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# Critical Evaluation of Thin Film Composite Membrane on Pesticide Removal

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## ABSTRACT

This study focuses on how operating pressure, pesticide characteristics, membrane materials, feed solution and draw solution affect the performance of thin film composite membranes on pesticides removal. The membrane separation discussed in this review involve nanofiltration (NF), reverse osmosis (RO) and forward osmosis processes (FO) (i.e., FO mode and pressure retarded osmosis (PRO) mode). High pressure shows positive effects on NF and RO membranes flux performances, but it could deform PRO membranes. Hydrophobic pesticides that are larger in size, negatively charged with small dipole moments will result in higher retention. Besides, 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. This paper is crucial to give an overview on ways to improve the removal of pesticides with various thin film composite membranes.

*Keywords:* Nanofiltration, reverse osmosis, forward osmosis, pressure retarded osmosis, pesticide

## 1.0 INTRODUCTION

High demand of water from the modernization of many developing and industrialized countries are causing pollution to the environment and lead to water scarcity problem [1, 2]. Landfill leachate and other wastewater effluents from various industries such as manufacturing, agriculture, mining, sewage treatment plants and domestic livestock farms are the point and non-point sources for surface water and groundwater contamination [3, 4].

According to Food and Agriculture Organization of the United Nations [5], 70 % of freshwater globally is used for agriculture purpose. Large volume of water is required in the agricultural field as irrigation for crops [2]. This has brought about water contamination issue due to the build-up of biowastes, heavy metals, pesticides and fertilizers residues in agricultural runoff [6, 7]. These contaminants have aroused several problems in both ecosystem and the wellbeing of most life beings including humans.

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'

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growth to achieve higher yield of crops [8]. According to Marican and Durán-Lara [9], "pesticide" is a general name for herbicides, insecticides, fungicides, bactericides and miticides. They are used by farmers in repelling, preventing, mitigating and eliminating weeds and pests.

Pesticides can be categorised based on their chemical structures such as organochlorines, organophosphorus, carbamates, chlorophenols and synthetic pyrethroids [9]. High level of these pesticides from agriculture and landscape cause pollution in river water and groundwater. Pesticide-contaminated water is difficult to treat due to its variability of both chemical and physical structures, composition, and high range of pH from 0.5 (highly acidic) to 14 (highly alkaline). Depending on the sources of the water, the pesticide level can vary between 0.1 to 107 mg/L [10]. The wellbeing of various living organisms is at risk due to the persistence of the toxic pesticides in the environment. Exposure to these pesticides can cause various negative impacts to our body system. It was reported that pesticides are poisonous to humans' body and cause neurological, respiratory, reproductive and dermalogical issues [11]. Thus, it is imperative to control the concentration of pesticides in drinking water within the allowable limit for humans' consumption. The legal standard of individual pesticide in drinking water is 0.1 μg/l and the total pesticides concentration is 0.5 μg/l as set by the European Union [12].

Among the wide range of pesticides being used in the agricultural field, several pesticides are 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.

NF, RO and FO processes utilise thin film composite membrane as separation medium. The membrane consists of polyamide active layer rests on porous membrane support for separation purpose. NF and RO membranes are pressure driven membranes [13]. At high osmotic gradient, large pressure is exerted upon the membrane feed side, forcing water to infiltrate the membrane while efficiently rejecting the solutes. RO membranes have smaller pore size compared to NF membranes, hence lower solute permeability. To overcome the low membrane permeability, the operating pressure in RO process is higher than NF membrane. On the other hand, FO membrane is an emerging membrane filtration method. It utilise osmotic pressure difference instead of hydraulic pressure in the separation process [14]. 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. Draw solution is highly concentrated with salt which is either being regenerated or serve other purposes after the process. 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 [15].

Recent studies have been focusing on membrane separation to remove pesticides and other micropollutants in wastewater [8]. Due to its cost-effectiveness, 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, the performances of the membrane in terms of rejection and permeability are highly dependent on the properties of the pesticides, the membrane materials and the operating conditions. Besides, low chlorine tolerance is another limitation of membrane separation. Therefore, it is imperative for researchers 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 NF, RO, and FO processes including FO and PRO mode in the removal of pesticides and their respective permeate fluxes under various operating variables are presented in this study. The operating variables studied are operating pressure, pesticide characteristics, membrane characteristics, feed solution and draw solution. 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.

