Recovery of the Diluted Draw Solution of Os-MBR and Production of Purified Water by Membrane Distillation

By

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"I dedicate my dissertation work to my family, friends and teachers. Without whom none of my success would be possible. A special gratitude to my loving parents whose words of encouragement and push for tenacity ring in my ears"

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(Aamir Shahzad)

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LIST OF ABRIVATIONS

AGMD	Air gap membrane distillation
$CaCl_2$	Calcium chloride
CH_3COONa	Sodium acetate
DCMD	Direct contact membrane distillation
DS	Draw solution
ED	Electrodylasis
FO	Forward osmosis
FS	Feed solution
LMH	Liters per square Meter per Hour
M	Molar concentration
MBR	Membrane bioreactor
MD	Membrane Distillation
MF	Micro filtration
$Mg(CH_3COO)_2$	Magnesium acetate
mg/L	milligram per liter
$MgCl_2$	Magnesium chloride
MW	Molecular weight
NaCl	Sodium chloride

NF	Nano filtration
Os-MBR	Osmotic membrane bioreactor
PP	Polypropylene
PTFE	Polytetrafluoroethylene
PVDF	Polyvinyl fluoride
RO	Reverse osmosis
TDS	Total dissolved solids
UF	Ultrafiltration
VMD	Vacuum membrane distillation
WW	Wastewater
WWF	World wild life fund

ABSTRACT

This study investigates the application of direct contact membrane distillation (DCMD) for concentrating diluted draw solution (DS) from osmotic membrane bioreactor (Os-MBR). A flat sheet PTFE hydrophobic membrane with a pore size of 0.2 µm was used to perform the experiments. The effect of circulation velocity, temperature, and channel spacer effect on permeate flux were investigated. Results indicated that the permeate flux increased with feed temperature and velocity. Spacers enhanced permeate water flux up to 35% and the sequence of spacer design in terms of flux was: diamond design > ladder design > without spacer. DCMD process was also applied during long period for reconcentration of synthetic aqueous draw solutions of two organic (sodium acetate & magnesium acetate) and three inorganic salts (sodium chloride, magnesium chloride, & calcium chloride) under the optimal operating conditions. The optimal DCMD condition was achieved using aqueous NaCl solution. Organic salts $Mg(CH_3COO)_2$ gave prolong operational period in OsMBR-MD and required more MD membrane flushing. MD membrane flushing followed the order as $Mg(CH_3COO)_2$ > CH_3COONa > $CaCl_2$ > $MgCl_2$ > NaCl. NaCl gave better performance in terms of flux and recovery as compared to all other salts. For all organic and inorganic DS, the DCMD system was able to achieve DS recovery as per Os-MBR requirement and also produced good quality product water due to high TDS and contaminant rejection (>99%).

Chapter 1

INTRODUCTION

1.1 Background

Water is the main source of life, necessary for human survival and substantial economic development of a country. The exponential and continuous growth of world population has raised considerable concerns of water sustainability (Chekli et al., 2016). According to WWF two-third of the world's population may face water shortage by 2025. Therefor a sustainable solution is needed for clean water production. Membrane bioreactor (MBR) is considered as the most effective wastewater treatment technology combining biological treatment with membrane separation (Wang et al., 2016). Compared with conventional treatment process, MBRs has many advantages such as less sludge production, smaller foot prints, and better effluent quality (Le-Clech et al., 2006; Meng et al., 2009). Despite these advantages, MBR has several draw backs such as external source of energy to pressurize the water through the membrane, membrane fouling results in performance reduction, rapid flux decline, frequent membrane cleaning leading to increase operating and maintenance cost (Wang et al., 2016).

Forward osmosis is an emerging green membrane technology that can be used for desalination, water treatment, and wastewater treatment. Recently, FO process integrated with MBR called osmotic membrane bioreactor (Os-MBR) has been developed for wastewater treatment. Compared to conventional MBR process, Os-MBR has less membrane fouling, low energy consumption and high rejection (Nguyen et al., 2016a). Forward osmosis is driven by osmotic pressure generated by highly concentrated draw

solution (DS) to extract water from wastewater using a semi permeable membrane. The driving force is therefore created by the difference of osmotic pressure between the DS and the feed solution (FS) (Rastogi, 2016). In forward osmosis, water flows from the FS by osmosis through a semi permeable membrane into the DS and dilutes the higher concentration of DS on the permeate side and lower the osmotic pressure gradient. Diluted DS requires a further treatment process to maintain osmotic pressure gradient across the membrane (Bruggen and Luis, 2015).

Therefore, FO process requires further integration with reconcentration process to recover the water from the DS. Forward osmosis generally has been coupled with other membrane separation processes like electrodylasis (ED), reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), and membrane distillation (MD) to separate the DS from the permeate water (Ling and Chung, 2011; Luo et al., 2014; Zhang et al., 2013; Zhao et al., 2012). Membrane distillation (MD) is an ideal and attractive option for recovery of DS because of its advantages such as less capital cost, high permeate quality and less affected by feed salinity (Luo et al., 2014). MD is a thermally driven water separation process, which allow water vapor, not liquid, to pass through micro porous hydrophobic membrane. The main driving force of MD is vapor pressure difference generated by the temperature difference between feed and permeate surface of the membrane (Boubakri et al., 2014a) which is different from conventional membrane separation processes. MD has lower membrane fouling as compared to other membrane separation processes due to its large pore size of hydrophobic membrane. Pore size of MD membrane is in the range of 0.001 to 1 μm (Khayet and Matsuura, 2011). Separation process takes place in three steps; from feed side of membrane evaporation take places,

the water vapor moves through the membrane from hot to cold side due to pressure difference across the membrane, and finally the condensation take place on permeate side which depend on the module configuration (Bouchrit et al., 2015). DCMD is the most widely used and simplest form of MD configuration, mostly used in desalination and concentration process and proven to be more efficient in terms of permeate flux (Boubakri et al., 2014a).

The aim of this study was to examine the performance of DCMD process for the re-concentration of different draw solutions for osmotically driven membrane process. The impact of operating parameters on permeate flux and salt rejections were studied. DCMD was applied for recovery of diluted draw solutions in which two organic and three inorganic salts were examined.

1.2 Objectives of study

- Evaluate the performance of DCMD system in terms of flux, removal efficiency at different temperature, velocities, and salt concentration
- Study the impact of spacer on performance of Membrane distillation (Ladder and Diamond design)
- Investigate recovery of the concentration of diluted organic and inorganic DS for Os-MBR

1.3 Scope of study

Research work was divided into two phase, Phase one was the optimization of DCMD and phase two was the recovery of draw solution of osmotic membrane bioreactor.

In this research, flat sheet PTFE hydrophobic membrane having a pore size 0.2 µm was used for the experimental work. Synthetic solutions were prepared by using 0.25M of NaCl, $MgCl_2$, $CaCl_2$, CH_3COONa and $Mg(CH_3COO)_2$. Study was conducted with lab scale DCMD setup and research were set as follows:

- DCMD performance was evaluated on the basis of permeate flux and TDS rejection. The variables which were included are feed temperature, circulation rate of feed and permeate, spacer and salt type.
- Suitable temperature and velocity were determined to maintain desired Os-MBR DS concentration.
- The performance of organic and inorganic DS was compared in terms of recovery, flux, and membrane flushing.

Chapter 2

LITERATURE REVIEW

2.1 Membrane bioreactor

Membrane bioreactor (MBR) is the biological degradation process followed by membrane separation like micro filtration (MF) or ultrafiltration (UF) and widely used for municipal and industrial wastewater treatment. MBR process use a semipermeable membrane as a filter, rejecting organic matter or nutrient from wastewater, resulting in a clarified product effluent (Lee et al., 2002). Over conventional processes, MBR can produce effluent of high quality, smaller foot prints, and less sludge production (Bernal et al., 2012). Pictorial view of pilot scale MBR plant installed at NUST is shown in Fig. 1.

Fig. 1. NUST MBR plant

2.2 Forward osmosis

Forward osmosis technology has gained increasing popularity since the beginning of 2000. It is a most favorable technology in the 21st century for desalination, water and wastewater treatment (Luo et al., 2014) due to its low operating cost and less membrane fouling compared to other membrane separation processes. Like reverse osmosis (RO), forward osmosis (FO) is an osmotic process, uses a semi permeable membrane to separate water from wastewater. Instead of high pressure, the driving force of FO is an osmotic pressure generated by high concentrated draw solution (DS). The DS consist of single or multiple salts. Draw solution of FO is the driving force to attract water from FS while rejecting solutes through a semi permeable membrane by osmotic pressure difference. Fig. 2 shows the process of forward osmosis.

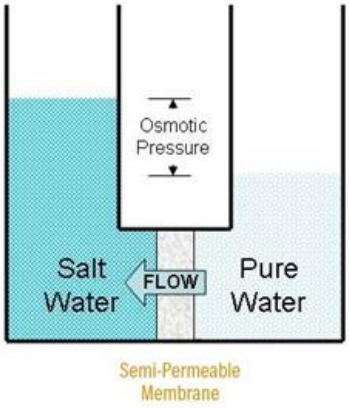


Fig. 2. Forward osmosis process

2.3 Osmotic membrane bioreactor (Os-MBR)

Os-MBR is an innovative MBR process using forward osmosis (FO) membrane instead of microporous (conventional) membrane. Os-MBR can reduce fouling, enhanced rejection of dissolved particles and smaller species (Nguyen et al., 2016a). Advantages of FO membrane are: (i) use of osmotic pressure as the driving force (low energy consumption process); (ii) high rejection of contaminants, (good quality product water); (iii) low fouling (due to dense and tight surface structure of membrane) (Nguyen et al., 2016b, 2015; Yin Tang and Ng, 2014). Os-MBR process is shown in Fig. 3.

