# UNIVERSITY OF SOUTHAMPTON

FACULTY OF ENGINEERING AND THE ENVIRONMENT

Water and Environmental Engineering

# Wastewater Treatment by Forward Osmosis (FO) Based System for Resource Recovery

by

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# ABSTRACT

Resource recovery from wastewater has attracted significant attention in the circular economy. Among different technologies, forward osmosis (FO) as an emerging membrane technology has the potential to transform municipal wastewater treatment plants into factories for water, nutrients and energy production by concentrating very diluted municipal wastewater for direct nutrients recovery and subsequent water and energy recovery.

Although FO membrane has much lower fouling propensity than reverse osmosis (RO) due to much lower pressure applied to membrane, fouling is still one of the barriers to the FO application. The first technical chapter of this thesis investigated the concentration of synthetic and real municipal wastewater to 90% water recovery rate by two different configurations, i.e., hollow fiber and flat sheet thin film composite (TFC) FO membranes, and their associated membrane fouling and cleaning. Results show that the FO membrane had high rejection rates of COD, phosphate, $Ca^{2+}$ and $Mg^{2+}$ with concentration factors at around 8 when achieving a 90% water recovery rate, which facilitated downstream phosphate recovery by direct precipitation and energy production by anaerobic digestion (AD). The significantly increased $Ca^{2+}$ and phosphate concentrations after FO filtration with 90% water recovery was found to be the main factor contributing to inorganic scaling, which was harder to be cleaned by physical cleaning compared with cellulose particles used to simulate suspended solids (SS) in synthetic wastewater. Both hollow fibers and flat-sheet configurations are found not to be suitable for treatment municipal wastewater without prior SS removal although flat sheet configuration was still able to achieve a 90% water recovery rate but with water flux of only 7.5 $L/m^2{\cdot}hr$ at 90% water recovery rate while hollow fiber FO was completely clogged with operation failure. The use of a spacer in the flat sheet configuration did not alleviate membrane fouling during the membrane filtration process, but it improved the efficiency of the following physical cleaning by around 15%. This study highlighted the importance of the chemistry of feed solution (FS) and draw solution (DS) and FO membrane configuration on membrane fouling particularly at high water recovery rates and the necessity of pre-treatment of municipal wastewater.

For wastewater treatment with FO, it has been widely reported that FO has very low ammonium rejection primarily due to the negative charge nature of membrane. This restricts the application of FO for wastewater treatment particularly with a purpose of ammonium and water recovery. The second technical chapter in this thesis thus aimed to enhance ammonium rejection in the FO process by selecting DSs with different physiochemical characteristics. Results show that under the same osmotic pressure divalent cation DS (i.e.

$Mg^{2+}$) with larger hydrated radius resulted in a higher ammonium rejection than monovalent cation DS (i.e. $Na^{+}$) with lower hydrated radius. For the same cation based DS, DS with lower diffusion coefficient showed higher ammonium rejection. These results imply that impeding the exchange of cation in DS with ammonium in FS by increasing cation radius or reducing diffusion coefficient could minimize the ammonium permeation to DS. Non-ionic DS such as glucose, glycine and ethanol are able to minimize cation exchange between feed and draw solutions, leading to a 98.5-100% ammonium rejection rate. This further validate that even with negative charge of membrane, cation exchange between FS and DS is critical for ammonium permeation. The treatment of filtered municipal wastewater and sludge digestate with glucose and NaCl as DSs, respectively, proved that the non-ionic nature of glucose resulted in a high rejection rate not only for ammonium, and other cations such as $Ca^{2+}$ and $Mg^{2+}$ but also for anion such as $PO_4^{3+}$. This is for the first time that a generic guideline could be proposed based on cation exchange mechanism for the selection of DS in wastewater treatment especially when ammonium and water recovery is a concern.

To recover water from municipal wastewater, FO is usually needed to combine with other technologies. Membrane distillation (MD) offers a promising solution for simultaneous water recovery from DS and DS regeneration when waste heat is easily available. Although the integrated FO-MD system was studied in literature, temperature effects and heat balance in such integrated system are unclear. In the third technical chapter, the effect of FS and DS temperatures was examined. In addition, ammonium permeated from FS to DS was studied in the MD configuration for its potential contamination to the recovered water. It is found that higher FS and DS temperatures resulted in a higher water flux and a higher RSF from either NaCl or glucose as DS due to the increased diffusivity of molecules. However, the water flux increased at a higher rate with glucose DS than with NaCl DS by 10-14.8%, while the RSF increase rate with NaCl DS was two times higher than glucose DS. In addition, the use of NaCl DS at higher DS and FS temperatures such as 50 and 42 °C, respectively, resulted in more ammonium permeation from the FS to the DS, whereas ammonium was completely rejected with glucose DS even at high temperature. These results are very important because in the integrated FO–MD system at higher temperatures such as 50 °C, the advantage of high flux of NaCl as DS was not increased significantly while the disadvantages of high RSF of NaCl and lower ammonium rejection were greatly amplified. On the contrary, the disadvantage of low water flux of glucose as DS was overcome at 50 °C while 100% ammonium rejection was still maintained. This implies that temperature needs to be an important factor for the consideration in selecting DS in FO-MD system. Furthermore, a simple heat balance calculation suggests that if there was no heat recovery in the FO-MD system, waste heat from power plants is far less than the heat

demand in such systems for municipal wastewater treatment. An internal heat exchange between different streams was proposed to maximize the efficiency of heat utilization, but unarguably it would increase the complexity of the FO-MD system. Further study is needed regarding heat efficiency.

Overall, this project shows that the FO membrane fouling, the associated cleaning methods and ammonium rejection can be enhanced by understanding the feed and draw solutions chemistry. In addition, this project highlights the importance of the operation temperature when selecting the DS and the necessity of internal heat recovery in the FO-MD system.

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# Declaration of Authorship

Name: Khaled Almoalimi

**Title of thesis**: **Wastewater Treatment by Forward Osmosis (FO) Based System for Resource Recovery**

I declare that this thesis and the work presented in it are my own and has been generated by me as the result of my own original research.

I confirm that:

1. This work was done wholly or mainly while in candidature for a research degree at this University;
2. Where any part of this thesis has previously been submitted for a degree or any other qualification at this University or any other institution, this has been clearly stated;
3. Where I have consulted the published work of others, this is always clearly attributed;
4. Where I have quoted from the work of others, the source is always given. With the exception of such quotations, this thesis is entirely my own work;
5. I have acknowledged all main sources of help;
6. Where the thesis is based on work done by myself jointly with others, I have made clear exactly what was done by others and what I have contributed myself;
7. Parts of this work have been published as:
    - Almoalimi, K. and Liu, Y. (2022) 'Fouling and cleaning of thin film composite forward osmosis membrane treating municipal wastewater for resource recovery', Chemosphere. Elsevier Ltd, 288(P1), p. 132507. doi: 10.1016/j.chemosphere.2021.132507.
    - Almoalimi, K., Liu, Y., Booth, A. and Heo, S. (2022) 'Temperature effects of MD on municipal wastewater treatment in an integrated forward osmosis and membrane distillation process', Processes, 10.2, p. 355. doi: https://doi.org/10.3390/pr10020355.
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Parts of this work have been presented in the following conferences:

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- 5th Annual CDT-SIS conference “Creating a Sustainable Future” 20th November 2019 - Oral presentation.
- The EBNet Research Colloquium 2020 University of Edinburgh, 22-23 January - Poster Presentation.
- EBNet Early Career Research conference (25 June 2020) - Oral presentation.

Signature: Date: 09/06/2022

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# Definition of Abbreviations

| | |
|---|---|
| AD | Anaerobic digestion |
| AGMD | Air gap membrane distillation |
| AL-DS | Active layer facing draw solution |
| AL-FS | Active layer facing feed solution |
| CAS | Conventional activated sludge |
| CF | Concentration factor |
| COD | Chemical oxygen demand |
| CP | Concentration polarization |
| CTA | Cellulose triacetate |
| DCMD | Direct contact membrane distillation |
| DI | Deionised |
| DS | Draw solution |
| EBPR | Enhanced biological phosphorus removal |
| ECP | External concentration polarization |
| FO | Forward osmosis |
| FO-AnMBR | Anaerobic membrane bioreactor with forward osmosis |
| FS | Feed solution |
| ICP | Internal concentration polarization |
| LEP | Liquid entry pressure |
| MD | Membrane distillation |
| MF | Microfiltration |

| | |
|---|---|
| MF-FOMBR | Microfiltration-forward osmosis membrane bioreactor |
| OMBR | Osmotic membrane bioreactor |
| PTFE | Polytetrafluoroethylene |
| RO | Reverse osmosis |
| RSF | Reverse solute flux |
| SGMD | Sweeping gas membrane distillation |
| SI | Saturation index |
| TFC | Thin film composite |
| TSS | Total suspended solids |
| VMD | Vacuum membrane distillation |
| VSS | Volatile suspended solids |
| WWTP | Wastewater treatment plant |

# Chapter 1: **Introduction**

## 1.1 Research motivation

Water, energy and nutrients are essential resources for the development of economic and social aspects (Valladares et al., 2013; Mehta et al., 2015). Owing to population growth and industrial activities, the demand for these resources has recently increased significantly, leading to their scarcity (Ray et al., 2018). Only around 2.5% of Earth's water is fresh, and 97.5% is saltwater. As a large part of freshwater is either frozen or difficult to access, only 0.007% of Earth's water is accessible and available for direct use (Le and Nunes, 2016). Water pollution caused by industrial activities, oil exploration, mining and pesticide residue used in agriculture affects part of this freshwater (Le and Nunes, 2016). As a result, around 1.79 billion people live in areas with a high shortage of water, and this number is expected to increase to 3.59–6.22 billion by 2050 (Grafton, 2017). Water reclamation and reuse from municipal wastewater can help minimise the high demand for freshwater worldwide. For example, water recovery from municipal wastewater helped to supply around 25% of the potable water needed in the city of Windhoek in Namibia (Verstraete and Vlaeminck, 2011). In Chennai, India, 15% of the population's water demand was covered by reusing municipal wastewater (Kehrein and Garfí, 2020). Xi'an University in China reported that treatment of water from toilet flushing, gardening and landscaping helped reduce 50% of freshwater consumption on campus (Kehrein and Garfí, 2020).

Currently, the global energy problem is mainly related to the limited fossil energy supply and its environmental impacts: energy lifecycle, mining, emissions, waste disposal and recycling (Zhao et al., 2012). Developing sustainable technology that can gradually replace non-renewable fossil fuels is essential to solving these issues. Energy sustainability can be achieved by converting energy from natural and renewable resources (e.g. biomass and water) into useful energy (e.g. electricity) and energy storage systems for remote or long-term usage (Le and Nunes, 2016). For example, energy recovery from municipal wastewater can significantly save the total energy consumption of wastewater treatment plants (WWTPs). In fact, the chemical energy in typical sewage wastewater is five times higher than that needed for its treatment (Kehrein and Garfí, 2020).

Protecting downstream users from health hazards is the main reason for the treatment of wastewater (Kehrein and Garfí, 2020). In the past decades, nutrient pollution in the receiving water bodies (eutrophication) has been controlled with strict regulations to protect the natural and aquatic systems (Bloem et al., 2017). Therefore, technologies to remove phosphorus and nitrogen have been applied to WWTPs (Kehrein and Garfí, 2020). The conventional activated sludge (CAS) process is the most widespread technology used to achieve this target (Batstone and Virdis, 2014). Even though CAS treatment can meet the legal effluent standards for phosphorus and nitrogen, its low potential for resource recovery, high-energy demand, large footprint and high cost make this process unsustainable (Kehrein and Garfí, 2020). Recently, phosphorus demand has increased due to population growth (Qiu et al., 2015). After 2040, the production rate of economically available phosphorus reserves is expected to peak, and demand will exceed supply. Consequently, the depletion of rock phosphate reserves could occur in the next 50–100 years (Cordell et al., 2009; Desmidt et al., 2015). Thus, more attention has been paid to large-scale phosphorus recovery that is economically feasible. Municipal wastewater is considered one of the main sources to achieve this target, as the world demand for phosphate rock could be reduced by 20% by recovering phosphorus from municipal wastewater (Yuan et al., 2012). Furthermore, nutrient recovery from municipal wastewater not only reduces the speed of phosphorus depletion but also helps to save water and energy. Recovering nutrients decreases the demand for fossil-based fertilisers; therefore, the water and energy used to produce traditional fertilisers are conserved (Mo and Zhang, 2013).

Although different techniques have been adopted to recover nutrients, energy and water from municipal wastewater such as by digesting excess sludge, applying stabilised sludge to land and filtrating treated water by RO, the recovery efficiency is very low due to indirect resource recovery approaches used. If very diluted municipal wastewater could be concentrated cost-effectively, a direct recovery of nutrients by chemical precipitation, a direct energy recovery by anaerobic digestion with high COD at even mesophilic and thermophilic conditions and a recovery of water could be feasible easily and economically.

Many countries around the world consider desalination to be a sustainable water process, especially in the Middle East (Zhang et al., 2016). For example, the water supply in Kuwait and Qatar for industrial and domestic uses can be 100% satisfied through the desalination process (Le and Nunes, 2016). According to Markets (2020), the membrane market is estimated to increase from $5.4 billion in 2019 to $8.3 billion by 2024. Saudi Arabia, Brazil and India are expected to rank the highest in membrane consumption in the future. Several reasons can explain the rise of the membrane market, such as the shift from chemical to physical water treatment, strict regulations of water standards, population growth, rapid industrialisation and increasing awareness of wastewater reuse (Markets, 2020). With a high rejection of contaminants, the RO membrane is the widest membrane used in WWTPs (Voorthuizen et al., 2005; Holloway et al., 2007; Boo et al., 2013). However, pre-treatment prior to the use of RO membranes (e.g. nanofiltration) is required to control membrane fouling (Lutchmiah et al., 2014). Furthermore, the RO process is energy intensive, as hydraulic pressure is the driving force of RO (Lotfi et al., 2018). Desalination processes consume around 75.2 TWh per year, most of which are related to the RO process (Chaoui et al., 2019). Therefore, looking for advanced separation technologies that can concentrate organics and nutrients from municipal wastewater to facilitate their further recovery and achieve low fouling propensity and energy consumption is critical to develop a sustainable wastewater treatment process.

FO is a membrane separation technology that works without hydraulic pressure (Korenak et al., 2017). It transmits water from the FS, which is the side where the concentration of soluble substances is low, through a semi-permeable membrane to the DS, which is the side where the concentration of soluble substances is high (Nicoll, 2013). This movement, which takes place under the osmotic pressure gradient, happens spontaneously. The technology presents several benefits, including eliminating a high quantity of pollutants, producing high-quality permeate and conserving energy while producing low membrane fouling (Chaoui et al., 2019). Based on this concept, an innovative idea for the treatment of municipal wastewater has recently been proposed. Using this idea, the FO process is used to concentrate municipal wastewater before it is transmitted to the struvite or hydroxyapatite crystallisation or anaerobic reactor for the recovery of nutrients and the production of biogas (Yang et al., 2019). The use of FO requires another step in which the DS is reconcentrated and clean water is recovered (Wang et al., 2011). An external energy supply is needed for this second step. In the entire FO process with DS regeneration, separating the permeate water from the DS uses most of the required energy (Minier-Matar et al., 2016). Based on the regeneration method of this DS, this second step can be accomplished with the use of low-grade energy, which could also be renewable. An example of a technology that uses low-grade heat to facilitate separation MD. An amalgamation of FO and MD can be used to treat municipal wastewater and high-salinity water with a low consumption of energy (Husnain et al., 2015). Owing to the absence of applied hydraulic pressure, the fouling propensity of both FO and MD is expected to be lower than that of RO (Chaoui et al., 2019).

Even though the integrated FO-MD system has the potential for resources recovery application from municipal wastewater, there are still challenges to overcome. These include FO membrane fouling, how to enhance ammonium rejection by the TFC FO membrane, the ability of the MD membrane to reject ammonium in the DS, and temperature effects on the integrated FO-MD system.

## 1.2 Knowledge gaps

FO is still in the early stages of development, and several challenges need to be overcome to make concentration by FO membrane more viable and sufficient. Firstly, fouling is a crucial issue for all membrane processes, as it affects membrane performance. There was no clear investigation of the fouling and performance of the FO membrane to treat municipal wastewater by combining both nutrients and organics enrichment and water recovery at a higher rate (90%) that is required to achieve the desired concentrations of COD and phosphorus from low strength municipal wastewater to facilitate their subsequent recovery. In addition, most FO studies focused on the use of synthetic FS without suspended solids (SS) or filtered municipal wastewater in the plate and frame configuration as it is easy to install. Membrane configuration plays an important role in the FO system. Recently, the hollow fiber FO configuration has been developed and could offer potential advantages over plate and frame configuration such as higher packing density, lower manufacturing cost and better hydrodynamics conditions that can enhance the shear forces on the membrane surface (Minier-matar et al., 2016). Until now, there have been limited studies on the hollow fiber configuration due to manufacturing complexity. Thus, further research is required on the hollow fiber FO configuration to be compared with the plate and frame configuration in terms of membrane fouling. $Ca^{2+}$ is an essential factor that could cause inorganic fouling during the FO process. Lastly, comparing the up-concentration of synthetic wastewater with real wastewater by the TFC membrane in different FO configurations is lacking of study.

Secondly, most available studies to concentrate municipal wastewater in the FO process focused on using NaCl as the DS because it is highly soluble, non-toxic at low concentrations, and relatively easy to re-concentrate using conventional desalination processes. A higher diffusion of cations relative to anions for the TFC membranes than CTA membranes was reported, attributing this phenomenon to different surface charges of TFC and CTA membranes (Coday et al., 2013; Lu et al., 2014). As a result, several studies had reported that ammonium ($NH_4^+$) was not effectively rejected by the TFC membrane when NaCl was used as a DS in the FO process. The lower $NH_4^+$ rejection is attributed to bidirectional diffusion of $NH_4^+$of FS and $Na^+$ cations of DS (Arena et al., 2014; Hu et al., 2017). To further improve $NH_4^+$ rejection in the TFC FO membrane process, most researchers focused on improving the membrane properties. Whereas introducing another DS with different physiochemical properties could help to minimize cations exchange between FS and DS and enhance $NH_4^+$rejection by the TFC FO membrane filtration process. However, and to the best of the author's knowledge, no previous studies have evaluated the effect of different DSs types (ionic and non-ionic) with different physiochemical properties DS on ammonium rejection during the TFC FO filtration process.

Thirdly, most previous studies for FO and MD systems were operated separately without considering the effect of FS and DS temperatures on the FO process (DS replacement cost, fouling and contaminate rejection). Further study is needed to investigate whether the FS and DS temperatures will have different effects when using ionic and non-ionic DSs (i.e. NaCl and glucose). In addition, although that previous studies demonstrated the feasibility of the integrated FO-MD process for following resources recovery application, a heat balance is important to understand if internal heat recovery is necessary for the integrated FO-MD system.

## 1.3 Aim and objectives

This study aimed to investigate the performance of municipal wastewater treatment using TFC membrane based FO technology for the potential recovery of water, nutrients and energy in the downstream. To achieve this overall aim, the project was conducted with the specific objectives as shown below:

Objective 1: Investigate the technical aspects of concentrating municipal wastewater using TFC FO membrane filtration with a purpose for the downstream recovery of water, nutrients and energy.

Objective 2: Understand the effects of physiochemical properties of the DS on the rejection of pollutants especially ammonium cations contained in municipal wastewater to facilitate downstream water and nutrient recovery.

Objective 3: Examine the temperature effects of FS and DS on municipal wastewater treatment in an integrated FO-MD system for DS regeneration and water recovery and its implication on heat demand and the design of FO-MD systems.

## 1.4 Thesis structure and the correlation between different chapters

This thesis is structured as follows (Fig 1.1):

- Chapter 1 defines the research motivation, knowledge gaps, aim and objectives and significance and novelty of this research.
- Chapter 2 explains the current situation and problems during municipal wastewater treatment for a resources recovery application. In addition, the current technologies used for resources recovery and the state of the art of the FO and MD membranes with the focus on the treatment of municipal wastewater to identify the knowledge gaps are summarized in detail.
- Chapters 3 evaluates the ability of the selected TFC FO membrane to concentrate phosphate and COD in the FS at a high water recovery rate (90%). The effects of the selected FO membrane on the water flux, ammonium, $Ca^{2+}$, $Mg^{2+}$ and $K^{+}$ rejections, pH and membrane fouling of the concentrated FS are investigated. In addition, the effects of SS and $Ca^{2+}$ concentrations on TFC membrane fouling for resource recovery applications during the TFC FO filtration process are also studied. The efficiency of different membrane cleaning methods during synthetic and real municipal wastewater filtration is also investigated.
- Chapter 4 focuses on enhancing the poor ammonium rejection by the TFC FO membrane obtained from Chapter 3 by selecting the appropriate DS. The effect of FS chemistry using synthetic municipal wastewater, real municipal wastewater and sludge digestate on ammonium rejection is also investigated.
- Chapter 5 elucidates the temperature effects on the integrated FO-MD system. These include the key challenges presented in Chapters 3 and 4, such as water flux, reverse solute flux (RSF), membrane fouling and ammonium rejection. In addition, internal heat recovery is proposed to maximize the efficiency of the integrated FO-MD process.
- Chapter 6 presents the conclusions and recommendations for further research.

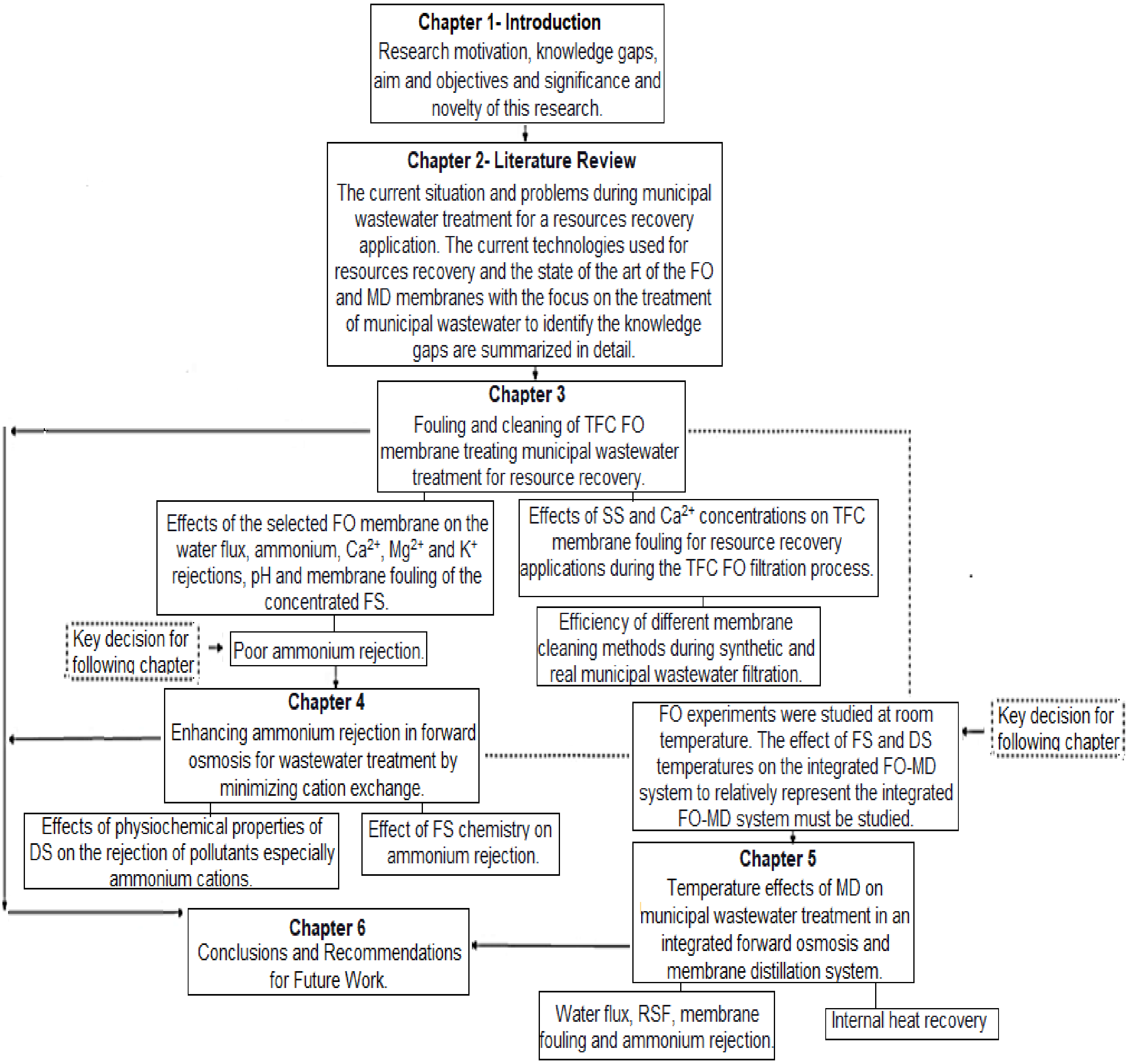

**Fig. 1.1.** Thesis structure.

## 1.5 Significance and novelty

The present study investigated FO membrane fouling in two configurations, i.e. flat sheet and hollow fiber, treating municipal wastewater with the purpose of resource recovery. In this case, the water recovery rate must be around 90%. How FO membrane fouling develops and how the membrane could be cleaned, how particle and inorganic precipitation contribute to fouling and affect cleaning under the high water recovery rate (i.e. 90%) have not to be studied so far. This study reports the results and conclusions on these research questions for the first time.

Forward ammonium diffusion to DS in TFC FO is still one of the barriers to real application. Significant efforts have been put to modify functional groups of the FO membrane surface from negative charge to positive charge to improve ammonium rejection, but the change in charge could cause other unfavourable consequences such as reduced anion rejection. The present study aims to develop an alternative but practical strategy to enhance ammonium rejection by selecting an appropriate DS based on the study of the mechanism of ammonium permeation. To the best of the author’s knowledge, the fourth chapter in the current study reports the enhancement of ammonium rejection for the first time by selecting DS based on physiochemical properties of chemicals and less possible cation exchange, which contributes to the criteria of DS selection. The findings in this study could also be used to develop or select more effective and cost-effective DS for wastewater treatment with ammonium rejection and recovery considered. Furthermore, the study sheds light on the mechanisms of FO for the rejection of small ions, which could be used to develop better FO membrane in future.

Thirdly, how the FS and DS temperatures affect the FO process in terms of membrane fouling and the rejection of nutrients and organic matter (COD) needs further investigation. In addition, as the volatility of ammonium increases with the increase in pH, temperature and ammonium concentrations in the DS (Vaneeckhaute et al., 2017; Bae et al., 2020), further research is still needed to understand the effect of the DS pH and ammonium concentration on ammonia vapour pressure to produce a clean water by the MD membrane. Results from this study can be used as guideline for the development of the integrated FO–MD system by understanding how the variation of FS and DS temperatures will have different effects on the FO process with different DSs, how the DS type and pH will affect ammonia vapour during the MD membrane filtration process and how the use of internal heat recovery helps to reduce the external heat demand for the integrated FO-MD process.

# Chapter 2: **Literature Review**

Different wastewater treatment processes have been used in order to minimize water pollution, such as chemical precipitation, enhanced biological phosphorus removal (EBPR) and membrane filtration. This chapter contains a literature review of the characteristics of municipal wastewater and the current state of resources recovery from municipal wastewater. A comparison of the advantages and disadvantages of each technology is listed. Moreover, the use of FO in wastewater is criticality evaluated, including the factors that affect the overall performance of this process. In addition, this chapter provides the state of art of the integrated FO- MD system for wastewater treatment.

## 2.1 Municipal wastewater characteristics

Wastewater from residential activities, such as human body wastes (urine and faeces), water for flushing toilets, personal washing, laundry and cleaning of kitchen utensils, is called municipal wastewater (Pelaz-Pérez, 2016). Table 2.1 shows the typical characteristics of municipal wastewater.

**Table 2.1:** Typical municipal wastewater composition (Metcalf and Eddy, 2008).

| Pollutant | Concentration (mg/L) | | |
|---|---|---|---|
| | Weak | Average | Strong |
| Total solids | 350 | 720 | 1200 |
| Total suspended solids (TSS) | 100 | 220 | 350 |
| Total dissolved solids (TDS) | 250 | 500 | 850 |
| Volatile suspended solids (VSS) | 80 | 165 | 275 |
| Volatile dissolved solids (VDS) | 105 | 200 | 325 |
| Ammonia nitrogen | 12 | 25 | 50 |
| Total nitrogen | 20 | 40 | 85 |
| Phosphorus | 4 | 8 | 15 |
| Oil and grease | 50 | 100 | 150 |
| Five-day biochemical oxygen demand | 110 | 220 | 400 |
| Chemical oxygen demand (COD) | 250 | 500 | 1000 |
| Total organic carbon | 80 | 160 | 290 |
| Alkalinity (as CaCO3) | 50 | 100 | 200 |
| Chlorides | 30 | 50 | 100 |
| Sulphate | 20 | 30 | 50 |

Treating municipal wastewater is important to avoid health hazards and environmental pollution (Ordóñez et al., 2014). As previously mentioned, nutrients are one of the main sources of eutrophication that adversely affect the receiving water bodies, and removing them from municipal wastewater is important (De-Bashan and Bashan, 2004; Zhu et al., 2021). As shown in Table 2.1, the phosphorus concentration is 4-15 mg/L, and the ammonia nitrogen concentration is 12-50 mg/L. The type of treatment process depends mainly on the effluent quality standards set by law. The European Water Framework Directive sets a maximum allowable effluent concentration of 1 mg/L (10.000–100.000 p.e.) for nitrogen and 2 mg/L (more than 100,000 p.e.) for phosphorus (Ye et al., 2017).

A major limitation that restricts resource recovery from municipal wastewater is the low concentrations of phosphorus, ammonium and organic matter. As shown in Fig. 2.1, the solids content of municipal wastewater is approximately 0.5%, which does not make nutrients and energy recovery economically applicable (Ansari, 2017). Therefore, nutrients and organic matter must be concentrated before they are recovered from municipal wastewater.

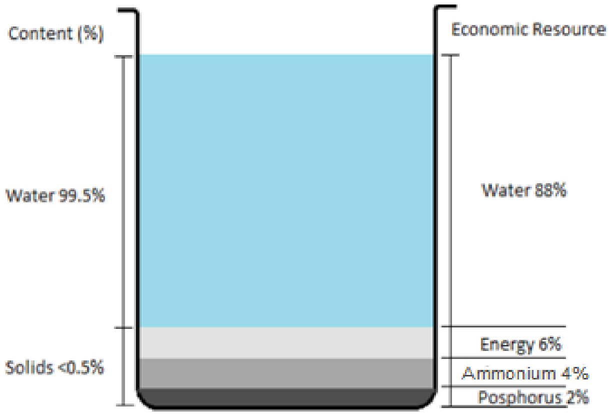

**Fig. 2.1.** Resource content and economic value of municipal wastewater (adapted from Ansari, 2017).

## 2.2 Recovering fresh water from municipal wastewater

The primary motivation for water reclamation is to produce the highest water quality to protect human health and avoid operational risks. Among the different wastewater treatment technologies, membrane processes have the advantage of meeting the effluent standards for municipal WWTPs (Ordóñez et al., 2014). Several membrane processes, such as nanofiltration and RO, can effectively recover water from waste streams. However, they are limited by membrane fouling and high energy demand (Mehta et al., 2015). FO is a novel membrane separation process that is gaining increasing interest. Not only is FO a high rejection process, it can also effectively concentrate nutrient and organic contents in the waste stream effluent, providing a favourable condition for subsequent recovery (Ansari et al., 2017). In the FO system, the membrane is placed between two solutions: FS and DS. As the DS has a much higher concentration of solutes than the FS, the osmotic pressure difference across the membrane naturally moves the water from the FS to the DS (Fig. 2.2) (Zhang et al., 2014a; Rayet al., 2018; Zhu et al., 2021).

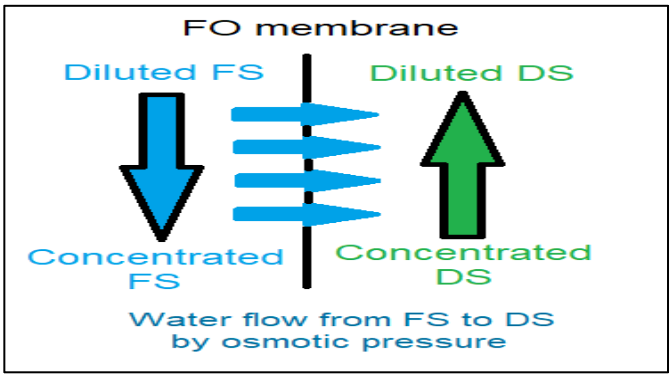

**Fig. 2.2.** Water extraction in the FO filtration process.

In comparison with other membrane processes, FO has the following main advantages (Nguyen et al., 2016; Ansari, 2017; García, 2018; Nascimento et al., 2018; Ray et al., 2018):

1) Lower fouling propensity (Fig. 2.3).
2) Lower energy consumption as water moves to the highly concentrated solution through osmotic pressure (Fig. 2.4).
3) Longer lifespan of the membrane.

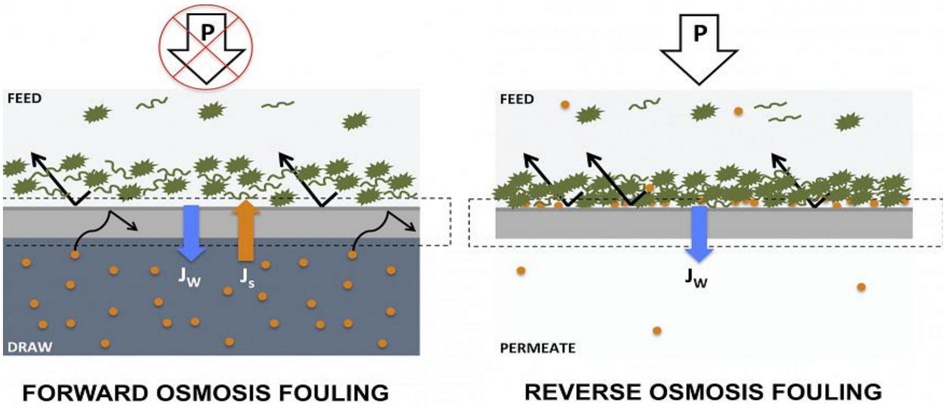

**Fig. 2.3.** Membrane fouling in the FO and RO processes (adapted from Perry, 2014).

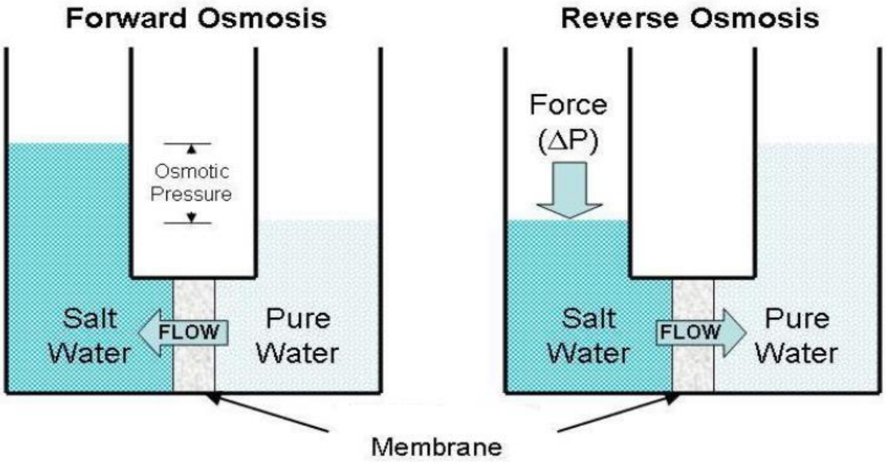

**Fig. 2.4.** Schematic diagrams of the FO process illustrating the direction of water flux in the FO and RO systems (adapted from Muzhingi, 2016).

Siddiqui et al. (2018) compared the fouling behaviour between FO and the RO processes at the same initial water flux of 18 L/m$^2$·hr by using 200 mg/L alginate, 45 mM NaCl and 5 mM $CaCl_2$ as FS. The results from the comparison showed that although the FO and RO had similar water flux decline during fouling tests, the FO foulant resistance was found to be greater than RO. These results suggest that the water flux stability against fouling for the FO membrane is better than the RO membrane. Another study by Field et al. (2021) focused on fouling and cleaning both FO and RO membranes by using 200 mg/L alginate, 45 mM NaCl and 5 mM$CaCl_2$ as FS. After 1000 min of filtration, the normalized water flux of the FO membrane was 17.34% greater than the RO membrane. After membrane flushing, the initial water flux recovered for the FO membrane was 99.89% greater than 83.78% for the RO membrane. These results indicated that the FO membrane was less sensitive to fouling than the RO membrane. Notwithstanding the several benefits for the FO process, large scale implementation is hampered by a lack of economic feasibility analysis and proper membranes, which constitute the primary conditions for commercial success (Zarebska-Mølgaard et al., 2021). Moreover, there are current limitations regarding developing a large-scale operational process because of the dearth of appropriate DS. The leading problem in developing a suitable DS is their separation and reclamation from the product water, particularly for applications involving drinking water. It is important that the recovery process is not expensive or consumes high amounts of energy. If that were the case, the advantages of the FO process in comparison to other membrane technologies like RO would not be realised (Shon et al., 2015).

FO must be integrated with another filtration process (e.g. RO or MD) to recover fresh water from the DS and to re-concentrate the diluted DS (Husnain et al., 2015; Xie, 2015). For more sustainable desalination technology, MD is the most favourable process that can be integrated successfully with the FO process (Wang, 2018). In the MD non-isothermal membrane process, thermal energy is used to provide a vapour phase of volatile molecules on the feed side and condensing the permeated vapour on the other side. Thus, the driving force in the MD process is the temperature difference between the feed and permeate sides (Shirazi and Kargari, 2015). The low-grade heat (e.g. waste heat or solar heat) can be used in MD processes for an economical and energy-efficient desalination process (Xie et al., 2013a; Husnain et al., 2015). In comparison with the RO process, the MD has the following advantages (Husnain et al., 2015; Wang, 2018):

1- MD has lower energy consumption than RO.
2- Membrane fouling is lower than RO.
3- MD has high rejection factors.

Membrane fouling is a severe problem for stand-alone MD processes. However, when integrating FO and MD into a single system, FO helps to reduce membrane fouling in the MD process by removing substances from the FS (Husnain et al., 2015).

Although the integrated FO-MD is a promising technology for resources recovery from municipal wastewater, there are challenges as well to overcome:

1- The FO membrane fouling.
2- Ammonium rejection by the TFC FO membrane.
3- Effect of operating temperatures on the integrated FO process (i.e. FO–MD).

Each of these challenges is discussed in the following sections.

## 2.3 Nutrient recovery from municipal wastewater

Nutrient recovery from municipal wastewater not only controls eutrophication but also reduces the speed of phosphorus depletion (Tran et al., 2014). For economic reasons, phosphorus recovery from municipal wastewater is now practised only in a few WWTPs in developed countries. Experts expect that recovering phosphorus from municipal wastewater will be widely practised in industrialised countries over the next 20 years (Sartorius et al., 2012).

Phosphorus recovery provides many advantages to the environment and society. For example, recovering phosphorus from wastewater or sewage sludge can potentially help control eutrophication and provide a source of fertiliser (Kumar and Pal, 2015). Additionally, phosphorus recovery from wastewater reduces the clogging problem in pumps and pipes (Tarayre et al., 2016). To recover phosphorus from municipal wastewater, phosphorus has to be pre-concentrated or transformed from a liquid to a solid phase (Mayer et al., 2016). Chemical precipitation is the most popular technology used to remove phosphorus from wastewater due to its high removal efficiency, which meets the discharge standard (Melia et al., 2017). Conversely, EBPR is the most environmentally friendly technology for the luxury uptake of phosphorus to sludge under aerobic conditions; it releases phosphorus to liquid during anaerobic digestion (AD) to facilitate struvite precipitation for nutrient recovery (Manyumba et al., 2009). When the phosphorus concentration in wastewater is high, chemical precipitation is considered more efficient (Melia et al., 2017). Therefore, chemical precipitation is preferred to EBPR when strict effluent regulations are enforced on WWTPs (Nancharaiah et al., 2016). However, chemical precipitation technology has two main disadvantages: the cost and requirement of chemical additions and the generation of huge volumes of sludge that are unsuitable for reuse (Melia et al., 2017). Furthermore, phosphorus in aluminium-P and ferric-P solids is considered unrecoverable for possible industrial processing into fertiliser (De-Bashan and Bashan, 2004; Melia et al., 2017).

Currently, EBPR processes provide the pre-accumulation of phosphorus required in most full-scale phosphorus recovery technologies. In the EBPR process, the anaerobic process is the first step where the organisms in the wastewater or activated sludge hydrolyze polyphosphates and release phosphorus from cells in the form of orthophosphates, absorbing simple organic compounds from the environment and storing them in the form of poly-b-hydroxybutylic acid. Following the previous step, the wastewater or activated sludge go into an aerobic process, where the bacteria which have the ability to store larger amounts of phosphorus that is necessary for their physiological needs begin to retain phosphorus in the form of polyphosphate (Egle et al., 2016; Cieślik and Konieczka, 2017). EBPR processes can typically remove up to 85% of phosphorus in municipal wastewater influents (Ramasahayam et al., 2014). Compared to chemical precipitation, EBPR is considered more sustainable and can offer significant economic advantages for large WWTPs (Manyumba et al., 2009). With less or no chemical addition, EBPR has the potential for full-scale phosphorus recovery (Melia et al., 2017). However, when legislation requires low phosphorus concentrations in effluent discharge, chemical precipitation is coupled with EBPR to ensure that effluent requirements are met (Kim and Chung, 2014). EBPR must be installed and operated for subsequent struvite formation. Approximately 20% of European WWTPs use EBPR for phosphorus removal, considerably limiting the application of struvite recovery technology (Bluetech Research, 2015). Additionally, EBPR has complex operations and large space and energy requirements (Melia et al., 2017).

For an economic struvite recovery, the phosphorus concentration should be more than 50 mg/L in the wastewater influent (Qiu et al., 2015). The liquid effluent produced from anaerobically digested sludge is a promising opportunity for nutrient recovery in WWTPs. However, it is still insufficient to provide an economically viable recovery (Ansari et al., 2017). Currently, chemical precipitation using magnesium and calcium ions is the most widely used process to recover phosphorus from wastewater because of its high stability and efficiency (De-Bashan and Bashan, 2004; Corre *et al.*, 2009). Magnesium and calcium react with phosphate to form struvite and hydroxyapatite, respectively. The recovered struvite can be directly applied in agriculture, while hydroxyapatite can be used in the phosphate industry (Ye et al., 2017). However, as the recovered phosphate comes directly from sewage sludge, there is a risk of introducing hazardous organic pollutants or pathogens. Thus, further treatment processes may still be needed for the obtained materials (Cieślik and Konieczka, 2017). Another way to recover phosphorus is through the direct use of sewage sludge as a fertiliser. However, it may affect the food supply by introducing chemical and biological contaminants into the environment. Moreover, a huge amount of sewage sludge must be transported, which is very costly (Melia et al., 2017).

Recently, phosphorus recovery from thermo-chemical applications has gained wide interest. The incineration of sewage sludge at a temperature below 700°C results in ash-rich residue with phosphate, which can be applied to the struvite recovery process (Yuan et al., 2012). However, the presence of other elements, such as copper, mercury, aluminium and iron, requires further pre-treatments (mechanical, thermal and chemical) for phosphorus separation (Mehta et al., 2015). As a result, the direct use of sewage sludge ash as a fertiliser is limited. From an economic point of view, note that phosphorus recovery through a thermo-chemical application can only be operated on a large scale WWTPs (Kataki et al., 2016; Melia et al., 2017).

For a cost-effective recovery of nitrogen as ammonium from wastewater through struvite precipitation or ion exchange, $NH_4$-N concentration must be more than 5 g/L in the influent (Deng et al., 2021). However, municipal wastewater contains less than 0.50 g $NH_4$-N/L.

