CRITICAL EVALUATION OF THIN FILM COMPOSITE MEMBRANE FOR PESTICIDE REMOVAL

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

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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 :

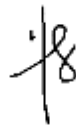Name : SHIRLEY LEE SZE YING

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APPROVAL FOR SUBMISSION

I certify that this project report entitled **"CRITICAL EVALUATION OF THIN FILM COMPOSITE MEMBRANE FOR PESTICIDE REMOVAL"** was prepared by **SHIRLEY LEE SZE YING** 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.

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ABSTRACT

Pesticides are widely used by farmers in the agricultural field to control the proliferation of pests growth to achieve higher yield of crops. However, high level of these pesticides cause negative effects on the environment and wellbeing of living organisms. Membrane separation is an efficient way to remove both pesticides and other micropollutants in wastewater. This study presents a critical evaluation of thin film composite membranes on pesticides removal. Different types of processes using thin film composite membranes discussed were nanofiltration (NF), reverse osmosis (RO) and forward osmosis (FO) (i.e. FO mode and pressure retarded osmosis (PRO) mode) processes. This paper mainly focuses on how certain parameters such as operating pressure, system configuration, pesticide characteristics, membrane characteristics, feed solution and draw solution affect the performance of the membrane. The effects of these parameters on pesticides rejection and permeate flux are studied by comparing the results and findings obtained from various literatures to conclude on the optimum operating conditions for the membranes to achieve high removal efficiency. It was found that the effects of the parameters mentioned varies according to the type of membranes. Generally, high pressure showed positive effects on NF and RO membranes flux performances but could deform PRO membranes. In terms of system configuration, cross-flow configuration in the pressure-driven membranes and FO mode are desired. Besides, hydrophobic pesticides that are larger in size, negatively charged with small dipole moments showed higher retention. The intensity of membrane fouling which reduces membrane performance can be affiliated to its materials. Humic acid has a positive effect on membrane fouling. Ions in the feed solution increased the rejection efficiency and permeate flux of membrane whereas pesticides concentration has a negative effect on their retention. pH of feed solution determines the zeta potential of membrane. As for the draw solution, NaCl at higher concentration is recommended. Thus, it can be concluded that membrane processes are among the prominent approaches to reduce pesticides levels in agricultural wastewater to below the legal standard of pesticides in drinking water set by WHO.

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LIST OF SYMBOLS / ABBREVIATIONS

$log\ K_{ow}$	n-octanol/water partition coefficient
d_s	Stokes diameter, nm
Δ	delta
π	pi
2,4 D	2,4-dichlorophenoxyacetic acid
AOP	advanced oxidation process
BC	Before Christ
BHC	benzene hexachloride
BW30	BW30 reverse osmosis membrane
$CaCO_3$	calcium carbonate
CO_2	carbon dioxide
DDE	1,1-dichloro-2,2-bis(4-chlorophenyl)ethene
DDT	1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane
DO	dissolved oxygen
e.g.	exempli gratia/for example
e_{CB}^-	conductive band electrons
EDC	endocrine disrupting compound
EDTA	ethylendiaminetetraacetic acid
eV	electronvolt
FAO	Food and Agriculture Organization of the United Nations
FO	forward osmosis
H_2O	water
HCH	1,2,3,4,5,6-hexachlorocyclohexane
h_{VB}^+	positive valence band hole
i.e.	id est/in other words
ICP	internal concentration polarization
LiCl	lithium chloride
M	molarity
MCPP	2-(4-Chloro-2-methylphenoxy)propionic acid
$MgCl_2$	magnesium chloride

MgSO$_4$	magnesium sulphate
mV	millivolt
MOH	Ministry of Health
MWCO	molecular weight cut off, Da
NF	nanofiltration
NF200	NF200 nanofiltration membrane
NF270	NF270 nanofiltration membrane
NF90	NF90 nanofiltration membrane
$^{\cdot}$OH	hydroxyl radical
PhAC	pharmaceutically active compound
POP	persistent organic pollutant
ppm	parts per million
PRO	pressure retarded osmosis
RO XLE	reverse osmosis cross-linked membrane
RO	reverse osmosis
SEM	scanning electron microscopy
SW30	SW30 reverse osmosis membrane
TDS	total dissolved solids
TFC	thin-film composite
TiO$_2$	titanium dioxide
TOM	trace organic matter
UF	ultrafiltration
USA	United States of America
US EPA	United States Environmental Protection Agency
UV	ultraviolet
VOC	volatile organic compounds
WEPA	Water Environment Partnership in Asia
WHO	World Health Organization

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CHAPTER 1

INTRODUCTION

1.1 Background

Alongside the modernization of human civilization throughout the past centuries, technologies and industries have been flourishing at an astounding rate to provide a better lifestyle and life quality for all living beings on Earth. New innovations are being invented, often incorporating new technologies and being mass-produced to accommodate the evergrowing of human needs. Nonetheless, the advancement and mass-production often brought about detrimental effects to the environment. High demands of water from the modernization of many developing and industrialized countries causing problems such as water pollution and water scarcity have been major issues (Mekonnen and Hoekstra, 2016; Almuktar, Abed and Scholz, 2017). Water plays a prominent role in various industries, production of both energy and food, economy of a country and wellbeing of the environment. Through the proliferation of technological advancements, there have been a surge of contaminants flowing into various water sources, polluting and rendering them unusable as a water supply (Shannon et al., 2008). This has led to water scarcity and inadequacy of drinkable water access in many areas where these water supplies are being highly depended on. In the United Nations World Water Development Report 2018, it was mentioned that approximately 3.6 billion people suffer from water crisis each year. It was believed that by year 2050, this number will increase to 4.8-5.7 billion people (WWAP, 2018).

Landfill leachates and other wastewater effluents from various industries such as manufacturing, agriculture, mining, sewage treatment plants and domestic lifestock farms are the point and non-point sources for surface water and groundwater contamination (Mohamed et al., 2009; Li, Wang and Du, 2010; Department of Environment Malaysia, 2018; Zhang et al., 2020). According to Food and Agriculture Organization of the United Nations (FAO) (2019), 70 % of freshwater globally is used for agriculture purpose as depicted in Figure 1.1. Large volume of water is required in the agricultural field as irrigation for crops (Almuktar, Abed and Scholz, 2017). This has brought about water

contamination issue due to the build-up of biowastes, heavy metals, pesticides and fertilizers residues in agricultural runoff (Ng, 2017; Beltrán-flores, Caminal and Blánquez, 2020). These contaminants in agricultural runoff have arised a number of problems in both ecosystem and the wellbeing of most life beings including humans. When excess nutrients from agriculture i.e. fertilizers flow into rivers, they cause eutrophication which is the excessive growth of algae and planktons, intaking large amount of dissolved oxygen (DO). These microorganisms compete DO with other living organisms in the water and "collapse" the ecosystem (Ng, 2017). On the other hand, heavy metals and pesticides have a higher impact on groundwater and surface water which are the primary source of water for most humans and animals. Adverse health issues in humans from drinking contaminated water and ingesting marine animals with these toxins in their bodies are one of the direct impacts (Mohamed et al., 2009; Plakas and Karabelas, 2012).

Share of freshwater withdrawals by sector (%) in 2014
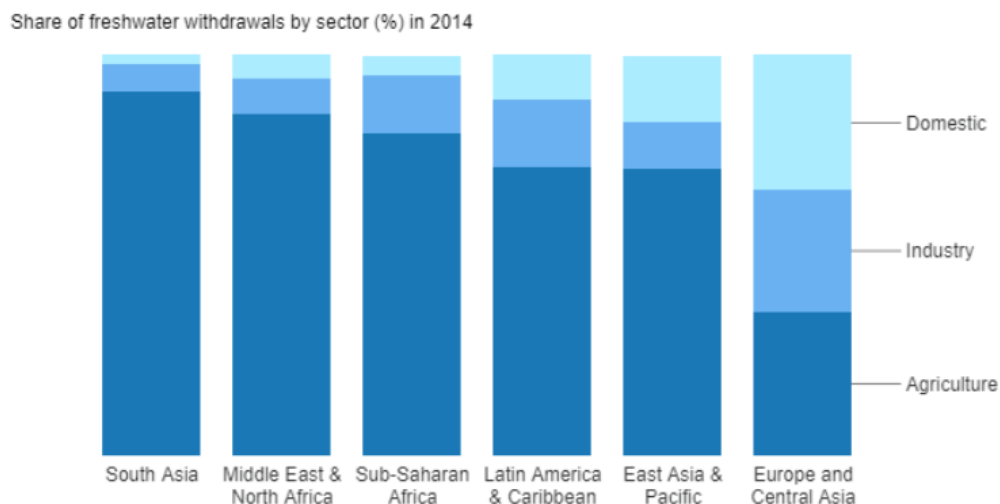
Figure 1.1: Statistics for Freshwater Usage in 2014 (FAO, 2019)

Water scarcity and water pollution problems can be curbed using several approaches like constructed wetlands, bioremediation, adsorption using activated carbon and photocatalysis degradation. Recently, many studies have been focusing on membrane separation to remove pesticides and other micropollutants in wastewater (Mudhoo et al., 2019). Membrane technology had been widely used in sectors such as food, pharmaceutical, biotechnology, chemical and especially in wastewater or drinking water treatment. Membrane

separation utilises different types of membranes to counter different conditions as illustrated in Figure 1.2. Due to its cost-effectivenes, readily available membrane materials, high removal capacity and less energy requirement, this technology is favoured by scientists and engineers over conventional wastewater treatment method. However, membranes are susceptible to fouling which is the blockage of membrane pores by deposition of colloids, particles, salts and macromolecules. Membrane fouling causes decline of permeation flux, affects selectivity and shortens the lifespan of the membrane (Jhaveri and Murthy, 2016). To increase the efficiency of a membrane, many improvements have been made to modify membrane structure such as low pressure, submerged air-sparged membranes but membrane fouling is still a challenge yet to be overcome (Baker, 2012a).
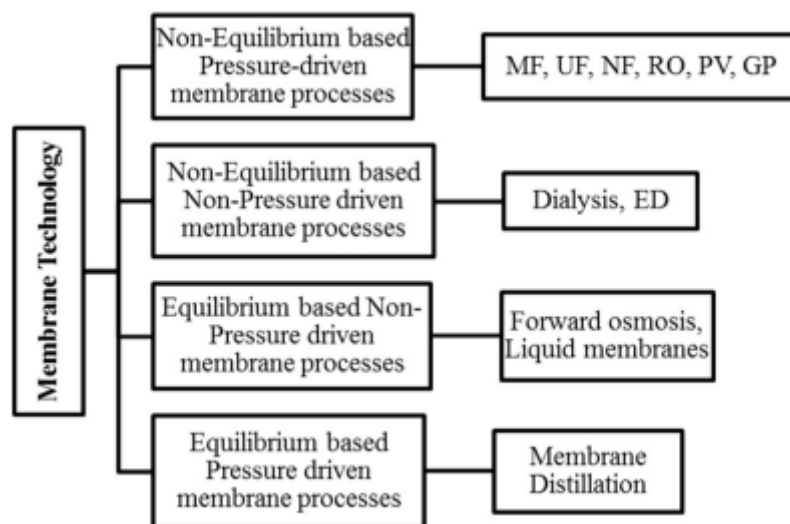
Figure 1.2: Schematic Diagram of Membrane Separation (Jhaveri and Murthy, 2016)

1.2   Importance of the Study

Membrane separation has been widely used in the wastewater field to remove pesticides of small sizes but there are certain limitations for membranes like membrane fouling and low chlorine tolerance. Therefore, it is imperative as a chemical engineer to study the efficiency of membrane under various conditions to optimize the optimum operating condition in which the membrane functions at its top efficiency.

A critical evaluation of the performance of thin film composite membranes in nanofiltration (NF) processes, reverse osmosis (RO) processes, forward osmosis (FO) processes including FO and pressure retarded (PRO) mode in the removal of pesticides and their respective permeate fluxes under various operating variables is presented in this study. Due to certain limitations, this evaluation is conducted through review-based from a number of literatures. The operating variables that are studied are operating pressure, system configuration, pesticide characteristics, membrane characteristics, feed solution and draw solution. These variables are critically reviewed from different literature sources for their effects on pesticides removal and permeate flux. It is crucial to determine the optimum operating parameters to increase the removal of pesticides through NF, RO, FO and PRO membranes to meet the legal standards of allowable pesticides concentration in raw drinking water. The legal standard of individual pesticides in drinking water is 0.1 µg/l and 0.5 µg/l for total pesticides concentration set by the European Union (Van Der Bruggen et al., 2001; Verliefde et al., 2007; Plakas and Karabelas, 2012).

Through these reviews, we may gain further insight on the thin film composite membranes' pesticide removals and these findings may help other researchers in the field of membrane separation in developing NF, RO and FO membranes with quality membrane performance.

1.3   Problem Statement

Pesticides and fertilizers have been widely used in modern agricultural practices for decades. Throughout the century, pesticides have played a huge role in sustainable food production by controlling the proliferation of pests growth to achieve higher yield of crops (Mudhoo et al., 2019). Other than agricultural fields, pesticides are also used in the public health sector to treat diseases such as malaria or dengue (Kim, Kabir and Jahan, 2017). However, the wellbeings of various living organisms like humans, floras and faunas are at risk due to the persistence of pesticides in the environment and their toxicity. Exposure to these pesticides causes various negative impacts to our body systems. It was reported that pesticides are poisonous to humans' body and cause neurological, respiratory, reproductive and dermalogical issues (Kim, Kabir and Jahan, 2017). Hence, the high level of pesticides residues in food has become a critical food safety concerns in countries like China (Grung et al., 2015). Agriculture is the largest consumer of pesticides in the world, thus it is imperative to control the concentration of pesticides in drinking water within the allowable limit established by World Health Organization (WHO) for humans' consumption. Therefore, a range of pesticide abatement methods such as bioremediation, photocatalysis degradation, adsorption and membrane separation are used.

Among the wide range of pesticides being used in the agricultural field, a number of pesticides are either banned in the Stockholm Convention or the production have ceased due to their hazard properties towards the environment and human health. However, traces of them could still be found in certain water sources because of their high persistence in the environment. Therefore, a suitable approach needs to be employed to remove these pesticides efficiently using membrane separation. In this study, membrane separation processes using NF, RO, FO and PRO membranes are studied to investigate the removal of pesticides. The performance of the membranes vary with different conditions and operating parameters. Hence, a review was carried out to identify the operating parameters and evaluate their effects to achieve maximum rejection for the membranes. Besides, other foreign substances that could affect the membrane performance are discussed.

1.4 Aim and Objectives

This study is aimed to critically evaluate the performance of thin-film composite membranes, e.g. nanofiltration (NF) process, reverse osmosis (RO) process, forward osmosis (FO) process including FO mode and pressure retarded osmosis (PRO) mode on the removal of pesticides from wastewater. The objectives of this study are listed as follows:

    i.   To identify the effects of operating pressure on membranes' permeate flux and rejection.

    ii.   To evaluate the effects of system configuration on membranes' permeate flux and rejection.

    iii.   To determine the effects of pesticide and membrane characteristics on membranes' permeate flux and rejection.

    iv.   To investigate the effects of feed and draw solutions on membranes' permeate flux and rejection.

1.5 Scope and Limitation of the Study

In this study, NF, RO, FO and PRO membranes were studied for their efficiency in pesticide removal in aspect of rejection rate and permeate flux under various operating conditions such as operating pressure, system configuration, pesticide characteristics, membrane characteristics, feed solution and draw solution. The scope of this study is listed as follows:

    i.   The performances of NF, RO, FO and PRO membranes in terms of their rejection performances and permeate fluxes are studied.

    ii.   Permeate flux and pesticides rejection efficiency at different operating pressure are identified.

    iii.   The effect of system configuration (i.e. dead-end and cross-flow configuration for NF and RO processes and FO and PRO modes for FO processes) on permeate flux and pesticides rejection efficiency are evaluated critically.

    iv.   Pesticides characteristics are identified and compared for their flux performance and rejection efficiency in terms of molecular size, ionic charge and hydrophobicity.

v. Membrane are characterized based on the fouling intensity and membrane materials when determining their effects on permeate flux and pesticides retention.

vi. The permeate flux and pesticides rejection efficiency in feed solutions are evaluated and compared based on the feed solution ionic charge, concentration, pH and presence of trace organic matter.

vii. Draw solutions in FO processes are also studied on the types and concentration.

A few limitations are present during the study which are listed as follows:

i. Due to the COVID-19 pandemic, the study which was initially lab-based was forced to switch to review-based. Hence, time is a constraint in the second half of the research due to a number of changes to be made in the previous work.

ii. Since all information are based on previous research work found online, certain information may not be readily available. For example, lesser information on FO processes using thin film composite membrane are available because TFC FO membranes are relatively new so less researches and journals can be obtained.

iii. The results and findings from different research work may vary from one to another due to various reasons like different operating conditions, system configurations or types of membrane used in the experiments.

CHAPTER 2

LITERATURE REVIEW

2.1   Water Pollution and Wastewater Issue

Water plays a crucial role in human's everyday life as an indispensable resource of sustainable lifestyle for human and a prominent necessity for the survival of wildlife. However, boost in human population and water consumption behavior have diminished the water quality and supply (Nazemi and Madani, 2018). Immense population growth is normally interrelated with advancement of agricultural field. In a study by Taiz (2013) on how population growth advanced with agriculture since 8,000 Before Christ (BC) until the modern ages, the enhancement in agricultural field comes at certain environmental cost. Pesticides and fertilizers are used widely in modern agricultural practices. Despite being catalysts for high quality food and fibre, their traces remain in agricultural runoff which cause contamination to both surface and ground water.

China having its economy in most areas governed by agriculture is one of the highest pesticide usage country in the world. Thus, China faces serious contamination in both water and soil. Nie et al. (2020) mentioned that 1.46 million tonnes of pesticides are consumed within the year 2005. Roughly 25 % of the water in China is polluted by DDT to class IV pollution (25-250 ng/l) with certain river basins up to class V (> 250 ng/l) (Grung et al., 2015). In India, pesticide residues are still a major problem in the drinking water industries. It was discovered that the most commonly-used pesticides in India, organochlorine and organophosphorus pesticides were detected in bottled drinking water at above permissible limit. This is due to the lack of pesticide concentration in drinking water standards. Yamuna River which used to be a primary source of drinking water is now heavily polluted by untreated or partially treated wastewater and this has risen concerns from environmentalists (Agrawal, Pandey and Sharma, 2010).

Groundwater and surface water are considered as a major drinking source to humans. Consumption of contaminated water may lead to adverse health issues like kidney disease, neuro-development disorders, defects in genetics and immune system damage (Plakas and Karabelas, 2012). The

pesticide-contaminated water is toxic to marine lives when the water flows into river or sea. Thus, it is in the interest of the public, authorities, environmental engineers and those involved in drinking water production to tackle this problem.

2.1.1   Water Pollution in Malaysia

Langat River is one of Malaysia's principal river flowing through the developed and densely populated area of Selangor (Juahir et al., 2011). It serves the people of Selangor by means of domestic, agriculture and industrial. Hence, its pollution level has always been highly monitored and a number of studies are focused on contamination of the river. According to a study by Mohamed et al. (2009), the ecosystem of Langat river basin is largely affected by farming and industrial activities around the area. The nearby oil palm plantations as non-point sources of pollutants use large amount of pesticides, diminishing the ground water and soil quality. In 1997, agro-based industries pollution comprises of 10.04 % of the overall pollution and the figure largely dropped to 0.03 % in 2013. It was also classified as class III pollution for both years (Farid et al., 2016). Although agro-based industries are not the highest source of pollution at the river, it should not be overlooked.

The pesticide concentration and distribution at Langat river delta was also studied by Wee et al. (2016). Traces of organophosphorus pesticides were detected along the river. It was found that at all sampling points, the concentration of both individual and total pesticides are kept within the drinking water limit appointed by European Union (0.1 µg/l for individual pesticides; 0.5 µg/l for total pesticides). This huge improvement from the previous study implies that corrective actions were taken over the years possibly by the local authority or farmers to reduce water contamination due to pesticides.

Water pollution by agricultural runoff is also present at Tanjung Karang located in Kuala Selangor as one of the largest land rice cultivation area in Malaysia due to farming irrigation flowing into the river (Elfikrie et al., 2020). It was found that among the pesticide residues present in the water sample, propiconazole holds the highest mean concentration of 4493.1 ng/l which is out of range for legal standard of individual pesticides in drinking water. Hence, a drinking water treatment plant is set up to treat the irrigation water into drinking water in which 86 % removal efficiency of propiconazole is achieved.

2.1.2   Regulatory Actions on Water

According to the Malaysia Environmental Quality Report 2018, there were a total of 13 wells distributed around farming areas in Malaysia to monitor groundwater pollution due to agricultural runoff in 2018. This operation was carried out in conjunction with the National Groundwater Quality Monitoring Programme which was initiated in 1997. The groundwaters are tested for the presence and concentration of volatile organic compounds (VOCs), pesticides, heavy metals, anions, bacterias like coliform, phenolic compounds, total hardness, total dissolved solids (TDS), pH, temperature, conductivity and dissolved oxygen (DO). In the same year, a total of 76.8 metric tonnes of pesticides were generated as scheduled waste into our environment (Department of Environment Malaysia, 2018).

Unlike our neighbouring countries like Singapore and Thailand, there is no local establishment of any specific regulations on soil and groundwater pollution in Malaysia to date (Huang et al., 2015). Malaysia adopts the groundwater and drinking quality standards of Water Environment Partnership in Asia (WEPA) which was initiated by the Ministry of Environment, Japan in 2003. WEPA addresses the overall water environment in the Asia continent through the establishment of water environmental governance. According to WEPA (2013), the allowable pesticides concentration in surface water and groundwater quality standards are listed in Table 2.1 and Table 2.2.

Table 2.1: Allowable Pesticides Concentration in Surface Water Quality
Standards (WEPA, 2013)

Pesticides	Standard value (mg/l)
Total organochlorine	0.05
DDT	1.0
Alpha-BHC	0.02
Dieldrin	0.1
Aldrin	0.1
Heptachlor and Heptachlor Epoxide	0.2
Endrin	None

Table 2.2: Allowable Pesticides Concentration in Groundwater Quality
Standards (WEPA, 2013)

Pesticides	Standard value (mg/l)
Chlordane	0.0002
Dieldrin	0.00003
Heptachlor	0.0004
Heptachlor Epoxide	0.0002
DDT	0.002
2,4 D	0.03
Atrazine	0.002
Lindane	0.0002
Pentachlorophenol	0.001

In comparison to groundwater and surface water quality standards, drinking water quality standard poses a stricter control on the maximum allowable concentration of pesticides. The World Health Organization (WHO) and United States Environmental Protection Agency (US EPA) has adopted the guideline by the European Unions on pesticides concentration in drinking water quality standards in Malaysia. Under the Drinking Water Directive (98/83/EC), the legal standard of individual pesticides in drinking water is 0.1 µg/l and 0.5 µg/l for total pesticides concentration (Van Der Bruggen et al., 2001; Verliefde et al., 2007; Plakas and Karabelas, 2012) Referring to a document by Engineering Services Division MOH Malaysia (2004), selected pesticides concentration allowable in Malaysia drinking water quality standards are adopted from WHO and are presented in Table 2.3 while the complete list can be obtained in Appendix B.