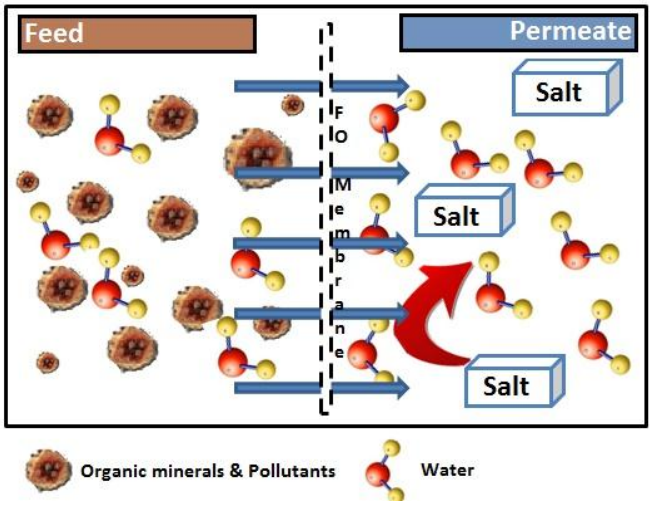


Fig. 3. Os-MBR process

Water flows from the feed by osmosis through a semi permeable membrane into the DS and dilutes the higher concentration of DS on the permeate side and lower the osmotic pressure gradient. Diluted DS requires a further treatment process to maintain osmotic pressure gradient across the membrane. FO application needs draw solution separated from water or reconcentration of DS for reuse.

Different technologies have been used for separation of draw solution such as thermal separation, membrane separation, precipitation, combined process and direct use without recovery (Luo et al., 2014). Fig. 4 shows schematic of Os-MBR with reconcentration unit.

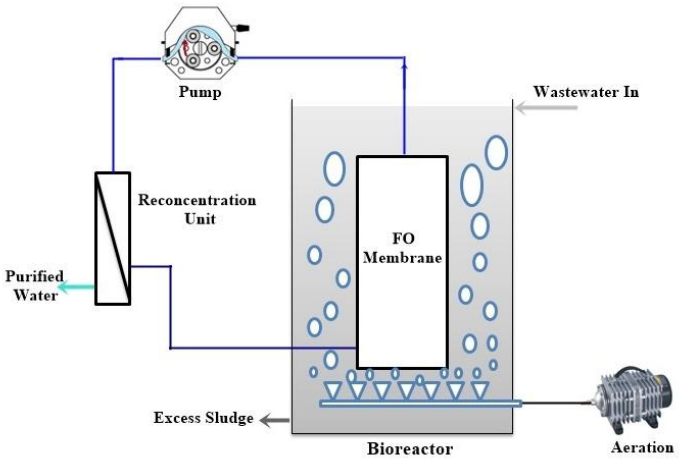


Fig. 4. Schematic diagram of Os-MBR with reconcentration unit

2.4 Approaches to DS recovery

2.4.1 Thermal separation

In thermal separation, volatile solutes such as SO_2 were added in seawater or fresh water to create high pressure osmotic DSs. After FO diluted DS was separated from water by heating. Thermal separation is an easy but energy intensive process. Water recovery rate is high but quality is not good (Luo et al., 2014).

2.4.2 Precipitation

Perceptible salts of acids like manganic acid, valeric acid, and glucuronic acid and metal ions like sodium, calcium, potassium, barium and cesium were used as a draw solution of FO for sea water desalination. There solubility changed with pH and temperature resulting in a separation from DS by precipitation. This recovery process did not require energy but heavy metals residues in product water can make it unsafe (Alnaizy et al., 2013).

2.4.3 Membrane Separation

2.4.3.1 Reverse Osmosis (RO)

Reverse osmosis is the finest membrane having a pore size range from 0.0001 to 0.001 µm. RO is able to mostly retained all of the contaminants except water due to its small pore size. The required operating pressure is greater because flows goes against the concentration gradient (forcing water to go from low pressure to high pressure) (Shenvi et al., 2015).

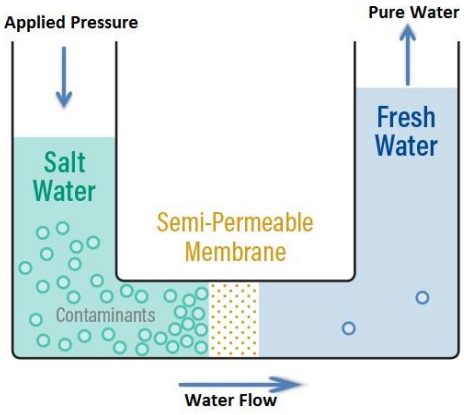


Fig. 5. Reverse Osmosis

Reverse osmosis (RO) is a pressure driven membrane separation process where a semi permeable membrane rejects contaminants present in feed water and only fresh water passes through the membrane. Pump is used to create pressurize feed that flows through the membrane to the product side. Salt retained into the feed side of reactor is known as brine (Garud et al., 2011). RO can be used with FO as a post treatment process, to recover DS from water and to produce purified water due to its high water recovery and high salt rejection. RO membrane is protected from fouling and scaling as most of the contaminants are rejected from FO membrane and only diluted draw solutes are sent to the RO membrane for reconcentration. The use of FO-RO hybrid system for desalination of saline or brackish water and wastewater is energy saving and economically feasible. Cath et al. (2010) studied the FO-RO hybrid system, FO treated wastewater first with draw solution, and then diluted DS transferred to the RO process to produce clean water. Fig. 6 shows schematic diagram of FO-RO integrated system.

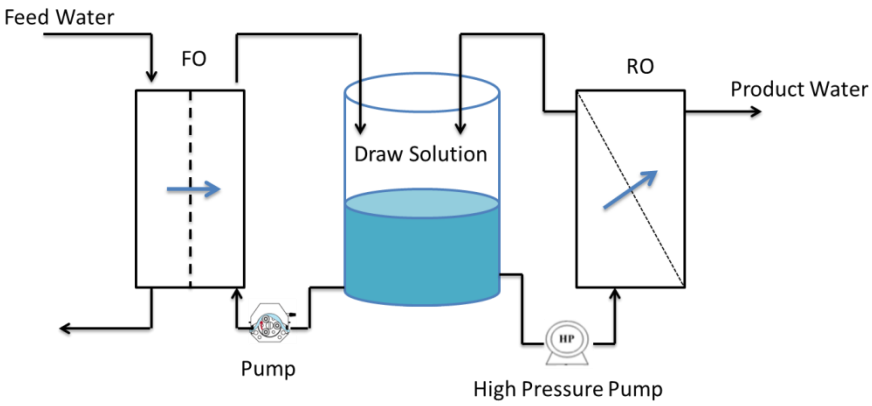


Fig. 6. Schematic diagram of FO and RO integrated system

Hybrid FO-RO process is most competent to the alone RO process, especially for the desalination of high saltwater, as the energy saving of RO for recovery of diluted DS can be achieved. But the RO may be discouraged due to its high operating cost (Luo et al., 2014).

2.4.3.2 Nano filtration (NF)

Nano filtration (NF) membrane pore size vary from 0.001 to 0.01 µm (Marszałek et al., 2016). NF membrane filters synthetic dyes, multivalent ions, specific salts and sugar. Having larger pore size than RO, NF requires less pressure to operate (Walha et al., 2007). Application of NF membrane becomes popular because of many reasons such as low operating pressure, less capital and maintenance cost, and high rejection of salts. Salt rejection could be achieved upto 99% for divalent salts such as $MgCl_2$, $MgSO_4$, and Na_2SO_4. So, NF recovery process for the DS may be good option when multivalent ions are used as draw solutes (Chekli et al., 2012).

2.4.3.3 Ultrafiltration (UF)

Pore sizes of ultrafiltration (UF) membranes ranges from 0.1 to 0.01 µm and are able to retain silica, versus, endotoxins, and proteins. It can also be used in pharmaceutical industries for wastewater treatment. UF membrane has attracted attention for drinking water production due to its low energy cost compared to NF and RO (Clever et al., 2000). UF process is widely used to concentrate solutions, but, the application for water separation or concentration of aqueous solutions are lacking due to large pore sizes of membrane (Crini et al., 2014). UF membrane was proposed for the recovery of polymeric substances have various molecular weights (MW) and expanded structure. However, the effective use of UF membrane is not suitable for DS with low MW (Bai et al., 2011).

2.4.3.4 Microfiltration (MF)

Microfiltration (MF) membrane has a pore size 0.1 to 10 µm and mostly served for the pre-treatment of other water separation process such as UF, and NF, and a post treatment for granular media filtration. Due to large pore size of MF membrane, it is not suitable for post treatment of FO or recovery of any DSs (Luo et al., 2014). Separation ranges of RO, NF, UF, and MF membrane is shown in Fig. 7.

