Applications Study of Membrane Distillation for the Dairy Industry

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Abstract

Membrane technology has been used for food processing for many years. Of the range of membrane technology types, membrane distillation is relatively new to industry. Membrane distillation (MD) is a thermal membrane separation process which was introduced in the 1960s. It is considered to be an alternative to conventional separation processes like distillation and membrane reverse osmosis (RO), and has been mostly studied for desalination and water treatment processes. Its application in the treatment of dairy process and waste streams has not, however, been fully explored. MD is regarded to offer potential to be a cost effective membrane technique for concentration of dairy process and waste streams and recovering useful water. Dairy waste treatment has become more important in dairy industry at present due to reasons such as importance of preserving water and reduction of waste produced. Therefore, it is important for the dairy industry to invest in cost effective and energy efficient membrane processes for dairy waste treatment to recover water and concentrate the waste streams. MD could be a useful membrane separation process which can concentrate the dairy waste streams and recover water.

MD is a thermally driven separation process working on vapour pressure gradient across the hydrophobic porous membrane. The ability to harness thermal energy (either waste or heat flows within the dairy plant) is the key reason researchers are promoting MD as a cost saving compared to pressure driven processes like RO. In the basic operation of MD, the liquid to be treated is fed to one side of the membrane, but the hydrophobic nature of the membrane prevents the liquid from entering the membrane pores. The vapour transported from feed side to the permeate side is condensed and produces water. The aim of this study is to investigate specific applications of MD in the dairy industry and assess its viability to save water or offer benefits against competing technologies.

A direct contact MD (DCMD) setup was used for the experiments as it is the widely used MD configuration. Dairy industry members were consulted, where meetings and site tours revealed several potential applications for MD. The dairy waste streams selected were RO retentate of NF permeate of UF permeate of sweet whey (SWROR), salty whey UF permeate (SUFP), ion exchange (IX) regeneration solution and combined dairy effluent, i.e. pre and post anaerobic digestion wastewater streams (Pre-AD and Post-AD). Each feed stream was initially analysed for its chemical composition to understand the chemical nature of each feed stream. The main feed stream quality analyses performed were total solids (TS), chemical oxygen demand (COD), total organic carbon (TOC), total nitrogen (TN), main minerals, lactose, proteins and fat. Due to the presence of fats, and other hydrophobic chemistries (i.e. proteins) in dairy streams, membrane wetting was a focus in this research. Membrane wetting is loss of the essential hydrophobic property of the membrane due to the adsorption of hydrophobic organics on the membrane, that link to hydrophilic chemistries allowing water to pass through the membrane and compromising performance.

MD performance of each feed stream was tested using membranes with different chemistries to address the potential wetting issues: hydrophobic polytetrafluoroethylene/PTFE (HP), hydrophilic coated PTFE (HCP) and hydrophobic and oleophobic acrylic copolymer (HOA) , depending on the nature of the feed. The MD performance was assessed on the basis of permeate flux, concentration factors (F_T)/water recovery, rejection of solutes and permeate quality. Fouling of membranes by different feed streams were analysed using scanning electron microscopy (SEM), fourier-transform infrared (FTIR) and synchrotron infrared. Fouling composition analysis was also performed by dissolving the fouling layer followed by the component analysis.

All three membranes tested (HP, HOA, HCP) worked well for MD treatment of SWROR. They achieved high concentration factors: > 7, > 5 and > 4 for the HP, HOA and HCP membranes respectively. They also produced high quality permeate with solute rejection above 99%. The HP membrane was selected as the best membrane as it showed the highest initial permeate flux (17 kg/m^2/h) and selected for further testing of MD of SWROR. The FTIR and chemical analyses of the fouling layer formed by SWROR on HP membrane gave indication of organic fouling by proteins and lactose. Calcium phosphate was also found to be present in small quantities. As the fouling was

a combination of largely organic species , the conventional dairy clean-in-place (CIP) process which involves alternate NaOH and HNO_3 rinses was selected as the most suitable membrane cleaning method to run under the semi-continuous mode operation with daily cleaning. This conventional CIP method was found to be suitable for cleaning of SWROR fouled HP membrane which did not cause membrane wetting and could recover much of the original permeate flux.

The HP membrane was not found to be suitable for SUFP treatment as membrane wetting appeared to be a major issue. MD treatment of this process stream was found to result in high permeate conductivity and low solute rejection of fat (72.8%), protein and lactose. The incidence of wetting was clearly evident from visual inspection of the membrane after treatment. The wetting and poor membrane performance were attributed to hydrophobic interactions of the PTFE membrane and organic compounds, accelerated by the increasing concentration of organic matter in the retentate with time. This was confirmed by the analysis of the foulants on the wetted membrane where relatively higher concentration of organic matter like fat, protein and lactose was detected. The use of the HCP membrane on SUFP, however, was found to avoid the wetting problems exhibited when using the HP membrane on this process stream. This was attributed to reduced interactions between the hydrophilic membrane and the organic matter in the feed, thereby minimizing fouling and subsequent wetting.

The HP membrane was found to be suitable for the treatment of IX regeneration acid stream. The permeate flux was not observed to decrease even at a concentration factor about 3.4 which is a 70% water recovery. The permeate conductivity was, however, found to increase from 33 µS/cm to 309 µS/cm due to volatile HCl acid penetration. The solute rejection for all solutes except HCl was above 99.9%. Recovery of HCl in clean water is a possibility here, but would require further optimisation to explore its potential.

The HP membrane treatment of Pre-AD wastewater was ineffective due to high amount of organic matter, particularly fats, which led to membrane wetting. The permeate flux was observed to decrease from the beginning and then showed negative values after a few minutes. Wetting was confirmed by the appearance of the final membrane which appeared transparent. The FTIR results showed some significant peaks related to fats and proteins, however, peaks for fats were more significant. Better performance was achieved on this process stream by using the HOA membrane. The maximum flux achieved with HOA membrane was 4 kg/m^2/h and concentration factor reached about 1.7 after 83 hours where the flux decreased to 2 kg/m^2/h. Conventional CIP was, however, found to be ineffective at restoring the flux as it caused wetting. Replacing the membrane with a new HOA membrane to further concentrate the retentate, concentration factor of up to 2.6 was achieved. For all solutes tested, rejection was above 99%.

The HP membrane treatment of Post-AD wastewater was found to be much more effective. Even after 30 hours of operation, the flux was 14 kg/m^2/h. The concentration factor was approximately 5 at the end of the test and the permeate conductivity rose from 1.5 µS/cm to 95.6 µS/cm during the test. The increase in the permeate conductivity could be possibly due to penetration of ammonia in the retentate as there was an increase in permeate pH from 8.4 to 9.5 and TN rejection was 87%. Apart from ammonia penetration, all the other solutes showed a rejection above 98% and the final membrane did not appear wetted.

Overall, MD was found to be a suitable membrane process to concentrate the tested dairy streams and recover potable water. In summary, MD using conventional HP membranes was found to effective for dairy process streams and wastewater streams with low organic matter and fat content, giving relatively high flux and good fouling mitigation via CIP. MD treatment of process streams with high organic matter and fat content are better treated using hydrophilic coated membranes/HCP, but the flux for these membranes is considerably less than that of conventional HP membranes. Finally, MD with hydrophobic and oleophobic acrylic co-polymer/HOA membranes having a similar flux to HCP membrane for the treatment of dairy streams with high organic matter and fat content avoids wetting, but further research is required to find a CIP procedure that preserves hydrophobicity.

Student Declaration

“I, Thilini Randika Hettiarachchi, declare that the Master by Research thesis entitled Applications Study of Membrane Distillation for the Dairy Industry is no more than 60,000 words in length including quotes and exclusive of tables, figures, appendices, bibliography, references and footnotes. This thesis contains no material that has been submitted previously, in whole or in part, for the award of any other academic degree or diploma. Except where otherwise indicated, this thesis is my own work”.

Signature: Date:

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List of Publications and Awards

Oral Presentation

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Chapter 1. Introduction

1.1. Background

Membrane technology has been used for food processing for many years. The dairy industry is one of the major utilisers of membrane technology within the foods industry, which started from the1970s [1-3]. The typical membrane separations include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). Compared to these well adopted operations, another separation type, membrane distillation, is only just being explored.

Membrane distillation (MD) is a thermal membrane separation process and it was introduced in 1960s [4, 5]. With the growth of membrane engineering, the developments of MD started in the early 1980s [6-10]. MD is found to be an emerging separation technique which can use low-grade waste and alternative energy. MD is considered to be an alternative to conventional separation processes like distillation and RO [11]. Although MD has been studied for more than 40 years, it is still in development stage and has not been applied at industrial scale. MD has been mostly studied for desalination and water treatment where purified water is produced from the sea, brackish water or industrial wastewater. However there are some studies in foods applications, for concentrating salt and sugar solutions and fruit juice [12-14]. Despite this progress, industrial application of MD in treatment of dairy streams has not still been discovered, despite that it can be a useful cost effective membrane technique for concentration of dairy process streams and dairy waste treatment. Meanwhile, there are emerging issues in dairy waste treatment that could benefit from the MD process.

Dairy waste treatment has become a key focus in the dairy industry. Further, there are growing costs for purchasing potable water. These conditions will be more severe as the local regulations continuously become more stringent on water consumption and waste disposal to the environment. The predictions of decreases in rainfall due to drought and climate changes have created a great pressure on the need of conserving the limited water resource.

Dairy processing plants in Australia consume an average of 386ML of potable water per annum and produce an average of 452 ML of waste water per annum [15]. This indicates the magnitude of water consumption in dairy plants and the importance of dairy waste treatment. The treated wastewater is a resource for irrigation of recreational reserves, agricultural lands and in factories for cleaning equipment and utensils. Wastewater reuse not only reduces the overall water consumption, but also offers an environmental and cost saving due to reduced discharged waste volume. This wastewater however requires processing to make it suitable for reuse, which in turn requires energy. According to Australian Dairy Industry Council, the energy cost is another major challenge for the dairy industry. This is due to the increase in cost of energy and the cost of emission to the environment that have resulted from climate change policies [16, 17].

Dairy wastewater has become an issue in countries other than Australia [18]. Preserving water and dairy wastewater treatment is important in United States as the cost for incoming water and also surcharge for dairy waste disposal has increased over the years [19, 20]. Similarly, the production of large quantities of dairy wastewater has created much pressure in countries such as New Zealand [21] and India [22] to find better treatment solutions. With the increased demand for dairy industry in India, the production of dairy in India is expected to grow rapidly and in parallel to this waste generation and related issues are also expected to increase if innovative wastewater treatment technologies are not in place.

With the challenges mentioned above, therefore, it is important for the dairy industry to invest in cost effective and energy efficient membrane processes for dairy waste treatment. MD could be a good option for this purpose as it is a thermally driven separation process working on vapour pressure gradient across the membrane. Hence, MD can be operated under low temperatures and could be coupled with low-grade waste or renewable energy. Solar power is the most widely experimented alternative energy coupled with MD and most of these studies have been targeted at sea water desalination [23-27].

According to a study based on using MD for desalination, the estimated water production cost with heat recovery was $\$1.17\text{m}^{-3}$, which is comparable to the cost of water produced by conventional thermal processes that was around $\$1.00\text{m}^{-3}$ for multiple effect distillation (MED) and $\$1.40\text{m}^{-3}$ for multi-stage flash (MSF). It is expected to have cost savings if a low-grade thermal energy source is used which reduces the cost and this can be comparable to the cost of water produced by RO, which is about \$0.50m^{-3} [28].

Therefore, MD could be an economical technology to be used in dairy waste treatment while also producing reusable clean water. However, lack of full understanding about the technical and economical features has caused MD not being applied in industrial scale. Thus, the aim of this study is to investigate the applicability and viability of MD into dairy industry and specially in dairy waste treatment.

This will be done exploring a few key specific industry examples as part of this collaborative project with Dairy Innovation Australia Ltd.

1.2. Objectives

The main objective of this research is to investigate the viability of MD for dairy waste treatment to concentrate dairy waste streams and recover potable water. Based on this, there are specific objectives;

- To work with Australian dairy industry representatives and identify potential opportunities for MD for closer investigation;
- To measure MD performance of different membranes against various dairy waste streams in terms of permeate flux, concentration factors, solute rejection and permeate quality
- To explore the chemical interactions between feed components, membrane cleaners and different membrane materials and the effect of these interactions to avoid fouling and wetting

1.3. Outline of the Thesis

The thesis consists of eight chapters described as follows:

- Chapter 1 “Introduction” - introduces MD and background to the study;
- Chapter 2 “Literature Review” - reviews theoretical aspects and applications of MD and related previous studies in the literature;

- Chapter 3 “Materials and Methods” - describes the materials and methods used in the experiments;
- Chapter 4 “Sweet Whey Processing by MD” - explains the viability of MD to concentrate RO retentate of NF permeate of UF permeate of sweet whey and recover good quality water;
- Chapter 5 “Salty Whey UF Permeate Processing by MD” - investigates the performance of the UF permeate of salty whey to be processed by MD;
- Chapter 6 “Processing of Ion Exchange Regeneration Stream by MD” - describes the MD performance of the acid stream of the ion exchange regeneration solution as to investigate MD as a concentration and water recovering technique;
- Chapter 7 “Combined Dairy Effluent Treatment by MD” - investigates the MD performance to process combined dairy effluent streams before and after anaerobic digestion as for volume reduction of the waste streams and to recover potable water;
- Chapter 8 “Conclusions and Recommendations” - concludes and recommends the possible applications in the dairy industry to be performed under MD.

Chapter 2. Literature Review

2.1. Membrane distillation

MD is a thermal process in which only vapour passes through a hydrophobic porous membrane. The liquid feed is in direct contact with one side of the membrane and the hydrophobic nature of the membrane prevents the liquid from entering the membrane pores. This is due to high surface tension between the membrane and liquid. This forms a liquid/vapour interface at the entrance of membrane pores. The driving force for vapour transportation from feed side to the permeate side is the vapour pressure difference across the membrane. Volatile components driven by this vapour pressure gradient evaporate from feed side and are condensed on the permeate side leading to permeate flux [29-31]. Figure 2.1 shows a schematic of MD.

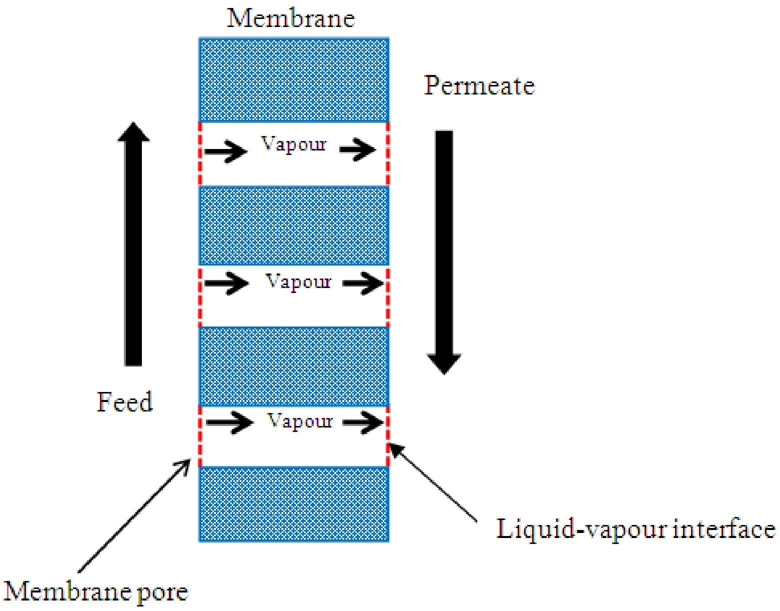


Figure 2.1 Schematic of MD

2.2. Configurations of MD

There are four main MD configurations which are based on the mode of creating the driving force/vapour pressure difference across the membrane. The four main MD configurations [11] shown in Figure 2.2 are described as follows:

I. Direct contact MD (DCMD)

In DCMD, both liquid feed and liquid permeate are in direct contact with the membrane and vapour pressure gradient is created by the temperature difference between the hot feed and the cold permeate . DCMD is the simplest and one of the most widely used forms of MD as it yields the highest fluxes.

II. Air gap MD (AGMD)

A stagnant air gap is interposed between the membrane and the condensation surface. The volatile compounds evaporated from the feed side cross both membrane and the air gap and then condense on the cold permeate side. This configuration is popular in high thermally efficient designs.

III. Sweeping gas MD (SGMD)

A cold inert gas sweeps the permeate side of the membrane by carrying the evaporated molecules. These volatile compounds then pass through a condenser that is situated outside the membrane module where they undergo a phase change to the liquid state.

IV. Vacuum MD (VMD)

A vacuum is maintained in the permeate side of the membrane using a vacuum pump. The applied vacuum pressure is lower than the pressure of the volatile molecules of the feed solution. These volatile compounds then pass through a condenser that is situated outside the membrane module where they undergo a phase change to the liquid state. This configuration is popular for its simple module design and high thermal energy efficiency.

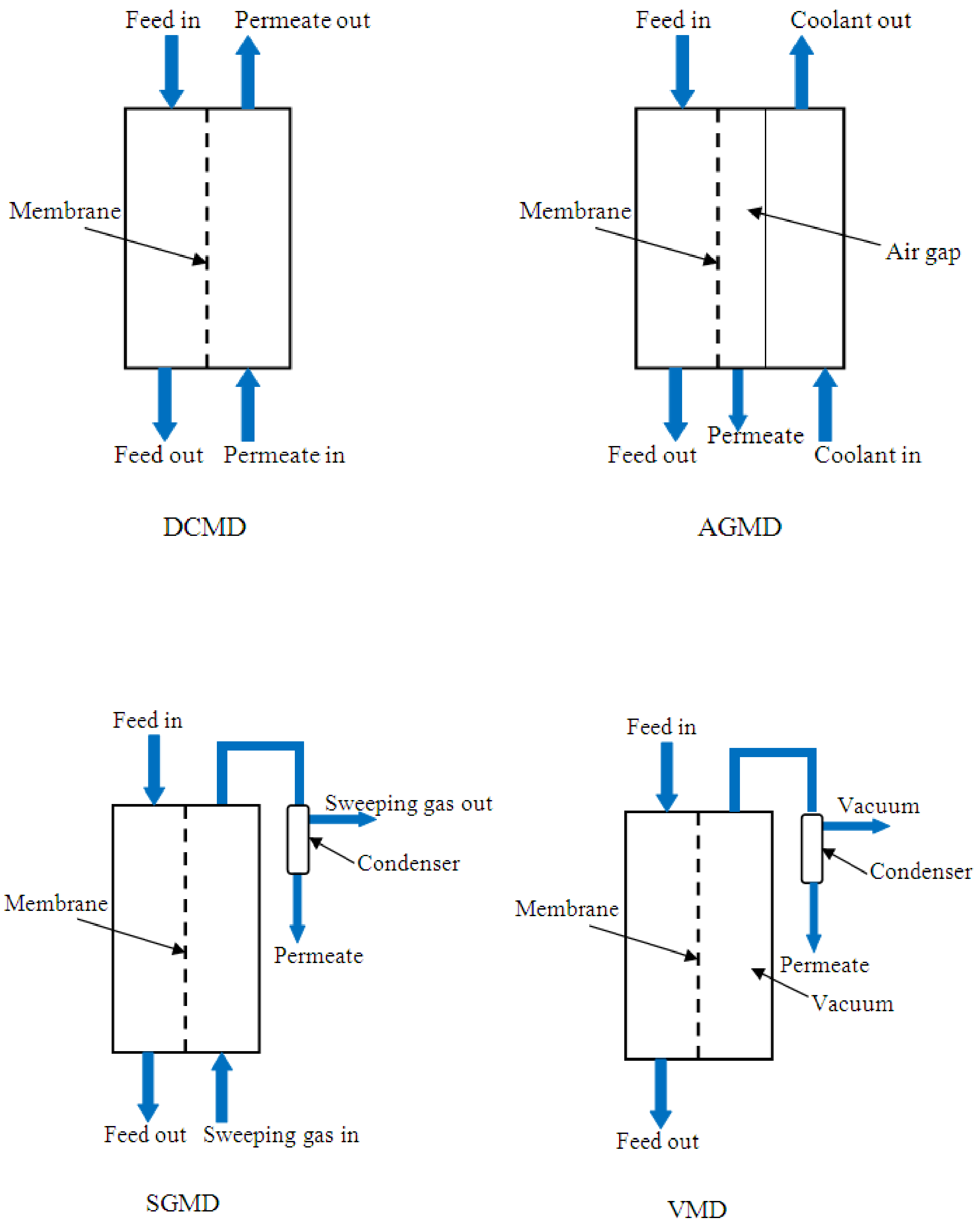


Figure 2.2 The four common configurations of MD

2.3. MD membranes

There are several material requirements of membranes to be used for MD [32]. The characteristics that influence the performance of MD membranes are:

I. Membrane structure and thickness

The thickness of the membrane is inversely proportional to the mass transport (flux) and the heat transport. While mass transport is favourable for MD, heat transport through the membrane is a heat loss. Hence, there should be an optimum thickness to maximise the mass transport and minimise the heat transport. The thermal conductivity of the membrane material should also be as low as possible to minimise the heat conducted through the membrane [31, 32].

II. Hydrophobicity, porosity, pore size, pore distribution and tortuosity factor

The membrane should be porous and made out of a hydrophobic material. Porosity is defined as the area open for the evaporation. Porosity of the membrane should be high as possible as this is directly proportional to the permeate flux.

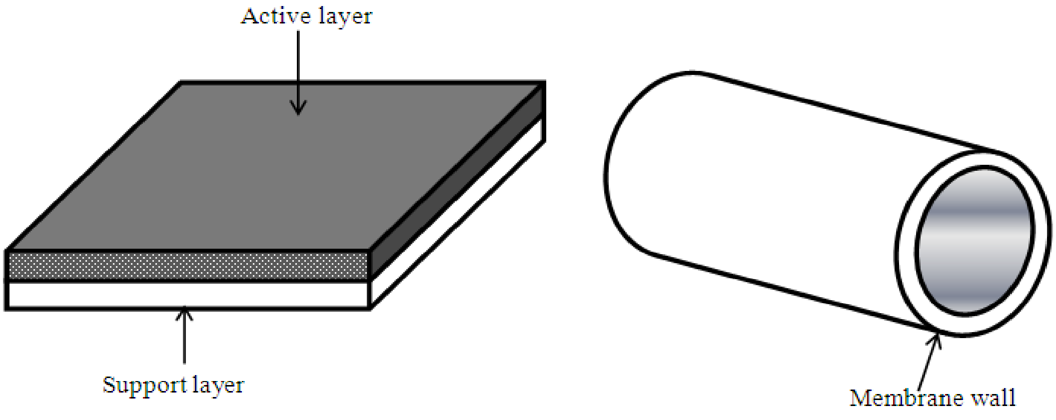
The pore size range may vary from several nanometers to few micrometers. Although the flux (or membrane permeability) is proportional to the pore size, pores should be narrow as possible to avoid feed liquid from penetrating through the membrane. The minimum transmembrane pressure required for feed liquid to enter pores is known as liquid entry pressure (LEP) and this LEP should be high as necessary for practical operation in a process (i.e. hundreds of kPa). The LEP is a characteristic of each membrane and a high LEP can be achieved by using materials having low surface energy or high hydrophobicity (i.e. large contact angles to water and feed solutions) and small maximum pore size. Therefore, the pore size should be a compromise between membrane permeability and a high enough LEP [31]. For example Polytetrafluoroethylene (PTFE) membranes with pore size of 0.2 μm and 0.45 μm have LEP of 368 kPa and 288 kPa respectively [33].

The tortuosity, a measure of the deviation of the pore structure from straight cylindrical pores, is inversely proportional to the permeability and therefore should be small as possible [32].

III. Fouling resistance, thermal stability and chemical resistance

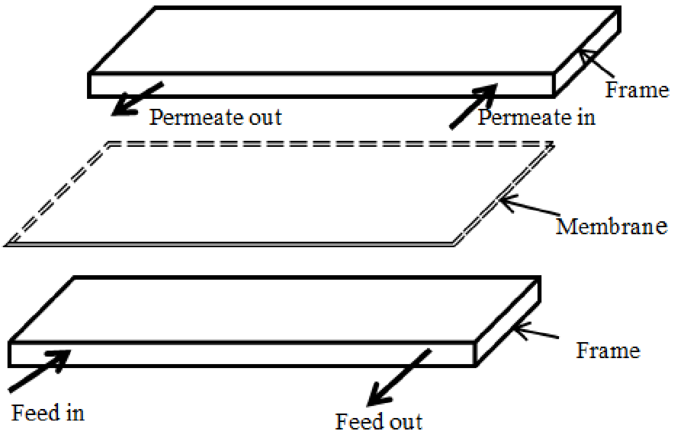
The membrane surface contacting the feed solution will need to resist the chemistry of the feed and cleaning solutions and be able to operate at the required temperatures for MD. Membrane surface modification can be done to make the membrane surface more resistant to fouling depending on the feed solution to be treated. They should have a good thermal stability to withstand the high temperatures such as 100 °C and should have the ability to resist various chemicals in different feed solutions and membrane cleaning agents like acids and base. They should also be able to function with a stable MD performance for a long period [31].

The membranes used in MD are generally made of hydrophobic materials such as polypropylene (PP), polyvinylidene fluoride (PVDF) and polytetrafluoroethylene (PTFE). These membrane are available in both flat-sheet and capillary/hollow fibre forms [34] (see Figure 2.3). They vary from 0.2 μm to 1.0 μm in pore size, 0.02 mm to 0.2 mm in thickness and 30% to 90% in porosity [35].

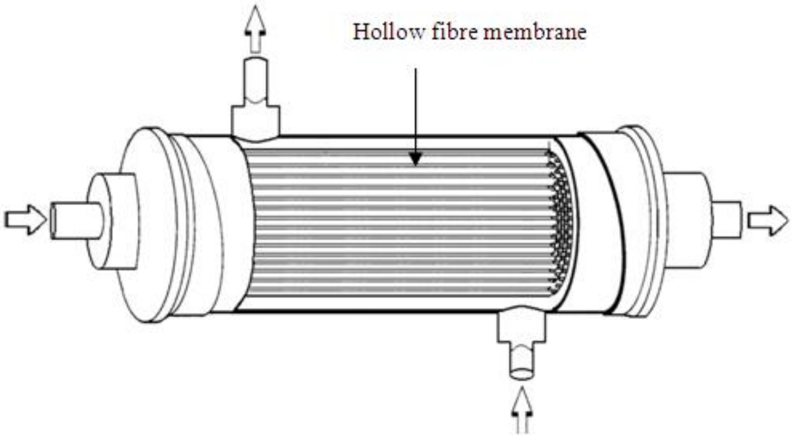


(a) (b)

Figure 2.3 Forms of membranes (a) Flat-sheet membrane (b) Hollow fibre membrane



(a)



(b)

Figure 2.4 MD membrane modules (a) Flat-sheet module (b) Tubular

PTFE is the most widely used material for flat-sheet modules due to its highest melting point (327 °C) [36] and the low surface energy and high hydrophobicity. In addition to this, PTFE membranes have good thermal stability, high chemical resistance and good mechanical strength [37]. PTFE also exhibits better performance in terms of permeate flux due to its higher mass transfer coefficient than PVDF membranes [38].