Therefore, it is more feasible to use nitrification/denitrification processes to remove nitrogen from wastewater (Ansari, 2017).

Recently, special attention has been paid to emerging osmotically driven membrane processes (e.g. FO), which have a high rejection of contaminant solids and the ability to enrich nutrients for subsequent recovery (Gao et al., 2018; Xiao et al., 2018; Kumar et al., 2019). Qiu et al. (2015) reported that phosphorus could be directly recovered from municipal wastewater by combining a microfiltration (MF) membrane within an osmotic membrane bioreactor (OMBR) in the form of calcium phosphate using brine as a DS. Although that previous studies showed the ability of the FO membrane to concentrate phosphorus from municipal wastewater for following recovery by struvite or hydroxyapatite precipitation (Qiu et al., 2015; Xue et al., 2015; Wang et al., 2016; Ansari et al., 2017), however, membrane fouling and the low ammonium rejection in the TFC FO membrane are still issues that need further study.

## 2.4 Energy recovery from municipal wastewater

As mentioned in Chapter 1, treating municipal wastewater to meet statutory standards is energy intensive. The energy demand for WWTPs is expected to increase in the future due to population growth and effluent requirements (Stillwell et al., 2010). AD is the most effective technology used to recover energy from WWTPs (Batstone and Virdis, 2014). Additionally, AD not only recovers energy by producing methane-rich biogas but also addresses the sludge management requirements in WWTPs (about 50% of the total operating cost) (Ansari, 2017). However, producing biogas from municipal wastewater through AD is feasibly ineffective due to the low organic matter concentration (Zhang et al., 2014b). Pre-treatments, such as FO, that concentrate the organic content in municipal wastewater are necessary to increase the overall energy recovery in the AD (Verstraete et al., 2009). As shown in Fig. 2.5, the biogas produced from the AD can be used to supply the energy requirements of the proposed integrated FO system. Moreover, anaerobic treatment enhances the chemical availability of phosphorus and ammonium for subsequent recovery.

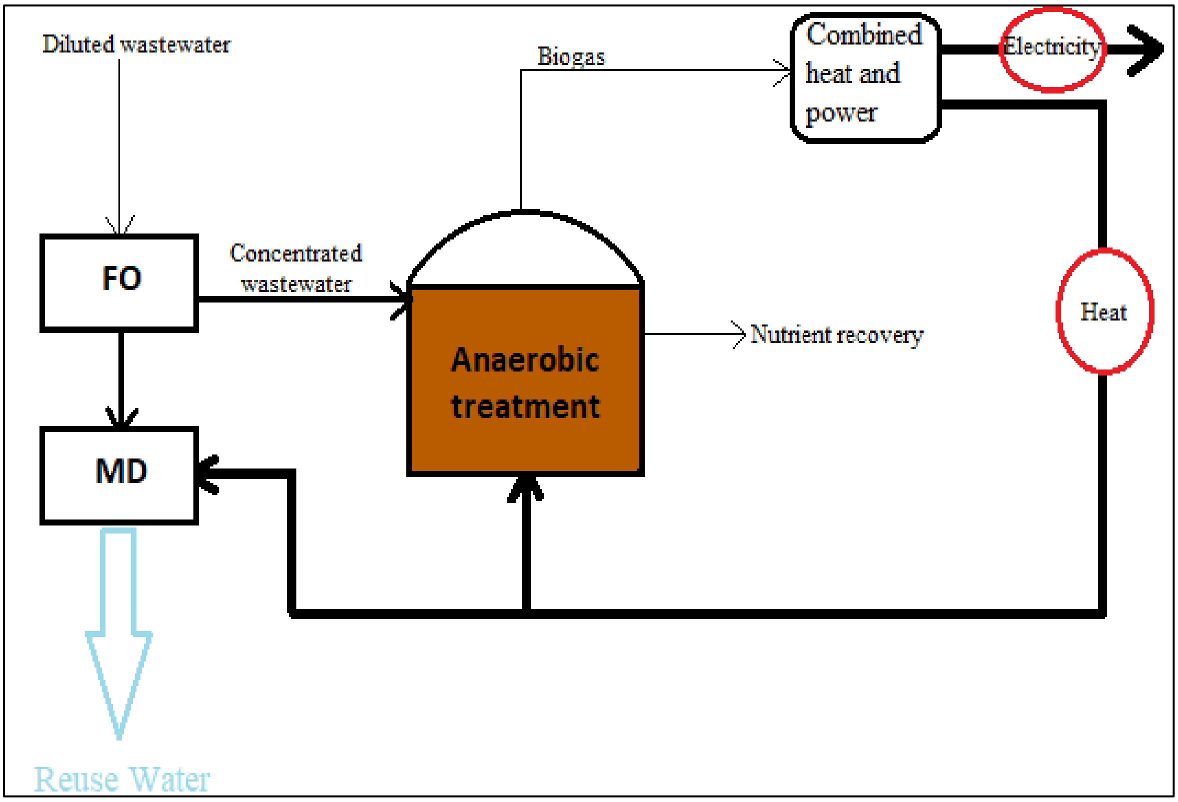

**Fig. 2.5.** Schematic of the integrated FO–MD system for energy and nutrient recovery through anaerobic treatment.

## 2.5 FO for wastewater

Recently, FO has gained much interest as an emerging desalination process. The concept of the FO process using an osmotic pressure difference as the driving force has led to a reduction in energy consumption. FO has better membrane fouling resistance than other membrane processes (Xie et al., 2014). In addition, the ability of FO to reject emerging substances, pathogens, saline water and total dissolved solids from complex solutions has been reported (Lutchmiah et al., 2014). FO is still in the early stage of development, with fewer than 420 publications published in 2021 (Fig. 2.6). The data in Fig 2.6 clearly show that the FO process has gained much attention recently for the advancement of water treatment and desalination (Ray et al., 2018).

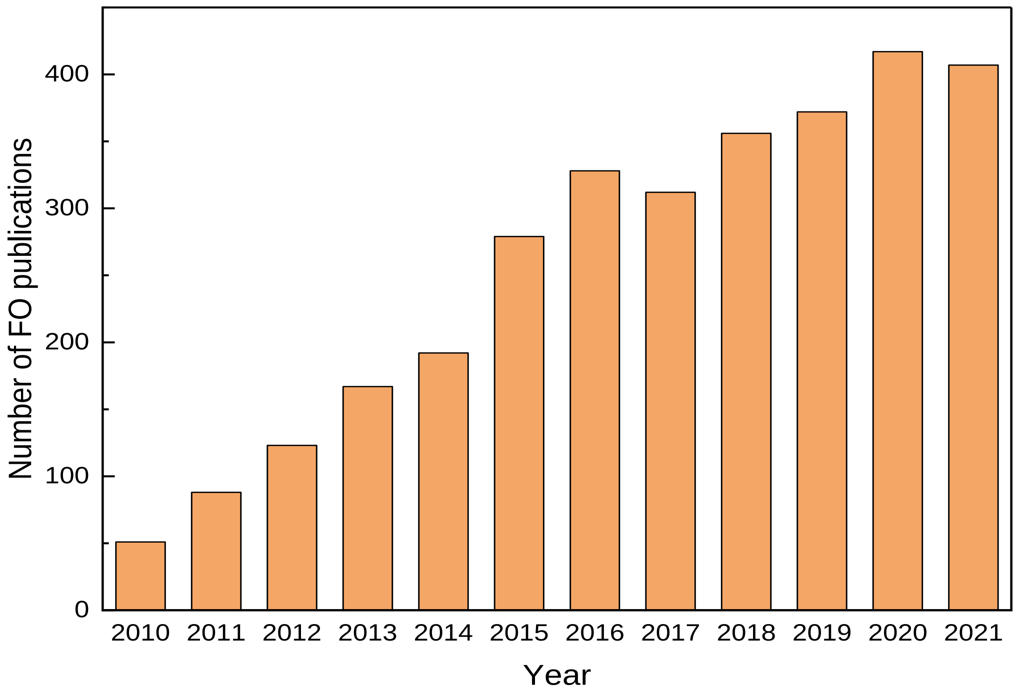

**Fig. 2.6.** Publications related to FO from 2010 to 2021 (numbers of the FO publications were extracted from Scopus).

During the FO process, the water transport is driven by an osmotic pressure difference between the FS and DS across a semipermeable membrane. The water flux ($Jw$) can be expressed using the following equation:

$$Jw = A\ (\pi_{D,b} - \pi_{F,b}) \qquad \text{Equation 2.1}$$

where A is the water permeability coefficient of the membrane (L/m$^2$·hr.bar), $\pi_{D,b}$ is the bulk osmotic pressure of the DS (bar) and $\pi_{F,b}$ is the bulk osmotic pressure of the FS. This equation assumes that an ideal membrane is used whereby the DS does not reverse to the FS, as well as the existence of an ideal osmotic pressure gradient between both sides of the FO membrane. Other factors such as concentration polarization (CP), RSF and membrane fouling contribute to the lower water flux than expected water flux behaviour observed during FO operation (Ansari et al., 2017).

In comparison with conventional wastewater treatment (Fig. 2.7), the proposed FO–MD process requires much lower energy (Fig. 2.8). In addition, the FO–MD process not only focuses on water recovery but also facilitates nutrient and energy recovery.

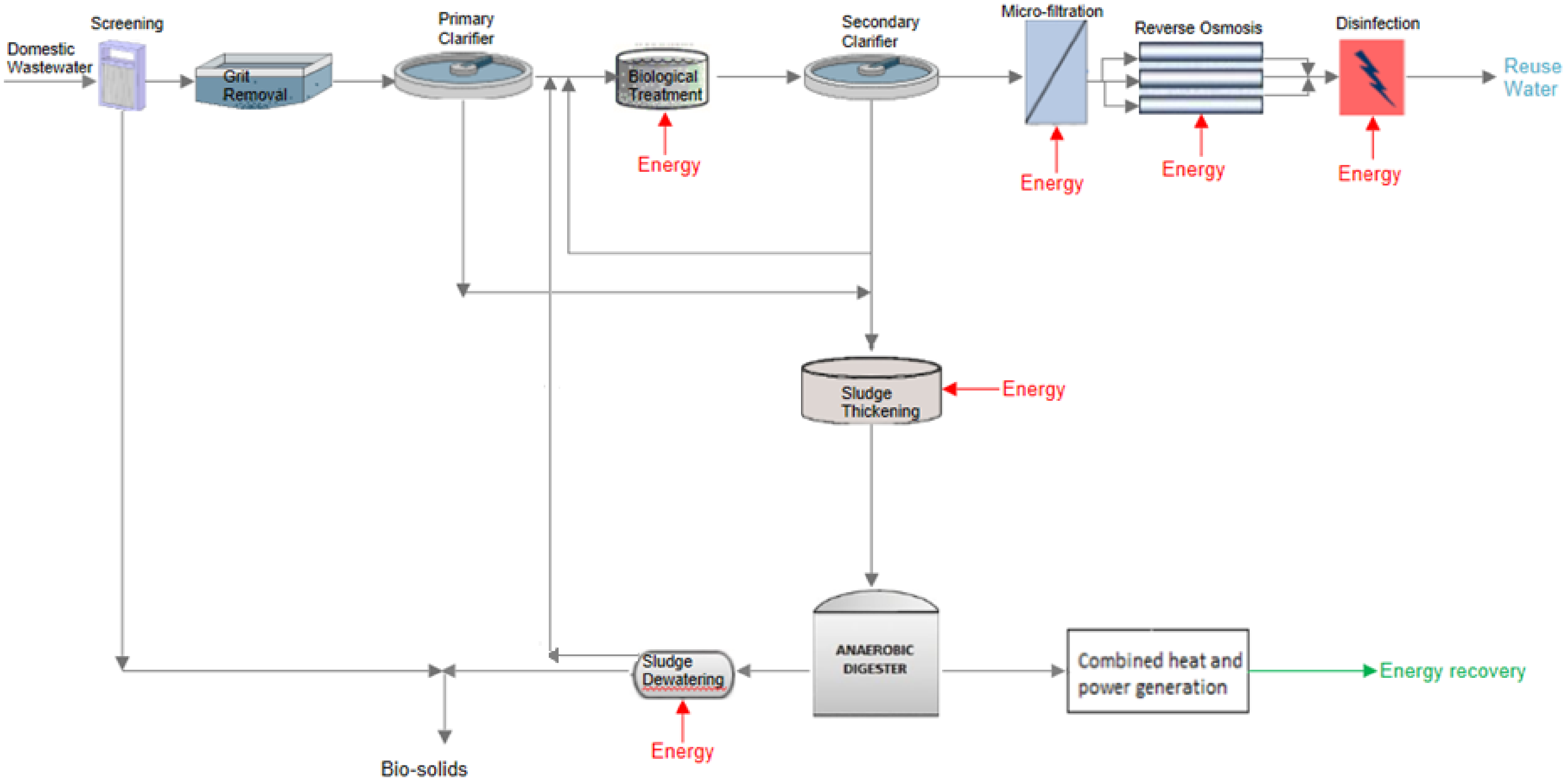

**Fig. 2.7.** Conventional wastewater treatment plants consume significant energy and do not effectively manage nutrients (adapted from Verstraete and Vlaeminck, 2011) .

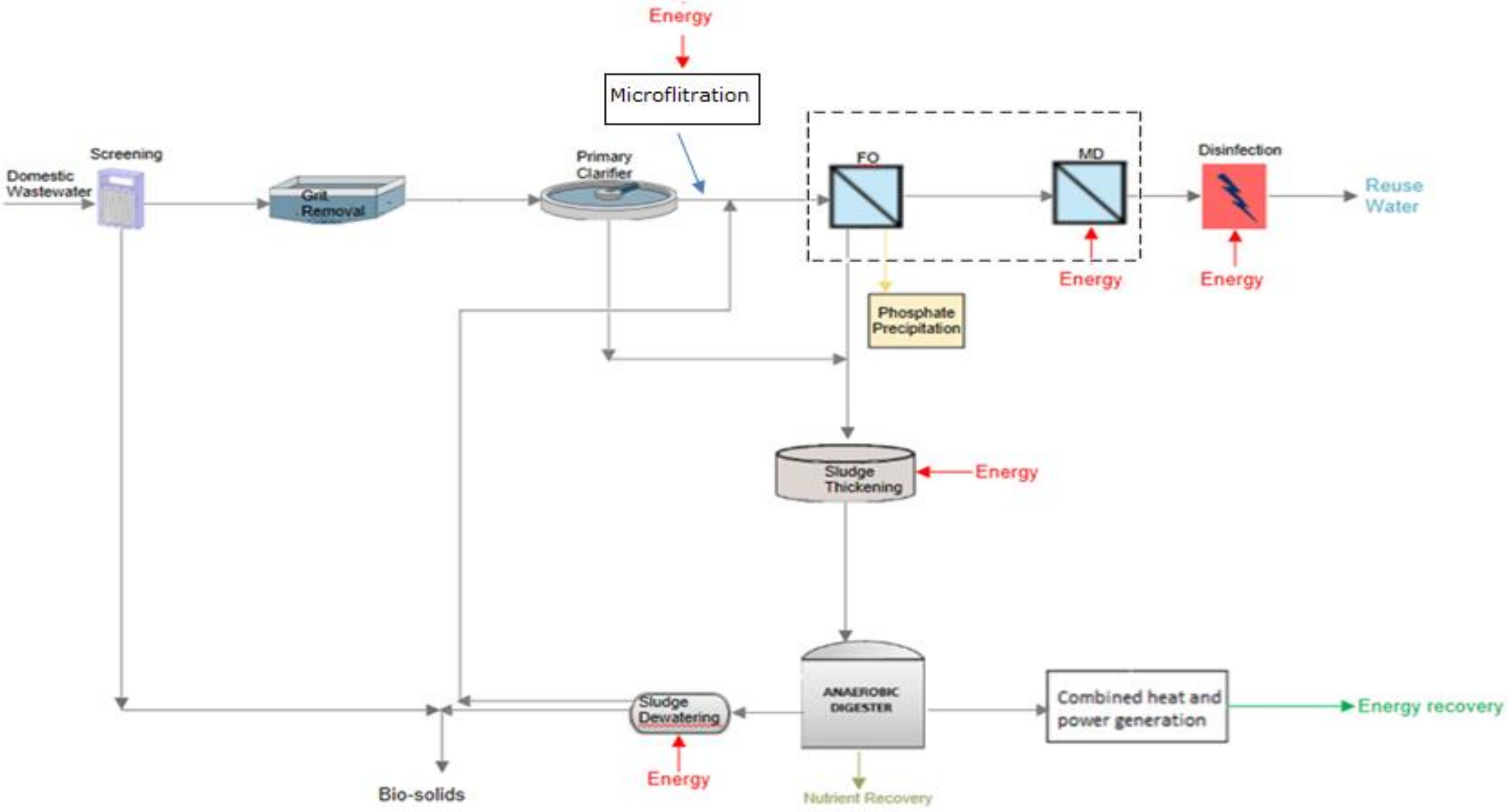

**Fig. 2.8.** The proposed FO–MD process consumes less energy and facilitates nutrient and energy recovery.

## 2.6 Factors affecting the FO process

It is important to understand the factors affecting the FO process's performance. This process is affected by several factors, such as membrane properties, membrane configuration, DS properties, CP, membrane fouling and process conditions (Mamisaheby et al., 2012; Lutchmiah et al., 2014). Each factor will be described in the following subsections.

### 2.6.1 Membrane properties

Feed solute transport and water permeability are highly related to membrane properties (Xue et al., 2015). A typical FO membrane material must have a better water flux, be appropriate to the selected DS, and be able to tolerate different operating conditions (e.g. pH and temperature) (Xie et al., 2014). The most widely used membrane fabricated for the FO process is asymmetric porous membranes. The thickness of the dense or active layer in the asymmetric membrane is 0.1–1 μm, while the support layer thickness is 100–200 μm. The narrow pores of the selective layer FO membranes (i.e. 0.4-1 nm) are designed to transport water from the FS to the DS and reject containments and solutes in the feed and draw solutions. At the same time, the support layer provides the mechanical strength for the selective layer of the FO membrane, which is also designed to reject containments and solutes in the feed and draw solutions (Arslan et al., 2018). The ideal FO membranes require specific criteria: high water flux, solute rejection, mechanical strength and chemical stability and low concentration polarisation (Cath et al., 2006). Other factors such as the surface charge of the membrane, membrane hydrophilicity and roughness, and the support layer thickness and tortuosity also affect the performance of the FO membrane (Zheng et al., 2015; Wang and Liu, 2021). Normally, the FO membranes are negatively charged, which impacts the retention of contaminants by electrostatic interactions. The anti-pollution performance could be improved by increasing the membrane's hydrophilicity. Moreover, the FO membrane's hydrophilic layer improves the water flux and lowers the internal concentration polarization (ICP) through adding the support layer's porous wettability. The membrane's roughness could have an impact on the membrane fouling because it is easy for the foulants to deposit on the rough membrane surface. The support layer's tortuosity and thickness could also impact the performance of the FO by affecting CP. It is on this basis that it is posited that optimising the support layer's structure parameters could play an important role in the reduction of the CP, improving the efficiency of the membrane (Wang and Liu, 2021).

The asymmetric structure of FO membranes allows for two options for membrane orientation (Zhao et al., 2022):

1- Active layer facing FS (AL-FS) mode.
2- Active layer facing DS (AL-DS) mode.

The selected orientation significantly affects the FO process in terms of flux behaviour and membrane fouling (Tiraferri et al., 2011). A larger water flux can be obtained when operating the FO process in the AL-DS mode as the DS is in contact with the active layer and is therefore not affected as severely by the ICP. However, membrane fouling in the AL-DS mode is more prominent, as the support layer is in contact with the FS (Arslan et al., 2018; Zhao et al., 2022). As a result, the AL-FS mode is widely used for wastewater applications (Ansari, 2017). For this reason, the AL-FS mode was applied exclusively in the current study.

The widest membranes used and examined in the FO process are cellulose triacetate (CTA) membranes (Lutchmiah et al., 2014; Eyvaz et al., 2018). However, the relatively low water flux and salt rejection of CTA membranes limit their use in the FO process (Comas and Blandin, 2017). Recently, TFC membranes have devolved and have been preferred to CTA membranes because of their higher water permeability and greater pH tolerance (Klaysom et al., 2013; Wang et al., 2015a). A lab-scale experiment by Comas and Blandin (2017) reported that the TFC membrane had a higher water flux and better reverse salt diffusion than the CTA membrane. Corzo et al. (2017) also confirmed that the TFC membrane had a higher water flux and salt rejection than the CTA. Conversely, previous studies showed that the use of the TFC membrane in the FO process resulted in a greater fouling tendency than the CTA membrane (Muna et al., 2016; Li et al., 2018). Table 2.2 shows the comparison between the CTA and TFC FO membranes with regard to water permeability, rejection, membrane fouling and chemical and biological stability.

**Table 2.2:** Comparison in the performance and properties of CTA and TFC FO membranes (Vu et al., 2019).

| Parameters | CTA | TFC |
|---|---|---|
| Water permeability | Low | High |
| Rejection | Low | High |
| Membrane fouling | Lower fouling propensity | Higher fouling tendency |
| Chemical stability | Highly resistant to chlorine<br>A narrow range of pH tolerance (3–8) | Stability at broad pH values (2-12) Sensitive to chlorine |
| Biological stability | High biodegradable tendency | Low biodegradable propensity |

Currently, several companies are manufacturing FO membranes, the status of which is either pre-commercial or under development, as shown in Table 2.3 (Nicoll, 2013).

**Table 2.3:** Commercial status of FO membranes (Nicoll, 2013).

| Company | Country | Membrane type | Status |
|---|---|---|---|
| GKSS | Germany | TFC | Development |
| Oasys Water | USA | TFC | Pre-commercial |
| Porifera | USA | TFC | Pre-commercial |
| Toray | Korea | TFC | Development |
| Toyobo | Japan | CTA | Pre-commercial |
| Woojgin-CSM | Korea | TFC | Development |

Most researchers reported that the fouling of TFC FO membranes could simply be cleaned using physical cleaning methods with a single or few inorganic, organic and colloidal foulants (Mi and Elimelech, 2010; Yu et al., 2017; Xiao et al., 2018, Minier-Matar et al., 2016; Wang et al., 2016; Gao et al., 2018; Yang et al., 2019, Pramanik et al., 2019). However, there is a lack of study on the use of complex and real wastewater to examine the TFC membrane fouling and the effectiveness of different cleaning methods to recover the initial water flux.

### 2.6.2 Membrane configurations

Several membrane configurations have been developed in the last decade for the FO process, such as plate and frame, hollow fiber and spiral wound configurations (Fig. 2.9).

The plate and frame module is the simplest configuration, consisting of two end plates, a flat sheet membrane and spacers. The hollow fiber modules used for seawater desalination consist of bundles of hollow fibers in a pressure vessel. The spiral wound module is the most popular for nanofiltration or RO (El-ghaffar and Tieama, 2017). The choice of membrane configuration module depends on several factors, such as cost, fabrication simplicity in the module design and fouling severity. Table 2.4 summarises some of the advantages and disadvantages of each configuration (Lutchmiah et al., 2014).

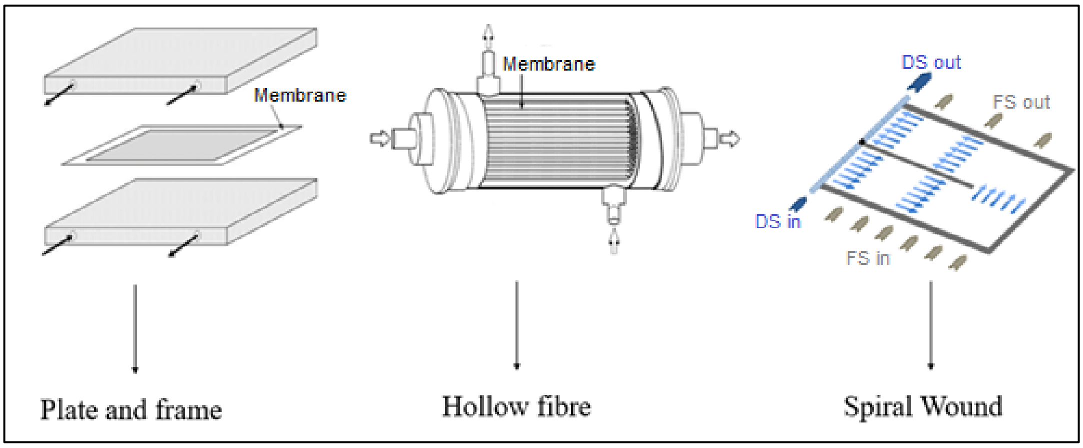

**Fig. 2.9.** Schematic representation of FO membrane configurations.

**Table 2.4:** Advantages and disadvantages of FO configurations (Lutchmiah et al., 2014; Minier-Matar et al., 2016).

| Configuration | Advantages | Disadvantages |
|---|---|---|
| Plate and frame | 1- Appropriate for wastewater applications.<br>2- Less complicated in design.<br>3- Better backwashing.<br>4- High cross-flow velocities. | 1- More expensive per $m^2$ of membrane area. |
| Hollow fiber | 1- High packing density.<br>2- Self-supported membranes eliminate the need for spacers, lowering manufacturing cost.<br>3- The fouling deposits can be easily cleaned. | 1- Clogging problems. |
| Spiral-wound | 1- Suitable flow patterns.<br>2- High packing density. | 1- Slow mixing on the membrane surface. |

Most FO applications use the plate and frame configuration because it is easy to install and commercially available (Minier-Matar et al., 2016). Although the hollow fiber FO configuration offers potential advantages over other configurations, there are limited commercial hollow fiber membranes available that can be used for the FO system. Private companies are largely focused on the flat sheet membranes. This indicates the need for further research on the hollow fiber FO before applying it to a large-scale module.

### 2.6.3 DS properties

An appropriate DS must be chosen to improve the overall FO process performance and save costs for subsequent DS recovery and replenishment (Ge et al., 2013). In addition, osmotic pressure is highly related to DS characteristics (Lutchmiah et al., 2014). Therefore, the following criteria must be met when selecting a DS (Ge et al., 2013; Xie et al., 2014; Nguyen et al., 2018; Wu et al., 2022):

1) Must produce high osmotic pressure to increase the water flux.
2) Lower RSF.
3) Consumes less energy during reclamation recovery to reduce the operation cost.
4) Non-toxic.
5) Highly soluble.

The physical and chemical characteristics of the DS are important for the selection of the ideal DS. Table 2.5 summarises the effect of different DS parameters on the FO process.

**Table 2.5:** Effects of DS characteristics on the FO process (Yasukawa et al., 2015; Sreedhar et al., 2018).

| Parameter | Effect on the FO process |
|---|---|
| Molecular weight and viscosity | A DS with a smaller molecular weight and lower viscosity leads to higher diffusion coefficient and therefore a higher water flux. |
| | A DS with a higher molecular weight and viscosity decreases the diffusion coefficient in the aqueous solution. However, these properties have the advantage of having a lower RSF. |
| Osmotic pressure | A DS that can generate a higher osmotic pressure at a lower concentration is desirable for a better FO process. |
| Solubility | A DS with a high solubility in water can produce a high osmotic pressure and facilitate the DS recovery. |

The search for the ideal DS was studied intensively in the past decades. Qiu et al. (2015) reported laboratory-scale experiments for direct phosphorus recovery from municipal wastewater by using a hybrid microfiltration-forward osmosis membrane bioreactor (MF-FOMBR), using seawater brine as the DS. The nutrient rejection efficiency of the CTA membrane was more than 90% at pH 9. As a result, the nutrient was enriched in the bioreactor, leading to the recovery of phosphorus without any chemical addition. However, salinity accumulation in the bioreactor remains the main challenge. Another lab-scale experiment by Ansari et al. (2016) demonstrated recovery of up to 92% of the initial phosphate concentration as calcium phosphate from digested sludge centrate using an FO membrane without chemical addition. CTA was the membrane used in this study, and the DS was seawater. However, another DS with a lower RSF and a higher osmotic pressure is desirable. In previous studies, inorganic salts were investigated as possible DSs in the FO process because they their availability, low cost and could potentially create high osmotic pressure at lower concentrations. However, the low charge and small hydrated radius of the monovalent ions in the DS (e.g. NaCl)  could result in a high RSF (Trung et al., 2017). In Chen et al. (2014) study, batch experiments involving a submerged anaerobic membrane bioreactor with forward osmosis membrane (FO-AnMBR) were conducted to treat low-strength wastewater using 0.5 M NaCl as the DS. The FO-AnMBR was found to have higher removal efficiency (phosphorus, organic carbon and ammonia nitrogen) than the conventional anaerobic membrane bioreactor. However, it was not suitable for long-term operation, as the CTA membrane had a low tolerance to biological attachment and high solution temperatures. Moreover, the salinity effects on the process remained a significant challenge. The lab-scale experiment of Gao et al. (2018) on FO with a direct concentration of municipal wastewater used NaCl as the DS at different concentrations. Membrane fouling and flux were found to increase when the DS was increased. Some studies on FO processes with different DSs are summarised in Table 2.6.

**Table 2.6:** Summary of different DSs used in the FO process for wastewater treatment.

| Feed solution | Draw solution | Membrane module | Draw solution recovery | Membrane configuration | Performance | Ref |
|---|---|---|---|---|---|---|
| Municipal wastewater | Seawater brine | CTA | Conductivity controller | Plate and frame | COD removal = 90%<br>Phosphate removal = 98% | (Qiu et al., 2015) |
| Low-strength wastewater treatment | 0.5 M NaCl | CTA | Conductivity controller | Plate and frame | COD removal = 96.7%<br>Phosphate removal = 100%<br>Ammonia nitrogen removal = 62% | (Chen et al., 2014) |
| Domestic wastewater | Ethylenediaminetetraacetic acid disodium | CTA | MD membrane | Plate and frame | Phosphate removal = 99.7% | (Nguyen et al., 2016) |
| Digested sludge centrate | Seawater | CTA | A large DS-to-FS volume ratio | Plate and frame | Phosphate removal = 92% | (Ansari et al., 2016a) |
| Secondary treated effluent and sewage | 1.5 M $MgCl_2$ | CTA | Conductivity controller | Plate and frame | Phosphate removal = 97% | (Xie, 2015) |
| Low-strength municipal wastewater | 0.5 M NaCl | CTA | Conductivity controller | Spiral wound | COD removal = 99.8%<br>Phosphate removal = 99.7%<br>Ammonia nitrogen removal = 48.1% | (Wang et al., 2016) |
| Low- and moderate-strength wastewater | 1.27 M NaCl | CTA | Conductivity controller | Plate and frame | COD removal = 100% | (Ansari, 2017) |

**Table 2.6:** Summary of different DSs used in the FO process for wastewater treatment.

| | | | | | | |
|---|---|---|---|---|---|---|
| Effluent following primary sedimentation | 3 M NaCl | CTA | Conductivity controller | Plate and frame | TOC = 94.3%<br>Phosphate removal = 98.6%<br>Ammonia nitrogen removal = 88.3% | (Ansari, 2017) |
| Digester centrate | Seawater | TFC | Conductivity controller | Plate and frame | Phosphate removal = >99% | (Kedwell et al., 2018) |
| Synthetic domestic wastewater | 0.5 NaCl | TFC | Conductivity controller | Plate and frame | Ammonia was not rejected | (Hu et al., 2017) |

Sugar DSs have also been used as a DS in FO processes. Kravath and Davis (1975) investigated the use of glucose as a DS in the FO process for the desalination of seawater. As the diluted DS could be used safely, recovering the DS was not proposed. Kessler and Moody (1976) proposed the use of a mixture of glucose and fructose as a DS. Compared to pure glucose DS, the proposed DS showed better FO performance (Ge et al., 2013; Alaswad, 2015). Su et al. (2012) evaluated the use of a sucrose DS for wastewater treatment. The results showed that 1 M sucrose as the DS had a water flux similar to that created by 1 M $MgCl_2$. A negligible reverse sucrose flux was also obtained. Alaswad et al. (2018b) investigated the performance of sucrose DS and glucose DS in the FO process against deionised (DI) water FS. The water flux decreased with an increase in the glucose and sucrose DS concentrations due to the effect of ICP on the active layer of the membrane. The water flux increased when the FS and DS flow rates increased. Ansari (2017) examined the effect of an RSF of two different DSs (i.e. 0.65 M NaCl and 1.13 M glucose) on the FO process in the following anaerobic treatment. The results showed that 0.65 M NaCl had a higher RSF (3 $g/m^2$ h) than glucose (0.3 $g/m^2$ h). Moreover, NaCl showed a negative effect on methane production, whereas glucose proved to enhance methane production. However, there is a lack of study on whether the use of sugar DSs will affect the FO membrane stability due to membrane fouling. Table 2.7 summarises the performance of the different types of sugars used as DS in the FO process.

**Table 2.7:** Overview of sugars used as a DS in the FO process.

| Feed solution | Draw solution | Membrane module | Membrane configuration | Draw solution recovery | Performance | Ref |
|---|---|---|---|---|---|---|
| DI water | Concentrated glucose | CTA | Plate and frame | RO | ICP | (Yaeli, 1992) |
| Tomato juice | 2 M Glucose | TFC | Plate and frame | Direct application | Low RSF<br>ICP | (Petrotos et al., 1999) |
| DI water | 5–6 M Fructose | CTA | Plate and frame | Direct application | ICP | (Ng and Tang, 2006) |
| DI water | 1 M Sucrose | CTA | Hollow fiber | Nanofiltration | Low water flux | (Su et al., 2012) |
| DI water | 1.13 M Glucose | CTA | Plate and frame | - | Low reverse salt flux<br>Relatively low water flux | (Ansari et al., 2015) |
| DI water | 170–400 g/L Sucrose | TFC | Plate and frame | - | CP (high viscosity) | (Alaswad et al., 2018a) |
| DI water | 90–250 g/L Glucose | TFC | Plate and frame | - | CP (high viscosity) | (Alaswad et al., 2018a) |
| Milli-Q water containing 40 mg/L TOC | 3 M glucose | CTA | Plate and frame | - | Low RSF | (Xie et al., 2012) |

Table 2.8 shows the different types of DSs with their main advantages and disadvantages.

**Table 2.8:** Advantages and disadvantages of different types of DSs for the FO process (Ge et al., 2013; Lutchmiah et al., 2014).

| Draw solution type | Advantages | Disadvantages |
|---|---|---|
| Inorganic salts | Inexpensive and creates a high osmotic pressure at lower concentrations | RSF and recovery problem<br>May negatively affect AD |
| Organic salts | Low RSF | Low water flux |
| Sugars | Recovery is not necessary<br>Beneficial for anaerobic treatment | ICP |
| Volatile compounds | High water flux | Corrosive, and their solutions are acidic and unstable |
| Nutrient-rich substances (e.g. fertilisers) | Recovery is not necessary | Significant CP |
| Available sources (e.g. seawater) | Available source | Must be near to the available source (e.g. coastal area) |
| Synthetic compounds | High osmotic pressure | Expensive and RSF |

Understanding the characteristics of each DS is essential to guidance the exploration of successful DS during the FO filtration process (Long et al., 2018). In addition, further research is still needed with the focus on how the properties of DS could affect nutrient rejection during the FO process.

### 2.6.4 Concentration polarisation (CP)

CP is one of the factors affecting the performance of the FO process. There are two types of CP: external concentration polarisation (ECP) and ICP (Chun et al., 2017). ECP takes place on the surface of the active layer, while ICP occurs within the porous membrane support layer (Xu et al., 2010). ECP leads to the reduction of the osmotic pressure between the FS and DS and can occur on both sides of the membrane's active layer. Concentrative ECP occurs when the AL-FS, while dilutive ECP occurs when the AL-DS. However, the effect of ECP can be minimised by increasing the cross-flow velocity due to the increase of the shear force near to the at the membrane boundary layer (Ansari et al., 2016b; Nascimento et al., 2018). Both concentrative and dilutive ICP occur within the porous support layer of the membrane, depending on the membrane orientation. Concentrative ICP occurs when the DS faces the active layer, leading to the accumulation of solutes in the pores of the membrane support layer, while dilutive ICP occurs when the support layer faces the DS, causing a decrease in the effective driving force inside the pores of the support layer (Alaswad, 2015; Nascimento et al., 2018). As a result, the water flux in the FO system decreases significantly. Unlike ECP, it is difficult to reduce the effects of ICP, and this remains a major challenge in the FO process (Ansari, 2017).

### 2.6.5 Operating conditions

The effect of different operating conditions such as FS pH, cross-flow velocity and FS and DS temperatures on the FO process is described in the following subsections.

#### 2.6.5.1 Feed solution pH

The pH of FS is another critical factor affecting membrane fouling and the rejection of nutrients and organic matter in the FO process. Boo et al. (2012) studied the relationship between FS pH and colloidal fouling propensity. At high pH 9, the water flux for the polydisperse suspension suddenly decreased, whereas a mild water flux decline was observed at pH 4 for an identical polydisperse suspension. The increase in the radius of the hydrodynamic particles at a high pH causes them to aggregate to each other, resulting in fouling formation. Qiu et al. (2015) suggested that the ideal pH for municipal wastewater in the FO process should be 6–6.5 to keep the phosphate minerals in soluble form in the bioreactor. Another study reported that overall phosphorus removal from digested sludge centrate increased with an increase in FS pH due to the formation of phosphorus precipitates (Ansari, 2017). Other compounds (e.g. heavy metals and suspended solids) generally precipitate at high pH ranges or dissolve at a low pH (Lutchmiah et al., 2014). The saturation index (SI), which is an indicator of phosphate mineral precipitation, increases when the pH of wastewater increases (Song et al., 2002). As a result, possible fouling caused by inorganic precipitates could occur. Therefore, it is necessary to evaluate the change in pH in the concentrated FS during the FO filtration process.

#### 2.6.5.2 Cross-flow velocity

In the FO process, cross-flow velocity is closely related to membrane fouling in terms of CP and mass transfer (Lotfi et al., 2018). Cath (2009) reported that a higher water flux was reached at higher and equal FS and DS cross-flow velocities (i.e. 110 cm/s). The results showed a lower water flux (around 20% from its maximum value) when the DS velocity was high and the FS was low. Devia et al. (2015) reported the effect of cross-flow velocity on nutrient rejection from a secondary treated effluent using $MgCl_2$ as a DS. The water flux was increased by 30% and 60% by increasing the cross-flow velocity from 17 cm/s to 25 cm/s and 34 cm/s, respectively. Lee et al. (2010) found that fouling propensity decreased as cross-flow velocity increased from 17.1 to 34.2 cm/s due to the additional shear force that reduce the accumulation of foulants on the FO membrane. Additionally, an appropriate cross-flow velocity must be chosen to reduce the effect of CP, which can increase at a lower cross-flow velocity, and the RSF, which has been found to increase at a higher cross-flow velocity (Kedwell et al., 2018). In terms of membrane fouling and physical cleaning, previous studies have demonstrated that an appropriate cross-flow velocity must be chosen to enhance the FO process in terms of water flux decline and flux recoverability. The effects of fouling mitigation by increasing the cross-flow velocity are shown in Table 2.9.

**Table 2.9:** Effects of fouling by increasing the cross-flow velocity cleaning method.

| Foulants | Fouling duration | FO configuration | Cleaning duration | Cross-flow velocity | Efficiency | Ref |
|---|---|---|---|---|---|---|
| Organic | 40.8 h | Flat-sheet | - | 32.1 cm/s | Reversible | (Boo et al., 2013) |
| Organic | 20–24 h | Flat-sheet | 15 min | 21 cm/s | Reversible | (Mi and Elimelech, 2010) |
| Organic fouling and biofouling | 24 h | Flat-sheet | 30 min | 9.9 cm/s | Almost reversible | (Chun et al., 2015) |
| Inorganic and organic | 10 h | Flat-sheet | 30 min | 13.32 cm/s | Reversible | (Nguyen et al., 2019) |

#### 2.6.5.3 Feed and draw solution temperatures

Temperature is an additional factor that plays a vital role in the FO process as it affects the mass transfer on the membrane (Xie, 2015). Several studies have shown that water flux increases when the FS and DS temperatures increase (Lutchmiah et al., 2014). Phuntsho et al. (2012) reported a water flux increase of 12% and 45% when the FS and DS temperatures increased from 25 °C to 35 °C and 45 °C, respectively. Wang et al. (2014) found that the water flux in the FO process increased 10 times when the DS temperature increased from 3 °C to 50 °C. Arifin et al. (2015) reported an increase in the water flux in the FO process at a higher temperature due to the lesser effect of the ICP. Devia et al. (2015) tested three different temperatures of 20 °C, 25 °C and 30 °C for both FS and DS sides by using CTA membrane. Nutrient rejection was more than 90% at all operating temperatures, indicating no significant effect of temperature on overall nutrient removal efficacy. However, water flux was higher at a high temperature, and wastewater concentrated faster when the temperature increased in the FO process. Nevertheless, greater fouling of the membrane could be expected at higher temperatures (Lutchmiah et al., 2014). The following reasons could explain the increase of the water flux at higher FS and DS temperatures (Lutchmiah et al., 2014; Ray et al., 2018):

1- The solute diffusivity will increase with increasing the solution temperature.
2- The DS osmotic pressure will increase at higher temperatures according to the following equation:

$$\Pi = iMRT \qquad \text{Equation 2.2}$$

where $\Pi$ (bar) is the osmotic pressure, i is the van’t Hoff factor of the solute, M (mol/L) is the molar concentration, R is the universal gas constant (0.08206 L.atm/mol.K), and T is the absolute temperature in K.

3- The viscosity of the solution decreases with the increase in temperature, reducing the ICP effects and enhancing the water flux.

In the integrated FO–MD process, the DS must be operated at a higher temperature (e.g. 35–70 °C) so that the vapours can pass to the permeate side at a lower temperature. The increase in the DS temperature also increases the FS temperature on the FO side. Most previous studies used a cooler for the FS side, which would lead to more energy consumption in the integrated FO–MD process (Wang et al., 2011; Husnain et al., 2015; Al-furaiji et al., 2019). Conversely, other studies did not control the FS temperature or operate the FO and MD systems separately without considering the effect of the DS temperature on the FO process (Zhang et al., 2014a; Nguyen et al., 2018). Table 2.10 presents the FS, DS and permeate temperatures used in the integrated FO–MD process.

**Table 2.10:** FS, DS and permeate temperatures used in the integrated FO-MD process.

| FS Temp | DS Temp | Permeate Temp | Ref |
|---|---|---|---|
| Not reported | 33-60 ºC | 15-18 ºC | (Wang et al., 2011) |
| 20 ºC | 50 ºC | 20 ºC | (Al-furaiji et al., 2019) |
| 20 ºC | 40-70 ºC | 15-30 ºC | (Husnain et al., 2015) |
| 50–70 ºC | 50-70 ºC | 20 ºC | (Ge et al., 2012) |
| Not reported | 23 ºC or 60 ºC | 12 ºC | (Zhang et al., 2014a) |
| 25 ºC | 40-55 ºC | 25 ºC | (Lu et al., 2018) |
| 25 ºC (for the FO system) | 25 ºC (FO system) | 25 ºC | (Nguyen et al., 2018) |
| | 55 ºC (MD system) | | |

As hydroxyapatite precipitation increases with an increase in phosphate and calcium concentrations, pH and temperature (Song et al., 2002), this could affect the FO membrane in terms of inorganic fouling. Thus, the effect of the FS temperature during the integrated FO–MD process for treating municipal wastewater must be studied.

## 2.7 Membrane fouling and cleaning

Membrane fouling is a serious problem that degrades membrane performance (i.e. decreases water flux and shortens membrane lifespan) (Chun et al., 2017; Suzaimi et al., 2019). Even though FO has a lower fouling propensity than pressure-driven membranes, membrane fouling is still a major concern for the FO process because it significantly affects membrane performance in terms of water flux and solute rejection (Xie et al., 2014; Ansari et al., 2018a; Wu et al., 2022). Moreover, the quality of the water product and the operating costs, such as cleaning chemical costs, labour requirements and frequent membrane replacements, are also affected by membrane fouling (Majeed et al., 2016a). Therefore, further research is needed to develop an effective strategy to minimise the effects of membrane fouling and to enhance the effectiveness of different cleaning methods in the FO process.