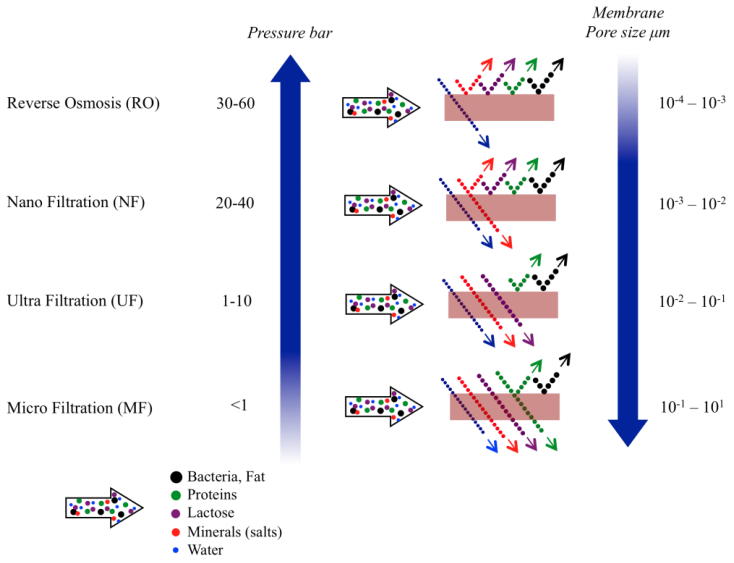


Fig. 7. Principles of membrane separation

2.4.3.5 Electrodialysis (ED)

Electrodialysis (ED) is the transportation of salt ion from one solution to another solution through ion exchange membrane under the influence of applied electric potential, which has been used for desalination process Fig. 8 shows ED system (Strathmann, 2010). As compared to other separation process like RO and NF, ED has the advantages of requiring neither pressure nor energy conversion process and also has high water recovery with less membrane fouling (Xu et al., 2013). But, there is also several

disadvantages of ED, such as uncharged compound cannot be removed with it, high capital cost, short membrane life, and unsuitable to treat high by saline water. ED with solar energy has attracted great interest for brackish water treatment but the cost of electrode and membrane remains a serious issue for long term operation.

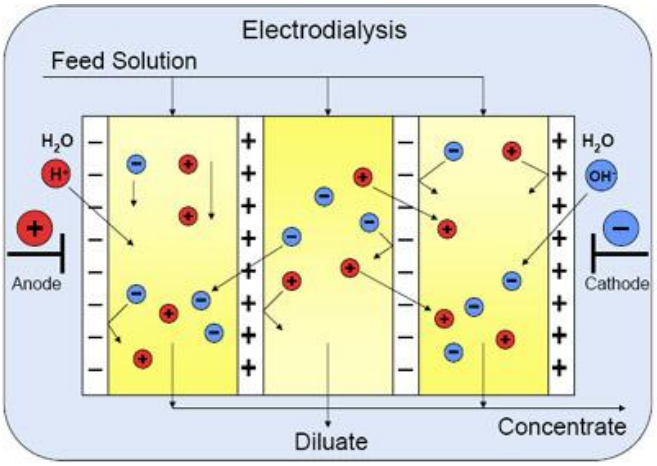


Fig. 8. Electrodylasis system

2.4.3.6 Membrane Distillation

Membrane distillation (MD) is mass transfer process driven by a vapor pressure difference due to temperature difference across the membrane. Fig. 9 shows hydrophobic MD membrane just allowing water vapor not liquid to pass through it. To produce distilled water a temperature difference between feed and permeate side of 10 to 20 ^{o}C can be considered enough (Adham et al., 2013). Due to many attractive features MD is a promising technology for desalination. MD requires low capital and operating cost as it is not a pressure driven process (Wang and Chung, 2012; Warsinger et al., 2015). Membrane distillation performance of desalination is less affected with feed salinity compared with other membrane separation processes such as NF and RO. MD give rise

to 99.99% rejection of nonvolatile solutes and produce high quality product water equal to that of distilled water (Adham et al., 2013; Wang and Chung, 2012).

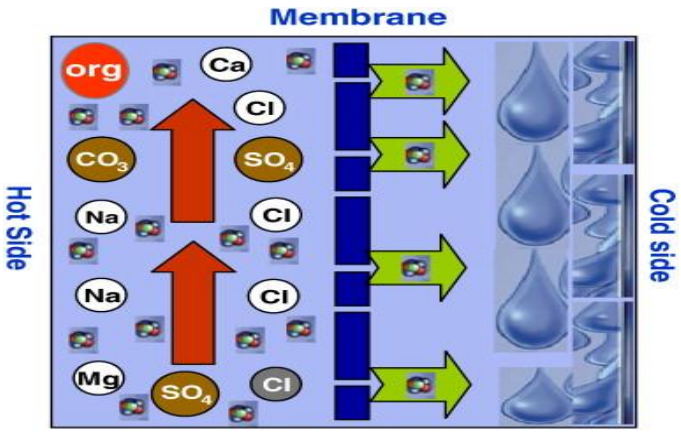


Fig. 9. Schematic diagram of membrane distillation

2.5 MD configuration

Membrane distillation has four different major configurations that have been utilized to separate FS which are direct contact membrane distillation (DCMD), sweeping gas membrane distillation (SGMD), air gap membrane distillation (AGMD), and vacuum membrane distillation (VMD) as shown in Fig. 10. The main difference between these configurations is the kind of processing of the permeate side (Khalifa, 2015).

2.5.1 Direct contact membrane distillation (DCMD)

DCMD is the simplest and famous MD configuration, where both hot feed and cold permeate aqueous solution is in direct contact with membrane surface. Therefore, at the feed membrane surface evaporation take place, vapor moves across the membrane to permeate side by the vapor pressure difference and condenses inside the membrane module. This configuration has been used in food industries for concentration of aqueous solutions and also used for desalination processes (Alves and Coelhoso, 2006; Hsu et al.,

2002). The major drawback of this system is that the cool aqueous solution results in conductive heat loss through the membrane (Summers et al., 2012).

2.5.2 Air gap membrane distillation (AGMD)

In AGMD only FS is in direct contact with feed side of membrane. Stagnant air is introduced between the membrane and permeate surface, vapor crosses that air gap and condense over the cold surface inside the membrane module. The advantage of this design is reduced heat loss by conduction however the main disadvantage is due to air gap additional resistance to mass transfer is created (Yarlagadda et al., 2009). AGMD is suitable for desalination and removing of volatile substances from aqueous solutions (Alkhudhiri et al., 2012a; García-Payo et al., 2000).

2.5.3 Sweeping gas membrane distillation (SGMD)

In SGMD, an inert gas is used to sweep vapor at permeate side and condense that vapor outside of the membrane module. Similar to AGMD there is gas barrier which reduce the heat loss and enhance mass transfer resistance. This configuration is suitable for removal of volatile compounds. The main disadvantage of this configuration is a large volume of inert gas required to just diffuse a small volume of permeate and thus requires a large condenser. Like AGMD, SGMD also used for removing volatile substances from aqueous solutions (García-Payo et al., 2002).

2.5.4 Vacuum membrane distillation (VMD)

In VMD, pump is used to create a negative pressure in the permeate membrane side. This configuration enhances the pressure difference between two sides of membrane leading to increase the permeate flux. Condensation of vapor takes place outside of membrane

module. In this configuration the heat loss due to conduction is also negligible (Alkhudhiri et al., 2012a).

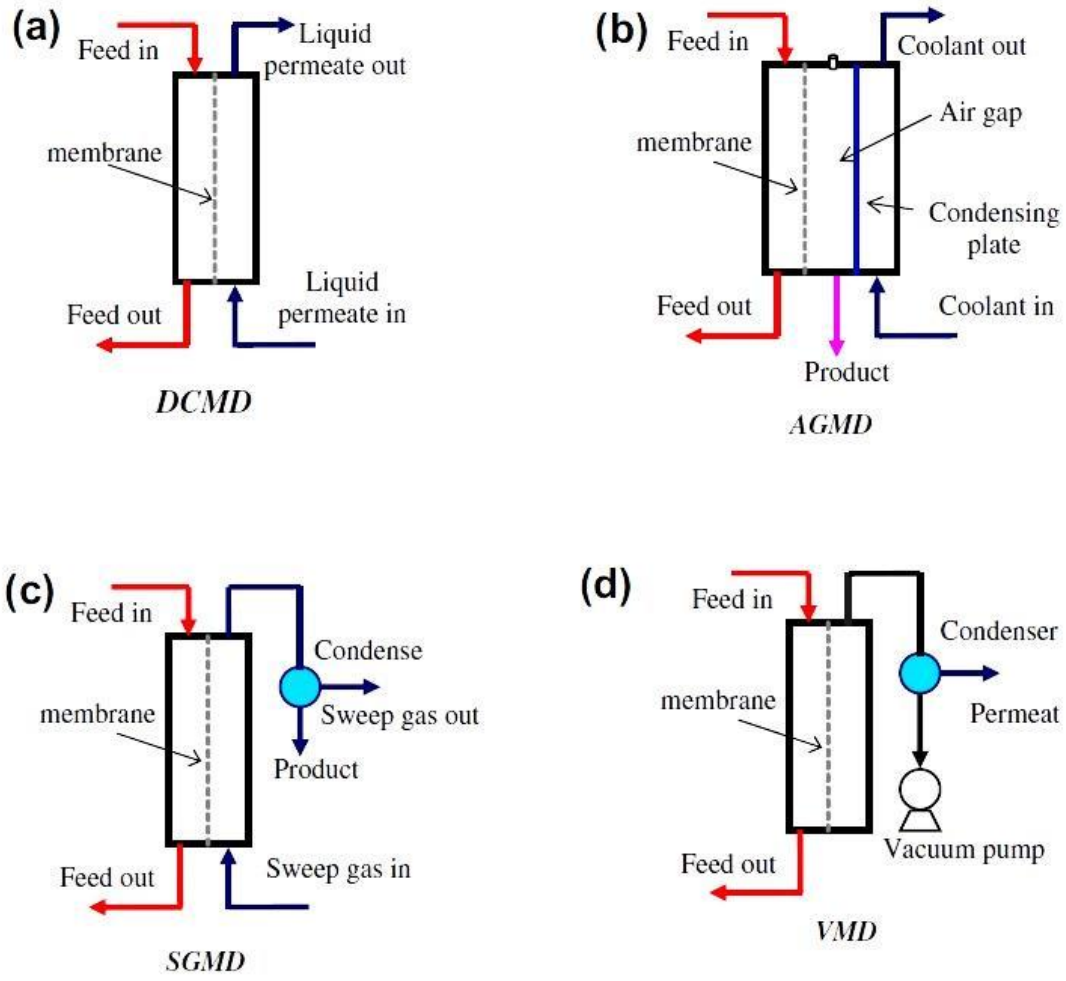


Fig. 10. MD configuration

2.5.5 Comparison among four configurations of MD

Apart from the change in nature of permeate side, all MD configurations have similar benefits and limitations. As the simplest configuration, DCMD has been widely investigated at laboratory scale. In commercial application of DCMD low energy efficiency is consider as the main problem. Among all four configurations, DCMD has highest heat loss due to higher heat transfer coefficient on permeate side and relatively