## 2.0 EFFECT OF OPERATING PRESSURE

Operating pressure is also referred to transmembrane pressure. Membranes are normally studied in a pressure range of 5 to 20 bar for NF, RO and FO membranes. Riungu *et al.* [16] investigated the effect of pressure using several NF membranes which are NF270, NF90 and NTR7250. It was found that the retention of an herbicide, atrazine improved along with the pressure. 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 %. The retention was higher at high pressure because water flux in the membrane resulted in 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 with the increment of the operating pressure [16]. Similar trend was observed in the study by Musbah *et al.* 2013 [17] the rejection of four pesticides eg. atrazine, DEA, simazine and diuron are over 74% with pressure varied from 10 to 25 bar.

Besides, Ajao *et al.* [18] also agreed that pressure had a very high influence on permeate flux in RO membrane. From the findings, the applied pressure and pure water flux showed a linear relationship. The trend of water flux coincided with the solution-diffusion model where pressure was directly proportional to water flux [19].

On the other hand, the effect of high pressure was opposite 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 [20–22]. When 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 [20]. This was caused by “shadow effect” which was the membrane compressing against the feed spacer, blocking the channel for water permeation at high pressure [21]. Furthermore, water flux increased as the osmotic pressure increased which was related to concentration of draw solution. The non-linear pattern was probably due to reverse salt flux [23].

From the above studies, 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-membranes like FO, high pressure may lead to deformation of membranes and weaken the membrane performance.

## 3.0 EFFECT OF PESTICIDES CHARACTERISTICS

### 3.1 Size of Pesticides Molecules

Molecule size is a dominant factor in determining the efficiency of 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.

In many studies, micropollutants with larger molecular weight had better rejections compared to micropollutants with smaller molecular weight [17, 23–27]. In the study by Wang *et al.* [26], 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 [27]. In another study by Musbah *et al.* [17], diuron had the smallest molecular length and width (9.19 A length and 4.87 A width) achieved the retention of roughly 74 % while 97 % of atrazine with the largest molecular length and width (10.36 A length and 8.02 A 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.* [24] reported that atrazine which had a smaller molecular weight showed a relatively low 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.* [25] in 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.* [23]. It was explained that micropollutants with smaller size was able to adsorb onto the porous surface of the membrane and penetrate the membrane easily.

From our review, most of the papers 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.

### 3.2 Pesticides Ionic Charge

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 [28]. 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 [25].

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 [23, 26, 27, 29]. Interestingly, Salamanca and co-researchers [23] reported that micropollutants with positive charge had an unexpectedly high rejection (≤ 99.99 %) for its molecular weight in FO mode. They claimed that this might be due to high electrostatic attraction where positively charged molecules were easily deposited on the active layer surface of the membrane, which was of opposite charge, causing low permeate flux. However, most studies stated that the presence of electrostatic attraction decreased the overall rejection of membranes [27, 30]. On the other hand, low adsorption rate thus high rejection in RO membranes was seen in the case of negatively charged molecules because of high electrostatic repulsion [28–30].

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 [31, 32].

According to the 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.* [23].

### 3.3 Pesticides Hydrophobicity

Other than the molecular sieving factor, hydrophobicity was also one of the parameters affecting pesticides retention and permeate flux during membrane filtration [33, 34].

NF membranes were normally hydrophilic due to the presence of polar amide and carboxyl functional groups in the thin film active layer [35]. Pesticides like endosulfan and atrazine were hydrophobic in nature, so they were able to adsorb and diffuse through the membrane surface by steric interaction. As a result, hydrophobic pesticides showed lower removal rate in thin film membrane separation [36].

However, Tan *et al.* [32] claimed otherwise despite both studies were carried out using NF90 membrane. They mentioned that pesticides with higher hydrophobicity exhibited better removal in which atrazine ($log\ K_{ow}$ of 2.34) was rejected better at 99 % than dimethoate ($log\ K_{ow}$ of 0.70) which showed only 81% rejection. This finding was in line with the results from the two other studies [35], [15]. It was then explained that a pure water layer was easily formed on the highly hydrophilic surface of the membrane. This had avoided the hydrophobic pesticides from being adsorbed or deposited on the membrane surface, hence exhibited high rejection [37]. Licona *et al.* [13] added that hydrophilic compounds favoured adsorption onto the membrane surface or diffusion through the membranes, resulted in low rejection.