Table 2.3: Allowable Pesticides Concentration in Malaysia Drinking Water
Quality Standards (Engineering Services Division MOH Malaysia,
2004)

Pesticides	Standard value (mg/l)
Aldrin/Dieldrin	0.00003
DDT	0.002
Heptachlor and Heptachlor Epoxide	0.00003
Lindane (BHC)	0.002
Endosulfan	0.03
Chlordane	0.0002
Pentachlorophenol	0.009
Atrazine	0.002
2,4 D	0.03
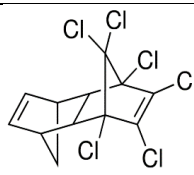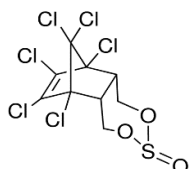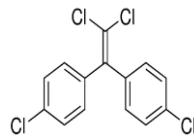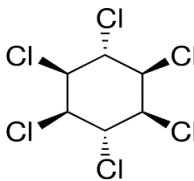
2.2 Pesticides

For decades, pesticides are used by farmers for pest control in the agricultural field. According to Marican and Durán-Lara (2018), "pesticides" is a general name for herbicides, insecticides, fungicides, bactericides and miticides. Pesticides play a huge role in the agricultural field by repelling, preventing, mitigating and eliminating weeds and pests. Herbicides are generally used for eradicating weeds or unwanted vegetation while insecticides controls insects. Furthermore, fungicides can be used to curb germination of moulds and mildew and disinfectants to prevent bacteria growth (National Institute of Environmental Health Science, 2020).

Pesticides can be categorized based on their chemical structures such as organochlorines, carbamates, chlorophenols, organophosphorus and synthetic pyrethroids (Marican and Durán-Lara, 2018). High level of these pesticides from agriculture and landscapes cause pollution in river water and groundwaters. Pesticides-contaminated water is difficult to treat due to its variability of both chemical and physical structures, compositions and high range of pH from 0.5 which is highly acidic to 14 which is highly alkaline. Depending of the sources of the water, the pesticides level can vary between 0.1 to 107 mg/L (Saleh, Zouari and Al-Ghouti, 2020).

Pesticides are normally characterized based on their water solubility at 25 °C, n-octanol/water partition coefficient ($log\ K_{ow}$), polarizability and molar volume. The characteristics of several selected pesticides are listed below in which the $log\ K_{ow}$ and the polarizability of the pesticides were obtained from CompTox Chemicals Dashboard of United States Environmental Protection Agency (US EPA). For $log\ K_{ow}$, both experimental and predicted average were recorded; for polarizability, only predicted average were recorded. In the chemical dashboard, the experimental values were obtained from studies by other researchers while the predicted values were average from datas obtained from several chemical softwares like ACD/Labs, OPERA and EPISUITE. The details of the pesticides are presented in Table 2.4 and Table 2.5 below.

Table 2.4: Different Types of Pesticides

Types of Pesticides	CAS* Number	Chemical Formula	Molecular Weight (g/mol)	Molecular Structure
Aldrin	309-00-2	$C_{12}H_8Cl_6$	364.91	
α-endosulfan	959-98-8	$C_9H_6Cl_6O_3S$	406.93	
DDE	72-55-9	$(ClC_6H_4)_2C$ $=CCl_2$	318.03	
Lindane	58-89-9	$C_6H_6Cl_6$	290.83	

*CAS: Chemical Abstracts Service

Table 2.5: Physicochemical Properties of the Pesticides (US EPA, 2020)

Types of Pesticides	Water solubility at 25 °C (mg/l)	*log K_{ow}**	Polarizability (Å^3)	Molar volume (cm^3/mol)
Aldrin	0.2	Experimental: 6.50 Predicted: 5.91	30.8	228.1
α-endosulfan	0.53	Experimental: 3.83 Predicted: 3.58	31.1	233.2
DDE	292	Experimental: 6.73 Predicted: 6.38	31.7	227.2
Lindane	7.3	Experimental: 3.72 Predicted: 3.95	22.5	157.2

* log K_{ow} > 2 indicates pesticide is hydrophobic

2.2.1 Aldrin

A more commonly name known for 1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4:5,8-exo-dimethanonaphthalene is aldrin which is an organochlorine pesticide. It is a colourless crystalline solid used as a soil insecticide for the wellbeing of food crops. It is most widely used in between 1950s to early 1970s for worms, beetles and termites control (Berntssen, Maage and Lundebye, 2017). Farmers coat the seeds of the crops with aldrin to ward off ants. Aldrin is insoluble in water and volatile. Furthermore, aldrin has a moderately high persistence in the environment with a half-life in soil of two to fifteen years. Its volatility nature allows it to degrade into dieldrin after disposal which will remain in the earth for a much longer period. Hence, despite the banned usage of aldrin, dieldrin still bioaccumulates and acts as a toxicology threats to animals (Deck, Reinke and McCain, 2015). Aldrin and dieldrin residue in soil may be ingested by grass-eating animals like sheeps and cows. Other than soil bioaccumulation, these pesticides also bioaccumulates in aquatic animals while travelling along the river and sea currents.

When human consume the chemical-contaminated animals, health issues may arise. Long term exposure of aldrin may affect the central nervous system (CNS) and hyperexcitation. Due to these environment and health concern, in 1972, the usage of aldrin was limited to only in non-edible plant roots, termite control and moth control in manufacturing processes. After that, any usage of aldrin is entirely banned by US EPA in 1987 and is neither manufactured nor imported to the US ever since then (Honeycutt and Shirley, 2014).

2.2.2 α-endosulfan

α-endosulfan is an isomer of endosulfan which is a cyclodiene insecticide. It is a crystalline solid that appears to be colourless to brown colour. Endosulfan are one of the most commonly detected pesticide in air and surface waters. The semi-volatility and high persistence of endosulfan allow it to remain in the environment for decades without breaking down, thus contaminating the water, soil, air and vegetation in the particular place. Its high volatility allows it to undergo a long range of transport in the air and water. Traces of endosulfan can be found at places far away from its original location (Kim et al., 2020). This

statement is supported by Weber, et al. (2010) who stated that endosulfan was detected bioaccumulating in Arctic marine foodwebs.

α-endosulfan exhibits carcinogenic effects in human bodies after long term of exposure. It can also act as our body's estrogen receptor, disrupting our endocrine system (Ghosh et al., 2018). Other than endocrine system, endosulfan affects humans' reproductive system and cause physiological disorders (Mudhoo et al., 2019). α-endosulfan was widely used in the 1900's but was banned in more than 80 countries since 2012. Stockholm Convention listed endosulfan as one of the persistent organic pollutants (POPs) due to its negative impact on the environment and human health. However, several countries like China and India are still producing and extensively using endosulfan because of its cost-effectiveness and the high performance in pest controlling (Singh, Volger and Gordon, 2014).

2.2.3   1,1-Dichloro-2,2-bis(4-chlorophenyl)ethene (DDE)

1,1-dichloro-2,2-bis(4-chlorophenyl)ethene (DDE) is degraded from 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane (DDT) which is used as an insecticide. Innitially, DDT was used to repel disease-spreading insects like mosquitoes and lice. It was then used by farmers to eliminate pests in their crops before being banned in the Stockholm Convention in 1970s for its persistence in the environment and bioaccumulation. Losing its agricultural purpose, DDT is being used in households as an insect repellent (Burr, 2014).

DDT has high hydrophobicity and is water insoluble. In water, DDT breaks down photocatalytically or by biodegradation. The residues bioaccumulate and remain in the environment for a long period, causing adverse effects to humans' health at the same time. DDE has a longer half-life in humans which is 7-11 years as compared to DDT which is 2-15 years. With DDE being an anti-androgen, DDT and DDE cause reproductive issues in. These pesticides cause estrogenic effects and affect fertility rate (Bonde and Toft, 2011).

As a breakdown product of DDT, DDE has no commercial use but it has higher persistence in the environment and is much more harmful to human health and environment. Thus, it is being focused more in the following studies and is used as one of the pesticides that are to be removed through membrane separation in this research.

2.2.4 Lindane

The eight monomers of 1,2,3,4,5,6-hexachlorocyclohexane (HCH) are α-, β-, γ-, δ-, ε-, ζ-, Z- and ψ-HCHs. Among the monomers, 1α,2α,3β,4α,5α,6β-Hexaclorocyclohexane (γ-HCH) also known as lindane is the most commonly used as pesticides in the agricultural field. Lindane appears as a white solid substance and can evaporate easily. Lindane is a type of insecticide for crops and animals that are widely used in the agricultural field towards the late 20th century. With high persistence in the environment, it appears in vapour form in the air for a long period. It is stated in the safety data sheet of lindane that lindane is highly toxic to marine lives in which the effects are long lasting (Sigma-Aldrich, 2020).

In human body, lindane may affect the nervous system and it is carcinogenic which is cancer-inducing. Due to environmental and health hazards, the production of lindane in the United States has ceased since 1976. Yet, lindane is still being utilised in medicinal field to treat scabies and body lice on human body (Chen, 2014). Since lindane has high persistence and can bioaccumulate in the environment,abundance of lindane residues still can be found in the manufacturing plants that have been shut down (Chen et al., 2020).

2.3 Pesticide Abatement Methods

Ever since pesticides were introduced into the agricultural field for the sake of high quality crops and enhancement of agricultural yield, various pesticides abatement methods have been developed to treat pesticide residues in water sources from agricultural runoff. In a review of pesticide removal by Marican and Durán-Lara (2018), it was concluded that pesticide remediations are classified into three main groups: biological, physical and chemical methods. In this section, one remediation method from the three classifications are reviewed. Firstly, bioremediation is discussed as the biological method for pesticides mineralization. Secondly, the physical remediation which will be reviewed is adsorption method. Last but not least, advanced oxidation processes (AOPs) will be reviewed as the chemical remediation.

2.3.1 Bioremediation

In recent years, bioremediation has appeared as one of the most promising approach to remove harmful pesticides and organic pollutants from water. Bioremediation can be carried out using bacteria, fungi or phytoremediation depending on the composition of the pesticides. Since a more natural approach is taken, it is comparably more environmental friendly and cheaper at the same time able to remove a wide range of pesticides than other pesticide abatement methods (Mudhoo et al., 2019; Marican and Durán-Lara, 2018).

The species of bacteria used for the elimination of pesticides and their removal mechanisms differ by the types of target pesticides. Bacterias can be coupled with microalgae to increase their adaptability in extreme environments. Oxygen produced through photosynthesis by microalgae promotes growth of bacterias while respiration of bacterias produces carbon dioxide as a carbon substrate for microalgae (Kumari, Ghosh and Thakur, 2016). On the other hand, fungal biodegradation is carried out through pathways like esterification, hydroxylation, demethylation, dehydrochlorination, dichlorination, oxidation and dioxygenation with different enzymes (Maqbool et al., 2016). In phytoremediation, vegetation is exploited to clear up pesticide contamination. The products from phytoremediation could be reused to achieve the benefit in eco-friendliness thus gaining recognition in green engineering aspect (Mudhoo et al., 2019).

In spite of the superiority of bioremediation in eco-friendliness, it can be labour intensive and a lot of time is required to achieve the desired result. It is also challenging to be up-scaled to real field scenarios and in-depth knowledge and experience are required (Mudhoo et al., 2019). The sensitivity of microorganisms to pH, temperature, organic solvents and severe environmental conditions still remain a challenge for bioremediation to be commercially and industrially applied as a general pesticide removal method (Marican and Durán-Lara, 2018).

2.3.2 Adsorption

Adsorption of pesticides from water is another reknowned method of pesticide removal. This process is simple, fast and inexpensive with high quality of treated effluent produced compared to other pesticide abatement methods (Ibrahem, 2012; Ariffin et al., 2017). Adsorption may be driven by electrostatic attraction or carried out through physicsorption which is driven by weak Van der Waals forces or chemisorption by covalent bonding. It utilizes a highly porous material which is the adsorbent for solutes to be accummulated on the surface through the intermolecular forces of attraction between liquid and solids (Rashed, 2013).

A wide range of safe adsorbents available in the market prompts the advancement of the adsorption method. The criterias of a suitable adsorbent material are its commercial availability, non-toxicity, low cost, high susceptibility on abrasion, high surface capacity and stability in various environmental conditions (Shamsollahi and Partovinia, 2019). According to Mojiri et al. (2020), activated carbon, graphene, biochar, bentonite, zeolite, chitosan and nanoparticle adsorbents are the commonly used adsorbents in the removal of organic pollutants. Among these adsorbents, activated carbon is claimed by US EPA as an excellent adsorption material due to its high adsorption capacity, and high porosity at large surface area but at a high cost (Rashed, 2013). Bandala et al. (2006) concluded that aldrin elimination efficiency of 95.3-95.57 % can be achieved through the adsorption using activated carbon. On the other hand, El-Kady et al. (2013) managed to obtain 98.6 % of lindane removal within 3 hours using activated carbon. Nonetheless, activated carbon has the disadvantage of being expensive. Thus, alternatives

bearing high efficiency and lower cost are still being studied to replace activated carbon as an adsorbent material.

2.3.3 Photocatalytic Degradation

AOPs include several different reactions for pesticides removal in water treatment industry. Generally, radical species which are very reactive and oxidizing like hydroxyl radicals ($^\cdot$OH) interact and degrade the organic pollutants. More biodegradable intermediates or complete mineralization of micropollutants can be achieved through AOPs (Vagi and Petsas, 2017). The reactions classification of AOPs are shown in Figure 2.1. Among the various AOPs, heterogeneous photocatalysis or photocatalytic degradation using titanium dioxide (TiO_2) with ultraviolet (UV) light is discussed.
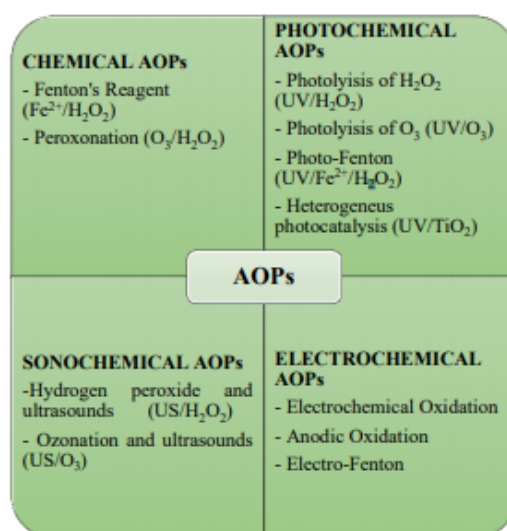
Figure 2.1: Classifications of Advanced Oxidation Processes (Vagi and Petsas, 2017)

Photocatalytic degradation utilizes a semiconductor oxide photocatalyst as the catalyst. The utilization of TiO_2 in the removal of pesicidies in water has gained recognition around the globe due to its stability in photochemical conditions, commercial availability, minimal toxicity and high efficiency in pesticides absorption (Mudhoo et al., 2019; Devipriya and Yesodharan, 2005). However, the wide band gap (3.2 eV) of pure TiO_2 only allows it to be photoactive in UV light which only accounts for a mere 8 % in sunlight

compared to visible light which accounts for 45 % in sunlight (Xiong et al., 2015). Jagadale et al., (2008) reported that doping TiO_2 with nitrogen extends the spectral reponse to allow efficient harnessing of visible light to undertake the photocatalytic reactions.

The mechanism of photocatalytic degradation is as follows:

$$TiO_2 + h_v \ (< 387 \ nm) \rightarrow e_{CB}{}^- + h_{VB}{}^+ \tag{1}$$

$$h_{VB}{}^+ + R \rightarrow intermediates \rightarrow CO_2 + H_2O \tag{2}$$

$$H_2O + h_{VB}{}^+ \rightarrow \cdot OH + H^+ \tag{3}$$

$$\cdot OH + R \rightarrow intermediates \rightarrow O_2 + H_2O \tag{4}$$
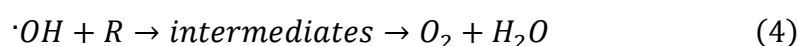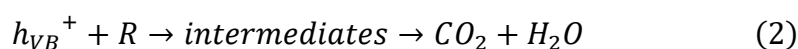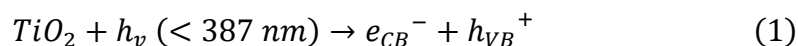
According to Umar and Aziz (2013) and Devipriya and Yesodharan (2005), when the semiconductor catalyst is irradiated with light larger than the band gap, conductive band electrons (e_{CB}^-) and positive valence band hole (h_{VB}^+) are generated (Eq. 1). Then, the h_{VB}^+ undergo oxidation either with organic compounds to produce carbon dioxide (CO_2) and water (H_2O) (Eq. 2) or with water to form a hydroxyl radical ($\cdot OH$) (Eq. 3). The electrophilic nature of $\cdot OH$ promotes oxidation on most organic compounds then convert them into CO_2 and water (Eq. 4).

Despite the wide usage of this method in pesticide abatement, the drawbacks faced are the formation of by-products. When used at large scale, the cost of the process is high due to large energy usage (Mudhoo et al., 2019; Devipriya and Yesodharan, 2005). To counter this drawback, cost minimization can be done through process optimization in catalyst separation and recycling (Abdennouri et al., 2016).

2.4 Nanofiltration (NF) Membrane

As an alternative to the conventional method to remove pesticides from agricultural wastewater, nanofiltration (NF) membrane is one of the technology that scientists have been studying in recent years to improve pesticides removal (Karimi, Rahimpour and Kebria, 2016). NF membrane is a type of asymmetric thin-film composite (TFC) membrane made up of a "skin" upper layer deposited on top of a thick support layer (Wang, 2016). The "skin" upper layer is a polymer layer e.g. polyamide or poly(piperazine-amide) whereas the support layer is a polysulfone porous ultrafiltration membrane. The function of the support layer is to carry out mechanical loads and to protect the "skin" layer which allows permeate to pass through and perform the main separation process (Kowalik-Klimczak, Bednarska and Grądkowski, 2016). The cross-sectional view of the assymetric TFC membrane is illustrated in Figure 2.2.
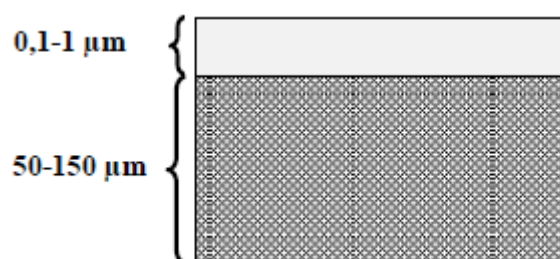
Figure 2.2: Cross-sectional View of Assymetric Thin Film Composite
Membrane (Kowalik-Klimczak, Bednarska and Grądkowski, 2016)

With the properties ranging in between ultrafiltration (UF) and reverse osmosis (RO) as illustrated in Figure 2.3, nanofiltration membrane is a pressure-driven membrane (Al-Zoubi et al., 2007; Madaeni, 2016). According to Baker (2012), NaCl rejections of NF membrane is 20-80% while its molecular weight cut off (MWCO) is between 200-1000 Da for dissolved organic solutes. Filtration of NF membrane is highly dependent on size exclusion and Donnan exclusion effects. Size exclusion plays a huge role for uncharged solutes. However, the pore size of NF membrane is larger compared to RO membrane, leading to coarser filtration. This might cause the removal of smaller pesticides to be ineffective (Khairkar et al., 2020). In Donnan exclusion, multivalent ions of the same charge are rejected while oppositely charged multivalent ions are

freely permeable through the membrane (Baker, 2012). It was mentioned by Cathie Lee et al. (2014) that the charge of NF membrane depends on its pH condition. This is further elaborated in Chapter 3.

Size, μm	Ionic	Molecular	Macromolecular	Microparticle	Macroparticle
	0.001	0.01 0.1	1.0	10	100 1,000
Approximate Molecular Weight	100 200 1,000	10,000 20,000 100,000 500,000			
Relative Size of Various Materials in Water	Dissolved Solids	Viruses Humic Acids	Bacteria Algae Cysts Clays Silt		Sand
Separation Process	ED/EDR RO NF	Ultrafiltration	Microfiltration		
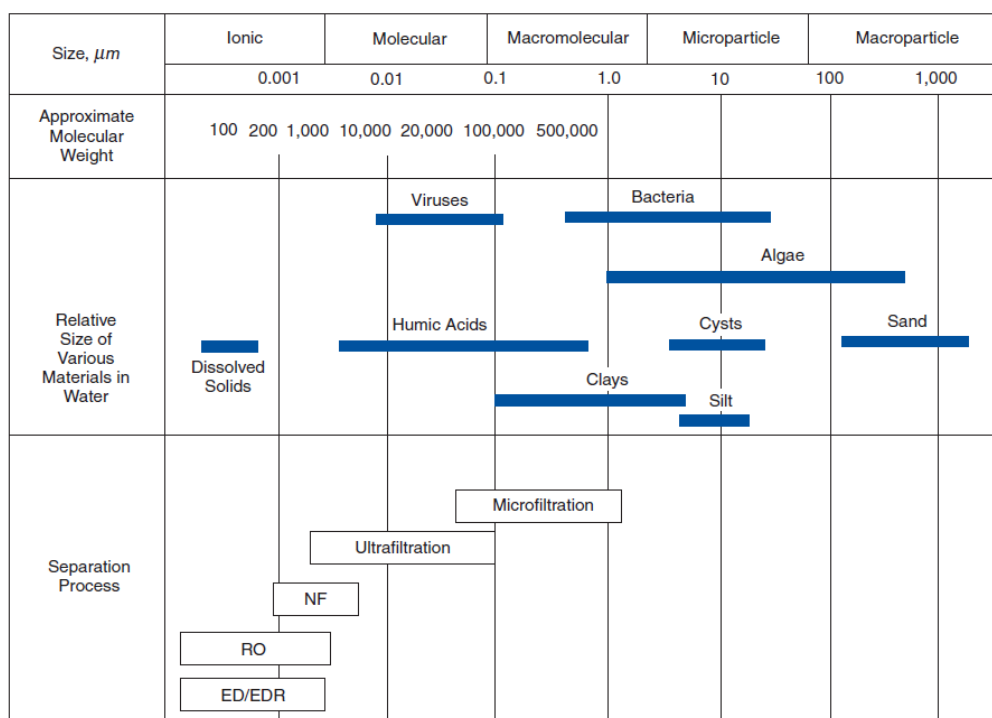
Figure 2.3: Overview of Membrane Separation Processes (Foley, 2007)

In the interest of cost effectiveness, NF membrane is favoured by wastewater engineers compared to RO membranes. The low cost is due to low operating pressure of the membrane with high permeate flux (Karimi, Rahimpour and Kebria, 2016). Licona et al. (2018) stated that high retention of inorganic ionic salts and small organic molecules can be achieved without any phase change within the membrane. Furthermore, Al-Zoubi et al. (2007) also explained that NF process is easy to operate with high reliability. In comparison to RO membranes, NF process consumes less energy with high efficiency in removing pollutants. Because of these advantages, NF process is mainly applied in surface water and groundwater treatment, for instance, water softening and micropollutants removal (Karimi, Rahimpour and Kebria, 2016). It is also being used to reduce salt concentration in water and remove organic compounds with low molecular weight. Other than water purification process, NF membranes can also be utilised to treat industrial wastes. It is able to achieve excellent

efficiencies when separating metal ions, mono and multivalent ions and removing dyes (Kowalik-Klimczak, Bednarska and Grądkowski, 2016). Several common commercial NF membranes that can be found in the market are studied and compiled in Table 2.6. In order to facilitate the comparison, the membrane specifications are compiled from the same membrane manufacturer which is DOW FILMTEC[TM]. This manufacturer is selected because most of the membranes in the literature reviewed are purchased from it.