The importance of membrane fouling on the FO process has led to many studies attempting to understand the fouling mechanisms. There are three types of FO membrane fouling in wastewater as the FS (Ansari, 2017; Nguyen et al., 2019): (1) organic fouling, (2) inorganic fouling and (3) biofouling. Several factors in the FO process affect membrane fouling: FS chemistry, operating conditions and hydrodynamics, foulant characteristics and DS type and concentration (Lee et al., 2010). FO membrane fouling exists in different forms such as blockage of membrane pores, cake layer formation, inorganic precipitation due to high concentrations that build near the membrane surface and biofouling due to the growth of microorganisms (Ang and Mohammad, 2015; Muzhingi, 2016). Table 2.11 shows the various factors affecting membrane fouling in the FO process.

**Table 2.11:** Factors affecting different types of fouling in the FO process (Chun et al., 2017; Korenak et al., 2017; Wang et al., 2022).

| Fouling | Major factors | Causes | Other factors |
|---|---|---|---|
| Organic | Calcium binding | Organic macromolecules found in the FS | pH |
| | Hydrodynamic shear force | | |
| | Permeation drag | | |
| Inorganic | Feed water chemistry | Inorganic scaling occurs when the concentration of soluble salts in the FS exceeds their solubility at high product water recovery. | DS type and concentration |
| | Membrane characteristics | | |
| Biofouling | Membrane surface properties | Bacterial adherence with growth forming a biofilm | Cross-flow velocity |
| | Feed water chemistry | | |
| | Microbial properties | | |

In terms of the effect of FS chemistry, pH and divalent cations are two important factors in FO fouling (Arkhangelsky et al., 2012). The up-concentration of municipal wastewater through FO membrane filtration for resource recovery can result in a significant increase in all pollutants, causing inorganic precipitation. For example, $Ca^{2+}$ and $Mg^{2+}$ can be more easily precipitated with phosphate or ammonium at elevated concentrations. Wang et al. (2015) reported that during the up-concentration of municipal wastewater, water flux declined by 45.7%, from 9.2 to 5 $L/m^2 \cdot hr$ when the initial calcium concentration in the FS increased from 35 to 250 mg/L, with an initial phosphorus concentration of 3.18 mg/L in the CTA FO membrane. Other operational conditions, such as the initial water flux, cross-flow velocity and membrane orientation and configuration, also play a role in FO fouling formation and cleaning (Honda et al., 2015; Hong, 2015; Kim et al., 2015; Ansari et al., 2018a). In addition, crossflow direction plays an important role in the FO process. Operating the FO process in a counter-current crossflow mode offers several advantages over the co-current mode such as gradual decrease in the water flux, higher average water flux and higher water extraction capacity of the DSs (Phuntsho et al., 2014). Thus, the counter-current crossflow mode is exclusively applied throughout this thesis.

Different physical techniques, such as normal flushing, high flow flushing and osmotic backwash (Fig. 2.10) have been evaluated to restore the water flux of the FO membranes (Majeed et al., 2016a; Ansari et al., 2018a; Gao et al., 2018). Previous studies showed that physical cleaning methods could achieve high water revocability when treating municipal wastewater (Mi and Elimelech, 2010; Zhao et al., 2012; Boo et al., 2013; Minier-Matar et al., 2016; Wang et al., 2016; Gao et al., 2018; Yang et al., 2019). In addition, others studies showed that inorganic and organic fouling could be successfully controlled using physical cleanings (Mi and Elimelech, 2010; Zhao et al., 2012; Boo et al., 2013). However, these studies focused on the use of synthetic FS without SS or filtered municipal wastewater in the plate and frame configuration. In addition, as the FO membrane has a high rejection of contaminants, the severity of membrane fouling increases at a higher water recovery rate. Nevertheless, limited studies have evaluated FO membrane fouling and the effectiveness of different membrane cleaning methods at a high water recovery (90%), which is required to achieve viable phosphorus and energy recovery from municipal wastewater. In this case where the FO membrane is used to treat municipal wastewater with SS until a high water recovery rate, chemical cleaning might be needed to clean the fouled FO membrane which is undesirable (Wang et al., 2022). In addition, more detailed studies on the chemistry of municipal wastewater in terms of the FS and DS in inorganic scaling remain lacking. Therefore, determining the effect of FS chemistry on the performance of the FO fouling is necessary to better understand whether pre-treatment is needed for the FO membrane when treating municipal wastewater. In addition, investigating the effectiveness of different physical cleaning techniques to recover the water flux in the FO membrane is also required. This necessary to understand when chemical cleaning should be used for TFC FO membranes. Table 2.12 presents the fouling and cleaning methods used for the FO filtration process.

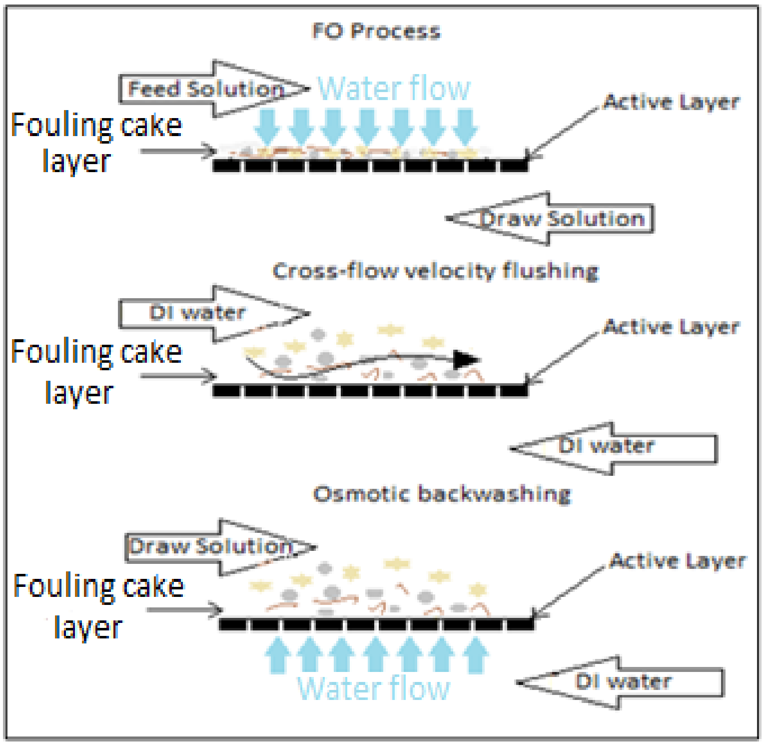

**Fig. 2.10.** The fouled FO membrane and physical cleaning methods such as cross-flow velocity flushing and osmotic backwashing used to clean the fouled FO membrane.

**Table 2.12:** Summary of studies on fouling in the FO process for wastewater treatment.

| Feed solution | Duration | Membrane | Flux decline | Foulants | TSS (mg/L) | Cleaning | Ref |
|---|---|---|---|---|---|---|---|
| Treated municipal wastewater | 60 days | CTA | 5% | Biofouling and slight inorganic scales | - | - | (Xue et al., 2016) |
| Sewage collected from the aeration grit chamber | 25 h | CTA | Depends on the DS concentration and cross-flow velocity | Humic acid, protein, carbon, calcium, magnesium, silicon, aluminium and phosphorus | - | Online air–water washing, 15 min for all DS concentrations (recovery 90%) | (Gao et al., 2018) |
| Municipal wastewater | 17 h | CTA | 45.10% | Cake layer | 400–800 | - | (Zhang et al., 2014b) |
| Municipal wastewater | - | TFC | Depends on the DS concentration and cross-flow velocity | Not reported | - | Chemical cleaning using different reagents (recovery 62%–100%) | (Wang et al., 2015b) |
| Municipal wastewater | 12 days | CTA | After a 12-day operation, the sever water flux decline was around 71% | Cake layer<br>Polysaccharides | - | Physical cleaning using cross-flow velocity (50% recovery)<br>Chemical cleaning using 1% sodium hypochlorite, 0.8% sodium ethylenediaminetetraacetic acid and 0.1% sodium dodecyl sulphate in sequence (58%–67% recovery) | (Sun et al., 2016) |
| Digested sludge | 12 h | CTA | 86% | Cake layer<br>High solids and mineral content (i.e. calcium and magnesium) | 1160 | Very high cross-flow velocity for 30 min (62.5% recovery)<br>Ultrasonic for 30 min (87.5%) | (Ansari et al., 2018a) |

**Table 2.12:** Summary of studies on fouling in the FO process for wastewater treatment.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Raw wastewater | 12 h | CTA | 42% | - | 640 | - | (Ansari, 2017) |
| Synthetic municipal wastewater | Up to 50% water recovery rate | CTA | 90% | Organic fouling | - | Osmotic backwash for 12 h (100% recovery) | (Valladares et al., 2013) |
| Municipal wastewater | 20% water recovery rate for three cycles | TFC | 45% | Organic fouling | - | Osmotic backwash for 30 min (96% water recovery) | (Pramanik et al., 2019) |
| Municipal wastewater (Pre-treatment with coagulation) | 20% water recovery rate for three cycles | TFC | 15% | Organic fouling | - | Osmotic backwash for 30 min (99% water recovery) | (Pramanik et al., 2019) |

## 2.8 Ammonium rejection during the TFC FO membrane filtration process

Although the TFC FO membrane has the advantages of having a higher water flux, greater contaminant rejection and better chemical stability over the CTA FO membrane, its lower cation rejection (especially ammonium) is still a major challenge (Lu et al., 2014; Jafarinejad et al., 2018). The DS contamination by ammonium ions may negatively affect the final water quality when water recovery is targeted and cause membrane fouling in the integrated FO process in the DS regeneration process after long-term operation (Ansari, 2017). Coday et al. (2013) found that cation diffusion from the FS to the DS was greater using the TFC membrane than the CTA membrane. Furthermore, the RSF of $Na^+$ ion was higher than that of $Cl^-$ in all experiments with the TFC membrane. This phenomenon can be explained by the more negative charges of the TFC membrane compared with the CTA membrane (Xie et al., 2013b; Li et al., 2018; Rood et al., 2020). Therefore, most studies have focused on improving membrane properties to increase ammonium rejection in the TFC FO process (Castrillón et al., 2014; Li et al., 2014; Akbari et al., 2016; Jafarinejad et al., 2018). For example, creating a positively charged membrane that repeals the positively charged ammonium ions is one of the techniques used to overcome the leakage of ammonium from the FS side to the DS side (Li et al., 2014; Akbari et al., 2016; Xu et al., 2017; Jafarinejad et al., 2018). However, to be positively charged, membrane modification will negatively affect the rejection of anions such as phosphate and sulphate. Akbari et al. (2016) reported that only 25% rejection of sulphate was obtained with a positively charged FO membrane. Membrane modification also increases membrane fabrication costs and concerns related to safety requirements (Xu et al., 2017). Therefore, it is necessary to look for alternative solutions to increase ammonium rejection.

One possible solution is the appropriate selection of a DS that reduces or prevents ammonium exchange with ions in the DS. Rather than modifying or changing the membrane property, DS selection plays a vital role in rejecting ammonium during the FO process. Hu et al. (2017) investigated ammonium rejection in a TFC FO membrane using NaCl and $MgCl_2$ DSs for the treatment of municipal wastewater. $NH_4^+$-N, which was not concentrated in the FS, decreased when NaCl was used as a DS, while the ammonium rejection rate was 58%–87% when using the $MgCl_2$ DS. Using NaCl with a higher diffusion coefficient than $MgCl_2$ has been reported to result in a higher cation exchange between $Na^+$ and ammonium from the FS to the DS. However, the validity of this observation is limited, as only two DSs were used in this study.

Using ammonia–carbon dioxide ($NH_3$–$CO_2$), Lu et al. (2014) showed that the RSF of ammonium increased when 0.2 M NaCl was used as FS. Wang et al. (2016) reported that the low rejection of ammonium was attributed to the bidirectional diffusion of ammonium of the FS and $Na^+$ cation of the DS (Fig. 2.11). Cheng et al. (2018b) reported that when 0.1 M KCl was used as FS and 1 M NaCl was used as DS, the RSF of $Na^+$ and the forward solute flux of $K^+$ were nearly equal by 1.9 mol/m$^2$.hr to maintain electricalneutrality between FS and DS. On the other hand, when DS with divalent cation $Ca^{2+}$ (i.e. 1 M $CaCl_2$) was used with 0.1 M KCl as FS, the forward solute flux of $K^+$ was decreased to 0.9 mol/m$^2$.hr. Cheng et al. (2018b) study also showed that the forward $K^+$ flux from the FS and the RSF of $Na^+$ from the DS were between 1.9-4.5 mol/m$^2$.hr when DS with monovalent cation was used (i.e. 1 M NaCl, 1 M $NaNO_3$ or 1 M $Na_2SO_4$), while the presence divalent cations in the FS (0.1 M $CaCl_2$, 0.1 M $Mg(NO_3)_2$ and 0.1 M $MgSO_4$) resulted in a lower $Na^+$ RSF (1-1.8 mol/m$^2$.hr). In addition, it was reported the RSF of $Na^+$ was significantly increased when the FS contains cations in the FS compared with DI water FS. From these results, it was suggested that the RSF of $Na^+$ was determined by the DS diffusion coefficient when DI was used as FS, while $Na^+$ RSF was affected by the cations hydrated radius when the FS contains cation such as $K^+$, $Ca^{2+}$ and $Mg^{2+}$. These suggest that the physiochemical properties of DS, and the presence of cations in the FS (e.g. ammonium) could affect other cations such as ammonium. However, further research is still needed to understand how the DS type could affect ammonium rejection during the TFC FO process.

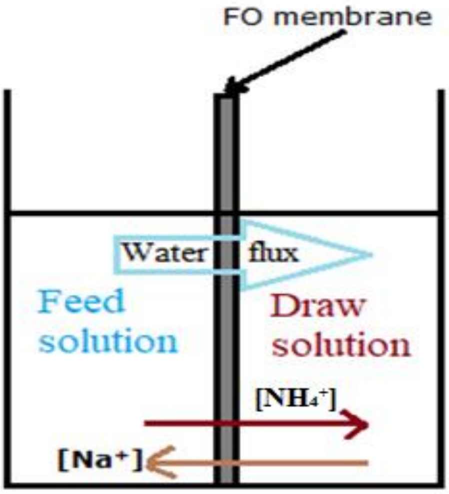

**Fig. 2.11.** Bidirectional diffusion of ammonium from the FS to the DS side during the FO process with ionic DS such as NaCl.

## 2.9 Effect of FS chemistry on the FO process

In the FO filtration process, FS chemistry greatly affects overall performance in terms of contaminate rejection and membrane fouling. For example, Gao et al. (2018) reported that the $NH_4^+$-N rejection rate was 93.3% using the CTA FO membrane for treating municipal wastewater, with an initial $NH_4^+$-N concentration of 42.3 mg/L and 1 M NaCl. A lower $NH_4^+$-N rejection rate was achieved (83%) for treating digested sludge, with an initial $NH_4^+$-N concentration of 922 mg/L using 1 M brine as the DS (Soler-cabezas et al., 2018). The $NH_4^+$-N rejection rate was found to be higher due to the low $NH_4^+$-N concentration in real municipal wastewater compared to digested sludge (Gao et al., 2018). Membrane fouling was found to be more severe when digestion sludge was used as the FS rather than municipal wastewater due to the higher initial contaminants concentrations (Cornelissen et al., 2008; Ansari et al., 2018b; Gao et al., 2018; Soler-cabezas et al., 2018). Although these studies showed differences in the FO process in terms of contaminate rejection and membrane fouling, the membrane properties, DS type and concentration also had a significant effect on the FO filtration process. Thus, it is important to use the same FO membrane (which has the same properties) to treat two different wastewater (municipal wastewater and digestion sludge) with different DSs at the same osmotic pressure to better understand the effects of FS chemistry and DS type on the FO process.

## 2.10 Membrane distillation

As mentioned before in section 2.2, MD has the advantageous over other desalination processes to be integrated with the FO process for following water recovery. The following subsections review the MD membrane characteristics, materials, modules and configurations.

### 2.10.1 Membrane characteristics

The major requirement of the MD membrane process is hydrophobicity (Husnain et al., 2015). Therefore, MD membranes are fabricated using hydrophobic polymers (Shirazi and Kargari, 2015). Aside from its good chemical resistance to acids and bases, the stability of MD membranes must be good at high temperatures (Alkhudhiri et al., 2012). Two important features of MD membranes are required: high permeability and high liquid entry pressure (LEP) (Shirazi and Kargari, 2015). The thickness of the MD membranes must be sufficiently thin to allow vapours to pass through them in a shorter time. LEP, which is the minimum hydrostatic pressure that blocks liquid solutions from entering the membrane pores, can be obtained by using a membrane with high hydrophobicity and a small maximum pore size (i.e. 0.1-0.6 µm) (Alkhudhiri et al., 2012; Biniaz, Ardekani and Makarem, 2019).

### 2.10.2 Membrane materials and modules

MD membranes come in different materials: 1) polypropylene, 2) polyvinylidene fluoride, 3) polytetrafluoroethylene (PTFE), 4) polyethylene, 5) inorganic materials and 6) carbon nanotubes (Biniaz et al., 2019). These membranes can be used in the plate and frame, hollow fiber, spiral wound and tubular modules. Recently, the PTFE membrane has been widely applied in MD process applications because of its high hydrophobicity and good resistance under different operating conditions (Zhang et al., 2011; Camacho, 2013; Biniaz et al., 2019). Table 2.13 shows the different MD membrane modules, along with their advantages and disadvantages.

**Table 2.13:** Advantages and disadvantages of different MD modules (Biniaz et al., 2019).

| Membrane module | Advantages | Disadvantages |
|---|---|---|
| Plate and frame | 1- Widely used in MD processes because it is easy to operate and install.<br>2- Membrane cleaning and replacement are easy. | 1- Low packing density.<br>2- Membrane support is needed. |
| Hollow fiber | 1- High packing density.<br>2- Low energy consumption. | 1- High fouling tendency.<br>2- Difficult to clean and maintain. |
| Spiral wound | 1- Good packing density.<br>2- Acceptable energy consumption. | 1- Fouling tendency. |
| Tubular | 1- Low fouling tendency<br>2- Easy to clean. | 1- Low packing density.<br>2- High operating costs. |

### 2.10.3 MD configurations

Four different configurations are used in the MD process: 1) direct contact membrane distillation (DCMD), 2) sweeping gas membrane distillation (SGMD), 3) air gap membrane distillation (AGMD) and 4) vacuum membrane distillation (VMD) (Shirazi and Kargari, 2015). Fig. 2.12 shows a schematic diagram of the different configurations used in the MD process. In the DCMD configuration, the MD membrane is in direct contact with liquids (i.e. feed and permeate solutions). In the SGMD configuration, a stripping cold inert gas or air is used as the carrier for the vapour molecules produced on the permeate side. AGMD uses a stagnant air gap on the permeate side to be interposed between the MD membrane and the condensing plate. In the VMD configuration, the permeate side is vapour or air under a vacuum (Shirazi and Kargari, 2015). The DCMD configuration is the most commonly used because of its simple operation and less equipment requirement (Shirazi and Kargari, 2015; Biniaz et al., 2019).

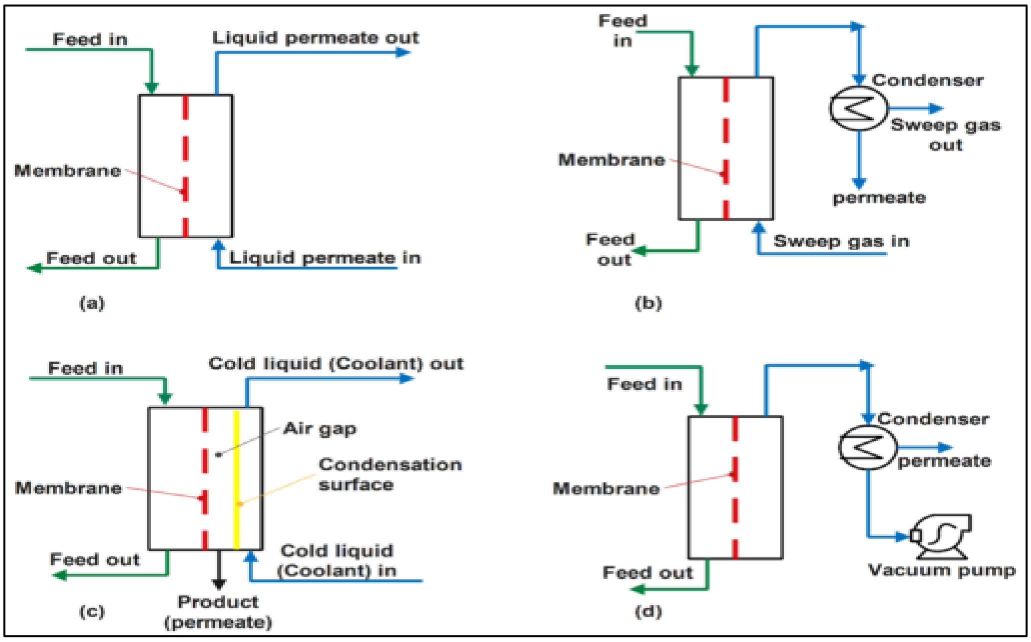

**Fig. 2.12.** Schematic diagram of the MD membrane configurations: (a) DCMD, (b) SGMD, (c) AGMD and (d) VMD (adapted from Biniaz et al., 2019).

Table 2.14 shows a comparison between different MD configurations.

**Table 2.14:** Advantages and disadvantages of different MD configurations (Biniaz et al., 2019).

| Membrane configuration | Advantages | Disadvantages |
|---|---|---|
| DCMD | 1- Simple operation.<br>2- Required less equipment. | 1- Not suitable for removing dissolved gasses.<br>2- High heat loss by conduction. |
| SGMD | 1- Suitable for the removal of volatile component and dissolved gasses.<br>2- Low thermal polarization. | 1- Large condenser is needed.<br>2- Low water flux. |
| AGMD | 1- Less conductive heat loss and fouling tendency.<br>2- High water flux. | 1- Difficult module design.<br>2- Creation of additional resistance to mass transfer. |
| VMD | 1- Heat loss is negligible.<br>2- High water flux. | 1- Pore wetting risk and high fouling tendency.<br>2- Require vacuum pump and external condenser. |

## 2.11 Advantages of the MD process

In addition to its high rejection rate of contaminants (100% rejection of non-volatile contaminants) (Wang et al., 2011), the MD process also consumes less energy and has less capital costs and footprint compared to the RO filtration process (Ray et al., 2018; Chaoui et al., 2019). In the MD process, it is not necessary to heat the solution above its boiling temperature, which results in less heat being lost to the environment (Mahdi et al., 2014a). Furthermore, low-grade waste and/or alternative energy sources, such as solar and wind, can be coupled with MD systems for an economical and energy-efficient desalination process (Yuan et al., 2015; Biniaz et al., 2019; Chaoui et al., 2019). It has been proven that the MD process powered by solar energy has a lower operational cost than the RO process (Shirazi and Kargari, 2015). The other advantages of the MD process over other desalination processes are easier operating conditions, less fouling tendency and operability at ambient pressure, which increases safety (Mahdi et al., 2014b).

## 2.12 Integrated FO–MD

The application of the integrated FO–MD process was examined previously for concentrating dye wastewater (Ge et al., 2012), protein solution (Wang et al., 2011) and municipal wastewater (Husnain et al., 2015). The results from Xie et al.'s (2014) lab-scale FO–MD system showed the potential for recovering phosphorus, DS and water from sludge digestate. However, future studies on contaminant accumulation in DS are still needed (Xie et al., 2014). Husnain et al. (2015) investigated the removal of nitrogen from the AD process using the FO–MD system. The FO–MD system was able to achieve approximately 98% rejection of $NH_3$-N. Water flux decreased significantly because of fouling problems in the FO membrane. However, by cleaning the FO membrane with tap water, more than 75% water flux recovery was achieved. The overall results showed that the FO–MD system is an active process for nutrient treatment.

Al-furaiji et al., (2019) analysed the feasibility of integrating FO with the MD process in treating hypersaline-produced water. Four DSs were used in this study: 1) NaCl, 2) KCl, 3) LiCl and 4) $MgCl_2$ at concentrations near their saturation limits. The temperatures of the DS and permeate solutions were maintained at 50 °C and 20 °C, respectively. This study aimed to select the most appropriate DS that could make the FO−MD process work in parallel in terms of water flux to obtain similar transfer rates in both FO and MD, so that the water transferred through FO is extracted using MD at the same rate. $MgCl_2$, at a concentration of 4.8 M, showed comparable fluxes for both FO and MD for 20 h of operation. Wang et al. (2011) examined the concentration of protein solutions through the FO–MD process using NaCl DS at temperatures of 33–60 °C and permeate solutions at temperatures of 15–18 °C. The results showed no significant leakage of NaCl from the DS side to the permeate side, resulting in pure water as a by-product. However, ammonium leakage may occur from the FS to the DS during the TFC FO membrane filtration process when using inorganic DS (e.g. NaCl). As the volatility of ammonia increases with increasing pH, temperature and ammonia in the DS, further research is still required to evaluate the effects of DS type, ammonium concentration and DS pH on the overall performance of the integrated FO–MD process to produce clean water. Furthermore, the low water flux associated with the use of organic DS (e.g. glucose) can be enhanced by increasing the temperature. However, there is a lack of research on the effect of FS and DS temperatures on the overall FO performance in terms of water flux and contaminate rejection when using glucose as the DS. Even though the integrated FO-MD system can potentially treat complicated wastewaters, the integrated system has not been applied on a large scale due to the lack of economic analysis study (Zarebska-Mølgaard et al., 2021). In addition, the lack of internal heat recovery for the MD process is the major limitation for the development of this process (Zaragoza et al., 2018). Thus, more attention must be paid to the internal heat recovery in the integrated FO-MD system to maximise heat utilization efficiency.

## 2.13 Summary

FO is a promising technology that can reject a wide range of contaminants and concentrate resources (i.e. phosphorus and organic matter) from municipal wastewater for subsequent resources recovery. In addition, the use of osmotic pressure as the driving force for the FO process reduces energy consumption. It results in a better membrane fouling resistance than other desalination processes (e.g. RO). Water recovery can also be achieved when the FO process is integrated with the MD process. The less energy consumption, capital cost and footprint of the MD process compared to the RO process makes it more favourable.

Despite the potential of the integrated FO-MD system to be applied as a promising technology for resources recovery application from municipal wastewater in the future, technical questions remain and need further study. Firstly, how FO membrane fouling develops, how the membrane can be cleaned, how particle and inorganic precipitation contribute to fouling and affect cleaning at a high water recovery rate (i.e. 90%) need further investigation. This is important to understand if a pre-treatment prior to the FO membrane is required. Secondly, how the use of different DSs with different physiochemical properties will affect ammonium rejection during the TFC FO filtration process also needs attention. The successful demonstration of how the DS type and properties can enhance ammonium rejection without FO membrane modification will provide general guidance on selecting DS from the perspective of ammonium rejection in wastewater treatment. Moreover, there is a need to consider how the operational temperatures affect the integrated FO–MD process. How the operational temperatures will affect the FO process in terms of water flux, RSF, membrane fouling and contaminates rejection is still unclear. In addition, addressing or reducing the heat demand of the integrated FO-MD process needs further study. It helps develop the integrated FO–MD system by understanding how the variation of FS and DS temperatures will have different effects on the FO process with different DSs and how the internal heat recovery can decrease the external heat demand. The following chapters present the research questions' methods, results, and conclusions.

# Chapter 3: Fouling and cleaning of thin film composite forward osmosis membranes used for treating municipal wastewater for resource recovery

## 3.1 Introduction

Municipal wastewater is an important source for the recovery of water, energy, and nutrients in the circular economy. It was estimated that one cubic meter of municipal wastewater had the potential to produce freshwater for 5-10 persons per day, around 2 kWh-equivalent of energy and sufficient nutrients for at least 1 $m^2$ of agriculture production area per year (PUB, 2013). Currently, energy and nutrients are recovered mainly through sludge digestion with very low efficiency. Water is mainly recovered through expensive tertiary treatment including membrane technology (Yuan et al., 2015). Also, the direct use of biosolids as nutrient fertilizer poses concerns about the contamination of agricultural land (Mehta et al., 2015). To improve efficiency and reduce the cost of resource recovery from municipal wastewater, new technologies are desirable.

FO as an emerging osmotically driven membrane technology is recently attracting great attention for resource recovery from municipal wastewater due to its high rejection rates of contaminants and a low propensity of membrane fouling compared with RO (Ahmed et al., 2018; Ansari et al., 2016a; Chekli et al., 2016; Ray et al., 2018). Like any type of membrane filtration, however, membrane fouling is still a major concern for the FO process as it could affect the membrane performance and operation regarding membrane cleaning and maintenance (Xie, 2014, Majeed et al., 2016b).

FO membrane fouling could be caused by organic molecules, inorganic scaling and biofilm growth (Ansari et al., 2017), therefore, the chemistry of FS and DS plays an important role to determine what type of fouling would be dominant. Municipal wastewater contains suspended solids (SS), organic molecules, phosphate, ammonium, metal ions, and anions. Concentrating municipal wastewater by FO membrane filtration for resource recovery could result in a significant increase in all pollutants, which can result in inorganic precipitation. For example, $Ca^{2+}$, $Mg^{2+}$, and $Fe^{3+}$ could be more easily precipitated with phosphate or ammonium at elevated concentrations. Wang et al. (2015) reported a water flux decline from 9.2 to 5 L/m$^2$·hr when $Ca^{2+}$ concentration in the FS increased from 35 to 250 mg/L with an initial phosphorus concentration of 3.18 mg/L during the CTA FO filtration process for concentrating municipal wastewater. However, a more detailed study on the chemistry of municipal wastewater as FS and DS on inorganic scaling is still lacking.

In addition, membrane chemistry and membrane structure are important too because membrane surface chemistry could have some interaction with chemicals in FS and DS, and/or bacteria attachment for biofilm growth while membrane structure could affect foulant retention. It has been reported that newly developed TFC membrane is preferred over cellulose CTA membrane due to its higher water permeability, wider pH tolerance, higher salt rejection and resistance to biological degradation (Lu et al., 2014; Wang et al., 2015b), but a more severe fouling tendency was found in TFC FO membrane due to its highly porous and asymmetric support structure (Comas and Blandin 2017; Li et al., 2018). However, the effect of FS chemistry on the TFC FO membrane fouling were not clearly presented compared with CTA membrane and needs further investigation.

Membrane fouling can be controlled by either physical or chemical cleaning. It was reported that membrane configuration affected cleaning effects. For example, hollow fiber FO configuration was reported to be favourable over other configurations as it is a self-supported membrane (eliminate the need for spacers, lowering manufacturing cost) and a higher shear force could be achieved within the narrow membrane lumen, helping remove fouling deposits easily when being cleaned (Majeed et al., 2016b; Minier-Matar et al., 2016; Chen et al., 2018). But studies on the hollow fiber FO configuration are much less than flat-sheet membrane configuration, resulting in a difficulty to compare two configurations directly or with sufficient data.

Regarding membrane cleaning methods, many studies (Mi and Elimelech, 2010; Yu et al., 2017; Xiao et al., 2018, Minier-Matar et al., 2016; Wang et al., 2016; Gao et al., 2018; Yang et al., 2019, Pramanik et al., 2019) reported that FO membranes fouling could be simply cleaned by using physical cleaning with 96-100% water flux recovery. Among several physical cleaning methods, osmotic backwashing was found to be the most effective. However, osmotic backwashing is reported to be less effective than chemical cleaning when dealing with complex FS (i.e. real wastewater) (Hafizah et al., 2018). Wang et al. (2015) investigated chemical cleaning for TFC flat sheet FO membrane and reported that the most effective chemical cleaning was by a mixture of 0.1% NaOH and 0.1% sodium dodecyl sulfate (SDS) for 10 min followed by acid cleaning with either 2% citric acid or 0.5%

hydrochloric acid for 10 min, with a focus on removing acidic and alkaline foulants in sequence. Other studies suggested that each alkaline and acid cleaning could last for 60 min to improve the cleaning efficiency (Padmanaban et al., 2020; Ezugbe et al., 2021). Obviously, chemical cleaning is more suitable to more persistent foulants which could not be removed by physical cleaning (Wang et al., 2015b; Majeed et al., 2016a). However, information on when chemical cleaning should be used for TFC FO membranes is limited.

Although membrane fouling and cleaning have been studied by some researchers, these studies have constraints with a focus on synthetic FS without SS. In addition, most FO process studies on concentrating municipal wastewater focused on the operation time of the FO process rather than the water recovery rate achieved (Qiu et al., 2015; Sun et al., 2016; Rood et al., 2020). Generally, fouling experiments lasted only for 1 cycle or 24 h (or less) (Mi and Elimelech, 2010; Zou et al., 2011; Arkhangelsky et al., 2012; Chun et al., 2015; Majeed et al., 2016a; Gao et al., 2018) without long-term fouling studies. In practice, membrane cleaning is often conducted after a long-term operation. Thus, it is necessary to study the membrane fouling and cleaning after multiple cycles with high water recovery rates.

To the best of the author’s knowledge, there are no studies on the effects of initial TSS concentration in FS on TFC FO membrane fouling, the efficiency of corresponding physical and chemical cleaning methods at a 90% water recovery rate with possibly more severe membrane fouling, and what level of a pre-treatment for the TFC FO membranes is needed. In addition, comparing how representative synthetic wastewater is for real wastewater in different FO configurations is still lacking.

This study thus aimed to investigate the concentration of municipal wastewater by TFC FO membrane filtration for resource recovery and its associated effects from SS and $Ca^{2+}$ concentrations in municipal wastewater on membrane fouling with NaCl as DS. Furthermore, different membrane cleaning methods were studied.

## 3.2 Materials and methods

### 3.2.1 Forward osmosis membranes and experimental setup

Hollow fiber TFC membranes developed by the Singapore Membrane Technology Centre with an effective membrane area of 90 $cm^2$ were used in this study. The hollow fiber membrane modules contained 15 fibers each and the active layer was located on the lumen.

The inner and outer diameters of the hollow fiber are 870 and 1180 µm, respectively. Flat sheet TFC membrane with an active membrane area of 42 $cm^2$ was used. According to the method reported by Kim et al. (2017) and Cath et al. (2013) , the pure water permeability (A), the solute permeability (B), and the structural parameter (S) of FO membranes used in this study were measured as 1.65 $L/m^2 \cdot hr.bar$, 0.16 $L/m^2 \cdot hr$, and 242 µm, respectively, for hollow fiber FO, and 0.96 $L/m^2 \cdot hr \cdot bar$, 0.16 $L/m^2 \cdot hr$, and 204 µm, respectively, for flat sheet FO.

A lab-scale cross-flow FO membrane system was run as shown in Fig. 3.1 with the orientation of active AL-FS. When flat-sheet membrane was used, the hollow fiber module was replaced by a membrane cell (Sterlitech CF042D-FO Cell, USA) consisting of structured rectangular channels with outer dimensions of 12.7 cm long, 10 cm wide and 8.3 cm deep on both sides of the membrane with or without a diamond spacer shape (spacer thickness: 1.19 mm) (Sterlitech, US) placed in contact with the membrane in the FS side.

In both hollow fiber and flat-sheet membrane configurations, counter-current recirculation of the feed and draw solutions was applied on each side of the FO membrane via two peristaltic pumps with a cross-flow velocity of 13.4 cm/s. The FS tank containing wastewater was placed on a digital balance (Kern, Germany), and the water flux was calculated based on the recorded weight changes during the experiment periods. To avoid the settlement SS in the FS tank, a mechanical mixer (IKA Labortechnik, RW 20.n, Germany) was installed in the FS tank with a stirring speed of 600 rpm. In the DS tank, a conductivity probe (Hanna HI700 instrument, HI7639 probe, UK) was installed for online measurement. All experiments were carried out at room temperature (18-20 $^oC$).

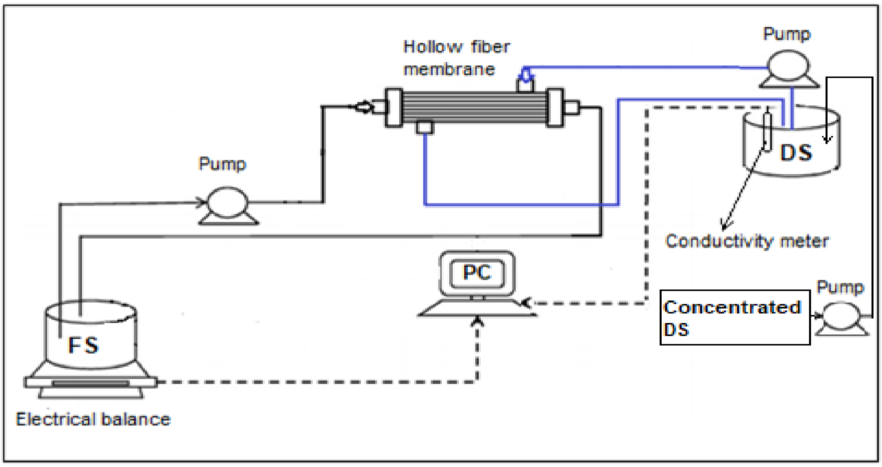

**Fig. 3.1.** Schematic illustration of the hollow fiber forward osmosis membrane filtration system.

### 3.2.2 Feed solution and draw solution

A synthetic municipal wastewater was prepared with 486 ± 5.73 mg/L COD (with NaAc.3$H_2O$ as COD), 8.91 ± 0.49 mg/L $PO_4^{3-}$-P (with $KH_2PO_4$ for P), 37.57 ± 1.07 mg/L ammonium-N (with $(NH_4)_2SO_4$ for N), 6.24 ± 0.32 mg/L $Mg^{2+}$, and 11.45 ± 0.67 mg/L $K^+$. To study effects of $Ca^{2+}$, three different $Ca^{2+}$ concentrations, i.e., 0, 13, and 61 mg/L, respectively, were added to the synthetic wastewater. To study effects of suspended solid, cellulose was added to simulate SS with a concentration 115 ± 7 mg/L, which was reported as a typical SS concentration by Bukhari (2008) and Nakhla et al. (2010).

For real municipal wastewater treatment experiments, the municipal wastewater after the primary settlement tank at Millbrook Municipal WWTP, Southampton, UK, was collected with a reduced SS concentration compared with crude sewage. The collected municipal wastewater consisted of 232.44 ± 36.54 mg/L COD, 3.91 ± 1.6 mg/L $PO_4^{3-}$-P, 34.88 ± 5 mg/L $NH_4^+$-N, 60.49 ± 4.70 mg/L $Ca^{2+}$, 4.07 ± 0.28 mg/L $Mg^{2+}$, 7.89 ± 1.02 mg/L $K^+$, 484.25 ± 16.62 mg/L TSS, and 399 ± 4.24 mg/L VSS. Unless otherwise stated, all FO experiments were conducted using a constant 3 M NaCl DS (144 bar of osmotic pressure). It needs to point out that the location and climate changes in Millbrook municipal Wastewater Treatment plan resulted in a higher TSS concentration than 115 mg/L reported in the literature.

### 3.2.3 Operation of the experimental systems

All FO membrane filtration experiments were run until a water recovery rate of 90% was achieved unless specified. Before the membrane fouling experiments for synthetic or real wastewater, baseline tests were conducted with DI water as FS and 1 M NaCl DS to determine the flux and RSF of the membrane. After the membrane fouling experiments for synthetic or real wastewater, the flux with DI water was tested again to determine the water flux decline extent by comparing it with the baseline flux. After this, three different physical methods were used to clean the membrane, which are i) normal flushing by replacing FS and DS with DI water with the a flow rate of 0.6 L/min for 30 min, ii) high cross-flow velocity flushing with the same method of normal flushing but with the increased flow rates to 1.8 L/min for 30 min to increase hydraulic turbulence and shear force, and iii) osmotic backwashing by substituting DS with DI water and FS with 1 M NaCl with AL-DS for 30 min at flow rates of 0.6 L/min to induce opposite crossflow to remove foulants on/in the membrane. For chemical cleaning, the membrane after fouling tests was immersed in 0.2%

sodium hydroxide solution for 60 min followed by being immersed into 0.5% hydrochloric acid solution for another 60 min before the membrane was flushed with DI water for 5 min.

1 M NaCl was used as DS without controlling the DS to access the concentration of the synthetic sewage with initial volumes for both FS and DS tanks of 4 L. While 3 M NaCl was used as DS for fouling experiments to increase the driving force for an improved water flux. In this case, the DS concentration was maintained at 3 M during the whole experiment period using a peristaltic pump connected to the online conductivity controller (Hanna HI700 instrument, HI7639 probe, UK) which automatically dosing 5 M NaCl with 2 L working volumes for feed and draw solution reservoirs.

### 3.2.4 Analytical methods

TSS, VSS, COD, ammonium, and phosphate were measured in accordance with standard methods by American Public Health Association (APHA). Conductivity was measured by using Hanna HI700 instrument and HI7639 probe (Hanna, UK). The concentration of soluble elements ($Ca^{2+}$, $Mg^{2+}$ and $K^{+}$) were analyzed using ion chromatography (882 Compact IC plus, Metrohm, Switzerland). Particle size distribution was measured with a Malvern 300 Mastersizer analyser (Malvern, UK). The fouled membrane after FO filtration with synthetic wastewater at initial $Ca^{2+}$ of 61 mg/L was characterised using scanning electron microscopy (ZEISS Merlin FEG-SEM) equipped with an Extreme EDS detector (Oxford, UK).

### 3.2.5 Calculations

Water flux across the FO membranes was calculated from the volume change of FS by using equation 3.1:

$$J_w = \frac{\Delta V}{\Delta t \times A_m} \qquad \text{Equation 3.1}$$

where $J_w$ ($L/m^2 \cdot hr$) is the water flux across the membrane, $\Delta V$ (L) is the volume change in the FS, $\Delta t$ (hr) is the filtration time and $A_m$ ($m^2$) is the active membrane area. FS volume was calculated by dividing FS weight with density, i.e. 1 kg/L.

The concentration factor (equation 3.2) (CF) was calculated as the ratio between the FS concentration at time t ($C_t$) after filtration and the initial FS concentration ($C_0$) at time 0:

$$CF = \frac{C_t}{C_0} \qquad \text{Equation 3.2}$$

The RSF ($J_s$) was determined based on the electrical conductivity variation of the FS (DI water as FS and 1 M NaCl as DS) with time and was calculated from the following formula (equation 3.3):

$$J_s = \frac{V_{t2}.C_{t2} - V_{t1}.C_{t1}}{\Delta t \times A_m} \qquad \text{Equation 3.3}$$

where $J_s$ ($g/m^2 \cdot hr$) is the reverse solute flux, $V_{t2}$ (L) is the volume of FS at recording time interval $t_2$, $V_{t1}$ (L) is the FS volume at recording time interval $t_1$, $C_{t2}$ (g/L) is the salt mass concentration in FS at $t_2$, $C_{t1}$ (g/L) is the salt mass concentration in FS at $t_1$. The concentration of reverse NaCl was obtained by measuring conductivity of FS at different times according to the calibration curve between NaCl concentration and solution conductivity.

## 3.3 Results and discussion

### 3.3.1 Concentrating synthetic wastewater by hollow fiber forward osmosis membrane for resource recovery

Before the experiments, baseline water flux of membrane was tested with DI water as FS and 1 M NaCl as DS. It was found that the initial water flux and RSF of the hollow fiber FO membrane were 22.12 $L/m^2 \cdot hr$ and 4.96 $g/m^2 \cdot hr$, respectively (as shown in Fig. A1). The initial water flux reduced from 22.12 to 10.67 $L/m^2 \cdot hr$, while the conductivity of DS dropped from 86.10 to 48.90 mS/cm after a 90% water recovery. The decrease of DS conductivity indicates the dilution of DS by the FO membrane extracting water from the FS by osmotic pressure, leading to reduced driving force (i.e. the osmotic pressure difference between FS and DS) over time and thus reduced water flux over time as the conductivity of DS in this study was not controlled. Thus, maintaining a constant concentration of DS benefits a more relatively constant water flux. In the vast majority of studies, however, the concentration of DS was not controlled for a simpler process and operation (Yuan et al.,2015; Valladares Linares et al., 2013). Thus, in this section of this study where the main focus was on the concentration of synthetic sewage, the concentration of DS was 1 M NaCl and was not controlled.