It was worthy to mention that the rejection performance of a membrane could be eventually weakened when the adsorption capacity was impoverished [26]. This was agreed that lower rejection could be seen once the steady-state conditions respecting adsorption were reached [34]. At this state, size exclusion played the dominant factor instead. Therefore, 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.* [15] 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.

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 reduced. This can be affiliated with membrane fouling.

## 4.0 EFFECT OF MEMBRANE CHARACTERISTICS

The removal efficiency and permeate flux of membrane varies according to membrane types such as NF, RO, FO or PRO membranes. The active layer of these membranes could be made up of different materials.

Even though NF 90 and NF 270 membranes made up of similar materials, they exhibit different performance. The active layer of NF90 membrane was made up of fully-aromatic polyamides while NF270 membrane possessed a semi aromatic 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. Besides, NF90 was more hydrophobic and more susceptible to fouling issues because the membrane surface is rougher as compared to NF270 [38]. 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.* [13] and Riungu *et al.* [16]. 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 membrane pore size of NF90 is lower (0.55 nm) compared to NF270 (0.71 nm)[16].

It was mentioned in the study by Fini, Madsen and Muff [39] 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 (both are commercial RO membranes from Dow Chemicals), higher pesticides adsorption was noticed in BW30 membrane. For instance, 10.2 % of 2-methyl-4-chlorophenoxy propionic acid (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.

The effect of hydrophobicity on the rejection efficiency and permeate flux was in line with the study by Khairkar *et al*. [40]. It was also claimed that XLE membrane displayed a larger flux than BW30 membrane, classifying XLE membrane as a low pressure reverse osmosis (LPRO) membrane [41]. Hence, ions rejection using BW30 was slightly higher than XLE membrane.

Even though the difference in flux performance and pesticides retention were not distinct, the effect of membrane materials on membrane performance 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.

## 5.0 EFFECT OF FEED SOLUTION

### 5.1 Feed Solution Ionic Charge

Other than pesticides ionic charge, ions in feed solutions could also influence permeate flux and membrane performance.

Fini *et al.* [39] 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.* [42]. Deionized water, tap water and field water were tested with diuron and isoproturon pesticides using self-fabricated thin film composite membranes 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 the 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 the field water. This result was consistent with the study by Palma *et al.* [36]. Using 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.* [32] in which river water with the most ions displayed the highest retention and lowest permeate flux of atrazine and dimethoate pesticides using DK, NF270, NF200 and NF90 membranes. For instance, the retention and permeate flux of atrazine in deionised water 50% and $2.1\times10^{-5}$ m$^3$/m$^2$·s, respectively. On the other hand, the retention and permeate flux in river water was 60% and $1.6\times10^{-5}$ m$^3$/m$^2$·s, respectively. 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 [39]. This claim was supported by another study through the analysis of zeta potential for different membranes in vary pesticide concentrations [41]. It was reported that zeta potential increased with the ionic concentration of the feed solution and this increment was due to the adsorption of ions onto the membrane surface, resulting in pore blocking and increased rejection of pesticides.

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 using different types of water sources. 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 are achieved at an environment with high ionic strength.

## 5.2 Pesticides Feed Concentration

Feed solution concentration indicates how saturated the feed solution is with pesticides. The higher the feed concentration, the higher the number of pesticides in the feed solution. The amount of pesticides contain in the feed solution will affect the permeability and the rejection efficiency of membrane.

In another study by Fini, Madsen and Muff [39], 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 2-methyl-4-chlorophenoxy acetic acid (MCPA) when the feed concentration inclined from 1 µg/l to 10 mg/l. 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.

For FO membranes, Nguyen *et al.* [43] reported 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.* [44] 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. It was explained that this was caused by the decline of the difference in osmotic pressure between the feed and draw solutions [44]. This findings coincided with the study by Fini *et al.* [39] where the rejection value of pesticide MCPP dropped from 97.1 % to 95.8 % when the feed concentration rose from around 940 µg/l to 1050 µg/l as shown in Figure 1.