2.4. Recent developments in MD membrane design

To address fouling and wetting problems that are problematic for MD, researchers have attempted membrane modification through techniques such as surface coating, phase inversion and plasma modification. The main objectives behind these membrane modification are to improve membrane durability, and/or fouling resistance, and/or to increase the permeate flux.

Preparation of hydrophobic/hydrophilic composite membranes has been researched by many to enhance the permeate flux. Essalhi and Khayet (2012) prepared such membrane by blending fluorinated hydrophobic surface modifying macromolecules into the hydrophilic host polymer polyetherimide by phase inversion to increase the hydrophobicity [39]. Qtaishat et.al. (2009) also prepared a porous hydrophobic/hydrophilic polysulfone membrane through phase inversion method by blending the hydrophilic polysulfone with hydrophobic surface modifying macromolecules for desalination by DCMD. They could observe higher permeate flux than commercial PTFE membranes [34]. Here, the top hydrophobic layer controlling the membrane performance is made as thin as possible which reduces the mass transfer resistance and heat conductivity of the membrane and thereby increase the flux [40]. However the application to reduce fouling and wetting has not been fully explored.

It is well known that the fouling by proteins, fats/oils and other organic matter is greater in hydrophobic membranes than hydrophilic membranes because of their higher affinity with hydrophobic chemistries. Interaction of the hydrophobic membrane surface with the hydrophobic functional groups of the foulants leads to reorientation of the foulant molecules such that the hydrophobic parts of the molecule adheres to the membrane, leaving the hydrophilic parts of the molecule oriented towards the solution. As a result, the membrane can lose its hydrophobicity, resulting in membrane wetting– i.e., the feed solutes penetrate the membrane and contaminate the permeate. One solution to minimise organic fouling is to make the top layer hydrophilic which reduces the interactions with the organic foulants [41]. Alginate coated PTFE and chitosan coated PVDF membranes have been tested in treatment of oily feeds using osmotic distillation and were found to have no wetting compared to the uncoated hydrophobic membranes [42, 43]. During the alginate coated PTFE test, the reduction of the mass transfer coefficient of the coated membrane due to the hydrophilic coating was found to be less than 5% compared to the uncoated membrane. However, in the chitosan coated PVDF test, they observed a flux enhancement if the chitosan concentration and cross linking on the coating were not very high. Another very recent research developed a hydrophilic and oleophobic membrane by blending the base PVDF polymer with an additive polymer having both hydrophilic and oleophobic properties [44]. The oleophobic nature increases the membrane resistance to organic fouling as it has a very low free surface energy than that of oils and other organic foulants. Therefore, this modified membrane exhibited better resistance to organic and biological fouling, lower flux decay and higher flux recoveries after membrane cleaning than the normal hydrophilic membrane [44].

Plasma modification is another new technique for surface modification of membranes. According to a recent study, N_2/H_2 plasma has been used to modify the surface of PTFE UF membrane for desalination by DCMD [45]. It was found that the plasma treatment affected the surface polarity and thereby enhanced the hydrophilicity of the membrane. This could lead to the increase in permeate flux. However, there was a decrease in salt rejection. The use of plasma is still very early, but hydrophilic and dual property (hydrophobic and oleophobic) membranes are commercially available, but the membranes are yet to be tested in MD to avoid fouling and wetting.

2.5. Heat and mass transfer of MD

There are three main steps of mass transfer taking place in MD [46]. Those are;

1. Evaporation of water from the hot feed side of the membrane,
2. Transportation of water vapour through the non-wetted pores,
3. Condensation of water vapour transported at the permeate side of the membrane.

For the purpose of demonstrating the heat and mass transfer concepts in MD, the DCMD configuration will be used. Figure 2.5 describes the simultaneous heat and mass transfer mechanism in DCMD.

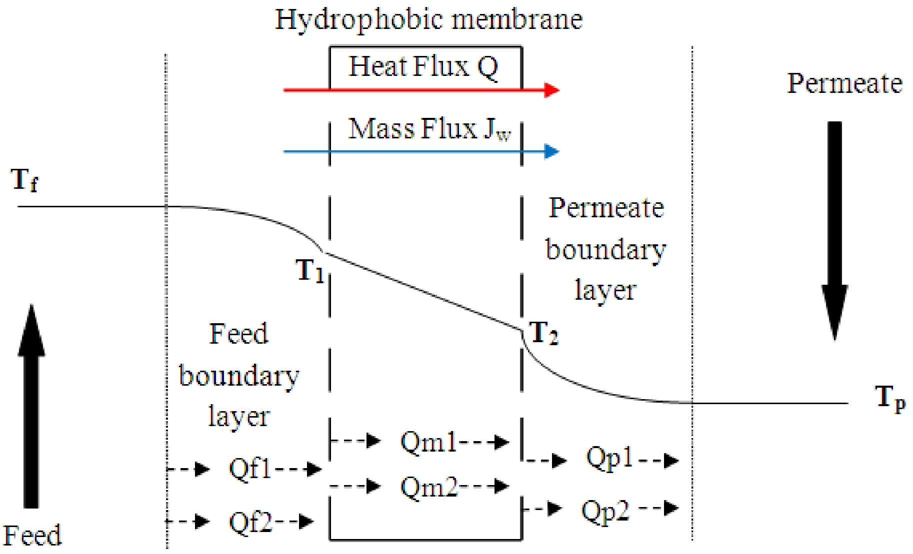


Figure 2.5 Heat and mass transfer in DCMD

The driving force for water vapour transportation through the membrane pores is the temperature difference between the feed temperature (T_f) and the permeate temperature (T_p). Due to the heat losses in DCMD process (primarily conductive and latent), the membrane/interface temperatures (T_1 and T_2) are different from the bulk feed/permeate temperatures (T_f and T_p).This phenomenon is known as temperature polarization and this is considered as a drawback in DCMD due to the drop in the theoretical driving force. The temperature polarization coefficient (τ) is defined as the ratio between the actual driving force and the theoretical driving force and is given by Equation 2.1 [47]. Ideally τ should be unity, but values between 0.4 – 0.7 are expected [47].

$$\tau = \frac{T_1 - T_2}{T_f - T_p} \qquad (2.1)$$

Heat transfer in DCMD can be divided into three regions (Figure 2.5) as follows.

1. Feed region - convectional heat transfer in the feed boundary layer (Q_{f1}) and the heat transferred due to mass transfer across the feed thermal boundary layer (Q_{f2})
2. Membrane region – conductive heat transfer through the membrane (Q_{m1}) and heat transferred due to water vapour migration through the membrane pores (Q_{m2})
3. Permeate region - convectional heat transfer in the thermal permeate boundary layer (Q_{p1}) and the heat transferred due to mass transfer across the permeate thermal boundary layer (Q_{p2})

Therefore, based on the above mechanism heat transfer can be expressed [46] as follows.

Heat transferred through the feed boundary layer;

$$Q_f = Q_{f1} + Q_{f2}$$

$$Q_f = h_f\,(T_f - T_1) + J_w \,.\, H_f \left\{\frac{T_f + T_1}{2}\right\} \tag{2.2}$$

Heat transferred through the membrane;

$$Q_m = Q_{m1} + Q_{m2}$$

$$Q_m = h_m(T_1 - T_2) + J_w \,.\, H_v \tag{2.3}$$

Heat transferred through the permeate boundary layer;

$$Q_p = Q_{p1} + Q_{p2}$$

$$Q_p = h_p\left(T_2 - T_p\right) + J_w \,.\, H_p \left\{\frac{T_2 + T_p}{2}\right\} \tag{2.4}$$

In the above equations, h_f is the feed boundary layer heat transfer coefficient, h_p is the permeate boundary layer heat transfer coefficient, h_m is the heat transfer coefficient of the hydrophobic membrane, J_w is themass/permeate flux, H_f is the enthalpy of the feed solution, H_v is the enthalpy of the vapour and H_p is the enthalpy of the permeate solution.

The average bulk temperatures of feed and permeate (T_f and T_p) can be calculated using following equations.

$$T_f = \frac{T_{f,in} + T_{f,out}}{2} \qquad (2.5)$$

$$T_p = \frac{T_{p,in} + T_{p,out}}{2} \qquad (2.6)$$

In the two equations above, $T_{f,in}$ and $T_{f,out}$ are feed inlet and feed outlet temperatures respectively, whereas $T_{p,in}$ and $T_{p,out}$ are permeate inlet and outlet temperatures respectively.

The dominating mechanism for heat transfer in both feed and permeate thermal boundary layers is convectional heat transfer. Furthermore, the enthalpy of vapour (H_v) is almost equal to the latent heat of vaporization (ΔH_v) [46, 48].

Therefore equations (2.2), (2.3) and (2.4) can be rewritten as follows:

$$Q_f = h_f (T_f - T_1) \qquad (2.7)$$

$$Q_m = h_m (T_1 - T_2) + J_w \,.\, \Delta H_v \qquad (2.8)$$

$$Q_p = h_p \left(T_2 - T_p\right) \qquad (2.9)$$

When the heat lost to the environment is negligible (at steady state);

$$Q = Q_f = Q_m = Q_p \qquad (2.10)$$

When describing the mass transfer in DCMD, researchers assume that the mass flux is proportional to the vapour pressure difference across the membrane. Therefore, the mass flux (J_w) is explained using following relationship [49].

$$J_w = C \left(P_{T_1} - P_{T_2}\right) \qquad (2.11)$$

In the above equation, C is the membrane distillation coefficient and P_{T1} and P_{T2} the vapour pressure at feed/membrane interface temperature and permeate/membrane interface temperature respectively.

Vapour pressure (P) is a function of temperature (T) and P at a given temperature and is given by the Antoine equation below [50, 51] where P is expressed in Pascal and T is expressed in Kelvin.

$$\mathrm{P} = \exp\left[23.273 - \frac{3481.2}{\mathrm{T} - 45}\right] \qquad (2.12)$$

The mass transfer through the MD membrane can be considered as gas transport in a porous media. This process has been described in three different mechanisms- Knudsen diffusion, Molecular diffusion and Poiseuille-flow [31].

1. Knudsen-diffusion

This is where either the gas density is very low or the pore size is very small and the collisions between molecules can be ignored compared to collisions between molecules and the inside walls of the porous membrane.

2. Molecular-diffusion

Collisions between molecules dominate over collisions between molecules and membrane wall and a mixture of molecules move relative to each other under a concentration gradient.

3. Poiseuille-flow

Gas transport is described as a move of a continuous fluid driven by a pressure gradient. Here also molecule-molecule collisions dominate over molecule-membrane wall collisions.

In experiments performed by Schofield et al. (1987), it was shown how the membrane distillation coefficient (C) varies with different flow mechanisms [49].

2.6. Advantages of MD

According to literature, MD has many advantages over other separation processes. MD is considered as cost effective due its lower electrical energy, capital and land requirement compared to the conventional distillation [31]. The vast vapour space and the high vapour velocities in conventional distillation are replaced by the microporous hydrophobic membrane in MD. The MD process requires very low temperatures ranging between 30°C – 90°C and this, combined with small surface area, reduces the heat lost to the environment [31, 52]. The lower operational temperatures of MD also avoids undesirable heat related changes in feed, for example denaturing of proteins or loss of flavour.

Unlike RO, MD does not depend on electrical energy to drive the separation, but instead is driven by thermal energy in the form of temperature. Low grade, waste or alternative energy can be integrated with MD. Solar energy has been the mostly used alternative energy for MD operations and most of them were based on desalination [23-27, 53]. Use of solar energy has been proved as technically feasible for desalination by MD [54] and some studies have shown that its water production cost can be comparable with the cost involved in conventional thermal processes and RO [28]. Lower operating pressures in MD compared to RO offer benefits in cost, safety and less demand for membrane mechanical properties [31, 33].

The salt rejection is higher (theoretically 100%) in MD than other membrane processes and a good quality permeate can be achieved even at higher concentration of feed [31]. Cath et al. (2003) observed a salt rejection above 99% even at a high feed salt concentration such as 73 g/L in desalination by DCMD [55]. Another desalination study of DCMD done by Dumée et al. (2010) showed a salt rejection of 99% with a high flux rate about 12 kg/m^2/h [56]. Khayet and Mengual (2004) [57] also compared DCMD for its higher salt rejection against NF in treatment of humic acid solutions.

2.7. Applications of MD to non-dairy streams

Most of the knowledge of MD from researchers are based on desalination of brackish water or sea water. These studies have shown that MD is a successful application for desalination and they have also deeply analysed different MD configurations, modules, membrane types and different operating conditions and their suitability and effect towards MD performance in desalination.

In a study based on desalination by DCMD, PTFE appeared to be the most suitable membrane due to its higher hydrophobicity and permeate flux than PP and PVDF membranes. In the same study the thinnest DCMD module was shown as the most efficient module over other two DCMD modules as the thinnest one can provide the largest linear velocity and thereby highest permeate flux [12].

During several studies in desalination by MD, feed temperature has been emphasized as a critical operating parameter as higher feed temperatures lead to higher transmembrane temperature difference which ultimately increases the vapour pressure difference across the membrane [12, 58, 59].

A research based on application of MD to desalinate brines from thermal desalination plants has proven MD is a feasible technology which can consistently produce a pure quality water confirmed by a very low permeate conductivity (< 10 µS/cm) throughout the test [58]. Here, salt concentrations upto 70 g/L did not cause any drops in permeate flux, however, there was a 20% flux drop at salt concentrations above 70 g/L. For all these salt concentrations, fouling was not observed on tested membranes and therefore stable fluxes could be achieved. Nevertheless, it has shown that direct application of MD in sea water would require pH adjustment and/or addition of antiscalants to minimize the precipitation of calcium carbonate on the membrane.

With the developments in research studies based on desalination by MD, there are several studies have been carried out at pilot plants in relatively larger scale than laboratory experiments [60-62]. In addition, as mentioned in the Section 2.6 many studies have experimented solar energy as an alternative energy to be used in desalination and evaluated its feasibility. These studies have shown that coupling solar energy with MD is technically feasible and cost for such application can be comparable with the water production cost in RO or other conventional thermal processes.

Apart from desalination, MD has also been studied in the applications of concentrating salt/sugar solutions, fruit juices and wastewater. Jensen et al. (2011) demonstrated a possible application of DCMD for the concentration of black currant juice [63]. This study describes a predictive model for concentrating commercial black currant juice by DCMD and its applicability for commercial scale-up.

There are few studies conducted on osmotic membrane distillation (OMD) which applies the similar principle like MD, however, the vapour transportation is driven by the difference in water activity between the two aqueous solutions contacting with two sides of the hydrophobic porous membrane. This method usually uses concentrated inorganic salt solutions having low water activity such as NaCl, $CaCl_2$, $MgCl_2$ or organic solvents such as glycerol, polyglycerol as stripping solutions. OMD has been successfully applied by using PTFE membranes for concentration of sugar solutions and fruit juices like grape juice [64, 65].

In addition, Gryta and Karakulski (1999) applied MD to separate water from oil-water emulsions [29]. Capillary membranes made from polypropylene were used in this study. An oil concentration up to 1000 ppm in the feed was found to be practical not causing any penetration of oil to the permeate. However, oil concentrations above this level can also be applicable if the feed oil concentration can be maintained below 1000 ppm using a combined system with MD to separate oil.

2.8. Application of MD to processing of dairy streams

Compared to desalination based MD applications, MD has not been widely studied in dairy applications. However, there are some recent studies related to MD in dairy applications. Christensen et al. (2006) applied DCMD for whey protein concentration from 20% dissolved solids to 34% dissolved solids with limited denaturation of whey proteins [66]. Another paper has been published by Hausmann et al. (2011) on applying DCMD for concentration of different dairy streams like whole milk, skim milk, whey and lactose solution and to understand membrane performance [67]. As an extension to this study Hausmann et al. (2013) have recently studied fouling behaviour of whey and skim milk fouled PTFE membranes in DCMD of whey and skim solutions [68, 69]. Finding of these fouling studies have been described further in section 2.8.

The application of MD to dairy industry process and waste streams and the integration of MD with other membrane processes in dairy processing is an area which holds a great potential for concentration of dairy process and waste streams and production of good quality water. This area is still remaining as an unexplored area of dairy based MD research. As outlined in the Chapter 1 (Introduction), dairy waste management is one of the key challenges to the industry. Identification of the high volume dairy streams and investigation of the feasibility of MD treatment of these streams to reduce waste volume and recover high quality water addresses this challenge. The energy demand for this MD treatment could be met by utilising the large amount of low-grade waste heat within dairy plants such as evaporators, lactose crystallisers and anaerobic digesters.

There are possible existing MD opportunities identified within dairy processing such as sweet whey, salty whey, ion exchange regeneration streams and also combined dairy effluent stream which can be utilised to concentrate dairy feeds and recover potable water via concentration by MD.

2.8.1. Application of MD to sweet whey processing

Cheese production is one of the main processes generating dairy waste in the form of whey. Cheese whey is the most complex waste generated in the production of cheese. Whey is green-yellowish liquid remaining after coagulation of caseins in milk [70]. Cheese whey can be generated in two methods such as acid whey and sweet whey depending on the coagulant (acids or enzymes) used for curdling. Sweet whey is the liquid remaining after coagulation of milk caseins by the rennet enzyme. Sweet whey mainly contains lactose (≈5%), proteins (≈1%), and minerals (≈0.5%) [71, 72]. In terms of minerals, NaCl and KCl are the main contributors making more than 50% of the mineral content while calcium salts (primarily calcium phosphate) are also present in considerable amount [70].

In the past, dairy plants did not have proper whey management systems and discharged their effluents by land application or direct discharge to receiving waters (rivers, lakes, ocean) without any pre-treatment. As whey contains high amount of organic matter (chemical oxygen demand/COD and biological oxygen demand/BOD) and creates a serious environmental issues this direct disposal to sewer is no longer possible with the intensive wastewater regulatory requirements [70, 73]. Therefore, the dairy industry has now approached whey management process through different techniques. Membrane technology is one of the main techniques used for whey processing. Membrane treatment of whey not only reduces the volume of dairy waste but also separates whey proteins and lactose which are used as valuable ingredients in food processing. Ultrafiltration (UF) is used to separate the whey proteins from whey. The UF permeate is then processed by nanofiltration (NF) to isolate lactose. RO can be then used for the NF permeate as a waste volume reduction process [1, 74-78]. Figure 2.6 shows the full process of sweet whey processing.

The marine evaporators recover water from the RO retentate which can be reused in dairy plants and concentrate the dairy minerals/salts which will be sent to salt ponds. The possible MD opportunity for the sweet whey is to concentrate the RO retentate (concentrate) and recover pure water that can substitute the marine evaporators which have a relatively high operating cost and energy demand.

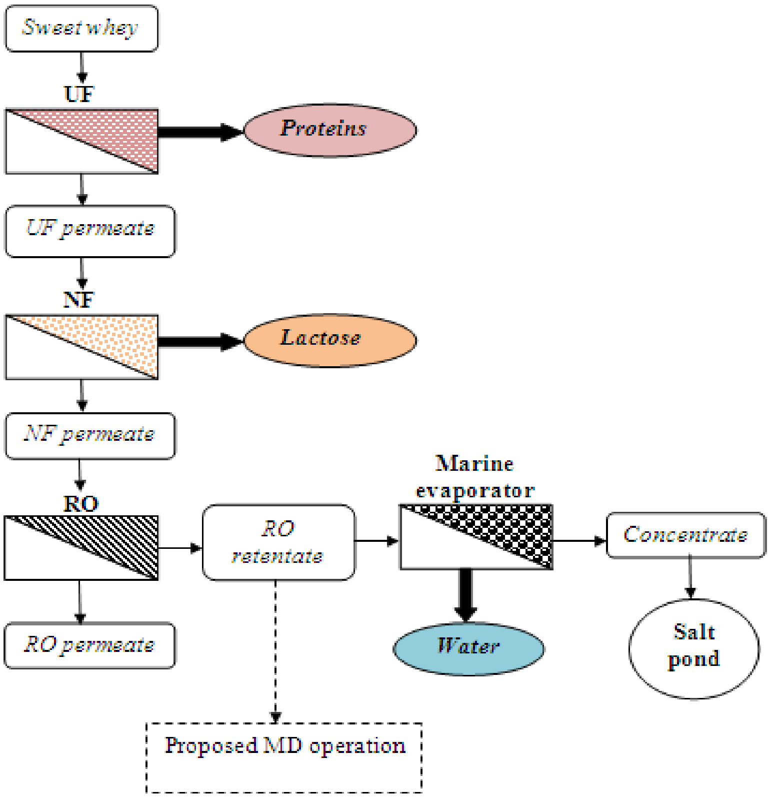


Figure 2.6 Sweet whey processing

2.8.2. Application of MD to salty whey processing

Salting is a final step of producing cheeses such as cheddar. Salt is added to cheese in order to expel the excess whey from cheese. When salt is dispersed on the curd, it dissolves with the moisture and diffuses into the curd which causes the expulsion of whey. This whey is known as “salty whey” and it contains high amount of salts [79, 80].

Salty whey contains about 4% - 6% NaCl which makes it impossible to be reintroduced to normal cheese whey. Moreover, it consist of about 6% whey solids and BOD of 45,000 ppm which again creates great environmental issues if discharged directly to the sewer [81]. Therefore, dairy industry uses UF to separate whey solids from salty whey which can then be reintroduced to cheese whey [76, 82, 83]. UF permeate can then be further processed by marine evaporators to recover water and capture salts. Figure 2.7 shows the process diagram for salty whey.

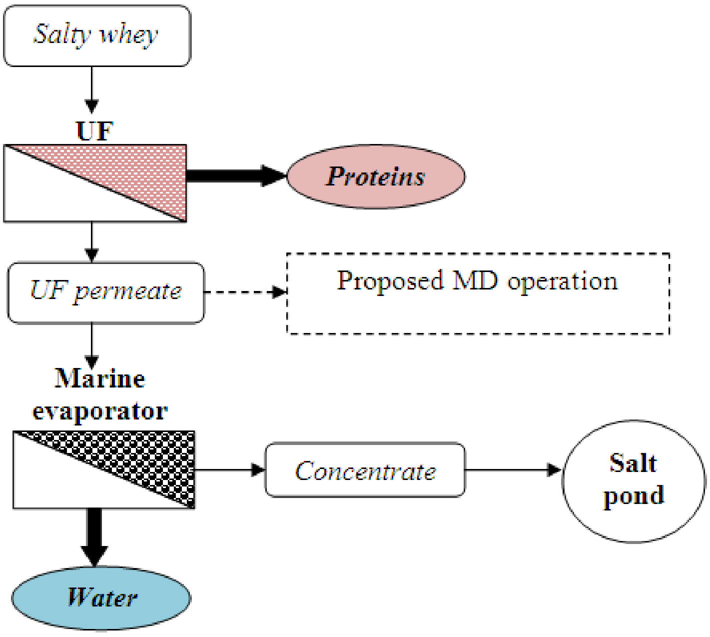


Figure 2.7 Conventional approach to salty whey processing

As for sweet whey, MD can be a substitute for marine evaporators which can concentrate the UF permeate in order concentrate the salts and produce water.

2.8.3. Application of MD to ion exchange regeneration stream

As outlined in the section 2.8.1. whey is a valuable source of whey proteins and lactose. However, due to its salt concentration whey has to be demineralised before separating proteins or lactose. Dairy industry uses ion exchange (IX) resins for whey demineralisation [84].

When the whey is first passed through the cation resin all the cations in whey (e.g. Na^+, K^+, Ca^{2+}, Mg^{2+}) are replaced by the H^+ of the cation resin. Similarly, whey is then passed through the anion resin where all the anions in whey (e.g. Cl^-, SO_4^{2-}) are replaced by the OH^- of the anion resin. This process makes the whey demineralised as all the cations and anions are removed from the whey. Whey is passed through these resin beds until the resin beds are saturated with cations and anions. After the resins beds are saturated the next step is the regeneration process where the resin beds are treated with an acid to replace the absorbed cations by H^+ and with an alkaline to replace the absorbed anions with OH^-. This regeneration solution contains all the dairy minerals and may contain some proteins which have been purged from demineralised whey [85, 86]. Figure 2.8 shows the process diagram of the demineralisation of whey by ion exchange process. Ion exchange regeneration solution contains high amount of dairy minerals (salts) which can be concentrated and water in the solution can be recovered by a membrane separation process like MD.

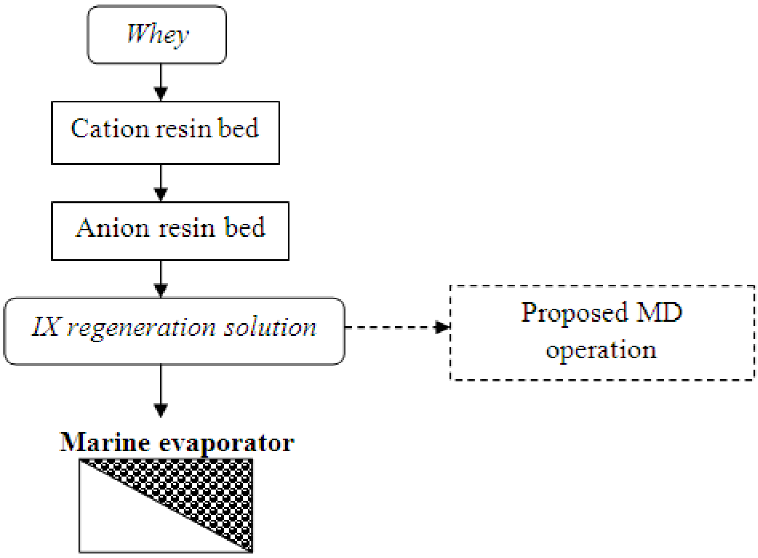


Figure 2.8 Ion exchange process of whey demineralisation

2.8.4. Application of MD to combined dairy effluent stream

Some dairy plants use anaerobic digestion in a bulk volume fermenter (BVF) as a biological process for dairy waste treatment in which most of the organic matter present in the combined dairy waste are broken down [87]. The conventional dairy waste treatment process is shown in Figure 2.9.