Table 3.1 shows the up-concentration of synthetic wastewater with a 90% water recovery rate by hollow fiber FO membrane. It was found that FO membrane had similar concentrating effect for COD, $PO_4^{3-}$-P, $Ca^{2+}$, and $Mg^{2+}$ with concentrating factors ranging from 7.75 to 8.09 while with a concertation factor of only 2.10 for $K^+$. This is in agreement with previous studies that the FO membranes were more permeable to monovalent ions (e.g. $K^+$) than divalent ions such as $Ca^{2+}$ and $Mg^{2+}$ (Ansari, et al., 2016; Gao et al., 2018). However, monovalent ammonium was not concentrated at all by the FO membrane, with the $NH_4^+$-N concentration in the FS decreased from 37.57 ± 1.07 to 13.12 ± 0.33 mg/L after the 90% water recovery rate, indicating that ammonium could not be rejected by the FO membrane used in this study. In addition, it was noticed that ammonium concentration in DS was even higher than that in FS, thus, the theory of substance diffusion from high to low concentration alone can't explain this phenomenon. The negative concentration factor for ammonium, i.e. -2.86, obtained in this study is similar to the concentration factor of -3 reported by Ortega-bravo et al. (2016) and -2.40 reported by Xue et al. (2015) using TFC FO membrane to concentrate municipal wastewater although TFC membranes in these studies were from different suppliers. No rejection or poor rejection of ammonium by TFC FO membrane was reported in many studies (Lu et al., 2014; Devia et al., 2015; Hu et al., 2017). This poses a challenging problem for wastewater treatment because ammonium in municipal wastewater could contaminate DS and further affect the quality of recovered water in the process of regeneration of DS. Furthermore, the loss of ammonium from the concentrated municipal wastewater could result in the difficulty of struvite precipitation if nutrients in municipal wastewater are targeted for recovery after concentration by FO membrane. Therefore, some studies have been done to improve ammonium rejection by modifying TFC membrane surface with poly (ethylene glycol) diglycidyl ether (PEGDE) or dicyclohexylcarbodiimide (DCC) to create a positively charged membrane to improve ammonium rejection (Akbari et al., 2016, Xu, Chen et al., 2017, Jafarinejad et al., 2018). With the modified TFC membrane 99% ammonium rejection in synthetic wastewater and 89.3% in real wastewater could be obtained (Jafarinejad et al., 2018). However, as Akbari et al. (2016) pointed out, the use of positively charged membrane resulted in a poor divalent anionic rejection ($Na_2SO_4$ = 25%) compared with divalent cationic ($CaCl_2$ = 85.5%) due to aggregation of positive charges on the membrane surface. Therefore, the modification of membrane surface may lead to a negative impact on the rejection rate of other ions (e.g. divalent anion), a higher membrane fabrication cost and concerns related to safety requirements (Xu et al., 2017). Thus, a cost-effective process for ammonium rejection during the FO process by using different DS (e.g. non-ionic DS) needs further investigation.

**Table 3.1.** Summary of initial and final concentrations of pollutants in synthetic wastewater as feed solution and 1 M NaCl as draw solution, and concentration factors of each pollutant with a 90% water recovery rate after TFC hollow fiber FO membrane filtration.

| Pollutants | Initial concentration in FS (mg/L) | Final concentration in FS (mg/L) | CF | Theoretical concentration in FS assuming 100% rejection (mg/L) | Final concentration in DS***** (mg/L) |
|---|---|---|---|---|---|
| COD | 486 ± 5.73 | 3766 ± 7.75 | 7.75 | 4860 | 57.58 |
| $PO_4^{3-}$-P | 8.91 ± 0.49 | 72.10 ± 0.78 | 8.09 | 89.10 | 0 |
| $NH_4^+$-N | 37.57 ± 1.07 | 13.12 ± 0.33 | -2.86 | 375.70 | 19.08 |
| $Ca^{2+}$ | 13.33 ± 0.72 | 103.51 ± 5.91 | 7.76 | 133.30 | 1.57 |
| $Mg^{2+}$ | 6.24 ± 0.32 | 48.80 ± 1.11 | 7.82 | 62.40 | 0.72 |
| $K^+$ | 11.45 ± 0.67 | 24.04 ± 1.73 | 2.10 | 114.50 | 4.76 |

*Final concentrations of each pollutant in the draw solution were calculated based on the loss of pollutants from FS

The biggest advantage of using FO membrane filtration to concentrate municipal wastewater is to facilitate resource recovery from municipal wastewater for the transformation of energy-intensive WWTPS into refinery plants for water, energy and nutrient recovery in the circular economy. From Table 3.1, it can be seen that wastewater volume of FS was reduced by 90%, and concentrations of COD and $PO_4^{3-}$-P were increased by 7.75-8.09 times with a water recovery rate of 90%. In the practice, for RO membrane filtration, the water recovery rate is usually maintained at around 70% or below instead of 90% to alleviate membrane fouling (Matin et al., 2021). To understand the optimal water recovery rate for FO filtration operation to facilitate resource recovery from municipal wastewater, concentrations of COD and $PO_4^{3-}$-P were monitored with different water recovery rates as shown in Fig. 3.2. As reported, a higher COD concentration is preferred for AD at ambient temperature and 2000 mg/L COD was recommended as the minimum (Verstraete et al., 2009). To achieve this value, the water recovery rate should be above 78%. For direct phosphorus recovery by struvite precipitation, phosphate-phosphorus concentration should be above 50 mg/L (Desmidt et al., 2013), which corresponds to the water recovery rate of 86% in Fig. 3.2. From both COD and phosphate-phosphorus data in this study with a purpose to facilitate cost-effective recovery of energy and phosphorus from municipal wastewater, a 90% water recovery rate is recommended based on the results in Fig. 3.2. Experiments in this study on treating real municipal wastewater showed that simply adjusting pH of concentrated FS after a 90% water recovery rate to 11 resulted in a 99.3% phosphorus recovery by forming phosphate precipitates without any additional chemical dose (Fig. A2). In addition, achieving a 90% water recovery rate in the FO filtration process can reduce the feed volume by 90%, which allows a possible anaerobic treatment even under mesophilic or thermophilic condition due to significantly reduced heat requirement (Ansari et al., 2016a). However, such a high water recovery rate might cause more serious fouling, thus, membrane fouling and cleaning at the water recovery rate of 90% was studied in the subsequent sections.

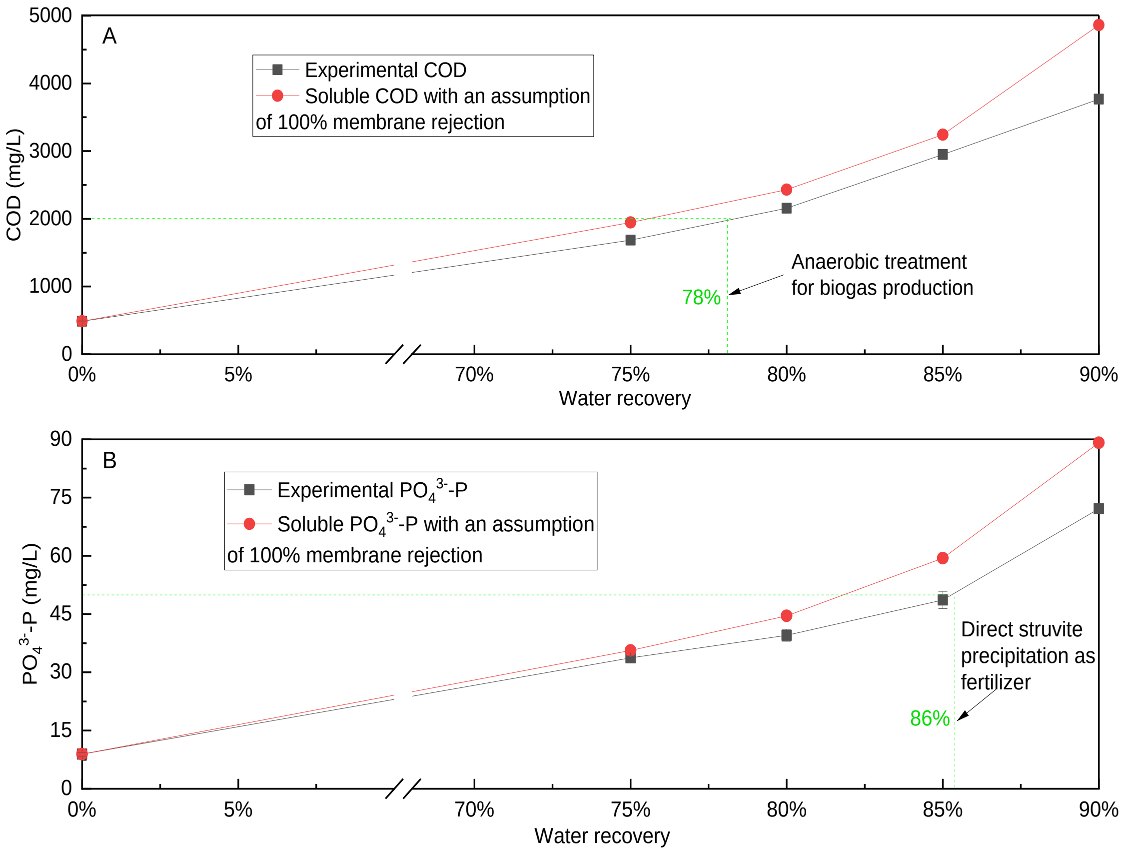

**Fig. 3.2.** Concentration profiles of COD and $PO_4^{3-}$-P in the synthetic sewage feed solution over time until 90% water recovery rate was achieved in the hollow fiber FO system with 1 M NaCl as draw solution.

In addition, it was noted that both COD and $PO_4^{3-}$-P concentrations in FS were lower than those with the assumption of 100% membrane rejection and the difference between experimental data and assumed data became larger at higher water recovery rates particularly when above 75%. A control experiment with synthetic wastewater maintained under the same conditions but without membrane filtration was run in parallel to investigate COD loss. It was found that 6% of the total COD in FS was lost by biodegradation during

25-hr membrane filtration period, which resulted in 292 mg/L COD loss in FS if there was 100% membrane rejection. However, COD concentration in FS at 90% water recovery rate was 3766 ± 7.75 mg/L, indicating that some COD was still lost by passing through membrane to DS.

Assimilation of phosphorus for the loss of 6% of COD due to biodegradation is negligible while no phosphorus was detected from DS, suggesting phosphorus rejection by the membrane was 100%. It was believed that the negative charge of the TFC membrane prevented the diffusion of the negatively charged phosphate ions. This performance is consistent with previous reports that a complete rejection of $PO_4^{3-}$-P by TFC FO membrane for concentrating municipal wastewater or anaerobically treated dairy manure (Wang et al., 2016; Gao et al., 2018; Kumar et al., 2019). The actual lower phosphorus concentration than it is supposed to be by 100% rejection might be caused by the precipitation of calcium phosphate because the concentrations of both $Ca^{2+}$ and $PO_4^{3-}$ increased by 8 times at the water recovery rate of 90%, which is beneficial for the precipitation. Furthermore, an obvious pH increase of FS from 6.56 at the beginning to 7.15 at the end of filtration with the 90% water recovery rate was observed, which is conducive to the precipitation of calcium phosphate too. The increase in pH of FS was reported for both synthetic and real wastewater when using NaCl as DS (Cath, 2009; Xie et al., 2014). It was speculated when $Na^+$ diffused from the DS to the FS via so-called RSF, $H^+$ in the FS diffused from FS to the DS to maintain the electroneutrality of the solutions (Cath, 2009). Another possible reason is that the presence of NaCl ions in the FS as a result of RSF could affect the pH of the FS. This was validated by measuring pH of pure NaCl solution with different concentrations. It can be seen from Fig. A3 that pH increased from 6.91 to 7.6 accordingly when the NaCl concentration increased from 0 to 0.2 M. Kaiserslautem and Hr (1994) and Zhao et al. (2015) reported that the increase in the salt concentration caused a reduction in the dissolution of $CO_2$ and thus increased pH. In addition, dissolved $CO_2$ could precipitate more easily with increased metal ions concentrated by membrane filtration to increase pH. In one word, salt reverse flux particularly when salt as DS could change the chemistry of FS such as pH and ionic strength, and thus affect the inorganic fouling of the membrane. In this study, it is reasonable to believe that the lower soluble phosphate concentration than it is supposed to be with 100% rejection rate is purely caused by the precipitation of calcium phosphate under elevated pH, and $Ca^{2+}$ and $PO_4^{3-}$ concentrations when membrane filtration was going on. The higher water recovery rate implies a high precipitation rate of calcium phosphate due to higher concentrations of $Ca^{2+}$ and $PO_4^{3-}$. The concentrations of $Ca^{2+}$ in municipal wastewater in different regions are quite different, which might be ranging from

10 mg/L to 150 mg/L. The precipitation of phosphate with $Ca^{2+}$ with a high concentration would result in inorganic scaling on membrane. In addition, $Ca^{2+}$ could also induce organic fouling by binding with organic molecules to form larger net structure (Lutchmiah et al., 2014; Wang et al., 2015a; Gao et al., 2018). Effects of $Ca^{2+}$ on membrane fouling when concentrating municipal wastewater were further investigated in this study

### 3.3.2 Fouling and cleaning of hollow fiber forward osmosis membrane for concentrating synthetic wastewater with two different $Ca^{2+}$ concentrations

As shown in Fig. 3.3, the water flux declined more steeply when the initial $Ca^{2+}$ concentration in synthetic wastewater was 61 mg/L compared with that without $Ca^{2+}$ in three batch membrane filtration cycles. In addition, the initial water flux was reduced by 12.5% from the first cycle to the second cycle and by 66.7% from the second cycle to the third cycle with 61 mg/L $Ca^{2+}$ while it was by 23% and 11.9%, respectively, with 0 mg/L $Ca^{2+}$. This indicates that TFC membrane fouling was much more severe when $Ca^{2+}$ concentration was higher but fouling still occurred even when $Ca^{2+}$ concentration was 0. As discussed, the decline of water flux was mainly attributed to inorganic scaling on the membrane by calcium precipitates such as calcium carbonate and/or calcium phosphate due to the increased concentrations of $Ca^{2+}$ and $PO_4^{3-}$ and pH as all the other conditions were the same in the two scenarios. Even without $Ca^{2+}$, the initial water flux was around 24 $L/m^2 \cdot hr$ which is much lower than the initial flux with 61 mg/L of $Ca^{2+}$ (33 $L/m^2 \cdot hr$). However, it was hypothesised that this flux difference could be the effect of fouling caused by previous experiment with 61 mg/L $Ca^{2+}$ (the same membrane was used in the hollow fiber FO experiments for the effect of $Ca^{2+}$ on membrane fouling).

From Fig. 3.3, it can be seen that the deposit of inorganic precipitates on the membrane surface affected the membrane fouling and water flux in the subsequent cycles as well. Similar results of $Ca^{2+}$ effects on CTA FO membrane fouling were reported by Wang et al. (2015) when concentrating municipal wastewater, from which CTA FO fouling was negligible with the initial $Ca^{2+}$ concentration of 35 mg/L and the initial phosphorus concentration of 3.18 mg/L while the initial water flux declined by 45% when the initial $Ca^{2+}$ concentration increased to 250 mg/L (water recovery rate and initial pH were not reported). This suggests that the inorganic scaling is similar for both CTA and TFC membranes.

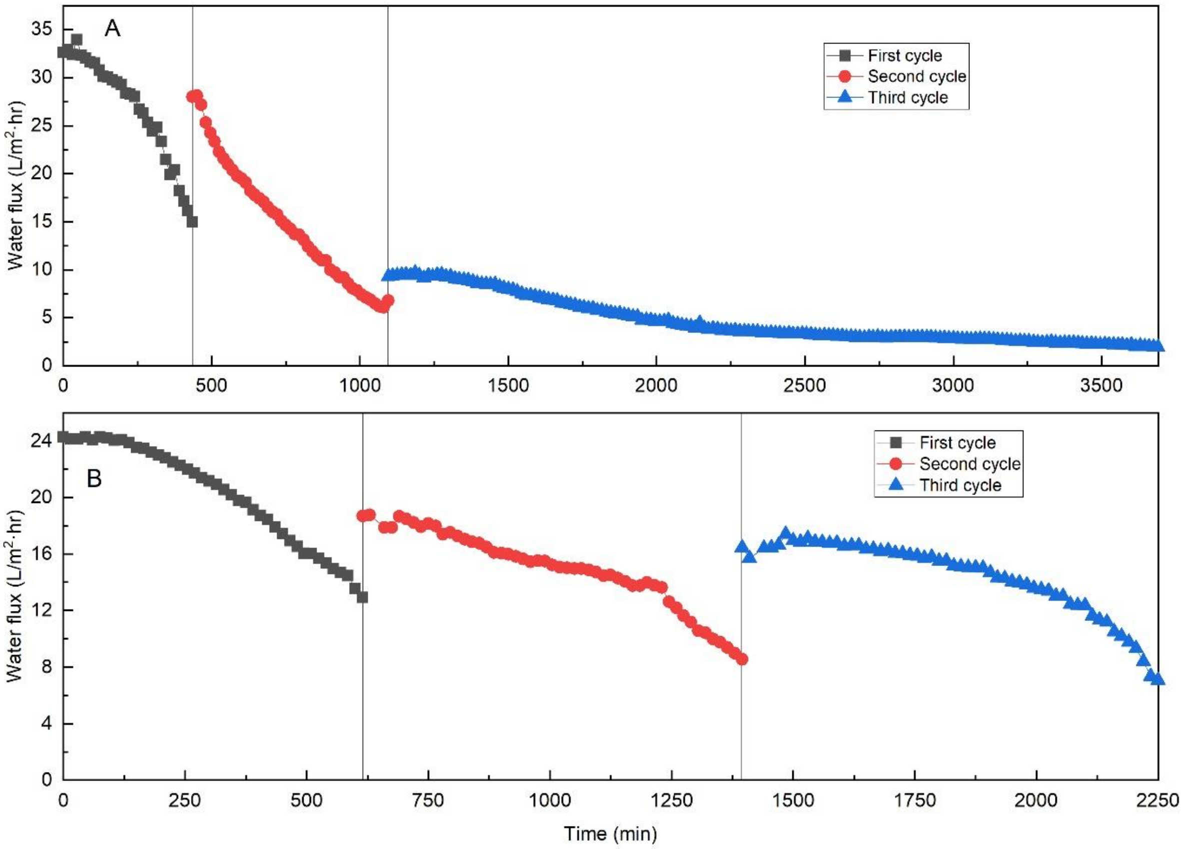

**Fig. 3.3.** The declines in water flux in three batch hollow fiber FO membrane filtration cycles with 90% water recovery rate each when concentrating synthetic sewage containing an initial $Ca^{2+}$ concentration of A) 61 mg/L, B) 0 mg/L.

In addition, although the initial pH of FS was around 6.6 for both scenarios, the final pH of FS with the presence of $Ca^{2+}$ at 90% water recovery rate was increased to 8.02 while it was increased to only 7.31 in the absence of $Ca^{2+}$ at the end of cycles. This is mainly because that more than double of the time required to achieve a 90% water recovery rate (Table A1) for the scenario with 61 mg/L $Ca^{2+}$ resulted in more total reverse salts to FS, leading to higher effects on the chemistry of FS by DS and thus on higher pH increase and precipitation of $Ca^{2+}$. From this perspective, the largest disadvantage of salts as DS for concentrating municipal wastewater is the interaction of salt ions with chemicals in municipal wastewater due to RSF, which might induce inorganic fouling on the membrane and be unfavourable to maintain stable water flux. Furthermore, a longer filtration time due to fouling worsens membrane fouling further when the operation is batch.

To investigate the membrane flux recovery after inorganic scaling, osmotic backwashing was used for membrane cleaning for 30 min after three batch membrane filtration cycles with a 90% water recovery rate each. As shown in Fig. 3.4A, only 45% of the initial water flux was recovered by using the osmotic backwashing method with the presence of 61 mg/L $Ca^{2+}$ in synthetic swage while it was 121% of the initial water flux recovery in the absence of $Ca^{2+}$ (Fig. 3.4B), indicating that osmotic backwashing for 30 min was not enough to recover the membrane flux fully and more vigorous cleaning methods are necessary. In addition, since that osmotic backwashing was able to recover 121% of the initial water flux in the absence of $Ca^{2+}$, this indicates that fouling in the FO process with the absence of $Ca^{2+}$ was negligible and verify the previous hypothesis that flux decline in the absence of $Ca^{2+}$ was mainly caused membrane fouling from inorganic precipitates during the FO filtration with 61 mg/L $Ca^{2+}$.

In osmotic backwashing, the DS was replaced with DI water, and the permeate flows from DS to FS side. As a result, the deposited foulants were possibly washed away by this opposite cross flow. Most of the FO fouling studies showed that FO membrane fouling is completely reversible and backwashing could recover initial water flux (Chekli et al., 2017; Pramanik et al., 2019). For example, Valladares et al. (2013) reported that osmotic backwashing was able to remove almost all organic foulants from the FO membrane surface when treating synthetic municipal wastewater as FS and 0.65 M NaCl as DS. In addition, Holloway et al. (2007) studied the efficiency of osmotic backwashing to clean FO membrane after concentrating anaerobic digester centrate. It was suggested that osmotic backwashing could be an efficient cleaning method for the FO membranes. However, osmotic backwashing in Fig. 3.4A proved to be not effective enough for cleaning fouling caused by inorganic scaling. Longer osmotic backwashing might be needed, but longer cleaning implies lower treating capacity. In addition, osmotic backwashing might not strong enough to remove more complex fouling from wastewater (Hafizah et al., 2018; Zhu et al., 2021). The active layer of the fouled FO membrane after cleaning was further characterized by SEM images combined with EDS. As shown in Fig. A4 and A5, the phosphorus and $Ca^{2+}$ peaks after osmotic backwashing for 30 min confirmed that inorganic scaling still covered the active layer of the FO membrane. This implied that calcium phosphate precipitates were not removed after osmotic backwashing used in this study. Thus, chemical cleaning may be needed to remove calcium phosphate precipitates from the hollow fiber membrane surface. Therefore, chemical cleaning method was further investigated for treating raw sewage wastewater in this study.

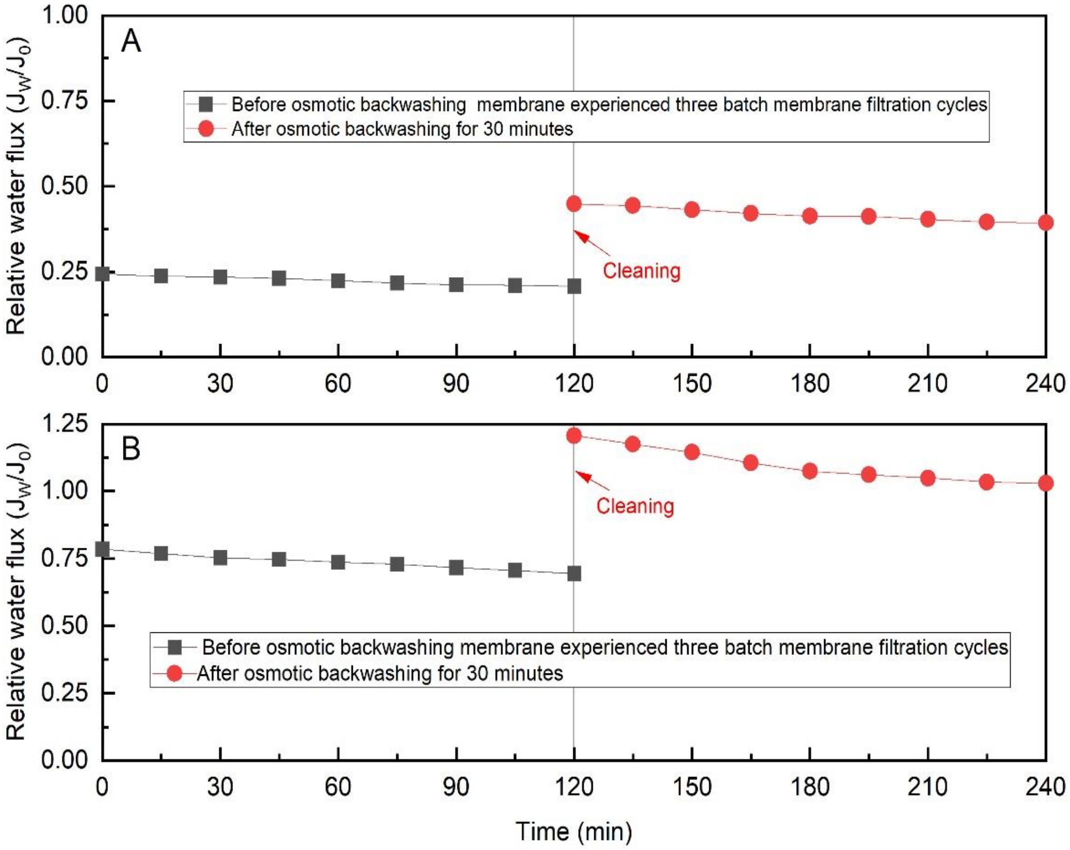

**Fig. 3.4.** Relative DI water fluxes before and after osmotic backwashing to clean hollow fiber FO membrane after three batch membrane filtration cycles with/without $Ca^{2+}$ for concentrating synthetic sewage with 90% water recovery rates in each cycle A) 61 mg/L $Ca^{2+}$, B) 0 mg/L $Ca^{2+}$.

### 3.3.3 Fouling and cleaning of hollow fiber forward osmosis membrane for concentrating synthetic wastewater with/without suspended solids

Municipal wastewater contains SS, which would cause the deposits of solids on the membrane for fouling. In this study, cellulose was used to simulate SS in synthetic wastewater with a concentration of 115 ± 7 mg/L. Meanwhile, $Ca^{2+}$ concentration in the synthetic wastewater was around 13 mg/L. It can be seen from Fig. 3.5A that no flux decline was observed after three batch membrane filtration cycles with a water recovery rate of 90% in each cycle for treating synthetic wastewater without SS. However, when initial SS concentration was 115 ± 7 mg/L, the initial water flux declined slightly by 6.7% from the first cycle to the second cycle, but by 30% from the second cycle to the third cycle (Fig. 3.5B). In addition, the water flux in the third cycle dropped significantly, resulting in 29 h for the third cycle (i.e. 3.68 times longer than the second cycle) to obtain a 90% water recovery rate. The total duration for three batch membrane filtration cycles without SS was 20 h while it was extended to 44 h with 115 ± 7 mg/L SS. The slight drop in the second cycle and the significant drop in the third cycle indicate that only when the deposit of SS on the membrane reached a certain level, i.e. critical point, the water flux started to drop significantly.

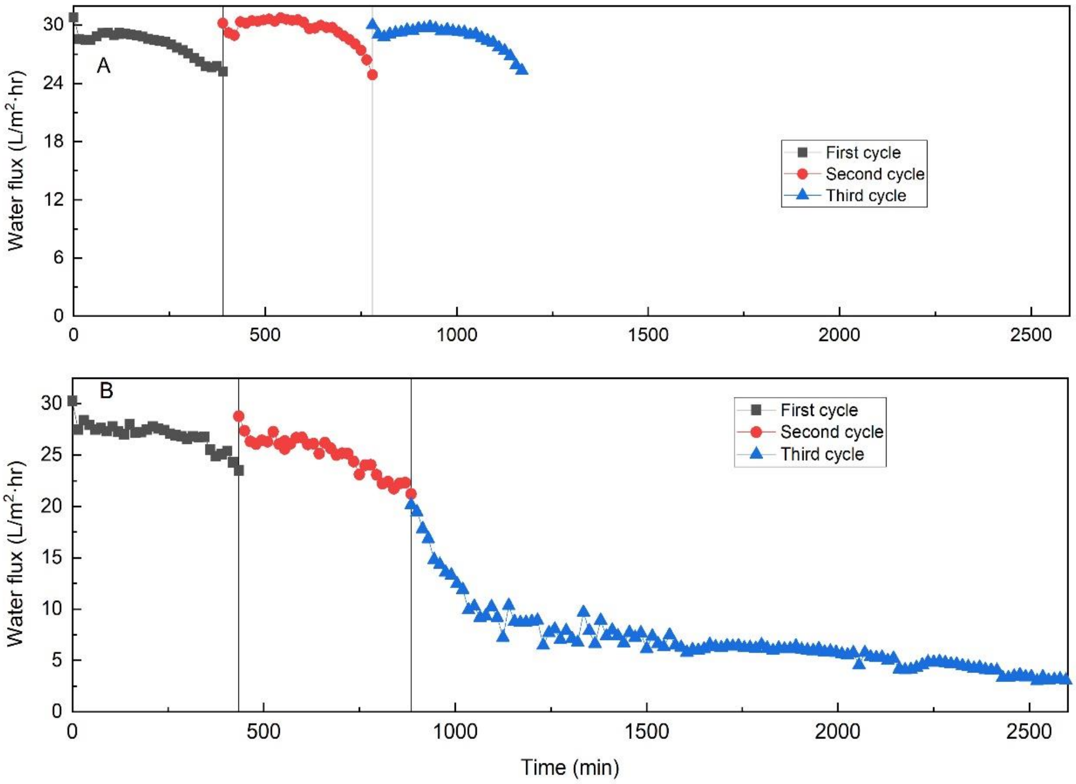

**Fig. 3.5.** Water fluxes in three batch hollow fiber FO membrane filtration cycles with a water recovery rate of 90% for concentrating synthetic sewage A) without suspended solids, and B) with 115 ± 7 mg/L of initial suspended solids.

To understand the recovery of the fouled membrane, three different membrane cleaning methods were used , which are normal flushing with DI water for 30 min, high cross-flow velocity flushing with three times higher water flow velocity for 30 min and osmotic backwashing for 30 min. These physical cleaning methods were used in most FO studies due to their high efficiency to clean the FO membranes in some cases (Arkhangelsky et al., 2012; Valladares et al., 2013; Xie et al., 2014; Ansari et al., 2018a) and simplicity for operation. From Fig. 3.6A, it can be known that after running three batch membrane filtration cycles of synthetic wastewater without SS, there was only a 5% flux decline, which might be due to the small amount of calcium precipitates. The initial water flux was fully recovered after normal flushing with DI water for 30 min, suggesting that the precipitates of calcium deposited only on the hollow fiber membrane surface loosely, and can be removed easily. For synthetic wastewater with 115 ± 7 mg/L SS, the initial water flux after three cycles dropped by around 37%. After normal DI water flushing for 30 min, 82.5% of the initial water flux was recovered. This indicates that the vast majority of SS deposits on membrane loosely, but the much longer duration of three batch cycles might result in more compact deposits. Compared with the cleaning of membrane fouling caused by calcium precipitates in Fig. 3.4, membrane fouling caused by SS was much easier to be recovered. A further flushing with high cross velocity for another 30 min (see Fig. 3.6B) only slightly improved water flux to 88.4% although much more turbulence was created with higher shear force by using higher velocity to enhance the hydrodynamic conditions near the membranes surface (Boo et al., 2013). But subsequent osmotic backwashing for 30 min fully recovered the initial water flux to 100%, suggesting that the membrane fouling caused by SS during three batch cycles was still reversible and osmotic backwashing was more effective than high cross velocity flushing.

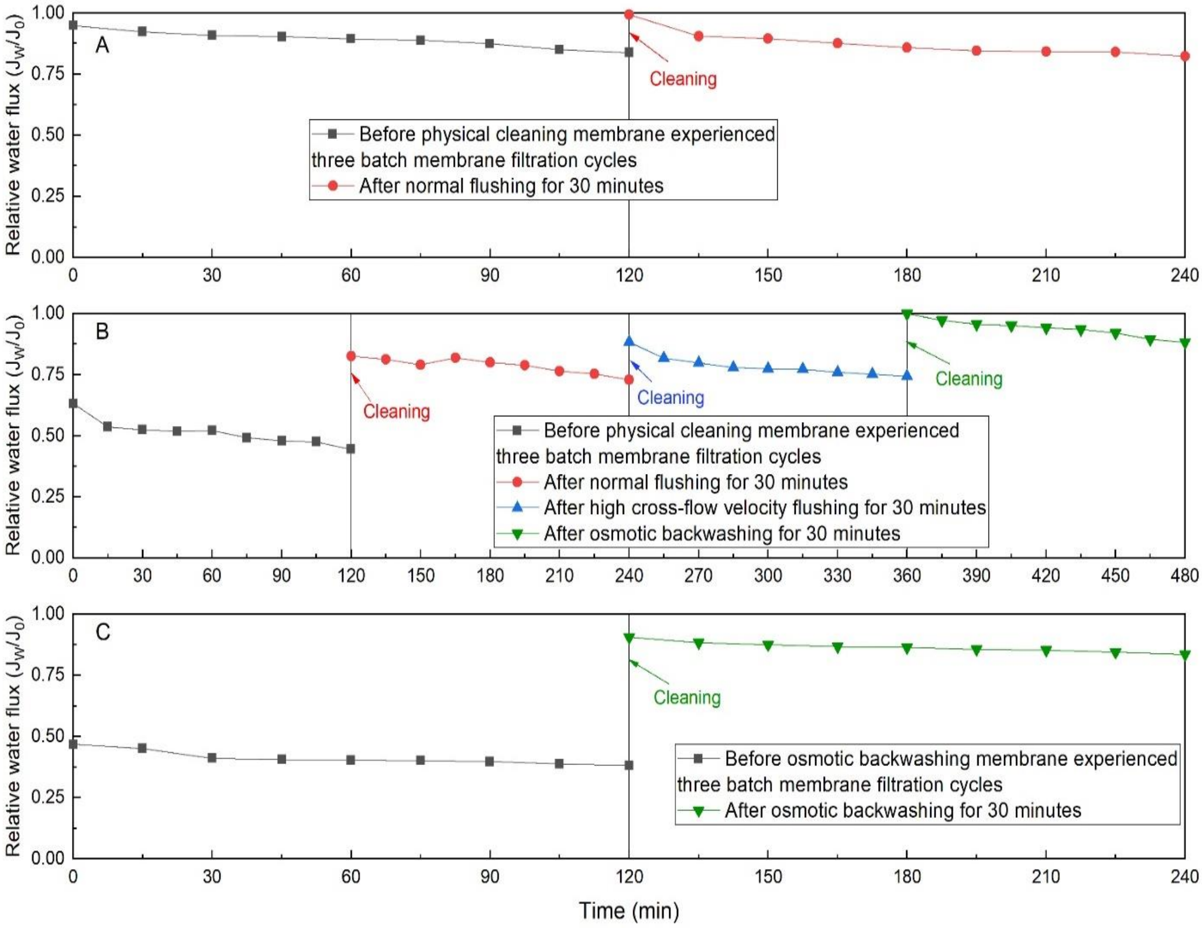

**Fig. 3.6.** Relative water fluxes before (i.e. after three batch membrane filtration cycles for concentrating synthetic wastewater A) without suspended solids, and B and C) with a suspended solid concentration of 115 ± 7 mg/L with a water recovery rate of 90% in each cycle) and after different physical cleanings.

100% water flux recovery was achieved after sequential physical cleaning methods with normal flushing followed by high cross velocity flushing and osmotic backwashing as shown in Fig. 3.6B, but it is unclear if backwashing alone could recover 100% water flux. Thus, another three batch cycles same as Fig. 3.5B was conducted to get a similar level of membrane fouling as in Fig. 3.6B. As shown in Fig. 3.6C, single osmotic backwashing for 30 min recovered 91% water flux while a combined cleaning of normal flushing for 30 min with high cross-velocity flushing for 30 min recovered 88.4% water flux, suggesting osmotic backwashing for 30 min was more effective in cleaning than the combined normal flushing and high cross-velocity flushing (30 min each) when treating synthetic sewage with SS with less cleaning time (down time) and lower energy consumption. Results on cleaning of fouling caused by SS in this study are in agreement with previous studies by Holloway et al. (2007) on membrane fouling caused by digester centrate and Yu et al. (2017) on membrane fouling caused by synthetic wastewater containing slica particles, implying backwashing is more effective to remove SS foulant from the TFC membrane as well as CTA membrane

### 3.3.4 Fouling and cleaning of hollow fiber and flat-sheet forward osmosis membrane for concentrating real municipal wastewater

The fouling of membrane by real municipal wastewater with complex organic and inorganic chemicals and ions might be more challenging. Organic matters in municipal wastewater such as proteins, lipids, amino acids, colloidal particles, and humic acid are responsible for the membrane organic fouling in treatment of raw wastewater (Padmanaban et al., 2020). In addition, it was reported that both scaling and biofouling are anticipated when treating real wastewater (Zhang et al., 2012). Since batch test with less 21 h was done in this study, it was assumed that bio-fouling could be negligible because biofilm growth takes time. Regarding inorganic fouling, water hardness level could affect membrane fouling due to high calcium and magnesium concentrations. It is well known that 60% of the UK is classed as having hard or very hard water with high calcium concentration (Theobald, 2005). In this study, real municipal wastewater after the primary clarifier (removal of most SS) from Southampton, Southeast England, was collected, which contained around 60 mg/L calcium, 484 mg/L SS and other pollutants.

As shown in Fig. 3.7, when treating real municipal wastewater, the hollow fiber FO membrane was immediately clogged with the water flux reduced from 14 to 0.80 L/m$^2$·hr within 60 min and only a 10% water recovery rate was obtained after around 51-hr filtration.

This result is different from that with the synthetic wastewater by using cellulose as SS in Fig. 3.5. A particle size analysis found that the particles size in real wastewater distributed between 2.42 and 1850 µm with an average particle size of 290 µm while cellulose particle to simulate SS distributed between 1.45 to 163 µm with an average particle size of 36 µm (Fig. A6). The wide particle size distribution up to 1850 µm could easily clog the hollow fiber as the internal diameter of the fiber was only 870 µm. Thus, it is reasonable to believe that the rapid and significant drop of water flux with real wastewater was mainly caused by particle clogging instead of membrane fouling.

To further look into the fouling and clogging of hollow fibers by real municipal wastewater, the membrane orientation with AL-DS was tested to contrast with AL-FS conducted above. It can be seen from Fig. 3.7 that the initial water flux was 22.96 L/m$^2$·hr, much higher than in AL-FS filtration (14 L/m$^2$·hr). A rapid decline of water flux to 11.83 L/m$^2$·hr within 30 min was observed as well due to the foulant deposit on the membrane, but from 45 min, the water flux reduced steadily and 540 min were taken to reach a 75% water recovery rate. Since the support layer of the hollow fiber membrane faced FS, particles in FS could move freely in the hollow fiber membrane shell with much less restriction than the lumen in the case of AL-FS. The water flux decline was thus much less than that in the AL-FS case, but the clogging and fouling still occurred with the final water flux of 4.75 L/m$^2$·hr at the water recovery rate of 75%.

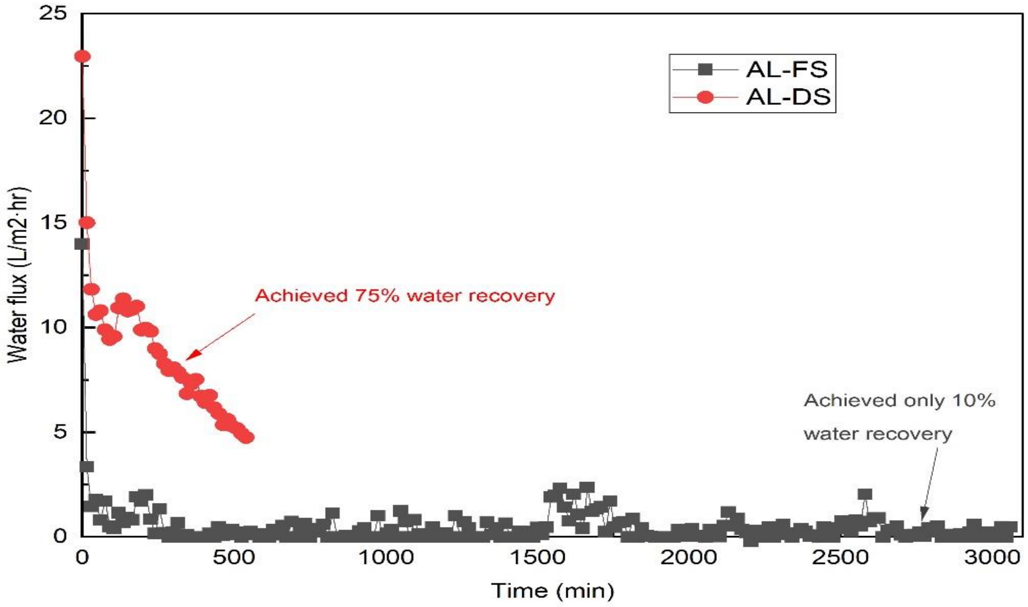

**Fig. 3.7.** Water flux changes in the single batch hollow fiber membrane filtration cycles for concentrating real municipal wastewater with the AL-FS and the AL-DS, respectively.

The cleaning effects of osmotic backwashing for two scenarios with AL-FS and AL-DS, respectively, were shown in Fig. 3.8. It can be seen that in the case of AL-FS, the water flux resumed to 100% after a simple osmotic backwashing for 30 min, indicating that only particle clogging occurred. In addition, the rapid formation of a cake layer in hollow fiber membrane lumen could prevent the membrane fouling from large organic molecules or other inorganic precipitates although the small diameter of hollow fiber membrane lumen is prone to clogging (Majeed et al., 2016b). In the case of AL-DS, a water flux decline by 82.6% was observed after one batch membrane filtration cycle. Only 40% of the initial water flux was recovered after osmotic backwashing for 30 min. It has to be pointed out that channels and pores in the support layer were much larger (Majeed, et al., 2016b; Yee et al., 2019), thus, particles and organic molecules in real municipal wastewater were easily stuck inside of the membrane support layer, resulting in poor effects from physical cleaning such as osmotic backwashing. A further chemical cleaning by 0.2% NaOH and 0.5% HCl for 60 min each followed by 5-min membrane flushing with DI water resumed the water flux to only 69% of the initial value, suggesting that the support layer of the membrane became a barrier for both physical and chemical cleaning. In addition, the concentrative ICP increased when the support layer faced FS (Su et al., 2012; Honda et al., 2015; Fan et al., 2018) because soluble organic molecules in wastewater were trapped in the support layer with higher concentrations, resulting in reduced water flux. Thus, AL-DS is not a recommended hollow fiber membrane orientation for the filtration of wastewater when the active layer is in the lumen.