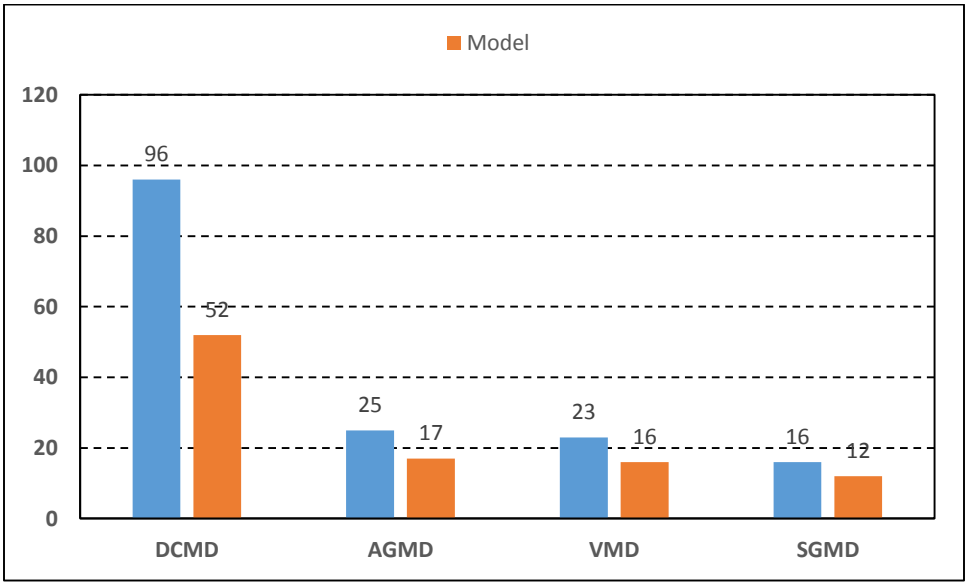
less thermal efficiency (Camacho et al., 2013). In AGMD, both heat and mass transfer are controlled by air gap, between membrane and cold permeate, which outcomes in more mass and thermal transfer resistance. In view of conductivity and thickness of membrane, AGMD is much thicker (2,000 to 10,000 μm) and less thermal conductivity. Thus, heat loss in AGMD is more as compared to DCMD. AGMD has less flux due to less temperature difference and hence, require a greater surface area of membrane (Chouikh et al., 2005). In SGMD configuration, the vapors are stripped from the feed side to the permeate side and condensed in external condenser outside the membrane module. Mass transfer rates in SGMD are higher than AGMD due to more driving force coming from permeate side and less heat loss through the membrane as compare to DCMD. Requirement of an external condenser and inert gas for SGMD cause rising of energy consumption, investment, and running cost (Khayet et al., 2000). In VMD, vacuum is applied in permeate side and vapor is taken out continuously from permeate side. Vapor pressure on permeate side is largest driving force of VMD.

Table 1. Comparison among MD configurations

Configuration	Permeate Side	Flux	Heat Loss	Energy Consumption	Applicability	
					Purification	Intensification
DCMD	Cold Solution	✓	✓✓✓	✓	✓✓✓	✓
AGMD	Air Gap	✓	✓	✓	✓✓	✓
SGMD	Sweeping gas	✓✓✓	✓	✓✓	✓	✓✓✓
VGMD	Vacuum	✓✓✓	✓	✓✓	✓	✓✓✓

Legend: ✓✓✓ very strong; ✓✓ medium and; ✓✓weak

Literature indicates that DCMD is the most popular and attract most studies at laboratory scale research as half of the published papers are based on DCMD (El-Bourawi et al., 2006; Khayet et al., 2000).



(El- Bourawi et al., 2006)

Fig. 11. MD configuration studies and other relating theoretical work

2.6 MD membrane material and module type

MD configuration selection depends on the purpose of application. The considerate factors are given consistence of permeate flux, removal efficiency, pore size, porosity, thermal conduction, and thickness of membrane (Alkhudhiri et al., 2012a).

2.6.1 Materials of MD membrane

Microporous hydrophobic membranes are applied in MD process to resist wetting phenomena. The membrane are made from hydrophobic material generally polypropylene (PP), Polytetrafluoroethylene (PTFE), and polyvinylidene fluoride (PVDF) (Laganà et al., 2000) following requirements for MD membrane such as less thermal conductivity and low resistance to mass transfer. Also, the selected membrane should have good chemical resistance and necessary heat tolerance (Alkhudhiri et al., 2012a; Khayet and Matsuura, 2011).

2.6.2 MD membrane module

There are many different types of MD membrane modules have been designed and used per demand. These modules are classified as flat sheet and frame module, tubular module, spiral wound module, and hollow fiber module.

2.6.2.1 Flat sheet module

Flat sheet membrane is placed in between two plates of module. In general, this module is mostly use at lab scale for desalination and purification due to its suitability as it can be replaced and cleaned simply. However, in flat sheet module the ratio between membrane area and module volume is very low (Alkhudhiri et al., 2012a).

2.6.2.2 Tubular module

In tubular module, tube shape membrane is placed between feed and permeate cylindrical chamber. This membrane module is more attractive due to larger surface area, less fouling tendency and easy cleaning. But, it requires high operational cost. This type of module mostly made from ceramic and investigated for DCMD, AGMD, and VMD with above 99% of salt rejection (Cerneaux et al., 2009).

2.6.2.3 Hollow fiber module

For this type of module, many hollow fibers are bundled and sealed in a shell tube. Operating mechanisms of this type of module are outside-in and inside-out. In outside mechanism, the outlet solution is fed on outer surface of membrane while permeate collected at inner surface. And reverse direction is described for inside-out. The major advantages of this type of module are high packing density and less energy consumption (Curcio and Drioli, 2005).

2.6.2.4 Spiral wound module

In this type of module, membranes are rolled around a perforated tube. In an axial direction feed moves across the membrane surface and the permeate flow radially to the center and exits through the tube. Spiral wound module has good packing density and acceptable energy consumption. In this type of module feed solution is pumped tangentially to the membrane in cross flow and permeate produces through the membrane when feed is re-circulated (Alkhudhiri et al., 2012a).

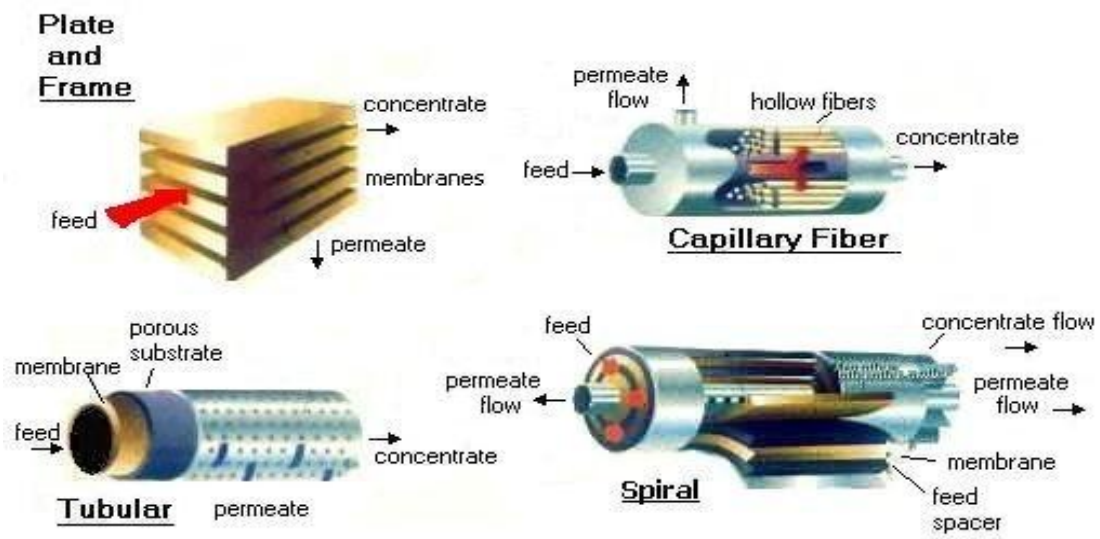


Fig. 12. Types of membrane module

2.7 Advantages, disadvantages, and application of MD

2.7.1 Advantages

MD process has following advantages over other membrane separation processes

- Theoretically a 100% rejection of ions, colloids, macromolecules, cells and non-volatiles compounds can be achieved.
- Compared with conventional distillation, MD operate at low temperature.
- Lower operating pressure in MD than other pressure driven process.
- Less affected with feed salinity.
- Produce a good quality of product water and does not require pretreatment.