The organics are converted to methane in the anaerobic digester. Ammonia (NH_3) is also produced as a result of conversion. Methane is an energy source which can be burnt on site and used to provide heat for the anaerobic digesters themselves or to produce electricity. After the anaerobic digestion, the treated waste may be further treated by induced air floatation (IAF). Here, the waste is mixed with air and fats and other solid materials are preferentially removed. The final effluent from treatment plant enters a common trade pipeline where the charges for the waste are based on volume, BOD and suspended solids [15, 88, 89].

Thus, it is a vital task for the dairy plant to reduce the dairy waste volume and BOD levels as much as possible in order to minimise the cost incurred. MD could be a viable application to be used before and/or after anaerobic digestion as a concentration technique to reduce the dairy waste volume. This not only reduces the cost for waste volume , but also the cost for purchasing incoming water if good quality water can be achieved by MD. Figure 2.9 shows how MD could fit in with anaerobic digestion in a dairy plant.

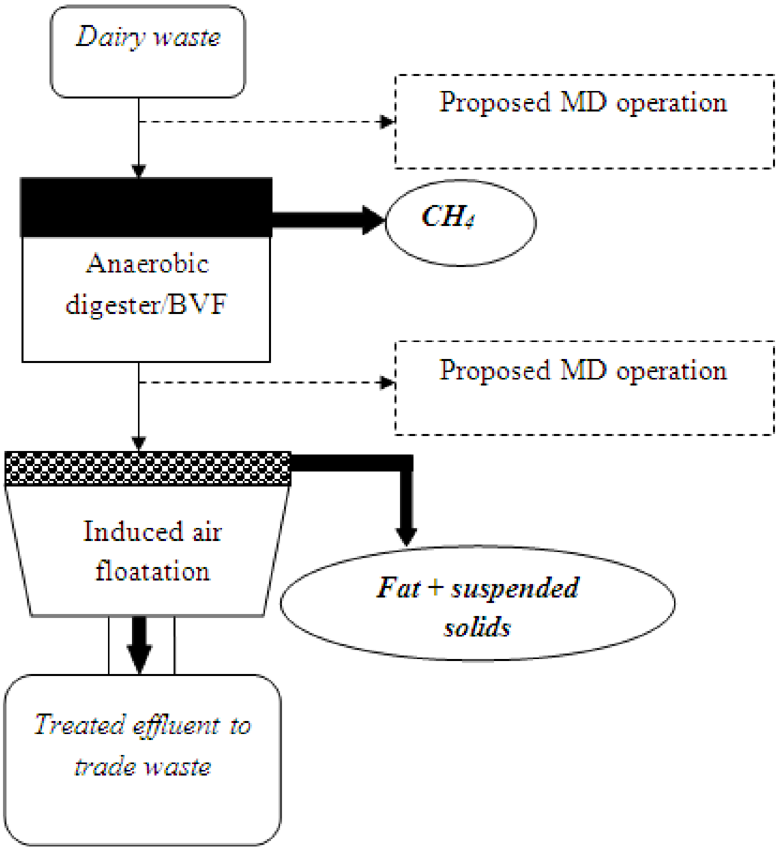


Figure 2.9 Dairy waste treatment process

2.9. Challenges for MD

Although MD has been seen as a promising membrane process for different applications mentioned above it has to overcome some key challenges before it can be successfully applied. Among these, membrane fouling and membrane wetting are key challenges to be overcome. These will be discussed in detail below in Section 2.9.1. and Section 2.9.2.

2.9.1. Membrane fouling

One of the major challenges for membrane technologies is membrane fouling. Fouling is deposition of suspended or dissolved substances on membrane surface or inside membrane pores. Fouling can be organic, inorganic/scaling, biological or colloidal. A fouling layer formed on the membrane surface can be either porous or non-porous [90].

Initial fouling is caused by the hydrodynamic forces and interactions between foulants in feed and the clean membrane. Once a fouling layer has been deposited, interactions between foulants in feed and the fouled membrane then become significant [91].

The ultimate result of fouling is reduced membrane permeability and thereby permeate flux. The permeate flux decline is due to pore blocking, cake formation or concentration polarization [92]. For MD, membrane wetting is also a special type of fouling, but will be discussed in Section 2.9.2. In regards to conventional fouling for MD, the reason for the negative effect of fouling towards permeate flux is the decrease in the partial vapour pressure on the active side of the membrane due to deposition of foulants on the evaporation surface/active side. Increasing the feed concentration can enhance fouling, hence, a feed concentration below the saturated concentration of the feed solution enables a better MD performance with less fouling [93]. The long term effect of fouling can cause irreversible microbiological action on membrane and reduce the lifetime of membrane [94, 95].

Fouling in MD process have been studied for different applications by several researchers. A study by Gryta (2008) looked at the fouling on polypropylene capillary membranes when treating wastewater containing proteins, bilge water and brines [90]. The main contributors for fouling were proteins and $CaCO_3$. Protein fouling was found to be less if the feed was first filtered before heating. The permeate flux drop was mainly caused by the increase in heat resistance of the fouling layer. It was found that fouling was not only formed on the membrane surface, but also inside membrane pores due to scaling. Salt crystallisation ($CaSO_4$) inside pores caused wetting where feed liquid penetrated through the membrane and also cause a mechanical damage to the membrane structure. The intensity of the fouling was found to be limited by decreasing the feed temperature and increasing the feed flow rate.

Humic acid, a substance commonly found in surface waters, was found to foul PVDF membranes in MD has been studied by Srisurichan et al. (2004). The flux declines were negligible before introducing Ca^{2+} to the feed, however, it could be seen a considerable flux decline due to formation of a complex by Ca^{2+} with humic acid and coagulation on the membrane surface [96].

Another study has found the importance of a pre-treatment before MD processing of wastewater containing NaCl and proteins, and also effluents from ion exchange regeneration as it could be seen a severe fouling on the membrane due to organic matter, scaling inorganics and also bio-fouling. The major reason for fouling was found to be the increase of the feed concentration which occurs as part of the MD processing, and the higher temperatures used to cause evaporation [97]. Gryta et al. (2001) also explained the importance of a pre-treatment of the feed solution in their MD research in treating a NaCl solution containing organic matter. There, they have found that the pre-treatment proposed removed proteins and Cl^{-} ions by heating the feed solution followed by filtration. This could be able to significantly overcome the fouling issue [93]. Therefore, the process of heating and filtration may be a way to combat fouling. The filter may be included within the standard MD hot cycle loop instead of a standalone pre-treatment.

Membrane fouling by dairy components on various types of membranes have been studied by several researchers, and has some resemblances to the fouling chemistry observed for water treatment applications. The influence of feed pH and operating temperature on the fouling behaviour during NF of fresh dairy UF permeate was examined in 2009 by Rice et al. [98]. Overall, a minimum flux decline could be observed at low temperatures and pH values, where precipitation of calcium phosphate salts was minimised. Another main finding here was that the chemistry of calcium in the bulk feed in terms of being insoluble or precipitated form can affect the fouling mechanism. Cake layer formation was more dominant than the surface scaling when the calcium phosphate precipitation was initiated in the bulk feed before filtering. However, at low temperatures where the calcium phosphate precipitation has not initiated in the bulk feed, the scaling is more dominant. Scaling deposits on the membrane add to the flux resistance, and are more strongly bound to the membrane surface and more difficult to be removed [99].

So far, studies related to dairy fouled MD membranes are very limited. A recent study of application of DCMD in skim milk and whey solution on PTFE membrane by Hausmann et al. (2013) found that proteins contribute to most of the fouling and this is faster when salts are present in the solutions [69]. While all proteins are likely to adsorb to hydrophobic surfaces due to their hydrophobic and amphoteric nature [41, 100], interactions between casein proteins with the hydrophobic PTFE seem to be stronger than that of whey proteins and hence caseins form a more extensive fouling layer [69]. Lactose seems not to interact directly with the membrane, however can interact with other components and contribute to fouling.

In terms of fouling mechanism of skim milk and whey on PTFE membrane studied by Hausmann et al (2013) [68], skim milk fouling is initiated by proteins and salts where lactose contributes later to the fouling. Whey fouling also shows a similar mechanism. Whey fouling layer seems to be thinner than the skim milk layer. Skim milk fouling happens much quicker forming a homogenous fouling layer whereas whey fouling occurs slowly and remains reversible for a longer time. Moreover, whey fouling first starts in several spots and then extents across the membrane. As whey proteins have weaker interactions with the membrane than caseins they tend to interact with each other to form a thick fouling layer. Caseins however, adsorbs to the membrane stronger and faster. Minerals and proteinaceous material appear to penetrate into the membrane during whey test in which calcium plays a major role on adhesion to the membrane with whey proteins.

While the drop in permeate flux caused by decreased membrane permeability being the initial effect of fouling in MD, deposition of organic and inorganic materials on hydrophobic membrane can cause membrane to lose its hydrophobicity and thus facilitates progressive wetting of the membrane which is known as the penetration of feed solutes to the permeate side through the membrane pores [90]. Wetting is a critical fouling issue in MD and will be discussed in the following Section 2.9.2.

2.9.2. Membrane wetting

In MD, the hydrophobic membrane acts as a barrier between two liquids and the feed liquid does not penetrate until the pressure difference across the membrane exceeds liquid entry pressure (LEP). LEP is defined as the minimum pressure required for feed liquid to penetrate through the hydrophobic membrane pores [101].

LEP is correlated to the liquid surface tension (γ_L), contact angle of the liquid on the membrane surface (θ) and the radius of the membrane pore (r). The relationship between operating pressure difference across the membrane (ΔP) and largest allowable pore radius (r_{max}) is given by the following Laplace Young equation where G is the geometric factor determined by the pore structure [101].

$$\Delta \mathrm{P} = -\,\mathrm{G}\,\frac{2\,\gamma_{\mathrm{L}}}{\mathrm{r}_{\max}}\cos\theta \qquad (2.13)$$

The contact angle (θ) of a liquid droplet on an ideal homogeneous surface is described by the following equation where γ_L is the liquid surface tension, γ_S is the surface tension of the solid (membrane surface) and γ_{SL} is the solid-liquid surface tension [102].

$$\gamma_L \cos\theta = \gamma_S - \gamma_{SL} \qquad (2.14)$$

If a liquid has a contact angle larger than 90° on a hydrophobic surface (PP, PVDF, PTFE) it is called as a non-wetting liquid whereas a liquid with a contact angle below 90° is called a wetting liquid [103]. Figure 2.10 presents a graphical expression of a non-wetting and wetting liquid.

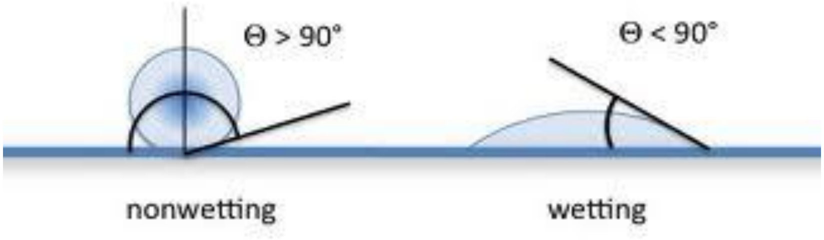


Figure 2.10 Non-wetting and wetting liquids

Water and inorganic solutions have high values of surface tension and contact angle for hydrophobic microporous membranes such as PP, PVDF and PTFE with pore size of 1µm or less. However, when organic solutes are present in an aqueous solution, the liquid surface tension (γ_L) and contact angle (θ) will decrease rapidly. Therefore, according to equation 2.21 and 2.22, if the concentration of organic matter exceeds some critical value and $\Delta P > LEP$, the feed liquid can penetrate through the membrane pores which is called membrane wetting. After this stage MD will no longer be possible unless the membrane is thoroughly cleaned and dried. Therefore, organic molecules/surfactants like proteins, fats, oils, sugars and polysaccharides can act as wetting agents after a certain concentration [43, 102].

As a remedy for membrane wetting caused by organic matter in wastewater treatment by MD, Goh et al. (2012) have looked at the application of a MD bioreactor (MDBR).

MDBR was found to minimise the organic fouling and delay the wetting caused by organics by removing carbohydrates and proteins from the retentate. The MDBR did not show a severe bio-fouling issue and was able to maintain the permeate flux above 6.8 $kg/m^2/h$ although this was 8% lower than the average MD flux [104].

In terms of wetting caused by dairy feeds in MD, Hausmann et al. (2011) could observe slight wetting due to fats in DCMD of whole milk on PTFE membrane. It was believed to be more because of unstable fat globules in milk. Therefore, homogenisation was recommended before the experiment in order to minimise wetting caused by fats. It has also highlighted that even with more stable fats wetting can be enhanced with the increased fat concentration in the feed [67].

2.10. Membrane cleaning

Membrane cleaning is commonly performed to reverse fouling on the membrane and restore performance. Selection of a membrane cleaning agent depends on the nature of fouling material. Cleaning efficiency can be examined by methods such as recovery of permeate flux, analysis of the foulants in the cleaning solution and membrane surface analysis before and after cleaning [105, 106].

Acids, alkalines, oxidants/disinfectants, chelating agents and surfactants are among different types of cleaning agents used based on the nature of fouling [107, 108]. Alkaline agents are more effective in removing organic fouling whereas acids are found to be effective in inorganic fouling. Oxidants/disinfectants are commonly used for minimising bio-fouling. Nevertheless, the interactions between different cleaning agents and foulants and between cleaning agents and the membrane, have not been fully understood [109-111].

Concentration of the cleaning agent, pH of the cleaning solution, operating pressure, flow rate and time are important factors affecting the cleaning efficiency of a particular cleaning agent [109].

In the MD research conducted by Gryta (2008) where proteins and $CaCO_3$ were main foulants on PP membranes treated by wastewater, it was found that periodic cleaning to remove the fouling layer would be beneficial to reduce the negative impact on the membrane performance [90]. However, complete dissolution of fouling was found to facilitate the penetration of feed liquid to membrane pores which enhanced wetting. As a result internal scaling could be observed. Therefore, in this study it was recommended to remove only a part of fouling from the membrane surface.

Another research based on fouling on PVDF membrane in treating humic acid by MD where the main fouling was due to formation of a complex between Ca^{2+} and humic acid, explained that rinsing the fouled membrane with clean water and 0.1 M NaOH was effective in removing the foulants and can achieve a 100% flux recovery [96].

For the polypropylene capillary membranes fouled by organic matter present in a NaCl solution, the gel-like fouling layer mainly consisted of proteins and Cl^{-} ions. This fouling could be partially removed by cleaning the fouled membrane with 2 wt.% citric acid solution [93].

Nigam et al. (2008) found that caustic solution and elevated temperatures were effective in the cleaning of polysulfone UF membranes that were fouled by whey protein concentrate [112]. Many plants, including dairy plants, regularly use clean-in-place (CIP) process for membrane cleaning which involves minimal manual handling. Dairy plants are unique in that they clean the food handling equipment on a daily basis so the membranes in the food processing lines must withstand daily cleaning. However equipment in the waste treatment side of the dairy plant will only require cleaning to maintain performance, which is typically much less often than daily. CIP for membranes can vary significantly depending on the membrane materials and fouling. Often costly proprietary cleaners are used to ensure membranes are not harmed during cleaning. However, conventional dairy plant CIP is preferred due to its existing use, simplicity and cost effectiveness. The conventional CIP process uses temperature, caustic (sodium hydroxide) and acid (nitric acid) solutions with water rinse in-between [113, 114].

There are no published studies on the cleaning of dairy fouled MD membranes. Some unpublished recent research studies at the Institute for Sustainability and Innovation (ISI) in Victoria university, Melbourne, have found that conventional dairy plant CIP can lead to membrane wetting when MD membranes (PTFE) were fouled by whey and skim milk. Enzymatic cleaners, however, were highly effective for these fouled membranes and didn’t lead to membrane wetting. Another ISI MD study has shown that conventional dairy CIP works well for PTFE membranes fouled by the evaporator condensate of milk.

2.11. Conclusions and research gaps in dairy related MD applications

According to this literature review, MD has been studied for more than 40 years in many applications. Compared to the applications such as desalination and wastewater treatment, utilisation of MD in dairy is very limited .However, it can be a viable opportunity for concentration of dairy waste streams and production of good quality water. Therefore, there are research gaps in application of MD in different dairy streams and in investigation of its viability in terms of permeate flux behaviour, concentration factor/water recovery and membrane rejection. There are also gaps in identification of stream specific issues related to MD treatment such as fouling and wetting and exploring suitable membrane chemistry to propose viable cleaning routines.

As highlighted in sections 2.8.1 – 2.8.4 there are possible opportunities for MD within the dairy industry which have not been studied before. These applications are worthwhile of exploring by MD as they can minimise the dairy waste and recover resources, which is a key topic for dairy processors today. At the same time , successful MD treatment of the applications mentioned above would require a full study of the membrane performance (permeate flux, concentration factor/water recovery, salt rejection, permeate quality) and associated challenges around those applications such as fouling and wetting. Hence, investigation of fouling behaviour, cleaning methods and wetting issues and possible remedies (suitable membrane material, cleaning methods) to minimise those issues are also important.

Thus, the overall aim of this research is to identify the opportunities for MD in the treatment of real time dairy waste streams mentioned above and to investigate the viability of MD as a concentration and water recovery technique for the dairy industry in terms of applications such as sweet whey, salty whey, IX regeneration solution and combined dairy effluent. The research will explore the MD performance of these dairy streams in terms of permeate flux behaviour, concentration factors/water recovery, salt rejection and permeate quality. The research will also deal with identifying the specific issues (fouling and wetting) related these dairy streams and coming up with possible solutions (suitable membrane materials and cleaning methods) to overcome those issues.

Chapter 3. Materials and Methods

3.1. Materials and Equipment

3.1.1. Dairy feeds

Following are the main dairy streams tested which were obtained by several dairy plants located in Australia.

- RO retentate of NF permeate of UF permeate of sweet whey
- Salty whey UF permeate
- Ion exchange regeneration solution
- Combined dairy effluent

3.1.1.1. RO retentate of NF permeate of UF permeate of sweet whey

Sweet whey is the liquid remaining after coagulation of caseins by enzymes in cheese making. The tested sweet whey had been filtered through UF, NF and RO respectively. Therefore, the tested solution was the RO retentate of NF permeate of UF permeate of sweet whey (SWROR). This solution was supplied by ‘Site A in Australia’. The solution was stored in the freezer at -20 °C until tested.

3.1.1.2. Salty whey UF permeate

Salty whey is the expelled whey from cheese as a result of salting process. UF permeate of salty whey (SUFP) was supplied by ‘Site A in Australia’. The solution was stored in the fridge at 4 °C until tested.

3.1.1.3. Ion exchange regeneration solution

Acid stream of the ion exchange regeneration solution (IX-Regen) was supplied by ‘Site A in Australia’. The solution was stored in the fridge at 4 °C until tested.

3.1.1.4. Combined dairy effluent

Combined dairy effluent was collected from ‘Site B in Australia’. These solutions were stored in the freezer at -20 °C until tested. This combined dairy effluent consisted of overall waste produced by the dairy plant. There were two streams collected. i.e. ;

1. Combined dairy effluent before anaerobic digestion (Pre-AD)
2. Combined dairy effluent after anaerobic digestion (Post-AD)

3.1.2. Membrane set-up

Feed solutions were tested using a direct contact membrane distillation (DCMD) set-up as shown in Figure 3.1.

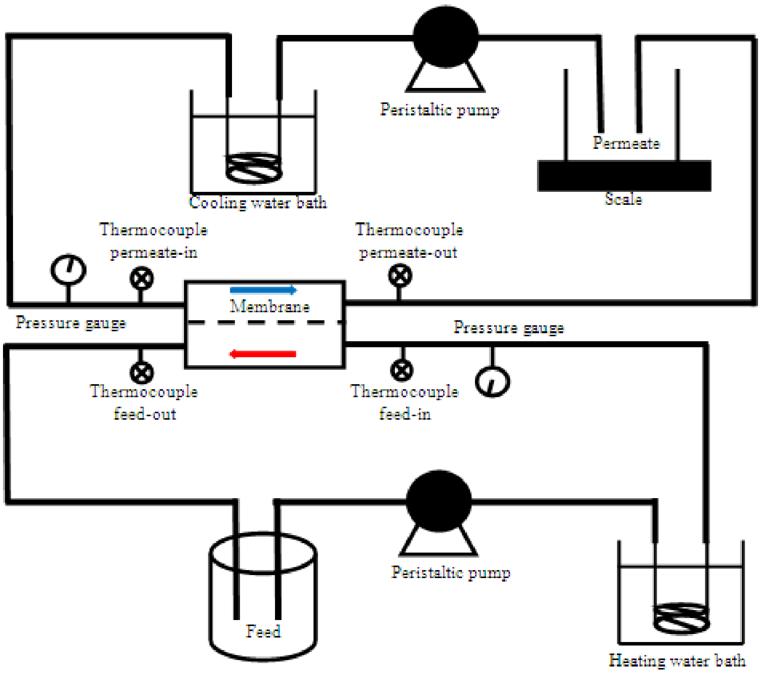


Figure 3.1 Direct contact membrane distillation set-up

The flat sheet laboratory scale membrane module (Osmonics SEPA CF) used had an area of 0.014 m^2. The feed inlet temperature was maintained approximately at 55 °C using a water bath. The permeate inlet was maintained at 5 °C using another water bath. The high temperature choice of 55 °C represents a compromise between performance and practical use in dairy as the temperature is low enough to prevent the protein denaturation which starts to occur from 60 °C.

Feed and permeate flow rate was set at 200 mL/min using a peristaltic pump (Cole-Parmer Masterflex L/S). The inlet and outlet temperatures of both feed and permeate were monitored by thermocouples and data were connected to the computer (software-PLW). The inlet pressures of feed and permeate were monitored by pressure gauges. The weight of the collected permeate was continuously recorded using a scale (AND GP-32K) and this was connected through data logger to the computer(software-Rs Weight). The pH, conductivity and temperature of the retentate were monitored(using TPS Smart CHEM meter)and recorded using the software Win TPS V1.35. The conductivity of the permeate was also recorded(using HANNA HI 8733 conductivity meter) where the images were captured by a web camera (Logitech) and recorded using the software Flix V3.3.

During salty whey and ion exchange solution experiments two cartridge filters (IBC Water SSEDP1-10) having a pore size of 1 µm were installed on the feed side, just before heating (Cold filter) and after heating (Hot filter). The pressure changes across the filters were monitored by analogue pressure gauges. The purpose of incorporating filters was to separate any suspended solids heading towards the membrane, thus, to minimise the fouling. Also, the precipitating salts captured by the filters could be isolated and potentially reused as an alternative product.

3.1.3. Membranes

Table 3.1 summarises the characteristics of all the membrane types tested and Table 3.2 presents all the feed streams against relevant membranes that they were tested on. Conventional polytetrafluoroethylene (PTFE) membrane was initially tested for all the feeds as it is a common type for MD applications. To explore alternative chemistries to typical hydrophobic surfaces, a hydrophilic coated PTFE (provided by Bruck Textiles, Australia) and hydrophobic/oleophobic (provided by Pall Corporation, Australia) membranes were also tested.

Table 3.1 Characteristics of tested membranes

Membrane	Manufacturer	Membrane material	Surface properties	Pore size (µm)
HP	Ningbo Changqi Porous Membrane Technology CO. LTD	Polytetrafluoroethylene (PTFE)	Hydrophobic	0.45
HOA(0.45)	Pall Corporation	Acrylic copolymer	Hydrophobic and oleophobic	0.45
HOA(0.8)	Pall Corporation	Acrylic copolymer	Hydrophobic and oleophobic	0.8
HOA(1.2)	Pall Corporation	Acrylic copolymer	Hydrophobic and oleophobic	1.2
HCP	Bruck Textiles	Hydrophiliccoated PTFE	Hydrophilic coating on hydrophobic membrane	0.45

Table 3.2 Dairy feeds and tested membranes

Dairy feed	Tested membrane
Sweet whey RO retentate	HP HOA(0.45) HCP
Salty whey UF permeate	HP HCP
Ion exchange regeneration solution	HP
Combined dairy effluent Pre-AD	HP HOA(0.8) HOA(1.2)
Combined dairy effluent Post-AD	HP

3.2. Methods

3.2.1. Feed analysis

Following tests were carried out to analyse the composition of each dairy feed stream and following sections describe the importance of these tests in identifying the chemical nature of different dairy streams.

- Total solids
- Chemical oxygen demand
- Total organic carbon
- Total nitrogen
- Minerals
- Lactose
- Proteins
- Fat

3.2.1.1. Total solids

Total solids (TS) of feeds were analysed according to ISO standard method for food analysis [115].

About 20 g of sand was placed in a clean crucible. The crucible with sand was then dried in an oven for about 30 min, cooled in a desiccator and weighed along with a small glass rod. The weight of the crucible + sand + glass rod was recorded (w_1). Then approximately 4 to 6 g of the feed sample was weighed into the crucible and the weight of the crucible + sand + glass rod + sample was recorded (w_2). A small amount of water was added to the crucible and mixed using the glass rod. The purpose of adding water was to aid mixing. Next , the excess amount of water was evaporated in a water bath and the contents were then dried in an oven at 102 °C overnight. After drying the contents were cooled in a desiccator and the weight of the crucible + sand + glass rod + sample after drying was recorded (w_3).

The moisture percentage and the total solids were calculated using following equation. Three replicates from each solution were analysed and the average value was calculated.

$$Moisture\ \% \quad = \frac{w_2 - w_3}{w_2 - w_1} \times 100 \tag{3.1}$$

$$Total\ solids\ \% \ = 100 - Moisture\ \% \tag{3.2}$$

3.2.1.2. Chemical oxygen demand

Chemical oxygen demand (COD) of feed solutions was analysed as an indicator of the amount of organic matter present in the feed. COD analysis was carried out according to HACH method (HACH Company USA- COD Method 8000) for COD analysis for water and wastewater [116]. The concentration range of 20 to 1,500 mg/L COD digestion reagent vials was selected. The samples were diluted according to this range and mixed well before the analysis.

The sample digester (HACH DRB200 Reactor) was preheated to 150 °C. A volume of 2 mL of the sample was transferred to COD digestion reagent vials using a volumetric pipette. A blank sample was prepared by transferring 2 mL of deionized water to another vial. The vials were then closed with caps tightly fitted, rinsed with water and wiped with a clean paper towel. The vials were then inverted gently several times to mix the contents inside followed by placing the vials in the pre-heated digester.