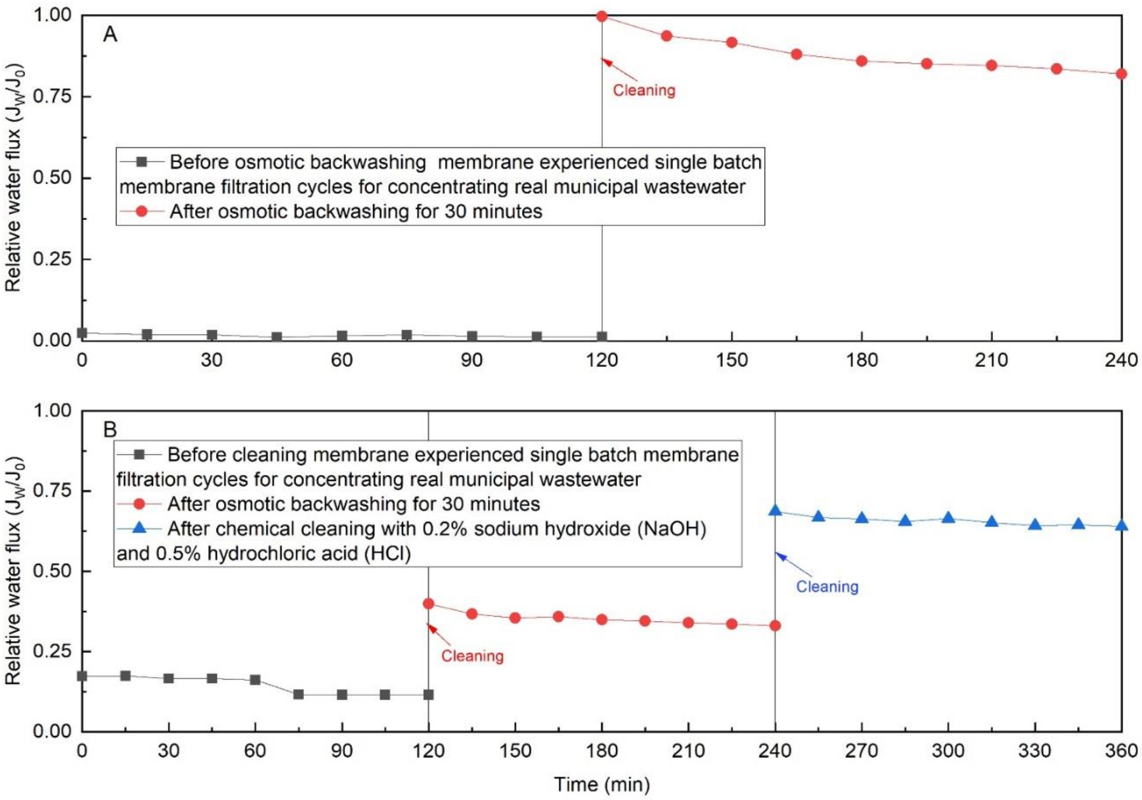

**Fig. 3.8.** Relative water fluxes before (i.e. after single batch membrane filtration cycles for concentrating real municipal wastewater with A) AL-FS, and B) AL-DS, and after different cleanings.

Given the constraints of hollow fiber membrane for the filtration of wastewater containing particles, flat sheet membrane was tested to compare with hollow fiber membrane. From Fig. 3.9, it can be seen that the flat sheet membrane was able to achieve 90% water recovery for concentrating the same real municipal wastewater and the spacer did not play a noticeable role to alleviate the flux decline. This phenomenon is different from that reported by Alanezi et al. (2007) that in the absence of feed spacer, the membrane would experience a severe ECP, which can promote ICP and thus lead to a dramatic flux decline. Wang et al. (2010) also reported that the use of feed diamond-patterned spacer enhanced the initial flux of the CTA FO membrane, and significantly improved the flux stability during FO fouling by using synthetic wastewater as FS with SS (had a mean particle diameter of 3 μm). However, Yu et al. (2017) didn't find a significant difference between two FO systems with or without a spacer for the CTA membrane when investigating the effect of spacer (shape was not reported) for treating DI water with 5,000 mg/L silica particles (diameter 1–5 μm) and 200 mg/L humic acid. The contradictory results about the effects of a spacer on water flux during membrane filtration processes are probably due to different types of membrane and wastewater used with different characteristics. For example, Wang et al. (2010) and Yu et al. (2017) used CTA FO membrane to treat synthetic wastewater as FS and the this study used TFC FO membrane for the treatment of real wastewater with much higher particle sizes. Thus, the studies on spacer effects should be further conducted to find the most suitable circumstances for the use of a spacer.

Linear regressions were used to better understand how the FO membrane fouling was devolved for the treatment of real sewage with/without spacers. From two overlapping lines with/without spacers in Fig. 3.9, the flux decline could be divided into two distinct regions with one from 0 to 18% water recovery rate with a water flux declining rate of 0.46 L/m$^2$·hr per % water recovery rate while the other from 18% to 90% water recovery rate with a water flux declining rate of 0.15 L/m$^2$·hr per % water recovery rate. This indicates that once the initial cake layer or fouling layer was formed, the flux decline rate reduced by 67% afterwards. A similar result was observed in Fig. 3.5 with the synthetic wastewater containing SS, but in Fig. 3.5, two batch cycles were needed to form this initial fouling layer and the two distinct regions with different flux decline rates were seen in the third cycle. The deposits of organic foulants on the FO membrane surface restricted the water permeability (Padmanaban et al., 2020). In addition, the cake layer developed when treating raw municipal wastewater. Both of these resulted in a severe concentrative ECP, leading to the increase in feed solute concentration of FS at the active membrane surface and thus the reduction in the effective osmotic pressure driving force (Xiao et al., 2018). This water flux behaviour in agreement with previous study reported by Gao et al. (2018) who studied the CTA membrane fouling for direct concentration of municipal sewage (initial TSS concentration was not reported) at different NaCl concentrations. Gao et al. (2018) reported that when 4 M NaCl was used as DS, flux decline was significantly higher at 350 min compared with 1 M NaCl where the flux began to decline at 1200 min. These results showed that fouling caused by SS is similar for both CTA and TFC membranes at higher NaCl DS concentrations.

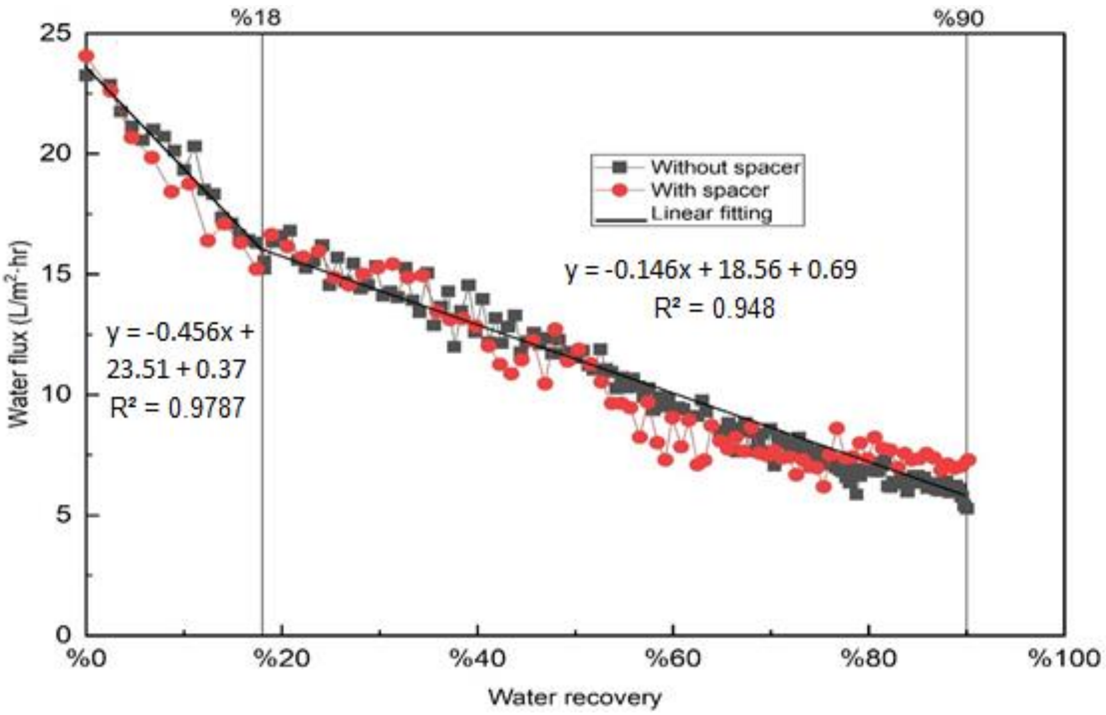

**Fig. 3.9.** Water flux changes in the single batch flat sheet FO membrane filtration cycles for concentrating real municipal wastewater with/without the use of spacer, respectively.

Although there was no noticeable difference regarding water flux during the membrane filtration processes, it was found that the membrane surface (as shown in Fig. A7) looks much cleaner without an obvious deposit layer when the spacer was used. In addition, the membrane water flux recoverability after the filtration with the spacer was improved by 84% after osmotic backwashing while it was only 60.5% without spacer as seen in Fig. 3.10. This further indicates that the existence of the spacer did result in a less compact foulant deposit which could be partially removed by osmotic backwashing. To enhance membrane water flux recovery rate of the FO membrane, high cross-velocity was further applied resulting in a further 69% improvement for the membrane without a spacer. The chemical cleaning could restore the initial water flux to around 94% for both cases. From the results, it can be known that the use of spacer in the flat sheet membrane filtration did improve the recovering capacity of physical cleaning and thus reduce the operation cost.

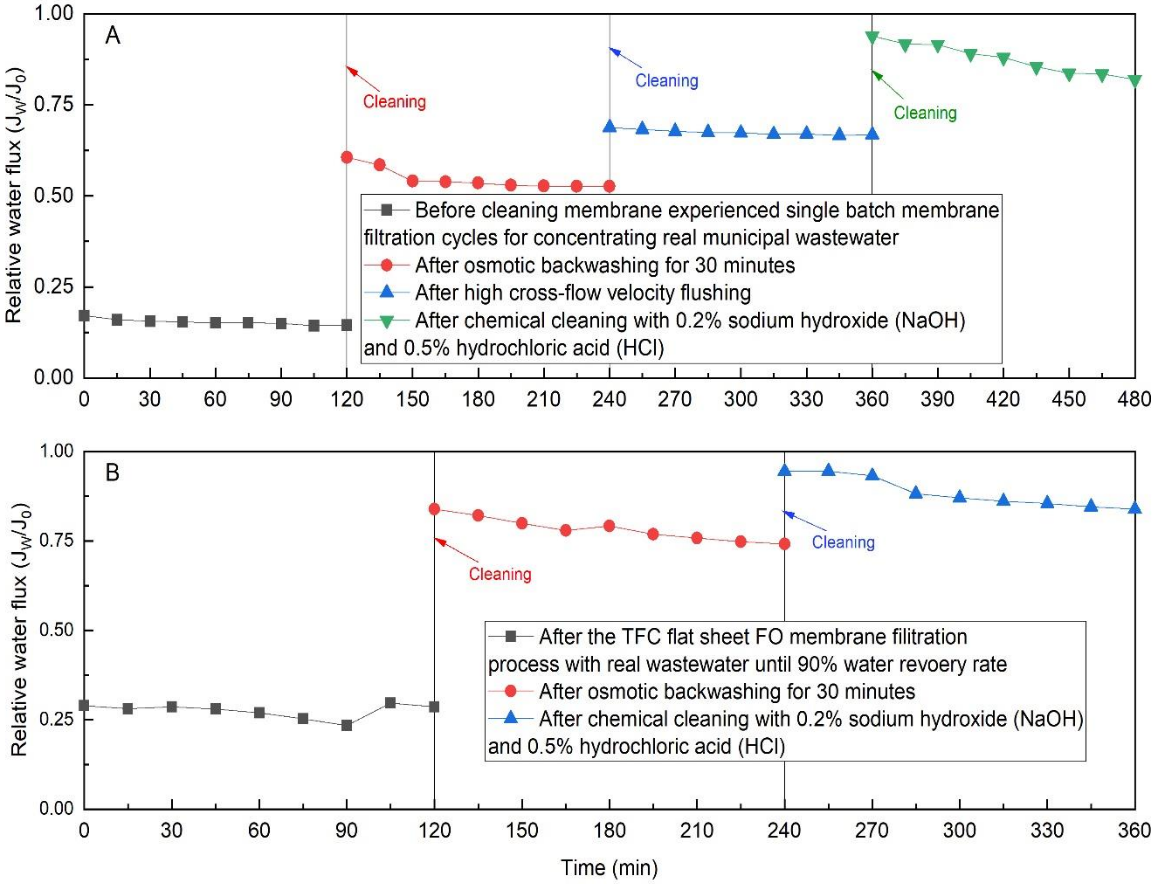

**Fig. 3.10.** Relative water fluxes before (i.e. after single batch membrane filtration cycles for concentrating real municipal wastewater with 90% water recovery rate in a flat sheet FO membrane configuration A) without spacer, and B) with spacer , and after different cleanings.

## 3.4 Conclusions

Concentrating municipal wastewater by FO membrane filtration for resource recovery and associated membrane fouling and cleaning were investigated. The following conclusions can be drawn:

- A 90% water recovery rate was needed to get sufficient COD and phosphate concentrations to facilitate direct phosphate precipitation for phosphors recovery and anaerobic treatment for energy recovery from wastewater.
- The two TFC FO membranes used in this study have high rejection rates for COD, phosphate, $Ca^{2+}$, $Mg^{2+}$ with concentration factors at around 8 while lower rejection rate for $K^+$ and no rejection at all for ammonium. Simple physical cleaning is more

effective to remove deposits on the membrane caused by SS than inorganic scaling caused by calcium precipitates during membrane filtration periods.

- Membrane fouling caused by real municipal wastewater is more complicated and harder to be cleaned by physical cleanings. Pre-treatment such as micro-filtration has to be done to ensure stable and relatively long-term membrane filtration and to increase the membrane life-span.
- The use of a spacer in the flat sheet configuration for concentrating municipal wastewater did not alleviate membrane fouling and improve water flux during the membrane filtration process, but it improved the efficiency of the following physical cleaning method by 15%. However, chemical cleaning was still needed to enhance the recovery of the initial water flux, which will increase the operating costs and reduce the membrane life-span.

# Chapter 4: Enhancing ammonium rejection in forward osmosis for wastewater treatment by minimizing cation exchange

## 4.1 Introduction

With the more stringent environmental consents are being imposed to minimize eutrophication , nutrients such as ammonium and phosphate in municipal wastewater need to be removed from treatment (Koyuncu, 2007; Jafarinejad et al., 2018). Meanwhile, ammonium and phosphorus in wastewater are important resources that could be recovered as fertilizers. Thus, combining wastewater treatment with nutrients recovery from wastewater has gained growing interests (Jorgensen and Weatherley, 2003; Xue et al., 2015). Among different technologies, the emerging FO technology appears promising due to the high rejection rates of pollutants, simple process, potential of lower energy consumption, lower membrane fouling propensity and possibilities for the direct recovery of nutrients from wastewater by concentrating (Gao et al., 2018; Yang et al., 2019).

In FO process, DS is believed to be the most critical because it affects water flux, rejection of pollutants and the cost of DS including regeneration when necessary (Yong et al., 2012; Ray et al., 2020). An ideal DS should be able to generate higher water flux, lower reverse RSF, meanwhile, be easy to regenerate and preferred to have a low molecular weight and viscosity to reduce the effect of CP (Ge et al., 2013; Zohrabian et al., 2020). These requirements are usually contradictory, and a compromise has to be made. This is one of the reasons that DS is being studied intensively. However, there is little research on DS regarding the rejection of ammonium, a major pollutant in wastewater.

It has been widely reported that ammonium in FS could easily permeate into DS due to the nature of negative charge of the FO membrane, positive charge of ammonium and similar size with water (Arena et al., 2014; Xue et al., 2015). The permeation of ammonium from FS into DS could cause DS contamination and the accumulation of ammonium in DS during the regeneration process (Volpin et al., 2018). In addition, the permeated and accumulated ammonium in DS could further escape into the water when water recovery from DS is conducted (Ray et al., 2020; Rood et al., 2020). Thirdly, the escape of ammonium from FS also results in less recovery efficiency when nutrient recovery from wastewater is targeted.

Thus, how to improve ammonium rejection in FO process for wastewater treatment and resource recovery is very important.

So far, two types of FO membranes, i.e. CTA and TFC membrane have been developed. TFC, as the second generation of FO membrane, becomes preferable to CTA due to higher water flux, lower RSF and lower biodegradable tendency (Kedwell et al., 2018). Although TFC FO membranes can achieve a more than 95% phosphate rejection rate for different types of wastewaters such as municipal and industrial wastewaters and sludge digestate (Valladares et al., 2013; Ortega-bravo et al., 2016; Wang et al., 2016; Gao et al., 2018; Volpin et al., 2018), it shows a very poor ammonium rejection (Lutchmiah et al., 2014; Rood et al., 2020). In most cases, ammonium in FS was even diluted with a lower concentration than the initial concentration in FS. For example, for municipal wastewater treatment, a negative ammonium concentration factor of -3 was reported by (Ortega-bravo et al., 2016) with 0.6 M NaCl as DS and of -2.4 with seawater as DS (Xue et al., 2015). From the perspective of municipal wastewater treatment, this is unacceptable.

To tackle this critical issue, some researchers modified the membrane surface by using poly (ethylene glycol) diglycidyl ether or dicyclohexylcarbodiimide to create a positively charged membrane surface to increase ammonium rejection (Akbari et al., 2016; Xu et al., 2017; Jafarinejad et al., 2018). Ammonium rejection rates of 99% for a synthetic solution with 50 mg/L $NH_4^+$ and of 89.3% for a return activated sludge (RAS) were obtained after membrane surface modification (Jafarinejad et al., 2018). When the membrane surface was modified to be positively charged, however, the rejection of anions such as phosphate and sulphate could be reduced. Akbari et al. (2016) reported that a positively charged FO membrane resulted in only 25% sulfate rejection. Phosphate rejection has not yet been reported for the modified FO membranes (Akbari et al., 2016; Shen et al., 2017; Jafarinejad et al., 2018), but creating a positively charge membrane could negatively affect phosphate rejection. Levchenko and Freger (2016) reported that $PO_4^{3-}$ rejection for the negatively charged nanofiltration (i.e. NF270) membrane was 95%, while $PO_4^{3-}$ rejection decreased significantly to 40% with a positively charged NF (p-NF) membrane for the treatment of secondary wastewater. Thus, it is reasonable to speculate that modifying the FO membrane surface to create a positively charged membrane might negatively affect the rejection of phosphate or other small anions, which would increase the contamination of DS and jeopardize the nutrient recovery efficiency from wastewater. Another possible solution to increase ammonium rejection is to adjust the pH of FS to a lower value such as 3. It was found by Engelhardt et al. (2019) that ammonium rejection was increased from around 52% at pH of

6 to more than 90% at pH 3 (with initial ammonium concentration of 1 g/L as FS, and 0.5 M NaCl as DS, for 80% water recovery rate). The pH effect could be explained by the change in the membrane surface charge from more negative to less negative due to more protonated carboxylic groups (COOH) at pH of 3 than deprotonated carboxylate groups ($COO^-$) at pH of 6. Thus, at lower pH, the forward ammonium flux and the RSF of $Na^+$ were reduced, leading to the increase in ammonium rejection rate. It can be seen that adjusting pH to increase ammonium rejection is essentially due to change membrane surface charge as well. Since wastewater is usually bulk and highly diluted, adjusting bulk solution pH is impractical. Alternatively, an after-thought solution was proposed to overcome the DS contamination problem by removing permeated ammonium by microorganisms. For example, Rood et al. (2020) proposed to introduce an algal strain in the synthetic seawater DS to take up ammonium. However, the proposed algal FO system was not very effective with only 35.4% ammonium removal in total. In addition, introducing algae in DS could lead to potential membrane fouling problems by forming biofilm on the membrane surface. Therefore, a cost effective, efficient, and easy-to-implement solution is badly desired for ammonium rejection without causing other negative effects. It has been reported that different DSs could have different rejection rates for a same type of contaminant (Lu et al., 2014; Zheng et al., 2019). Hu et al. (2017) investigated the impact of ionic DSs such as NaCl and $MgCl_2$ on ammonium rejection by using the TFC FO membrane for treating municipal wastewater. $NH_4^+$-N concentration in the FS decreased during the FO process, i.e., not effectively rejected, with NaCl as DS while ammonium rejection rate reached between 58-87% with $MgCl_2$ as DS. It was explained in the study that the higher diffusion coefficient of NaCl compared than $MgCl_2$ resulted in a higher reverse $Na^+$ than $Mg^{2+}$ flux to FS, and thus caused more forward ammonium permeation from the FS to the DS to maintain electroneutrality. Since this study only investigated NaCl and $MgCl^2$ as DSs, it is hard to draw a solid conclusion that diffusion coefficient of DS plays a critical role for ammonium rejection. An investigation on more different types of DSs is needed for validation. Furthermore, multiple physiochemical properties are changed when DS is different. Thus, it would be very beneficial if the critical physiochemical properties of DS affecting ammonium rejection could be identified. If so, a rule could be found to guide the selection of DS for ammonium rejection without compromising the rejection of anions. In addition, it still unknown if other factors such as wastewater quality and ammonium concentration in wastewater affect ammonium rejection.

Thus, the objective of this study was to evaluate what properties of DS could be used to enhance ammonium rejection with TFC FO membrane for wastewater treatment. The investigated DSs included ionic DSs such as NaCl, $MgCl_2$, $MgSO_4$, $Na_2SO_4$ and non-ionic DSs such as glucose, glycine and ethanol. The effects of FS chemistry on ammonium rejection were also investigated by using synthetic wastewater, real municipal wastewater and sludge digestate.

## 4.2 Materials and methods

### 4.2.1 Forward osmosis membrane and experimental setup

Hollow fiber TFC membranes developed by the Singapore Membrane Technology Centre were used in this study. Details of the FO membrane and the experimental protocol can be found in section 3.2.1.

### 4.2.2 Feed solution and draw solution

Two different types of synthetic wastewater were used in this study. To investigate the effects of DS type in FS on ammonium rejection, synthetic water containing only ammonium with a concentration of 34.30 ± 0.61 mg/L ammonium-N (with $(NH_4)_2SO_4$ for N) was used. To investigate ammonium rejection with the presence of other main pollutants in municipal wastewater, a synthetic municipal wastewater was prepared to simulate municipal wastewater that was reported by (Metcalf and Eddy, 2008) with 496.82 ± 34.78 mg/L COD (with NaAc. $3H_2O$ as COD), 8.72 ± 0.43 mg/L $PO_4^{3-}$-P (with $KH_2PO_4$ for P), 38.33 ± 1.10 mg/L ammonium-N (with $(NH_4)_2SO_4$ for N), 8.57 ± 0.24 mg/L $Ca^{2+}$, 7.75 ± 0.16 mg/L $Mg^{2+}$, 8.75 ± 0.39 mg/L $K^+$.

Two different $NH_4^+$-N concentrations, i.e., 17.87 ± 0.15 and 1293.95 ± 10.68 mg/L, respectively, in synthetic wastewater were used to simulate $NH_4^+$-N concentration in municipal wastewater and sludge digestate for the study of effects of initial ammonium concentration in FS on ammonium rejection in the TFC FO process.

In addition, real municipal wastewater and sludge digestate were tested with 0.6 M NaCl and 1.2 M glucose as DSs, respectively, under the same osmotic pressure of 29 bar. Both municipal wastewater after the treatment by primary settlement tank and sludge digestate from anaerobic digester were collected from the Millbrook Municipal WWTP, Southampton, UK. To avoid the FO hollow fiber membrane clogging from SS, both real municipal wastewater and sludge digestate were pre-treated by centrifugation and filitration to minimize SS concentrations. Specifically, the municipal wastewater was centrifuged

(Sorvall Legend T, Sorvall) for 10 min at 4100 g/min, followed by filtration with 1.2 um filter (Whatman, UK) and finally with 0.45 um filter (Whatman, UK). The same procedure was used to filter the sludge digestate with the addition of chemical coagulant such as aluminium chloride prior to the filtration. The filtered municipal wastewater contained 119.96 ± 3.39 mg/L COD, 2.26 ± 0.12 mg/L $PO_4^{3-}$-P, 16.74 ± 0.16 mg/L $NH_4^+$-N, 63.83 ± 0.49 mg/L $Ca^{2+}$, 13.07 ± 0.27 mg/L $Mg^{2+}$ and 17.16 ± 1.41 mg/L $K^+$ mg/L, while the filtered sludge digestate consisted of 959.70 ± 33.93 mg/L COD, 1 ± 0.02 mg/L $PO_4^{3-}$-P, 1255.13 ± 87.56 mg/L $NH_4^+$-N, 21.02 ± 0.32 mg/L $Ca^{2+}$, 18.96 ± 0.82 mg/L $Mg^{2+}$, and 93.38 ± 2.36 mg/L $K^+$ mg/L.

Four different types of inorganic salts such as NaCl, $MgCl_2$, $MgSO_4$ and $Na_2SO_4$ were used as DSs due to their different diffusion coefficient, molecular size and hydrated cation radius. Non-ionic chemicals such as glucose, glycine and ethanol with different molecular weight and diffusion coefficient were chosen as three types of DSs with minimal cation exchange potential. The main physiochemical properties of DSs were summarized in Table B1. In addition, Table B2 shows the estimated transport parameters, atomic weight and estimated cation hydrated radius in the inorganic DSs. Different DS concentrations were prepared by dissolving the osmotic agents in DI water to rule out the effects of other ions from DSs.

### 4.2.3 Operation of the experimental systems

The water flux performance of the TFC membrane with three different types of DSs (i.e. NaCl, $MgCl_2$ and glucose) was evaluated by using the lab-scale, hollow fiber FO system to determine water flux ($J_w$) and RSF ($J_S$). These DSs were chosen as a reference to evaluate the effect of DS physiochemical properties (i.e. diffusion coefficient, molecular weight and viscosity) on the FO water flux and RSF. The solute was dissolved in DI water to prepare DSs with different concentrations, which corresponded to different osmotic pressure such as 24, 48, 96 and 144 bar. The molar concentration of 6 M glucose as DS to obtain 144 bar osmotic pressure wasn't evaluated in this study as this concentration exceeds its solubility limit in water. To determine the RSF of the DS in the FO process, the conductivity (Hanna HI700 instrument, HI7639 probe, UK) of the FS was measured every 15 min when using ionic salts as DSs and DI water as FS, while a 10 mL sample was withdrawn from the FS tank every 15 min for the subsequent COD analysis when non-ionic DSs were used. All FO experiments to determine water flux and RSF were lasted for at least 2 h.

FO membrane filtration experiments were run until a water recovery rate of 50% to investigate the effect of DS type on ammonium rejection by TFC FO membrane. The initial

FS and DS volumes were set as 1 L for the effect of DS type on ammonium rejection, while the initial volumes for synthetic wastewater and real wastewater were set as 0.7 and 0.7 L, respectively, for the investigation of ammonium rejection in different types of wastewater. To investigate the effects of other ions on ammonium rejection, a synthetic municipal wastewater was used as FS (2 L) with 1 M of glucose (2 L) as DS until 90% water recovery. Unless otherwise stated, the pH of both FS and DS were adjusted to around 7 by using sodium hydroxide (NaOH) or hydrochloric acid (HCl) prior to each experiment.

Before the membrane experiments for synthetic or real wastewater, baseline tests were conducted with DI water as FS and 1 M NaCl DS to determine the baseline water flux. After the membrane experiments for synthetic or real wastewater, the flux was tested again with DI water to determine the water flux decline extent by comparing it with the baseline flux. After this, two different physical methods were used to clean the membrane, which are i) normal flushing by replacing FS and DS with DI water with flow rates of 0.6 L/min for 30 min, and ii) osmotic backwashing by substituting DS with DI water and FS with 1 M NaCl with AL-DS for 30 min at flow rates of 0.6 L/min to induce opposite crossflow to remove foulants on/in the membrane.

### 4.2.4 Analytical methods

COD, ammonium, and phosphate were measured in accordance with standard methods by American Public Health Association (APHA). Conductivity was measured by using Hanna HI700 instrument and HI7639 probe (Hanna, UK). pH was measured  using the pH probe from Jenway 3010 meter (Bibby Scientfic Ltd, UK). The concentration of cations such as $Ca^{2+}$, $Mg^{2+}$ and $K^{+}$ were analyzed using ion chromatography (882 Compact IC plus, Metrohm, Switzerland).

### 4.2.5 Calculations

Water flux across the FO membranes was determined by using equation 4.1:

$$J_w = \frac{\Delta V}{\Delta t \text{ x } A_m} \qquad \text{Equation 4.1}$$

where $J_w$ (L/m$^2$·hr) is the water flux, $\Delta V$ (L) is the volume change of the FS, $\Delta t$ (hr) is the time elapsed and $A_m$ (m$^2$) is the effective membrane area. To obtain the FS volume, FS weight was divided by the density, which was assumed to be 1 kg/L.

The concentration factor (equation 4.2) (CF) was calculated as the ratio between the FS concentration at time t ($C_t$) after FO experiment and the initial FS concentration ($C_0$) at time 0:

$$\mathrm{CF} = \frac{C_t}{C_0} \qquad \text{Equation 4.2}$$

Contaminant rejection rate (R) was calculated based on the mass balance between FS and DS (equation 4.3):

$$\mathrm{R} = \left(1 - \frac{V_{df} \times C_{df}}{V_{fi} \times C_{fi}}\right) \times 100\% \qquad \text{Equation 4.3}$$

Where $V_{df}$ (L) is the final volume of the DS, $C_{df}$ (mg/L) is the final contaminate concentration in the DS, $V_{fi}$ (L) is the initial FS volume, $C_{fi}$ (mg/L) the initial contaminate concentration in the FS.

The RSF (Js) was calculated from the following formula (equation 4.4):

$$\mathrm{Js} = \frac{V_{Ft2}.C_{Ft2} - V_{Ft1}.C_{Ft1}}{\Delta t \times A_m} \qquad \text{Equation 4.4}$$

Where Js ($g/m^2 \cdot hr$) is the RSF, $V_{Ft2}$ (L) is the volume of FS at recording time interval $t_2$, $V_{Ft1}$ (L) is the FS volume at recording time interval $t_1$, $C_{Ft2}$ (g/L) is the solute mass concentration in FS at $t_2$, $C_{Ft1}$ (g/L) is the solute mass concentration in FS at $t_1$. The salt concentration in the FS of due to RSF was obtained by measuring conductivity of FS at different times according to the calibration curve between salt concentration and conductivity of solution. The concentration of reverse non-ionic solute was obtained by measuring COD of FS at different times according to the calibration curve between non-ionic solute concentration and COD.

The osmotic pressures for different DSs at different concentrations were calculated using Van't Hoff equation 4.5 (Cornelissen et al., 2008; Altaee et al., 2013; Altaee and Hilal, 2014; Devia et al., 2015; Corzo et al., 2017):

$$\Pi = iMRT \qquad \text{Equation 4.5}$$

where Π (bar) is the osmotic pressure, i is the van't Hoff factor of the solute, M (mol/L) is the molar concentration, R is the universal gas constant (0.08206 L.atm/mol.K) and T is the absolute temperature in K.

The SI was calculated by using Visual MINTEQ (v. 3.1) software to estimate potential precipitates in the concentrated FS. The SI for synthetic municipal wastewater FS and 1 M glucose DS was calculated at 90% water recovery rate, while SI for real municipal wastewater and sludge digestate was calculated at 50% water recovery rate.

## 4.3 Results and discussion

### 4.3.1 Effects of draw solution type on water flux and reverse solute flux

Fig. 4.1 shows the effects of DS type, e.g. monovalent, divalent inorganic and non-ionic organic DS, on water flux and RSF under different osmotic pressures. A liner regression between the water flux and the DS osmotic pressure was used to show flux increase rate for each DS. It can be seen that water flux increased linearly with the increase in the osmotic pressure of three different types of DSs, however, the water flux increased with the highest rate of 0.21 $L/m^2·hr·bar$ when using NaCl as DS, followed by $MgCl_2$ with a rate of 0.098 $L/m^2·hr·bar$ and glucose with a rate of nearly 0. This indicates that enhancing water flux by simply increasing the osmotic pressure of DS is not always workable, which highly depends on the type of DS. Among DSs such as NaCl, $MgCl_2$ and glucose used in this experiment, diffusion coefficients are $1.47 \times 10^{-9}$, $1.07 \times 10^{-9}$ and $0.67 \times 10^{-9}$ $m^2/s$, respectively, and viscosity of liquid under the same osmotic pressure are 0.94, 1.14 and 1.45 cP, respectively, and molecular weight of solute are 58.44, 95.21 and 180.16 g/mol, respectively (Phang and Stokes, 1980; Miller et al., 1984; Achilli et al., 2010; Salva et al., 2013; Holloway et al., 2015; Yasukawa et al., 2015). It has been reported that lower diffusion coefficient, higher viscosity and larger molecule size of DS could cause more serious both ICP and ECP (Ansari et al., 2015; Parveen and Hankins, 2019) since solute molecules in DS are unable to quickly diffuse from the bulk solution to the diluted zone in the support layer of membrane facing DS. This would reduce effective driving force created by osmotic pressure difference between FS and DS, lowering water flux. Thus, glucose results in the lowest water flux due to the most severe ICP caused by the highest viscosity and the lowest diffusivity coefficient under the same osmotic pressure compared with NaCl and $MgCl_2$. When the concentration of DS increases, viscosity further increases. The positive impact from the increased osmotic pressure of glucose is likely offset by the negative impact from more severe ICP, leading to negligible water flux increase as shown in Fig. 4.1A. Although no quantitative relationship could be obtained between water flux and draw solution's viscosity, and diffusivity coefficient and molecular size of solute, physiochemical properties of DS such as diffusion coefficient, viscosity and molecular size could be used to qualitatively estimate water flux and corresponding water flux increase with the concentration of DS. This is helpful for the selection of DS for different application scenarios. In addition, it should be noted that draw solution's viscosity and diffusivity coefficient could be significantly changed for an increased water flux at higher. Thus, besides what mentioned above, temperature should be also considered when selecting DS.

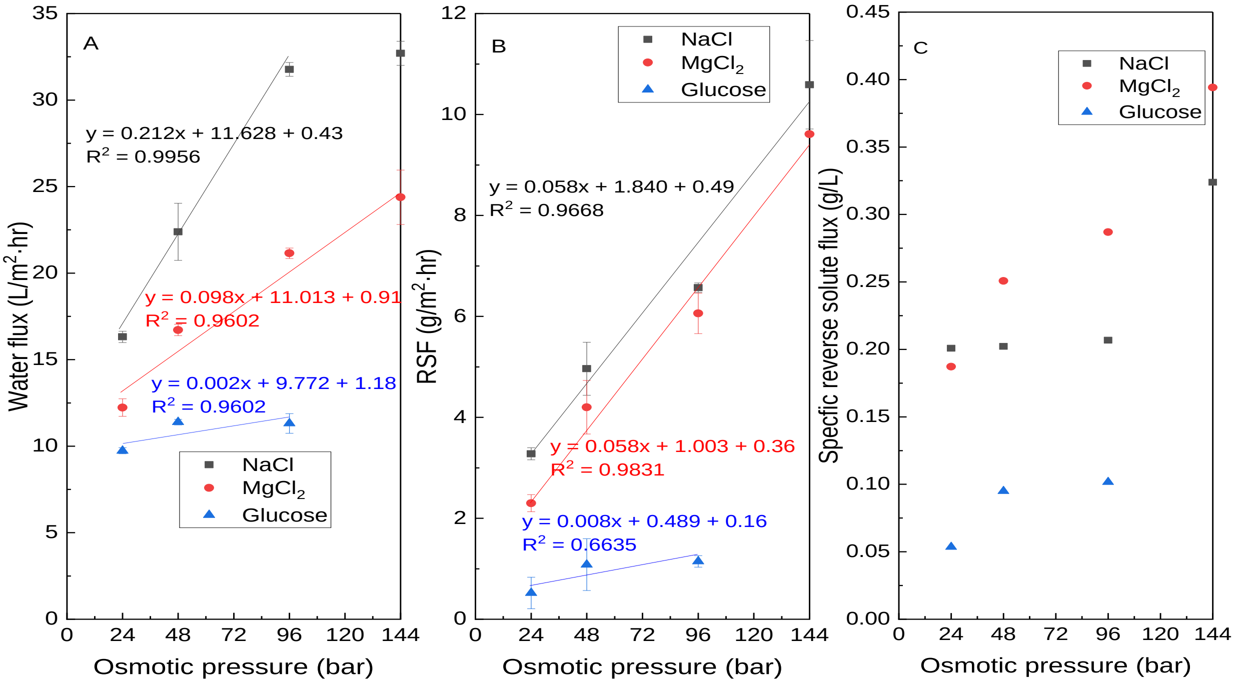

**Fig. 4.1.** The dependence of water flux, RSF and specific reverse solute flux on the osmotic pressure of draw solutions such as NaCl, $MgCl_2$ and glucose and DI water as FS.

RSF is another important factor which needs to be considered for the selection of DSs. It can be seen from Fig. 4.1B that RSF increased linearly with the rise of the osmotic pressure of NaCl, $MgCl_2$ and glucose but RSF of NaCl and $MgCl_2$ were much higher than that of glucose. Again, RSF could depend on diffusion coefficient, molecular size of solute in DS, and viscosity. The larger effective diameter of hydrated $Mg^{2+}$ (i.e. 800 $10^{-12}$ m, almost two times of $Na^+$ (Devia et al., 2015)) and lower diffusivity of $Mg^{2+}$ might result in the lower passage of $Mg^{2+}$ ion through the FO membrane compared with $Na^+$. Glucose has the larger molecular size as non-ionic organic and lower diffusivity coefficient, leading to the lowest RSF. These results are in good agreement with previous studies with NaCl, magnesium acetate, $MgCl_2$, sodium acetate and glucose as DSs, whereby DSs with lower diffusion coefficient have a lower water flux and RSF (Achilli 2010; Ansari et al., 2015; Adnan et al., 2019; Gulied et al., 2019). In addition, it is found that the RSF from NaCl and $MgCl_2$ changed at a similar rate of 0.058 g/m$^2$·hr·bar with the osmotic pressure, which is different from water flux. From this perspective, NaCl is better than $MgCl_2$ as DS.

When considering DS loss (or replenishment demand) or total contamination of FS by the solutes of DS after a certain operation period, specific reverse solute flux ($J_s/J_w$), i.e. how much solute loss from DS due to RSF for per liter permeate, is a more useful parameter than RSF. As shown in Fig. 4.1C, glucose had the lowest specific reverse solute flux at 24, 48 and 96 bar compared with NaCl and $MgCl_2$. However, $MgCl_2$ demonstrates higher specific reverse flux than NaCl although it has lower RSF than NaCl as the increasing rate of RSF was higher than the increasing rate of water flux. As shown in Table B3, the replenishment cost of glucose is lower than NaCl and $MgCl_2$ at the osmotic pressure of 24 bar, however, with the increase in osmotic pressure, NaCl becomes more economic than glucose and $MgCl_2$. From the practical point of view, seawater or brine could be obtained for free particularly in the regions close to coasts. However, with the development of saccharification from organic wastes, glucose or sugar solutions could be available at an acceptable cost. In this case, an FO process with sugar solution as DS could be integrated with a fermentation process to reduce the cost of sugar.

### 4.3.2 Effects of draw solution type on ammonium rejection

Unlike COD and phosphate, ammonium is usually ineffectively rejected by the TFC FO membrane due to the negative charge of membrane surface. Pre-tests of DSs of NaCl, $MgCl_2$ and glucose showed ammonium rejection rates as 32.46%, 70.72% and 100%, respectively (Fig 4.2B). From this result, it can be known that selecting appropriate DSs could be an alternative to the modification of membrane surface from negative to positive charge as reported to selectively reject ammonium.

To better understand which physiochemical properties of solute of DS affect ammonium rejection most, two additional ionic DSs (i.e. $Na_2SO_4$ and $MgSO_4$), and two neutral DSs (i.e. glycine and ethanol) were further investigated for ammonium rejection. Glycine and ethanol were selected because they are neutral at the studied pH but with higher diffusion coefficient than that of glucose while $Na_2SO_4$ and $MgSO_4$ were selected as they are ionic as NaCl but with different diffusion coefficients and hydrated cation radium. 9 DSs for the study could be classified into groups for the comparison of different hydrated cation radius such as $Na^+$ and $Mg^{2+}$, different diffusion coefficients with the same cation such as between NaCl and $Na_2SO_4$, $MgCl_2$ and $MgSO_4$, different diffusion coefficients for neutral chemicals such as glycine, ethanol and glucose. Fig. 4.2 shows water flux and ammonium rejection with 9 different DSs. It can be seen that sodium-based DSs have higher water flux than magnesium-based DSs but with lower ammonium rejection. Neutral chemicals as DSs have ammonium rejection rates of 100% or close to 100% with middle range or low range water flux.

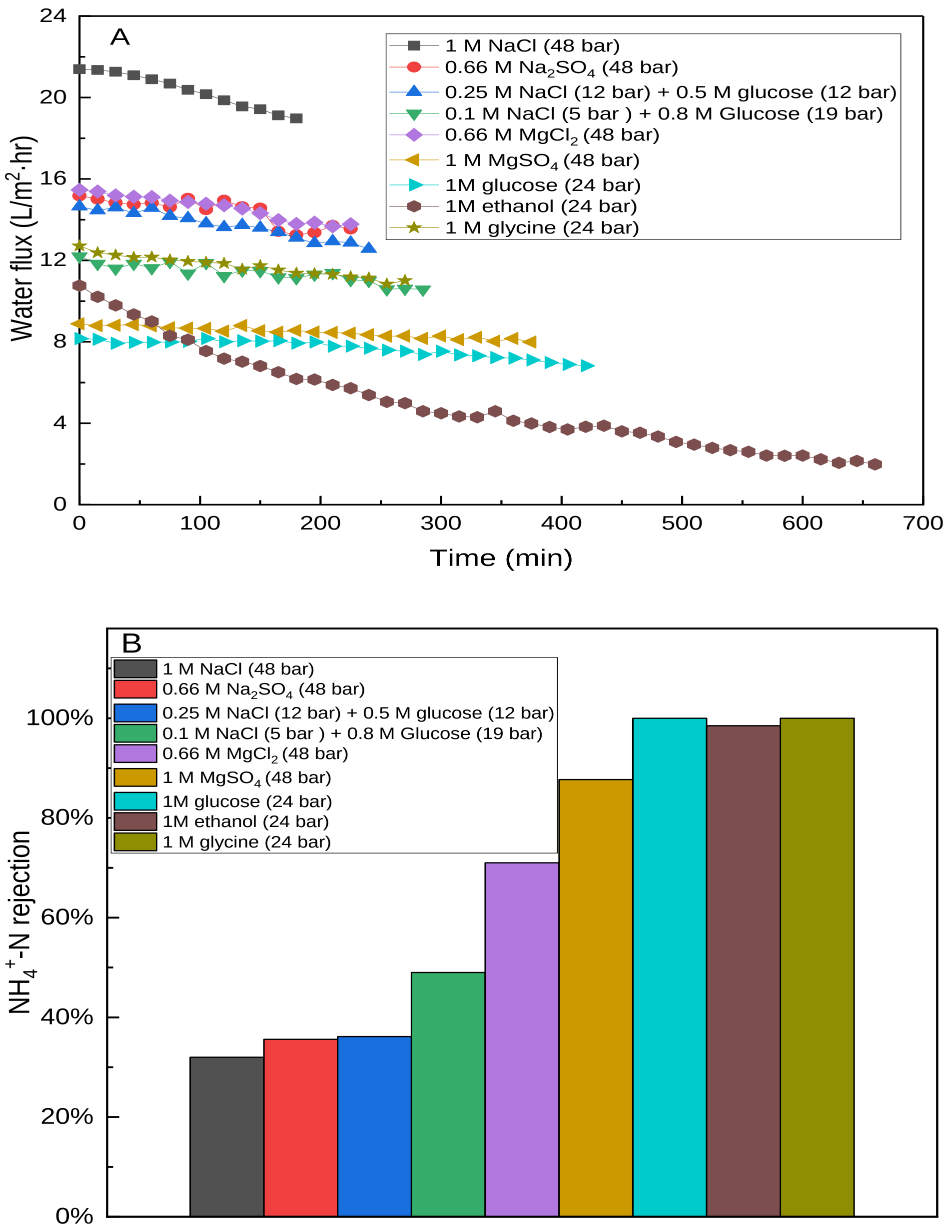

**Fig. 4.2.** Water flux and $NH_4^+$-N rejection rate in the synthetic FS with different DSs during the TFC FO membrane filtration process until 50% water recovery with 34.30 ± 0.61 mg/L of initial $NH_4^+$-N.

Different from the mechanism of ammonium rejection by modified membrane surface with repulsion between ammonium and positive charge on the membrane surface, the higher ammonium rejection rates with magnesium-based DSs and neutral chemicals as DSs are most likely due to reduced cation exchange between ammonium in the FS and cations in the DS. Irvine et al. (2013) reported solute-solute interaction via ion exchange could have a dramatic impact on the permeation of solutes through dense polymeric membranes and they found that identity of anions in DS had a significant impact on forward nitrate permeation from FS. Thus, the current study focused on forward ammonium permeation. Similarly, it was found in this study that the identity of cation such as $Na^+$ and $Mg^{2+}$ have significant impact on forward ammonium permeation via cation exchange with magnesium based DS having higher ammonium rejection.