2.7.2 Disadvantages

MD process has many advantages but it has some disadvantages which are

- The tendency to separate two or more solutions in a mixture is not possible in MD where both have higher vapor pressure.
- External energy required in MD process to heat FS which may be expensive.
- Membrane wetting and heat loss by conduction is another drawback of MD process.

2.7.3 Applications of membrane distillation

MD processes is commonly applied in the fields of separation and purification. That include trace volatile organic substance from water, separation of ionic or non-volatile substance and extraction of organic substances from liquid solution (El-Bourawi et al., 2006; Lawson and Lloyd, 1997). Typical MD application are illustrated in Table 2.

Table 2. Application of Membrane distillation

Applications Area	Configurations			
	DCMD	AGMD	SGMD	VMD
Desalination and Purification	✓	✓	✓	✓
Concentration of aqueous solutions and wastewater treatment	✓			
Removal of dyes in textile industry	✓			✓
Concentration of acid and removal of VOCs in chemical industry	✓	✓	✓	✓
Pharmaceutical and biomedical industry	✓			
Food industry	✓	✓		✓

Source: (El-Bourawi et al., 2006)

Chapter 3

METHODOLOGY

Details about materials and methods are described in this chapter which were used for the investigation purpose of the study. Research work was performed in Water and Wastewater laboratory of IESE, NUST. Following sections represent the detail of specific experiments and all conditions of this study.

3.1 Experimental Unit

A process flow diagram of DCMD experimental setup used in this study coupled with Os-MBR is shown in Fig. 15. The flat sheet module made of acrylic constituted of two channels. Each channel was 0.3cm × 4.5cm × 10.6cm (depth, width, and length) with 48 cm^2 of total membrane effective area for mass transfer. Membrane module was placed in a horizontal position for all the experimental runs. Feed and permeate solutions were circulated by using two peristaltic pumps (Masterflex, 7524-45, Cole Parmer, USA) in a countercurrent direction through each channel. The circulation velocity of feed and permeate sides were maintained similarly.

Heat exchanging coil of stainless steel submerged into a hot water tank was used to heat the feed solution connected with temperature control unit to regulate the temperature of feed. Two temperature sensors (TPM-900, SANHNG, China) were used to measure the inlet and outlet temperature of feed water. Feed or draw solution TDS was checked by TDS meter (Sension, HACH, USA). A chiller was used to control the distillate temperature. Two in line TDS meters (KOMATSU, Japan) with temperature sensor were used to measure the inlet and outlet temperature and TDS of the permeate water. A digital

balance (UX 6200H, SHIMADZU, Japan) connected with computer was used to measure the increase in distillate. Draw solution used for regeneration purpose was obtained from an Os-MBR which was coupled with DCMD for continuous supply of diluted DS.

3.2 Microporous membrane characteristics

A flat sheet hydrophobic microporous membrane from Ningbo Changqi Porous Membrane Technology Co. Ltd was used in this study. The membrane had a thin polytetrafluoroethylene (PTFE) active layer on top of polypropylene (PP) supported layer. The active layer thickness, porosity, and average pore size of this membrane were 12 µm, 70%, and 0.2 µm respectively (Duong et al., 2015). A new membrane sample was used for each experimental run.

3.3 Feed solution characteristics

Synthetic DS with initial concentration of 0.25M was prepared by using two organic and three inorganic salts. Sodium Chloride (NaCl), Magnesium Chloride ($MgCl_2$), Calcium Chloride ($CaCl_2$) were selected to represent inorganic draw solutes whereas Sodium Acetate (CH_3COONa) and Magnesium Acetate ($Mg(CH_3COO)_2$) were selected for organic draw solutes. The solutions were prepared by dissolving a suitable amount of salt into the distilled water. Initial membrane performance tests were conducted using aqueous solution of NaCl.

Table 3. Synthetic salts used for feed preparation

Salt Type	Molar Concentration (M)	TDS Concentration (g/L)
NaCl	0.25	14.610
$CaCl_2$	0.25	27.745
$MgCl_2$	0.25	23.802
CH_3COONa	0.25	20.508
$Mg(CH_3COO)_2$	0.25	35.598

3.4 Operating conditions

To investigate the circulation velocity and feed water temperature effect on flux, feed water temperature at inlet varied from 30 to 80^oC with an increment of 10^oC and circulation velocity was in the range of 2.8 to 14 cm/s. In the permeate tank, the cooling water temperature was fixed at 20^oC. In all other experiments the velocity was maintained at 14 cm/s. Two separator design (ladder and diamond) were used on both sides of the membrane having 1.08 mm thickness with mesh length of 4.2 mm and strand diameter of 0.7 mm for flux enhancement.

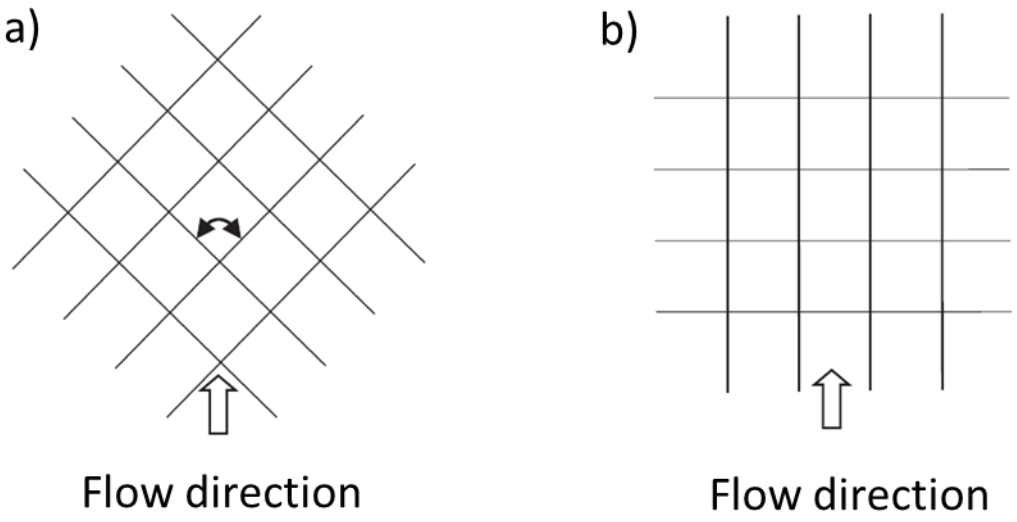


Fig. 13. Ladder (a) and diamond (b) spacer design with flow direction

Before the regeneration of draw solution DCMD was run with 0.25 M NaCl, $MgCl_2$, $CaCl_2$, CH_3COONa, and $Mg(CH_3COO)_2$ to investigate the effect of temperature on flux of these salts. For regeneration of DS, the cooling water temperature and circulation flow rate of DCMD were maintained at 10^oC and 14 cm/s respectively. For DS recovery, it was necessary to match water transfer rate of both Os-MBR and MD systems. The water transfer rate of MD membrane was adjusted to match that to Os-MBR by changing circulation velocity and water flushing of MD membrane. In previous studies, Luo et al. (2016) adjusted RO flux daily to match with FO by changing hydraulic pressure and Xie et al. (2014) flushed FO membrane with deionized water and reduced distilled temperature of MD to balance water fluxes of FO and MD. DS concentration was measured continuously to ensure that a constant concentration was maintained in the DS reservoir. MD circulation velocity was reduced when salt concentration increased in draw tank and MD membrane was flushed with distilled water when salt concentration

decreased in draw tank. During membrane cleaning, through the feed side of module, distilled water was circulated at cross follow velocity of 20 cm/s for one hour at temperature of 25^{o}C. Distilled water was also circulated through the permeate side at the same temperature and circulation rate to avoid any pressure difference across the membrane.

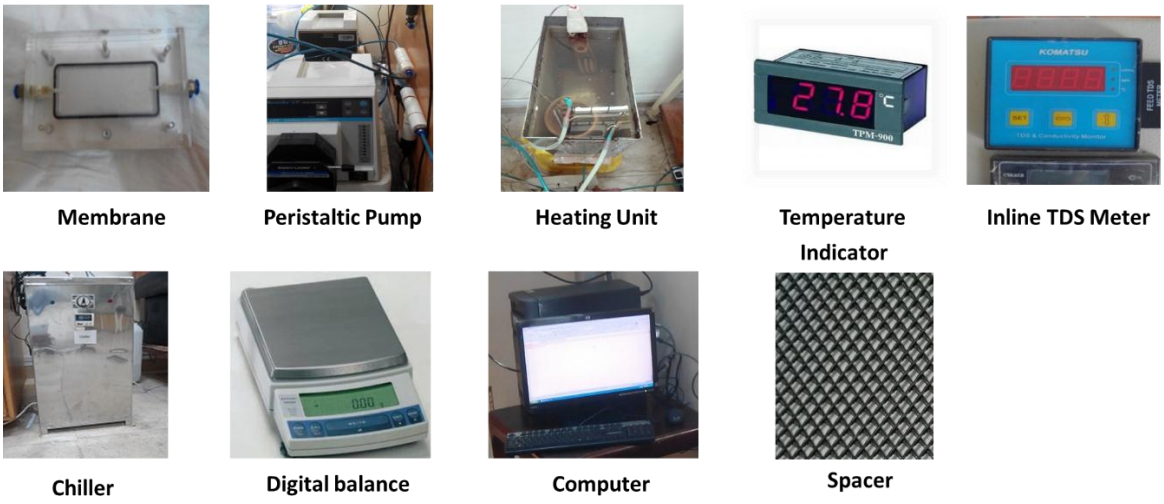


Fig. 14. Instruments used in DCMD process

3.5 Permeate water flux and salt rejection measurement

Permeate water flux can be measured by weight change of permeate over a selected time period. As the water transfer by vapor pressure across the membrane from feed side into the permeate side, the weight of permeate in tank increases. The rate at which volume increases over the membrane effective area yields the water flux.