Table 2.6: Membrane Specifications of Common NF Membrane (Racar et al., 2017; Plakas and Karabelas, 2008; Lenntech, 2021)

	NF90	NF200	NF270
Manufacturer	DOW FILMTEC[TM]		
Membrane Type	Polyamide thin-film composite		
Membrane Pore Size (nm)	0.55 ± 0.13	0.31	0.71 ± 0.14
MWCO (Da)	100-200	200	150-300
Water Permeability (L/m^2 h bar)	7.95	10.6 ± 0.7	13.45
pH Range	2-11	3-10	2-11
Maximum Operating Temperature (°C)	45	45	45
Maximum Operating Pressure (bar)	41	41	41

2.5   Reverse Osmosis (RO) Membrane

Reverse osmosis (RO) is a phenomenon where solutes flow against the concentration gradient from a less concentrated region to a more concentrated region. Osmotic pressure plays a huge in RO membranes due to the high concentration of solutes. Osmotic pressure occurs due to the effect of total dissolved solids (TDS) in the feed water and is overcome to generate product water flow (Baker, 2012). At high osmotic gradient, large pressure is exerted upon the membrane feed side, forcing water to infiltrate the membrane while efficiently rejecting the solutes (Shannon et al., 2008). RO membranes have smaller pore size compared to NF membranes, hence lower solute permeability. In order to overcome the low membrane permeability, the operating pressure in RO process is higher. Thus, it possesses a steeper fixed investment and greater operating cost, making it less favourable than NF membranes (Licona et al., 2018).

RO membranes can be made up of cellulose acetate or interfacial composites. Cellulose acetate membrane has an asymmetric structure made up of a thin separating functional layer on top of a coarse supporting layer (Kurihara and Sasaki, 2017). It has higher resistance to chlorine degradation but the salt rejection is relatively lower. On the other hand, interfacial composite membranes which are discussed in this study exhibit greater flux and salt rejection than cellulose acetate membranes. The drawback of this membrane is the low chlorine tolerance. Any exposure to chlorine may diminish the salt rejection properties of the membrane and lead to permanent loss in selectivity despite having a wide range of pH tolerance (Foley, 2007). The membrane structure for thin-film composite RO membranes are similar to NF membranes. The barrier layer or upper "skin" layer as mentioned in section 2.4 NF membrane utilises cross-linked aromatic polyamides which is sensitive to oxidants like chlorine. This active layer is placed on top of a polysulfone layer supported by a non-woven polyester web layer as illustrated in Figure 2.4 (Albergamo et al., 2020).
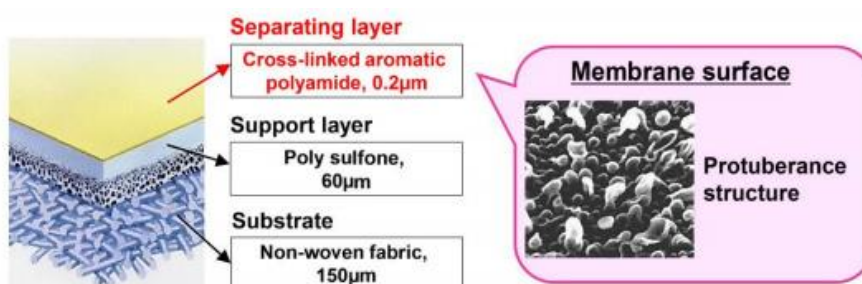
Figure 2.4: Structure of Polyamide Composite RO Membrane (Kurihara and
Sasaki, 2017)

The mechanism of RO process is the solution-diffusion model governed by concentration gradient as depicted in Figure 2.5 and Figure 2.6. The permeates dissolve in the material of the membrane then diffuse from a high concentration region to a low concentration region. The discrepancies in solubility and diffusion rate induce the separation mechanism of RO membranes. (Baker, 2012; Licona et al., 2018; Hasmadi et al., 2017). The advancement of RO membrane allows pesticide rejection of up to 94 % in deionized water, 97% in tap water and 95 % in field water (Mehta et al., 2015). Another study by Fini, Madsen and Muff (2019) achieved pesticides retention of more than 92 % using RO membrane and the value can be increased if feed recovery is applied. In Table 2.7, three commercial RO membranes from DOW FILMTEC[TM] are compared. The molecular weight cut off (MWCO) of SW30 membrane is undefined and cannot be found in any literatures. Hence, it is defined in terms of salt rejection which is obtained from the manufacturer (Palma et al., 2016). From the many literatures reviewed, the differences between NF membranes and RO membranes are enlisted in Table 2.8.
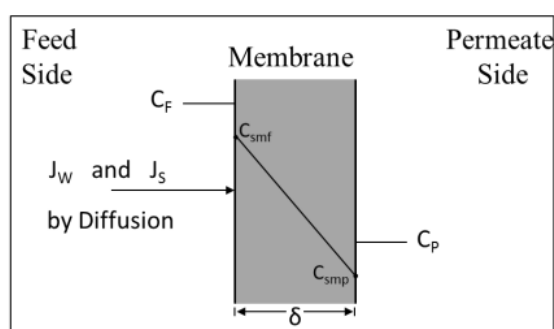
Figure 2.5: Solution-diffusion Model Schematic Diagram (Hasmadi et al.,
2017)

(a)   (b)
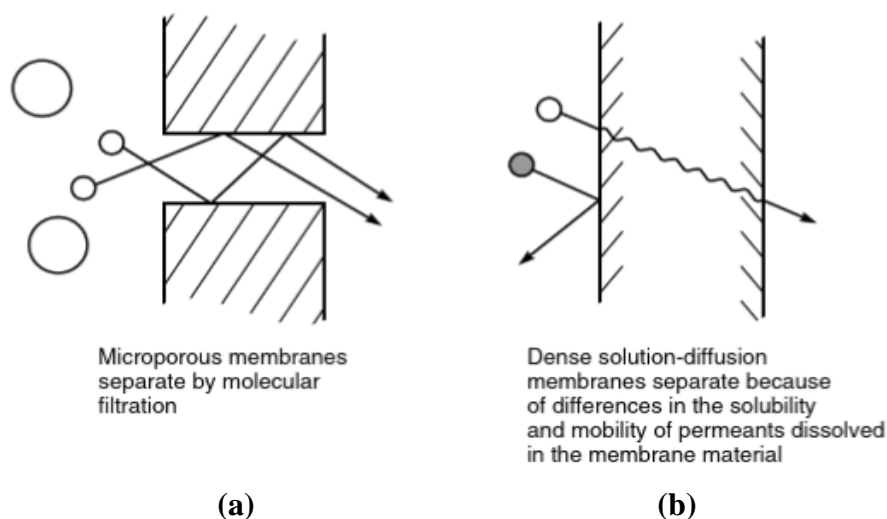
Figure 2.6: Transport of Molecules Through Membranes in (a) Pore-flow

Model or (b) Solution-diffusion Model (Baker, 2012)

Table 2.7: Membrane Specifications (Plakas and Karabelas, 2008; Licona et

al., 2018; Fini, Madsen and Muff, 2019; Palma et al., 2016)

	BW30	**RO XLE**	**SW30**
Manufacturer	DOW FILMTEC^{TM}		
Membrane Type	Polyamide thin-film composite		
MWCO (Da)	100	100	Salt rejection: 99.80 %
Water Permeability (L/m² h bar)	2.9 ± 0.2	5.7 ± 0.6	1.2
pH Range	2-11	2-11	2-11
Maximum Operating Temperature (°C)	45	45	45
Maximum Operating Pressure (bar)	41	41	69

Table 2.8: Comparison of NF and RO Membranes (Baker, 2012; Karabelas
and Plakas, 2011; Shon et al., 2013)

Characteristics	Nanofiltration (NF)	Reverse Osmosis (RO)
Driving force	Hydrostatic pressure	
Membrane material	Finely porous assymetric/composite	Nonporous assymetric/composite
Operating pressure	Low (5-20 bar)	High (10-100 bar)
Typical pore size (nm)	< 2	< 1
Permeability (L/m^2·h·bar)	1.4 - 12	0.05 – 1.4
Cost	Low	High due to high operating pressure
Mechanism	Sieving, Donnan exclusion and solution-diffusion model	Solution-diffusion model
Retention of solutes	Ineffective in monovalent ions retention	Effective in monovalent ions retention

2.6 Forward Osmosis (FO) Process

Forward osmosis (FO) is an emerging membrane filtration method which is shows great potential in water technology field like wastewater treatment and seawater desalination (Tan and Ng, 2013). Instead of utilizing hydraulic pressure as driving force like NF and RO membranes, osmotic pressure difference is used instead (Arjmandi et al., 2020). In FO processes, clean water is forced from a feed solution which is of low osmotic pressure to a draw solution with high osmotic pressure through a semi-permeable membrane as illustrated in Figure 2.7 (Arcanjo et al., 2020; Zhao et al., 2016; Zhang et al., 2017). Draw solution is highly concentrated with salt which is either being regenerated or serve other purposes after the process (Nikbakht Fini et al., 2020a). Similarly to pressure-driven membranes, solute rejections in FO processes are mainly governed by electrostatic interaction, steric exclusion and hydrophobic adsorption. Therefore, membrane characteristics and fouling still play significant roles in solute rejection (Zheng et al., 2019).

TFC membranes which are made up of a thin active layer placed on a thick mechanical support layer are the newer type of membranes used in FO processes in the recent few years. FO processes can operate in two modes with different membrane orientation. When the active layer faces the feed solution and the support layer faces the draw solution, the process is operated in FO mode. On the other hand, when the support layer faces the feed solution and the active layer faces the draw solution, then the process is operated in PRO mode (Zhao et al., 2016; Arjmandi et al., 2020; Khoo et al., 2020). Zhao et al. (2016) stated in his study that fouling in membrane support layer is more severe in PRO mode as compared to FO mode. This is because when pure water diffuses from the feed to draw side through the membrane, higher concentration of salt is retained in the support layer facing the feed side. In contrast, the salt concentration within the support layer which faces the draw side in FO mode is diluted hence the lower fouling. The difference between RO, FO and PRO modes is illustrated in Figure 2.8.
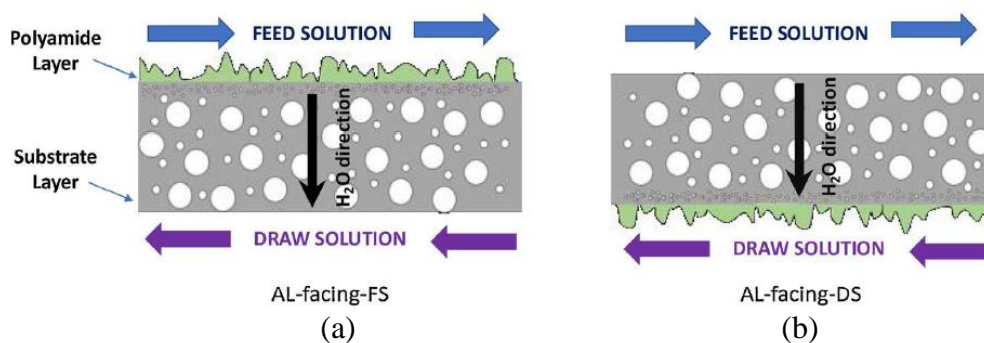
Figure 2.7: Illustration of Forward Osmosis Process in (a) FO Mode and (b) PRO Mode (Khoo et al., 2020)
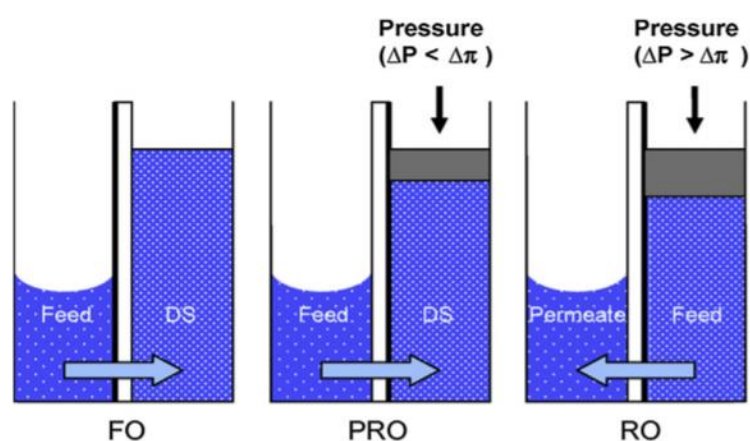
Figure 2.8: Solvent Flow in FO, PRO and RO (Touati and Tadeo, 2017)

Internal concentration polarization (ICP) is a main issue in FO membranes. Concentration polarization impairs the performance of osmotic membranes by causing a substantial decline in osmotic pressure difference possibly due to fouling issues. The flow of water into draw solution and salt into feed solution creates a salt gradient in the porous support layer (Touati and Tadeo, 2017). This results in the occurrence of ICP and is reported to be more severe in FO mode (Alsvik and Hägg, 2013; Khoo et al., 2020). In PRO mode, the ICP is called concentrative ICP where there is an accumulation of draw solute at the interface between active and support layer. On the contrary, the ICP in FO mode is called dilutive ICP where the draw solution in the support layer is diluted from water flux from feed solution (Alsvik and Hägg, 2013). The ICP in both FO and PRO modes are as depicted in Figure 2.9.
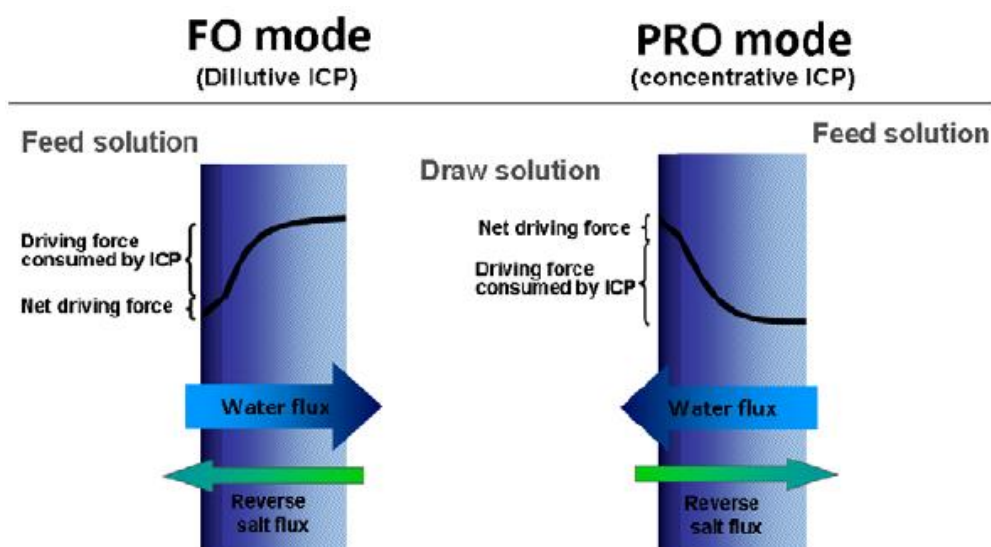
Figure 2.9: Dilutive ICP and Concentrative ICP in FO and PRO Modes

(Alsvik and Hägg, 2013)

FO shows great potential in the water treatment sector with additional advantages than NF and RO membranes such as low fouling tendency with reversible fouling and easy flux recovery. Considering FO uses natural osmotic pressure as driving force instead of hydraulic pressure, less energy is consumed and the cost is lower (Arcanjo et al., 2020; Tan and Ng, 2013; Liu et al., 2018). However, it is worthy to note that FO alone is yet to achieve the desired result of water reclamation due to its low selectivity and permeability. FO is merely used to withdraw clean water from the feed solution containing the contaminants (Zhang et al., 2017). Then, an additional step is required to recover or regenerate the downstream draw solution for water reuse. In most cases, reverse osmosis is used in the draw solution regeneration, forming an FO-RO hybrid system (Nguyen et al., 2018). With the additional process, additional energy is required and this may spike up the cost to be higher than alternative processes (Johnson et al., 2018). Therefore, FO process may be effective in seawater desalination or wastewater treatment but much research still needs to be done for potable water production.

2.7 System Configuration

2.7.1 NF and RO Processes

For membrane process, there are two main flow configurations which are cross-flow filtration and dead-end filtration. Feed flow is perpendicular to the membrane in dead-end configuration. After the feed is forced through the membrane, the left over matter accumulates on membrane surface (Calabrò and Basile, 2011). The accumulation of matter on membrane surface may form a cake layer which reduces flux because of the additional resistance (Van der Bruggen, 2018). At the same time, this cake layer may provide additional filtration effect to improve the separation efficiency. However, it is undesired because pressure drop within the membrane may increase and impair the membrane performance (Nagy, 2019). Dead-end system is normally equipped with a stirrer to reduce concentration polarization (Van der Bruggen, 2018). Dead-end configuration suffers from concentration polarization and extensive fouling. It is usually used in batch processes and lab-scale (Nagy, 2019). A typical dead-end flow configuration system is shown in Figure 2.10.
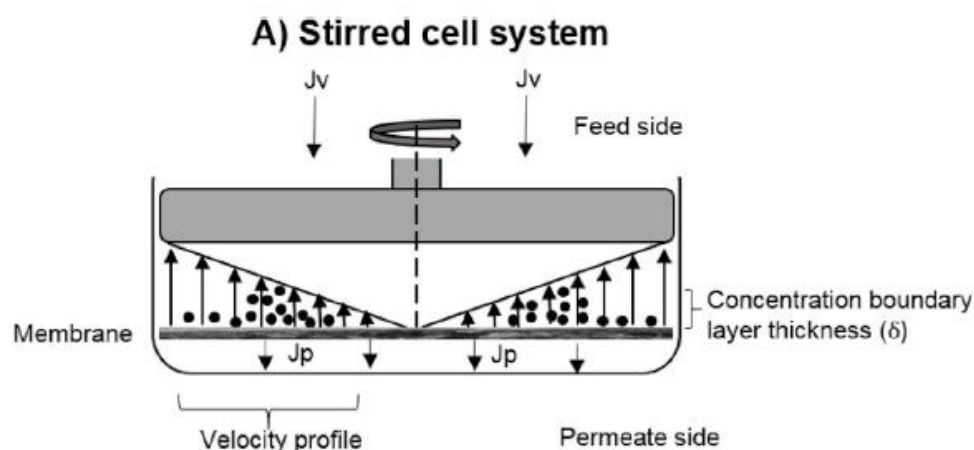
Figure 2.10: Dead-end Flow Configuration (Imbrogno and Schäfer, 2019)

A schematic diagram of a dead-end system using Sterlitech™ HP4750 dead-end stirred cell (SterlitechTM, USA) is depicted in Figure 2.11. Compressed high purity nitrogen gas is utilised to pressurize feed solution in the dead-end stirred cell. In the study by Mah et al. (2014), a wet flat sheet membrane with a total membrane area of $0.00152 \ m^2$ and effective membrane surface area of $0.00146 \ m^2$ is being situated at the bottom of the stirred cell. The

cell is supported by a porous support plate of stainless steel material. A magnetic stirrer coated with Teflon is equipped in the stirred cell to keep concentration polarization to a minimum. The collected permeate is weighed and permeate fluxes are monitored at the digital balance. The permeate weight is recorded as a function of time and the data is then transmitted to a personal computer. Prior to the experiment, a compaction process shall be conducted on the flat sheet membrane using distilled water for a certain amount of time to prevent any structural change in the membrane (Mah et al., 2014).

Figure 2.11: Schematic Diagram of SterlitechTM HP4750 Dead-end Stirred Cell Setup (Mah et al., 2014)

Unlike dead-end filtration, the suspension flow in cross-flow filtration is parallel to the membrane surface. A constant turbulent flow carries the retained particles forward and the retentate is removed at the end of the flow. At the same time, permeate is transferred to the opposite end of the membrane (Nagy, 2019). The turbulent flow parallel to the membrane surface prevents accumulation of matter hence diminishes fouling issues. Tube-shaped membranes with the active layer inside the wall of the tubes are normally used for this flow configuration. Pressure of cross-flow filtration are elevated to provide driving force for the separation process and high velocity are used to create a turbulent environment (Calabrò and Basile, 2011). Therefore, cross-

flow velocity is an important parameter in this configuration. When shear forces are applied on the membrane surface, flux stability and rejection are improved. Despite the less severe fouling, the main disadvantage for cross-flow configuration is that it requires higher energy thus higher cost (Van der Bruggen, 2018). A typical cross-flow configuration system is shown in Figure 2.12.
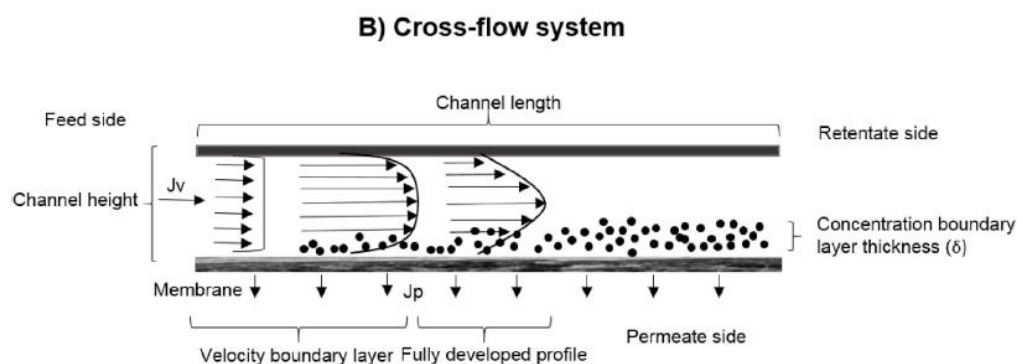
Figure 2.12: Cross-flow System (Imbrogno and Schäfer, 2019)