It is known that divalent $Mg^{2+}$ has a larger hydrated radius than that of monovalent $Na^+$ (i.e. 0.428 nm for $Mg^{2+}$ and 0.358 nm for $Na^+$, respectively) (Devia et al., 2015; Cheng et al., 2018a). Cheng et al. (2018b) also reported that divalent draw cations with larger hydrated radius could reduce cation exchange compared with monovalent draw cations when studying $K^+$ in the FS. Thus, it could be concluded that divalent draw cation is better for cation rejection in FS, and it is reasonable to speculate that trivalent draw cation could be even better than divalent cation regarding ammonium rejection. Secondly, it is found from Fig. 4.2 that the lower diffusion coefficient of DS led to higher ammonium rejection when the cation identity was same. For example, $Na_2SO_4$ with lower diffusion coefficient resulted in a 3% higher ammonium rejection rate than NaCl with higher diffusion coefficient. $MgSO_4$ with lower diffusion coefficient achieved more than 15% ammonium rejection rate than $MgCl_2$ with higher diffusion coefficient. This suggests that to enhance the ammonium rejection rate, it is better to use a multivalent cation-based DS with a lower diffusion coefficient.

Regarding neutral chemicals as DS without ion dissociation, it is found from Fig. 4.2 that ammonium was almost 100% rejected. The comparison of diffusion coefficient of ionic and non-ionic DSs used in this study in Table B1 shows that ethanol and glycine have much higher diffusion coefficient than $Na_2SO_4$ and $MgSO_4$, but ammonium rejection rates from ethanol and glycine are almost 100%. In addition, when NaCl concentration in the DS with a mixture of NaCl and glucose was higher than 0.25 M, ammonium rejection rate was slightly higher (i.e. 3%) than that with 1 M NaCl as DS. When NaCl concentration in the DS with a mixture of NaCl and glucose was reduced to 0.1 M, ammonium rejection rate was improved by 15% compared with 1 M NaCl due to the reduced $Na^+$ in DS and thus reduced reverse $Na^+$ permeation for cation exchange although the osmotic pressure of DS was controlled at the same level. Therefore, it could be seen from here that ammonium rejection rate does not rely on osmotic pressure but is negatively related with the NaCl concentration. In addition, it is found from Fig. 4.2 that the water flux of ethanol decreased more steeply compared with other DSs. In addition, it is found from Fig. 2 that the water flux of ethanol decreased more steeply compared with other DSs. The ethanol concentration in the DS after 50% water recovery rate was 19.41 g/L, lower than the theoretical ethanol concentration of 30.71 g/L assuming no ethanol transport to other solution or phases. The mass balance calculation by measuring COD in the FS after 50% water recovery rate indicates that 20.06% of the initial ethanol amount in DS transferred from the DS to the FS by RSF while around 4% of the initial ethanol was evaporated during the 11 hr FO operation given that ethanol was highly volatile. The more reverse ethanol permeation from DS to FS is the main reason for the steeper drop of water flux compared with other types of DSs. The significant loss of ethanol to the FS observed in this study is in agreement with (Kim et al., 2019) who showed that RSF obtained for ethanol DS was 240 $g/m^2 \cdot hr$, and was 40 times higher than 6 $g/m^{2 \cdot} hr$ for NaCl DS at the same osmotic pressure of 46.7 bar. This is mainly due to the small size of ethanol molecules and high diffusion coefficient. Even with such high reverse ethanol flux, there is almost no forward ammonium permeation. These results further confirm that cation exchange between DS and FS is the most critical factor for forward ammonium permeation while diffusion coefficient of DS might only play a minor role when ionic DS is used.

Apart from ammonium exchange with cations in DS, $H^+$ as a smaller positively charged ion could be more easily exchanged when ionic DSs are used, leading to pH change in both FS and DS. It can be seen from Fig. B1 that notable pH increase was observed in FS with NaCl, $MgCl_2$ and glucose as DSs during the period of the first 10% water recovery rate. After that, the pH of FS increased most with $MgCl_2$ as DS, while slightly with NaCl as DS and slightly decreased with glucose as DS. This is probably because that one $Mg^{2+}$ needs roughly 2 $H^+$ to exchange to maintain electroneutrality, and thus lead to higher pH increase in FS. The pH increase in the FS was observed in both synthetic and real wastewater during the FO process with different DSs (Cath, 2009; Xie et al., 2014; Ansari et al., 2016b, 2018). Ansari et al. (2016) reported that the pH of the FS increased from 6.5 to 8.0 with 1.27 M NaCl as DS after achieving 90% water recovery rate during the CTA FO process. Another study by Kumar and Pal (2015) showed that the pH of the FS with either NaCl or $MgCl_2$ as DSs at a 90 bar osmotic pressure was increased from 7 to 8 and 8.2, respectively. The pH change validates the ion exchange between DS and FS.

When DS is selected for enhanced ammonium rejection, water flux has to be considered as well because higher water flux can reduce membrane surface area required for specific treatment demand. From Fig. 4.2, it can be seen that for ionic DSs, it is difficult to find a type of DS with both relatively higher water flux and ammonium rejection rate. Since all neutral chemicals used in this study achieved almost 100% ammonium rejection rate, it is recommended to select a neutral chemical with the highest water flux as DS. Glycine is less practical as DS given its cost, but the findings in this study could be used as a guidance to select more suitable DS to meet the requirement of high ammonium rejection for wastewater treatment.

### 4.3.3 Concentrating synthetic municipal wastewater with glucose as draw solution until 90% water recovery rate

To further investigate if ammonium rejection with neutral chemicals as DS would be negatively affected by other ions and chemicals in wastewater, synthetic wastewater with multiple ions and chemicals was investigated with glucose as DS for 90% water recovery rate. As shown in Table 4.1, COD concentration was increased from 496.82 ± 34.78 to 6419.29 ± 69.57 mg/L with a concentration factor of 12.92. The final COD concentration was higher than the theoretical value for a complete COD rejection, i.e. 10 of concentration factor. Obviously, the extra COD was due to reverse solute permeation from DS. Although reverse glucose flux results in the cost for replenishment, the glucose lost to FS can be recovered as methane when concentrated municipal wastewater goes through post-treatment such as AD. No $PO_4^{3-}$-P, and $NH_4^+$-N were detected in the DS after 90% recovery rate, indicating 100% ammonium and phosphate rejection. However, as shown in Table 4.1, concentration factors of soluble $PO_4^{3-}$-P and $NH_4^+$-N in FS were 8.48 and 7.92, respectively, lower than theoretical value 10, for 100% rejection rate. At the end of the FO experiment with 90% water recovery rate, precipitates were observed in the concentrated FS, proving that a tiny proportion of soluble ammonium and phosphate were precipitated due to increased pollutant concentrations and pH. The SI values of struvite or hydroxyapatite at increased concentrations of $PO_4^{3-}$-P, $NH_4^+$-N, $Ca^{2+}$ and $Mg^{2+}$ and pH from 6.7 to 7.1 became positive, implying high potential for the formation of precipitates (Table B4). 100% rejection of $NH_4^+$-N and $PO_4^{3-}$-P by glucose DS can avoid forward nutrient permeation to contaminate DS and downstream recovered water and meanwhile guarantees maximum nutrient recoveries in the post-treatment. The final $PO_4^{3-}$-P concentration of 73.77 mg/L in the concentrated FS at 90% water recovery rate could be directly precipitated as struvite or hydroxyapatite precipitation for phosphorus recovery by adjusting pH to 9-11. In addition, since $NH_4^+$ and $K^+$ have the same hydrated radii (Guertal and Hattey, 1996) as 3.3 Å, similar rejection rates of $NH_4^+$ and $K^+$ were expected. However, it was noted that $K^+$ was enriched by only 4 fold from 8.75 to 35.04 mg/L. This indicates the complexity of forward permeability of small ions through membrane. The higher concentration factors reported in this study for $Mg^{2+}$ and $Ca^{2+}$ compared with $K^+$ align with previous studies in that monovalent cations are more permeable than divalent cations through FO membranes (Gao et al., 2018).

**Table 4.1:** Summary of initial and final concentrations of pollutants in synthetic wastewater as feed solution and 1 M glucose as draw solution, and concentration factors of each pollutant with a 90% water recovery rate after TFC hollow fiber FO membrane filtration.

| Pollutants | Initial concentration in FS (mg/L) | Final concentration in FS (mg/L) | CF | Theoretical concentration in FS assuming 100% rejection (mg/L) |
|---|---|---|---|---|
| COD | 496.82 ± 34.78 | 6419.29 ± 69.57 | 12.92 | 4968.20 |
| $PO_4^{3-}$-P | 8.72 ± 0.43 | 73.77 ± 0.09 | 8.48 | 87.20 |
| $NH_4^+$-N | 38.33 ± 1.10 | 303.53 ± 2.86 | 7.92 | 383.30 |
| $Ca^{2+}$ | 8.57 ± 0.24 | 66.20 ± 1.83 | 7.72 | 85.70 |
| $Mg^{2+}$ | 7.75 ± 0.16 | 64.21 ± 0.95 | 8.28 | 77.50 |
| $K^+$ | 8.75 ± 0.39 | 35.04 ± 1.14 | 4 | 87.50 |

Fig. 4.3 shows the dynamic water flux during FO process. Water flux decreased continuously mainly because of the reduced driving force between FS and DS by concentrating ions and chemicals in the FS and diluting DS. Fig. 4.3 shows varied water flux reduction rate, indicating membrane fouling could be involved in FO filtration process especially in the latter part of filtration. Based on the varying slopes of water flux reduction, the membrane filtration could be divided into four distinct periods, i.e. the first 330 min with water recovery rate from 0 to 23%, the period from 330 to 1125 min with water recovery rate from 23 to 68%, the period from 1125 to 1785 min with water recovery rate from 68 to 88.8%, and the last period from 1785 to 1860 min with water recovery from 88.8 to 90%. In the first period and the last period, water fluxes were relatively stable with little water reduction. This is because a certain time (i.e. 330 min) was needed for the development of membrane fouling, while in the last period (i.e. 88.8-90%) the fouling layer grew slowly. However, in the second period, water flux declined with a rate of 0.0031 L/m$^2$·hr per min from 8.72 to 6.28 L/m$^2$·hr while it became 0.0067 L/m$^2$·hr per min, a doubled declining rate, from 68% to 88.8% water recovery rate where the flux dropped by 69.4% from 6.28 to 1.92

L/m$^2$·hr. The increased water flux decline in the 2nd and 3rd periods should be from membrane fouling. Since the synthetic wastewater used in this study mainly contained sodium acetate, ammonium, phosphate $Ca^{2+}$, $Mg^{2+}$, and $K^+$, it could be speculated the membrane fouling was mainly caused by inorganic scaling from the phosphate precipitates instead of organic fouling or biofilm fouling. It is interesting to note that water flux decline rate was two times higher in the third period with water recovery rate above 68%, indicating that inorganic membrane fouling passed a tipping point. From this point of view, it would be better to operate FO filtration with a water recovery rate below 68% to maintain an acceptable water flux and treating capacity of FO system. It needs to point out that the recommended specific water recovery rate should be different for different wastewater with different fouling potential and different DSs, which should be obtained by monitoring water flux over the time.

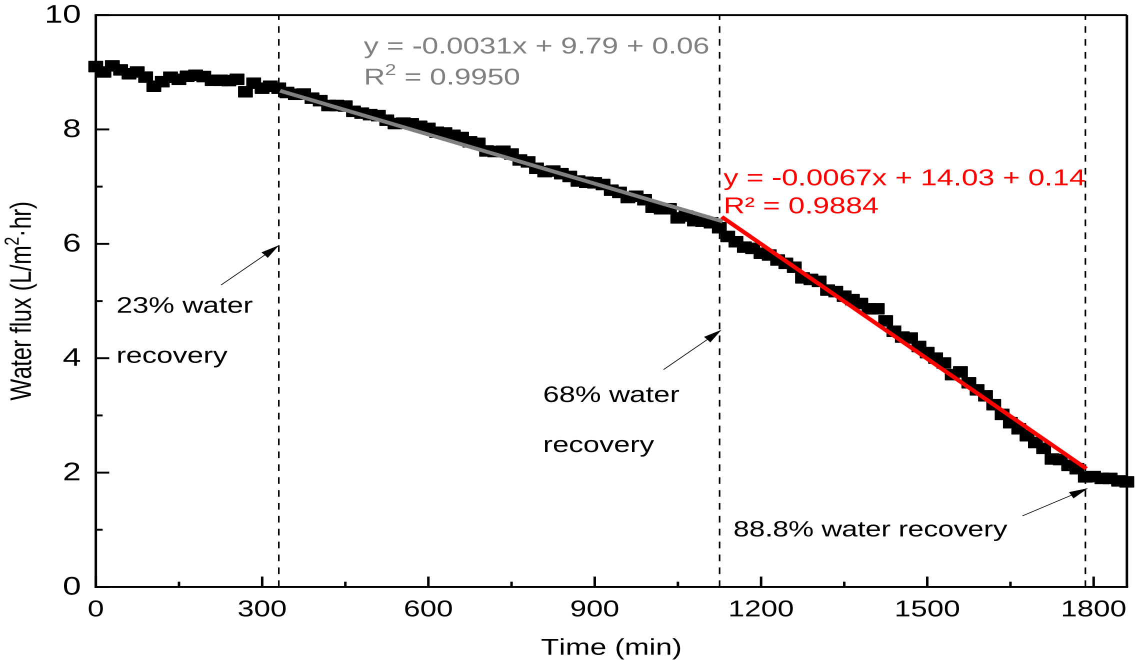

**Fig. 4.3.** Water flux behaviour with synthetic municipal wastewater as feed solution and 1 M glucose as draw solution for the TFC FO membrane until 90% water recovery rate.

After synthetic municipal wastewater treatment with 90% water recovery rate, the water flux was tested with DI water. It was found that water flux declined by around 34.5% as shown in Fig. B2. This further validated membrane fouling during the membrane filtration process. After osmotic backwashing for 30 min, around 99% of the initial water flux was restored, suggesting the reversibility of the TFC FO membrane after inorganic fouling.

### 4.3.4 Effect of initial ammonium concentration on ammonium rejection with NaCl and glucose as draw solutions

Real wastewater might contain different ammonium concentrations. In addition, real wastewater is more complex with more types of ions and chemicals. More tests were conducted to further investigate effects of ammonium concentration on ammonium rejection and enhanced ammonium rejection by neutral chemicals with different ammonium concentrations. Firstly, synthetic wastewater containing only ammonium was tested with NaCl as DS to study the effect of initial $NH_4^+$-N concentration on cation exchange (i.e. $Na^+$ and ammonium) during the FO process. Then, real municipal wastewater (i.e. sewage) and sludge digestate were tested with 0.6 M NaCl and 1.2 M glucose as DSs, respectively, under the same osmotic pressure. In practice, seawater could be used as an cost-effective DS, thus, the osmotic pressure of 29 bar was chosen in this section to simulate seawater (Volpin et al., 2018).

As shown in Fig. 4.4, higher ammonium concentration resulted in lower water flux due to the reduced driving force. In addition, water fluxes for treating synthetic wastewater with both initial 17.9 mg/L $NH_4^+$-N and 1294.0 mg/L $NH_4^+$-N were slightly higher than for treating real wastewater when NaCl was used as DS. Meanwhile, water flux decline percentages for real wastewater were higher than synthetic wastewater for achieving 50% water recovery rate. This is expected because the presence of other soluble organic or inorganic pollutants in real wastewater could result in reduced driving force cross membrane and cause more severe membrane fouling than synthetic wastewater. In addition, it is found that water fluxes with NaCl as DS were much higher than glucose even at the same osmotic pressure. This is closely related with ICP and ECP that specific type of DS creates. Due to higher viscosity, lower diffusion coefficient and larger molecular weight, glucose can create much higher ICP and ECP than NaCl. It is very interesting to note that water flux decline extents with glucose as DS were around 6% lower than NaCl for both real municipal and sludge digestate liquor although there was much longer membrane filtration duration. To further investigate if this was due to less membrane fouling, water flux was measured with DI water as FS.

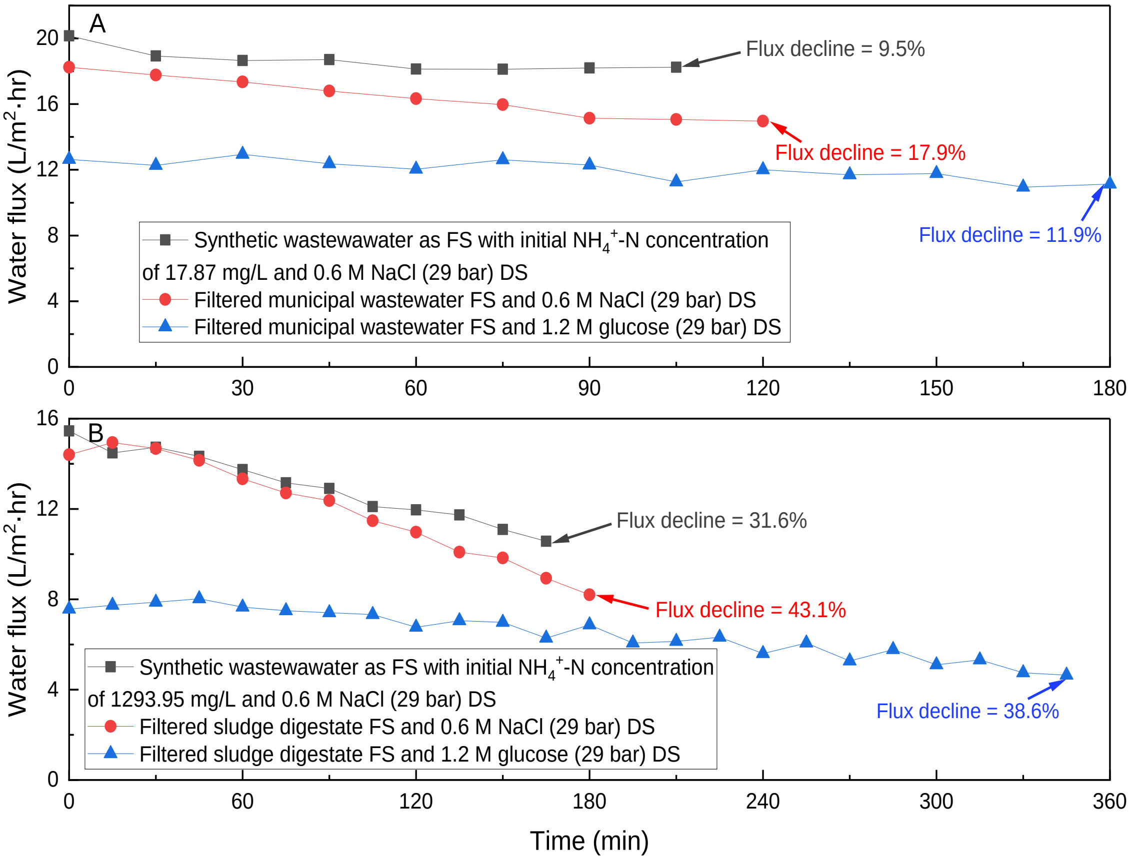

**Fig. 4.4.** Water flux decline with NaCl and glucose DSs at 29 bar osmotic pressure for the TFC FO membrane until 50% water recovery rate: A) with low initial ammonium concentration and B) with high initial ammonium concentration.

Relative water flux can be used to indicate the change of membrane performance. To understand how much flux drop at the end of each experiment was caused by membrane fouling, base-line water flux was measured with DI water as FS and NaCl as DS after each FO experiment and results were shown in Fig 4.5. It can be seen that relative water fluxes after the treatment of real wastewater are similar for DS with NaCl and glucose, which was around 0.98 for filtered municipal wastewater and 0.96 for filtered sludge digestate liquor. This result indicates that sludge digestate liquor did cause slightly more serious membrane fouling due to higher concentration of foulants than municipal wastewater, but the same level of relative water fluxes for the same type of wastewater with either NaCl or glucose as DS suggested that the less flux decline extent with glucose as DS could be caused by other factors. In addition, the complete recovery of water flux after the normal flushing indicates that membrane fouling is fully reversible even for real wastewater with 50% water recovery rate and pre-treatment by 0.45 µm membrane filtration to remove SS. This is highly in agreement with other FO studies on membrane fouling for treating filtered wastewater at a lower water recovery rate with NaCl as DS (Mi and Elimelech, 2010; Song et al., 2018; Pramanik et al., 2019). 100% membrane recoverability with glucose as DS also suggests that the membrane fouling and flux recoverability are not closely related with physical properties of DS.

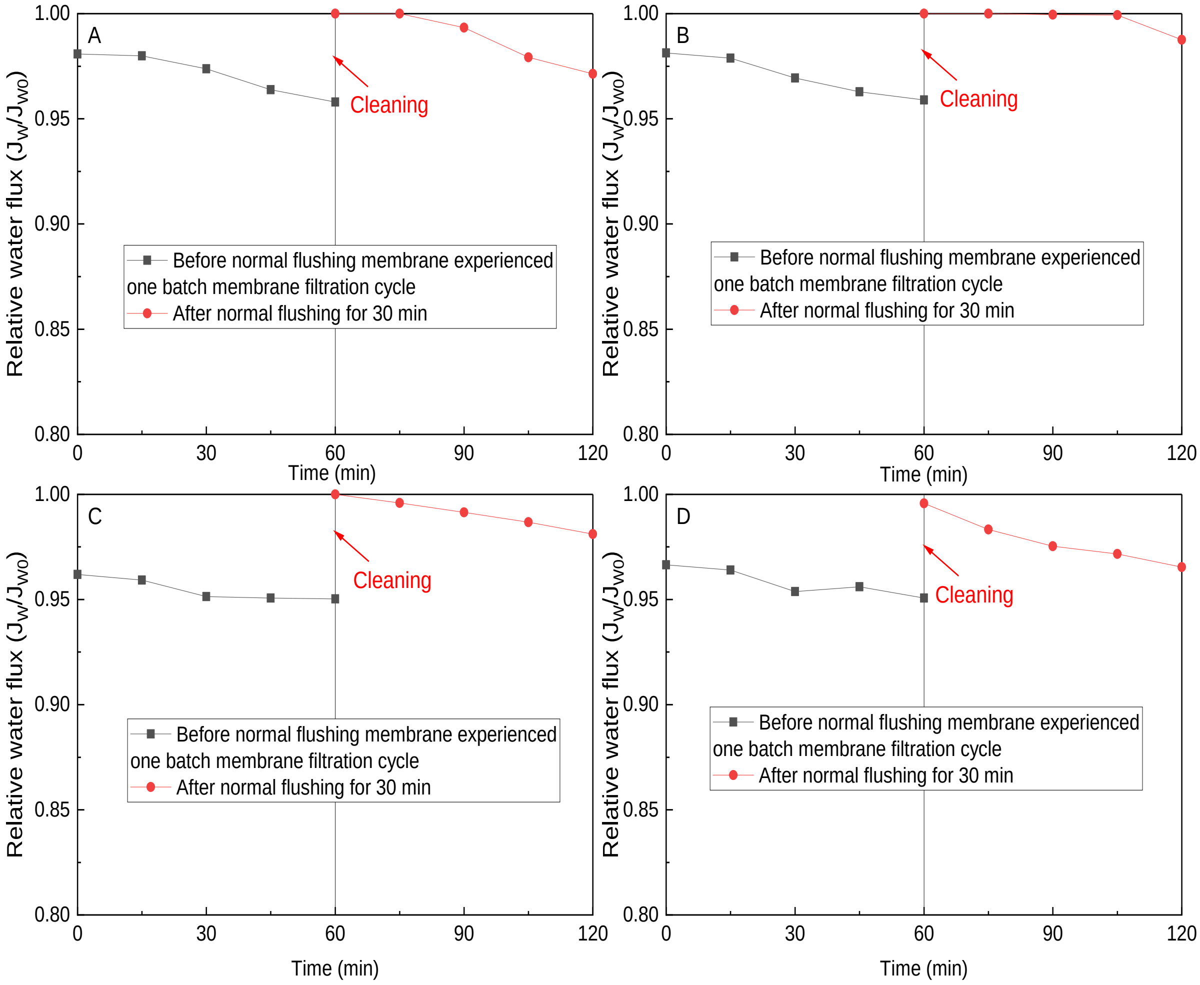

**Fig. 4.5.** Relative water fluxes before and after normal flushing to clean FO membrane after one batch membrane filtration cycle for until 50% water recovery rate with A) filtered municipal wastewater FS and 0.6 M NaCl DS, B) filtered municipal wastewater FS and 1.2 M glucose DS, C) filtered digestion sludge FS and 0.6M NaCl and D) filtered digestion sludge FS and 1.2 M glucose.

When synthetic wastewater with only ammonium was used as FS with 50% water recovery, it is found that ammonium rejection rate highly depended on initial ammonium concentration in FS (Table 4.2). For example, when the initial $NH_4^+$-N concentration was 17.87 mg/L, the final $NH_4^+$-N concentration dropped to only 6.72 mg/L with a rejection rate of 19.3% when NaCl was used as DS. However, when the initial $NH_4^+$-N concentration was 1293.95 mg/L, ammonium rejection rate reached 79.2% with a final $NH_4^+$-N concentration of 2044.89 mg/L. From the perspective of concentrating ammonium in FS, FO performs better with higher initial ammonium concentration. However, the actual ammonium permeated to DS at initial $NH_4^+$-N concentration of 1293.95 mg/L reached 188.27 mg while it was only 10.10 mg at initial $NH_4^+$-N concentration of 17.87 mg/L, causing more ammonium pollution to DS or possible problem for downstream water recovery from DS. In addition, higher ammonium permeation from FS to DS implies that more $Na^+$ in DS permeates to FS by cation exchange across membrane between $NH_4^+$ and $Na^+$ to maintain electroneutrality, resulting in high RSF. Cheng et al. (2018b) also reported that more cation exchange occurred for higher $K^+$ concentration in the FS in the TFC FO process when NaCl was used as DS. Thus, selecting appropriate DS to fully reject ammonium in FS or to be used for other benefits such as fertilisers.

**Table 4.2:** Summary of initial and final $NH_4^+$-N concentrations in the FS, rejection rate and final $NH_4^+$-N mass in the DS with 0.6 M NaCl as draw solution with a 50% water recovery rate after TFC hollow fiber FO membrane filtration for treating synthetic wastewater with only ammonium.

| Initial $NH_4^+$-N concentration in FS (mg/L) | Final $NH_4^+$-N concentration in FS (mg/L) | Rejection rate (%) | Final $NH_4^+$-N mass in the DS (mg) |
|---|---|---|---|
| 17.87 ± 0.15 | 6.72 ± 0.15 | 19.3 | 10.10 ± 0.82 |
| 1293.95 ± 10.68 | 2044.89 ± 1.53 | 79.2 | 188.27 ± 1.65 |

Table 4.3 shows the performance of wastewater treatment with FO. Due to the use of coagulant $Al_2(SO_4)_3$ for enhanced suspended solid removal during the pretreatment, phosphate concentration in filtered sludge digestate liquor was reduced to only 1 mg/L $PO_4^{3-}$-P. But for other dominant pollutants, their concentrations in sludge digestate liquor were much higher than municipal wastewater. It can be seen that glucose as DS obtained higher rejection rates of dominant pollutants and metal ions than NaCl for either municipal wastewater or sludge digestate liquor. Regarding ammonium, similar to results obtained with synthetic wastewater, ammonium in municipal wastewater with lower initial ammonium concentration was diluted while it was concentrated in sludge digestate liquor as FS with higher initial ammonium concentration with NaCl as DS. But ammonium rejection was still close to 100% for glucose as DS. Although glucose always resulted in better rejection than NaCl for any pollutants measured in this study as shown in Table 4.3, it was noted that concentration factors of $NH_4^+$ and $PO_4^{3-}$ in sludge digestate liquor were lower than those in

municipal wastewater. In addition, pH of FS increased from 7.0 to around 7.7-7.8. Due to the higher concentrations of pollutants and higher pH in FS during FO treatment period, it is possible for highly concentrated chemicals especially ammonium, phosphate, calcium and magnesium in FS to form inorganic precipitates such as calcium phosphate or struvite. To validate this assumption, pHs of the concentrated municipal wastewater and sludge digestate liquor were adjusted from 7.7-7.8 to 5.5 and $PO_4^{3-}$ concentrations were measured again. As shown in Table 4.3, concentration factors of $PO_4^{3-}$-P increased to around 1.92 or higher due to the release of phosphorus from possible precipitates (Cerozi and Fitzsimmons, 2016), suggesting inorganic phosphate precipitates at pH 7.7-7.8. In addition, SI, used as an indicator of possible mineral precipitation, of the concentrated FS at 50% water recovery rate showed oversaturation of phosphate precipitates for both municipal wastewater and sludge digestate liquor as FSs even at this $PO_4^{3-}$-P concentration level (i.e. 1.5-3.72 mg/L) (Table B5). However, concentration factor of 1.92 is still lower than the theoretical concentration factor of 2 although no phosphate was detected in DS. Thus, it is speculated that part of phosphate precipitates could be attached to the TFC membrane surface. For real wastewater treatment, it was found that higher pHs as shown in Table 4.3 were reached than DI water as FS as shown in Fig. B1. Higher pH results in higher possibility for inorganic precipitates, which contributes to membrane fouling. Unlike DI water, municipal wastewater and digestate FSs are more complex (Popa et al., 2012) suggested that the wastewater pH was greatly dependent on the physiochemical characteristics of wastewater. Therefore, it was speculated that the higher pH increase for the concentrated municipal wastewater and digestate in this study was due to the complex nature of real wastewater compared with DI water.

**Table 4.3:** Summary of initial and final concentrations of pollutants in municipal wastewater and digestion sludge wastewaters as feed solutions and 0.6 M and 1.2 M glucose as draw solutions, and concentration factors of each pollutant with a 50% water recovery rate after TFC hollow fiber FO membrane filtration.

| | | | $NH_4^+$-N | COD | $PO_4^{3-}$-P | $Ca^{2+}$ | $Mg^{2+}$ | $K^+$ | pH |
|---|---|---|---|---|---|---|---|---|---|
| | | | mg/L | | | | | | |
| Municipal wastewater | | Initial | 16.74 ± 0.16 | 119.96 ± 3.39 | 2.26 ± 0.12 | 63.83 ± 0.49 | 13.07 ± 0.27 | 17.16 ± 1.41 | 7 ± 0.03 |
| | 0.6 M NaCl | Final | 8.44 ± 0.56 | 239.93 ± 13.35 | 3.50 ± 0.06 | 110.67 ± 3.34 | 24.28 ± 0.61 | 18.96 ± 0.95 | 7.83 |
| | | CF | -1.98 | 2 | 1.55 | 1.74 | 1.86 | 1.07 | - |
| | | Final | - | - | 4.36 ± 0.23 | - | - | - | 5.5 |
| | | CF | - | - | 1.93 | - | - | - | - |
| | 1.2 M glucose | Final | 33.54 ± 0.25 | 263.92 ± 23.12 | 3.72 ± 0.17 | 116.43 ± 1.18 | 24.63 ± 1.46 | 26.33 ± 1.26 | 7.71 |
| | | CF | 2 | 2.20 | 1.65 | 1.81 | 1.89 | 1.63 | - |
| | | Final | - | - | 4.38 ± 0.16 | - | - | - | 5.5 |
| | | CF | - | - | 1.94 | - | - | - | - |
| Sludge digestate | | Initial | 1255.13 ± 87.56 | 959.70 ± 33.93 | 1 ± 0.05 | 21.02 ± 0.32 | 18.96 ± 0.82 | 93.38 ± 2.36 | 7.01 ± 0.02 |
| | 0.6 M NaCl | Final | 1422.31 ± 3.75 | 1919.38 ± 33.9 | 1.51 ± 0.04 | 38.08 ± 1.40 | 35.92± 0.89 | 128.19 ± 3.65 | 7.84 |
| | | CF | 1.13 | 2 | 1.51 | 1.81 | 1.89 | 1.37 | - |
| | | Final | - | - | 1.92 ± 0.04 | - | - | - | 5.5 |
| | | CF | - | - | 1.92 | - | - | - | - |
| | 1.2 M glucose | Final | 2409.82 ± 34.24 | 2159.34 ± 67.86 | 1.53 ± 0.06 | 40.24 ± 1.49 | 37.53 ± 0.75 | 172.51 ± 3.43 | 7.82 |
| | | CF | 1.92 | 2.25 | 1.53 | 1.91 | 1.98 | 1.81 | - |
| | | Final | - | - | 1.93 ± 0.04 | - | - | - | 5.5 |
| | | CF | - | - | 1.93 | - | - | - | - |

## 4.4 Conclusions

This study investigated the enhancement of ammonium rejection by the TFC FO filtration process for wastewater treatment by selecting appropriate DS. The following conclusions can be drawn:

- Lower reverse cation flux in DS resulted in higher ammonium rejection because ammonium rejection is related with the exchange of cation in DS and ammonium.
- Cation exchange between cation in DS and ammonium is the critical factor leading to lower ammonium rejection in FS. DS with multivalent cation and a larger hydrated radius resulted in higher ammonium rejection and non-ionic DSs lead to almost a complete ammonium rejection.
- Other physical properties of DS such as viscosity, molecular weight, and diffusion coefficient did not affect ammonium rejection very much. But for the same cation, (such as $NaCl$-$Na_2SO_4$ and $MgCl_2$-$MgSO_4$), ammonium rejection increased when the anion's diffusion coefficient was lower.
- More absolute ammonium in FS permeated to DS at higher initial ammonium concentration in the FS with ionic DS, but ammonium rejection rate increased.
- Concentration of ammonium, phosphate and other ions in FS as well as pH increase of FS due to cation exchange across membrane between $H^+$ and $Na^+$, led to more inorganic precipitates for membrane fouling. However, physical cleaning for 30 min could fully recover FO membrane fouled from one batch cycle filtration for the treatment of synthetic municipal wastewater, real municipal wastewater and sludge digestate liquor with MF pre-treatment.

# Chapter 5: Temperature effects of MD on municipal wastewater treatment in an integrated forward osmosis and membrane distillation system

## 5.1 Introduction

The increasing demand for fresh water with the growth of the world's population and industrialisation means that around 1.8 billion people would be in water shortage by 2025 (Zohrabian et al., 2020). To address this issue, alternative water sources such as seawater or treated wastewater are being explored. Desalination could pose serious brine discharge problem and also has higher cost (Panagopoulos, 2021) while recovery of fresh water from treated wastewater looks more economically promising. Currently, RO has been implemented in a few of areas to recover fresh water from treated municipal wastewater. However, RO process is usually used as the part of the tertiary treatment, which complicates the whole wastewater treatment process. Secondly, RO usually demands high energy because it is a pressure-driven membrane filtration process (Kim et al., 2015). By contrast, FO as a osmotic pressure driven process is attractive with the potential to replace conventional energy-intensive processes (Ali et al., 2018). FO has been reported to have the high rejection rates of nearly all contaminants from municipal wastewater, which could be directly used to treat municipal wastewater by concentrating pollutants for direct nutrient recovery through precipitation and direct energy recovery through AD (Wang et al., 2014). FO process usually cannot be used standalone, and another process is needed to regenerate DS unless diluted DS could be directly used for other purposes. MD is believed to be one of the most promising technologies to be integrated with FO for the regeneration of DS and water recovery given the fact that low-grade waste heat from power plants or other industrial processes could be used to provide the heat demanded in MD. Furthermore, MD has high rejection rates of contaminants (almost 100% rejection of non-volatile contaminants), less capital cost and a smaller footprint (Wang et al., 2011).

To regenerate DS from FO and recover water from DS in an integrated FO-MD process, the DS stream has to be heated to a higher temperature, such as 50 °C, to produce a water vapour pressure difference between DS and permeate as a driving force (Wang et al., 2011). Once the temperature of DS is increased, the contact between DS and FS in the FO module via membrane unavoidably results in a heat transfer between hot (DS) and cold (FS) streams, leading to an increased temperature of FS. In the vast majority of cases, to achieve a certain level of concentration of pollutants for wastewater treatment purpose, FS and DS have to be recirculated, which results in more heat transfer between FS and DS, more heat loss to FS and a higher temperature of FS.

The FS temperature in the integrated FO-MD process in previous studies was usually set at 25 °C or lower without considering the heat transfer between DS and FS (Wang et al., 2011; Zhang et al., 2014a). Additionally, a better contaminate rejection by FO was found at lower temperatures. For example, when the FS temperature increased from 20 to 40 °C, the rejection of neutral trace organic compounds (TrOCs) decreased significantly due to increased diffusivity of TrOCs at a higher FS temperature (Xie et al., 2013). The increase in the DS temperature results in higher reverse inorganic solute flux as well, due to the higher diffusivity of DS (Wang et al., 2019). Thus, from perspectives of contaminate rejection and of reverse solute flux in FO, the increase in temperature might exert negative effects. However, the previous studies were restricted to limited types of DS, and it is unclear if the negative temperature effects are applicable to a wide range of DS with different physico-chemical properties.

Another potential impact from higher temperature for FO is on ammonium. As reported, ammonium rejection by FO is usually poor due to the negatively charged membrane surface of TFC FO (Arena et al., 2014; Vu et al., 2019), leading to a higher ammonium concentration in DS. This ammonium in DS could permeate to a clean water stream during the filtration process by MD, affecting the quality of recovered water. Thus, understanding the effects of both FS and DS temperature on ammonium rejection is important for the improvement of ammonium rejection in the integrated FO-MD process for the treatment of municipal wastewater or other types of wastewater containing a higher ammonium concentration. In chapter 4 in this study, it was found that the use of non-ionic DSs, such as glucose, improved ammonium rejection to almost 100% at 20 °C. However, it is still unclear whether an increase in FS and DS temperatures can affect ammonium rejection using a non-ionic DS.

Temperature also affects FO membrane fouling, which is more complicated. Kim et al., (2015) reported that the increase in the FS temperature from 20 to 35 °C resulted in lower organic fouling of the FO membrane due to an increase in organic solubility as well as enhanced organic back diffusion from the membrane surface when using 3 M NaCl as DS. However, a temperature increase of FS would be beneficial for the precipitation of calcium phosphate, as the dissolvability of calcium phosphate is lower at high temperatures (Song et al., 2002), resulting in more severe inorganic fouling.

Apart from the above-mentioned potential impacts from temperature, water flux would be increased due to the increased diffusivity and decreased viscosity of both FS and DS at a higher temperature. However, so far there are no clear studies yet on the systematic evaluation of positive and negative effects that higher temperature might exert on municipal wastewater treatment in an integrated FO-MD process.

his study aimed to investigate temperature effects on FO and MD with three different types of DSs, i.e., NaCl, $MgCl_2$ and glucose for wastewater treatment. Water flux, ammonium rejection, contaminates rejection (i.e., COD, phosphate, $Ca^{2+}$, $Mg^{2+}$ and $K^{+}$) and membrane fouling in short periods were compared at different FO temperatures. Lastly, a simplified heat balance was conducted to discuss the practicality of an integrated FO-MD from the perspective of heat demand for municipal wastewater treatment.

## 5.2 Materials and methods

### 5.2.1 FO and MD membranes and the experimental setup

Hollow fiber TFC membranes developed by the Singapore Membrane Technology Centre (Singapore) were used in this study, and details of this FO membrane can be found in section 3.2.1. A PTFE flat-sheet hydrophobic membrane (Sterlitech, Auburn, WA, USA) was used for a direct contact MD with a membrane pore size of 0.2 µm, a thickness of 76–152 µm and an active area of 42 $cm^2$. The PTFE membrane can be operated at a pH range of 1–14 and a maximum operating temperature of 82 °C.

Lab-scale FO and MD experiments were conducted separately to study each individual processe. FO membrane experiments were run with the orientation of the AL-FS. In the MD experiments, a membrane cell (Sterlitech CF042D-FO Cell, Auburn, WA, USA) was used that consists of structured rectangular channels, with outer dimensions of 12.7 cm long, 10 cm wide and 8.3 cm deep. In the FO process, the FS and DS temperatures were set as follows: (i) both FS and DS at 25 °C to simulate an ambient temperature; (ii) FS at 25 °C and DS at 50 °C for simulating FS at an ambient temperature and high temperature of DS and (iii) the DS at 50 °C while FS without the control of temperature, which increases simply due to the heat gained by contacting the FO membrane with a high temperature DS. The FS temperature was controlled by going through a helical polyvinylchloride (PVC) tube coil immersed into a water bath with a pre-set temperature (Julabo, Stamford, UK) before recirculating, while the DS temperature was controlled by directly placing the DS tank into a water bath with a constant temperature (PolyScience, Niles, MI, USA), as shown in Fig. 5.1.

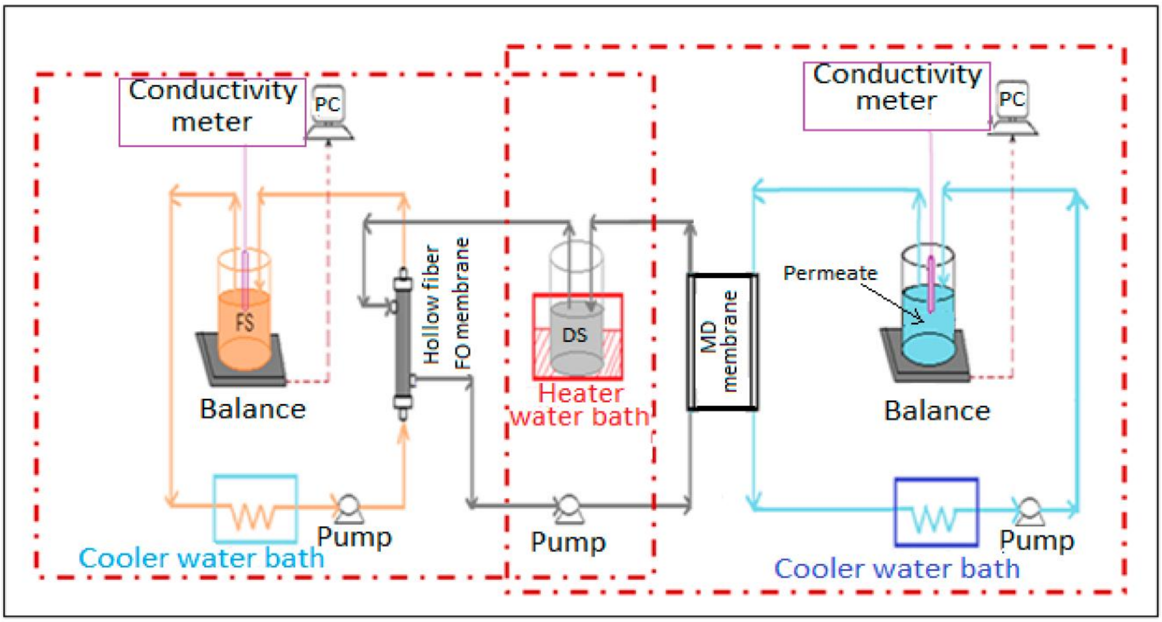

**Fig. 5.1.** Schematic diagram of the individual FO membrane process and MD membrane process in dashed rectangles and the integrated FO-MD process as a whole.

In both FO and MD rigs, counter-current recirculation of the FS and DS was applied on each side of the FO and MD membranes using two peristaltic pumps at flowrates of 0.6 L/min. The FS tank in the FO system and the permeate tank in the MD system were placed on a digital balance each (Kern, Kassel, Germany) connected to a PC, and the water flux was calculated based on the recorded weight changes from the balances during experimental periods.