The vials were heated at 150 °C for two hours and they were mixed again and allowed to cool to room temperature. The cooled sample vials were then subject to colourimetric determination method of COD (HACH DR 5000). The instrument was always first zeroed with the blank sample before placing the feed sample. The COD concentration could be recorded as a direct value and this value was then multiplied by the dilution factor. Three replicates from each solution were analysed and the average value was calculated.

3.2.1.3. Total organic carbon

As another measurement of organic matter in feeds, total organic carbon (TOC) was analysed using a total organic carbon analyser (Shimadzu V_{CSH}, Japan) with an autosampler (Shimadzu ASI-V, Japan) [117]. As the detectable range of the instrument was 0 to 100 ppm, the samples were diluted accordingly to be within the range. A 50 ppm solution of potassium hydrogenphthalate (KHP) was prepared as the standard solution to confirm the set calibration. Three replicates from each solution were analysed and the average value was calculated.

3.2.1.4. Total nitrogen

Total nitrogen (TN) of the feed were analysed as an indicator of proteinaceous matter present as TN measurement can be linked to proteins present in the feed [69]. TN was analysed using a total nitrogen analyser (Shimadzu TNM-1, Japan) connected to the TOC analyser and the autosampler mentioned above [117]. As the detectable range of the instrument was 0 to 50 ppm, the samples were diluted accordingly to be within the range. A 40 ppm solution of potassium nitrate (KNO_3) was prepared as the standard solution to confirm the set calibration. Three replicates from each solution were analysed and the average value was calculated.

3.2.1.5. Minerals

Main minerals present in milk such as K^+, Na^+, Ca^{2+}, Mg^{2+}, phosphorus (P) and sulphur (S) were analysed by inductively coupled plasma - atomic emission spectroscopy (ICP - AES) analysis using an ICP analyser (Shimadzu ICPE-9000, Japan) [118]. Feed samples were first subject to wet digestion in order to increase the solubility of the minerals. A volume of 0.5 mL the feed sample was mixed with 5 mL of concentrated HNO_3 acid (65% v/v) at 80 °C for about 3 hours until the solution was clear which confirmed the complete digestion. The digested sample was then transferred to a 50 ml volumetric flask and acidified with 5 mL of diluted HNO_3 acid (5% v/v) [119, 120]. The contents were then diluted up to 50 mL with deionised water and mixed well. The dilution was done to make the total solids below 1,000 ppm which is the instrument requirement. The final solution was filtered through 0.45 µm syringe filter before the ICP analysis to remove any solid particles in the solution.

A calibration series with one blank standard and five other standards having different concentrations was prepared for each element analysed using ICP standard stock solutions (Merck, Germany). The calibration solutions were also acidified with 5% v/v HNO_3 acid in the same concentration as feed samples to avoid any effects of sample acidification. Three replicates from each feed solution were analysed and the average value for each element was calculated.

3.2.1.6. Lactose

Lactose of the feed samples was analysed by the Dairy Technical Services, Victoria, Australia using the Enzymatic method [115].

3.2.1.7. Proteins

Proteins of the feed samples was analysed by the Dairy Technical Services, Victoria, Australia using the Kjeldahl method [115].

3.2.1.8. Fat

Total fat of the feed samples was analysed by the Dairy Technical Services, Victoria, Australia using the Mojonnier (NH_3 digestion) method [115].

3.2.1.9. Chloride ions

Chloride is the main anion present in milk and the chloride amount in each sample was analysed by the Dairy Technical Services, Victoria, Australia using the Volhard method [115].

3.2.1.10. Feed conductivity and pH

The initial conductivity and pH of each feed stream were measured by a combined conductivity and pH meter (TPS Smart CHEM). In addition, these feed conditions were also monitored continuously during MD tests which were connected to a data logger to the computer using the software Win TPS V1.35.

3.2.2. Initial membrane test

Prior to each MD test for every feed stream, an initial test with 1% NaCl (w/v) was performed for few hours to confirm the quality of the membrane. The permeate conductivity was monitored during this time as to see any salt penetration through the membrane. The quality of the membrane in terms of intactness was confirmed by stable (or declining) permeate conductivity, having typical values < 100 µS/cm.

3.2.3. MD batch tests

A known volume of the feed solution, typically between 2 and 5 litres at a time, was taken and run by the MD set-up in batch mode. The feed solution was continuously concentrated until the flux became very low or no sufficient volume left to run the test.

3.2.4. Continuous tests

A known initial volume of feed solution was taken and was run by MD in continuous mode for longer period (4 - 5 days) than batch mode. The extended operation was maintained by topping up the retentate with fresh feed when the volume reached a low level. The amount topped up was recorded each time.

3.2.5. Membrane cleaning

The conventional dairy CIP was utilised for membrane cleaning to restore flux after extended operation. First an initial deionised water flush was performed and then the system was cleaned with 1.5% w/w NaOH solution at 80 ˚C for 45 min. After that another deionised water flush was performed and this was followed by a clean with0.8% w/w HNO_3 acid at 60 ˚C for 45 min and then a final deionised water flush.

3.2.6. Determination of MD performance parameters

The determination of membrane performance of the MD process and a particular membrane was based on several parameters such as permeate flux, achievable concentration factors and water recovery, solute rejection of the membrane and the permeate quality.

3.2.6.1. Permeate flux

Permeate flux ($kg/m^2/h$) was calculated using the following equation [67]:

$$Permeate\ flux = \frac{\lfloor (m_2 - m_1)/1000 \rfloor \times 60}{A} \tag{3.3}$$

In the above equation, (m_2 - m_1) is weight of the permeate collected in1 minute intervals, recorded by the computer software Rs Weight. A is the area of the membrane which is 0.014 m^2.

3.2.6.2. Concentration factor and water recovery

Total concentration factor (F_T) was calculated to show the extent of concentration by MD [74].

$$F_T = \frac{V_{F0}}{V_{F(t)}} \tag{3.4}$$

Where V_{F0} is the total volume of the fresh feed added and $V_{F(t)}$ is the volume of the feed (retentate) at specific time, t, of the run.

Water recovery (R_W) was calculated by the ratio between the total volume of the permeate collected (V_P) and total volume of the fresh feed added (V_{F0}).

$$R_W = \frac{V_P}{V_{F0}} \times 100 \tag{3.5}$$

3.2.6.3. Solute rejection

Solute rejection for each component (TOC, TN, K^+, Na^+, Ca^{2+}, Mg^{2+}, P, S) was calculated by

$$Rejection\,\% = \left(1 - \frac{C_P}{C_R}\right) \times 100 \tag{3.6}$$

where C_R is the concentration of a particular component in the retentate and C_P is the concentration of the same component in the permeate [121, 122]. In terms of the permeate concentration the observed concentration was corrected to the actual concentration by reducing the volume of the initial deionised water taken as stripping water in the permeate side. Feed, retentate and permeate samples were collected during the test and analysed for concentration of each component using TOC, TN, ICP and chloride analysis mentioned in Section 3.2.1. Unlike feed/retentate samples, permeate samples were not diluted for the analysis. However, the same method was followed except diluting the permeate samples.

3.2.6.4. Permeate conductivity change

As another measurement of permeate quality in terms of salt penetration, the permeate conductivity was continuously monitored with time using a conductivity meter connected with a web camera where the images were recorded in the computer using the software Flix V3.3.

3.2.7. Fouling analysis

Fouling occurred on membranes with different feed streams was analysed by several techniques mentioned below.

- Scanning electron microscopy
- Fourier-transform infrared and synchrotron infrared
- Fouling component analysis

3.2.7.1. Scanning electron microscopy

The surface of both original and fouled membranes were observed under a bench-top scanning electron microscope (SEM- Nikon/JEOL Neo-Scope JCM-5000). Before SEM, the membranes were dried in an oven at 50 °C overnight to remove moisture. Then the sections of membranes were placed on small sample holders and gold coated(Nikon/JEOL Neo-Coater) for few minutes prior to observe under SEM. The SEM images of the original and fouled membranes were compared to identify the fouling behaviour.

3.2.7.2. Fourier-transform infrared and synchrotron infrared

The fouling layer components were analysed for its functional groups by ATR Fourier-transform infrared (FTIR- Shimadzu IRAffinity-1, Japan). Both original and fouled membranes were tested by FTIR and the corresponding IR spectra was compared against the reference samples to identify the material functional groups, which in turn identifies the fouling components present on the membrane.

For the original PTFE and sweet whey fouled PTFE membranes, synchrotron IR micro-spectroscopy was carried out at the Australian Synchrotron. The samples for this were prepared as thin sections at Hawthorn Histology, Melbourne to run under transmission mode. Cross sections of the fouled membrane were embedded in a block of paraffin wax and then it was cut at a thickness of 4 µm using rotary microtome. The cut sections were then transferred into a water bath at 50 °C and collected onto CaF_2 windows (Crystran Ltd, UK) followed by drying at 60 °C for about 20 minutes before analysing under IR. The IR spectra for original PTFE and sweet whey fouled PTFE were compared to identify the fouling materials on the fouled membrane.

3.2.7.3. Fouling component analysis

The fouling material was removed from the membranes and analysed [69]. This was carried out by cutting a fouled strip from the membrane having an area of 15 cm^2 and scraping then dissolving the fouling layer in a known volume of deionised water at 50 °C. The scraping and dissolving was done until the membrane looked clear without fouling and all the materials dissolved in the solution. The resulting solution was analysed for different components (TOC, TN, K^+, Na^+, Ca^{2+}, Mg^{2+}, P, S) by TOC, TN and ICP. The samples were diluted before the analysis to be within the instruments' detectable concentration range. Some fouling solutions (UF permeate of salty whey and IX-regen) were also analysed for proteins, lactose, fat and chloride ions by Dairy Technical Services Australia. Finally, the average fouling by each component on the membrane was calculated as µg/cm^2 of the membrane.

3.2.8. Analysis of cold and hot filters

The cold and hot filters having a pore size of 1µm used for UF permeate of salty whey and ion exchange regeneration solutions were analysed to study what the main solids captured in the filters separately. A piece of the filter media was cut and first treated with 1.5% w/w NaOH solution. The filter strip was kept in the solution for 2 hours at 80 °C and the substances in the filter were extracted to the NaOH solution. After that the same filter strip was placed in 0.8% w/w HNO_3 solution for 2 hours at 60 °C and the substances left in the filter were extracted to the HNO_3 solution. The same procedure was carried out for both cold and hot filters. The resulting NaOH and HNO_3 solutions were analysed for TOC, TN, ICP, proteins, lactose, fat and chloride ions.

3.2.9. Statistical Analysis

For the tests done with three replicate samples, standard error of the mean (*SEM*) is reported based on 95% confidence interval calculated from three replicate samples.

$$SEM = \frac{SD}{\sqrt{n}} \tag{3.7}$$

SD is the standard deviation of the value of 3 replicate samples and *n* is the number of replicate samples which is 3. The *SEM* calculated as per above formula covers only 68% of the population. Therefore, the *SEM* calculated as above has to be multiplied by 1.96 to obtain the *SEM* at 95% confidence interval. The *SEM* at 95% confidence interval is then calculated as a percentage and this percentage is shown with ± next to average value of three replicate samples for each component in tables.

Chapter 4. Sweet Whey Processing by MD

4.1. Introduction

As outlined earlier, sweet whey is the liquid remaining after coagulation of caseins by enzymes in cheese making [70]. The processing of sweet whey at the cheese making establishment where the sweet whey samples used in this study were sourced involves a number of membrane based separations. The sweet whey first goes through UF treatment where valuable proteins are recovered. The permeate then goes though NF treatment for lactose recovery. The last stage in this treatment process involves recovery of valuable water from the NF permeate by treating it using RO. This chapter describes the application of MD to the RO retentate left over from this process. The aim of this MD treatment is further recovery of valuable water and reduction of the volume to facilitate disposal. The RO retentate of sweet whey processing (SWROR) was first analysed for several components to study the chemical nature of the feed stream. The viability of MD to process SWROR was tested using three different membranes having different chemistries, i.e. Hydrophobic PTFE membrane (HP), hydrophobic and oleophobic acrylic copolymer membrane (HOA-0.45) and hydrophilic coated PTFE membrane (HCP). The membrane performance was determined by factors such as permeate flux, achievable concentration factor, water recovery, solute rejection and the permeate quality.

The membrane that achieved the highest flux and concentration factor prior to fouling was then further tested in continuous mode with conventional CIP membrane cleaning performed daily in order to study how CIP can affect the performance. The fouling layer formed on this membrane during MD treatment of SWROR was studied using chemical analysis, SEM imaging and FTIR spectroscopy.

4.2. Composition of SWROR

4.2.1. Total solids of SWROR

The total solids (TS) of the SWROR measured by the dry sand method was found to be 20,000 mg/L (2%) which was less than average TS value of sweet whey which is approximately between 5.3 – 7.9% [79]. In following sections, the main contributors for these total solids will be explained.

4.2.2. Chemical oxygen demand of SWROR

The chemical oxygen demand (COD) is an important parameter measured in dairy waste characterisation [87, 123]. COD is the amount of oxygen required to completely oxidise organic carbon to CO_2 [124, 125]. Therefore, COD is an indication of the amount of organic compounds present in a particular dairy stream.

The average COD level of SWROR measured by the HACH method was 19,200 mg/L. This value is lower than the COD of sweet whey on its own which is usually between 65,000 – 80,000 mg/L [126, 127]. This is because the tested sweet whey was already filtered through UF and NF which separates proteins and lactose respectively. However, there is still a considerable amount of organic matter present in SWROR as the COD value was about 19,200 mg/L. Therefore, it is important to analyse the concentration of organic components of SWROR.

4.2.3. TOC and TN of SWROR

The measured total organic carbon (TOC) and total nitrogen (TN) concentrations in the SWROR feed are shown in Table 4.1.

Table 4.1 TOC and TN of SWROR

Component	Concentration (mg/L)
TOC	6050 ± 1.5%
TN	987 ± 8.8%

Standard error of the mean is reported based on 95% confidence interval calculated from three samples

TOC was approximately 6050 mg/L and whereas the TN was about 987 mg/L which indicates that considerable amount of organic matter is present in the tested SWROR. Although TOC and TN values do not directly emphasize the exact organic matter present, these values could indicate the presence of compounds like lactose and proteins which are main organic compounds present in sweet whey. However, these TOC and TN values are lower than the expected values for sweet whey which usually contains about 5% lactose, 1% protein and 0.5% fat [71, 79].

The higher than expected TOC and TN may be attributed to less than total rejection of lactose and proteinaceous matter by UF and NF [74] which can depend on several factors such as membrane material, membrane cut-off and operating parameters like pH [128, 129]. A study based on two step purification of whey by UF and NF, for example, found that UF (cut-off of 2500 g/mol) could be able to reject almost all the whey proteins, however, it could allow penetration of some peptides, amino acids, non-protein nitrogen which were present in the UF permeate [130]. This study also showed that although NF of the UF permeate could separate the polypeptides, the purification is favoured by lower pH where the selectivity for peptides is higher than at higher pH values [130]. Therefore there is also the possibility for some polypeptides or other proteinaceous matter to pass through NF membranes as well. Furthermore, some studies have shown that lactose was present in NF permeate and that lactose rejection depended to some extent on the operating pressure. Higher lactose rejection (89%) has been observed at 2 MPa than at 1 MPa (85%) [71, 74].

4.2.4. Mineral analysis of SWROR

The measured concentrations of some of the major mineral components of the SWROR are shown in Table 4.2.

Table 4.2 ICP Mineral analysis of SWROR

Component	Concentration (mg/L)
K^+	7540 ± 1.4%
Na^+	1820 ± 5.4%
P	462 ± 8.6%
Ca^{2+}	41 ± 5.7%
Mg^{2+}	43 ± 9.2%
S	42 ± 7.1%

Standard error of the mean is reported based on 95% confidence interval calculated from three samples

Potassium was found to be the most abundant cation. This is consistent with the expected composition of milk [131], and the expected low rejection of monovalent ions by the preceding UF and NF membrane treatments. The relatively lower Ca^{2+}, Mg^{2+}, S (sulphate) and P (phosphate) concentration than that of milk (Ca^{2+} 1230 mg/L, Mg^{2+} 120 mg/L, S 300 mg/L) [132] may be attributed to the NF treatment [71, 99, 133, 134].

4.2.5. Conductivity and pH of SWROR

The initial pH of the SWROR was about 6.0 and the conductivity was approximately 16.2 mS/cm. This high conductivity could be mainly due to the high concentration of salts like Na^+, K^+ and other minerals (see Table 4.2).

4.3. MD tests of SWROR

4.3.1. MD performance of using HP membrane

The permeate flux and concentration factor (F_T) achieved during batch mode MD of the SWROR using the hydrophobic PTFE membrane are shown in Figure 4.1.

The initial flux was about 13 kg/m^2/h and this rapidly increased up to17 kg/m^2/h in the first hour. This initial rise and stabilisation of flux is due to the establishment of the temperature difference across the membrane and stabilisation of fluid dynamic conditions inside membrane module (vapour saturation inside membrane pores) [90, 135]. The flux declined gradually after approximately 5 hours as the concentration of the feed increased. This gradual flux decline is possibly a result of fouling of the membrane surface and/or the inside of the membrane pores caused by concentration polarisation and as a result of the continuous concentration of the feed which ultimately reduces the vapour transport through the membrane [66, 68, 90]. The rate of decline in flux was found to accelerate as the F_T approached 5. The sudden flux drop after 17.5 hours (as marked on the graph) was due to a sudden decrease in cross flow due to a pump malfunction, possibly leading to rapid build-up of a fouling cake layer when no cross flow existed across the membrane surface. The flux decline observed prior to interruption of flow was found to continue on resumption of flow, but from a lower flux value before the pump stopped.

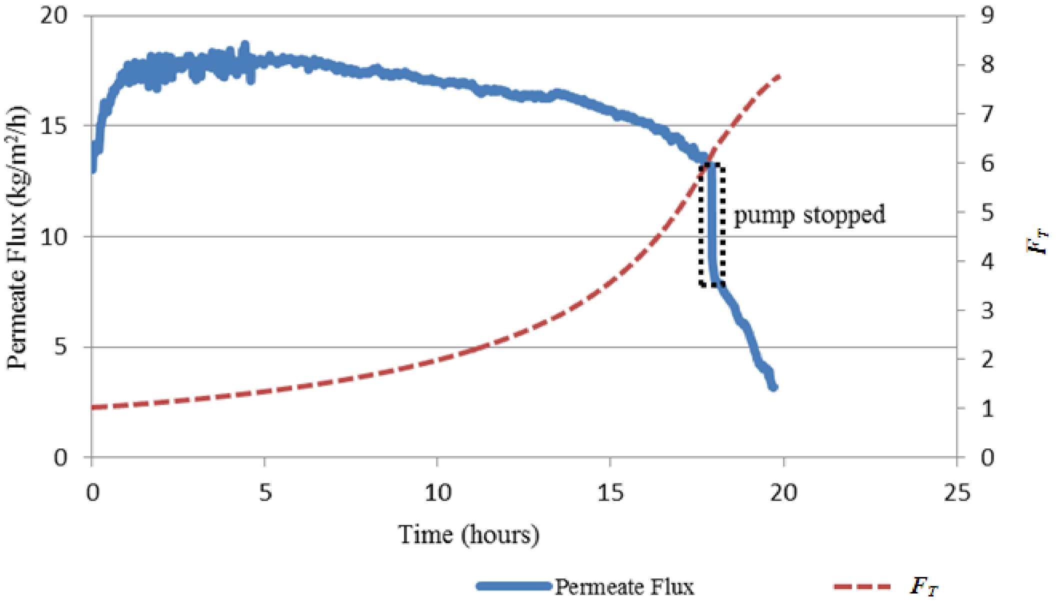


Figure 4.1 Permeate flux & F_T over time – HP membrane

Despite the permeate flux decline over time, the SWROR could be concentrated up to $F_T \approx 6$ when the flux was around 13kg/m^2/h. This is a practicable flux and not a significant flux decrease from the initial flux (17 kg/m^2/h). These results indicate that membrane cleaning after approximately 17 hours is required if higher F_T values are required. If, however, F_T values of 6 are sufficient, more treatment may be possible without membrane cleaning. It would be possible to maintain the flux at 13 kg/m^2/h if the retentate is diluted with more fresh feed before the F_T value exceeds 6.

The permeate conductivity is shown in Figure 4.2 and can be seen to increase from 2.1 µS/cm to 16.6 µS/cm during the test, which is expected when the retentate reaches high concentrations as observed by Hausmann et al. (2011) in MD of different dairy streams such as whole milk, skim milk, whey and lactose [67]. In addition, this permeate conductivity increase may be due to salt passage caused by operating at a pressure higher than the LEP of a small number of very large pores present in the membrane. However, if retentate salts penetrate to the permeate side in a large amount there should be a considerable sudden increase in the permeate conductivity which could not be observed in this case. This can be further confirmed by the rejection of solutes which remained high (see Table 4.3) and, the final appearance of the SWROR fouled HP membrane (see Figure 4.3) did not show any wetted spots/areas (the membrane becomes translucent when wet).

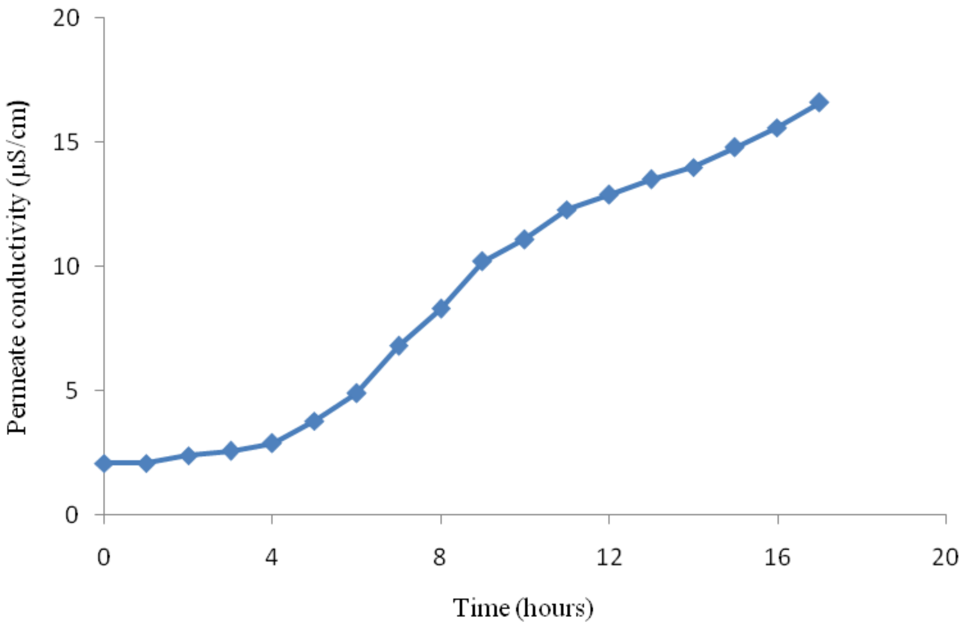


Figure 4.2 Permeate conductivity over time – HP membrane

As shown in Table 4.3 all the solutes tested showed a rejection above 99.9% even at high solute concentrations of the final retentate ($F_T > 7$) indicating the capability of MD to produce high quality permeate using the HP membrane.

Table 4.3 Solute rejection of HP membrane

Component	Final retentate concentration (mg/L)	Final permeate concentration (mg/L)	Rejection (%)
TOC	43,375 ± 2.9%	15 ± 3.8%	99.97
TN	7,002 ± 2.5%	2 ± 5.4%	99.97
K^+	54,300 ± 0.3%	3 ± 2.5%	99.99
Na^+	12,160 ± 2.0%	2 ± 1.4%	99.98
P	3,005 ± 3.9%	0.1 ± 7.5%	99.99
Ca^{2+}	201 ± 5.4%	0.1 ± 12.6%	99.95
Mg^{2+}	281 ± 6.9%	0.01 ± 7.0%	99.99
S	278 ± 6.3%	0.2 ± 9.4%	99.93

Standard error of the mean is reported based on 95% confidence interval calculated from three samples

Figure 4.3 SWROR fouled HP membrane

4.3.2. MD performance of SWROR on HOA-0.45 membrane

The permeate flux and concentration factor (F_T) achieved during batch mode MD of the SWROR using the hydrophobic and oleophobic acrylic copolymer membrane (HOA-0.45) are shown in Figure 4.4.

The initial flux was found to be about 6 kg/m^2/h which was quite stable up to approximately 16 hours due to the membrane stabilisation period. There was a slight increase in the flux (to ~ 7 kg/m^2/h) after this period possibly as a result of more saturation of the membrane pores with vapour. However, after this point the flux was found to decline due to fouling as the feed concentration increased. The sudden flux drops (as marked) can be attributed to pump malfunction leading to a rapid build-up of a fouling when no velocity existed across the membrane surface. The final flux reached (< 1 kg/m^2/h) where F_T was 5. These results indicate that membrane cleaning after approximately 35 hours is required if higher F_T values than 3 are required. If, however, F_T values of 3 are sufficient, more treatment may be possible without membrane cleaning by dilution of the feed with more fresh feed before the F_T value exceeds 3. The expected flux for this membrane is ~ 5 kg/m^2/h.

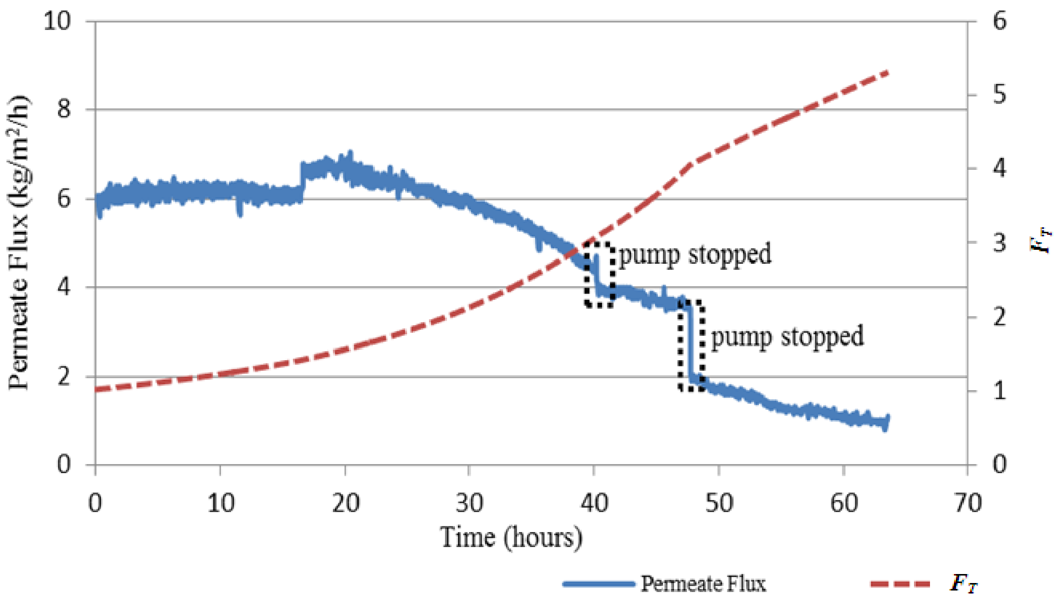


Figure 4.4 Permeate flux & F_T over time – HOA-0.45 membrane

In terms of the permeate quality, the permeate conductivity is shown in Figure 4.5. and can be seen to increase from 2.1 µS/cm to 46.7 µS/cm during the test which is possible when the retentate reach high concentrations (F_T > 5) or a slight salt passage caused by operating under higher pressure than LEP for a small number of large pores in the membrane as explained for the HP membrane. However, this permeate conductivity increase was not due to a severe wetting or salt penetration to the permeate side which could be further confirmed by the rejection of solutes shown in Table 4.4 and also the Figure 4.6, the final appearance of the SWROR fouled HOA-0.45 membrane which did not show any wetted spots/areas.