A schematic diagram of a cross-flow system using Sterlitech[TM] CF042 cross-flow filtration cell (SterlitechTM, USA) is illustrated in Figure 2.13. In the study by Mah et al. (2014), a wet flat sheet membrane with an effective membrane surface area of 0.0042 m^2 is being situated at the middle of the membrane cell. The membrane active layer is ensured to be placed facing the feed solution while the opposite surface faces the permeate. A high-pressure hydra-cell industrial pump is used to pump the feed solution from a feed tank to the membrane. A PolyScience chiller is installed at the feed reservoir to control the temperature of feed solution. Between the high-pressure pump and the feed tank, a pressure relief valve is installed to remove pressurized gas in the case of overpressure. A bypass valve and a concentrate valve are used to control the flow rare and pressure by adjusting the valve openings. The collected permeate is weighed and permeate fluxes are monitored at the digital balance. The permeate weight is recorded as a function of time using a data logger. Prior to the experiment, a compaction process shall be conducted on the flat sheet membrane using distilled water for a certain amount of time to prevent any structural change in the membrane (Mah et al., 2014).
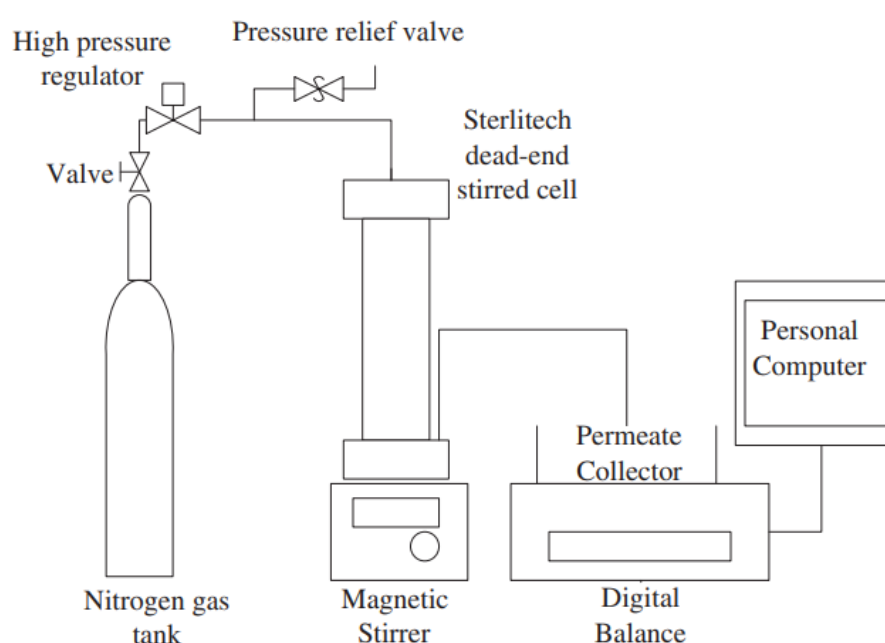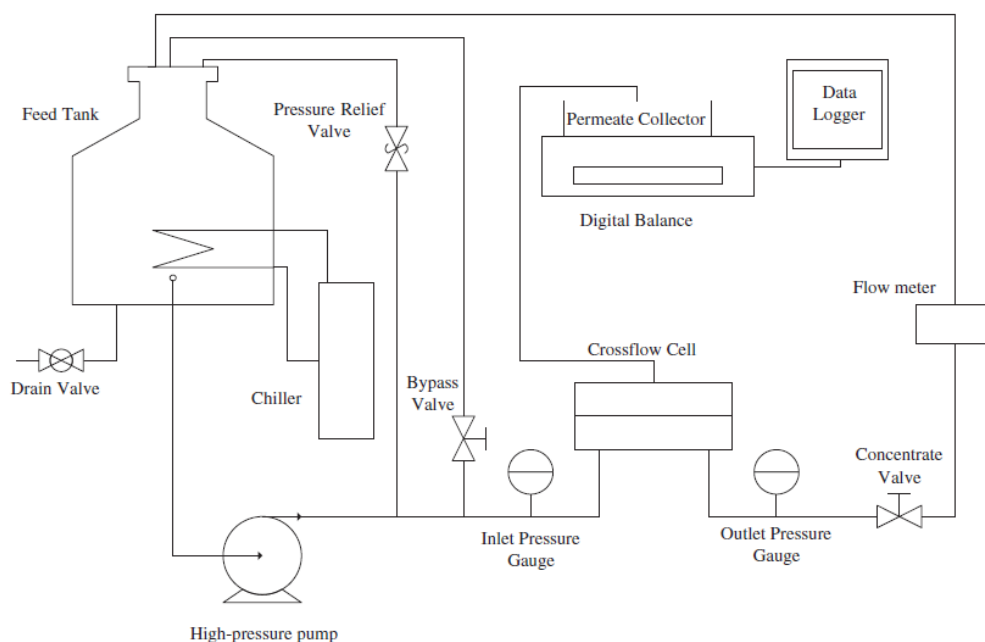
Figure 2.13: Schematic Diagram of a Crossflow Setup (Mah et al., 2014)

2.7.2 FO Process

The forward osmosis (FO) system depicted in Figure 2.14 is applicable for both FO and PRO mode. The only difference between these two modes are the orientation of FO membrane. When the active layer of the membrane faces the feed solution, the system operates in FO mode; when the active layer of the membrane faces the draw solution, the system operates in PRO mode (Zhao et al., 2016; Arjmandi et al., 2020; Khoo et al., 2020). In this set up by Zheng et al. (2019), a flat-sheet membrane is placed in the membrane cell and connected to two symmetrical and identical plastic flow chambers. The effective area of membrane in this study is 44.6 cm^2. Two gear pumps were used for the circulation of both feed and draw solutions across the membrane cell and back (Alturki et al., 2013). In pesticides removal, the feed solution is the solution containing pesticides while the draw solution is the salt solution. Flow meters were installed to monitor the flow rate of the solutions into the membrane cell. The volume of draw solution here is 0.5 L while the volume of feed solution is 2 L. The draw solution is weighed at the digital balance and the weight change is monitored and recorded as a function of time using a data logger. Another draw solution reservoir which is more concentrated is also placed on the digital balance to reduce any weight interference between the two draw solutions. A

conductivity probe connected to a peritaltic pump is used to control and maintain the concentration of both draw solutions. When the conductivity falls below a set point, the peristaltic pump is activated to transfer the concentrated draw solution to the draw solution reservoir, thus a constant concentration of draw solute is maintained (Alturki et al., 2013). Another conductivity probe is placed at the feed solution reservoir to monitor and maintain the concentration of feed solution.
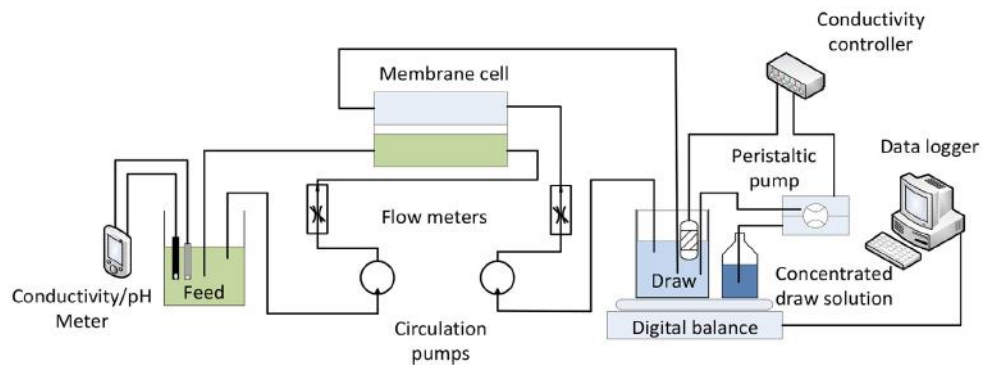
Figure 2.14: Schematic Diagram of a Lab-scaled Forward Osmosis System (Zheng et al., 2019)

2.8 Removal of Micropollutants with Thin Film Composite Membrane

In the environment, compounds that exist in trace amounts with concentrations of µg/l or ng/l are known as micropollutants. They consists of pharmaceuticals, pesticides, household chemicals, industrial agents and personal care products like perfumes and cosmetics. Their persistence and bioaccumulation in our water sources make them difficult to be eliminated which causes detrimental effects to various organisms (Das et al., 2017; Kim and Zoh, 2016).

The retention of particles are affected by feed solution pH, membrane hydrophilicity and humic acid. In a study by Riungu et al. (2012), humic acid increases rejection of atrazine in NF membrane through steric exclusion. However, this finding is not in agreement with Mehta et al. (2015) who uses RO membrane in the study. It is stated that the presence of humic acid is not significant in membrane performance because RO membrane has tighter pores compared to NF membrane, size exclusion plays a much more important role in particle rejection which downplays the effect of humic acid. Thus, humic acid only exhibits large influence on pesticide rejection in ionic condition.

Other than pesticides, there are also traces of other organic micropollutants like pharmaceutically active compounds (PhACs) and endocrine disrupting compounds (EDCs) in different water sources which is detrimental to human's health and the environment. In a study on PhACs removal by Licona et al. (2018), rejections above 88% can be achieved and neutral compounds like acetaminophen and caffeine depend on molecular size for the rejection. A similar study by Xu et al. (2020) also achieved retention higher than 80% for micropollutants with positive and neutral charge of molecular weight higher than 250 g/mol at room temperature. On the other hand, ibuprofen and dipyrone depend on medium pH to determine their hydrophobicity and electrostatic repulsion for solute retention (Licona et al., 2018).

Draw solution is crucial in FO processes because clean water is extracted from feed side to draw side. The types of salt in draw solution determines the separation efficiency and rejection performance of the membrane. Arcanjo et al. (2020) compared the membrane performance using several draw solutions like magnesium chloride, $MgCl_2$, sodium chloride, NaCl, magnesium acetate, $MgOAc_2$, sodium acetate, NaOAc and ethylenediaminetetraacetic acid

disodium salt, EDTA-Na$_2$. Among these draw solutions, the preferred draw solutions is ranked MgCl$_2$ > NaCl > NaOAc > EDTA-Na$_2$ > MgOAc$_2$ based on their rejection efficiency and flux performance. Xie et al. (2018) mentioned that the rejection of pesticide DEET is around 90 % when MgSO$_4$ was used as the draw solution but is increased to 96 % when NaCl was used as the draw solution. Draw solution concentration also displays a positive effect on the rejection efficiency of trace organic compounds in the same study.

Membrane fouling is studied in the study by Zheng et al. (2019). In the study, fouled membrane experienced a higher flux decline of 70 % while clean membrane only experienced a flux decline of 19 %. The cake layer developed on the surface of a fouled membrane may contribute to the additional filtration effect of the membrane. This claim is supported by Arcanjo et al. (2020). Other than membrane fouling, solute retention is also affected by ionic charge and hydrophobicity. When both micropollutants and membrane are of the same charge, electrostatic repulsion occurs and attribute to the rejection of the membrane (Nikbakht Fini et al., 2020a). It was also mentioned that hydrophobicity of a pesticide increases its rejection provided the membrane is not heavily saturated with pesticides. Table 2.9 summarizes the mentioned studies on micropollutants.

Table 2.9: Summary of Studies on Micropollutants

Thin Film Composite Membranes	Micropollutants	Membrane Performance and Main Findings	References
NF (DF30)	• Pharmaceutically active compounds (PhACs)	• Neutral and positively charged micropollutants with MWCO larger than 250 g/mol can be 80% rejected • Average rejection increases from 72.2 % to 87 % as recovery increases from 60 % to 80 % • Average rejection increases from 72.2 % to 88.6 % as temperature decreases from 25 ℃ to 13 ℃	(Xu et al., 2020)
FO (cellulose triacetate (CTA) membrane)	• Trace organic compounds	• The rank of desired draw solution is $MgCl_2 > NaCl > NaOAc > EDTA\text{-}Na_2 > MgOAc_2$. • Membrane fouling contributed to higher electrostatic repulsion between solutes and membranes, increasing solute rejection. • The reverse salt flux using $MgCl_2$ as draw solution is low due to large hydration radii.	(Arcanjo et al., 2020)

FO (aquaporin membrane)	• Pesticides (BAM, MCPA, MCPP)	• Pure water flux is 15.54 $L/m^2 \cdot h$ and reverse salt flux is 5.77 $g/m^2 \cdot h$. • Retention of larger pesticides (MCPA and MCPP) is 95-98 % while retention of small pesticide (BAM) is 93-94 %. • Electrostatic repulsion occurs between pesticides and membranes of the same charge, increasing rejection. • Hydrophobocity has a positive effect on pesticide rejection.	(Nikbakht Fini et al., 2020a)
FO (TFC)	• Trace organic compounds	• Internal concentration polarization reduces water flux. • For charged compounds, electrostatic interaction governs the solute rejection. • Flux decline in fouled membrane is 70 % while flux decline in clean membrane is 19 %. • Cake layer on membrane surface could increase rejection.	(Zheng et al., 2019)
NF (NF90) and RO (BW30)	• Pharmaceutically active compounds (PhACs)	• Rejection more than 88 % is achieved and hits its peak (> 90 %) at 20 bar and pH 5. • Non-ionic compounds depend on molecular size for the rejection while others depend on hydrophobicity and electrostatic repulsion at different pH	(Licona et al., 2018)

FO (aquaporin membrane)	• Endocrine disrupting compounds • PhACs • Industrial chemicals • Pesticides	• Pesticides rejection increased when concentration of draw solution increased (i.e. 67 % rejection of metronidazole at 0.5 M NaCl and 91 % rejection at 2 M NaCl). • Pesticide rejection is higher when NaCl was used as draw solution (i.e. When $MgSO_4$ is draw solution, pesticide DEET rejection is around 90 %; when NaCl is draw solution, rejection is increased to 96 %).	(Xie et al., 2018)
RO	• Phenyl urea pesticides	• Deionized water: 30 L/m^2h permeate flux and 94 % rejection • Tap water: 25 L/m^2h permeate flux and 97 % rejection • Field water: 23 L/m^2h permeate flux and 99 % rejection • The effect of humic acid is not significant	(Mehta et al., 2015)
NF (NF90, NTR7250, NF270)	• Pesticides	• At higher pressure, the increase in water flux causes higher pesticides retention at 25 °C • At pH 7, rejection is the highest • Humic acid increases rejection through steric exclusion	(Riungu et al., 2012)

CHAPTER 3

METHODOLOGY AND WORK PLAN

3.1   Overview of Methodology and Work Plan

In this chapter, the steps taken to in this study for a critical evaluation of thin film membranes for pesticides removal are discussed thoroughly. Figure 3.1 shows the flowchart of the steps taken to carry out this study to have a clear guideline when preparing for thesis writing. Since this study was conducted in review-based, ample time was required for searching of different journals and critically review them based on our problem statement and objectives. It was worthy to note that the results from journals may vary from one to another due to certain reasons like different operating conditions or duration of experiment. Therefore, it was important to review the journals critically and make a conclusion based on our understanding. The ability of judging the importance of information to be included was imperative to achieve a clearer analysis and discussion. By delivering a feasible judgement and providing possible recommendations, this may help future readers and researchers of the similar field.
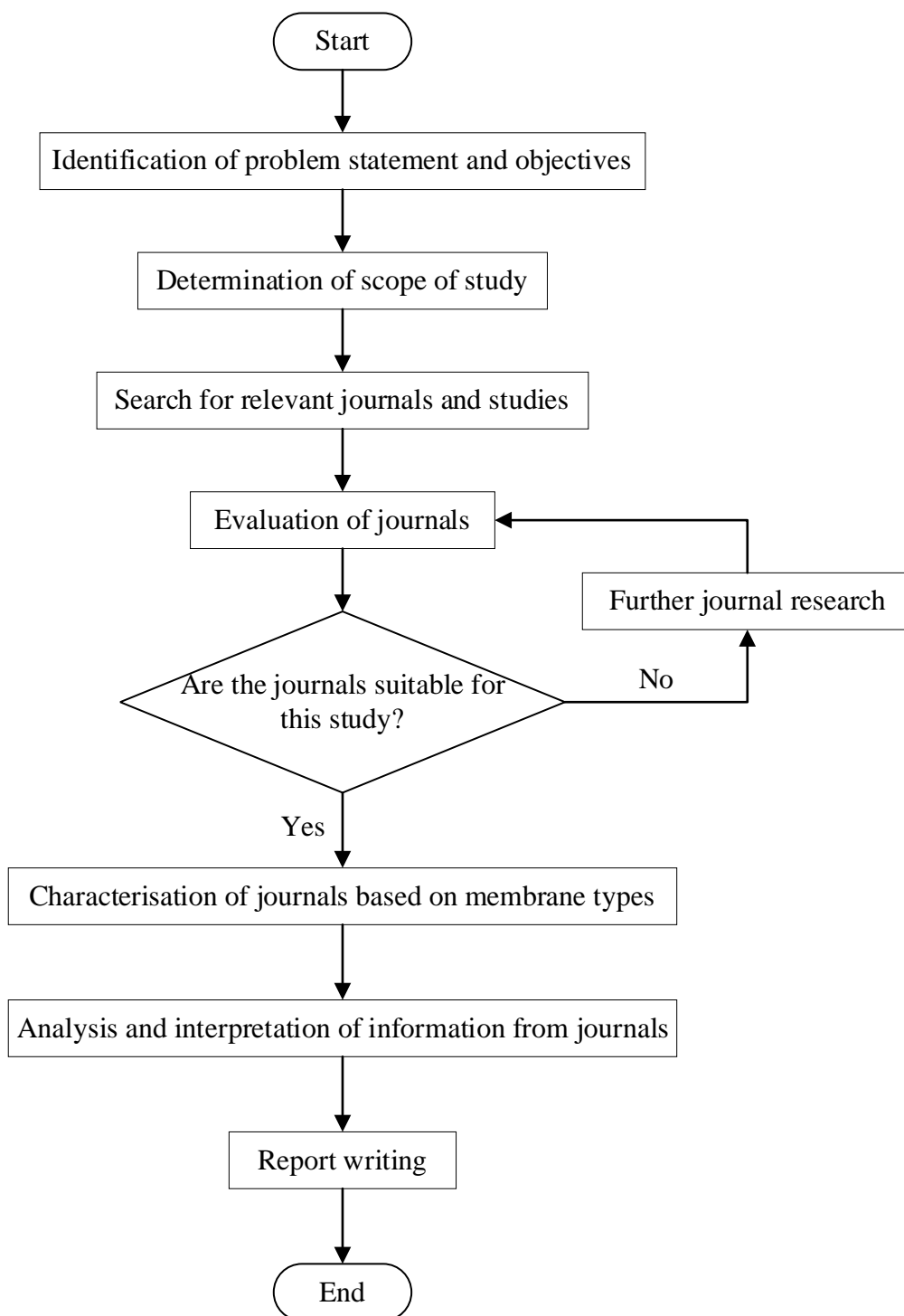
Figure 3.1: Flowchart of Review Project

3.2 Identification of Problem Statement, Objectives and Scope

The very first step in doing a review-based thesis was the identification of problem statement and objectives. It was crucial to identify and understand the research question and the purpose of this thesis first so we had a clear direction on what should be included in the thesis.

First and foremost, a discussion was held with the supervisor to understand the background of the field of interest, in this case, thin film membranes for pesticides removal. Different parameters affecting the membrane performance were discussed and listed. Membrane filtration is a very common research topic, hence the scope of study was defined to narrow down the field of interest to nanofiltration, reverse osmosis and forward osmosis processes. Other than that, the effect of the parameters on the removal of pesticides and permeate flux were discussed. The problem statement, aims, objectives and scope are listed in Chapter 1.

3.3 Search and Evaluation of Journals

Searching of sources for this review-based thesis could be conducted differently, either through online sources or hardcopies like textbooks or encyclopaedias. Most of the sources in this thesis were extracted online in which multiple search engines or databases were used. An effective search strategy allows accurate searching in minimal duration. It was imperative to understand the main topic and identify possible keywords for searching. Stages of developing the search strategy is listed in Figure 3.2.

Firstly, the main concepts were identified from the research title as shown in Figure 3.3. Identification of the main concepts gave us a clear idea of what to type into the search engine or databases. From the main concepts, possible keywords and similar terms that could be used to achieve a better searching result could be identified (Littlewood and Kloukos, 2019). For instance, keywords such as "nanofiltration", "reverse osmosis", "forward osmosis", "pressure retarded osmosis", "pesticides removal", "micropollutants retention" or "membrane performance" were used when searching in a library database. Abbreviations like NF, RO, FO and PRO were also used. The reference list of the research journals or review papers found could also allow

us to look for more similar journals or articles. The phrase searching technique narrowed down the search and we were able to obtain more accurate data or journals online (Tannebaum and Rauber, 2015). When quotation marks were added at the search term, the library databases were forced to carry out the search as a phrase instead of individual words. The main sources of information are:

(i) ScienceDirect (http://www.sciencedirect.com).

(ii) ResearchGate (http://www.researchgate.net).

(iii) SpringerLink (http://www.link.springer.com).

(iv) ACS Publications (http://www.pubs.acs.org).

(v) Wiley Online Library (http://www.onlinelibrary.wiley.com).

(vi) UTAR Library E-Journals (http://library.utar.edu.my).

(vii) Google Scholar (https://scholar.google.com).

The relevant journals found were downloaded for further evaluation. Various review papers were studied so the scope of the review-thesis does not overlap with other review papers in the field. It was ensured that the research done is able to contribute something new to the field.
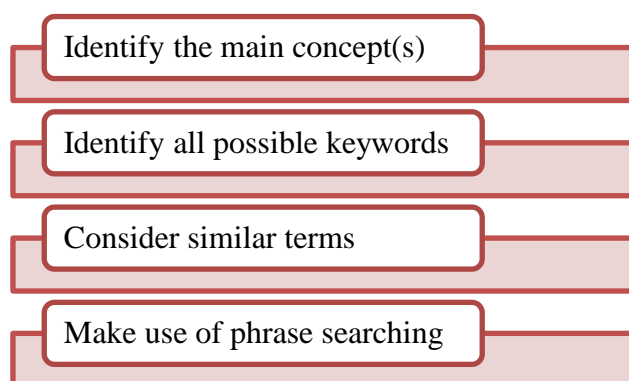
Figure 3.2: Search Strategy
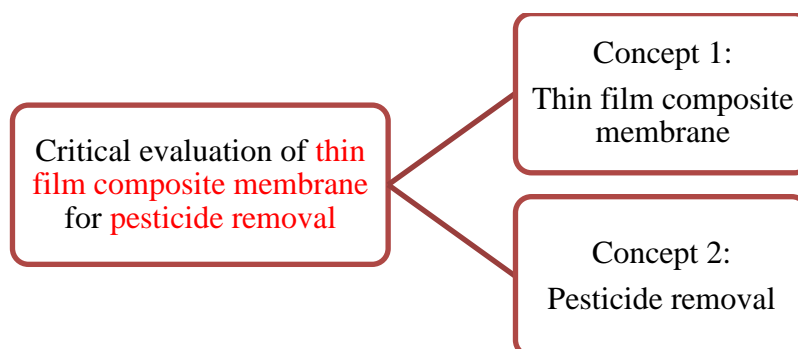
Figure 3.3: Identification of Main Concepts

3.4 Journals Characterization

After downloading all the relevant journals found online, the journals were organised and characterized based on the membrane types to facilitate future reference when doing literature review and results discussion as shown in Figure 3.4.
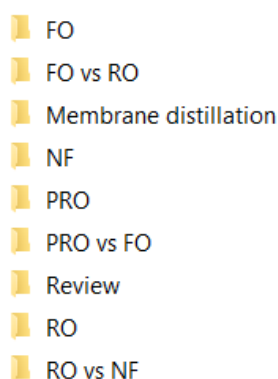
Figure 3.4: Characterization of Journals Based on Membrane Types

3.5 Analysis and Interpretation of Information

In the process of thesis writing, more than 100 journals were studied and downloaded. The journals and e-books downloaded were read thoroughly to gain insight on the scope. Reading abstracts in the papers were a good approach to understand the scope of the paper and the respective results achieved from the researchers. From the journals and e-books, the significant findings and data were extracted. These are usually contested findings, results and trends in the research papers and some back theories. Information that was deemed important and could be included in the thesis was highlighted for report writing later. The similarities and differences in findings between the studies were organized,

summarised and compared. Journals which were more recent were prioritised but relevant historical sources could still be taken into account during the analysis. As more information were extracted from the papers, new headings and subheadings were slowly developed at this stage to reflect the different findings. The structure of the thesis was outlined at this step.