Water flux across the membrane in $Lm^{-2}h^{-1}$ was calculated by using Eq. 1

$$\boldsymbol{J = \frac{\Delta V}{\Delta t \times A}} \quad (1)$$

Where ΔV is the change in permeate volume (L) over a sampling time Δt (h), and A is the effective membrane area (m^2).

For determining TDS rejection, the concentrations of TDS in feed water (C_f) and permeate water (C_p) were determined. The salt rejection (%) was calculated by using following equation Eq. 2

$$\boldsymbol{Rejection\ (\%) = \frac{C_f - C_p}{C_f} \times 100\%} \quad (2)$$

Where C_f and C_p feed and permeate concentrations, respectively in mg/L.

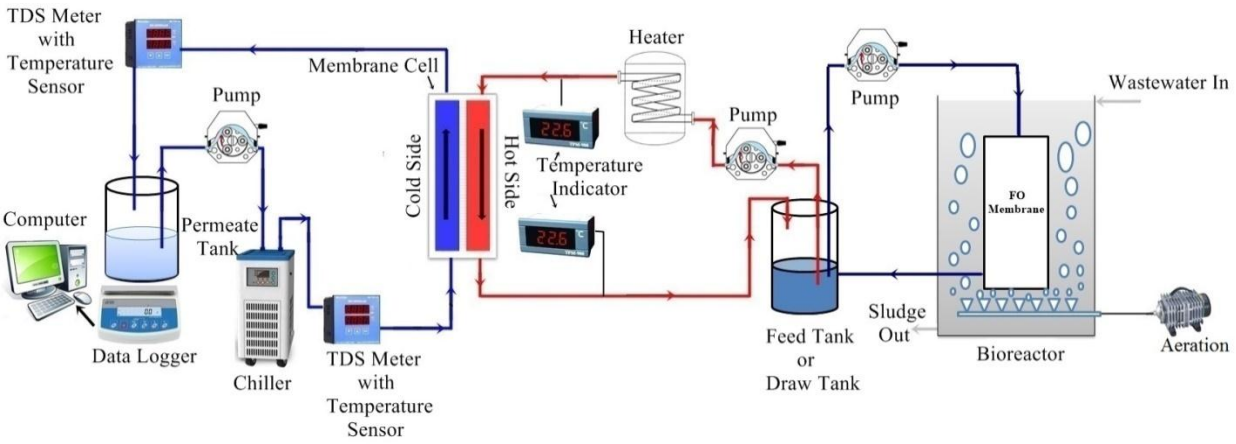


Fig. 15. Process flow diagram of the experimental unit

Fig. 16. Lab scale direct contact membrane distillation system at IESE, NUST

Chapter 4

RESULTS AND DISCUSSIONS

4.1 Effect of circulation velocity and temperature on DCMD performance

Fig. 17 illustrates the effect of circulation velocity under different feed inlet temperatures on permeate flux. Feed velocity and temperature were varied from 2.8 to 14 cm/s and 30 to 80^{o}C respectively. Feed inlet concentration and permeate temperature were kept constant at 0.25M NaCl and 20^{o}C respectively. It can be observed that the permeate flux increased with increase in feed water temperature and circulation velocity of feed and permeate.

Initially, permeate water flux increased noticeably with increase in velocity and asymptotic trends were observed at higher velocity. Fig. 17 shows that at feed water temperature of 30^{o}C, increase in velocity enhanced the permeate flux from 3.7 to 16 L $m^{-2}h^{-1}$. Similarly, at 80^{o}C increase in velocity lead to enhanced flux from 35 to 71 $Lm^{-2}h^{-1}$. This indicates that increases in velocity caused increase in permeate flux, but improvement was relatively less when the velocity approached to a certain level. Similar findings have been reported in previous studies (Boubakri et al., 2014b; Li et al., 2015) where the increase in feed velocity enhanced permeate flux and flux reached to plateau at higher velocity.

At start, the increase in velocity reduced the temperature polarization, causing an increase in water vapor pressure difference and caused an increase in permeate flux (Gryta, 2012;

Khayet and Matsuura, 2011). It was noted that there was relatively less incremental increase in flux when the velocity reached to certain limit, because at higher flow rate mass transfer resistance of membrane becomes predominant (Alkhudhiri et al., 2012a; Li et al., 2015).

Difference of vapor pressure across the membrane is the main driving force in membrane distillation and vapor pressure is the exponential function of the temperature (Li et al., 2015; Srisurichan et al., 2006). When the temperature increases the thermal efficiency and the driving force of mass transfer also increases accordingly. Fig. 17 shows the effect of feed inlet temperatures on flux, where higher the temperature resulted in the higher permeate water flux. For all the curves, permeate flux increases exponentially with increase in feed water temperature. At high temperature, temperature influence on permeate flux was more significant as compared to low temperature.

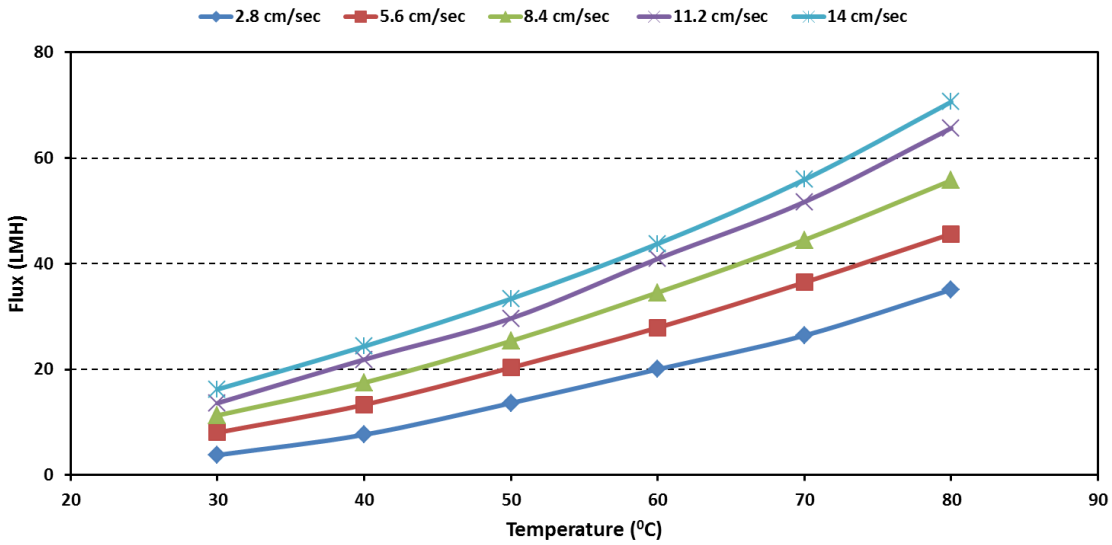


Fig. 17. Influence of temperature and circulation velocity on permeate water flux DCMD

4.2 Flux enhancement using spacer filled channel

To maximize flux, it was necessary to reduce temperature polarization effect or to increase vapor pressure difference on both sides of membrane. To reduce temperature polarization or to increase vapor pressure difference it was needed to decrease the resistance of thermal boundary layer across the membrane. By enhancing stream turbulence the thickness of thermal boundary layer can be reduced (Camacho et al., 2013). Spacer promotes turbulence and improves hydrodynamics condition in the channel.

Effect of spacer (ladder & diamond design) on flux was studied under different feed inlet temperatures. Salt concentration, circulation velocity on both side of membrane and permeate temperature were kept constant at 0.25M NaCl, 5.6 cm/s and 20^{o}C respectively. System was run with ladder design, diamond design, and without spacer. Fig. 18 show the results, where it can be observed that with spacer placed in module, permeate flux increased. For the same operating conditions (velocity, feed and permeate temperature) flux was higher when a diamond design separator was used as compared to ladder separator and empty channel. By using spacer, a 35% increase in flux with diamond design and 26% increase in flux with ladder design were observed at 80 ^{o}C of feed water temperature as compare to empty channel. The enhanced flux proved the appearance of turbulence and formation of eddies when the water passed via spacer strands. Similar findings were observed in previous studies (Martínez-Díez et al., 1998; Phattaranawik et al., 2003, 2001; Yun et al., 2011). Martínez-Díez et al. (1998) found that permeate flux in MD was higher when screen separator was used as compared to open flow separator. According to Yun et al. (2011) flux enhancement using spacer to increase flow regime

was better option as compared to increasing flow velocity. They also found that the coarse spacer has more effect on flux than fine spacer and without spacer. Phattaranawik et al. (2003) noticed flux enhancement in DCMD when spacer was used in the membrane channel due to improvement of heat transfer. Phattaranawik et al. (2001) achieved 31-41% higher flux in spacer filled channel than empty channel. This study was performed by using diamond design separator in module.