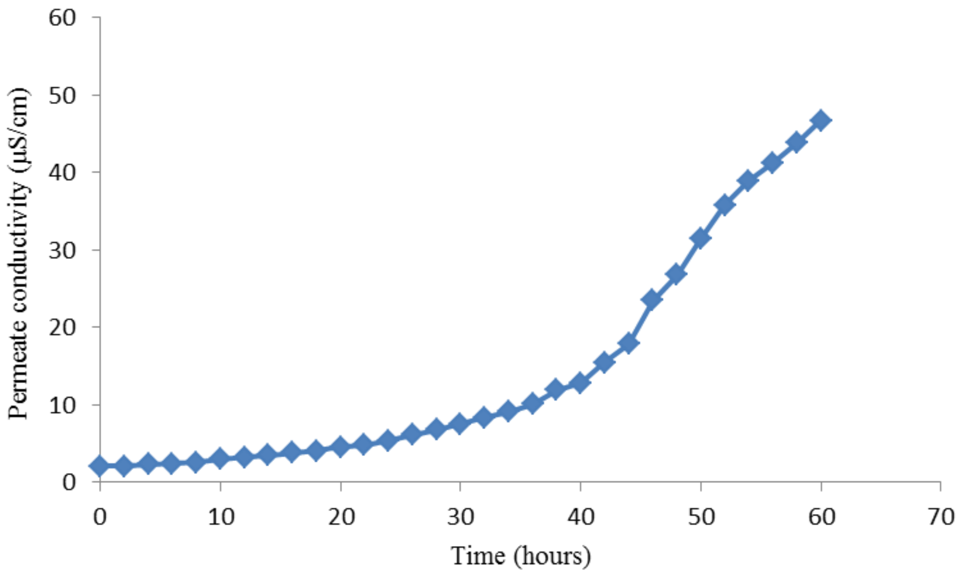


Figure 4.5 Permeate conductivity over time – HOA-0.45 membrane

As shown in Table 4.4 all the solutes tested showed a rejection above 99.8% even at high solute concentrations of the final retentate ($F_T > 5$) indicating the capability of MD to produce high quality permeate using the HOA-0.45 membrane.

Table 4.4 Solute rejection of HOA-0.45 membrane

Component	Final retentate concentration (mg/L)	Final permeate concentration (mg/L)	Rejection (%)
TOC	32,789 ± 3.4%	7 ± 3.9%	99.98
TN	5,930 ± 1.8%	8 ± 0.8%	99.87
K^+	39,187 ± 0.3%	16 ± 3.8%	99.96
Na^+	7,969 ± 1.8%	10 ± 4.8%	99.87
P	1,876 ± 10.4%	0.3± 6.1%	99.98
Ca^{2+}	226 ± 13.8%	0.1 ± 6.8%	99.96
Mg^{2+}	228 ± 15.2%	0.1 ± 12.6%	99.96
S	216 ± 8.7%	0.3 ± 10.3%	99.86

Standard error of the mean is reported based on 95% confidence interval calculated from three samples

Figure 4.6 SWROR fouled HOA-0.45 membrane

4.3.3. MD performance of SWROR on HCP membrane

A volume of 5 L of SWROR was taken as the initial feed and run by DCMD in batch mode using the HCP membrane. Figure 4.7 outlines the performance of the HCP membrane in terms of permeate flux and F_T over time.

The permeate flux started from about 6 kg/m^2/h and this was stable for first few hours due to stabilisation of the membrane conditions. After this period the flux started declining gradually due to fouling as explained in the section 4.3.1 as the feed is continuously concentrated. The final flux reached < 1 kg/m^2/h where the F_T was about 4. However, as of the HOA membrane this is not a practically viable flux. Thus, the F_T of SWROR has to be maintained below 2 in order to maintain a feasible flux which is 4 kg/m^2/h.

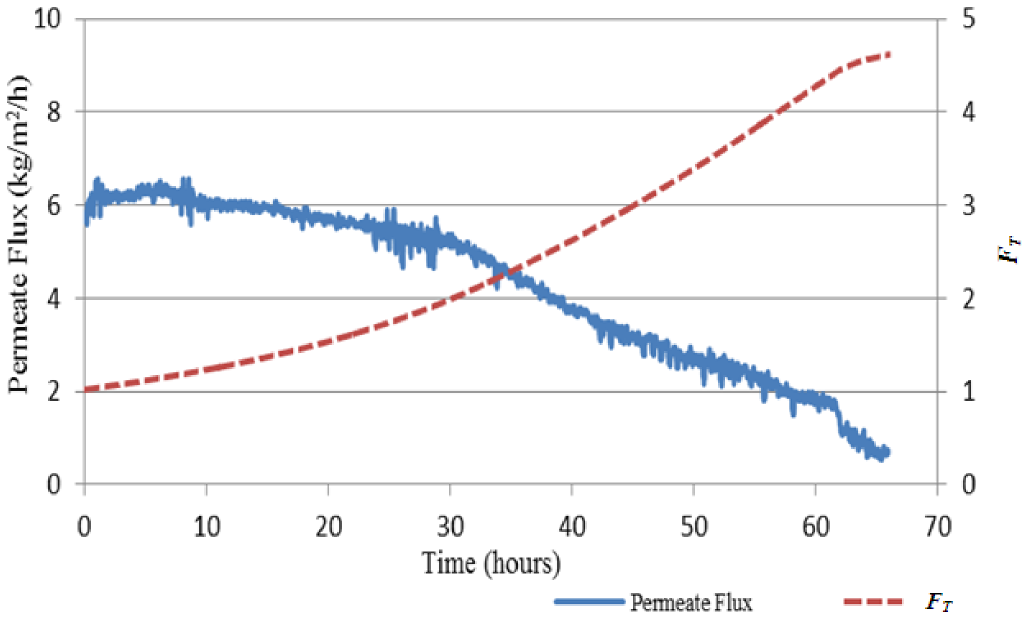


Figure 4.7 Permeate flux & F_T over time – HCP membrane

In terms of the permeate quality, permeate conductivity and the rejection of the solutes were mainly monitored. Figure 4.8 outlines the permeate conductivity over time. Permeate conductivity increased from 1.9 µS/cm to 52.2 µS/cm during the test which is possible when the retentate reaches high concentrations ($F_T > 4$) as explained for the HP and HOA-0.45 membranes. Thus, this permeate conductivity increase was not due to a severe wetting or salt penetration to the permeate side. This could be further confirmed by the rejection of solutes shown in Table 4.5 and also the Figure 4.9, the final appearance of the SWROR fouled HCP membrane which did not show any wetted spots/areas.

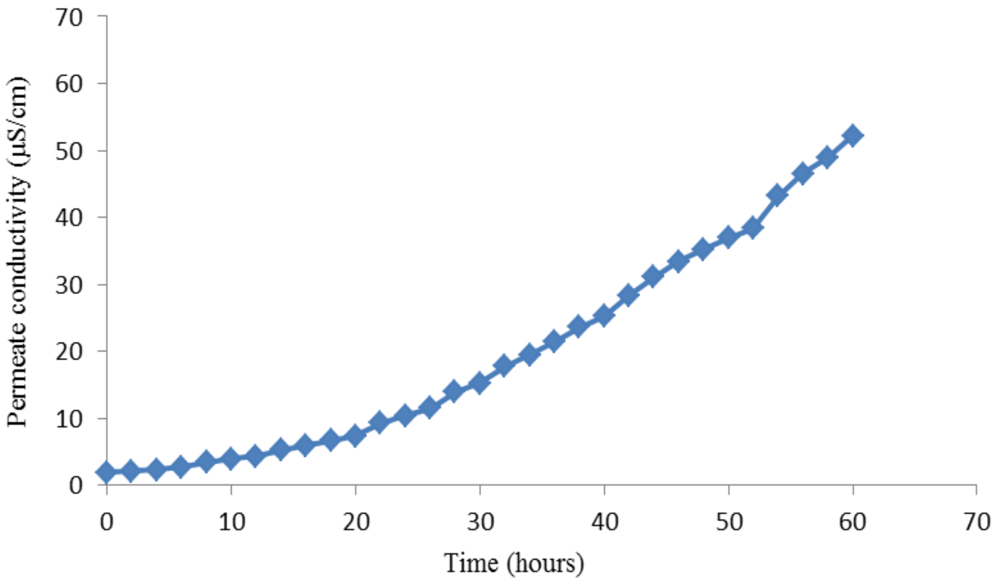


Figure 4.8 Permeate conductivity over time – HCP membrane

Table 4.5 Solute rejection of HCP membrane

Component	Final retentate concentration (mg/L)	Final permeate concentration (mg/L)	Rejection (%)
TOC	26,732 ± 1.8%	5 ± 7.6%	99.98
TN	4,698 ± 9.9%	2 ± 13.6%	99.96
K^+	32,367 ± 0.7%	18 ± 1.4%	99.94
Na^+	6,848 ± 4.3%	9 ± 5.0%	99.87
P	1,587 ± 9.7%	1 ± 8.5%	99.94
Ca^{2+}	203 ± 6.4%	0.5 ± 5.7%	99.75
Mg^{2+}	192 ± 5.7%	0.3 ± 14.9%	99.84
S	196 ± 14.8%	0.4 ± 8.2%	99.80

Standard error of the mean is reported based on 95% confidence interval calculated from three samples

Figure 4.9 SWROR fouled HCP membrane

As shown in Table 4.5 all the solutes tested showed a rejection above 99% even at high solute concentrations of the final retentate ($F_T > 4$) indicating the capability of MD to produce high quality permeate using the HCP membrane.

4.3.4. Selection of most suitable membrane for MD of SWROR

According to the membrane performance discussed above for HP, HOA-0.45 and HCP membranes, all three membranes seemed to work well for MD in terms of achieving high concentration factors where all three membranes could achieve F_T above 4. In addition, all three membranes showed final rejection above 99.8% for all the solutes tested indicating a good quality permeate. However, in terms of the permeate flux HP membrane showed the highest initial flux (17 kg/m^2/h) compared to the HOA-0.45 and HCP membranes. Hence, it can be stated that HP membrane is the most suitable membrane for MD of SWROR processing over the other two membranes as this can perform more efficiently in MD under tested conditions due to its highest permeate flux.

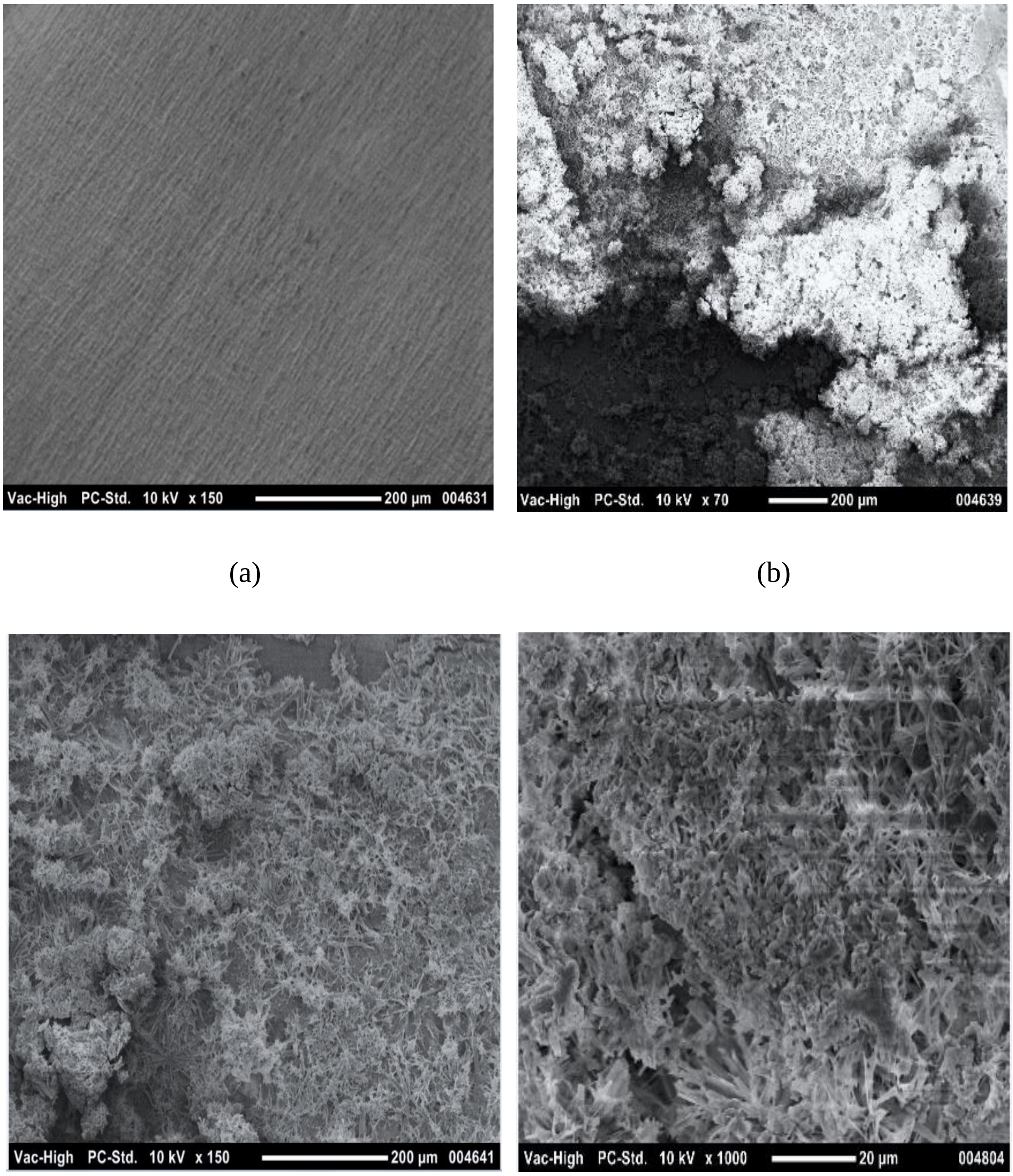
As HP membrane appeared to be the most suitable membrane for SWROR processing by MD, it was further studied to investigate the SWROR fouling characteristics on the HP membrane and also for its suitability for a long term test operated in continuous mode. This continuous mode test was performed with CIP each day to investigate the effects of CIP on the MD performance of the HP membrane.

4.4. SWROR fouling on HP membrane

The fouling layer formed on the HP membrane during the batch mode MD treatment of SWROR was analysed using SEM, IR analysis and chemical analysis.

4.4.1. SEM of SWROR fouled HP membrane

Figure 4.10 shows the SEM images of the original HP membrane surface and SWROR fouled HP membrane surface. The fouling seemed to be a combination of crystalline and filamentous material. Although these SEM images on its own cannot define the type of foulants, the morphology of the images shows somewhat similar fouling appearance observed by Hausmann et al. (2013) for whey fouled PTFE membrane [68, 69].



(a) (b)

(c) (d)

Figure 4.10 SEM of HP membrane (a) original (b)-(d) SWROR fouled

As shown in the Figure 4.10.b, 4.10.c and 4.10.d the fouling seemed to consist of crystalline-like structures which can be comparable to lactose crystals observed by

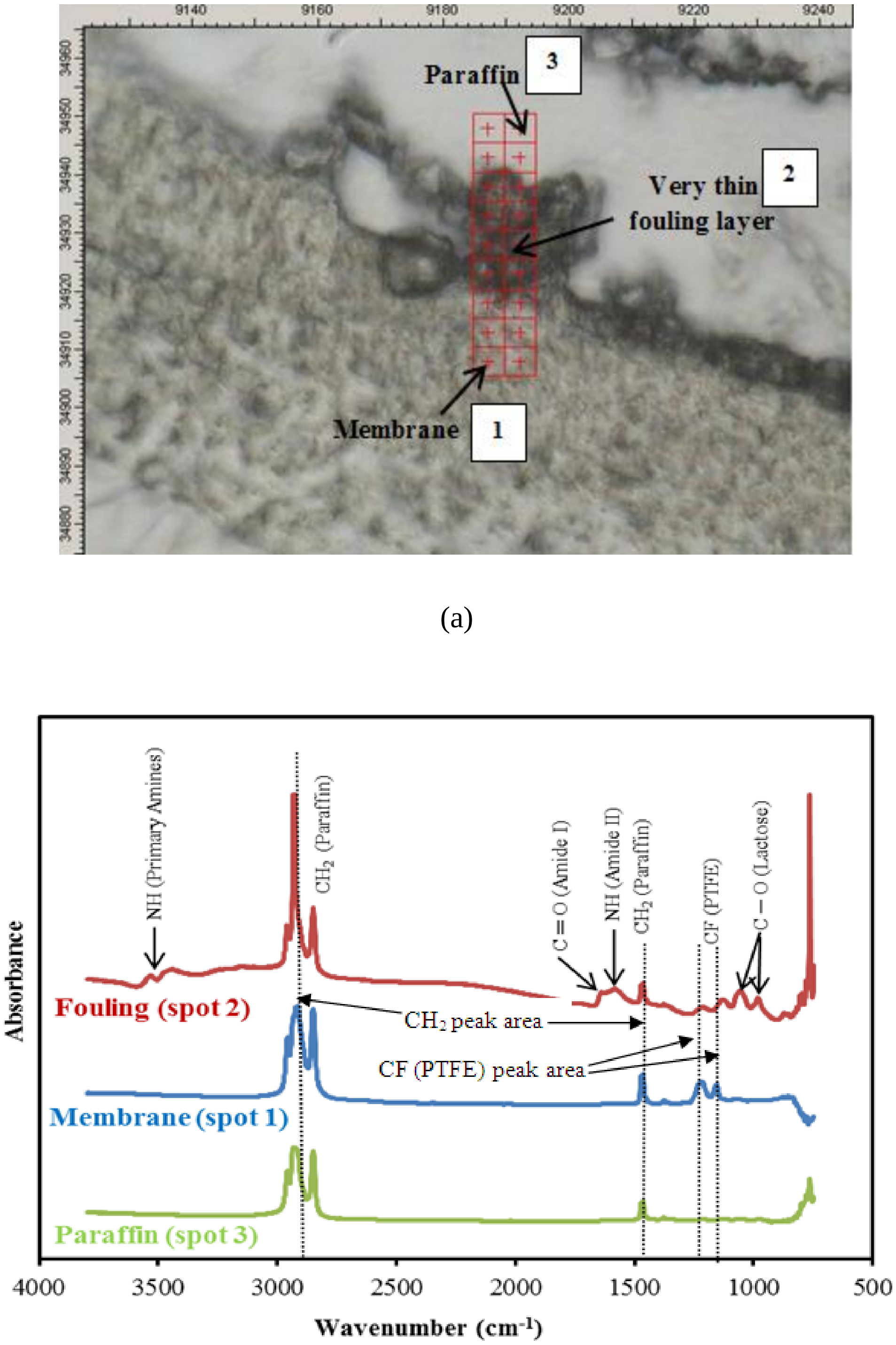
Hausmann et al. (2013) on whey fouled PTFE. In addition, there seemed to be proteins-like lumps spreading across the membrane which is also a similar observation to whey protein fouling observed by Hausmann et al. (2013)[68, 69].

4.4.2. IR analysis of SWROR fouled HP membrane

Figure 4.11.a shows the IR microscope grid map covering a cross section of the fouled membrane. Figure 4.11.b shows IR spectrum for spot 1, 2 and 3 (spots as marked in Figure 4.11.a) representing PTFE membrane, fouling layer and paraffin respectively.

The peaks for wavenumbers at 2916 cm^{-1} and 2856 cm^{-1} are related to H─C─H stretching in paraffin whereas 1466 cm^{-1} is related to H─C─H bending in paraffin [136, 137]. These peaks are common for all three spectra (paraffin, membrane, fouling) as paraffin interference across the entire sample is likely.

The two peaks for wavenumbers at 1221 cm^{-1} and 1156 cm^{-1} are for C─F stretching in PTFE [138] from the membrane material. This however is shown in fouling spectrum (spot 2) as well as the spot 2 can represent both membrane and fouling as marked in Figure 4.11.a. The peaks for wavenumbers at 1645 cm^{-1} and 1597 cm^{-1} could be related to Amide I and Amide II respectively and the double peak at 3484 cm^{-1} and 3398 cm^{-1} for N─H stretching of primary amines [136, 137, 139], indicating the presence of proteinaceous matter in the fouling. There are also peaks at 1058 cm^{-1} and 987 cm^{-1} which can be due to presence of lactose and crystallised lactose respectively [139, 140].



(a)

(b)

Figure 4.11 IR analysis of SWROR fouled HP membrane (a) grid map (b) IR spectra

4.4.3. Chemical analysis of fouling components

Chemical analysis of the fouling was performed by dissolving the fouling layer on a membrane strip in deionised water followed by the component analysis of the resulting solution. Table 4.6 shows the results of the chemical analysis of fouling in terms of average composition each foulant layer constituent per cm^2 of membrane area and their contribution to the fouling as a proportion of the feed composition.

The fouling layer was found to have relatively higher concentration of TOC and TN which is an indication of organic matter present in the fouling layer. TOC measurement may represents lactose and proteins in fouling confirmed by the IR analysis mentioned above. Although, TN measurement is not a direct indication of proteins, there can be some representation of proteins by TN as proteins was confirmed to be present in fouling by the IR analysis [69]. TN also shows the highest contribution for fouling as a proportion of the feed composition.

In terms of minerals, K^+ and Na^+ were the most abundant as they are also present in high amounts in the fresh feed. Although these ions mostly exist as free ions in milk, they can be bound with the membrane or proteins by charge interactions [69]. Similar to the IR spectra data which did not show any peaks for calcium phosphate, this chemical analysis also shows that phosphorus is not present in significant amounts in the fouling compared to TOC, TN, K^+ and Na^+. However, the contribution of Ca^{2+} as a proportion of the feed composition appears to be high which indicates that there can be some amount of calcium phosphate present in the fouling.

Table 4.6 Chemical analysis of SWROR fouling

Foulant layer constituent	Average fouling ($\mu g/cm^2$)	Fouling as a proportion of feed composition (%)
TOC	1700 ± 2.9%	0.79
TN	801 ± 1.3%	2.27
K^+	213 ± 3.7%	0.08
Na^+	92 ± 6.6%	0.14
P	9 ± 16.2%	0.05
Ca^{2+}	20 ± 11.3%	1.38
Mg^{2+}	3 ± 0.0%	0.20
S	3 ± 0.0%	0.20

Standard error of the mean is reported based on 95% confidence interval calculated from three samples

Overall, it can be stated that the fouling consists more of organic matter than inorganic matter. This can be related to findings of Hausmann et al. (2013) which confirmed that proteins could have direct interactions with the membrane and contribute to most of the fouling [69]. This fouling was found to be faster when salts are present in the feed. In contrast, lactose appeared not to interact directly with membrane, however, can interact with other components and contribute to fouling [69]. Therefore, the fouling could contain more with proteins and lactose. Although the fouling layer subject to IR did not contain much calcium phosphate to show any indicative peaks for, Table 4.6 results show a relatively high contribution of Ca^{2+} for fouling as a proportion of feed composition which indicates that Ca^{2+} is present in fouling.

As fouling was found to be mostly organic and slightly inorganic the best membrane cleaning method for SWROR fouled membrane is a combination of alkaline and acid cleaning which is the general CIP used in the dairy industry [113, 114]. Thus, for the continuous mode operation, the conventional dairy CIP was followed. This involved a NaOH clean to remove organic fouling followed by a HNO_3 acid clean to remove inorganic fouling [109, 110].

4.5. Semi-continuous mode test of SWROR on HP membrane

This semi-continuous mode test was performed for about 5 days with CIP each day where the retentate was diluted by adding fresh feed. The performance is shown in Figure 4.12. Flux started at about 17 kg/m^2/h, then remained stable for few hours after which started to drop gradually due to fouling in a similar trend to the batch test. At this point, the CIP was performed (CIP 1) but little improvement to flux was observed, suggesting incomplete removal of the fouling layer. Upon the addition of fresh feed into the feed container a short time after CIP 1, however, some of the flux was restored, suggesting that the residual fouling layer that was not removed by the CIP was partly removed by the now less concentrated retentate. The dilution of the retentate by fresh feed can be seen from the sudden drop in F_T.

Another CIP was carried out (CIP 2) which appeared to reduce flux. It is possible that accumulated solids where disturbed by the CIP which acted to block the flow channels of the MD module. The precipitation of solids during DCMD of groundwater has been found to yield similar tendencies, but the use of a filter to catch precipitating solids was found to greatly enhance flux potential at higher concentration factors [141]. Such a filter may offer similar advantages here.

Continued operation from this point saw three more CIPs, and the F_T reached 4. So while CIPs did not restore fluxes to a great extent, the critical feature is that to concentrate up to 4 –fold the incoming in concentration (i.e. MD recovery of around 75%), regular process CIPs did not compromise the MD performance and assisted slightly the flux return. Stable operation fluxes of between 12 and 14 kg/m^2/h were achieved over the 5 day run with daily CIPs.

Figure 4.13 shows the permeate conductivity changes over time throughout the run. The decrease in the conductivity from time to time is attributed to the points where fresh water was introduced to the container at the permeate side which caused the conductivity to decrease. As shown in Figure 4.13, there was an continuous increase in the permeate conductivity after 100th hour from 25 µS/cm to 580 µS/cm even after fresh water was introduced. This permeate conductivity increase may be a sign of showing membrane losing its rejection over a long term operation with daily CIPs. However, despite this permeate conductivity increase, the solute rejection for all solutes tested as shown in Table 4.7 was above 99.9% which indicates a high quality permeate. In addition, there were no wetted spots observed on the final membrane as shown in Figure 4.14 which confirmed that there was no membrane wetting caused by CIP which could be observed by some researchers at ISI in Victoria University in cleaning of whey and skim milk fouled PTFE membrane.