3.6   Report Writing

The final stage in this review-based thesis was report writing. The outlined structure of the thesis was used at this stage to write the final report. It was important to link one section to the previous section logically. A final checking was done after the report to ensure the thesis was free of grammar and other errors. The sources which were used in the thesis were cited and the references were listed at the end of this report to give credit to the authors and prevent plagiarism. Figure 3.5 shows the flowchart on the chapters which were included in the thesis and the steps of report writing.
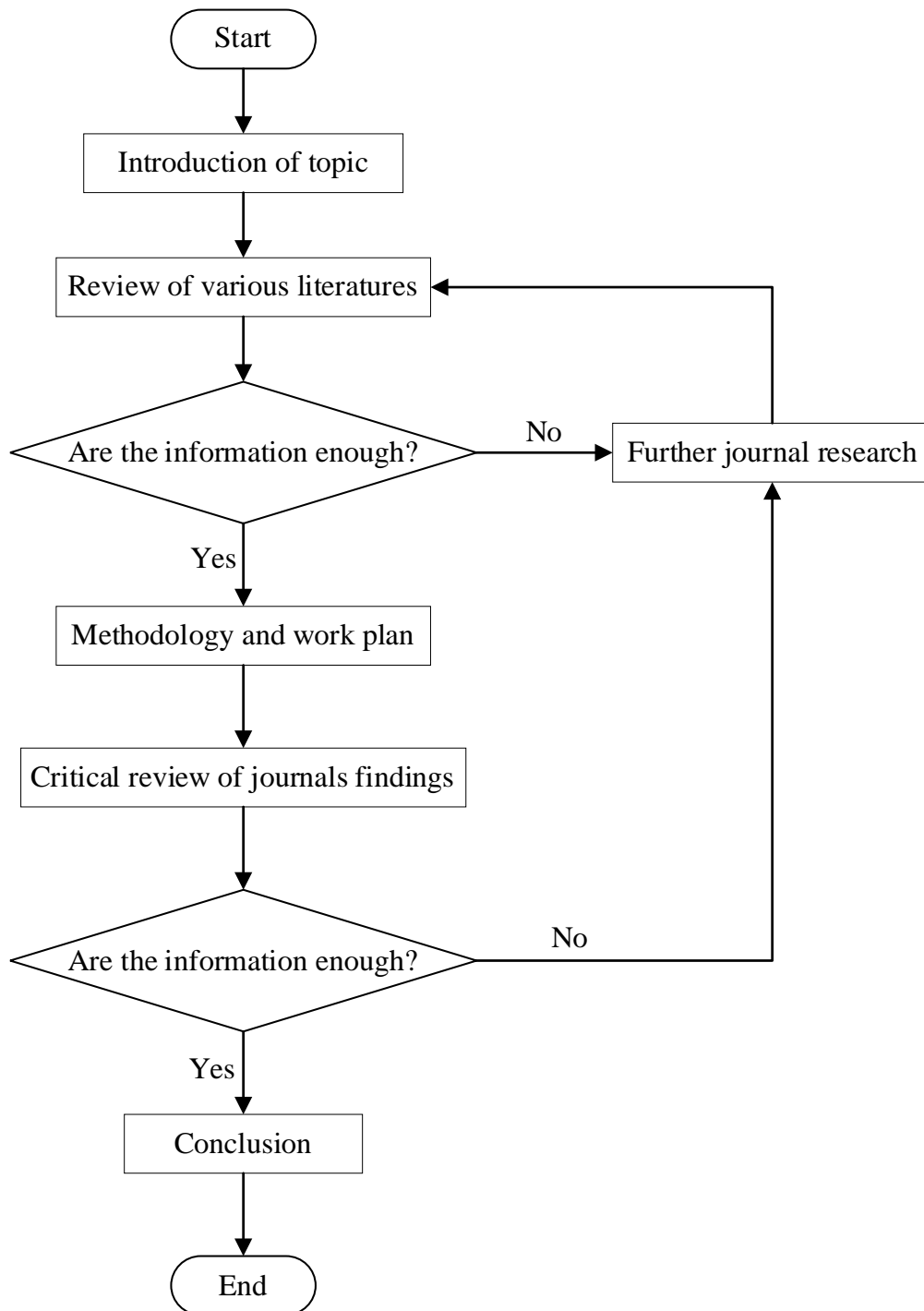
Figure 3.5: Flowchart of Thesis Writing

CHAPTER 4

RESULTS AND DISCUSSION

4.1   Introduction

In this section, the effects of different parameters on permeate flux and pesticides removal were discussed. Since this thesis was review-based, the results and findings from various journals were interpreted and compared. The findings of journals may vary from one to another, hence it was imperative to review them critically. At the end of each review for the respective parameters, short summaries of the findings were provided to wrap up the review. The parameters discussed were operating pressure, system configuration, pesticide characteristics, membrane charateristics, feed solution and draw solution. Graphs and charts were provided to provide a clearer view and understanding of the results and findings if possible. Journals on NF, RO, FO and PRO processes were included in the results and discussions. However, there were lesser research done on FO processes, especially PRO mode regarding micropollutants removal, possibly because FO and PRO were used more in seawater desalination instead of field water purification. For the effect of feed solution ionic charge, there were insufficient studies for FO and PRO to be critically reviewed so these membranes were not included in section 4.6.1. For draw solutions, only FO and PRO were discussed due to the fact that these membranes require both feed solution and draw solution to function while NF and RO membranes only require feed solution.

4.2 Effect of Operating Pressure on Permeate Flux and Pesticides Removal

One of the parameters affecting permeate flux and pesticides removal is operating pressure, also referred to transmembrane pressure in some studies. Findings of different journals and studies on pressure are included and critically reviewed. The membranes are normally studied in a pressure range of 5 to 20 bar which is applicable for NF, RO and FO membranes and the maximum allowable pressure for the membranes is 41 bar.

Riungu et al. (2012) investigated the effect of pressure using several NF membranes, e.g. NF270, NF90 and NTR7250. It was found that the retention of a herbicide, atrazine improved along with the pressure as depicted in Figure 4.1. For instance, as the pressure increased from 6 bar to 12 bar at a constant atrazine concentration of 10 ppm, the retention of NF270 membrane increased from 70 % to 80 %. At high pressure, the retention was higher because water flux in the membrane caused dilution of permeates when molecules were rejected by molecular sieving effect. Compared to retention efficiency, the effect of operating pressure was more obvious on permeate flux which was governed by membrane pore size. An almost double of permeate flux was achieved as shown in Figure 4.1 when the pressure increased (Riungu et al., 2012). Besides, Ajao et al. (2017) also agreed that pressure had a very high influence on permeate flux in RO membrane. In another study by Heo et al. (2013), there was a linear relationship between the applied pressure and pure water flux. As the pressure inclined from 0 to 20 bar, solute rejection rose from 82 % to 93 %. The trend of water flux coincided with the solution-diffusion model where pressure was directly proportional to water flux (Sivanantham et al., 2021).

The effect of high pressure was different in FO processes compared to in NF and RO membranes. It was reported in a number of studies that high pressure caused deformation of membrane in PRO mode, hence lowering their performance (Kim and Elimelech, 2013; Wan and Chung, 2015; Cheng and Chung, 2017). According to Figure 4.2, while pure water permeability was constant at 3.5 LMH/bar throughout the pressure fluctuations from 5 bar to 20 bar, solute permeability increased slightly from 0.28 LMH to 0.36 LMH. High solute permeability at high pressure was caused by defects in the membrane

layer (Wan and Chung, 2015). Kim and Elimelech (2013) added that this was caused by the membrane compressing against the feed spacer, blocking the channel for water permeation at high pressure. They called it the "shadow effect". Furthermore, Salamanca et al. (2021) mentioned that water flux increased as the osmotic pressure increased which was related to concentration of draw solution as depicted in Figure 4.3. The non-linear pattern was probably due to reverse salt flux. A summarise of the studies mentioned were tabulated in Table 4.1.
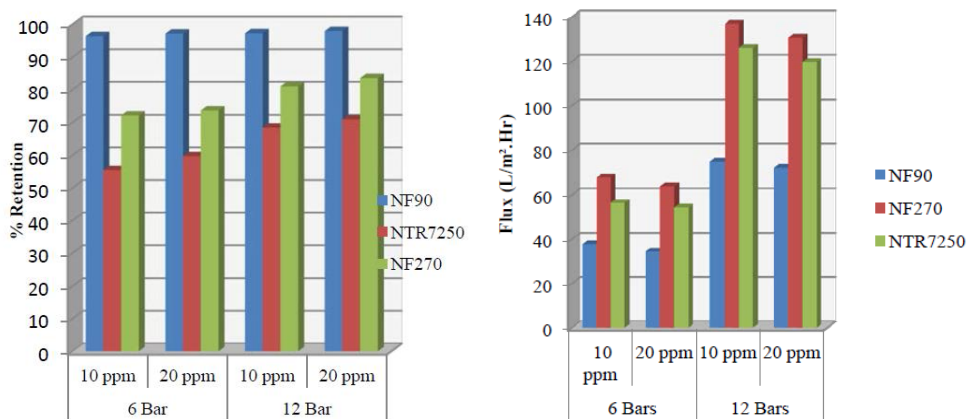
Figure 4.1: Effect of Pressure on Flux and Membrane Retention Performance (Riungu et al., 2012)
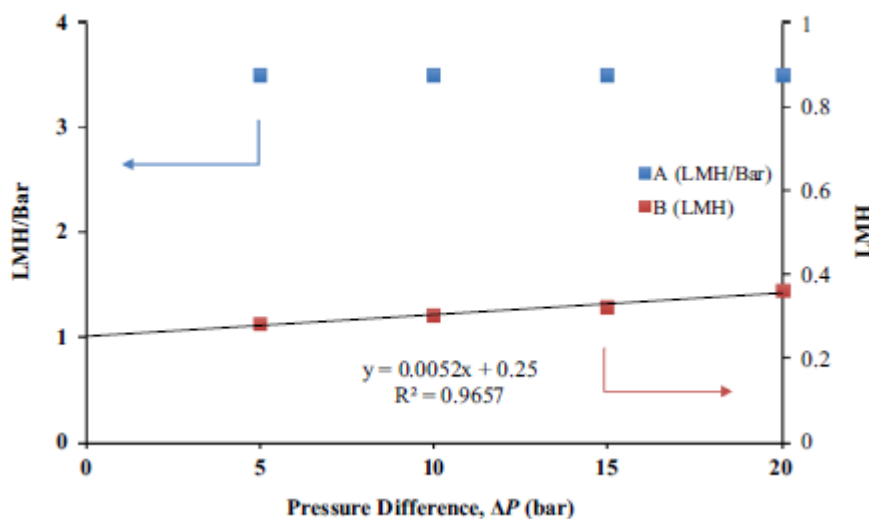
Figure 4.2: Pure Water Permeability (A) and Solute Permeability (B) as a Function of Pressure Difference (Wan and Chung, 2015)
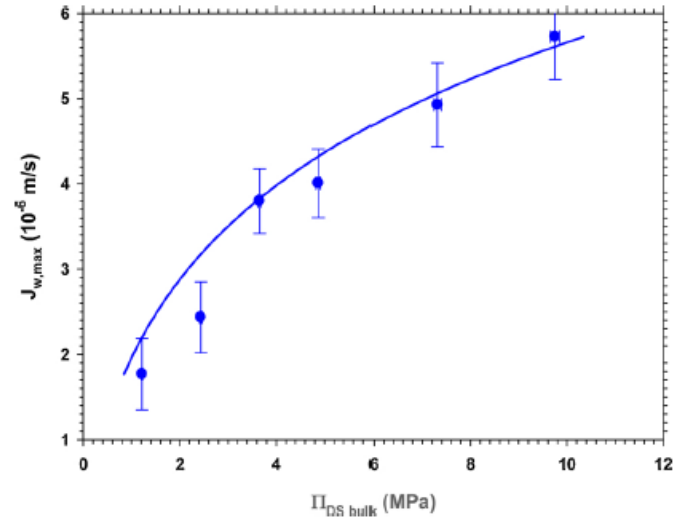
Figure 4.3: Water Flux as a Function of Osmotic Pressure (Salamanca et al., 2021)

From the studies mentioned, it is obvious that operating pressure has a positive effect on flux performance. In the pressure-driven NF and RO membranes, both permeate flux and pesticides rejection increased together with the operating pressure. The flux performance coincides the solution-diffusion model trend whereas the increased rejection is explained to be caused by permeates dilution by water flux in the membrane. In osmotically-driven membrane like FO, high pressure may lead to deformation of membranes and weaken the membrane performance.

Table 4.1: Some Recent Studies on the Effect of Operating Pressure on Retention and Flux Performances

Thin Film Composite Membranes	Main Findings	References
RO	• Rise in water flux around the membrane induced high chlorophenol rejection. • When pressure was doubled, a 14 % increment in rejection performance was observed. • The trend of water flux coincided with the solution-diffusion model where pressure was directly proportional to water flux.	(Sivanantham et al., 2021)
FO	• There was a 32.5 % increment in flux performance when pressure was doubled and this was related to draw solution concentration. • The non-linear pattern was probably due to reverse salt flux.	(Salamanca et al., 2021)
RO	• When pressure increased from 0 to 3500 kPa, permeate flux increased from 0 to 175 $L/m^2 \cdot h$.	(Ajao et al., 2017)
FO	• High pressure caused PRO membrane deformation and lowered membrane performance.	(Cheng and Chung, 2017)
FO	• There was a 16.13 % increment in flux performance when pressure was doubled.	(Wan and Chung, 2015)
FO	• "Shadow effect" occurred when membrane channels were blocked for water permeation at high pressure caused by membrane compression.	(Kim and Elimelech, 2013)

4.3   Effect of System Configuration on Permeate Flux and Pesticides Removal

In this section, system configurations in pressure-driven and osmotically-driven membranes were discussed. The system configurations discussed for pressure-driven membranes are dead-end and cross-flow configurations. For osmotically-driven membranes in FO process, membrane orientation is discussed since FO and PRO modes use the same filtration setup.

In the study by Imbrogno and Schäfer (2019), dead-end stirred cell configuration showed lower salt retention which the highest retention achieved was 77 % compared to macro and micro cross-flow configurations which the highest retention was 81 % and 83 % as presented in Figure 4.4. In a dead-end system, there was a constant decline in mass transfer from both cell wall to the centre of the stirred cell. The mass transfer at the middle is close to zero which was similar to no stirring. Therefore, larger concentration polarization was built-up here, reducing the separation efficiency. This finding was in line with another study by Tansel et al. (2006). In the study, the specific flux tested in dead-end filtration was higher (3.36 L/m^2·h·atm) than in cross-flow filtration (2.88 L/m^2·h·atm). This suggested that the higher resistance was formed against the water flux by the ions in the cross-flow filtration compared to in the dead-end filtration. Tansel et al. (2006) also related shear force of the system configuration to the flow conditions. It was claimed that base on the flow patterns, the size of hydrated radii of the ions determined whether their hydration water was retained in the hydration cell. Due to lower shear force in the cross-flow filtration, less ions were dehydrated in the process and larger amount of ions with large hydrated radius were rejected. This claim was in line with a more recent study by Tansel (2012).
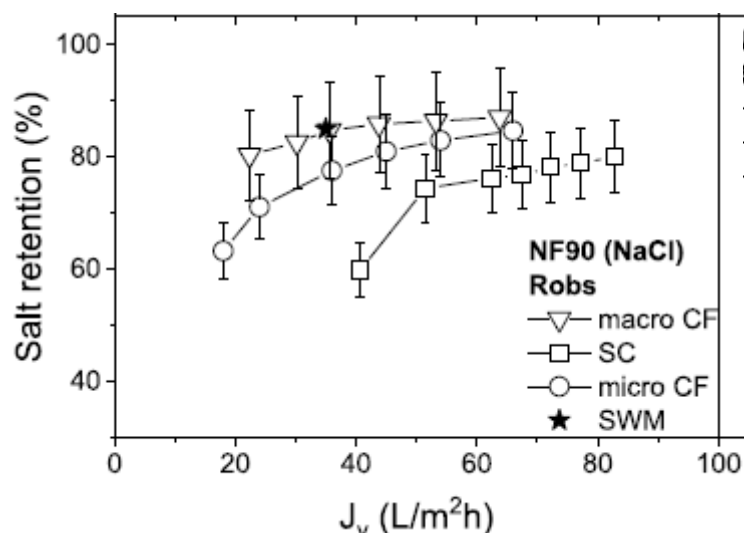
Figure 4.4: Salt Retention of Different Configurations as a Function of Flux
(Imbrogno and Schäfer, 2019)

For FO systems, the differences between FO and PRO modes were discussed. In the study by Zhao et al. (2016), membranes in PRO mode were more susceptible to fouling as compared to in FO mode. This was indicated through water flux measurement and scanning electron microscopic (SEM) images of mechanical layers of used membranes as depicted in Figure 4.5. It was obvious that the membrane in PRO mode underwent a much more severe scaling than in FO mode. It was then explained that the mechanical support layer faced the feed solution in PRO mode instead of the draw solution like in FO mode. Since permeates flowed from feed side to draw side in an FO process, the solutes were concentrated at the support layer facing the feed solution in PRO mode, leading to a more severe fouling issue. An illustration of cake formation in PRO mode was shown in Figure 4.6. Besides, Gao, Wang and Song (2019) also mentioned that water flux was more prominent in FO mode than in PRO mode. This was explained by the more severe ICP in PRO mode because salt did not readily diffused through support layer before active layer and osmotic pressure difference is reduced (Khoo et al., 2020; Alturki et al., 2013; Salehi et al., 2018). The studies mentioned were summarized into Table 4.2 which was shown below.

To conclude, higher membrane performance is obtained in cross-flow configuration than in dead-end configuration. The concentration polarization

effect in dead-end filtration is much more prominent. In cross-flow configuration, the high rejection is attributed to the low shear force while low flux is related to the high resistance of ions on water flux. For FO processes, FO mode is more desirable compared to PRO mode in the aspect of fouling intensity and low ICP.
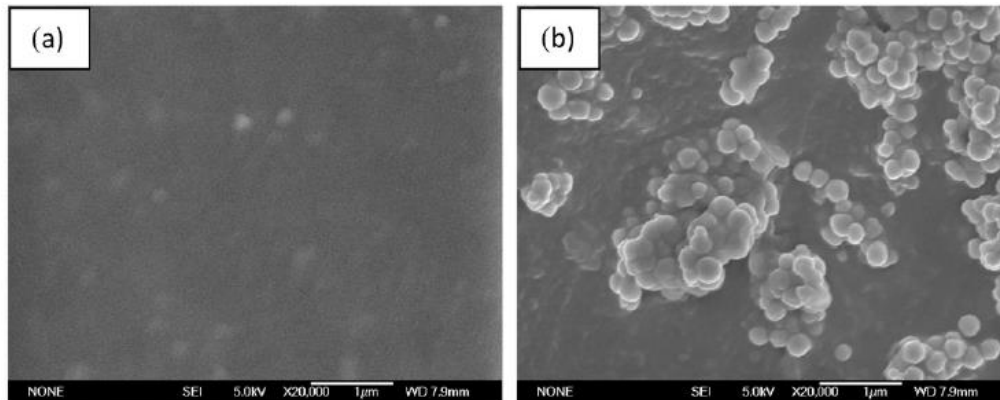
Figure 4.5: SEM Images of Mechanical Support Layer in (a) FO Mode and (b) PRO Mode (Zhao et al., 2016).
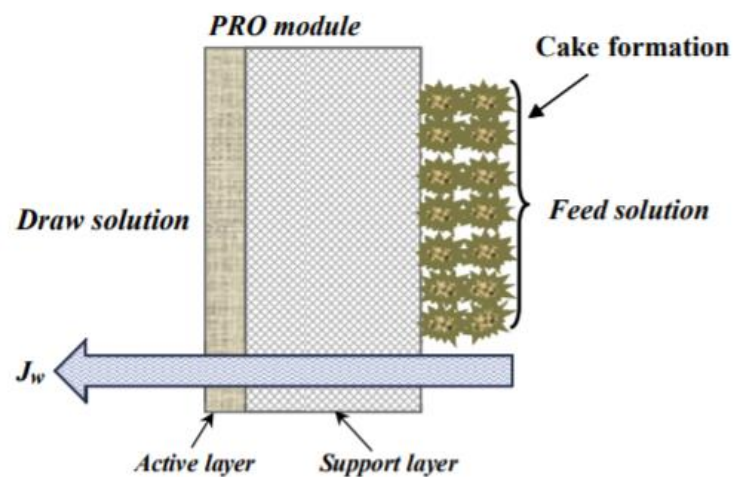
Figure 4.6: An Illustration of Fouling in PRO Module (Touati and Tadeo, 2017)

Table 4.2: Some Recent Studies on the Effect on Retention and Flux Performances at Different System Configuration

Thin Film Composite Membrane	Findings	References
FO	• ICP in PRO mode is more severe which caused osmotic pressure to decrease.	(Khoo et al., 2020)
NF	• Highest salt retention for dead-end stirred cell is 77 %. • Highest salt retention for cross-flow configuration is 83 %.	(Imbrogno and Schäfer, 2019)
FO	• Membranes in FO mode encountered higher water flux than in PRO mode.	(Gao, Wang and Song, 2019)
FO	• Water flux in FO mode is higher (22.1 $L/m^2 \cdot h$) than in PRO mode (16.3 $L/m^2 \cdot h$). • ICP is higher in PRO mode.	(Salehi et al., 2018)
FO	• Membranes in PRO mode was more susceptible to fouling than FO mode	(Zhao et al., 2016)
NF	• Specific flux in dead-end filtration (3.36 $L/m^2 \cdot h \cdot atm$) > cross-flow filtration (2.88 $L/m^2 \cdot h \cdot atm$). • Lower shear force in cross-flow configuration allowed better rejection of ions with large hydrated radii.	(Tansel et al., 2006)

4.4   Effect of Pesticide Characteristics on Permeate Flux and Pesticides Removal

4.4.1   Size of Pesticides Molecules/Pesticides Matrix

Molecule size was a dominant factor in determining the efficiency in pesticides removal for both NF and RO membranes. Theoretically, RO membranes had a smaller pore size (< 1 nm) than NF membranes (< 2 nm). Hence, RO membranes were more efficient in removing pesticides of small size than NF membranes. The size parameters used to determine molecular size were molecular weight, Stokes diameter (d_s), diameter derived from molecular volume, molecular width and molecular length (Karabelas and Plakas, 2011).

In many studies, micropollutants with larger molecular weight had better rejections compared to micropollutants with smaller molecular weight (Musbah et al., 2013; Heo et al., 2013; Alturki et al., 2013; Wang et al., 2015; Salamanca et al., 2021; Xu et al., 2020). In the study by Wang et al. (2015), micropollutants with molecular weight higher than 275 g/mol were able to achieve rejections more than 80 %. It was mentioned that the Stokes radii of the micropollutants increased linearly with their respective molecular weight. Smaller molecules had higher diffusivity through the membrane matrix, amplifying the mass transfer rate across the membrane (Xu et al., 2020). In another study by Musbah et al. (2013), diuron, having the smallest molecular length and width achieved the retention of roughly 74 % while 97 % of atrazine with the largest molecular length and width was retained by NF membrane. This further supported the fact that pesticide rejection increased as the molecular length and width increased.