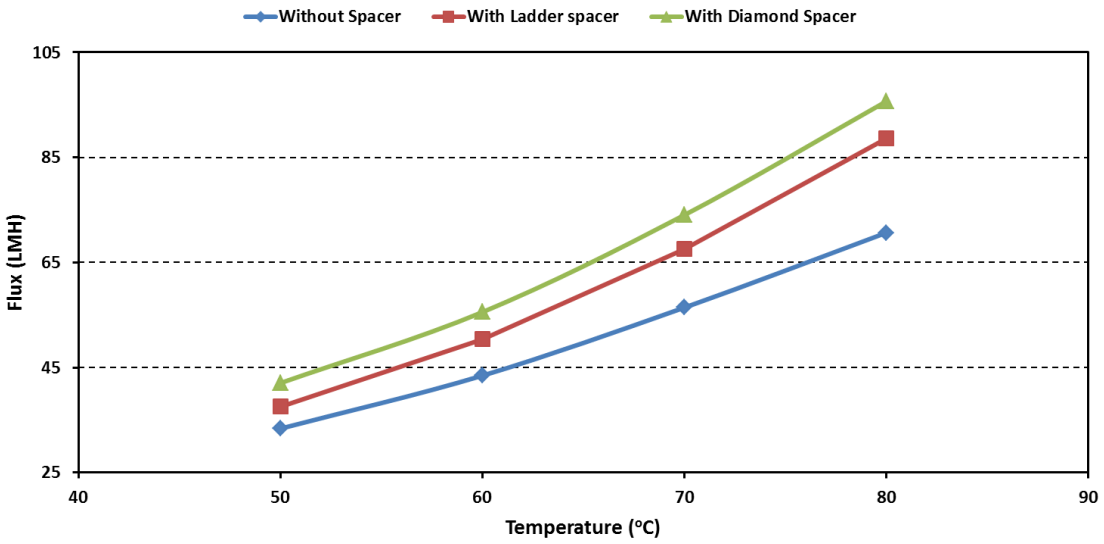


Fig. 18. Effect of spacer design on DCMD flux at different feed water temperature

4.3 Effect of temperature on flux for different salt solution

The effect of temperatures on three inorganic salts (NaCl, $MgCl_2$, and $CaCl_2$) and two organic salts (CH_3COONa, and $Mg(CH_3COO)_2$) having the same molar concentration were studied as replected in Fig. 19.

It shows that at same temperature NaCl produced highest flux then all other salts due to its lower TDS concentration. The concentration of salt solution affects MD flux, which

declined by increasing the feed water salinity. Reduction in flux was due to reduction of a water vapor pressure over the salt solution as a result reduction of the driving force for mass transfer was observed by increasing feed TDS concentration (Alkhudhiri et al., 2012b). The increase in feed water salinity also affects the temperature and concentration polarization phenomena resulting in a decline of flux (Gryta, 2002).

Under same operating conditions organic salts exhibited less flux as compare to inorganic salts, enhanced flux followed the order of NaCl > $MgCl_2$ > $CaCl_2$ > CH_3COONa > $Mg(CH_3COO)_2$. The remarkable difference between permeate flux of these salts was probably due to water activity. NaCl had maximum flux then all other salts at all the temperatures, because of water activity of NaCl being higher than all other salts. Water activity of any solution is the ratio between vapor of salty water to that of pure water at given temperature. The water activity magnitude reflects the avalibility of free water that is how easy water run away from the salt solution when it is evaporated. It has been reported that water activity for inorganic and organic salts follow the order of NaCl > $MgCl_2$ > $CaCl_2$ and CH_3COONa > $Mg(CH_3COO)_2$ respectively (Skalle, 2012). Similar findings have been reported in previous study (Li et al., 2015) for the salts of KCl, NaCl, and $MgCl_2$ where the water activity was the leading factors for influencing flux.

Results revealed that at temperature of 50^oC there was less difference for permeate flux between $MgCl_2$ and $CaCl_2$ and it became significant at 80^oC. On the controry, difference between the permeate flux of CH_3COONa and $Mg(CH_3COO)_2$ was reduced with increasing temperature. The main difference among the permeate fluxes was due to temperature dependence of their solubility. Solubility plays important role on membrane distillation flux, the salt having less solubility varies less with temperature and has more

flux (Guan et al., 2015). In comparision to $CaCl_2$ solubility of $MgCl_2$ varies little with increase in temperature and solubility of $Mg(CH_3COO)_2$ varies little with increase in temperature as compared to CH_3COONa (Mullin, 2001).

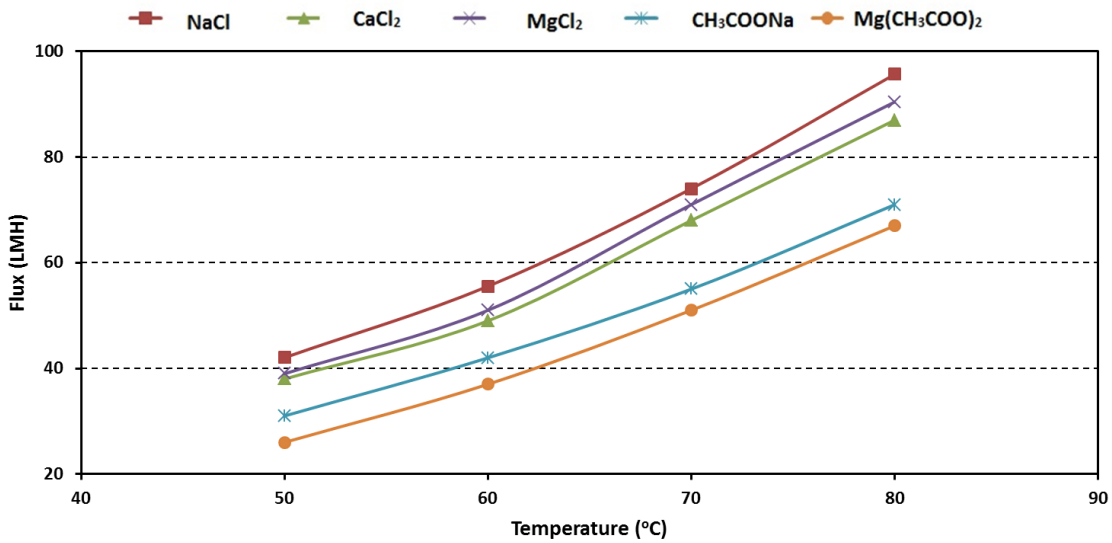


Fig. 19. Flux of different salts at different feed water temperature

4.4 Re-concentration of aqueous solution

Draw solution concentration is the main driving force of Os-MBR to extract the clean water across the semi permeable membrane. The DS concentration was diluted as function of operating time and MD recovery process was optimized accordingly. For a stable OsMBR and MD hybrid process, it was necessary to match water transfer rate in MD to that in Os-MBR process. Water transfer rates of both Os-MBR and MD systems at different salts solutions were shown in Fig. 20.

Once the optimum DCMD operating conditions were determined, long time experiments of hybrid OsMBR-MD system for reconcentration of DSs were conducted with different

salt solution NaCl, $MgCl_2$, $CaCl_2$, CH_3COONa, and $Mg(CH_3COO)_2$. The MD system for each of the above salt solutions was operated with feed water temperature of 70, 65, 70, 80, and 85^oC. Temperature of distilled water was 10^oC and initial circulation velocity of feed and permeate side was 14 cm/s.