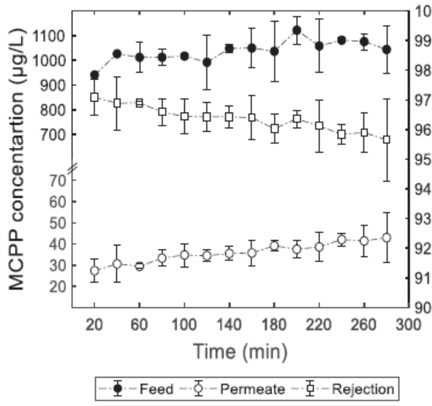

**Figure 1** Rejection of pesticide MCPP as a function of feed and permeate concentration [39]

From the above studies, as the feed concentration increases, the rejection of pesticides decreased. For NF and RO membranes, the decline of rejection is due to charge shielding of membranes caused by the deposition of pesticide on membrane surface and higher driving force at the feed side. While the lower rejection at higher feed concentration for FO processes 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.

### 5.3 Feed Solution pH

pH of the feed solution is interrelated to ionic charge of the membrane due to the dissociation of functional group [45]. pH and ionic charge are related to isoelectric point. Isoelectric point of a membrane is the pH when the membrane active layer is in neutral charge. When the pH is higher than the isoelectric point, the membrane is negatively charged. On the other hand, the membrane is positively charged when the pH is below the isoelectric point [46]. For instance, the isoelectric point of NF90 membrane is at pH 3.8 and pH 3 for BW30 membrane

pH of the feed solution also has effect on the hydrophobicity of pesticides. Licona *et al.* [13] claimed that micropollutants became less hydrophobic at high pH, allowing them to be more soluble. Besides, pH also affected the ionic charge of solutes. For instance, ibuprofen 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 and hence increased the rejection efficiency.

In another study by Liu *et al.* [30], the amount of solutes adsorbed onto the membrane varied according to pH. At pH 7.4, sulfamethoxazole 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 were adsorbed onto NF90 membrane at pH 3.8 while no solute was adsorbed at pH 7.4. This was because due to lacking electrostatic repulsion at the isoelectric point, causing inefficient rejection force of solutes. On the contrary, there was a substantial increment in rejection at pH 7.4 because electrostatic repulsion took place. As opposed to negatively charged solutes, positively charged solutes exhibited lower adsorption, hence higher rejection at isoelectric point for the reason that electrostatic attraction between the solutes and membrane was absent. Riungu *et al.* [16] suggested pH 7 as the most optimum condition giving the highest rejection using NF90, NTR7250 and NF270 membranes in the study. Comparing rejection of atrazine in feed solution with different pH, the rejection for pH 4, pH 7 and pH 10 was around 62%, 81% and 66%, respectively using NF270 membrane.

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, phenol permeation flux was around 880 mg/m$^2$·h at pH 7 and around 200 mg/m$^2$·h at pH 11. Dolar, Košutić and Strmecky [47] 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. Unlike permeate flux, there was insignificant effect of pH on reverse salt flux in FO membranes [46]. This claim was supported by Nikbakht Fini *et al.* [15]. On the other hand, FO membranes had shown higher rejection at high pH solution (alkali) as both phenolic compounds and FO membrane were negatively charged hence increased the electrostatic repulsion. Therefore, it is concluded that pH of feed solution has direct correlation with zeta potential of a membrane, and solute surface charge and hydrophobicity.

### 5.4 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. Natural organic matters (NOMs) exist in many natural water sources. One of the most studied NOM model is humic acid which is a dark brown organic matter [48].

The fouling extent of NOMs depends 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 [49]. Humic acid was found to increase tendency of membrane fouling. After the 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.* [16], when humic acids were added into 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 explained that humic acid was hydrophobic by nature so it was able to adsorb onto the surface of membrane and led to blockage of membrane pore, hence reducing membrane permeability. Humic acid also tended to leave a dark brown foulant layer on the membrane surface after the experiment which caused a significant impact in the membrane hydrophobicity and rejection [38].