Heo et al. (2013) carried out a study on flux behaviour and the removal efficiency of a few synthetic organic compounds which consisted of pharmaceutically active compounds and pesticides using FO and RO membranes. They mentioned that atrazine which had a smaller molecular weight showed a relatively lower retention in FO membrane. Similar trend could be seen using RO membrane in which organic compounds with larger molecular weight had a retention of more than 75 % while compounds with neutral charge and smaller molecular weight only achieved a retention of 47 % to 61 %. This claim was also agreed by Alturki et al. (2013) on another study using RO membranes and FO processes in PRO and FO modes. The results were also in

line with a more recent study on various micropollutants using FO mode by Salamanca et al. (2021). It was explained that micropollutants with smaller size was able to adsorb onto the porous surface of the membrane and penetrate the membrane easily. An example of the increment in rejection at larger pesticides size using NF270 membrane was illustrated in Figure 4.7 below. The studies on the effect of pesticides size on rejection and flux performance mentioned was summarized and tabulated in Table 4.3.
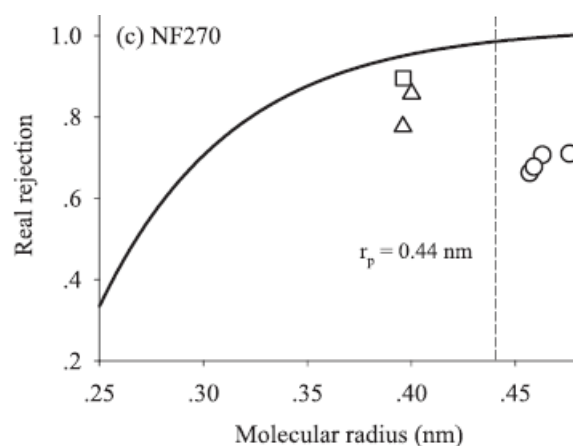
Figure 4.7: Rejection of Solutes as a Function of Molecular Radius (Liu et al., 2018)

Most of the journals used molecular weight as an indication for molecular size. As the micropollutants increased in their molecular size, the molecular weight increased. Micropollutants with larger size were able to be rejected by all types of membranes more efficiently at their uncharged state while smaller micropollutants could diffuse through the membrane matrix with ease.

4.4.2   Pesticides Ionic Charge

Other than molecular size of pesticides, ionic charge of pesticides also had an obvious effect in the retention and permeate flux. Pesticides could be neutral, positively or negatively charged depending on their nature. The negative charge of micropollutants was resulted from deprotonation of functional groups which were acidic within the molecular structures of the solutes (Albergamo et al., 2020). Other than size exclusion, rejection of charged solutes was also governed

by electrostatic interaction with the membrane surface. On the contrary, the rejection of neutral uncharged solutes depended only on size exclusion without the implication of electrostatic interaction (Alturki et al., 2013).

Pesticide polarity was interrelated with the molecular weight when it came to pesticides retention. More than one study showed that micropollutants which show low rejection shared common traits like low molecular weight and neutral charge (Wang et al., 2015; Xu et al., 2020; Nikbakht Fini et al., 2020; Salamanca et al., 2021). Referring to the study by Salamanca et al. (2021), micropollutants with positive charge had an unexpectedly high rejection (up to 99.99 %) for its molecular weight. This might be due to the ease of positively charged molecules to be deposited on the active layer surface of the membrane which was of opposite charge, causing low permeate flux. Liu et al. (2018) further explained that the high adsorption of molecules onto the NF and RO membranes was due to the high electrostatic attraction between the molecules and membranes while low adsorption rate was seen in the case of negatively charged molecules because of high electrostatic repulsion. It was stated that the presence of electrostatic attraction decreased the overall rejection of membranes (Liu et al., 2018; Xu et al., 2020). As for negatively charged molecules, Albergamo et al. (2020) and Nikbakht Fini et al. (2020) agreed that the micropollutants could be repelled from thin film membranes of the same charge, leading to high rejection in RO membranes.

The difference in charges within the molecular structure of a solute could cause dipole moments to occur. When there was a distance between two opposite charges of equal magnitude, the difference in electronegativity formed dipole moment. Hence, as the electronegativity of the molecular increased, the dipole moment increased. Like positively charged molecules, micropollutants with larger dipole moment could adsorb onto the charged membrane surface, making it possible for them to diffuse through the membrane. Hence, there was a lower retention of large dipole moment solutes (Rakhshan and Pakizeh, 2015; Tan et al., 2019). The studies mentioned was summarized and tabulated in Table 4.3.

According to the several studies on various micropollutants as mentioned above, it can be concluded that pesticides which are negatively

charged and with smaller dipole moment have better retention despite the discrepancy with the study by Salamanca et al. (2021).

4.4.3 Hydrophobicity/hydrophilicity

Other than the molecular sieving factor, hydrophobicity or hydrophilicity was also one of the parameters affecting pesticides retention and permeate flux during membrane filtration (Torres et al., 2018; Flyborg et al., 2017). Hydrophobicity of a solute particle could be determined through measurement of contact angle by using sensile drop method and indicated by octanal-water partition coefficient, $log \; K_{ow}$ as discussed in Section 2.2 (Tan et al., 2019). For solute particles with $log \; K_{ow}$ more than two indicated that they were hydrophobic and vice versa (Karimi, Rahimpour and Kebria, 2016).

NF membranes were normally hydrophilic as a result of the polar amide and carboxyl functional groups being strongly hydrophilic (Karimi, Rahimpour and Kebria, 2016). Pesticides like endosulfan and atrazine were hydrophobic in nature, so they were able to adsorb and diffuse through the membrane surface by steric interaction. Hence, hydrophobic pesticides had lower removal efficiency (Palma et al., 2016). However, Tan et al. (2019) claimed otherwise despite both studies were carried out using NF90 membrane. It was mentioned that pesticides with higher hydrophobicity exhibited better removal according to the study in which atrazine with $log \; K_{ow}$ of 2.34 was rejected better at 99 % than dimethoate with $log \; K_{ow}$ of 0.70 which only 81 % was rejected. This finding was in line with the results reported by Karimi, Rahimpour and Shirzad Kebria (2016) and Nikbakht Fini et al. (2020a). Kang and Cao (2012) further explained that it was easy for a pure water layer to form on the highly hydrophilic surface of the membrane. This avoided the hydrophobic pesticides from being adsorbed or deposited on the membrane surface hence the high rejection. Figure 4.8 gave a brief illustration of this claim. Licona et al. (2018) added that hydrophilic compounds favored adsorption onto the membrane surface or diffusion through the membranes, hence the low rejection.
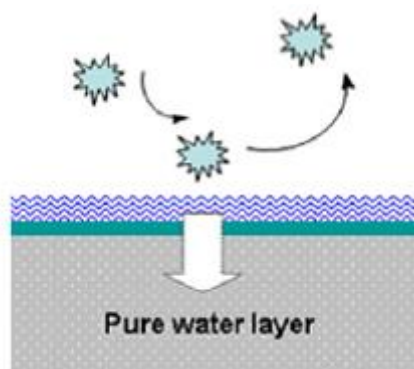
Figure 4.8: An Illustration of a Pure Water Layer Forming on a Membrane Surface (Kang and Cao, 2012)

It was worthy to mention that the rejection performance of a membrane could be eventually weakened when the adsorption capacity was impoverished (Wang et al., 2015). This was agreed by Flyborg et al. (2017) that lower rejection could be seen once the steady-state conditions respecting adsorption were reached. At this state, size exclusion played the dominant factor instead. In the study by Flyborg et al. (2017), newly purchased membranes showed higher rejection for hydrophobic compounds while negative effects were achieved for old membranes of the same brand. Other than the studies on NF membranes, the study by Nikbakht Fini et al. (2020a) on FO membranes also gave similar results. The rejection of hydrophobic pesticides reduced after the membrane was heavily saturated with pesticides which were severely adsorbed onto the surface. The pesticides molecules diffused from the feed solution side to the draw solution side through the membrane, reducing the retention. The studies on the effect of pesticides hydrophobicity on rejection and flux performance mentioned was summarized in Table 4.3.

From the various findings mentioned above, it can be concluded that pesticides hydrophobicity has a positive effect on pesticides retention for membranes with hydrophilic surfaces. However, once the adsorption sites of the membranes are fully saturated with molecules and the maximum capacity of adsorption are reached, membrane performance becomes lower. This can be affiliated with membrane fouling.

Table 4.3: Some Recent Studies on the Effect of Pesticides Characteristics on Retention and Flux Performances

Thin Film Composite Membrane	Findings	References
Size of Pesticides Molecules/Pesticides Matrix		
FO	• Compounds with low molecular weight can pass through membrane easily, hence lower rejection.	(Salamanca et al., 2021)
NF	• Mass transfer rate of small molecules is higher due to higher diffusivity through the membrane matrix.	(Xu et al., 2020)
NF	• Micropollutants with molecular weight higher than 275 g/mol were able to achieve rejections more than 80 %.	(Wang et al., 2015)
NF	• Diuron which was of smaller size achieved the retention of roughly 74 % while 97 % of atrazine which was of larger size was retained by NF membrane.	(Musbah et al., 2013)
FO	• Organic compounds with larger molecular weight had a retention of more than 75 %. • Neutrally-charged compounds with smaller molecular weight only achieved a retention of 47 - 61 %.	(Heo et al., 2013)
FO and RO	• Atrazine with molecular weight of 215.68 g/mol achieved a rejection of 40 %. • A PhAC with molecular weight of 454.6 g/mol achieved a rejection of 90 %.	(Alturki et al., 2013)

Pesticides Ionic Charge		
FO	• Positively-charged micropollutants had an unexpectedly high rejection (up to 99.99 %) due to the ease of deposition on membrane surface.	(Salamanca et al., 2021)
RO	• When both pesticides and membranes are negatively-charged, pesticides could be repelled which led to high rejection.	(Albergamo et al., 2020)
NF	• Electrostatic attraction decreased membrane rejection.	(Xu et al., 2020)
NF	• Low rejection could be seen in solutes with large dipole moments.	(Tan et al., 2019)
NF and RO	• Electrostatic attraction between positively-charged molecules and negatively-charged membranes increased adsorption of molecules. • Electrostatic repulsion between negatively-charged molecules and membranes decreased adsorption rate.	(Liu et al., 2018)
FO and RO	• Retention of neutral solutes depended only on size exclusion instead of electrostatic interaction.	(Alturki et al., 2013)
Hydrophobicity/Hydrophilicity		
FO	• When membrane was heavily saturated with pesticides, the rejection performance was reduced due to higher diffusion across the membrane.	(Nikbakht Fini et al., 2020a)

NF	• Atrazine with *log K_{ow}* of 2.34 was rejected better at 99 % than dimethoate with *log K_{ow}* of 0.70 with rejection of 81 %.	(Tan et al., 2019)
NF and RO	• Hydrophilic compounds could adsorb onto membrane surface with more ease, therefore the rejection was lower.	(Licona et al., 2018)
NF	• Lower rejection was observed once the adsorption steady-state was reached in which size exclusion played the dominant factor. • Newly purchased membranes showed higher rejection for hydrophobic compounds than used membranes.	(Flyborg et al., 2017)
NF and RO	• Hydrophobic pesticides were able to adsorb and diffuse through the membrane surface by steric interaction, hence lower retention.	(Palma et al., 2016)
NF	• After the adsorption capacity of membrane was reached, the rejection performance of a membrane could be eventually weakened.	(Wang et al., 2015)
RO	• A pure water layer formed on the highly hydrophilic membrane surface avoided the adsorption or deposition of hydrophobic pesticides on the membrane surface, hence the high rejection.	(Kang and Cao, 2012)

4.5   Effect of Membrane Characteristics on Permeate Flux and Pesticides Removal

4.5.1   Fouling

Membrane fouling is a common challenge in membrane filtration which were faced by almost all researchers in this field. It is one of the major drawbacks of membrane filtration which is yet to be solved. The undesirable deposition of colloid particles on surface of membrane or within the membrane pores gives rise to fouling issues (Dolar, Košutić and Strmecky, 2016). This induces pore blockage which degrades the membrane and reduces efficiency. Membrane fouling occurs after the membrane is used for a period of time. The severity of membrane fouling could be associated with the reduced permeate flux due to pore blockage.

Membrane fouling could be due to various reasons like particles in feed solutions. Membrane fouling was more severe in water sources with high ion concentration like wastewater compared to deionized water due to the more complex medium (Palma et al., 2016). With increased concentration of divalent ions in the feed solution, zeta potential became less negative. For instance, when divalent ions increased from 0 to 80 ppm, the negativity of zeta potential of feed solution decreased from -30 mV to -18 mV. This caused the negativity of the membrane to decrease owing to the cation adsorption onto the membrane surface and charge shielding. With lesser charge interaction between the cations and membrane, therefore membrane fouling was elevated and reduced the efficiency of membrane filtration, resulting in lower permeate flux (Mehta, Saha and Bhattacharya, 2017).

The occurrence of membrane fouling could be seen from flux decline overtime as depicted in Figure 4.9. In Figure 4.9, compared to NF90 and XLE membranes (average 50 $L/m^2 \cdot h$), NF270 displayed higher flux (average 100 $L/m^2 \cdot h$) due to looser membrane structure (Dolar, Košutić and Strmecky, 2016; Racar et al., 2017). This finding was in line with another similar study by Zhu (2015). Fouling had a positive effect on the rejection of organic micropollutant. Micropollutant rejection was 87.9 % for a clean NF90, 32.1 % for a clean NF270 and increased to 95 % for a fouled NF90, 65.8 % for a fouled NF270. The

increment of rejection in fouled membranes were attributed to enhanced sieving effect and pore blocking.
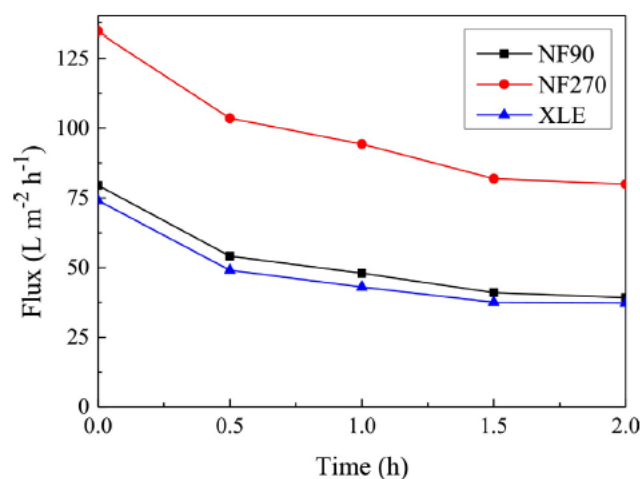
Figure 4.9: Permeate Flux as a Function of Time (Racar et al., 2017)

The influence of fouling in FO processes was similar to pressure-driven membranes. A large difference in water flux between clean and fouled membranes was seen in the study by Zheng et al. (2019). Fouled membrane experienced a 70 % decline in the water flux whereas clean membrane only experienced 19 % decline throughout the experiment. This was caused by the diminishing osmotic pressure gradient due to reverse salt diffusion. Pore blocking effect was induced by the formation of cake layer. Fouling of membranes also contributed to higher electrostatic repulsion between solutes and membranes, increasing solute rejection (Arcanjo et al., 2020). To summarize the studies mentioned in this section, Table 4.4 is tabulated.

Fouling can be a major problem for membrane separation processes because additional costs need to be incurred for backwashing or physical cleaning to discard the cake layer formed on membrane surface. Fouling leads to reduction of membrane pore size, inducing charge shielding effect and reduces flux performance. Membrane performance and membrane life will also substantially be diminished due to fouling. Hence, it is imperative that membrane fouling is mitigated to maintain membrane performance.

4.5.2   Membrane Materials

The removal efficiency and permeate flux of membrane varies according to membrane types such as NF, RO, FO or PRO membranes. The top layer of membrane or active layer allows permeate to pass through and perform the main separation process. The active layer could be made up of different material, hence the large variety of the same membrane type. For instance, NF 90 and NF 270 are both NF membranes but made up of different active layer material, thus the membrane performance varies as well. To this date, there were still no researches on the effect of membrane materials within thin film composite FO membranes on pesticides rejection and permeate flux. Most of the researches only focused on the effects of different types of membrane like cellulose acetate or biomimetic FO membranes. Therefore, FO membranes are not discussed in this section.

The active layer of NF90 membrane was made up of fully-aromatic polyamides while NF270 membrane possessed a semiaromatic piperazine-based polyamides active layer. Therefore, NF90 was relatively tight with the small pore diameter (0.68 nm) while NF270 was a loose NF membrane with larger pore diameter (0.84 nm). This allowed a higher salt rejection of 98.7 % using NF90 membrane while the rejection of NF270 membrane was 97.8 %. NF90 was also less permeable to solute particles (57.2 L/m^2·h) as compared to NF270 (85.5 L/m^2·h). NF90 exhibited 30 % decline of normalized permeate flux while NF270 only exhibited 20 % decline as shown in Figure 4.10. Besides, NF90 was more hydrophobic and more susceptible to fouling issues because the membrane surface is rougher as compared to NF270 (Zhu, 2015). On that account, membrane with rougher surface was more prone to fouling because particles were able to deposit on the rough surface with more ease. This finding was in line with another study by Licona et al. (2018) and Riungu et al. (2012). In the study by Riungu et al. (2012), the permeability of NF270 was 11.58 L/m^2·h while the permeability of NF90 was 5.89 L/m^2·h. With the lower solute permeability, the rejection of NF90 membrane was higher because the the membrane pore size of NF90 is lower (0.55 nm) compared to NF270 (0.71 nm) in the study.
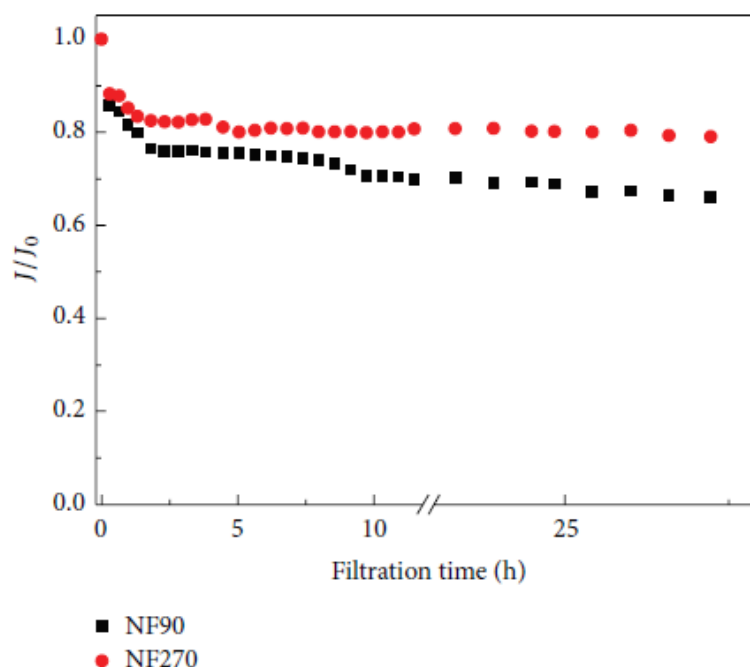
Figure 4.10: Normalized Permeate Flux of NF90 and NF270 Membrane (Zhu, 2015)

It was mentioned in the study by Fini, Madsen and Muff (2019) that pesticides adsorption were stronger in RO membranes as compared than NF membranes. This might be correlated to the higher hydrophobicity of RO membranes and the pesticides were adsorbed through electrostatic attraction. Among XLE and BW30 membranes, higher pesticides adsorption were noticed in BW30 membrane. For instance, 10.2 % of MCPP pesticides were adsorbed in BW30 while only 6.4 % of MCPP were adsorbed in XLE membrane. This may be attributed to the smaller pure water permeability hence slightly higher hydrophobicity of BW30 membrane. Pesticides rejection using BW30 membrane (red) and XLE membrane (black) was depicted in Figure 4.11. The effect of hydrophobicity on the rejection effiency and permeate flux was in line with the study by Khairkar et al. (2020). Madsen and Søgaard (2014) also claimed that XLE membrane displayed a larger flux than BW30 membrane, classifying XLE membrane as a low pressure reverse osmosis (LPRO) membrane. In the study, ions rejection using BW30 was slightly higher than XLE membrane too. A brief summary was provided in Table 4.4 regarding the studies mentioned.

Figure 4.11: Pesticides Rejection using Different Membranes (Fini, Madsen and Muff, 2019)

Even though the difference in flux performance and pesticides retention were not distinct, membrane materials still have a certain effect on membrane performance. This was correlated to the average pore size and hydrophobicity of the membrane. For active layers with smaller pore size and lower hydrophobicity, lower permeability thus higher pesticides retention can be achieved. Membranes with rougher surface are also proved to be more susceptible to fouling.

Table 4.4: Some Recent Studies on the Effect of Membrane Characteristics on Retention and Flux Performances

Thin Film Composite Membrane	Findings	References
Fouling		
FO	• High electrostatic repulsion was observed between solutes and fouled membranes, leading to high solute rejection.	(Arcanjo et al., 2020)
FO	• Fouled membrane experienced higher decline (70 %) in water flux. • Clean membrane only experienced 19 % decline in water flux.	(Zheng et al., 2019)
RO	• When divalent ions increased from 0 to 80 ppm, the negativity of zeta potential of feed solution decreased from -30 mV to -18 mV. • Reduced charge interaction between the cations and membrane elevated fouling issue and resulted in low permeate flux.	(Mehta, Saha and Bhattacharya, 2017)
NF and RO	• Membrane fouling was more prominent in wastewater compared to deionized water due to the more complex medium with higher ionic content.	(Palma et al., 2016)
NF	• Micropollutant rejection was 87.9 % for a clean NF90, 32.1 % for a clean NF270. • With similar condition but using fouled membranes, rejection increased to 95 % for a fouled NF90 and 65.8 % for a fouled NF270.	(Zhu, 2015)

Membrane Materials		
NF and RO	• Pesticides adsorption were stronger in RO membranes as compared than NF membranes. • Among XLE and BW30 membranes, 10.2 % of MCPP pesticides were adsorbed in BW30 membrane while only 6.4 % of MCPP were adsorbed in XLE membrane. • Membrane materials and their hydrophobicity may affect adsorption of pesticides.	(Fini, Madsen and Muff, 2019)
NF	• Higher salt rejection of 98.7 % was observed when a tight NF90 membrane was used while the rejection of a loose NF270 membrane was 97.8 %. • Solute permeability in NF90 was lesser (57.2 $L/m^2 \cdot h$) as compared to NF270 (85.5 $L/m^2 \cdot h$). • NF90 exhibited 30 % decline of normalized permeate flux while NF270 only exhibited 20 % decline.	(Zhu, 2015)
NF and RO	• XLE membrane was classified as a low pressure reverse osmosis (LPRO) membrane. • BW30 membrane displayed higher rejection than XLE membrane.	(Madsen and Søgaard, 2014)
NF	• The permeability of NF270 was 11.58 $L/m^2 \cdot h$ (lower rejection) while the permeability of NF90 was 5.89 $L/m^2 \cdot h$ (higher rejection).	(Riungu et al., 2012)

4.6   Effect of Feed Solution on Permeate Flux and Pesticides Removal

4.6.1   Feed Solution Ionic Charge

Other than pesticides ionic charge, ions in feed solutions could also influence permeate flux and membrane performance. Despite there were a number of studies on the effect of feed solution ionic charge on NF and RO membranes, there were insufficient information on FO processes to be critically reviewed. Hence, only NF and RO membranes were reviewed in this section.