Therefore, it can be stated that the PTFE membrane is a suitable membrane for SWROR processing by DCMD and suitable for operating over a considerable period of time (4 – 5 days).

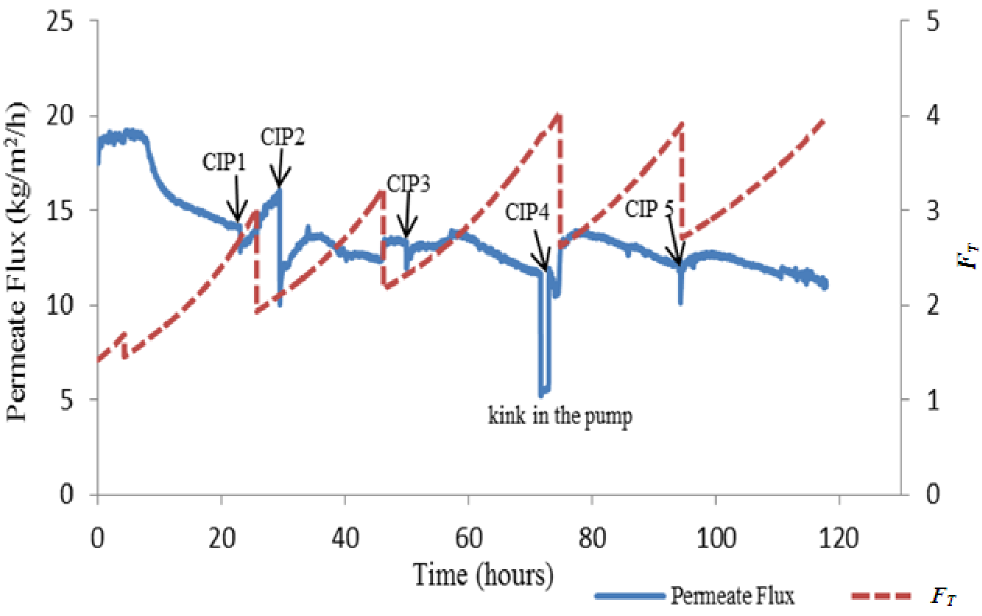


Figure 4.12 Performance of continuous mode test on HP membrane

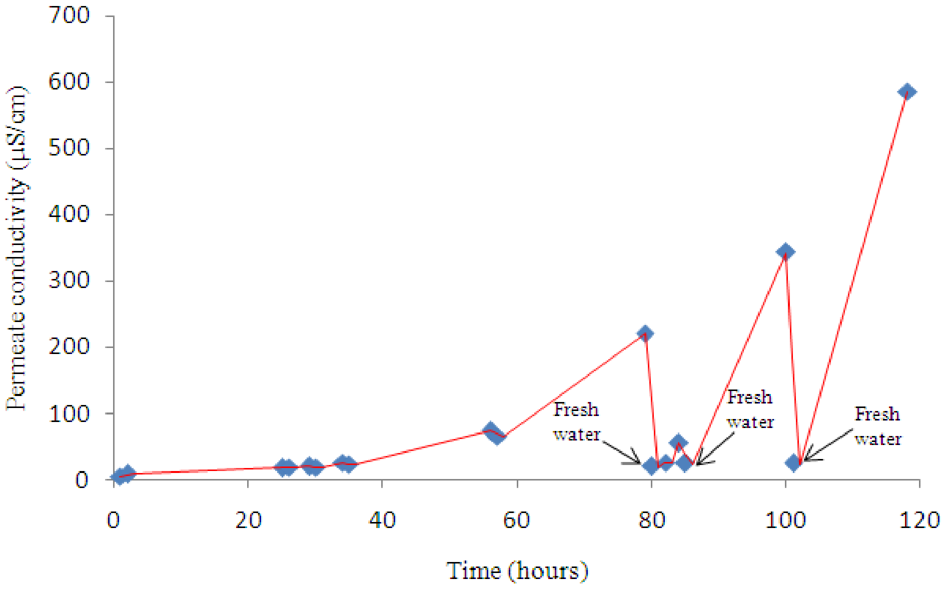


Figure 4.13 Permeate conductivity over time in continuous mode test on HP membrane

Table 4.7 Solute rejection of the continuous mode test

Component	Final retentate concentration (mg/L)	Final permeate concentration (mg/L)	Rejection (%)
TOC	36,218 ± 0.8%	27 ± 9.3%	99.93
TN	5,998 ± 12.4%	5 ± 11.4%	99.92
K^+	45,500 ± 1.8%	32 ± 5.5%	99.93
Na^+	11,800 ± 2.9%	8 ±7.7%	99.93
P	2,991 ± 4.8%	2 ± 8.6%	99.93
Ca^{2+}	180 ± 13.6%	0.1 ±14.0%	99.94
Mg^{2+}	257 ± 6.5%	0.1 ± 11.3%	99.96
S	263 ± 9.7%	0.1 ± 14.0%	99.96

Standard error of the mean is reported based on 95% confidence interval calculated from three samples

Figure 4.14 HP membrane after 5 CIPs in continuous mode test

4.6. Conclusions

Overall, MD was found to be a viable membrane separation technique to concentrate the SWROR and recover high quality potable water.

All three membranes (HP, HOA-0.45, HCP) worked well for MD treatment of SWROR as they could achieve high concentration factors:> 7, > 5 and > 4 for the HP, HOA-0.45, and HCP membranes respectively . Also, all three membranes could produce a high quality permeate with solute rejection above 99% for all the solutes tested. However, HP membrane (PTFE) was selected as the best membrane over the other two as this PTFE membrane showed the highest initial permeate flux (17 kg/m^2/h) which is more efficient in the long run. Thus, PTFE was further studied for its fouling behaviour and selected for the continuous mode operation.

The FTIR and chemical analyses of the fouling layer formed as a result of MD treatment of SWROR using the PTFE HP membrane gave indication of organic fouling by proteins and lactose. Calcium phosphate was also found to be present. This was, however, in relatively smaller quantity. As the fouling was a combination of largely organic and slightly inorganic, the conventional dairy CIP process which involves both NaOH and HNO_3 was selected as the most suitable membrane cleaning method to run under the continuous mode operation with daily cleaning.

In the semi-continuous mode operation with both CIP and concentration factor control via intermittent addition of fresh feed, MD treatment was effective over a 5 day continuous period of operation at concentrating the SWRO up to a 4 times the initial concentration. This equates to a 75% recovery of water for each fresh feed addition. The CIPs did not restore fluxes to a great extent, suggesting that they may not be necessary. The employment of CIP may, however, be desirable for hygiene. As regular process CIPs did not compromise the MD performance and assisted slightly the flux return where a stable operation fluxes of between 12 kg/m^2/hand 14 kg/m^2/h were achieved, CIP employment remains an option.

This study of MD treatment of SWROR has shown that the use of PTFE membrane allows semi-continuous concentration of SWROR to 4 times the original concentration and produce high quality permeate for reuse.

Chapter 5. Salty Whey UF Permeate Processing by MD

5.1. Introduction

This chapter investigates the viability of DCMD to concentrate salty whey UF permeate and recover good quality water. Salty whey is produced as a result of salting process in cheese making where salt is added to expel the excess whey from cheese. When salt is dispersed on the curd, it dissolves with the moisture and diffuses into the curd which causes the expulsion of whey known as salty whey [79, 80].

The tested salty whey had been filtered through UF and the feed solution used in these experiments was the salty whey UF permeate (SUFP). The SUFP was first analysed for several components to study the chemistry of the initial feed stream. The viability of DCMD to process SUFP was first investigated with the conventional hydrophobic PTFE membrane (HP membrane) and its suitability was identified using different parameters such as permeate flux, achievable concentration factor, water recovery, solute rejection and the permeate quality. A novel feature in this work is to include dead end filters to explore the concept of solids recovery during DCMD concentration. The fouling of HP membrane by salty whey UF permeate was analysed using different techniques in order to identify the fouling behaviour and its effects on membrane performance. Considering the risk of membrane wetting resulting from the deposition of fat-like materials onto the hydrophobic membrane surface, another membrane that has a hydrophilic surface coating was also tested.

5.2. Composition of SUFP

5.2.1. Total solids of SUFP

The total solids of the SUFP measured by the dry sand method was found to be 3.3% (33,000 mg/L). According to literature [79], the average amount of total solids in salty whey is between 8% to 10% and it can be seen that this value has reduced more than half due to UF separating most of the organic compounds such as proteins and fats. In following sections, the main contributors for these total solids will be identified and explained.

5.2.2. Chemical oxygen demand (COD) of SUFP

As explained in Chapter 4, Section 4.2.2, COD is an important parameter measured in dairy waste characterisation [87, 123]. COD gives an indication of organic matter present in the sweet whey UF permeate as COD is the amount of oxygen required to completely oxidise its organic carbon to CO_2 [124, 125].

The average COD level of SUFP measured by the HACH method was 15,170 mg/L. The COD of SUFP is lower than the COD of SWROR (19,200 mg/L) discussed in Chapter 4 indicating that SUFP has lower amount of organic matter than SWROR which could be due to the difference in generation of sweet whey and salty whey. Sweet whey is generated at the initial stage of cheese making where most of the whey proteins are separated whereas the salty whey is generated at the end of the process using salts to remove excess whey (see section 5.1). However considering the meaning of COD in this chapter, SUFP should contain a considerable amount of organic matter which will be important in understanding DCMD performance.

5.2.3.Organic composition of SUFP

Table 5.1 shows the average concentration of TOC, TN, proteins, lactose and fat in SUFP.

Table 5.1 Organic composition of SUFP

Component	Concentration (mg/L)
TOC	1975 ± 12.4%
TN	114 ± 7.9%
Protein	1400
Lactose	1000
Fat	268

Standard error of the mean is reported based on 95% confidence interval calculated from three samples

The presence of TOC seems to be mainly from proteins and lactose. However, there is some contribution of fat as well. Although fat and protein are supposed to be removed during UF, this indicates that protein and fat rejection of UF is not 100% [74] and can depend on factors like membrane material, membrane cut-off and operating conditions such as pH [128, 129].

5.2.4. Mineral analysis of SUFP

Table 5.2 shows the concentration of several minerals of SUFP measured by the inductively coupled plasma (ICP) and chloride ions by Volhard titration method.

Table 5.2 Mineral analysis of SUFP

Component	Concentration (mg/L)
K^+	1,455 ± 10.8%
Na^+	25,400 ± 1.5%
P	455 ± 10.7%
Ca^{2+}	1,235 ± 7.3%
Mg^{2+}	159 ± 11.8%
S	82 ± 11.1%
Cl^-	28,000

Standard error of the mean is reported based on 95% confidence interval calculated from three samples

In terms of cations, Na^+ is present in the highest concentration than other cations as this salty whey is treated with additional NaCl in cheese making to remove the excess whey from final cheese [80]. Therefore, unlike in sweet whey, Na^+ is higher than K^+ in salty whey.

Apart from Na^+ and K^+, Ca^{2+} is the other main cation present which had a less presence in SWROR due to removal by NF process. P, Mg^{2+} and S can also be seen in higher concentration than SWROR which could be possible due to absence of NF process to remove these minerals from SUFP. Cl^- is the main anion present which is due to addition of NaCl in cheese whey expulsion process apart from Cl^- ions already present in whey.

Overall, according to the mineral analysis, the total concentration of tested salts is approximately 57,000 mg/L which is in the range of salt concentration in salty whey explained in the literature (4% to 10%) by Blaschek et al. (2007) [79] and Kapoor and Metzger (2004) [80]. This is a high salinity for desalination processes, and RO may not be suitable as its upper limit of salinity is 70,000 mg/L limited by pressure. Thermal processes are more viable as they are not as sensitive to salinity in terms of driving force for evaporation. MD is regarded as a thermal process and thus is suitable for desalination of the salty whey stream.

5.2.5. Conductivity and pH of SUFP

The initial pH of the SUFP was about 4.7 and the conductivity was above 25 mS/cm. This high conductivity is mainly due to the high concentration of salts, specially Na^+ and Cl^- and also other salts like K^+ and Ca^{2+}.

5.3. MD performance of SUFP on HP membrane

A volume of 10 L from SUFP was initially taken as fresh feed and tested by the DCMD equipment. The main feature in this test is the installation of two filters in the feed side before heating (cold filter) and after heating (hot filter) in order to capture any precipitates during the run. The retentate was diluted with fresh feed at two points to run the test continuously for long period (80 hours).

Figure 5.1 outlines the performance of the HP membrane in terms of permeate flux and F_T over time. The additions of fresh feed are indicated on the figure. The flux started from 14 kg/m^2/h and this increased up to 16 kg/m^2/h within a few minutes. This initial flux increase is due to the membrane stabilisation period where the membrane pores are saturated with vapour with time [90, 135]. The reason for the initial F_T above 1 is the feed volume taken by the two filters which has to be taken into account for the calculation. After remaining stable for few hours in the stabilisation period, the flux started to decline gradually with time due to fouling while the feed is continuously concentrated as shown by the increase in total solution concentration factor, F_T. The sudden drop in F_T at about 4th hour was due to the dilution of the retentate by addition of fresh feed of 3.6 L.

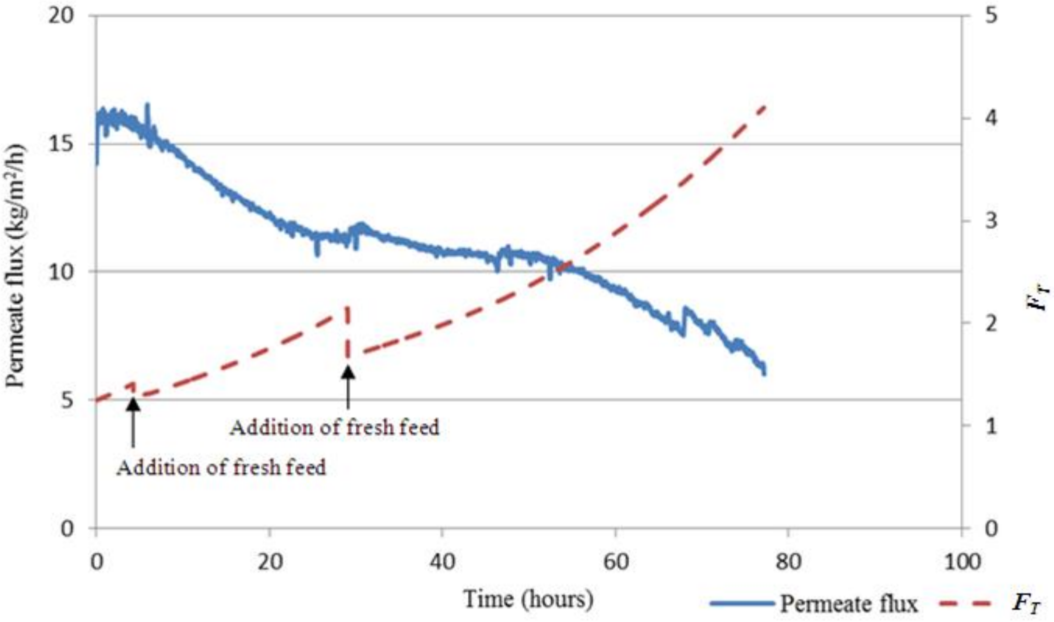


Figure 5.1 Permeate flux and F_T over time - SUFP on HP membrane

While flux declined, a slight increase was observed around the 28th hour. This coincided with the decrease in F_T where the retentate was diluted again with fresh feed of 2.4 L. This is most likely due to removal of some fouling on the membrane surface as the foulants see a drop in concentration in the bulk solution and thus redissolve. After this point, the retentate was continuously concentrated until the flux reach around 6 kg/m^2/h where the F was around 4 which is equivalent to 75% water recovery.

Figure 5.2 outlines the permeate conductivity change over time during the test. There was a continuous increase in the permeate conductivity stating from 0.3 µS/cm to 1415 µS/cm. The rate of increase appeared to occur in three main stages. In the first, the rise appears small until about 30 hours. This is at the point of the second feed addition. The rise become more rapid until around the 55th hour. Finally, from the 55th hour onwards, the rate of conductivity increase again, but a much faster rate than previously. The increase in permeate conductivity is expected as the feed concentration rises since rejection is not 100%. The LEP (see section 2.9.2) is a function of both pore size and hydrophobicity. If a membrane has a wide pore size distribution, the larger pores may have an LEP that is below that required for pumping the feed through the equipment, thus leaking of small quantities of concentrate through the small number of large pores will result. The higher feed concentration, however, does not account for the large conductivity rise. Doubling of the permeate conductivity is expected as the F_T increases from 2 at 22 hours to 4 at 75 hours if the increase is due to feed concentration alone. The conductivity increase is, however, much more from less than 100µS/cm to 1400 µS/cm. This suggests that fouling is lowering the hydrophobicity of the membrane, and hence its ability to retain the concentrate (i.e. wetting).This is further studied by the determination of final solute rejection outlined in the Table 5.3.

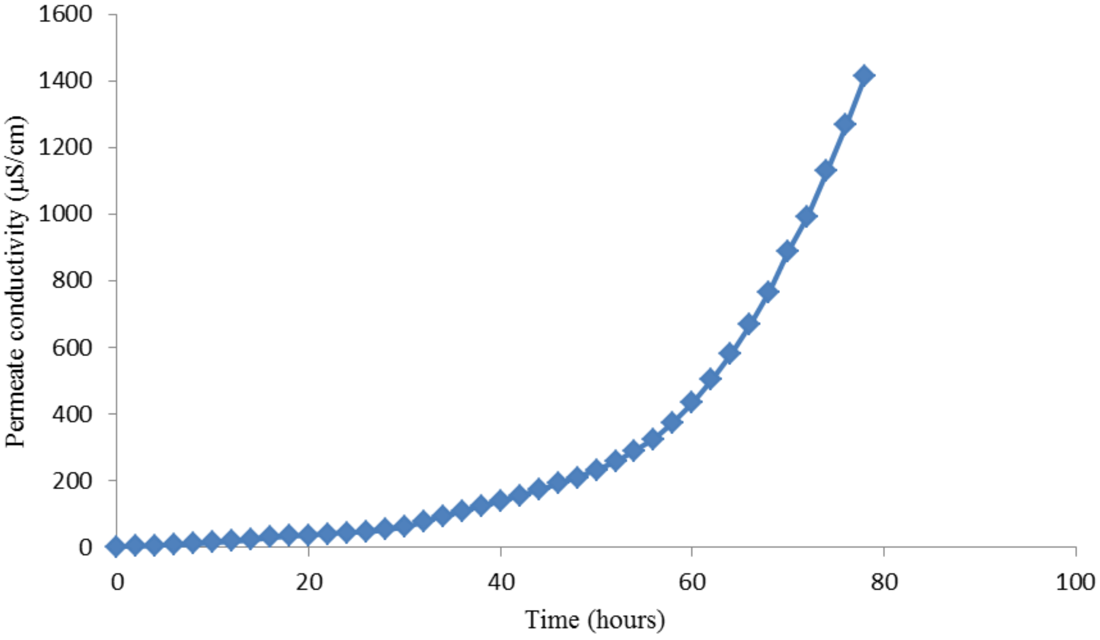


Figure 5.2 Permeate conductivity over time – SUFP on HP membrane

As outlined in the Table 5.3, the rejection of solutes has been compared with individual component concentration factor (F_i) which is calculated in the same way as F_T, but for individual components in the feed. The rejection of the tested solutes varies from 72.87% to 99.78%. Apart from S, inorganic salts show higher rejection than organic components such as protein, lactose and fat indicating some tendency of these organic matter to penetrate to the permeate side. The very low rejection of fat (72.87%) clearly confirmed that there should be a penetration of fats to the permeate side. However, protein and lactose may also have transferred through the membrane as 97% is not considered as a very good rejection in MD (> 99% is typically seen in the lab on clean NaCl solutions). Lower rejection of S could be due to penetration of SO_4^{2-} ions, however, this cannot be confirmed by the these data. According to literature, solute rejection was observed above 99% in well performing MD applications such as desalination and humic acid solution treatment [55, 57, 59, 142]. DCMD of different dairy streams like whole milk, skim milk, whey and lactose solution studied by Hausmann et al. (2011) could also show high rejection above 99% for TOC despite the slight membrane wetting occurred in whole milk test [67].

Therefore, although inorganic salts except S showed comparatively higher rejection, the rejection of fat, protein and lactose cannot be considered as an effective performance which could indicate some wetting issue.

This was clearly proven by the appearance of the final membrane after the test which showed wetted spots as shown in the Figure 5.3. The image shows the feed side and the permeate side of the wetted SUFP treated HP membrane. There were wetted spots in the feed side and also yellow coloured components appeared to transfer to the permeate side which is a clear indication membrane wetting. These yellow components maybe related to organic matter such as fat, protein and lactose showing lower rejection and this will be analysed and discussed in the component analysis of fouling on the wetted membrane in section 5.4. Interestingly, no deposit was found on the feed side indicating the function of the filters to inhibit scaling of the membrane. This effect is already understood for desalination of predominantly inorganic matter (ground water) where a filter after the heat exchanger on the hot loop of DCMD acted to remove precipitating salts prior to the membrane allowing for very high concentration factors to be achieved [141].

Table 5.3 Solute rejection and F_i – SUFP on HP membrane

Component	Final retentate concentration (mg/L)	F_i	Final permeate concentration (mg/L)	Rejection (%)
TOC	6870 ± 7.7%	3.5	103 ± 4.0%	98.50
TN	337 ± 11.8%	2.9	11 ± 5.7%	96.74
Protein	3,500	2.5	100	97.14
Lactose	4,000	4.0	100	97.50
Fat	505	1.9	137	72.87
K^+	4,095 ± 5.6%	2.8	54 ± 6.0%	98.68
Na^+	92,150 ± 1.4%	3.6	652 ± 2.6%	99.29
P	1,840 ± 6.7%	4.0	4 ± 11.6%	99.78
Ca^{2+}	3,150 ± 5.9%	2.6	22 ± 11.0%	99.30
Mg^{2+}	435 ± 10.0%	2.7	2 ± 7.7%	99.54
S	171 ± 13.0%	2.1	14 ± 4.5%	91.81
Cl^-	79,000	2.8	1,000	98.73

Standard error of the mean is reported based on 95% confidence interval calculated from three samples

(a)

(b)

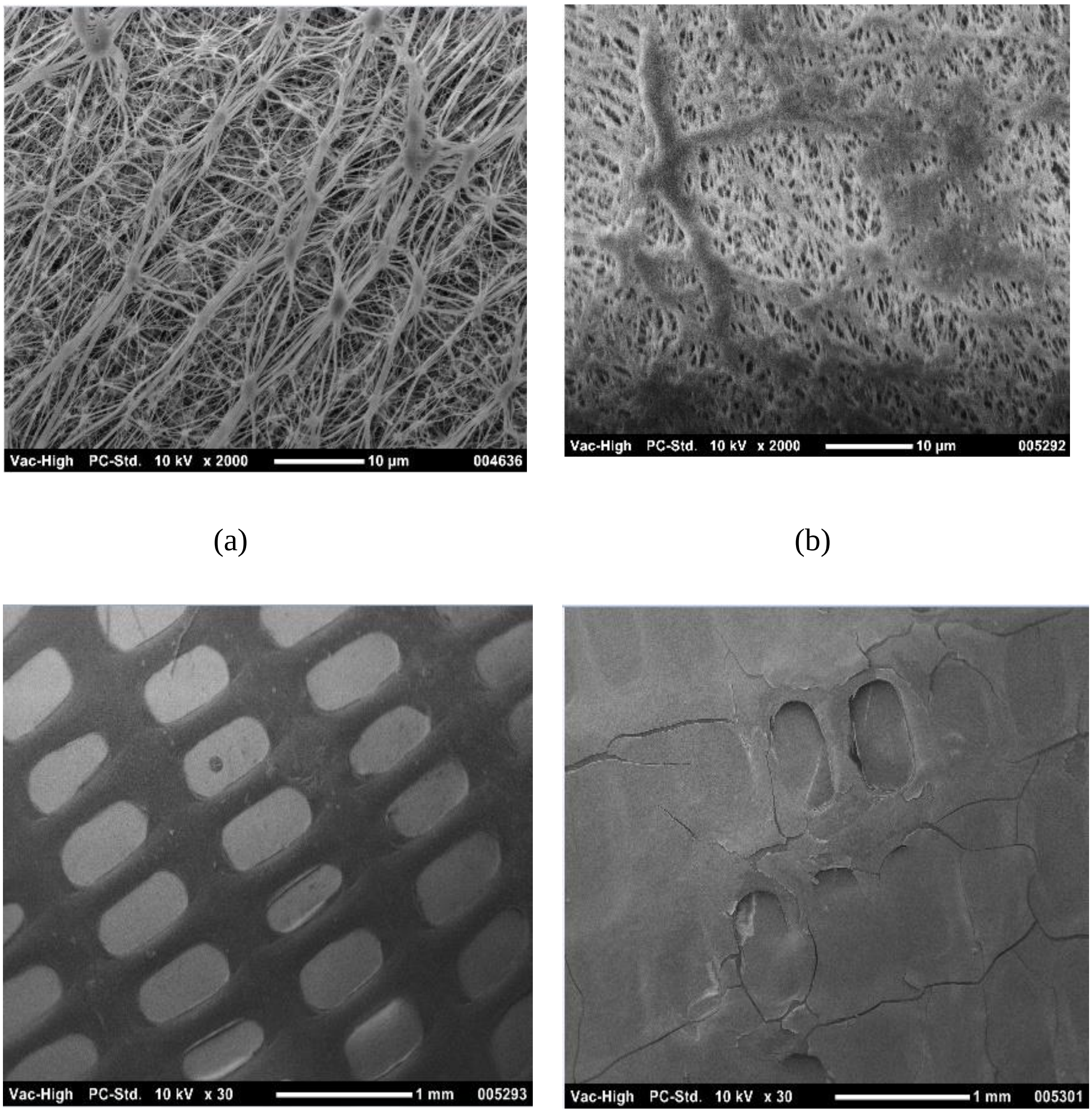
Figure 5.3 HP membrane wetted by SUFP (a) feed side (b) permeate side

5.4. Fouling analysis on HP membrane wetted by SUFP

Fouling on the wetted HP membrane was analysed using different techniques such as SEM, FTIR and chemical analysis of the fouling components.