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 % [42]. When the feed solution was switched to field water in a more recent study, there was a substantial increment in membrane fouling (14 %) [50]. The fouling was further aggravated to 23 % and 30 % when magnesium and calcium were added. It was explained that humic acid reduced the negativity of zeta potential and causing the membrane to be less negatively charged. This induced charge shielding and ion adsorption onto the membrane surface, hence enhancing fouling and reducing membrane performance.

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 further aggravates when ions are present in the water. Hence, backwashing or physical cleaning is necessary in diminishing fouling on membrane.

## 6.0 EFFECT OF DRAW SOLUTION

### 6.1 Types of Draw Solution

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 [51]. Since most of the journals were focused on using inorganic salts as draw solution, only the effect of different inorganic draw solution types is discussed.

Sodium chloride (NaCl) was one of the most common monovalent salt used as draw solutions [44, 46, 52, 53]. Zheng *et al.* [54] 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 internal concentration polarization (ICP) and lower water flux due to larger hydrated radius of lithium ion ($Li^+$) with lower diffusivity. The higher dilutive ICP resulted in lower 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 [55].

In another study by Xie *et al*. [55], 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 N, N-Diethyl-meta-toluamide (DEET) was around 90 % as compared to 96 % using NaCl. Later, magnesium chloride, $MgCl_2$ was preceded by NaCl as the recommended draw solution for FO membrane in the study by Arcanjo *et al*. [53]. This was because the overall rejection achieved by $MgCl_2$ was higher than NaCl with the lowest reverse salt flux due to larger hydration radii. With the same concentration, $MgCl_2$ was able to achieve higher osmotic pressure because more ionic species could be formed on dissociation [51]. Achilli *et al*. [56] further added that $MgCl_2$ had lower fouling potential which made it close to the ideal draw solution to be used. However, in terms of cost wise, $MgCl_2$ was not recommended since the replenishment cost was high due to its high unit cost. There are several qualities which a desired draw solution salt should possess, such as (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 re-concentration [51, 53]. 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.

## 6.2 Concentration of Draw Solution

Similar to feed solution concentration, draw solution concentration also affects water flux and micropollutants removal. Referring to the study by Cui *et al*. [44], when the NaCl draw solution concentration in FO mode was increased from 0.5 M to 2.0 M, the average water flux of phenol, aniline and nitrobenzene feed solutions doubled from around 10 $L/m^2 \cdot h$ to 20 $L/m^2 \cdot h$ using their self-fabricated thin film composite membrane. At the same time, there were also considerable improvements 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.

Later, Zhang *et al*. [46] 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 the commercial FO membranes. 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.* [57] reported 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 in this study was in agreement with the results by Touati *et al.* [59]. Xie *et al.* [55] 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.

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.

## 7.0 CONCLUSION

This paper describes characteristics of pesticides and membrane, as well as various operating parameters in removal of pesticides using thin film composite membrane. Most of these factors showed significant impact on the permeate flux and rejection. Hence, it is important to understand the interaction between them for better removal of pesticides.

Operating pressure has a positive effect on flux performance. There was a surge in permeate flux with increment of pesticides retention in NF and RO membranes when the operating pressure increased. However, high permeability at high pressure in FO process also affiliated with membrane compression, obstructing the membrane channel for water permeation. Generally, for pesticide characteristics, large and negatively charged pesticides can be retained more efficiently. Hydrophobicity of the pesticides also had a positive correlation with pesticides rejection due to repulsion with water layer on membrane surface. Besides, the average pore size of the hydrophilic active layer in the membrane showed positive effect to the reduction of permeability of the membrane.

In feed solutions, lower permeate flux and higher rejection was achieved at an environment with high ionic strength. Furthermore, the rejection of pesticides was determined by electrostatic interactions of both pesticides and membrane at the specific pH. Concentration of feed solution also increased the deposition of pesticides in the membrane, leading to lower rejection due to hindered electrostatic repulsion and charge shielding. There was also a positive increment in pesticides rejection as the concentration of draw solution increased. For FO processes, NaCl was selected to be the most desired inorganic salts to be used as draw solutions due to its cost-effectiveness, high availability and abundance existence.

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