Fini, Madsen and Muff (2019) mentioned that there was a slight increment in the rejection of pesticides along with decreased permeate flux at an environment with higher ionic charge even though the difference was not significant. In addition, the effect of ions in the water samples was also tested in a study by Mehta et al. (2015). Deionized water, tap water and field water were tested with pesticides and it was found that the average pesticide rejection for deionized water was the lowest (94 %) and the average permeate flux was the highest (30 L/m^2·h) while field water had the highest average rejection of 99 % and lowest average permeate flux of 23 L/m^2·h due to the high ion concentration in field water. Figure 4.12 gave a clearer view of the flux and diuron rejection difference between the different water samples used. This result was consistent with the study by Palma et al. (2016). For NF270 membrane, the permeability of wastewater (9.28 L/m^2·h·bar) was also the lowest as compared to drinking water (13.4 L/m^2·h·bar) and irrigation water (13.3 L/m^2·h·bar).

Similar trend was observed in another study by Tan et al. (2019) in which river water with the most ions displayed the highest pesticide retention and lowest permeate flux as shown in Figure 4.13. This might be due to the presence of other ionic compounds in the water blocking the membrane pores, restricting the exchange pathway of water and pesticide molecules (Fini, Madsen and Muff, 2019). This claim was supported by another study by Madsen and Søgaard (2014) through the analysis of zeta potential for different membranes in different pesticide concentrations. It was mentioned that zeta potential increased with the ionic concentration of the feed solution and this increment was due to the ions adsorbing onto the membrane surface, resulting in pore blocking and increased rejection of pesticides. Table 4.5 was provided as a summary table for the studies mentioned.

Ions in feed solution play a certain role in pesticides rejection and permeate flux through the membrane pores. Feed solution ionic charge are normally tested based on the type of water sources used in the experiments. It can be concluded that the presence of ions in feed solution could cause adsorption of ions on the membrane surface, blocking the solutes from passing through the membrane. Hence, lower permeate flux and higher rejection is achieved at an environment with high ionic strength.
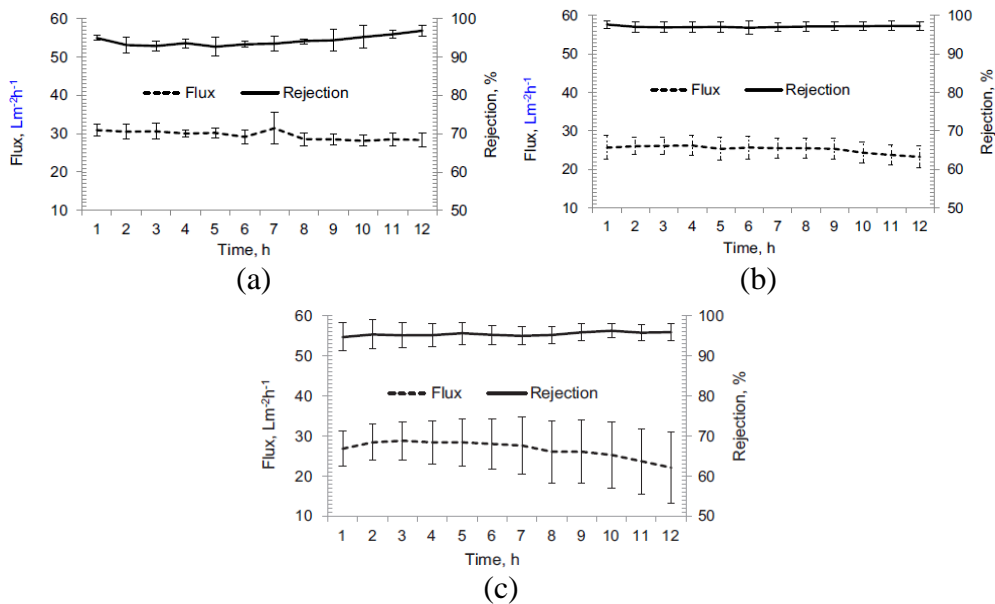
Figure 4.12: Diuron Flux and Rejection in (a) Deionized water, (b) Tap water and (c) Field water (Mehta et al., 2015).
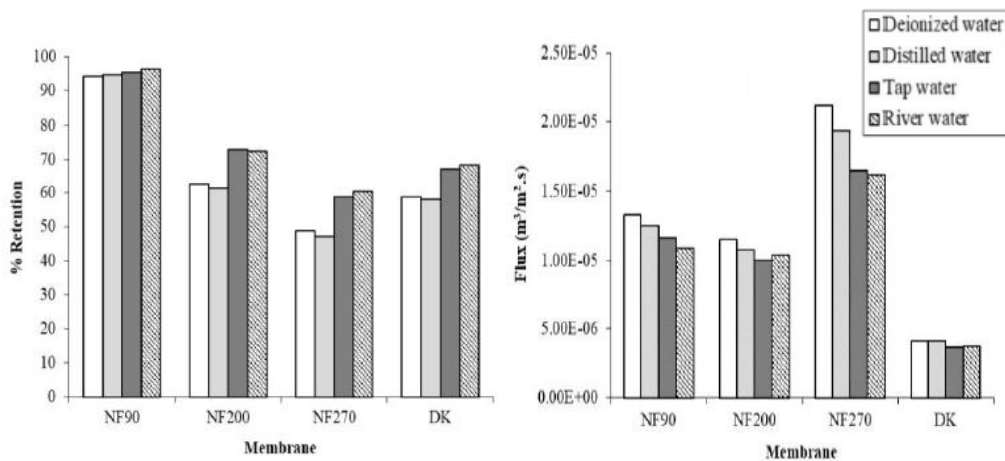
Figure 4.13: Effect of Different Water Matrixes on Atrazine Rejection and Flux Performance (Tan et al., 2019).

4.6.2 Pesticides Feed Concentration

Feed solution concentration determines how saturated the feed solution is with pesticides. The higher the feed concentration, the higher the amount of pesticides in the feed solution. It not only affects the permeate and water fluxes across the membranes, the rejection efficiency of pesticides can be affected as well.

According to Figure 4.14 by Hasmadi et al. (2017) using an RO membrane, feed concentration of 3.0 kg/m^3 achieved the highest solute permeate concentration (0.60 kg/m^3) after two hours, indicating the least rejection. The high concentration at feed side escalated the driving force for mass transfer, causing more diffusion of solutes through the membrane to permeate side. In another study by Fini, Madsen and Muff (2019), RO XLE membrane did not show any significant effect on different pesticides feed concentration. On the contrary, NF270 showed a dramatic decline in rejection efficiency from 92.6 % to a minimum of 37.3 % for pesticide MCPA when the feed concentration inclined from 1 µg/l to 10 mg/l as shown in Figure 4.15. This was further elaborated that the membrane surface charge was shielded by the increased deposition of pesticide molecules. Electrostatic repulsion between the charged compounds and the membrane was hindered, causing low rejections. This might imply that despite the low effect of concentration on pesticides retention, concentration gradient was still an important parameter for pesticides to transport through the membrane (Ahmad, Tan and Shukor, 2008).
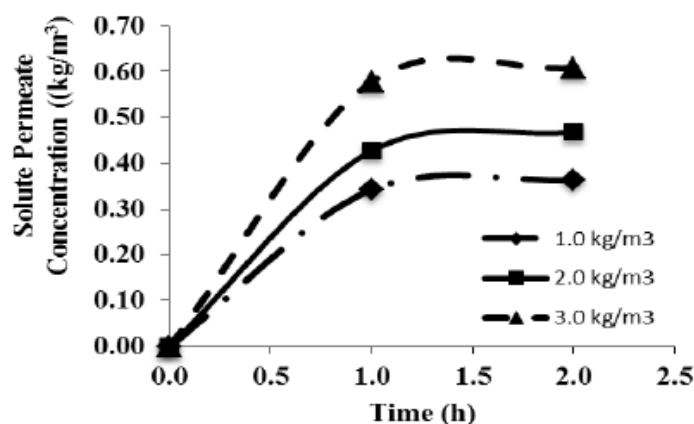
Figure 4.14: Solute Permeate Concentration at Different Feed Concentration (Hasmadi et al., 2017)
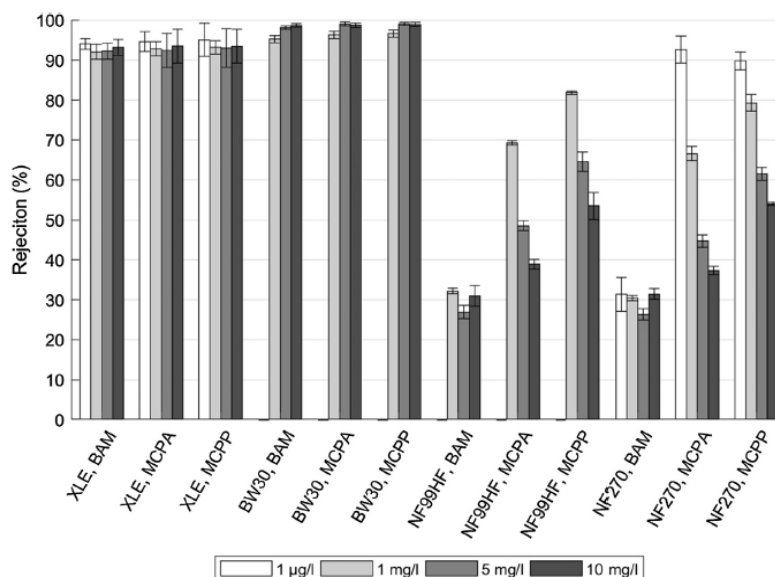
Figure 4.15: Rejection of Pesticides at Different Feed Concentrations (Fini, Madsen and Muff, 2019).

For FO membranes, Nguyen et al. (2018) mentioned that high feed concentration would brought about low water flux. In the study, there was a slight decline of water flux from 8.27 L/m^2·h to 7.04 L/m^2·h when feed concentration rose from 0.1 to 0.5 M. Using a lab fabricated FO membrane, Cui et al. (2016) also claimed that the water flux and rejection of pesticides decreased when the feed concentration increased. For instance, the water flux of phenol dropped from 17.9 L/m^2·h to 15.2 L/m^2·h when phenol concentration in the feed solution inclined from 500 ppm to 2000 ppm. At the same time, there was a 4 % drop in phenol rejection by the lab fabricated FO membrane. The effects of water flux and rejection by feed solution concentration were illustrated in Figure 4.16 below. Cui et al. (2016) explained that this was caused by the decline of the difference in osmotic pressure between the feed and draw solutions. This findings coincided with the study by Nikbakht Fini et al. (2020a) where the rejection value of pesticide MCPP dropped from 97.1 % to 95.8 % when the feed concentration rose from roughly 940 µg/l to 1050 µg/l as shown in Figure 4.17. In order to summarize the studies on the effect of pesticides feed concentration on permeate flux and pesticides removal, Table 4.5 is tabulated.
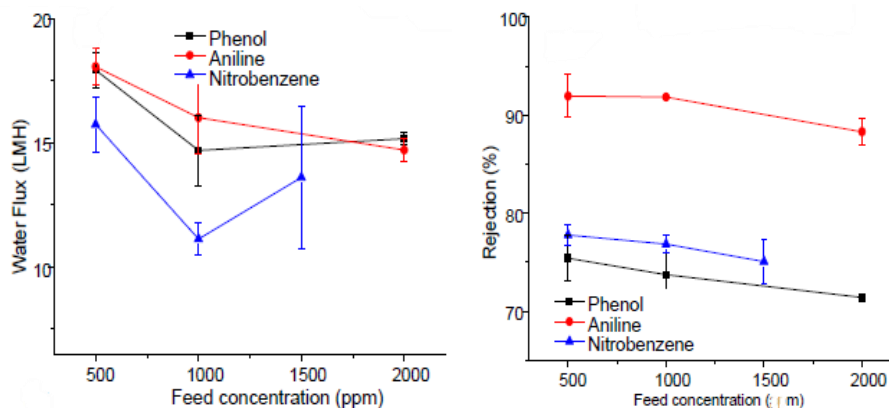
Figure 4.16: Effect of Feed Solution Concentration on Water Flux and Solute
Rejection (Cui et al., 2016)
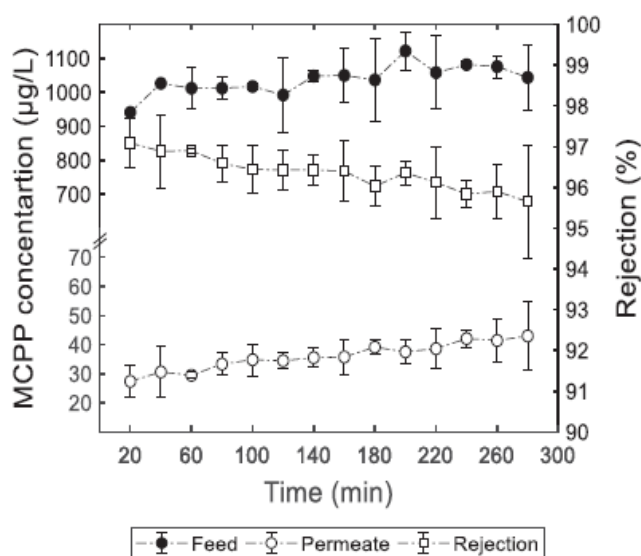
Figure 4.17: Rejection of Pesticide MCPP as a Function of Feed and Permeate
Concentration (Nikbakht Fini et al., 2020a)

From the various studied mentioned above, as the feed concentration
drops, the rejection of pesticides decreased as well due to different reasons. For
NF and RO membranes, the decline of rejection is due to charge shielding of
membranes caused by the desposition of pesticide on membrane surface. On the
contrary, the lower rejection at higher feed concentration could be caused by the
reduced osmotic pressure difference in feed and draw solutions. Since
membranes FO and PRO modes depend on osmotic pressure to function, this
reduced pressure difference could weaken the membrane performance.

4.6.3   Feed Solution pH

pH of the feed solution was interrelated to ionic charge of the membrane due to the dissociation of functional group (Karabelas and Plakas, 2011). pH and ionic charge were related with isoelectric point. Each membrane had its own isoelectric point which was the pH when the membrane active layer was at neutral charge. When the pH was higher than the isoelectric point, then the membrane was negatively charged. On the other hand, the membrane was positively charged when the pH was below the isoelectric point (Zhang et al., 2017). For instance, the isoelectric point of the membrane is at pH 3.8 for NF90 membrane and pH 3 for BW30 membrane shown in Figure 4.18.
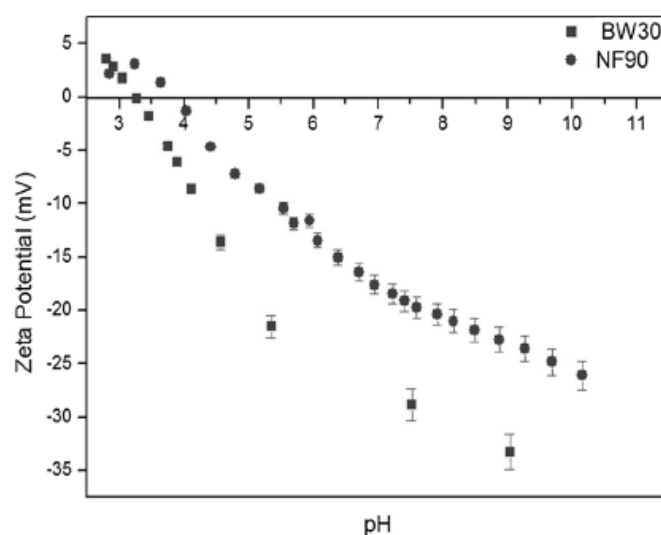
Figure 4.18: Zeta Potential Profile of BW30 and NF90 membranes as a
Function of pH (Licona et al., 2018)

pH of the feed solution also had effect on the hydrophobicity of pesticides. Licona et al. (2018) claimed that micropollutants became less hydrophobic at high pH, allowing them to be more soluble. Other than hydrophobicity, it was found that pH also affected the ionic charge of solutes. For instance, ibuprofen (PhAC) was neutral and anionic at pH 5 and retention was only based on steric exclusion and hydrophobic interaction between solute and membrane surface. When the pH was increased to 7, electrostatic repulsion took place, increasing the rejection efficiency. In another study by Liu et al. (2018), the amount of solutes adsorbed onto the membrane varied according to

pH. At pH 7.4 which was above the isoelectric point of NF90 membrane with zeta potential being highly negative, sulfamethoxazole (PhAC) was negatively charged. Therefore, more solutes were adsorbed and diffused through the membrane at isoelectric point of pH 3.8. 1.647 ng/cm^3 of sulfamethoxazole (PhAC) were adsorbed onto NF90 membrane at pH 3.8 while 0 solutes were adsorbed at pH 7.4. This was because there was a lack of electrostatic repulsion at the isoelectric point, causing inefficient rejection of solutes. On the contrary, there was a substantial increase in rejection at pH 7.4 because electrostatic repulsion took place. As opposed to negatively charged solutes, positively charged solutes displayed lower adsorption, hence higher rejection at isoelectric point for the reason that electrostatic attraction between the solutes and membrane was absent. Riungu et al. (2012) suggested pH 7 as the most optimum since the rejection of pesticides at pH 7 was the highest in the study.

The effect of pH on FO membranes were similar to NF and RO membranes. At a highly alkaline condition of pH 10 and above, the zeta potential was highly negative, causing both solutes and membrane to be negatively charged. On that account, the rejection of solutes depended on the effect of steric hindrance and electrostatic repulsion of the two negatively charged surface, leading to lower permeate flux. For instance, the solute permeation flux was around 880 mg/m^2·h at pH 7 and around 200 mg/m^2·h at pH 11 as shown in Figure 4.19. Unlike permeate flux, there was no effect of pH on reverse salt flux in FO membranes (Zhang et al., 2017). This claim was supported by Nikbakht Fini et al. (2020a). Dolar, Košutić and Strmecky (2016) further explained that there might be a possibility that the increment of pH could increase the potential of membrane scaling due to precipitation of calcium carbonate, CaCO$_3$ hence the low permeate flux. Table 4.5 was provided as a summary for the studies mentioned.

Therefore, it is concluded that pH has direct correlation to the zeta potential of a membrane and alters not only membrane charge but also solute charge and hydrophobicity. The effect of pH on the rejection efficiency of pesticides varies according to pesticides and membrane types. When both pesticides and membranes are negatively charged, electrostatic repulsion takes place and increases the rejection. When they are oppositely charged,

electrostatic attraction occurs instead which reduces the rejection efficiency. The optimum pH for pesticides removal based on the studies mentioned above is pH 7.
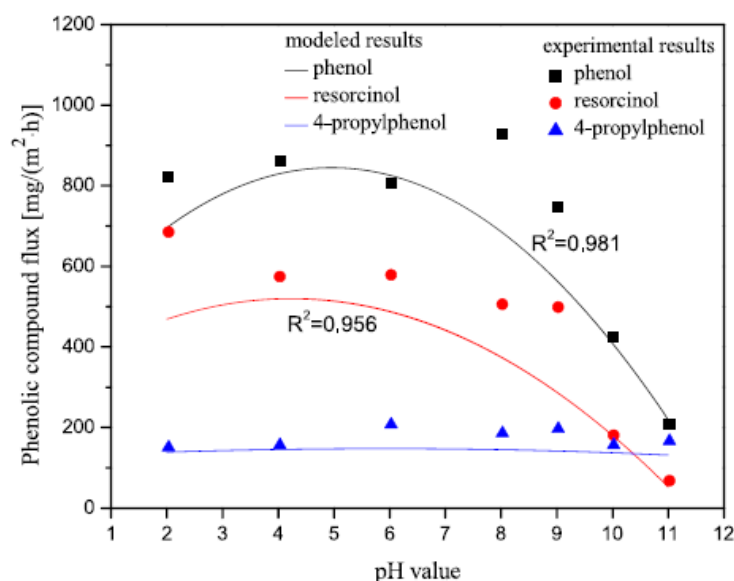
Figure 4.19: Phenolic Compound Flux as a Function of pH Value (Zhang et al., 2017)

4.6.4   Presence of Trace Organic Matters

In some studies, trace organic matters were added to improve pesticides rejection or to mimic properties of certain water sources. These trace organic matters could affect the membrane performance by either improving or weaken the performance. Natural organic matters (NOM) exist in many natural water sources. One of the most studied NOM is humic acid which is a dark brown organic matter which coagulates when acidified (Bleam, 2017).

As an NOM, humic acid is a membrane foulant. The fouling extent of natural organic matters depend on various properties like solution chemistry or molecular weight. It was reported that the hydrophobic fraction of an NOM was the main issue causing fouling and flux decline (Mehta, Saha and Bhattacharya, 2017). Humic acid was found to increase the tendency of membrane fouling. After addition of humic acid, a rapid flux decline could be seen in the membranes, indicating the presence of fouling. In another study by Riungu et al. (2012), when humic acids were added to feed solution containing atrazine, there was an obvious reduction of permeate flux from 77 $L/m^2 \cdot h$ to 41 $L/m^2 \cdot h$.

It was then explained that humic acid was hydrophobic by nature so it was able to adsorb onto the surface of membranes and led to reduction of pore sizes, hence decreasing membrane permeability. Humic acids also tend to leave a dark brown foulant layer on the membrane surface after the experiments which caused a significant difference in the membrane hydrophobicity and rejection (Zhu, 2015).

It was reported that humic acid had less influence on pesticide rejection in deionized water due to the absence of ions, hence fouling was less than 6 % (Mehta et al., 2015). When the feed solution was switched to field water in a more recent study, there was a substantial increment in membrane fouling (14 %) (Mehta, Saha and Bhattacharya, 2017). The fouling was further aggravated to 23 % and 30 % when magnesium and calcium were added as shown in Figure 4.20. It was explained that humic acid reduced the negativity of zeta potential causing the membrane to be less negatively charged. This induced charge shielding and ion adsorption onto the membrane surface, enhancing fouling and reducing membrane performance.
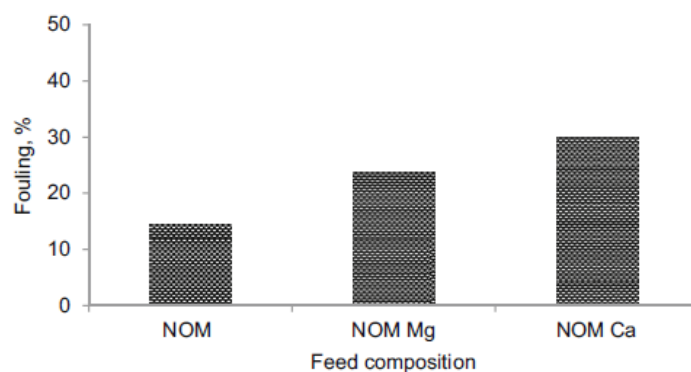
Figure 4.20: Effect of Divalent Ions Presence on Membrane Fouling (Mehta, Saha and Bhattacharya, 2017)

Hao et al. (2011) suggested the addition of ethylendiaminetetraacetic acid (EDTA) in the presence of metal ions to mitigate fouling since EDTA is a metal ion chelating agent. EDTA was able to form complex with calcium ions to reduce the interaction between the free calcium ions and humic acid. EDTA could also decompose the Ca^{2+}-humic acid complex to reduce fouling. However, the addition of EDTA was unable to fully restore the permeability of the

membrane hence backwashing was suggested for fouled membrane recovery instead. A summary of the journals discussed was tabulated in Table 4.5.