### 5.2.2 Feed solution and draw solution

Synthetic municipal wastewater was prepared with 460.66 ± 32.54 mg/L COD (with $NaAc{\cdot}3H_2O$ as COD), 7.90 ± 0.15 mg/L $PO_4^{3-}$-P (with $KH_2PO_4$ for P), 53.96 ± 0.66 mg/L ammonium-N (with $(NH_4)2SO_4$ for N), 37.25 ± 0.73 mg/L $Ca^{2+}$, 6.28 ± 0.35 mg/L $Mg^{2+}$ and 20.27 ± 1.36 mg/L $K^+$ to investigate effects of FS and DS temperatures on the FO membrane filtration. In addition, synthetic water containing only 50 mg/L ammonium-N (with $(NH_4)_2SO_4$ for N) was used to study effects of the DS type on ammonium rejection by MD.

Two DSs with the same osmotic pressure, i.e., 0.6 M NaCl as an ionic DS and 1.2 M glucose as a non-ionic DS, were used to examine effects of FS and DS temperatures on FO filtration. For ammonium rejection in the MD study, NaCl, $MgCl_2$ and glucose as DSs at 35 g/L were used to study DS regeneration and possible ammonium contamination on recovered clean water.

### 5.2.3 Operation of the experimental rigs

To test effects of FS and DS temperatures on water flux and RSF in the FO membrane filtration process, experiments were firstly conducted using DI water as FS and 0.6 M NaCl or 1.2 M glucose as DSs with initial volumes of 1 L for both FS and DS. To determine the RSF of the DS during the FO process, the conductivity (Hanna HI700 instrument, HI7639 probe, Bedfordshire, UK) of the FS was measured every 15 min when using NaCl as the DS, while a 10 mL sample was taken from the FS tank every 15 min for COD analysis to determine the reverse glucose flux from DS to FS. All FO experiments to determine the water flux and RSF in this study lasted for at least 2 h. When synthetic municipal wastewater was used, FO experiments at different FS and DS temperatures were conducted until a 70% water recovery rate was obtained. FO membrane fouling with synthetic municipal wastewater FS and 0.6 M NaCl DS was further investigated by applying three consecutive cycles with a 70% water recovery.

To test the effects of the DS type on MD membrane flux and ammonium rejection, the MD membrane was placed in a flat-sheet configuration. The initial volume for the permeate and DSs was 1 L, and the pH of both the permeate and DS was adjusted to 7. A sample of 15 mL was taken every 1 h from the permeate solution for analysis of the permeated ammonium. All MD experiments on ammonium rejection lasted for 6 h.

### 5.2.4 Analytical methods

COD, ammonium and phosphate were measured in accordance with standard methods (APHA 1998). The concentration of soluble elements (Ca2+, Mg2+ and K+) was analysed using ion chromatography (882 Compact IC plus, Metrohm, Herisau, Switzerland) by a Metrosep C4-250/4.0 column with eluent containing 1.7 Mm/L nitric acid and 0.7 mM/L dipicolinic acid.

### 5.2.5 Calculations

#### 5.2.5.1 Water Flux and Reverse Solute Flux

Water flux across the FO and MD membranes was calculated from the volume change of the FS or the permeate using the following equation:

$$J_w = \frac{\Delta V}{\Delta t \times A_m} \qquad \text{Equation 5.1}$$

where $J_w$ (L/m$^2$·hr) is the water flux across the membrane, ΔV (L) is the volume change in the FS or the permeate, Δt (hr) is the duration of the test, and $A_m$ (m$^2$) is the active membrane area.

The RSF (Js) was calculated using the following formula:

$$Js = \frac{V_{Ft2}.C_{Ft2} - V_{Ft1}.C_{Ft1}}{\Delta t \times A_m} \qquad \text{Equation 5.2}$$

where Js (g/m$^2$·hr) is the RSF, $V_{Ft2}$ (L) is the volume of the FS at the recording time interval $t_2$, $V_{Ft1}$ (L) is the FS volume at the recording time interval $t_1$, $C_{Ft2}$ (g/L) is the solute mass concentration in the FS at $t_2$, and $C_{Ft1}$ (g/L) is the solute mass concentration in FS at $t_1$. The concentration of reverse salt was obtained by measuring conductivity of FS at different times according to the calibration curve between NaCl concentration and conductivity of solution. The concentration of reverse glucose flux was obtained by measuring COD of FS at different times according to the calibration curve between glucose concentration and COD. The concentration of reverse glucose solute was obtained by measuring COD of FS at different times according to the calibration curve between glucose solute concentration and COD.

The osmotic pressures of the NaCl and glucose DSs were calculated using the van't Hoff equation (Cornelissen et al., 2008; Altaee et al.,2013; Altaee and Hilal, 2014; Devia et al., 2015; Corzo et al., 2017):

$$\Pi = iMRT \qquad \text{Equation 5.3}$$

where Π (atm) is the osmotic pressure, i is the van't Hoff factor of the solute, M (mol/L) is the molar concentration, R is the universal gas constant (0.08206 L.atm/mol.l), and T is the absolute temperature in K.

#### 5.2.5.2 Concentration Factor and Rejection Rate of Contaminates in FS

The CF (equation 5.4) was calculated as the ratio between the FS concentration at time t ($C_t$) after filtration and the initial FS concentration ($C_0$) at time 0:

$$CF = \frac{C_t}{C_0} \qquad \text{Equation 5.4}$$

The rejection rate (R) of the contaminants was calculated based on the mass balance between the FS and the DS:

$$R = (1 - \frac{V_{df} \text{ x } C_{df}}{V_{fi} \text{ x } C_{fi}}) \text{ x } 100\% \qquad \text{Equation 5.5}$$

where $V_{df}$ (L) is the final volume of the DS, $C_{df}$ (mg/L) is the final contaminate concentration in the DS, $V_{fi}$ (L) is the initial FS volume, and $C_{fi}$ (mg/L) is the initial contaminate concentration in the FS.

#### 5.2.5.3 Ammonia Pressure in the MD

The water vapour pressure in DS was calculated using the following formula (Alkhudhiri et al., 2012; Ray et al., 2018):

$$P_A = X_A P_A^* \qquad \text{Equation 5.6}$$

where $P_A$ (kPa) is the vapour pressure of the solution, $X_A$ is the mole fraction of the solvent, and $P_A^*$ (kPa) is the vapour pressure of the pure solvent.

The equilibrium between ammonium and ammonia in DS solution was affected by ammonium concentration, temperature and pH, which could be expressed using the following formula (Cao et al., 2017):

$$FA = \frac{17}{14} \times \frac{[NH_4{}^+ - N] \times 10^{pH}}{e^{(\frac{6334}{T})} + 10^{pH}} \qquad \text{Equation 5.7}$$

where FA is the free ammonia (mg/L), $NH_4^+$-N is the ammonium as nitrogen concentration (mg/L), and T is the temperature of the solution in K.

The vapour pressure of ammonia in DS is calculated using Henry's law (Dasgupta and Dong, 1985):

$$C = H\,P \qquad \text{Equation 5.8}$$

where P is the partial pressure of the ammonia (atm), H is Henry's law constant, and C is the concentration of ammonia in aqueous solution (M). Henry's law constant (H) is roughly calculated by using the following formula (Dasgupta and Dong, 1986): H = $e^{\left(\frac{4341}{T}-10.47\right)}$ with the assumption that ammonia solubility is not affected by solution salinity and pH. In addition, the equation neglects the autoprotolysis of water. By combining Equations (5.7) and (5.8), the pressure of ammonia could be estimated as below:

$$P_{\text{ammonia}} = \left[\frac{17}{14} \text{ X } \frac{[\text{NH}_4{}^{+}\text{−N}] \times 10^{\text{pH}}}{e^{\left(\frac{6334}{T}\right)} + 10^{\text{pH}}}\right] / \left[e^{\left(\frac{4341}{T} - 10.47\right)}\right] \qquad \text{Equation 5.9}$$

where $P_{\text{ammonia}}$ is the ammonia vapour pressure in atm.

#### 5.2.5.4 Heat Balance and Heat Demand in a FO-MD System without Internal Heat Recovery

Since single-pass water recovery in either FS or DCMD is very low, such as less than 10% (Swaminathan and Lienhard, 2018; Criscuoli, 2021), water recirculation as shown in Fig. 5.2A has to be conducted to achieve higher water recovery rate in an integrated FO-DCMD system. If it is assumed that no heat is lost in the whole system, the diagram of the FO-DCMD as shown in Fig. 5.2A could be simplified to Fig. 5.2B.

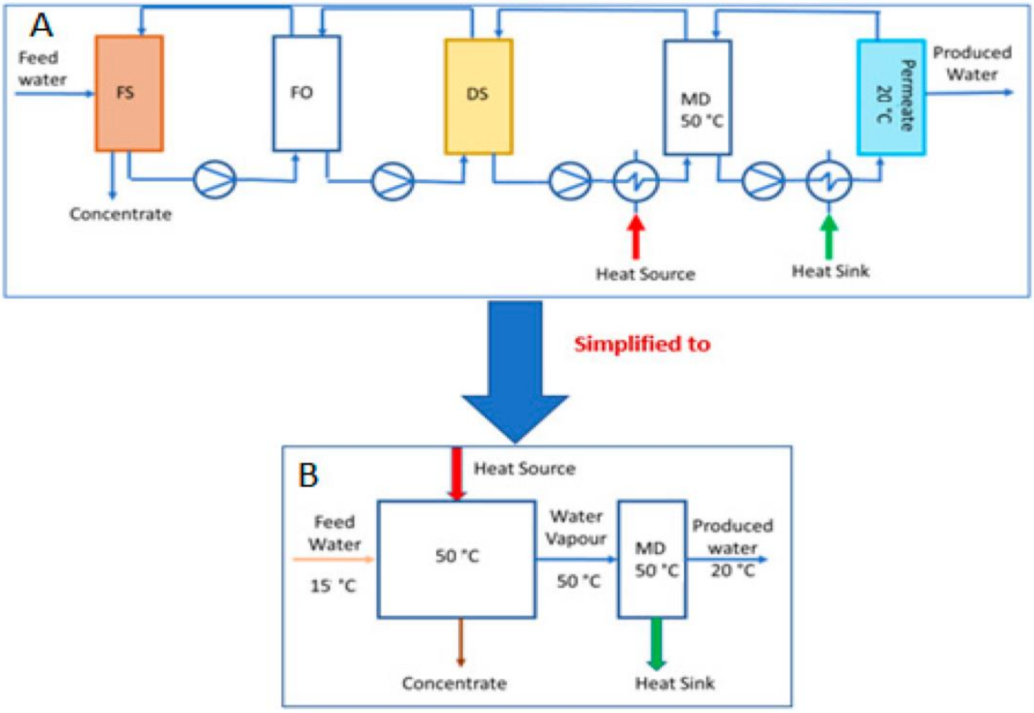

**Fig. 5.2.** An integrated FO-MD process for wastewater treatment and water production with external heat source and heat sink: (A) detailed and (B) simplified process flow diagram.

For water vaporisation in MD, the heat demand $Q_1$ for the increase in the temperature of DS from $T_1$ to a temperature $T_2$ and water evaporation at $T_2$ could be calculated by:

$$Q_1 = \mathrm{mR\Delta H} + \mathrm{cmR}(T_2 - T_1) = \mathrm{mR}(\Delta H + cT_2 - cT_1) \qquad \text{Equation 5.10}$$

The heat requirement $Q_2$ for the increase in concentrate temperature to 50 °C could be calculated by:

$$Q_2 = \mathrm{cm}(1 - R)(T_2 - T_1) \qquad \text{Equation 5.11}$$

where m is feed water mass, R is water recovery rate, $\Delta H$ is the latent heat of water vaporization, c is the specific heat capacity of water, $T_2$ is the temperature of heat stream in DCMD, $T_1$ is the temperature of feed water. Thus, the total heat requirement Q:

$$Q = Q_1 + Q_2 \qquad \text{Equation 5.12}$$

## 5.3 Results and discussion

### 5.3.1 Effects of Temperature of Feed and Draw Solutions on Water Flux and RSF with NaCl and Glucose as Draw Solutions and DI Water as FS

Fig. 5.3 shows the dependence of the water flux and RSF on different FS and DS temperatures with NaCl and glucose as DSs. It can be seen that the increased operating temperatures result in the increase in water flux and RSF for both DSs. These results are consistent with those from previous FO lab scale studies (Zhao and Zou, 2011; Phuntsho et al., 2012; Wang et al., 2014) with ionic DSs such as NaCl, KCl and $Na_2SO_4$ and by pilot scale FO study (Jalab et al., 2020). The increase in water flux and RSF is easy to understand because:

- The osmotic pressure of DS is proportional to temperature according to Equation (5.3);
- The diffusivity of both FS and DS increases with the increase in temperature, resulting in high water flux and reverse solute flux across the membrane (Chowdhury and Mccutcheon, 2018);
- The viscosity of the solutions decreases with the increase in the DS temperature, which is able to reduce both the ICP and ECP, enhancing the water flux (Lutchmiah et al., 2014; Chowdhury and Mccutcheon, 2018; Ray et al., 2018).

Although water flux increased with either NaCl or glucose as DS at an elevated temperature, it can be seen from Fig. 5.3 that the increasing extent of water flux with NaCl and glucose as DSs were different. The water flux with glucose as DS increased by 23% from 13.21 L/m$^2$·hto 17.15 L/m$^2$·h compared to 8.2% with NaCl as DS from 23.63 L/m$^2$·h to 25.74 L/m$^2$·h when the DS temperature increased from 25 to 50 °C with the FS temperature set at 25 °C. When the FS temperature was not controlled and the DS was set at 50 °C, the FS temperature increased from 18 °C and then stabilised at around 42.2 °C during a very short period, i.e., within the first 45 min, and the water flux increased by 25% from 17.15 L/m$^2$·h to 22.87 L/m$^2$·h with glucose as DS and by 15% from 25.74 L/m$^2$·h to 30.30 L/m$^2$·h with NaCl as DS. Although the previous studies have reported the increase of water flux and RSF of ionic DS at higher temperatures, this study is the first report to disclose that the difference of physico-chemical properties of NaCl and glucose could result in the different levels of increase in water flux and RSF when being used as DS. The difference in water flux between NaCl and glucose as DSs decreased when temperature was increased probably because the diffusivity and viscosity of glucose decreased more at elevated temperatures compared with NaCl. It was interesting to note that the RSF increased with glucose as DS at a rate of 0.07 g/m$^2$·h for every °C rise compared to 0.14 g/m$^2$·h for every °C rise for the NaCl as DS, even though both reverse solute fluxes from NaCl and glucose increased with temperature. In summary, the increase in the FS and DS temperatures enhanced the water flux with glucose as DS at a higher rate than with NaCl as DS, while the RSF increase rate was higher with NaCl as DS than with glucose as DS. In terms of water flux, glucose is inferior to NaCl as DS because of its high viscosity, low diffusivity and large molecule size with a higher corresponding ICP and ECP (Ansari et al., 2015). However, at an elevated temperature, glucose could be more suitable as DS especially when RSF is a big concern in FO. This conclusion could be applicable to other organic non-ionic chemicals with high viscosity, low diffusivity and large molecules, providing useful guidance for the selection of DS in a specific scenario.

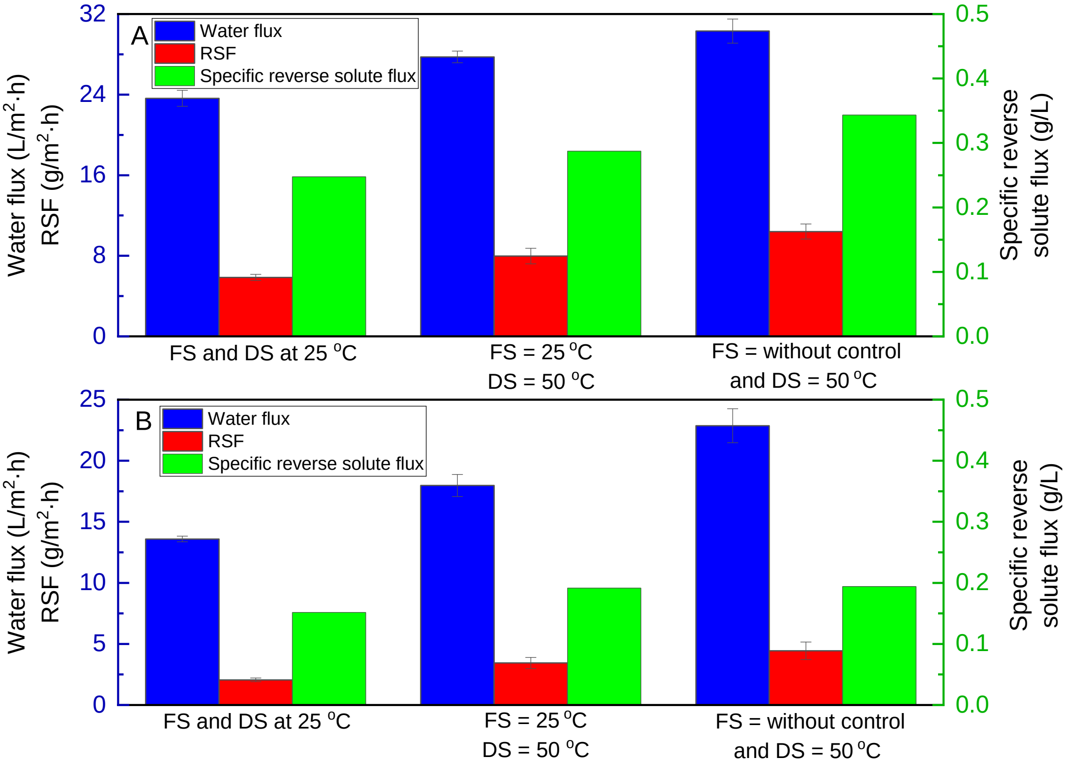

**Fig. 5.3.** Water flux, reverse solute flux and specific reverse solute flux at different operating temperatures with DI water as the FS and A) 0.6 M NaCl, and B) 1.2 M glucose as DS (note: temperature varying from 18 °C to 42.2 °C in FS without temperature control due to the heat transfer from DS to FS).

### 5.3.2 Effects of Temperature of Feed and Draw Solutions on FO Filtration with Synthetic Wastewater as FS

To understand FO filtration at an elevated temperature better, synthetic wastewater was used as FS to see how contaminates (i.e., COD, phosphate, ammonium, $Ca^{2+}$, $Mg^{2+}$ and $K^{+}$) were rejected and water flux was increased at a higher temperature. As shown in Fig. 5.4, the water flux with both DSs was proportional to the operating temperature. When the DS was set at 50 °C and the FS temperature was not controlled, the temperature of FS increased to 42 °C within the first 45 min due to the heat transferred from DS at 50 °C to FS, and then the temperature of FS stabilized at 42 °C during the remaining period of the filtration because of the heat balance between the heat loss to the surrounding environment and the heat gain from DS. After the FS temperature stabilised at 42 °C, the water flux with 0.6 M NaCl as DS increased by 19% from 25.36 $L/m^2 \cdot h$ to 30.25 $L/m^2 \cdot h$ and by 35% from 16.32 $L/m^2 \cdot h$ to 22.22 $L/m^2 \cdot h$ with 1.2 M glucose as DS. When the FS was set at 25 °C and the DS was set at 50 °C, the initial water flux with the NaCl as DS increased by 12% from 22.63 L/m$^2$·h to 25.36 L/m$^2$·h while it increased by 27% from 12.83 L/m$^2$·h to 16.32 L/m$^2$·h with glucose as DS compared to those with both FS and DS set at 25 °C. These increasing rates regarding water flux with temperatures for synthetic wastewater were very similar to those for DI as FS, indicating that contaminates in municipal wastewater do not affect heat balance obviously and temperature effects on water flux could be evaluated with DI water when the FO application is to municipal wastewater treatment.

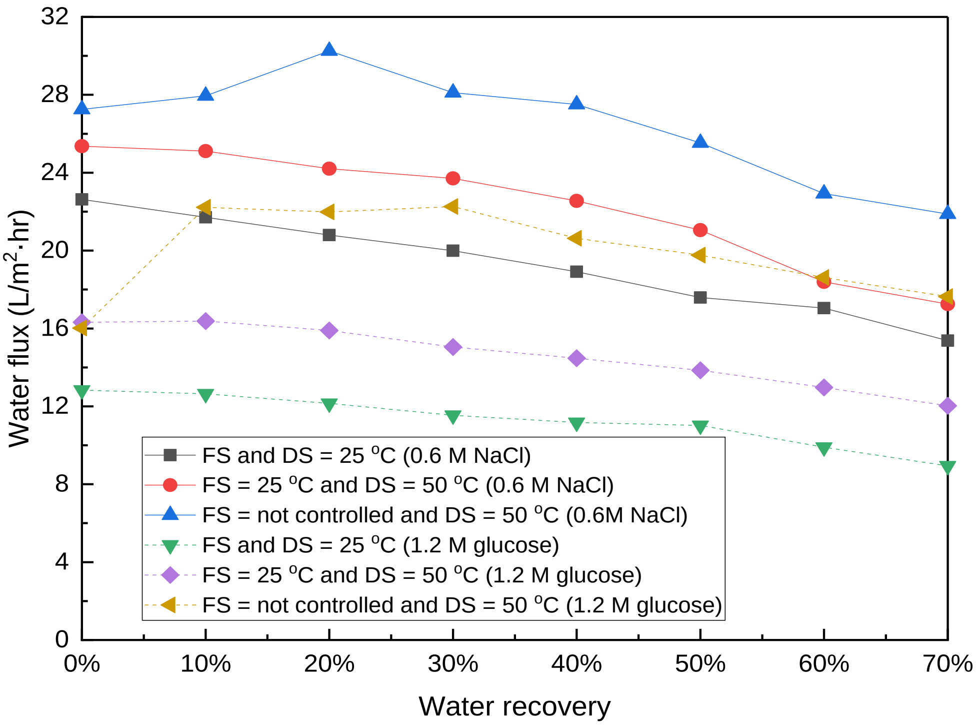

**Fig. 5.4.** Water flux at different FS and DS temperatures during the TFC hollow fiber FO filtration of synthetic municipal wastewater until a 70% water recovery rate.

From Fig. 5.4, it can be seen that the water flux with glucose as DS at an elevated temperature falls within the range of water flux with NaCl as DS at an ambient temperature, suggesting a much more acceptable water flux with glucose as DS at elevated temperatures regarding water flux. In addition, the shortened total filtration time to achieve a 70% water recovery rate with either NaCl or glucose as DS indicates a higher treating capacity per unit of membrane surface, implying lower wastewater treatment and water production costs. For example, Valladares et al. (2016) reported that when the water flux in FO increased from 10 to 20 L/m$^2$·h, the water production cost of each m$^3$ decreased from $0.637 to $0.611 for a production capacity of 100,000 m$^3$/d of potable water by an integrated FO and low-pressure RO process.

Table 5.1 shows the up-concentration of municipal wastewater by FO at different temperatures with either NaCl or glucose as DS. When NaCl was used as DS, it can be seen that the FS and DS temperatures did not have a notable effect on the up-concentration of both COD and $PO_4^{3-}$. Although it seems that CF of $PO_4^{3-}$ was lower than COD, no $PO_4^{3-}$ was detected in the DS after achieving a 70% water recovery rate, indicating that the TFC FO membrane used in this study had complete $PO_4^{3-}$ rejection at all operating temperatures, and the lower CF of $PO_4^{3-}$ was probably caused by precipitation in FS. These results showed that the TFC FO membrane had high stability to reject $PO_4^{3-}$ and COD at a relatively wide range of FS and DS temperatures. Conversely, ammonium was not concentrated in the FS with NaCl as DS at all operating temperatures. Even worse, the increase in FS and DS temperatures negatively affected $NH_4^+$ rejection when using 0.6 M NaCl as the DS. The $NH_4^+$ concentration factor was decreased from −1.59 with both FS and DS at 25 °C to −2.01 with FS at 25 °C and DS at 50 °C, and further to −2.96 with DS at 50 °C and FS at 42 °C. From previous studies (Cath, 2009; Arena et al., 2014; Lu et al., 2014; Ansari et al., 2017; Almoalimi and Liu, 2022), it was believed that low ammonium rejection was mainly caused by the cation exchange between $Na^+$ from DS and $NH_4^+$ from FS initiated by reverse $Na^+$ flux from DS. With the temperature increase of DS, as shown in Fig. 5.3, the RSF of NaCl increased due to higher NaCl diffusivity, which enhanced the exchange between $Na^+$ from DS and $NH_4^+$ from FS to maintain electroneutrality and thus deteriorated $NH_4^+$ rejection by FO.

When 1.2 M glucose was used as DS, as shown in Table 5.1, the increase in FS and DS temperatures improved the COD concentration factor CF. Given the fact that COD rejection at lower temperature was close to 100%, however, the increased CF was actually caused by high reverse glucose flux at a higher operating temperature. Both complete $PO_4^{3-}$ and $NH_4^+$ rejections were obtained at all operating temperatures as no $PO_4^{3-}$ and $NH_4^+$ could be detected in DS. The complete ammonium rejection rate by using non-ionic DS such as glucose in this study is significantly higher than previous studies with ionic DS (Cath, 2009; Arena et al., 2014; Lu et al., 2014; Almoalimi and Liu, 2022). The reduced concentration factors for $NH_4^+$-N in FS could be explained by the fact that ammonia vaporization was higher at a higher FS temperature and pH because the FS tank was not air-tight, resulting in the loss of ammonia during the FO filtration process. The controls validated this assumption that 0.65 mg N lost at 25 °C in the form $NH_3$ from FS while the ammonia loss increased to 2.5 mg N at higher FS temperatures (i.e., 42 °C). The results shown here again proved that the cation exchange between $Na^+$ from NaCl as DS and $NH_4^+$ in FS was the main reason for low ammonium rejection, which was enhanced by a higher temperature.

Once no cation exchange is present due to the undissociated molecule nature, such as glucose, ammonium rejection is not affected by temperature at all. Undissociated chemical is thus favourable as the DS at higher temperatures, when ammonium rejection is a concern.

For the rejection of cations in FS, when NaCl was used as the DS, it was found that concentration factors of $Ca^{2+}$, $Mg^{2+}$ and $K^+$ slightly decreased with the temperature increase in DS and FS, which could be related with the increased cation exchange as well as between cations in FS and $Na^+$ in DS at higher temperatures due to the higher diffusivity of both cations in FS and $Na^+$ in DS. $K^+$ is much smaller than $Ca^{2+}$ and $Mg^{2+}$; thus, it is easier to exchange with $Na^+$ in DS, leading to a lower CF of $K^+$ than those of $Ca^{2+}$ and $Mg^{2+}$ in FS. When glucose was used as DS, although higher concentration factors of $Ca^{2+}$, $Mg^{2+}$ and $K^+$ were obtained compared to NaCl as DS at all operating temperatures, CFs of $Ca^{2+}$, $Mg^{2+}$ and $K^+$ decreased slightly with the increase in temperature, probably due to the increased diffusivity of cations in FS. Due to the reverse salt permeation to FS and concentration of ions in FS over time in FO treatment with NaCl as DS, the salinity of the concentrate increased with temperature.

The increase in pH from the initial value of 6.98 in FS to 7.08–7.19 (Table 5.1) at the end of filtration indicates the ion exchange between DS and FS. The pH increase in the concentrated FS is beneficial for the phosphate precipitation with $Ca^{2+}$, $Mg^{2+}$, $NH_4^+$ and other ions over the filtration time with increased ion concentrations, which explains the lower final concentration factors for these ions compared to the theoretical concentration factors (i.e., 3.33) in the FS. The SI, which is used as an indicator of possible mineral precipitation of the concentrated FS at a 70% water recovery rate, was higher than 0, showing the oversaturation of phosphate precipitates. The formation of inorganic precipitates over FO membrane filtration time implies a fouling potential on membranes from inorganics. Thus, membrane fouling was further investigated in this study.

**Table 5.1:** Summary of the initial and final concentrations of pollutants in the synthetic municipal wastewater FS with 0.6 M and 1.2 M glucose as the DS and the concentration factors of each pollutant until a 70% water recovery rate after the TFC hollow fiber FO membrane filtration at different FS and DS temperatures.

| | | | COD | $PO_4^{3-}$-P | $NH_4^+$-N | $Ca^{2+}$ | $Mg^{2+}$ | $K^+$ | pH |
|---|---|---|---|---|---|---|---|---|---|
| | | | mg/L | | | | | | |
| Initial | | | 460.66 ± 32.54 | 7.90 ± 0.15 | 53.96 ± 0.66 | 37.25 ± 0.73 | 6.28 ± 0.35 | 20.27 ± 1.36 | 6.98 ± 0.02 |
| NaCl | FS and DS = 25 ℃ | Final (FS) | 1,427.55 ± 16.97 | 23.33 ± 0.06 | 34.66 ± 0.23 | 101.04 ± 1.77 | 19.97 ± 0.50 | 34.66 ± 0.93 | 7.10 |
| | | CF | 3.10 | 2.95 | -1.56 | 2.71 | 3.17 | 1.71 | - |
| | | Final (DS) | - | Not detected | 25.29 ± 0.43 | - | - | - | - |
| | FS = 2 5℃ and DS = 50 ℃ | Final (FS) | 1,415.56 ± 101.79 | 22.71 ± 0.03 | 26.89 ± 0.26 | 100.45 ± 1.81 | 19.67 ± 0.34 | 29.24 ± 1.46 | 7.16 |
| | | CF | 3.07 | 2.88 | -2.01 | 2.70 | 3.13 | 1.44 | - |
| | | Final (DS) | - | Not detected | 26.89 ± 0.37 | - | - | - | - |
| | FS = Not controlled and DS = 50 ℃ | Final (FS) | 1,439.55 ± 67.86 | 22.14 ± 0.15 | 18.21 ± 0.10 | 97.06 ± 1.36 | 18.89 ± 0.76 | 23.33 ± 0.48 | 7.19 |
| | | CF | 3.12 | 2.80 | -2.96 | 2.61 | 3.00 | 1.15 | - |
| | | Final (DS) | - | Not detected | 27.06 ± 0.49 | - | | - | - |
| Glucose | FS and DS = 25 ℃ | Final (FS) | 1,736.68 ± 33.93 | 23.63 ± 0.30 | 164.34 ± 1 | 110.16 ± 1.03 | 20.35 ± 1.04 | 63.44 ± 0.98 | 7.08 |
| | | CF | 3.77 | 2.99 | 3.05 | 2.96 | 3.24 | 3.13 | - |
| | | Final (DS) | - | Not detected | Not detected | - | - | - | - |
| | FS = 25 ℃ and DS = 50 ℃ | Final (FS) | 1,847.25 ± 16.97 | 22.91 ± 0.49 | 160.70 ± 0.50 | 107.22 ± 2.08 | 19.89 ± 0.76 | 63.65 ± 2.11 | 7.15 |
| | | CF | 4.01 | 2.90 | 2.98 | 2.88 | 3.17 | 3.14 | - |
| | | Final (DS) | - | Not detected | Not detected | - | - | - | - |
| | FS = Not controlled and DS = 50 ℃ | Final (FS) | 1,870.28 ± 33.93 | 22.68 ± 0.08 | 151.11 ± 0.37 | 104.30 ± 0.98 | 19.18 ± 0.23 | 62 ± 1.07 | 7.16 |
| | | CF | 4.06 | 2.87 | 2.80 | 2.80 | 3.05 | 3.06 | - |
| | | Final (DS) | - | Not detected | Not detected | - | - | - | - |

### 5.3.3 Membrane Fouling and Cleaning at Different Feed and Draw Solutions Temperatures in the TFC FO Filtration Process with Synthetic Municipal Wastewater

In practice, water recovery from RO filtration is usually not over 70% to alleviate membrane fouling (Matin et al., 2021). Although FO could be able to be operated with a higher water recovery rate than 70%, a 70% water recovery rate was used in three consecutive cycles in this study at different FS and DS temperatures to study FO fouling from inorganic precipitates in treating synthetic municipal wastewater. As shown in Fig. 5.5, under an isothermal condition (i.e., both FS and DS at 25 °C), three filtration cycles were finished after 675 min, while it took 585 min with FS at 25 °C and the DS at 50 °C and 450 min with FS stabilised at 42 °C and DS at 50 °C.

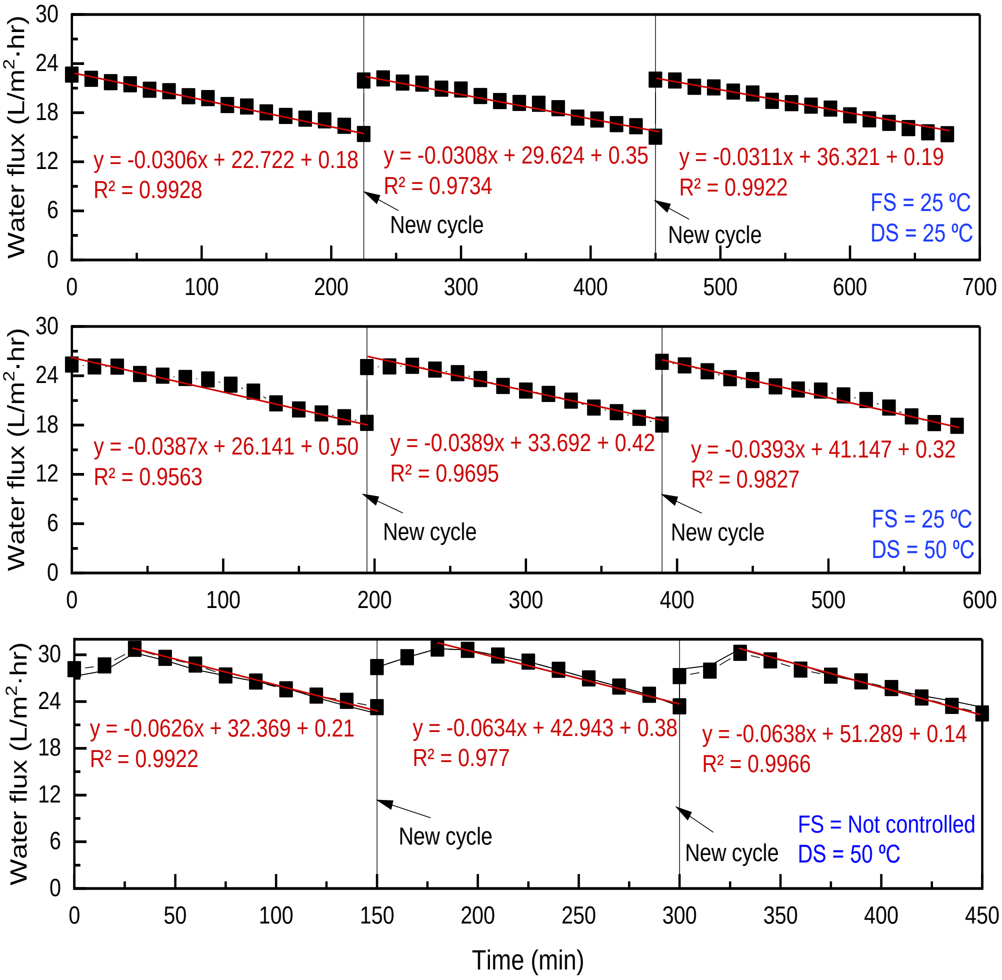

**Fig. 5.5.** The decline in water flux in three batches of FO membrane filtration cycles each at a 70% water recovery rate when concentrating synthetic municipal wastewater at different FS and DS temperatures.

Regression lines were used to show the water flux decline rate during the FO process for treating synthetic municipal wastewater at different operating temperatures. Only a slight decline in initial water flux was observed after each cycle at all operating temperatures, indicating that the decrease in the water flux in each individual cycle was mainly caused by the reduced driving force between the FS and DS due to the concentration of ions and organics in the FS and the dilution of the DS, and membrane fouling only contributed slightly to the flux decline. The water flux decline rate was 0.031 L/m$^2$·h per min under an isothermal condition, 0.039 L/m$^2$·h per min with the FS at 25 °C and the DS at 50 °C and 0.063 L/m$^2$·h with the FS temperature at 42 °C and the DS at 50 °C. The higher water flux decline at higher FS and DS temperatures could be attributed to higher water flux and a quick decrease in driving force between FS and DS instead of fouling.

As shown in Fig. 5.6, the water flux declined after three consecutive cycles by only 2.2% with the FS and DS at 25 °C, by 3.7% with the FS temperature at 25 °C and the DS at 50 °C and 3.8% with the FS at 42 °C and the DS at 50 °C. This indicates that membrane fouling was slightly more serious at higher FS and DS temperatures due to probably more inorganic phosphate precipitates at higher temperature. It has been reported that the dissolvability of hydroxyapatite is lower at higher temperatures (Song et al., 2002). The initial water flux of membranes was fully recovered after normal flushing with DI water for 30 min at all operating temperatures, suggesting that the inorganic precipitates deposited loosely on the membrane surface and could be easily removed. Based on these results, operating an FO process until 70% water recovery at different FS and DS temperatures did not cause obvious membrane fouling in treating synthetic municipal wastewater. However, it is necessary to study membrane fouling and cleaning after multiple cycles with long-term fouling durations by the use of synthetic or real municipal wastewater with higher initial contaminant concentrations.

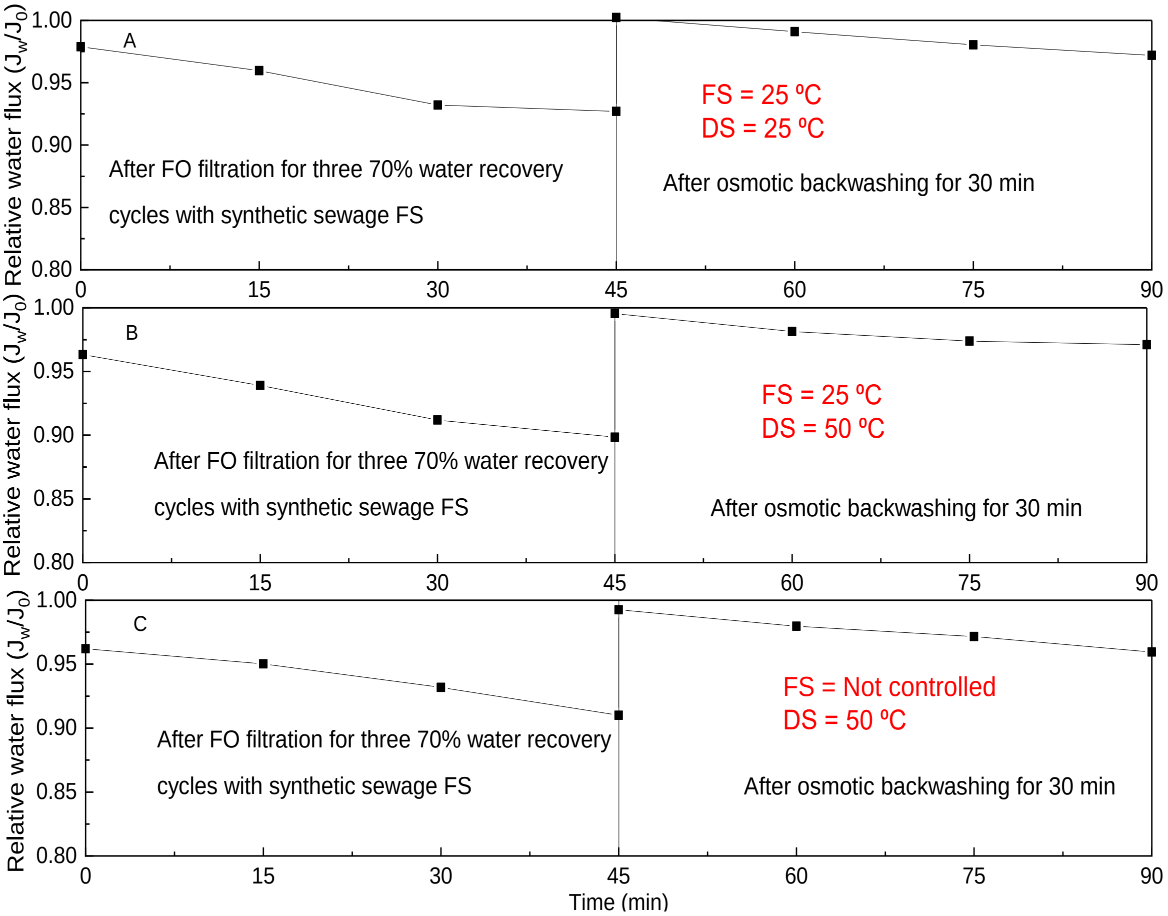

**Fig. 5.6.** Comparing the water flux recoverability after fouling test of three 70% water recovery cycles using synthetic municipal wastewater in the TFC FO process: A) FS and DS = 25 °C, B) FS = 25 °C and DS = 50 °C and C) FS = not controlled and DS = 50 °C.

### 5.3.4 Ammonia Vaporisation in a Direct Contact MD Membrane Filtration Process for Simultaneous DS Regeneration and Water Recovery

As mentioned before, an integrated FO-MD process could be promising for simultaneous DS regeneration and water recovery. The regeneration of different types of DSs, i.e., NaCl, $MgCl_2$ and glucose, in a direct contact MD process, was conducted. It was found that with 50 mg/L $NH_4^+$ in 1 L and 35 g/L NaCl, $MgCl_2$ or glucose as DS, the water flux was 5.72, 5.85 and 6.23 L/m$^2$·h, respectively, and the concentration of DS after 6 h of filtration was 40.65, 41.10 and 41.28 g/L, respectively, with a water recovery rate of around 14–15%. Since the initial concentration of all three types of DSs are the same, i.e., at 35 g/L, water flux from different types of DSs were supposed to be the same. It is thus believed that the slight difference in terms of water flux and water recovery rate might be due to errors, which are negligible.

Since FO has a low rejection of ammonium from FS with NaCl as DS, most ammonium in FS is permeated to DS. When DS containing ammonium is regenerated by MD, ammonium in DS could be converted to ammonia at equilibrium and vaporise and pass through MD membrane into the water side. As shown in Fig. 5.7A, the final $NH_4^+$-N concentration in the permeate of MD for all DSs was less than 1 mg/L after 6 h of operation. No effects from DS type were observed regarding ammonia permeation through MD to the clean water stream and ammonium rejection rate (Fig. 5.7B), indicating that solute type in DS does not affect ammonium–ammonia equilibrium and ammonia vapour pressure obviously.

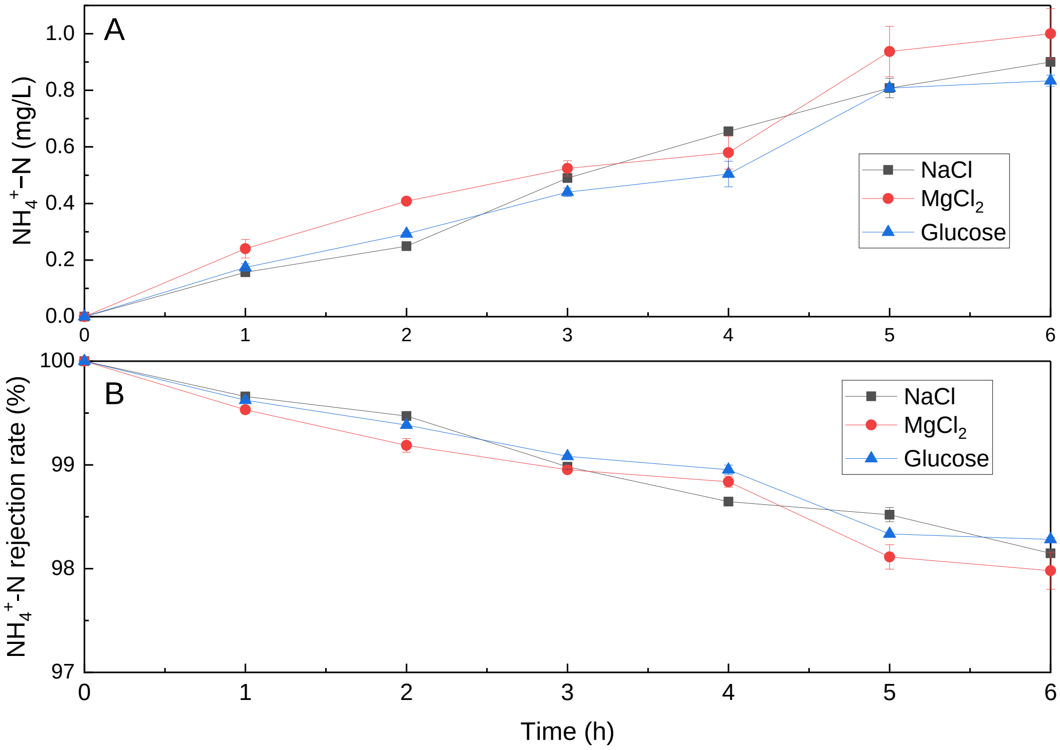

**Fig. 5.7.** Effect of the rate of NaCl, $MgCl_2$ and glucose DSs in the MD process at a permeate temperature of 20 °C and a DS temperature of 50 °C on A) the $NH_4^+$-N concentration on the permeate side and B) the $NH_4^+$-N rejection rate.