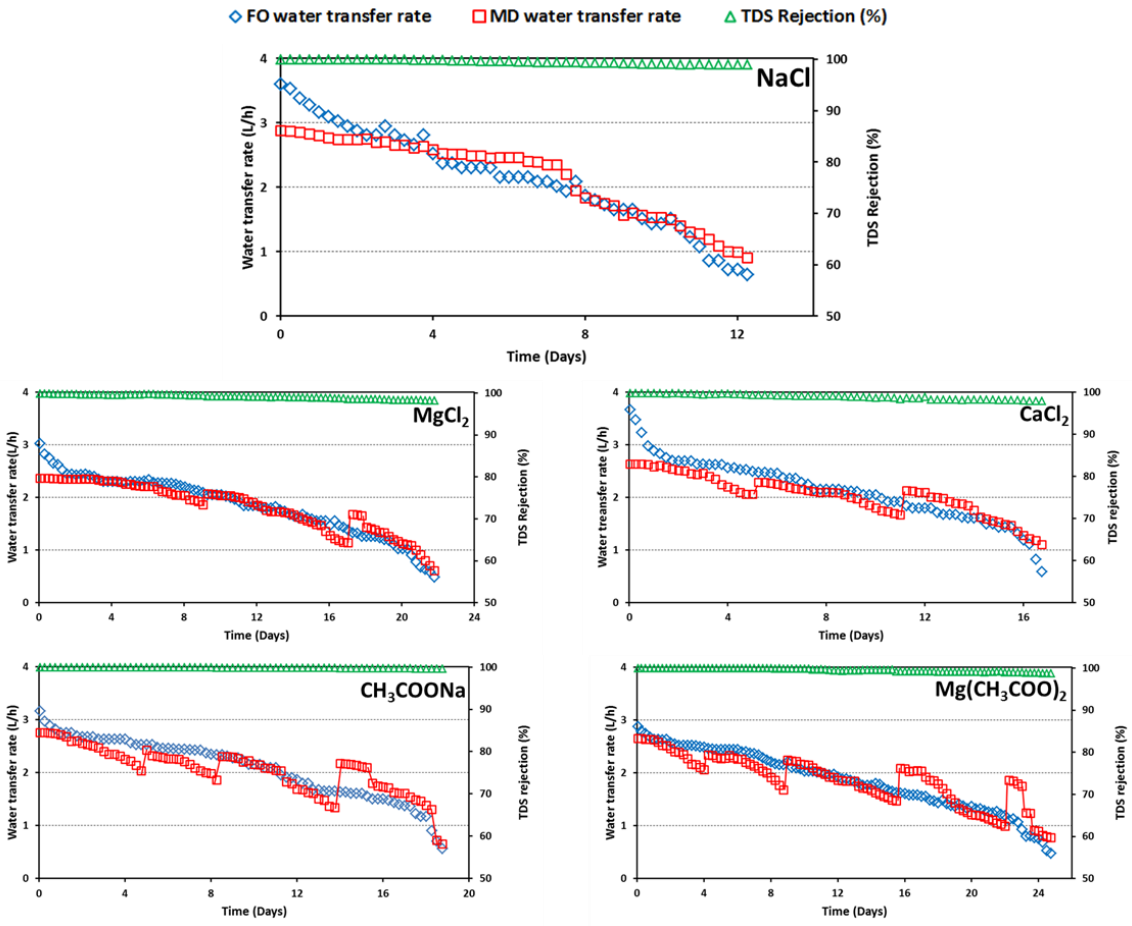


Fig. 20. Water transfer rate of Os-MBR and MD and TDS rejection from DCMD

In continuous operation of MD with Os-MBR, both Os-MBR and MD water fluxes declined as a function of operating time. DS concentration was maintained constant by maintaining stable equilibrium condition which was obtained by matching the water

transfer of both systems. Fig. 20 shows that water transfer rate of MD and Os-MBR for different salt solutions. The permeate flux of MD membrane was adjusted to match that to Os-MBR by changing circulation velocity and flushing of MD membrane. MD circulation velocity was reduced when salt concentration increased in draw tank and MD membrane was flushed with distilled water when salt concentration decreased in draw tank due to deposition. Crystal deposition on MD membrane leads to pore blocking that restricted the active surface area of membrane for transport of water vapor and also reduces the hydrophobicity of membrane (Alkhudhiri et al., 2012a; Gryta, 2008).

DCMD was run with osmotic membrane bioreactor process until fouling of FO membrane. Fig. 20 represent the recovery of NaCl, $MgCl_2$, $CaCl_2$, CH_3COONa, and $Mg(CH_3COO)_2$. NaCl shows better performance than all other salts in recovery by MD as it did not require membrane flushing throughout the system run, while $Mg(CH_3COO)_2$ required four time forward washing because of 0.25M $Mg(CH_3COO)_2$ having high TDS concentration than 0.25M NaCl and all other salts. Rapid flux decline was significantly dependent on density, viscosity, salt concentration, flow rate and operating temperature (Ramezanianpour and Sivakumar, 2014). Rapid flux decline in the MD process with $Mg(CH_3COO)_2$ was due to high temperature for obtaining high flux. Salt concentration was another factor effecting permeate flux, where flux decline rate raised proportionally with salinity and $Mg(CH_3COO)_2$ reflected highest salinity in water at 0.25M. For all other salts similar trends of flux decline indicate that above mention parameters are leading factors influencing flux. Membrane flushing frequency followed the order of $Mg(CH_3COO)_2$ > CH_3COONa > $CaCl_2$ > $MgCl_2$ > NaCl. For forward washing, MD membrane was flushed with distilled water with same temperature and circulated on both

sides of membrane. Fig. 20 shows that membrane flushing restored more than 87% of the initial water flux that was lost due to salt deposition on membrane. Similar findings of membrane washing were reported in Duong et al. (2015) in which 90% of initial water flux was restored when membrane was cleaned with 0.5% HCl solution while cleaning the scaled membrane with tap water, 85% flux restoration was achieved. Fig. 20 also shows that the organic salts rejection was higher in all the cases than inorganic salts, which was almost 99%. For all organic and inorganic solutes, the DCMD system was able to achieve DS recovery as per requirement.

4.5 Production of purified water and removal of contaminants

The purpose of DCMD to couple with Os-MBR was to successfully recover the draw solution of FO and the production of good quality product water. In the case of Os-MBR, retention rate of contaminants declined with increase of salinity in bio-tank and contaminants accumulated in draw tank (Liu et al., 2016; Luo et al., 2016; Xie et al., 2013). Any solute or contaminant passing through the FO membrane even in very small quantity was completely achieved with MD membrane. Fig. 21 shows that NH_4^+-N and PO_4^{3-}-P slowly diffused through the Os-MBR membrane into the DS tank. However they were moderately rejected by MD membrane and accumulated in draw solution tank. MD membrane completely rejects non-volatile solutes of feed water (Khayet and Matsuura, 2011). The DCMD permeate contained very less concentration of TDS and contaminants and this illustrated the ability of MD to produce good quality product water.

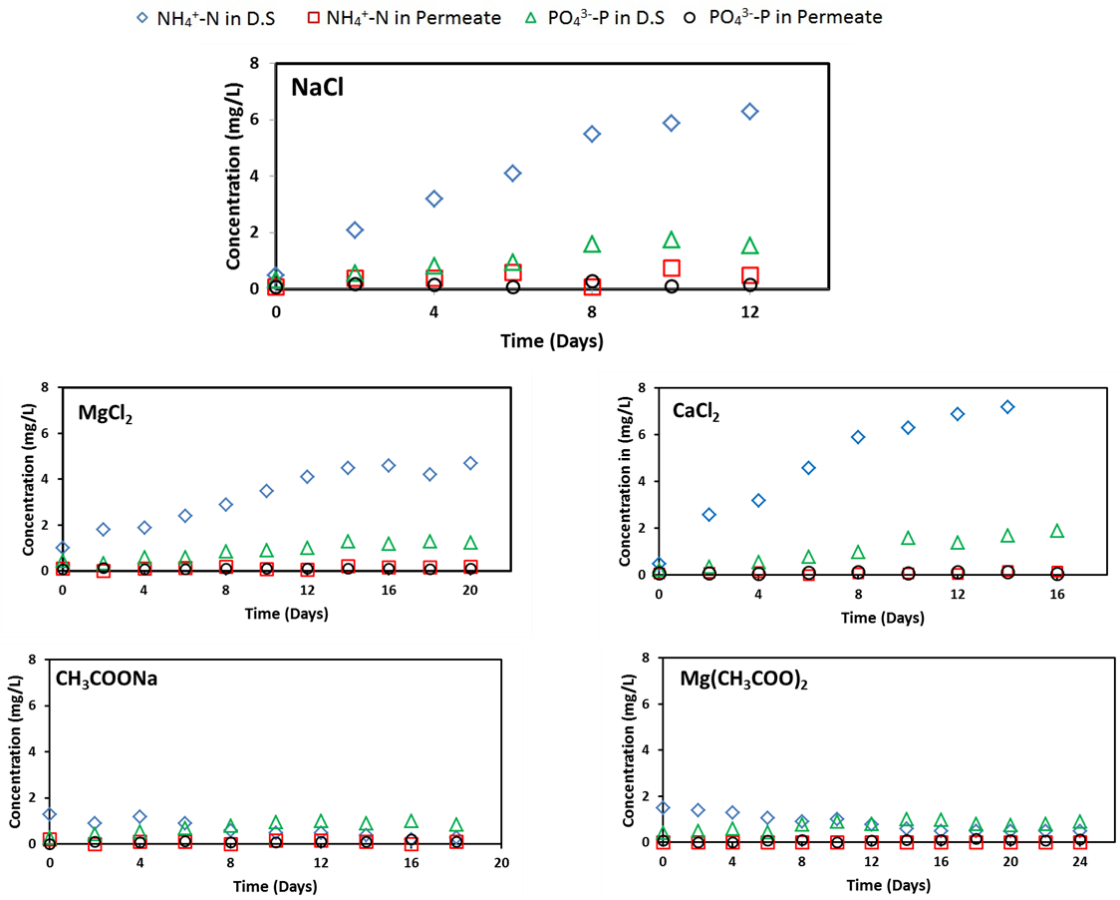


Fig. 21. Removal of NH_4^+-N and PO_4^{3-}-P with DCMD process

Chapter 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusions

In this study, DCMD system was able to reconcentrate aqueous salt solutions. The effects of operating parameters including feed temperature, circulation rate, effect of spacer, and feed salt concentration were studied to analyze the performance of DCMD. Most important findings are summarized as follows:

- For all draw solutes (organic & inorganic), DCMD system was able to achieve DS recovery as per requirement.
- Permeate flux increased exponentially with temperature; at high temperature influence of temperature on flux was more significant as compared to low temperature.
- Permeate flux was also affected by circulation velocity, but the flux improvement was relatively less when velocity increased to a certain level.
- Spacer produced turbulence and enhanced the water flux up to 35% and sequence of spacer design on flux was: diamond design > ladder design > without spacer.
- $Mg(CH_3COO)_2$ exhibited prolong operational period and also required more MD membrane flushing
- Membrane flushing followed the order of $Mg(CH_3COO)_2$ > CH_3COONa > $CaCl_2$ > $MgCl_2$ > NaCl.
- High quality of product water was produced by DCMD due to its high TDS and contaminant rejection

5.2 Recommendation

- Energy efficient system can be developed by identical size of OsMBR-MD membrane that can recover salt at low temperature.
- Mixture of salts can be tested as a draw solution of OsMBR-MD.
- Other configuration of MD can be tested for regeneration of draw solutions.

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