From the studies, it can be concluded that the membrane fouling issues are greatly affected by the existence of NOMs. The severity of membrane fouling is further aggrevated when ions are present in the water. In order to mitigate fouling caused by NOMs, EDTA can be added but its result is controversial. Hence, backwashing or physical cleaning is much more preferred in diminishing fouling in membranes.

Table 4.5: Some Recent Studies on the Effect of Feed Solutions on Retention and Flux Performances

Thin Film Composite Membrane	Findings	References
Feed Solution Ionic Charge		
NF and RO	• The rejection of pesticides was slightly higher with reduced permeate flux at high ionic charge environment.	(Fini, Madsen and Muff, 2019)
NF	• River water displayed the highest pesticide retention (roughly 92 %) and lowest permeate flux (roughly 1.1×10^{-5} $m^3/m^2{\cdot}s$).	(Tan et al., 2019)
NF and RO	• In NF270 membrane, the permeability of wastewater (9.28 $L/m^2{\cdot}h{\cdot}bar$) was the lowest as compared to drinking water (13.4 $L/m^2{\cdot}h{\cdot}bar$) and irrigation water (13.3 $L/m^2{\cdot}h{\cdot}bar$).	(Palma et al., 2016)
RO	• For deionized water, the average pesticide rejection was the lowest (94 %) and the average permeate flux was the highest (30 $L/m^2{\cdot}h$). • For field water, the average rejection of 99 % was the highest and the average permeate flux of 23 $L/m^2{\cdot}h$ was the lowest.	(Mehta et al., 2015)
NF and RO	• Zeta potential increased with the ionic concentration of feed solution due to adsorption of ions onto the membrane surface and increased pesticides rejection.	(Madsen and Søgaard, 2014)

	Pesticides Feed Concentration	
FO	• When feed concentration rose from roughly 940 µg/l to 1050 µg/l , pesticide MCPP rejection dropped from 97.1 % to 95.8 %.	(Nikbakht Fini et al., 2020a)
NF and RO	• NF270 showed a dramatic decline in rejection efficiency from 92.6 % to 37.3 % for pesticide MCPA when the feed concentration inclined from 1 µg/l to 10 mg/l. • When more pesticide molecules were deposited on the membrane, membrane surface charge was shielded and hindered electrostatic repulsion, causing low rejection.	(Fini, Madsen and Muff, 2019)
FO	• Water flux declined slightly from 8.27 L/m²·h to 7.04 L/m²·h when feed concentration rose from 0.1 to 0.5 M.	(Nguyen et al., 2018)
RO	• Feed concentration of 3.0 kg/m³ achieved the highest solute permeate concentration (0.60 kg/m³), indicating the least rejection. • Feed concentration of 1.0 kg/m³ achieved the lowest solute permeate concentration (0.35 kg/m³), indicating the highest rejection.	(Hasmadi et al., 2017)
FO	• The water flux of phenol dropped from 17.9 L/m²·h to 15.2 L/m²·h when phenol concentration in the feed solution inclined from 500 ppm to 2000 ppm.	(Cui et al., 2016)

Feed Solution pH		
NF and RO	• Pesticides hydrophobicity reduced at high pH, allowing them to be more soluble. • At a pH where micropollutants were neutral, retention was only based on steric exclusion and hydrophobic interaction between solute and membrane surface.	(Licona et al., 2018)
NF and RO	• 1.647 ng/cm^3 of sulfamethoxazole (PhAC) were adsorbed onto NF90 membrane at pH 3.8 (isoelectric point) while 0 solutes were adsorbed at pH 7.4 (above isoelectric point). • There was no electrostatic repulsion at the isoelectric point while at pH 7.4 above the isoelectric point, electrostatic repulsion took place.	(Liu et al., 2018)
FO	• The solute permeation flux was around 880 mg/m^2·h at pH 7 and around 200 mg/m^2·h at pH 11 where both solutes and membrane were negatively charged.	(Zhang et al., 2017)
NF and RO	• The increment of pH could increase potential of membrane scaling due to precipitation of CaCO$_3$ hence the low permeate flux.	(Dolar, Košutić and Strmecky, 2016)
NF	• pH 7 was suggested to be the optimum pH for pesticides rejection.	(Riungu et al., 2012)

Presence of Trace Organic Matter		
RO	• In field water, the effect of humic acid was obvious where membrane fouling was 14 %.	(Mehta, Saha and Bhattacharya, 2017)
RO	• There was no ions in deionized water, so the effect of humic acid was not obvious and fouling was less than 6 %	(Mehta et al., 2015)
NF	• Humic acids caused a significant difference in membrane hydrophobicity and rejection.	(Zhu, 2015)
NF	• After the addition of humic acids into atrazine solution, there was an obvious reduction of permeate flux from 77 $L/m^2 \cdot h$ to 41 $L/m^2 \cdot h$.	(Riungu et al., 2012)
UF (Ultrafiltration)	• Ethylendiaminetetraacetic acid (EDTA) in the presence of metal ions was suggested for fouling mitigation.	(Hao et al., 2011)

4.7   Effect of Draw Solution on Permeate Flux and Pesticides Removal

4.7.1   Draw Solution Types

FO processes in both FO and PRO modes were driven by osmotic pressure difference. One of the main aspects in FO and PRO pesticide retention was the salt selection for the draw solution. Draw solutions could exist in different forms such as gases or volatile compounds, inorganic salts, organic salts and functionalised nanoparticles (Johnson et al., 2018). Since most of the journals were focused on using inorganic salts as draw solution, only the effect of different inorganic draw solution types were discussed.

Among the many studies on inorganic draw solutions, sodium chloride, NaCl was one of the most common monovalent salt used as draw solutions (Zhao et al., 2016; Cui et al., 2016; Zhang et al., 2017; Arcanjo et al., 2020). Zheng et al. (2019) compared the rejection performance of FO membranes using two different draw solutions: NaCl and lithium chloride, LiCl. At the same concentration and pH of the draw solutions, LiCl exhibited more severe ICP and lower water flux due to larger hydrated radius of lithium ion, Li^+, hence lower diffusivity. The higher dilutive ICP resulted in the low water flux of LiCl. With lower reverse salt flux, the rejection of pesticides was higher when LiCl was used as the draw solution. The reason was that the forward diffusion was hindered by reverse salt flux through "retarded forward osmosis", causing lower permeation of micropollutants (Xie et al., 2018).

In another study by Xie et al. (2018), NaCl was compared with magnesium sulphate, $MgSO_4$ as draw solutions. It was found that the rejection of pesticides was lower when $MgSO_4$ was used as the draw solution for both non-ionic hydrophobic and hydrophilic compounds. When $MgSO_4$ was used as the draw solution, the rejection of pesticide DEET is around 90 % as compared to 96 % when NaCl was used as the draw solution. However, magnesium chloride, $MgCl_2$ was preceded by NaCl as the more recommended draw solution for FO membrane in the study by Arcanjo et al. (2020). This was because the overall rejection achieved by $MgCl_2$ was higher than NaCl with lowest reverse salt flux due to larger hydration radii as shown in Figure 4.21. With the same concentration, $MgCl_2$ was able to achieve higher osmotic pressure because more ionic species could be formed on dissociation (Johnson et al., 2018). Achilli,

Cath and Childress (2010) further added that MgCl₂ had lower fouling potential which made it close to the ideal draw solution to be used. In terms of cost wise, MgCl₂ was not recommended since the replenishment cost was high due to its high unit cost. Table 4.6 was tabulated to summarize the studies mentioned on draw solution types.
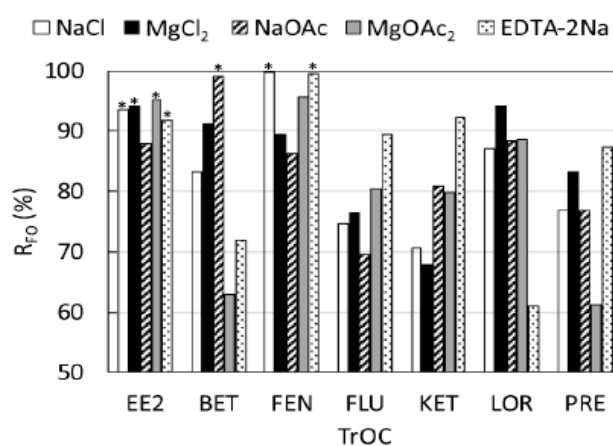
Figure 4.21: Comparison on the Rejection of TrOC using Different Draw
Solutions (Arcanjo et al., 2020)

There are several qualities which a desired draw solution salt should possess like (i) high solubility in the solution, (ii) high diffusivity through the membranes therefore lower ICP, (iii) high osmotic pressure, (iv) low viscosity for easy pumping and higher water flux, (v) low reverse salt flux, (vi) readily available at a decent cost and (vii) easy reconcentration (Johnson et al., 2018; Arcanjo et al., 2020). Based on the studies mentioned above, it appears that NaCl is one of the most desired inorganic salts to be used as draw solutions for FO and PRO membranes which are mostly used for desalination. It is also cost-effective, easily available and exists in abundance.

4.7.2   Concentration of Draw Solution

Similar to feed solution concentration, draw solution concentration also affected water flux and micropollutants removal. Figure 4.22 showed an example of the water flux and solute rejection for a lab-fabricated FO TFC membrane as a function of draw solution concentration. Referring to the study by Cui et al. (2016), when the draw solution concentration increased from 0.5 M to 2.0 M, the average water flux for all three organic compounds doubled from around 10 $L/m^2 \cdot h$ to 20 $L/m^2 \cdot h$. At the same time, there was also a considerable improvement for the solute rejection and reverse salt flux. As compared to permeate flux, the effect of draw solution concentration was more pronounced in water flux.
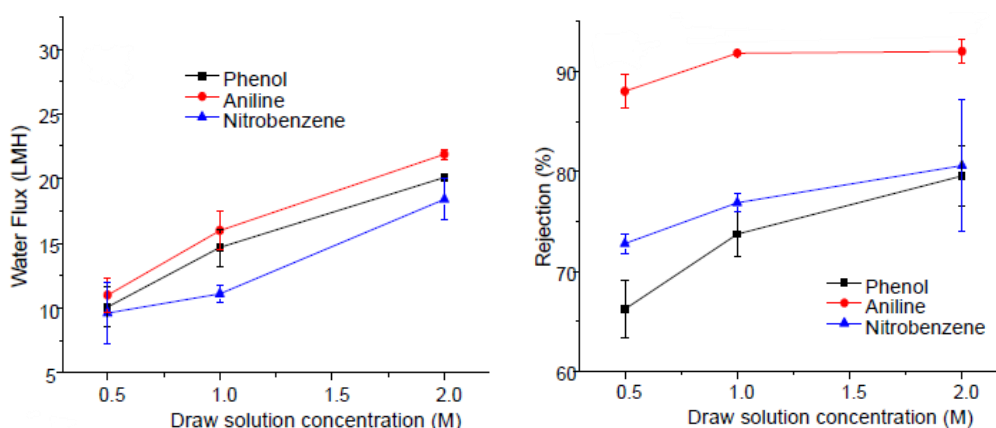
Figure 4.22: Effect of Draw Solution Concentration on Water Flux and Solute
Rejection (Cui et al., 2016)

Later, Zhang et al. (2017) had proven that there was no significant change of solute flux when the concentration of NaCl draw solution increased. Instead, there was a substantial increment in the water flux which may be attributed by the elevated osmotic pressure as the driving force for FO membranes as depicted in Figure 4.23. When phenol concentration increased from approximately 2 % to 10.5 %, the water permeation flux increased more than double from 6 $L/m^2 \cdot h$ to 13.3 $L/m^2 \cdot h$. It should be noted that there was a cap for draw solution concentration. The rise of water flux levelled off at high draw solution concentration as a consequence of dilutive ICP of the membrane surface. This phenomenon was ascribed to the reduced osmotic pressure

difference across the membrane. Sauchelli et al. (2018) mentioned that the charge shielding effect was most probably to occur at high draw solution concentration which he suggested to be higher than 0.5 M. The effect of draw solution concentration on water flux mentioned was in agreement with the results by Touati et al. (2015). Xie et al. (2018) further explained that the transfer of solutes across FO membranes was solution-diffusion model. Therefore, the increment of draw solution concentration had a positive effect on pesticides rejection. Table 4.6 summarized the studies discussed on draw solution concentration.
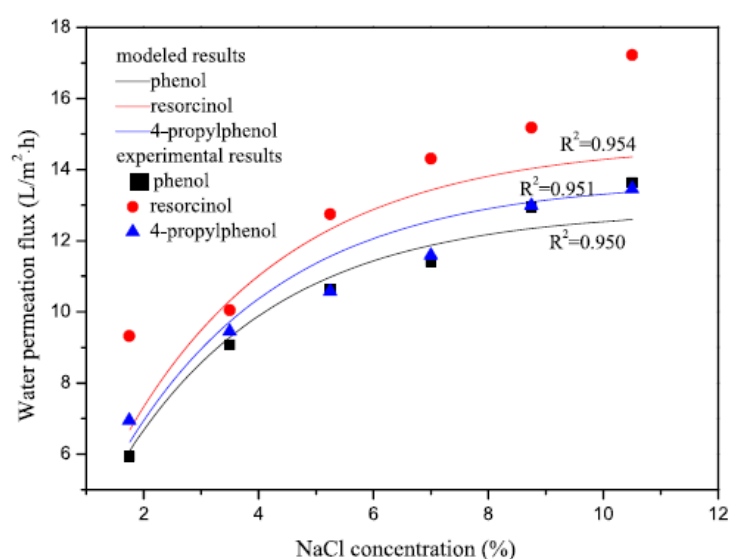
Figure 4.23: Water Permeation Flux as a Function of Draw Solution
Concentration (Zhang et al., 2017)

One may conclude that as the concentration of draw solution increases, pesticides rejection shows positive increment provided that the membrane is not saturated with salts. This could lead to membrane fouling which decreases the membrane osmotic pressure difference, impairing the membrane.

Table 4.6: Some Recent Studies on the Effect of Draw Solutions on Retention and Flux Performances

Thin Film Composite Membrane	Findings	References
	Draw Solution Types	
FO	• $MgCl_2$ was recommended as the draw solution due to lowest reverse salt flux.	(Arcanjo et al., 2020)
FO	• At the same concentration and pH of the draw solutions, LiCl exhibited more severe ICP and lower water flux. • The rejection of pesticides was higher with lower reverse salt flux when LiCl was used as the draw solution.	(Zheng et al., 2019)
FO	• $MgCl_2$ was able to achieve higher osmotic pressure because more ionic species could be formed on dissociation.	(Johnson et al., 2018)
FO	• The rejection of DEET pesticide (90 %) was lower when $MgSO_4$ was used as the draw solution compared to NaCl (96 %).	(Xie et al., 2018)
FO	• Despite the lower fouling potential of $MgCl_2$, it was not recommended as draw solution due to high replenishment and unit cost.	(Achilli, Cath and Childress, 2010)

Concentration of Draw Solutions		
FO	• At high draw solution concentration (> 0.5 M), charge shielding effect was most probably to occur.	(Sauchelli et al., 2018)
FO	• Draw solution concentration had a positive effect on pesticides rejection which coincided with the solution-diffusion model.	(Xie et al., 2018)
FO	• When phenol concentration increased from approximately 2 % to 10.5 %, water permeation flux increased more than double from 6 $L/m^2 \cdot h$ to 13.3 $L/m^2 \cdot h$. • The rise of water flux levelled off at high draw solution concentration as a consequence of dilutive ICP of the membrane surface.	(Zhang et al., 2017)
FO	• When the draw solution concentration increased from 0.5 M to 2.0 M, the average water flux for all three organic compounds doubled from around 10 $L/m^2 \cdot h$ to 20 $L/m^2 \cdot h$. • Draw solution concentration had a prominent effect on solute rejection and reverse salt flux.	(Cui et al., 2016)

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1   Conclusions

With the increasing demand in food and water quality, the development of agricultural field requires an extensive usage of pesticides. Despite being an asset to farmers to increase crop yields, these pesticides put the wellbeing of living organisms at stake due to their high persistence and toxicity in the environment. Therefore, approaches to eliminate pesticides in wastewater have become alarmingly crucial in the recent decades due to the strict regulations of permissible pesticides concentration in drinking water and also wastewater enforced by WHO. Membrane filtration processes comprising nanofiltration, reverse osmosis and forward osmosis are studied in this study. The process parameters posed great impact on the pesticides rejection and permeate flux. Operating pressure has a positive effect on flux performance. From the studies, when the operating pressure increased, there was a surge in permeate flux up to 32.5 % increment with 14 % increment of pesticides retention in NF and RO membranes. High permeability at high pressure in FO process was affiliated with membrane compression, obstructing the membrane channel for water permeation. NF and RO membranes show better performance in cross-flow configuration in terms of high pesticides rejection (83 %) and low permeate flux as compared to dead-end configuration (77 % retention). It is preferable for FO processes to operate in FO mode than PRO mode in the aspect of fouling intensity and low ICP. The water flux in FO mode is also higher (22.1 L/m^2·h) than in PRO mode (16.3 L/m^2·h).

The effect of pesticide characteristics in terms of pesticides size, ionic charge and hydrophobicity on rejection efficiency and permeate flux have been compared and discussed. It can be concluded that large and negatively charged pesticides can be retained more efficiently. From one of the journals, retention of diuron with smaller molecular weight was only 74 % while rejection of atrazine with larger molecular weight was 97 %. Hydrophobicity of the pesticides also have a positive correlation with pesticides rejection due to repulsion to the water layer on membrane surface. Hydrophobic atrazine was

rejected better at 99 % than hydrophilic dimethoate with rejection of 81 %. As for membrane characteristics, fouling on membrane layer reduces the average pore size which induces charge shielding effect and diminishes the flux performance despite providing additional filtration effects to increase pesticides retention. Besides, membranes with rougher surface further aggravates the fouling issue. The average pore size of the hydrophilic active layer in the membrane shows positive effect to the reduction of permeability of the membrane. NF90 with a smaller pore size exhibited pesticides rejection up to 98.7 % with low solute permeability of 57.2 $L/m^2 \cdot h$ while NF270 with a larger pore size was found to reject pesticides up to 97.8 % with higher solute permeability of 85.5 $L/m^2 \cdot h$.

In feed solutions, lower permeate flux and higher rejection up to 99 % is achieved at an environment with high ionic strength. Ionic strength of the membrane is directly correlated to pH. The rejection of pesticides are determined by electrostatic interactions of both pesticides and membrane at the specific pH. When both pesticides and membranes are negatively charged, electrostatic repulsion takes place and increases the rejection. The optimum pH depends on the membranes and pesticides charge and it was suggested to be pH 7. On the other hand, when they are oppositely charged, electrostatic attraction occurs instead which reduces the rejection efficiency. The presence of humic acid in feed solution brought about fouling issues which reduces permeate flux from 77 $L/m^2 \cdot h$ to 41 $L/m^2 \cdot h$. Serious deposition of humic acid on the membrane surface resulted in the formation of a cake layer that lowered the permeability of the membrane. Membrane fouling is exacerbated from 6 % to 14 % with the presence of ions in the water. Concentration of feed solution also increases the deposition of pesticides in the membrane, leading to lower rejection due to hindered electrostatic repulsion and charge shielding. For instance, when feed concentration inclined from 1 µg/l to 10 mg/l, pesticides rejection declined dramatically from 92.6 % to 37.3 %. The osmotic pressure differences in FO processes are also reduced at high feed concentration, weakening the membrane performance.

NaCl was selected to be the most desired inorganic salts to be used as draw solutions for FO processes due to its cost-effectiveness, high availability

and abundance existence. There was also a positive increment in pesticides rejection as the concentration of draw solution increased. When the draw solution concentration inclined by more than 400 % (e.g. 0.5 M to 2 M), a more than double increment was observed in water flux. To conclude, RO membranes surpassed NF and FO membranes in terms of pesticides rejection but NF membranes managed to achieve higher permeate flux.

5.2   Recommendations for future work

Since this is a critical review, the effect of process parameters are only studied based on previous studies by other researchers. The results of the studies may vary from one journal to the other due to different factors like different settings of experiments and membrane types used. Therefore, it is recommended that a lab-based study is conducted to verify the results and to come out with a set of optimum conditions for the parameters discussed. Furthermore, additional research on membrane cleaning approaches have to be executed in order to mitigate severe fouling issues which is the major deficiency of membrane separation processes. Due to limitation of resources on TFC-FO membranes, FO processes are not studied as thoroughly as NF and RO processes. Since TFC-FO is a relatively new membrane, there are considerably lesser research done. It is recommended that FO of other materials like cellulose acetate or aquaporin is included in the study for better evaluation of FO processes. Besides, research on hybrid processes can also be carried out to widen the range of membrane separation study. Last but not least, it was suggested that cost-benefit analysis is to be conducted to determine the financial feasibility of the membranes and operation of processes in future studies.

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APPENDICES

APPENDIX A: Figures

NO.	PARAMETERS	COLUMN I
		MAXIMUM ACCEPTABLE VALUE
		mg/l (unless otherwise stated)
	GROUP IV	
1	ALDRIN/DIELDRIN	0.00003
2	DDT	0.002
3	HEPTACHLOR & HEPTACHLOR EPOXIDE	0.00003
4	METHOXYCHLOR	0.02
5	LINDANE (BHC)	0.002
6	ENDOSULFAN	0.03
7	CHLORDANE	0.0002
8	1,2-DICHLOROPROPANE	0.04
9	1,3-DICHLOROPROPENE	0.02
10	HEXACHLOROBENZENE	0.001
11	PENTACHLOROPHENOL	0.009
12	ALACHLOR	0.02
13	ALDICARB	0.01
14	AMETRYN	0.05
15	ATRAZINE	0.002
16	BENTAZONE	0.3
17	CARBOFURAN	0.007
18	CHLOROTOLURON	0.03
19	CYANAZINE	0.0006
20	2,4-DICHLOROPHENOXY-ACETIC ACID (2,4D)	0.03
21	DIQUAT	0.01
22	1,2-DIBROMO-3-CHLOROPROPANE	0.001
23	1,2-DIBROMOETHANE	0.0004
24	ISOPROTURON	0.009
25	MCPA	0.002
26	METOLACHLOR	0.01
27	MOLINATE	0.006
28	PENDIMETHALIN	0.02
29	PERMETHRIN	0.02
30	PROPANIL	0.02
31	PYRIDATE	0.1
32	SIMAZINE	0.002
33	TRIFURALIN	0.02
34	2,4 DB	0.09
35	DICHLORPROP	0.1
36	FENOPROP	0.009
37	MECOPROP	0.01
38	2,4,5-T	0.009
39	TERBUTHYLAZINE	0.007

Figure A-1: Drinking Water Quality Standards in Malaysia (Engineering Services Division MOH Malaysia, 2004)