In addition, no variation of conductivity and COD was detected in the permeate side of the MD for NaCl, $MgCl_2$ and glucose as DSs, indicating that the MD membrane had a complete rejection of all solutes of DSs due to the non-volatility of solutes. The complete rejection of all types of solutes in DSs by the MD membrane used in this study is consistent with previous studies (Ge et al., 2012; Husnain et al., 2015; Nguyen et al., 2018) because of the unique vapour transfer mechanism of the MD membrane, which almost completely rejects all non-volatile compounds. Ammonium, however, due to its volatility nature, did result in the escape of ammonium from DS to the permeate through the MD membrane by vaporisation, thus imposing the potential risk to contaminate clean water. In this study, since

1 L of permeate and 50 mg/L $NH_4^+$-N in 1 L of DS were used to start MD experiment, ammonium concentration in the permeate after 6 h seems low. However, for per L water recovered, 7.7 mg $NH_4^+$-N was escaped from DS to clean water with the initial $NH_4^+$-N concentration of 50 mg/L in DS. When $NH_4^+$-N concentration in DS is higher due to a higher $NH_4^+$-N concentration in FS for FO filtration and the accumulation of ammonium in DS over time through a continuous FO-MD process, a more serious escape of ammonia from DS to the permeate side with reduced water quality would result.

Fig. 5.8 shows ammonia vapour pressure at different temperatures, pH and aqueous ammonium concentrations. It has to be pointed out that the Henry constant is affected by solution salinity, pH and other factors. In this part, the estimation of the Henry constant was significantly simplified with the purpose of getting an idea on how ammonia pressure varies with pH, temperature and aqueous ammonium concentration. It can be seen that the pH of DS, $NH_4^+$-N concentration in DS and temperature are three important factors that significantly affect ammonia pressure. Ammonia pressure increases with pH and temperature more steeply at higher aqueous ammonium concentrations than at lower ammonium concentrations. The suitable operating pH and temperature ranges (shown in deep and light purple area) are narrower at higher aqueous ammonium concentrations if a similar and low ammonia pressure needs to be maintained to minimize gaseous ammonia permeation from DS to a water side in MD. To avoid high ammonia pressure, the pH of DS could be reduced to a low level such as 5 or 6, but adjusting the pH of DS implies extra chemical costs and would affect the pH of FS as well. Alternatively, temperature could be reduced to less than 50 °C, but a lower temperature means a lower vapour driving force for water permeation through MD, with a reduced water flux and treating capacity of per unit membrane surface. Therefore, for an integrated FO-MD process, when the ammonium concentration in FS is high, such as in sludge digestate with a $NH_4^+$-N concentration of 1500 mg/L (Husnain et al., 2015), the best solution could be selecting non-ionic DS such as glucose to avoid ammonium escape from FS to DS in the first place and minimize ammonium contamination to the recovered water.

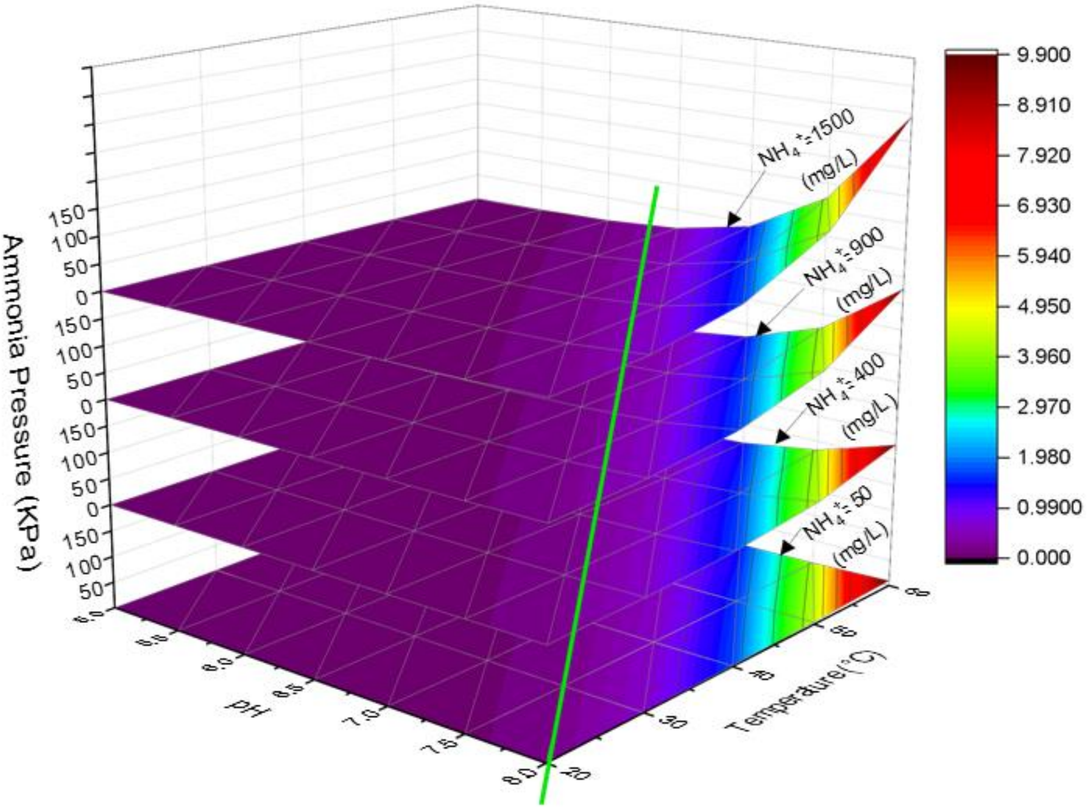

**Fig. 5.8.** Ammonia pressure profiles with temperature and pH at different aqueous ammonium concentrations in DS.

### 5.3.5 Heat Evaluation for an Integrated FO-MD Process in Treating Wastewater

Based on the diagram shown in Fig. 5.2 without internal heat recovery, for the treatment of 1 $m^3$ municipal wastewater with water recovery rates varying from 50% to 90%, the total heat requirement is varying accordingly from 1277–2181 MJ. When waste heat from power plant is used with an electricity generation efficiency of 40% and heat recovery efficiency of 50%, 1277–2181 MJ heat is equivalent to the heat from the generation of electricity of 255–436 kWh.

The Marchwood Power Plant in Southampton generates approximately 895 MW of electricity, which is equivalent to the needs of Southampton, the New Forest and Winchester, with a population of 456,500. If all the heat after electricity generation is recovered to provide heat sources for an integrated FO-MD system treating municipal wastewater, the water that could be treated is around 2052–3505 $m^3/h$. This is only equivalent to a population of 245,272–420,678 with domestic wastewater generation. Obviously, even with the waste heat available from power plants, the heat is far less than the heat demanded for an integrated FO-MD system to treat municipal wastewater. Thus, heat recovery from FO-MD systems should be considered. Given that the condensation of water vapour into water in MD releases a similar amount of heat demanded for vaporisation, the heat could be recovered from the produced water. The internal heat recovery was proposed as shown in Fig. 5.9 for an integrated FO-MD process, in which the discharged concentrate with a high temperature could be used to heat the stream that comes into the MD module while the heat in the permeate could be recovered by heating feed water. In this way, the external heat demand could be significantly reduced. However, how to maximize the internal heat recovery still needs further investigation.

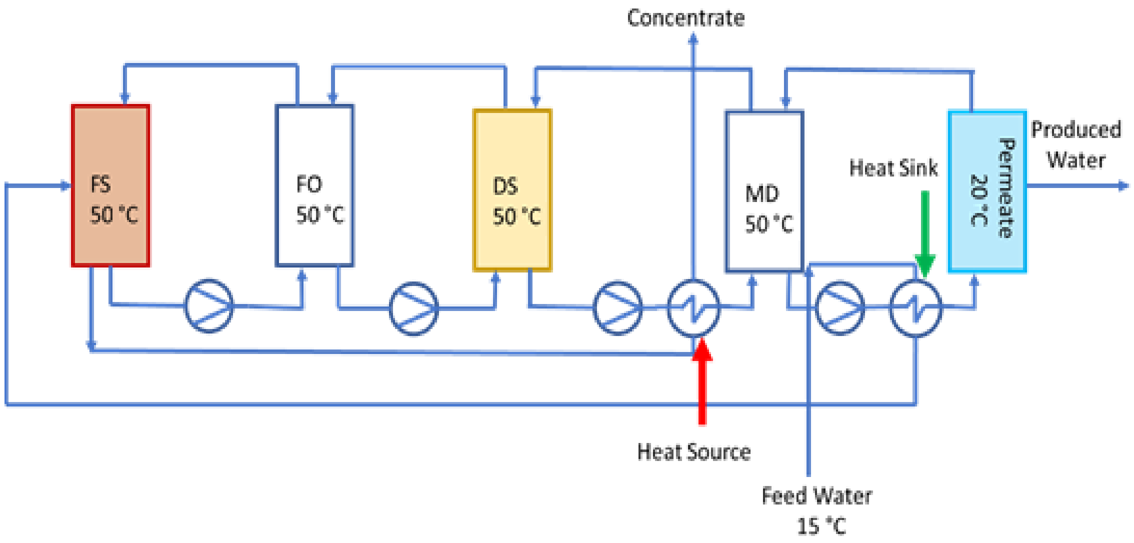

**Fig. 5.9.** The proposed integrated FO-MD process for wastewater treatment and water production with internal heat recovery.

## 5.4 Conclusions

The effect of FS and DS temperatures on the performance of the FO process was compared between ionic DS such as NaCl and non-ionic DS such as glucose, and the implications of ammonia escape and heat demand in an integrated FO-MD process were estimated for the first time. The results showed, at the elevated temperatures of FS and DS in FO, that a non-ionic DS such as glucose with a higher viscosity, lower diffusivity and larger molecules results in a much higher water flux increase (i.e., 23–35% vs. 8–19% by NaCl) but lower RSF increase compared with an ionic DS such as NaCl. The water flux at the elevated temperature with glucose as DS falls within the range of NaCl at ambient temperatures. Ammonium rejection with NaCl as DS for municipal wastewater was very low, and deteriorated at an elevated temperature, while there was not any forward ammonium permeation to DS at all operating temperatures with glucose as DS. The slightly higher water flux decline of the FO membrane at higher FS and DS temperatures could be due to the formation of inorganic precipitates. A normal flushing for 30 min was able to recover the water flux of FO membrane completely after three consecutive filtration cycles treating synthetic municipal wastewater with a 70% water recovery rate. The accumulation of ammonium in a DS such as NaCl, with a low ammonium rejection rate, imposes the risk of ammonium vaporization and escape to the recovered clean water stream in the MD process with reduced water quality, which is independent of the DS type. For treating DS with a 50 mg/L initial ammonium concentration, 7.7 mg ammonium permeated through the MD membrane for per liter clean water recovered. Thus, a non-ionic DS such as glucose is recommended to avoid ammonium contamination, especially for FS containing higher ammonium concentrations. From the perspective of heat demand, only with internal heat recovery, it is economically feasible to treat municipal wastewater in an integrated FO-MD process.

In summary, it can be conclude from the new findings above that temperature effects on FO greatly depend on the physico-chemical properties of DS. Ammonia permeation to recovered water side is decided by the pH, temperature and aqueous ammonium solution in wastewater when the ionic chemical NaCl is used as DS, making the operation control more difficult. However, non-ionic DS glucose shows better performance in terms of reverse solute flux, ammonium rejection and acceptable water flux in the FO unit at elevated temperatures and better quality of water recovered from the MD unit. The results could provide meaningful guidance for the selection of DS in an integrated FO-MD process with elevated temperature treating wastewater streams containing ammonium and suggest the necessity of internal heat recovery in FO-MD processes.

# Chapter 6: Conclusions and Recommendations for Future Work

## 6.1 Conclusions

This study aimed to investigate and enhance the performance of the TFC FO membrane for subsequent resource recovery applications from municipal wastewater in the integrated FO–MD process. The following conclusions can be drawn:

- The TFC FO membrane was able to concentrate COD and phosphorus to their desired concentrations that facilitated direct phosphate precipitation for phosphorus recovery and anaerobic treatment for energy recovery from municipal wastewater. However, it was found that the TFC FO membrane was not able to reject ammonium in the FS when NaCl was used as DS.
- Simple physical cleaning methods were more effective in removing fouling deposits on the membrane caused by SS than fouling caused by calcium precipitates.
- The use of real municipal wastewater resulted in more fouling issues and was harder to clean. This suggests that pre-treatment for the FO membrane to remove SS is important to ensure the stability of the FO membrane to achieve relatively long-term membrane filtration.
- Although the use of a spacer in the flat sheet configuration did not alleviate membrane fouling during the up-concentration of real municipal wastewater, the efficiency of the subsequent physical cleaning method increased by 15%. In addition, chemical cleaning was needed to enhance the initial water flux recoverability, which will adversely affect the membrane life-span and increase the operating costs.
- The use of a monovalent cation DS with a low hydrated radius resulted in an increase in cation exchange between the FS and DS, and therefore a lower ammonium rejection than the use of a divalent cation DS with a larger hydrated radius.
- The DS diffusion coefficient did not affect ammonium rejection with non-ionic DSs, while ionic DS with lower diffusion coefficient increased ammonium rejection for DS containing the same cation (i.e. NaCl-$Na_2SO_4$ and $MgCl_2$-$MgSO_4$).
- Almost a complete ammonium rejection rate was obtained using a non-ionic DS.

- Although that ammonium rejection rate was increased at higher initial ammonium concentration in the FS with ionic DS, however, more absolute ammonium was permeated to the DS.
- The increase of ammonium, phosphate and other ions (e.g. $Ca^{2+}$ and $Mg^{2+}$) in FS, as well as pH increase of FS, could induce inorganic fouling on the FO membrane. However, the initial water flux of the fouled FO membrane from one batch cycle filtration for the treatment of synthetic and real municipal wastewaters and sludge digestate with MF pre-treatment was fully recovered by using physical cleaning methods (i.e. normal flushing and osmotic backwashing) for 30 min.
- Increasing FS and DS temperatures improved the water flux and RSF for NaCl and glucose DSs. However, glucose DS showed a higher water flux increase rate at higher solution temperatures compared with NaCl by around 15%, while the RSF increase rate was two times higher for NaCl DS than glucose DS.
- Operating the FO filtration at higher temperatures resulted in a more passage of more ammonium ions into the DS with ionic DS such as NaCl. On the other hand, a complete ammonium rejection was obtained when glucose was used as the DS at all operating temperatures.
- Although the rate of flux decline was slightly higher at higher FS and DS temperatures, normal flushing for 30 min was able to recover the initial water flux for the FO membrane.
- Non-ionic DS such as glucose is recommended to avoid ammonium contamination in the FS, especially for FS containing higher ammonium concentrations.
- The proposed internal heat recovery in the integrated FO-MD process could help to reduce the external heat demand for the integrated process.

Overall, this study shows that understanding the FS characteristic will significantly help to optimize the FO membrane fouling and the associated cleaning methods. In addition, the current study contributes to the DS selection criteria by showing how ammonium rejection can be enhanced by the appropriate selection of DS based on the DS physiochemical properties during the TFC FO filtration. Finally, this study illustrates the importance of the FS and DS temperatures in the integrated FO-MD system and the necessity of internal heat recovery.

## 6.2 Recommendations for future work

Based on the results, the following recommendations are proposed for future work:

- Future studies could be conducted on the effect of inorganic scaling on the TFC FO membrane using real filtered municipal wastewater from hard water areas. Removing the SS may provide critical insight into how calcium phosphate precipitates affect membrane fouling, cleaning and whether pH adjustment in the FS to mitigate inorganic fouling is needed.
- The effect of $Mg^{2+}$ concertation can be studied by using real wastewater from areas with a high $Mg^{2+}$ concentration. How struvite precipitation can affect TFC FO membrane fouling and how effective physical and chemical cleaning methods are in cleaning the fouled membrane are lacking.
- The $Ca^{2+}$, $Mg^{2+}$ and $K^+$ concentrations in the DS after the FO filtration process could not be measured using DSs such as NaCl and glucose when applying the analytical facilities available in this study. Thus, to calculate $Ca^{2+}$, $Mg^{2+}$ and $K^+$ rejection using the TFC FO membrane, measuring these cations in the DS will be important in the future.
- This study focused on improving ammonium rejection by reducing cation exchange between FS and DS. However, more research is needed for the selection of an economically feasible DS that can achieve a high rejection of contaminates, high water flux and low replacement cost.
- To establish a full-scale FO system, continuous experiments must be performed to answer the following questions: how salinity build-up (e.g. NaCl) in the FS through long-term accumulation affects microbial toxicity for energy recovery through anaerobic treatment and membrane fouling, and how contaminate accumulation in the DS affects FO and MD membrane fouling and flux stability.
- A techno-economic assessment must be conducted to compare the integrated FO–MD process and the FO–RO process.

# Appendix A

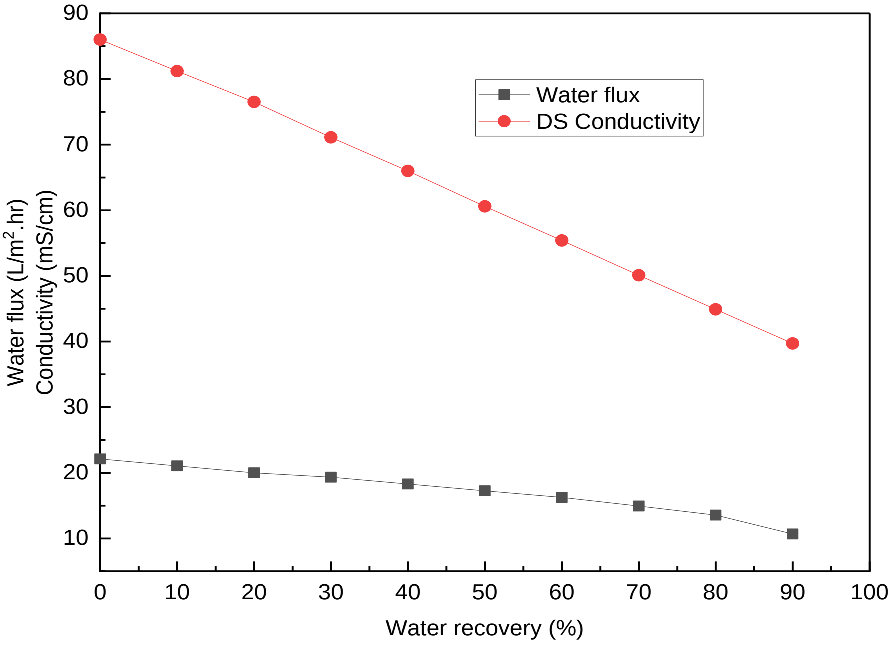

**Fig. A1.** Water flux and DS conductivity with DI water as FS and 1 M NaCl as DS during the hollow fiber FO filtration process until achieving 90% water recovery rate.

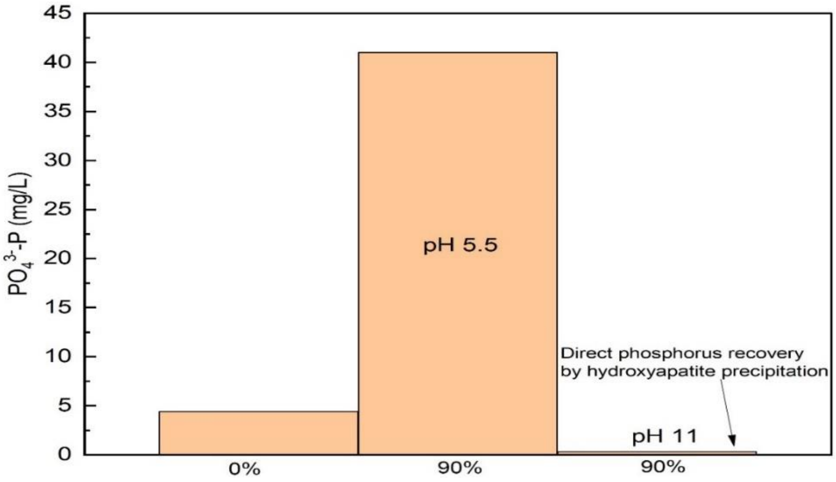

**Fig. A.2.** Initial and final $PO_4^{3-}$-P concentrations in the slat sheet FO process for treating raw sewage until 90% recovery rate after adjusting the pH of the concentrated feed solution to 5.5 and 11.

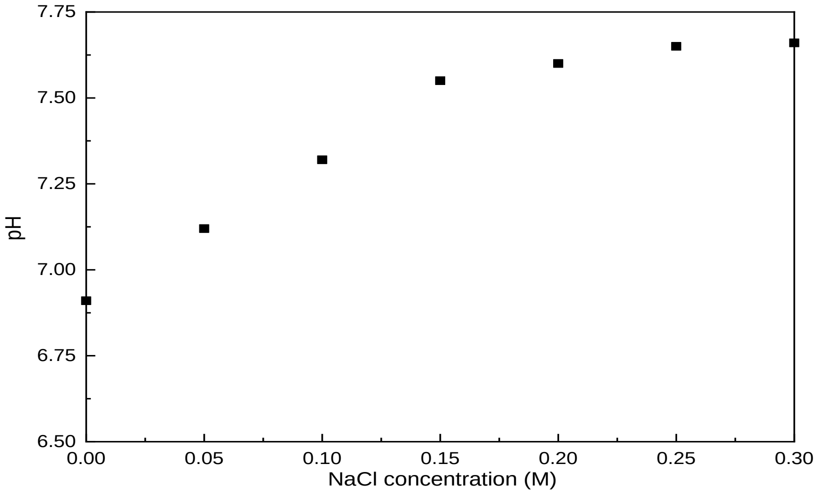

**Fig. A3.** pH of salt solutions at different NaCl concentrations (0 to 0.3 M).

**Table A1:** Variation of feed solution pH, conductivity and the time required to achieve 90% recovery rate at different initial $Ca^{2+}$ concentrations in the final cycle.

| Initial $Ca^{2+}$ (mg/L) | Initial pH (Final cycle) | Final pH (Final cycle) | Initial conductivity (mS/cm) (Final cycle) | Final conductivity (mS/cm) (Final cycle) | Time required to achieve 90% recovery rate (Final cycle) |
|---|---|---|---|---|---|
| 0 | 6.6 | 7.31 | 0.991 | 33 | 16.5 hr |
| 61 | 6.6 | 8.02 | 1.004 | 72 | 41.25 hr |

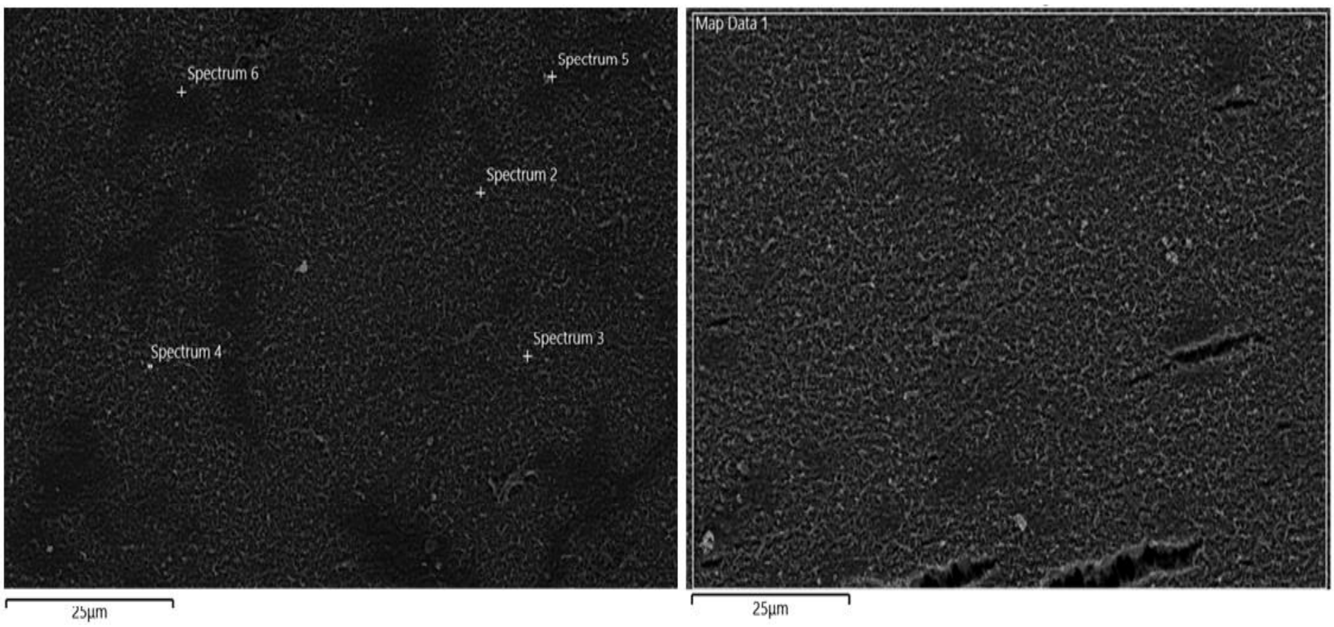

**Fig. A4.** Image produced by SEM for the hollow fiber FO membrane after three batch membrane filtration cycles with 61 mg/L $Ca^{2+}$ for concentrating synthetic sewage with 90% water recovery rates in each cycle followed by osmotic backwashing for 30 min.

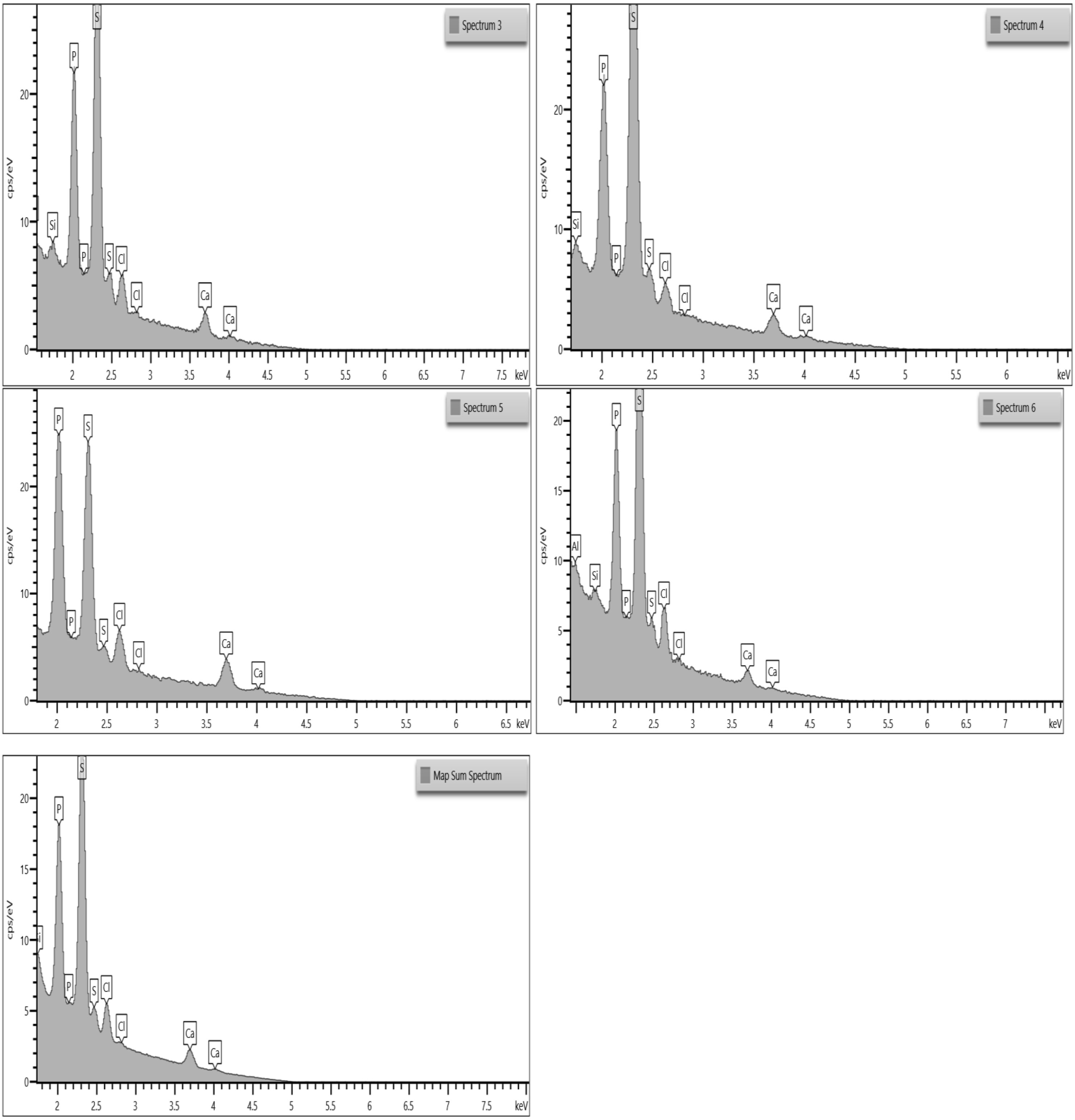

**Fig. A5.** EDS of the hollow fiber FO membrane after three batch membrane filtration cycles with 61 mg/L $Ca^{2+}$ for concentrating synthetic sewage with 90% water recovery rates in each cycle followed by osmotic backwashing for 30 min.

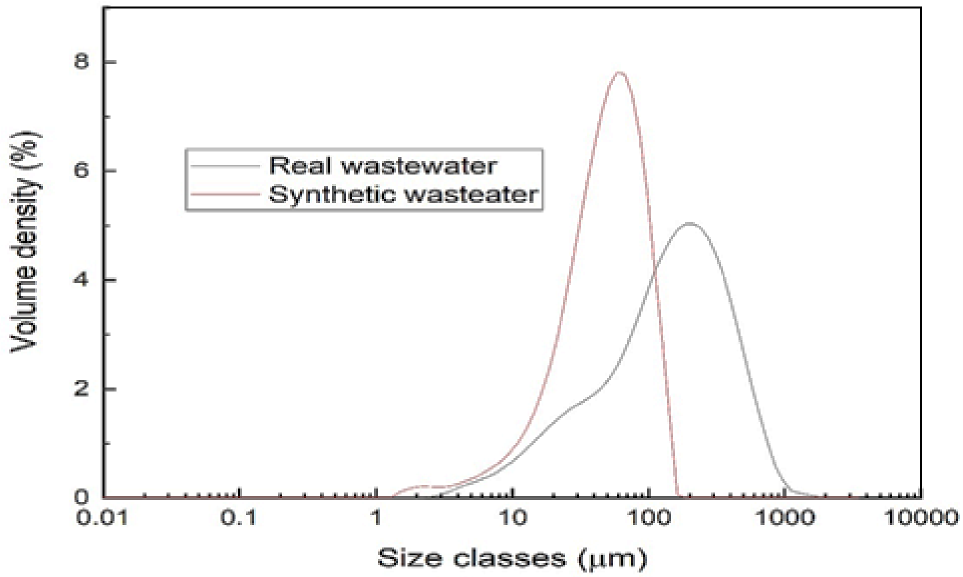

**Fig. A6.** Particle size distribution for wastewater with SS used for fouling tests in TFC FO process.

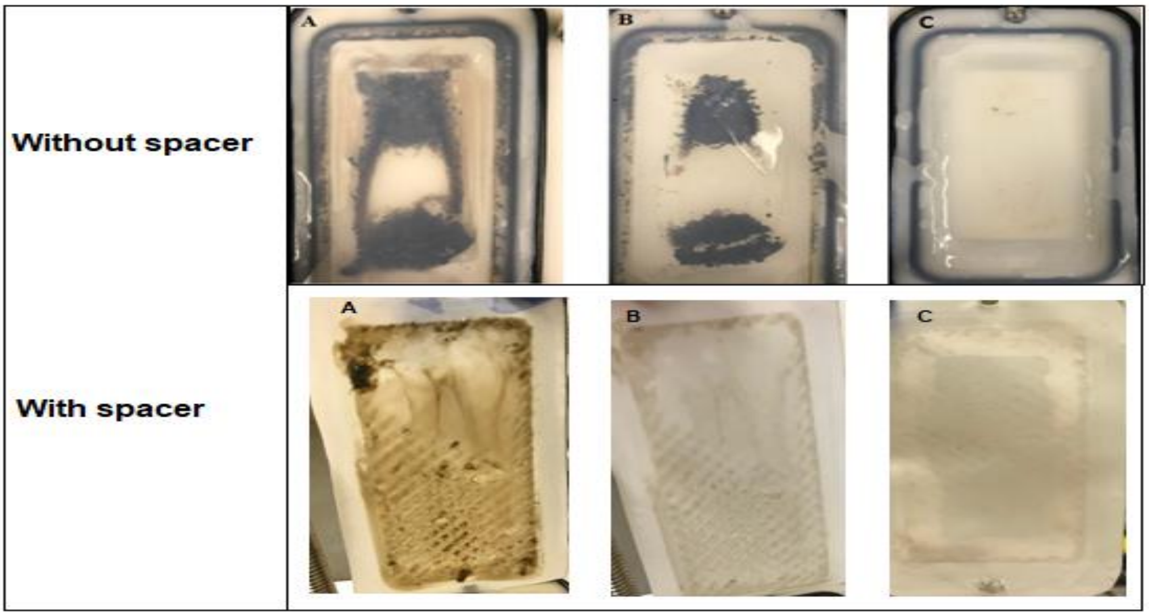

**Fig. A7.** FO membranes in the flat sheet configuration after single batch filtration A) without cleaning, B) After physical cleaning C) After combined physical and chemical cleaning.

# Appendix B

**Table B1:** Physic-chemical properties of NaCl, $MgCl_2$, $MgSO_4$, $Na_2SO_4$, glycine, ethanol and glucose (Achilli et al. 2010; Ansari et al. 2015; Holloway et al. 2015; Miller et al. 1984; Parveen 2018; Phang and Stokes 1980; Salva et al. 2013; Yasukawa et al. 2015).

| Property | Sodium chloride | Magnesium chloride | Magnesium sulphate | Sodium sulphate | Glycine | Ethanol | Glucose |
|---|---|---|---|---|---|---|---|
| Chemical formula | NaCl | $MgCl_2$ | $MgSO_4$ | $Na_2SO_4$ | $C_2H_5NO_2$ | $C_2H_5OH$ | $C_6H_{12}O_6$ |
| Molecular weight (g/mol) | 58.44 | 95.21 | 120.37 | 142.04 | 75.07 | 46.07 | 180.16 |
| Solubility in water at 25 °C (g/L) | 357 | 543 | 374 | 281 | 250 | Freely soluble | 910 |
| Diffusion coefficient ($m^2/s$) | 1.47 x $10^{-9}$ | 1.07 x $10^{-9}$ | 0.37 x $10^{-9}$ | 0.76 x $10^{-9}$ | 1.06 x $10^{-9}$ | 1.23 x $10^{-9}$ | 0.67 x $10^{-9}$ |

**Table B2:** Estimated transport parameters, molecular weight and estimated cation hydrated radius in the inorganic DSs.

| Cation | Diffusion coefficient ($m^2/s$) | Molecular weight (g/mol) | Hydrated radius (nm) |
|---|---|---|---|
| $Na^+$ | 1.334 x $10^{-9}$ | 22.99 | 0.358 |
| $Mg^{2+}$ | 0.706 x $10^{-9}$ | 24.31 | 0.428 |

**Table B3:** Estimated DS replenishment cost per litre of water filtrated at different osmotic pressures with different types of draw solutions.

| Draw solution | Osmotic pressure (bar) | Concentration (M) | DS cost* (\$/kg) | $J_S/J_W$ (g/L) | Replenishment cost (\$/L) |
|---|---|---|---|---|---|
| NaCl | 24 | 0.5 | 0.11 | 0.2008 | 0.00002209 |
| | 48 | 1 | | 0.2023 | 0.00002225 |
| | 96 | 2 | | 0.2068 | 0.00002275 |
| | 144 | 3 | | 0.3238 | 0.00003562 |
| $MgCl_2$ | 24 | 0.33 | 0.18 | 0.1872 | 0.00003370 |
| | 48 | 0.66 | | 0.2508 | 0.00004514 |
| | 96 | 1.32 | | 0.2869 | 0.00005164 |
| | 144 | 2 | | 0.3941 | 0.00007094 |
| Glucose | 24 | 1 | 0.41 | 0.0535 | 0.00002194 |
| | 48 | 2 | | 0.0950 | 0.00003895 |
| | 96 | 4 | | 0.1016 | 0.00004166 |

*DS cost is referred to industrial grade order. The prices are dependent on the provider and region, and can be modified.

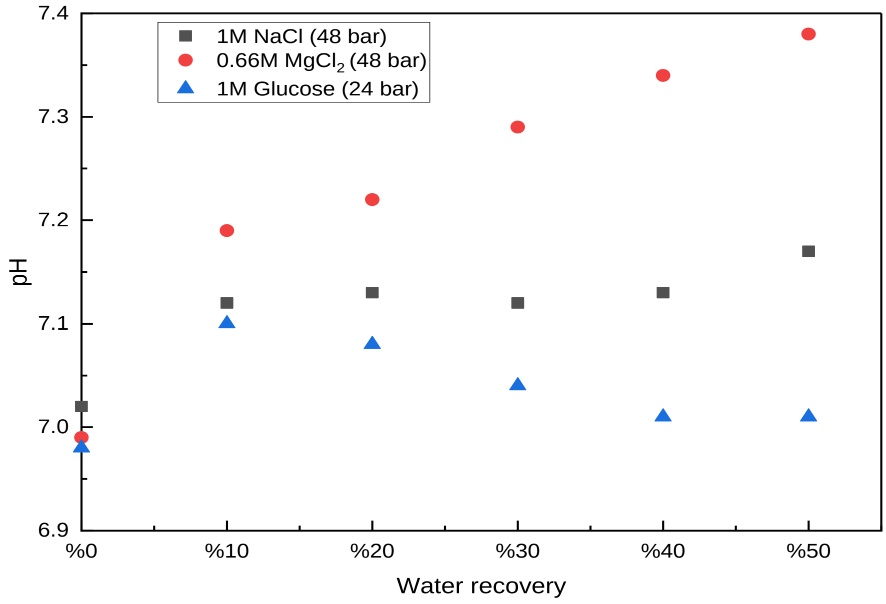

**Fig. B1.** pH change in the feed solution (DI water) for three different draw solutions until 50 % recovery rate during the TFC FO process.

**Table B4:** Saturation index values for the concentrated synthetic wastewater FS at 90% water recovery rate (i.e. 73.77 mg/L $PO_4^{3-}$-P, 303.53 mg/L $NH_4^+$-N, 66.20 mg/L $Ca^{2+}$, 64.21 mg/L $Mg^{2+}$ and 35.04 $K^+$ mg/L at pH 7.1) and 1 M glucose as DS.

| Mineral | SI |
|---|---|
| Brucite | -6.138 |
| $Ca_3(PO_4)_2$ (am1) | -1.188 |
| $Ca_3(PO_4)_2$ (am2) | 1.583 |
| $Ca_3(PO_4)_2$ (beta) | 2.674 |
| $Ca_4H(PO_4)_3$:$3H_2O$(s) | 2.471 |
| $CaHPO_4$(s) | 0.611 |
| $CaHPO_4$:$2H_2O$(s) | 0.306 |
| Hydroxyapatite | 10.275 |
| Lime | -22.173 |
| $Mg(OH)_2$ (active) | -7.491 |
| $Mg_3(PO_4)_2$(s) | -2.537 |
| $MgHPO_4$:$3H_2O$(s) | -0.386 |
| Periclase | -10.733 |
| Portlandite | -11.983 |
| Struvite | -0.045 |

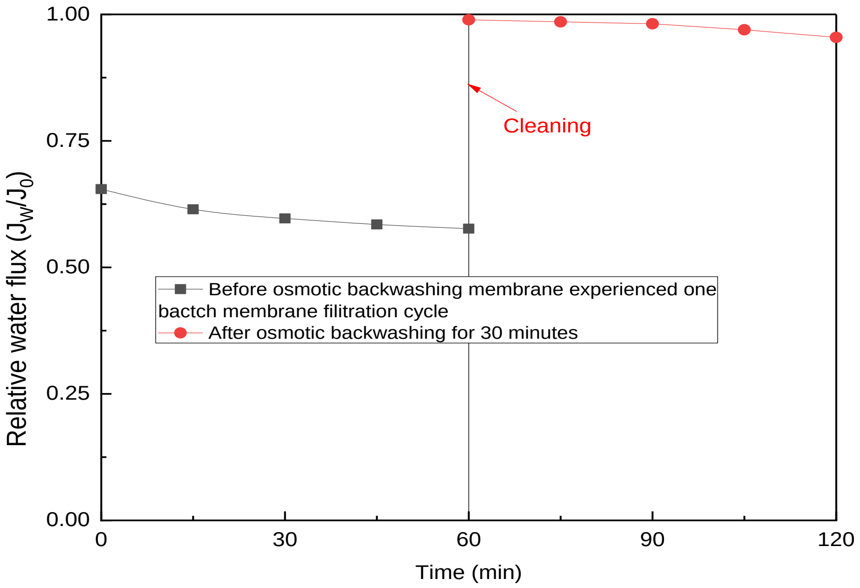

**Fig. B2.** Relative water fluxes before and after osmotic backwashing to clean FO membrane after one batch membrane filtration cycle for concentrating synthetic municipal wastewater until 90% water recovery rate with 1 M glucose DS.

**Table B5:** Saturation index values for the concentrated municipal wastewater and sludge digestate FS at 50% water recovery rate with NaCl and glucose DSs.

| Mineral | SI | | | |
|---|---|---|---|---|
| | Municipal wastewater at 50% water recovery with 0.6 M NaCl DS (pH 7.83) | Municipal wastewater at 50% water recovery with 1.2 M glucose DS (pH 7.71) | Sludge digestate at 50% water recovery with 0.6 M NaCl DS (pH 7.84) | Sludge digestate at 50% water recovery with 1.2 M glucose DS (pH 7.82) |
| Brucite | -4.949 | -5.193 | -4.922 | -5.002 |
| $Ca_3(PO_4)_2$ (am1) | -1.001 | -1.181 | -3.594 | -3.806 |
| $Ca_3(PO_4)_2$ (am2) | 1.77 | 1.590 | -0.823 | -1.035 |
| $Ca_3(PO_4)_2$ (beta) | 2.861 | 2.681 | 0.268 | 0.056 |
| $Ca_4H(PO_4)_3{:}3H_2O(s)$ | 1.839 | 1.682 | -1.749 | -2.031 |
| $CaHPO_4(s)$ | -0.209 | -0.186 | -1.202 | -1.271 |
| $CaHPO_4{:}2H_2O(s)$ | -0.513 | -0.490 | -1.508 | -1.577 |
| Hydroxyapatite | 11.47 | 11.086 | 7.276 | 6.920 |
| Lime | -20.345 | -20.572 | -20.953 | -21.028 |
| $Mg(OH)_2$ (active) | -6.303 | -6.546 | -6.275 | -6.356 |
| $Mg_3(PO_4)_2(s)$ | -4.268 | -4.496 | -4.953 | -5.177 |
| $MgHPO_4{:}3H_2O(s)$ | -1.845 | -1.837 | -2.204 | -2.277 |
| Periclase | -9.545 | -9.788 | -9.517 | -9.596 |
| Portlandite | -10.155 | -10.382 | -10.763 | -10.839 |
| Struvite | -2.311 | -1.824 | -0.476 | -0.355 |

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