5.4.1. SEM of HP membrane wetted by SUFP

As shown in the SEM images in Figure 5.4, some precipitation on membrane fibres on the feed side can be seen (b) when compared with the fresh membrane (a). Similarly, the SEM images (c) and (d) show the difference between the original membrane and the wetted membrane permeate side. The wetted membrane has a thick layer of some precipitate which was observed as the yellow material. In order to assess the chemistry of this fouling, the wetted membrane was further tested for FTIR and chemical analysis to identify the fouling and components passed through the membrane.



(a) (b)

(c) (d)

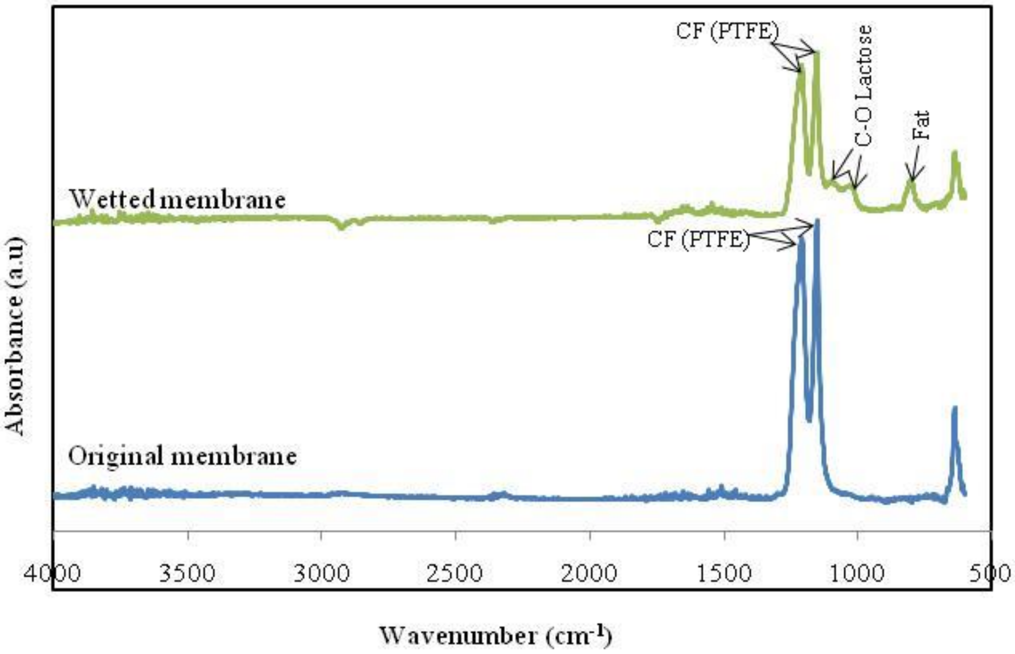
Figure 5.4 SEM of HP membrane wetted by SUFP (a) original feed side(b) wetted feed side (c) original permeate side (d) wetted permeate side

5.4.2. FTIR of HP membrane wetted by SUFP

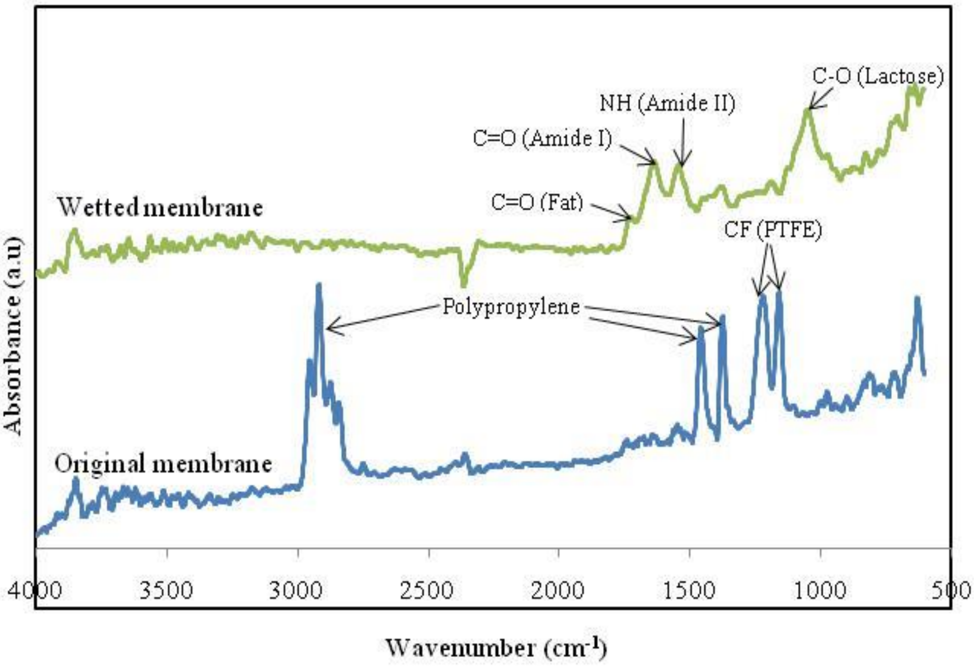
Figure 5.5.a shows the FTIR spectra for the feed side of the original membrane and the wetted membrane. The wavenumbers at 1149 cm^{-1} and 1207 cm^{-1} for both membranes can be related to C─F bond in PTFE membrane [138]. The wetted membrane shows additional peaks at wavenumbers 1045 cm^{-1}and1003 cm^{-1}which have been assigned to C-O bonds in lactose [139, 140]. There is also another clear peak appearing at 786 cm^{-1}

which has been assigned to C=O bonds in fat/oils present in the feed [139, 140]. Due to the hydrophobic nature of the PTFE, the wetting of the membrane could be mainly caused by these organic matter such as lactose and fat. This is a similar observation to wetting of PTFE membrane by fat in DCMD of whole milk observed by Hausmann et al. (2011) [67].

Figure 5.5.b shows the FTIR peaks for the permeate side of the original membrane and the wetted membrane, focussing on the yellow components transferred to the permeate side. The peaks appearing at 3000 cm^{-1} and 1400 cm^{-1} for the polypropylene of the scrim backing of the permeate side of the membrane are no longer visible in the wetted membrane which could be due to the presence of fouling layer. Peaks appearing on the original membrane at 1200 cm^{-1} to 1150 cm^{-1} for C─F in the PTFE membrane material have also become minor due to fouling [138]. There are clear peaks which could be related to fouling components transferred to the permeate side. The peaks at wavenumbers 1624 cm^{-1} and 1529 cm^{-1} are assigned to Amide I and Amide II, indicating proteins transferred through the membrane [136, 137, 139]. The slight peak for $C = O$ stretching at 1732 cm^{-1} is an indication of fat [140] and the clear peak at 1033cm^{-1}can be related to C-O bonds in lactose [139] which has also transferred through the membrane. Thus, the FTIR spectra indicate the presence of protein, lactose and fat in fouling and their penetration through the membrane caused by wetting.



(a)



(b)

Figure 5.5 FTIR of HP membrane wetted by SUFP (a) feed side (b) permeate side

5.4.3. Chemical analysis of fouling on HP membrane wetted by SUFP

Table 5.4 shows the composition of different components on 1 cm^2 of the membrane strip after dissolving components in deionised water according to the method explained in the Chapter 3.

Table 5.4 Chemical analysis of fouling on wetted SUFP treated HP membrane.

Component	Average fouling on membrane strip ($\mu g/cm^2$)
TOC	952 ± 11.2%
TN	60 ± 9.1%
Protein	714
Lactose	476
Fat	1184
K^+	3 ± 0.0%
Na^+	62 ± 16.6%
P	21 ± 12.3%
Ca^{2+}	249 ± 11.8%
Mg^{2+}	12 ± 7.0%
S	3 ± 0.0%
Cl^-	57

Standard error of the mean is reported based on 95% confidence interval calculated from three samples

As similar to the results from FTIR, Table 5.4 also shows that the fouling of the HP membrane is mainly caused by organic compounds than inorganic substances. The very low fat rejection was established by the highest concentration of fat on the fouled membrane strip. The hydrophobic interactions between the PTFE membrane and these organic compounds could be the reason for more organic fouling as it is well known that the fouling by proteins, fats/oils and other organic matter is greater in hydrophobic membranes because of their higher affinity of organic matter with hydrophobic membranes chemistries [41, 100]. Apart from fat, protein seems to be also present on the membrane in relatively high amount. Presence of proteins can also be confirmed by the TN value as TN can be linked to proteins according to Kjeldahl method used for protein analysis in food science and technology [68]. High tendency of protein to foul PTFE membrane has also been observed by Hausmann et al. (2013) in DCMD of skim milk and whey solution where they observed that the protein fouling was accelerated when salts are present in the solution[69]. Lactose has also contributed to fouling in a significant amount as confirmed by both FTIR and chemical analysis of fouling. As per findings of the study by Hausmann et al. (2013), lactose seems not to interact directly with the PTFE membrane, however can interact with other components and contributes to fouling [69].

Wetting observed on the membrane can be mainly because of the fat present in the UF permeate which could also been found in the fouling. Wetting of PTFE membrane by fat was observed by Hausmann et al. (2011) in processing whole milk by DCMD [67]. Including fat, other organic compounds like protein and lactose can also contribute for wetting as the organic concentration increases with time. Interaction of the hydrophobic membrane surface with the hydrophobic functional groups of the these organic foulants leads to reorientation of the foulant molecules such that the hydrophobic parts of the molecule adhere to the membrane, leaving the hydrophilic parts of the molecule oriented towards the solution. As a result, the membrane can lose its hydrophobicity, resulting in membrane wetting. Therefore, after a certain concentration these organic compounds can act as wetting agents [43, 102]. It is interesting to note that the data in Table 5.3 indicates that high rejection of all salt components except S is retained despite the wetting. Instead of allowing aqueous solution to pass the membrane, the only organics passed the membrane. If the wetting was predominantly hydrophobic, then this effect is possible as the membrane remains hydrophobic and resistive to aqueous solution transfer. So it is not certain whether this form of wetting is problematic for MD. Instead, the membrane still worked to reject salts, but passed fats.

In terms of minerals, Ca^{2+} is the main ion present in fouling. As shown by Hausmann et al. (2013) , Ca^{2+} is likely to adhere on the PTFE membrane with whey proteins [68, 69]. Ca^{2+} coupled with protein was also found to be a main contributor in fouling on polypropylene capillary membranes in DCMD of wastewater studied by Gryta (2008) [90]. In the same study , $CaSO_4$ crystallisation inside membrane pores was found to cause wetting of the membrane. Thus, $CaSO_4$ may also have played a role in wetting of PTFE membrane by SUFP. In a study conducted by Srisurichan et al. (2004) for MD of humic acid on PVDF membrane showed that the flux declines were negligible before introducing Ca^{2+} to the feed, however, it could be seen a considerable flux decline due to formation of a complex by Ca^{2+} with humic acid and coagulation on the membrane surface [96]. Therefore, Ca^{2+} may have played a significant role in forming a complex with organic compounds which lead to fouling and wetting of PTFE membrane in DCMD of SUFP. The presence of Na^+, K^+ and Cl^- on the fouled and wetted membrane was minor, as these ions can be bound with the membrane or proteins by charge interactions although they mostly exist as free ions in dairy solutions [69].

As fouling was found to be mostly organic coupled with some salts, the most suitable membrane cleaning method for DCMD of SUFP could be a combination of alkaline and acid cleaning which is the general CIP used in the dairy industry. This involves a NaOH clean to remove organic fouling followed by a HNO_3 acid clean to remove inorganic fouling [110, 113, 114] which may be beneficial to minimise fouling and wetting. Another way would be to maintain the retentate $F_T < 2$ by diluting with fresh feed, as it could be seen that the rate of permeate conductivity increase becomes greater at higher F_T values as shown in Figure 5.2 which could be a result of enhanced fouling at higher retentate concentration leading to wetting. But this would depend on the desired F_T from a practical point of view, as a high volume reduction target may be required.

Fouling is also influenced by the performance of the filters added to the hot loop to capture solids/precipitates heading towards membrane. The following section describes the solids captured in cold and hot filters of the DCMD of SUFP.

5.5. Analysis of solids captured in filters

Table 5.5 outlines the relative composition of each component captured on a strip having an area of $40cm^2$ in cold and hot filters which were situated before and after heating the feed respectively. While the amount captured depends on aspects such as the place of the sample taken, the results are reasonably comparable in absolute terms. The hot filter captured more material as a whole, with exceptions to fat and S. Despite the relative comparability, it is not possible to conclude that the hot filter captured more solids than the cold filter. However understandably, there was a slight preference for the cold filter to capture fat as it is less mobile at lower temperatures.

Protein was captured relatively more in the hot filter. Lactose shows a similar tendency towards both cold and hot. The overall the organic matter tended to be captured in hot filters than cold filters. Gryta et al. (2001) observed that during MD of feed solutions containing natural organic matter, they could remove the organic compounds like proteins to a great extent by filtering the feed solution after heating [93] caused by their lower solubility in hot solutions.

Although fat is removed for some extent from SUFP, fat was still one of the major reasons for membrane wetting as discussed above. Thus, using cartridge filters does not appear to be suitable solution to capture fat.

Table 5.5 Relative composition of solids captured in filters.

Component	F_i	Composition on cold filter strip (mg)	Composition on hot filter strip (mg)
Protein	2.5	20	40
Lactose	4.0	20	20
Fat	1.9	56	50
TOC	3.5	82	96
TN	2.9	43	47
K^+	2.8	52	73
Na^+	3.6	2064	2430
P	4.0	9	13
Ca^{2+}	2.6	33	50
Mg^{2+}	2.7	3	5
S	2.1	26	14
Cl^-	2.8	400	1300

Ca^{2+} and P have been captured more by the hot filter, which could be mainly calcium phosphate salts having less solubility at higher temperatures [98, 132]. Although inorganic salts of Na^+, K^+, Mg^{2+} and Cl^- generally exhibit higher solubility at high temperatures, these ions have been captured more in the hot filter. One reason could be the existence of these free ions on the feed solution which has been in contact with the filter. The other reason may be the ions (Na+, K+, Cl^-) forming complexes with either membrane or organic compounds such as proteins by charge interactions [69]. However, S could be seen more in cold filters which has less solubility at lower temperatures. The quantification of the free ions is more difficult in this analysis as their quantity could vary depending on the amount of free liquid that was part of the removed sample. This would vary according to handling. Despite this, the cold filter showed minimal Cl^-, but a value of Na^+ comparable to the hot filter. It would be expected that the more dominant ions Na^+ and Cl^- would be present in similar proportions to maintain charge neutrality. So the low presence of Cl^- in the cold filter is surprising and cannot be conclude based on the data here.

Although, cartridge filters seemed to remove some organic and inorganic compounds, it was not sufficient to remove the organic compounds such as protein, lactose and fat which could ultimately cause membrane wetting. However with a suitable membrane chemistry to avoid this wetting, the concept of solids capture was demonstrated in this study. Based on the F_i results, the filters appeared to capture the following components in order from highest to lowest: fat (1.9), S (2.1), protein (2.5), Ca^{2+} (2.6), Mg^{2+} (2.7), K^+ (2.8), Cl^-(2.8), TN (2.9), TOC (3.5), Na^+ (3.6), lactose (4.0), and P (4.0). The largest value of F_i (4.0) matched that of concentration shown in Figure 5.1 suggesting that the more soluble components concentrated with the bulk solution. While some fat penetrated the membrane (Table 5.3), the relative amount of fat and proteins to TOC in Table 5.5 does indicate that the filters were effective at removing them with lactose remaining more soluble in the bulk solution.

As outlined above, it seems that PTFE membrane is not suitable for processing of SUFP mainly due to wetting. But as discussed above, hydrophobic wetting did not compromise the membrane's rejection. However avoiding any wetting is preferred. Therefore, another membrane having a different chemistry was tested to investigate the viability of DCMD to process SUFP. That was hydrophilic coated PTFE (HCP) membrane which has a hydrophilic coating on the PTFE membrane.

5.6. MD performance of SUFP on HCP membrane

As observed above, the HP membrane appeared to be wetted by organic components. This is a similar finding to fouling and wetting observed by Hausmann et al. on HP membrane in DCMD of different dairy solutions like whole milk, skim milk and whey caused by the hydrophobic surface of HP membrane showing high affinity to organic matter [67-69, 143]. Testing of a membrane having hydrophilic surface would be interesting to see if avoidance of hydrophobic surface could minimise the hydrophobic interactions with organic components in the feed which would minimise wetting. Therefore, the HCP membrane which has a hydrophilic coated surface on PTFE membrane was selected to test with SUFP. Figure 5.6 outlines the performance of the HCP membrane in terms of permeate flux and F_T over time. The initial flux started from 3.3 kg/m^2/h and this increased up to 4.4 kg/m^2/h during the membrane stabilisation period. The initial flux is less than the conventional PTFE membrane. The reason could be the alteration in the hydrophobic surface of PTFE membrane by the top hydrophilic coating which has reduced hydrophobic interactions with feed components. However, more work is required to link these flux changes to theoretical models. After remaining stable in the stabilisation period for few hours, the flux declined gradually with the time due to fouling while the retentate concentration was continuously increasing.

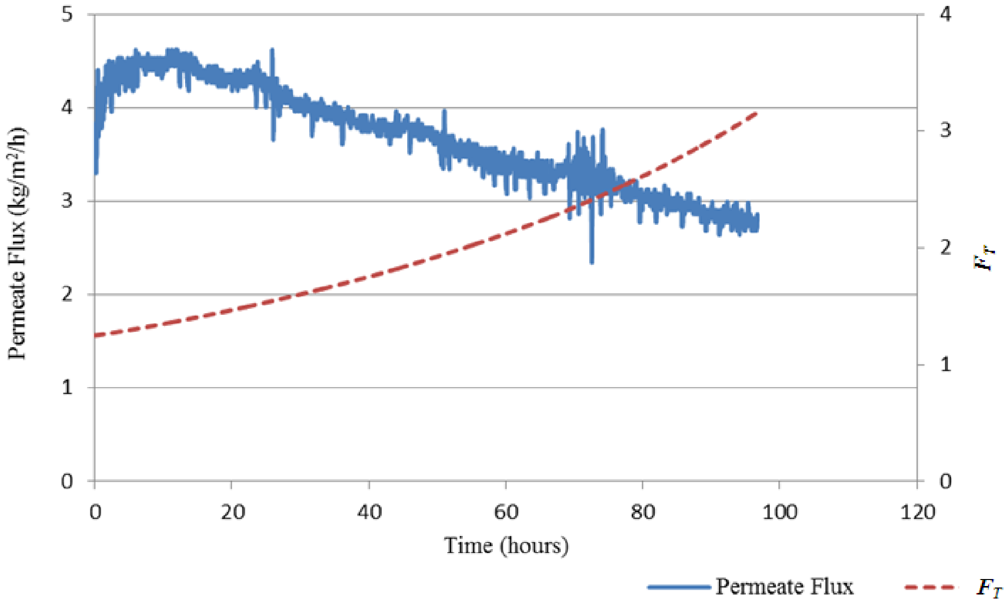


Figure 5.6 Permeate flux &F_T over time - SUFP on HCP membrane

The final F_T was about 3 when the permeate flux reached 2.8 kg/m^2/h. This final F_T was slightly lower than that achieved by HP membrane ($F_T \approx 4$), due to the lower flux of this membrane. Nevertheless, HCP membrane appeared suitable for processing of

SUFP as it did not show any signs of wetting indicated by the permeate conductivity in the Figure 5.7 and the appearance of the final membrane shown in the Figure 5.8.

As shown in Figure 5.7 the permeate conductivity increased linearly from 1.2 µS/cm to 38.8 µS/cm. However due to the linear nature of the increase, it is more likely this was due to what would be expected from a constant salt rejection value [67]. This fact was confirmed by the appearance of the final HCP membrane shown in Figure 5.8 where there were no wetted spots observed. The reason could be the hydrophilic chemistry of the top layer in HCP membrane which could minimise the hydrophobic interactions with the organic compounds present in the SUFP which could then avoid wetting [41].

Therefore, it can be stated that HCP membrane is more suitable for processing of SUFP as it did not show any membrane wetting like HP membrane and could perform with a reasonable flux exhibiting a comparable F_T to HP membrane.

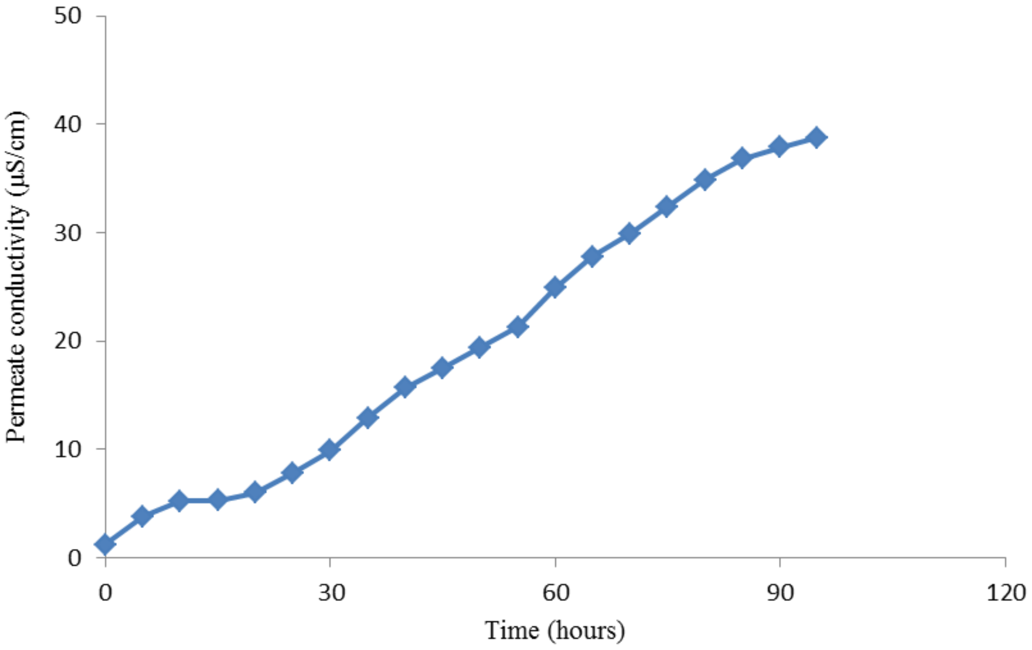


Figure 5.7 Permeate conductivity- SUFP on HCP membrane

Figure 5.8 SUFP fouled HCP membrane

5.7. Conclusions

SUFP was found to be a possible opportunity in the dairy industry to be processed by DCMD for concentration and recovering good quality potable water. Although, the conventional HP membrane performed well in terms of permeate flux (16 kg/m^2/h) and achievable concentration factor ($F_T \approx 4$), it did not appear to be suitable as it clearly showed the signs of membrane wetting indicated by the permeate conductivity increase from 0.3 µS/cm to 1415 µS/cm, low rejection of fat, protein, lactose and also the appearance of the final membrane where there were wetted spots with penetration of yellowish colour components to permeate side. The reason could be the hydrophobic interactions of the PTFE and organic compounds accelerated by the increasing concentration of organic matter in the retentate with time. This was confirmed by the analysis of the foulants on the wetted membrane where they were relatively higher concentration of organic matter like fat, protein and lactose. Although cartridge filters captured some amount of organic compound before the DCMD process it did not appear to be effective to minimise fouling.

The hydrophilic coated PTFE (HCP) membrane was found to avoid the wetting problems and could be a suitable membrane for SUFP. Due to the hydrophilic chemistry, it reduced the interactions with the organic matter in the feed and minimise fouling and subsequent wetting. Thus, it can be concluded that DCMD is a viable membrane process to concentrate SUFP and recover high quality distilled water using the tested hydrophilic coated PTFE membrane.

Chapter 6. Processing of Ion Exchange Regeneration Stream by MD

6.1. Introduction

This chapter investigates the MD treatment of ion exchange regeneration stream for concentration of the stream and recovering good quality potable water. The ion exchange process is used in the dairy industry to demineralisation of whey prior to separate protein and lactose from whey [84]. After whey is transferred through a bed of cation and anion resins to remove the selected components, the resin beds are then switched to regeneration mode where these components are stripped from the resins with acid and alkaline solutions (process discussed in detail in section 2.8.3). The spent acid and base solutions are considered the waste regeneration stream, which have extreme pH (typically < 1), but must be disposed of as waste. Thus, the ion exchange regeneration stream was selected as a feed stream to be tested by DCMD for its viability to reduce the waste volume and recovery clean water. The tested stream was the acid stream of the regeneration process [85, 86].

The provided ion exchange regeneration (IX regeneration) stream was analysed for its composition such as total solids, organic and inorganic matter in order to study the chemical nature of the feed stream. Initially it was tested by DCMD with the conventional HP membrane to investigate the performance in terms of permeate flux, concentration factor/water recovery, solute rejection and permeate quality. As used for salty whey UF permeate test (Chapter 5), two cartridge filters were used at the cold and hot side of the feed to capture any solid precipitates which could affect the performance of the DCMD. The fouled membrane were also analysed using various techniques to study investigate the main components contributing to fouling and to decide a suitable membrane cleaning method for a continuous operation of the stream by DCMD.

6.2. Composition of IX regeneration stream

6.2.1. Total solids of IX regeneration stream

The total solids of the tested IX regeneration stream measured by the dry sand method was found to be 8.2% which is about 82,000 mg/L. Main components contributing to this total solids will be discussed in following sections.

6.2.2. COD of IX regeneration stream

COD indicates the amount of organic matter present in the IX regeneration stream [87, 124]. The average COD level of the tested IX regeneration stream measured by the HACH method was 1440 mg/L. This is much lower than the COD level observed in SWROR (19,200 mg/L) shown in Chapter 4 and SUFP (15,170 mg/L) shown in Chapter 5. This indicates the lower presence of organic components in IX regeneration stream compared to the SWROR and SUFP.

6.2.3. Organic composition of IX regeneration stream

The average concentration of TOC, TN and organic compounds (proteins, lactose and fat) in the IX regeneration stream are shown in Table 6.1.

As indicated by lower COD, organic composition analysis also shows that IX regeneration stream contains lower TOC, TN, protein, lactose and fat than SUFP. Protein is the main contributor for organic compounds, which could be whey proteins as some amount of whey can cross over to the regeneration solution during ion exchange process.

Table 6.1 Organic composition of IX regeneration stream

Component	Concentration (mg/L)
TOC	916 ± 6.5%
TN	193 ± 6.4%
Protein	1,600
Lactose	< 100
Fat	180

Standard error of the mean is reported based on 95% confidence interval calculated from three samples

6.2.4. Mineral analysis of IX regeneration stream

Table 6.2 shows the concentration of several minerals IX regeneration stream measured by ICP and chloride ions by Volhard titration method.

