and ALG biopolymers. Both polyelectrolytes are biocompatible, adaptable material, versatile, non-toxic, easy to obtain and most importantly, biodegradable.

Thus, based on the findings obtained, continuous investigations can be carried out by using CHI and ALG as the deposition polyelectrolytes. Besides, zwitterionic PMPC-co-AA can also be added to reduce the membrane fouling and greater membrane performance, and this deposition can be assembled by using the spin-assisted LbL assembly due to its simplicity and effectiveness.

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