Table 6.2 Mineral analysis of IX regeneration stream

Component	Concentration (mg/L)
K^+	12,600 ± 4.6%
Na^+	4,450 ± 9.6%
P	10 ± 0.0%
Ca^{2+}	5,750 ± 7.6%
Mg^{2+}	1,330 ± 9.0%
S	199 ± 4.7%
Cl^-	51,000

Standard error of the mean is reported based on 95% confidence interval calculated from three samples

As shown in Table 6.2, Cl^- is present in very high concentration as the tested stream was the acid stream of the ion exchange regeneration process where the cation resins are treated with HCl acid. Apart from Cl^- ions already present in whey, the extremely high concentration of Cl^- could be a result of the acid treatment [85, 86]. In terms of the cations, K^+ is the most abundant ion followed by the Ca^{2+} and Na^+ which are also present in whey in larger proportions [85]. P showed the least presence which may be due to less presence of phosphate ions as the used regeneration solution was the cation resin bed/acid stream which is not expected to contain many anions.

6.2.5. Conductivity and pH of IX regeneration stream

The initial pH of the IX regeneration stream was about -0.01 indicating the extremely high acidity caused by the HCl acid. The conductivity was above 25 mS/cm which is mainly due to the high concentration of salts, specially Cl^- , K^+ and also other salts like Ca^{2+} and Na^+.

6.3. MD performance of ion exchange regeneration stream

A volume of 10 L from the provided ion exchange regeneration stream was taken as fresh feed and tested by the DCMD equipment. As for the salty whey UF permeate test, two filters with a pore size of 1μm in the feed side before heating (cold filter) and after heating (hot filter) were incorporated in order to capture any precipitates during the run. The feed was continuously concentrated and the test was carried out for about 16 hours. Unlike other tests, the main drawback of using ion exchange regeneration acid stream was its high acidity causing corrosion of metallic parts in the DCMD equipment. The stainless steel heating coil used to heat the feed had to be replaced by silicone tubing as the initial run with steel tubing lead to rapid corrosion. However, this can cause temperature variances in the feed inlet affecting the average temperature difference across the membrane. In addition, due to safety issues caused by the high acidic stream the test was not continuously run for 16 hours overnight. Instead, the test had to be carried out for two days with a stop in between.

Figure 6.1 outlines the performance of the HP membrane in terms of permeate flux, average temperature (T) difference across the membrane and F_T over time. As explained before, the typical MD flux pattern observed in SWROR and SUFP could not be observed here. The reason is the variation in average temperature difference across the membrane (calculated by the difference of average temperature in feed side and the average temperature in the permeate side) as shown in Figure 6.1. The feed temperature continuously changes as silicone tubing is not very effective compared to stainless steel in transferring heat from the water bath to the feed and cannot maintain a constant temperature throughout due to the difference of heat conductivity of these two materials i.e. stainless steel- 16 $Wm^{-1}K^{-1}$ and silicone rubber- 0.2 $Wm^{-1}K^{-1}$ [144]. Comparison of average T difference and the permeate flux pattern in Figure 6.1 clearly confirms this variability as these two parameters exhibit the same pattern over time.

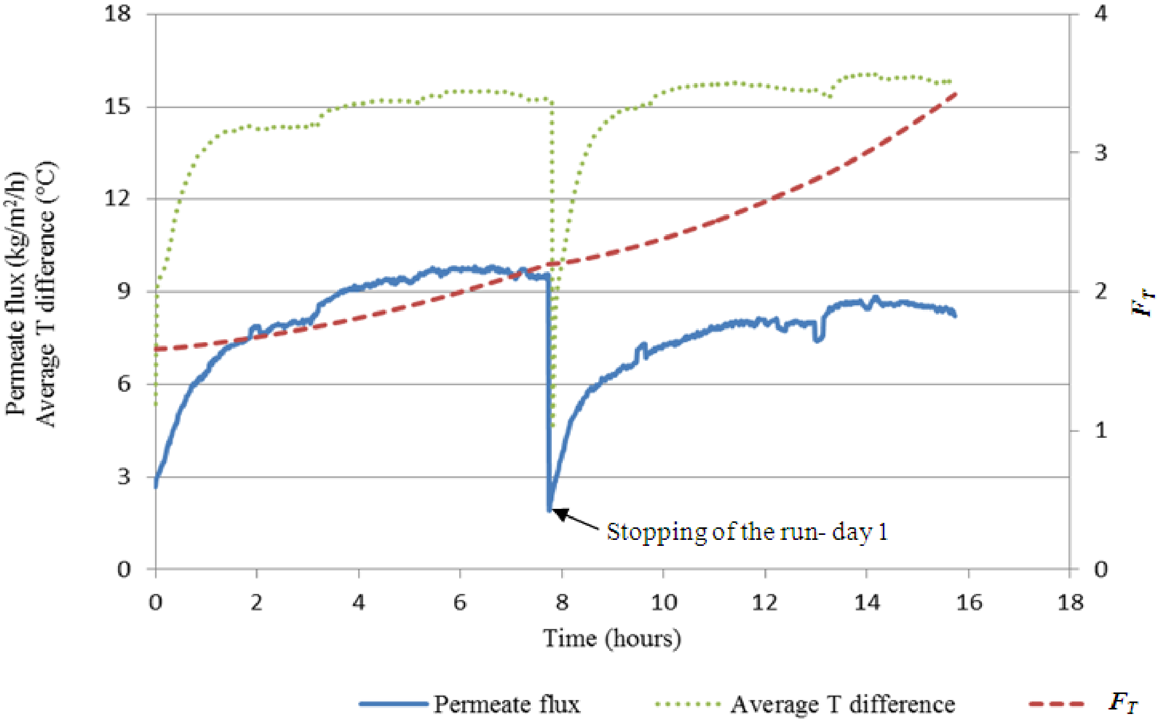


Figure 6.1 DCMD performance of IX regeneration stream on HP membrane

The initial flux started from 2.6 $kg/m^2/h$ where the average T difference was about 5.3 °C. For the DCMD tests of SWROR (Chapter 4) and SUFP (Chapter 5) on HP membrane operating at temperatures 55 °C and 5 °C for feed inlet and permeate inlet respectively where the average T difference across the membrane was about 28 °C, the typical permeate flux was found to be 15 $kg/m^2/h$. Hence, the observed DCMD initial flux for IX regeneration stream is proportional to the average T difference that it was operated at. The flux started to increase along with the increase average T difference.

The sudden drop in the flux after 7.5 hours was due to the stop of the test which could not be continued overnight due to safety issues considered with high acidic stream. After starting on the following day, the flux again started to increase over time as the average T difference also increased. By the end of the test, F_T was approximately 3.4 which is about 70% water recovery. However, it seems that fouling did not show any effect in flux decline as it could not be seen continuous flux decline. If the average T difference can be kept at a constant value the stream was able to be concentrated in a shorter time because of the higher flux at higher T difference. Thus, IX regeneration could be concentrated more and operated under continuous mode as there were no flux declines observed.

In terms of the permeate quality, permeate conductivity and solute rejection were considered. Figure 6.2 outlines the permeate conductivity change over time. The permeate conductivity continuously increased from 33 µS/cm to 309 µS/cm. The reason for this increase could be due to HCl acid present in the IX regeneration acid stream confirmed by the high amount of Cl^- ions in the feed as presented in the Table 6.2. Thus, this permeate conductivity increase is not because of membrane wetting which is penetration of feed solutes through the membrane and it is due to HCl as it is volatile and pass through the membrane [14].

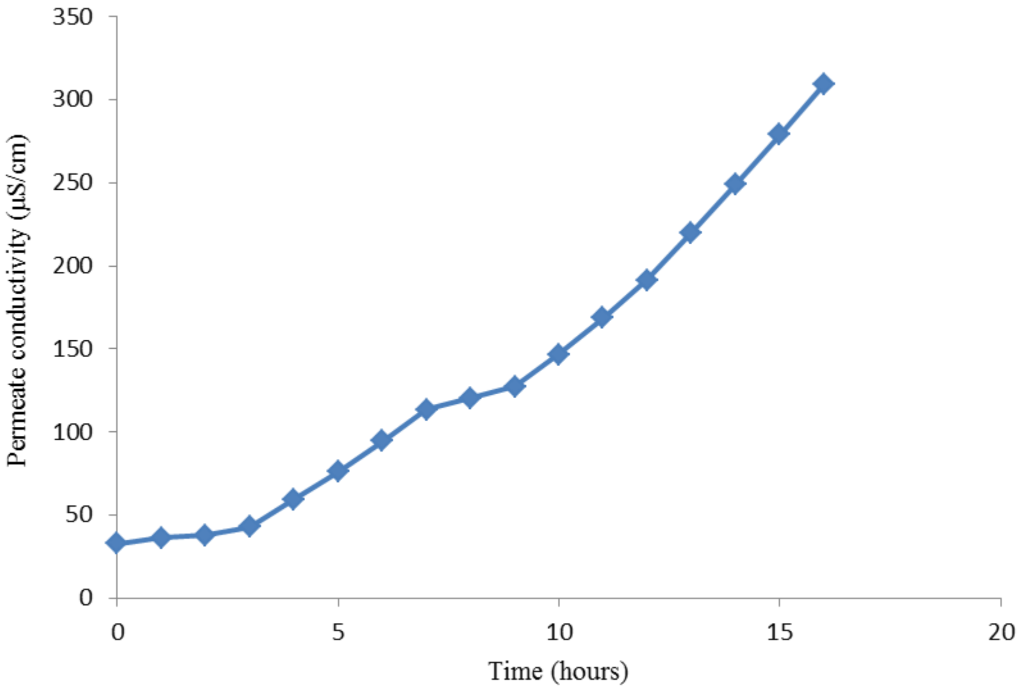


Figure 6.2 Permeate conductivity over time - IX regeneration stream on HP membrane

Table 6.3 outlines the rejection of the tested solutes which indicate that there was no wetting observed and the permeate conductivity increase is purely due to HCl gas penetration shown by the lowest rejection (98.97%) of Cl^{-}. Concentrations of protein, lactose and fat in the final permeate are shown as < 100 mg/L as these were out of the detectable range of the test method. However there should be very low concentration of these components in the final permeate as TN was not detected and TOC had a very low value of 1 mg/L. If protein, lactose and fat are present in significant amount there should be considerable concentrations for TOC and TN. Hence, it can be confirmed that DCMD of IX regeneration stream can produce a high quality permeate.

Table 6.3 Solute rejection – IX regeneration stream on HP membrane

Component	Final retentate concentration (mg/L)	Final permeate concentration (mg/L)	Rejection (%)
TOC	2,623 ± 12.9%	1 ± 4.1%	99.96
TN	503 ± 11.1%	0 ± 0.0%	100
Protein	4,600	< 100	> 99
Lactose	< 100	< 100	> 99
Fat	480	< 100	> 99
K^+	35,256 ± 1.6%	1 ± 5.4%	99.99
Na^+	13,100 ± 6.7%	0.1 ± 0.0%	99.99
P	28 ± 8.1%	0.1 ± 7.5%	99.97
Ca^{2+}	15,785 ± 2.6%	0.1 ± 7.5%	99.99
Mg^{2+}	3,897 ± 5.8%	1 ± 4.1%	99.97
S	573 ± 8.5%	0.1 ± 0.0%	99.98
Cl^-	78,000	800	98.97

Standard error of the mean is reported based on 95% confidence interval calculated from three samples

Figure 6.3 also confirms that membrane was not wetted by the IX regeneration stream as the final membrane appeared very clean and clear and did not show any wetted spots.

Figure 6.3 Final appearance of the HP membrane treated by IX regeneration stream

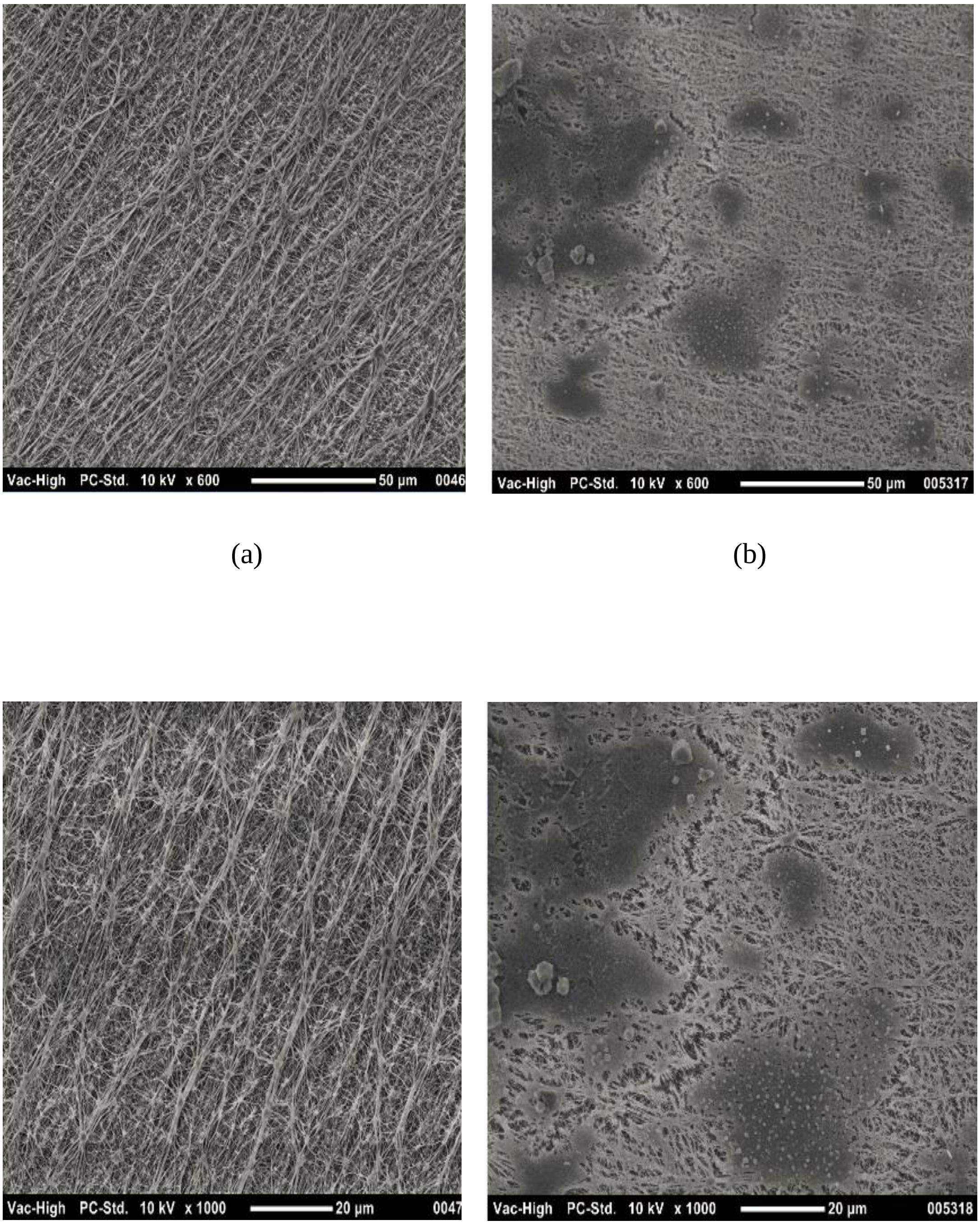
The final membrane looked clean and not fouled. However, the final membrane was analysed for several components in order to confirm more precisely the presence of fouling on the membrane.

6.4. Fouling analysis of IX regeneration stream fouled HP membrane

The final HP membrane was analysed using different techniques such as SEM, FTIR and chemical analysis of the fouling components.

6.4.1. SEM of IX regeneration stream fouled HP membrane

The SEM images of the original PTFE membrane and the IX regeneration stream treated PTFE membrane are shown in Figure 6.4.



(a) (b)

(c) (d)

Figure 6.4 SEM of IX regeneration stream fouled HP membrane. Figures (a) and (c) are original membrane, and Figure (b) and (d) are fouled membrane

Although the final membrane appeared to be very clean to the naked eye, it seems that there are some precipitation on the final membrane. Upon closer inspection, it appeared the PTFE structure may have been altered, evident by the difference in the underlying PTFE fibres compared to the control. Nevertheless, the fouling appeares porous in structure possibly explaining why it did not significantly affect the flux. The reason for this porous structure cannot be explained by the SEM images and hence, it was further analysed for fouling components.

6.4.2. FTIR of IX regeneration stream fouled HP membrane

Figure 6.5 outlines the FTIR peaks obtained for the original PTFE membrane and the IX regeneration stream fouled PTFE membrane.

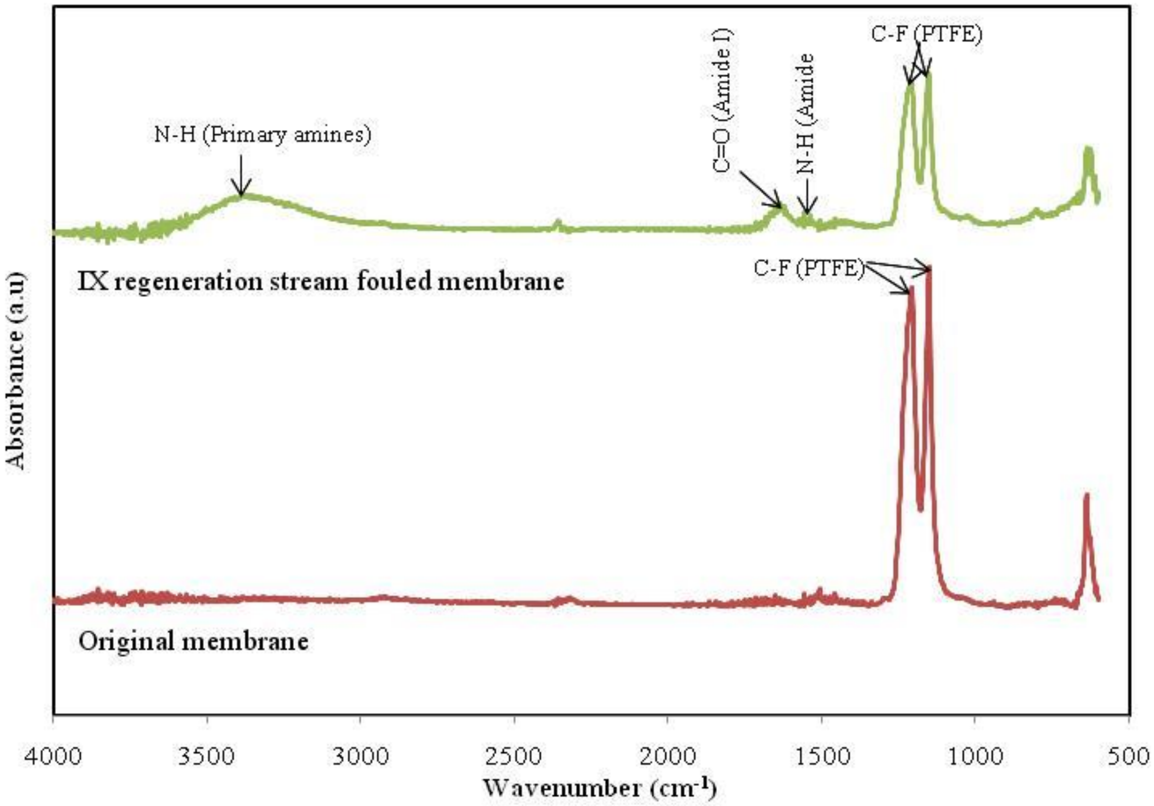


Figure 6.5 FTIR of IX regeneration stream fouled HP membrane

As outlined in Figure 6.5, compared to the original PTFE membrane, the fouled PTFE membrane revealed additional peaks. The two peaks for wavenumbers at 1205 cm^{-1} and

1150 cm^{-1} are for C─F stretching in PTFE [138] from the membrane material. Among additional peaks, the peaks for wavenumbers at 1633 cm^{-1} and 1530 cm^{-1} could be related to Amide I and Amide II respectively. The broad peak at 3331 cm^{-1}can be for N─H stretching of primary amines [136, 137, 139]. These peaks can be due to presence of proteins. These are the only peaks that could be visible and thus it indicates the fouling deposition of the hydrophobic PTFE membrane by IX regeneration stream is mainly due to protein.

6.4.3. Chemical analysis of IX regeneration stream fouled HP membrane

The fouling layer composition was determined by dissolving the layer from a membrane strip using deionised water and performing chemical analysis of the resulting solution. Table 6.4 shows the results.

Table 6.4 Chemical analysis of fouling by IX regeneration stream on HP membrane

Component	Average fouling on membrane strip ($\mu g/cm^2$)
TOC	383 ± 8.3%
TN	131 ± 9.6%
Protein	476
Lactose	Not detected
Fat	Not detected
K^+	0.5 ± 14.0%
Na^+	Not detected
P	Not detected
Ca^{2+}	133 ± 3.9%
Mg^{2+}	7 ± 12.3%
S	Not detected
Cl^-	95

Standard error of the mean is reported based on 95% confidence interval calculated from three samples

Similar to the FTIR results, the fouling was mainly found to be by protein and other proteinaceous matter as lactose and fat were not present in the fouling solution. Therefore, the contribution for TOC and TN can be from these proteinaceous matter.

In terms of minerals, Ca^{2+} and Cl^- are the only ions present in the fouling solution. Ca^{2+} and Cl^- can be assumed to be existing as either free ions or bound with the membrane or proteins by charge interactions. As shown by Hausmann et al. (2013) , Ca^{2+} is likely to adhere on the PTFE membrane with whey proteins [68, 69]. Ca^{2+} coupled with protein was also found to be a main contributor in fouling on polypropylene capillary membranes in DCMD of wastewater studied by Gryta (2008) [90].

As fouling was found to be mostly by proteins coupled with some salts such as Ca^{2+} and Cl^-, the most suitable membrane cleaning method for DCMD of IX regeneration stream could be a combination of alkaline and acid cleaning which is the general CIP used in the dairy industry which involved a NaOH clean to remove organic fouling followed by a HNO_3 acid clean to remove inorganic fouling [110, 113, 114] which may be beneficial to minimise fouling if the test is carried out for longer period or the IX regeneration stream is concentrated more where fouling can affect its performance. The other solution to minimise fouling could be using pre-treatment methods before the DCMD process.

As discussed in the Chapter 5, one of the main pre-treatment methods suggested to minimise fouling in continuous operation of DCMD is using filters before the membrane process in order to capture solids/precipitates heading towards membrane. The following section describes the solids captured in cold and hot filters of the DCMD of IX regeneration stream which will investigate the effectiveness of using cartridge filters for DCMD of IX regeneration stream.

6.5. Analysis of IX regeneration stream solids captured in filters

Table 6.5 outlines the relative composition of each component captured on a strip having an area of $40cm^2$ in cold and hot filters.

Protein and fat are mainly captured in the hot filter compared to the cold filter. Overall, the organic matter tend to be captured more in hot filters than cold filters as shown by Gryta et al. (2001) in MD of feed solution containing natural organic matter where they could remove the organic compounds like proteins to a great extent by filtering the feed solution after heating caused by their lower solubility in hot solutions [93].

Table 6.5 Relative composition of IX regeneration stream solids captured in filters

Component	Composition on cold filter strip (mg)	Composition on hot filter strip (mg)
Protein	50	70
Lactose	Not detected	Not detected
Fat	27	32
TOC	90	123
TN	44	58
K^+	299	270
Na^+	974	961
P	Not detected	Not detected
Ca^{2+}	121	129
Mg^{2+}	3	25
S	17	8
Cl^-	790	1800

Unlike in salty whey UF permeate where Ca^{2+} and P had been captured more in hot filter which could be mainly calcium phosphate salts having less solubility at higher temperatures [98, 132], the Ca^{2+} captured here in both filters were almost same and P was not present in either of the filters. This indicates that calcium phosphate is absent or slightly present in the IX regeneration stream. Therefore, these Ca^{2+} could be free ions existing in the feed or the Ca^{2+} bound with proteins.

As Na^+ and K^+ generally exhibit higher solubility at high temperatures, these ions have been captured more in cold filters. Nevertheless, Cl^- has been captured more in hot filer than cold filter. One reason could be the existence of these free ions on the feed solution which has been in contact with the filter while running through the filter. The other reason may be the Cl^- ions forming any complexes with proteins mostly captured in the hot filter by charge interactions [69].

According to above results, cartridge filters seemed to remove mostly proteins and probably Ca^{2+} bound with proteins which can contribute to fouling and reduce the membrane performance in the long run. Hence, the capturing of proteins looked effective under the operated period and concentration factor as there was not any significant fouling compromising the membrane performance was observed. However, more testing will be required to look its efficiency to run longer period to a higher concentration factor.

6.6. Conclusions

The tested IX regeneration acid stream is another possible opportunity for the dairy industry to apply DCMD to concentrate the stream and recovery good quality potable water. The chemistry of the conventional hydrophobic PTFE membrane looked suitable to process this stream as there was no significant fouling or any wetting issues were observed. As a result, the permeate flux was not observed to decrease even at a concentration factor about 3.4 which is a 70% water recovery. Despite the permeate conductivity increase from 33 µS/cm to 309 µS/cm due to HCl acid penetration which is largely present in the tested IX regeneration acid stream, the solute rejection for all solutes except Cl^- was above 99.9% thus producing a clean Cl^-solution. This could be a possible method of HCl recovery from IX regeneration solution. Cl^- ions also however showed relatively higher rejection above 98% under the operated conditions. Hence, it can be stated that DCMD of IX regeneration acid stream can produce a high quality permeate. Although fouling could not be seen by the appearance of the final membrane, there was evidence of proteins and Ca^{2+} to be present in the fouling layer from the fouling analysis. However, fouling could not cause a significant effect on permeate flux as there was no permeate flux decline observed. As pre-filters looked effective in removing proteins and bound Ca^{2+}, use of filters in continuous mode operation would be beneficial to minimise fouling and subsequent wetting.

Chapter 7. Combined Dairy Effluent Treatment by MD

7.1. Introduction

Chapter 7 is focused on the combined dairy effluent treatment by DCMD in order to reduce the waste volume and recover good quality potable water from dairy wastewater. Some dairy plants use anaerobic digestion (AD) as a biological process for dairy waste treatment in which most of the organic matter present in the combined dairy waste are broken down [87]. The final effluent may then be suitable for discharge to the sewer, as it meets the required water quality criteria such as BOD and suspended solids [15, 88, 89]. However removal of dissolved solids is not possible under the current treatment chain. As high dissolved solids can prevent the ability for the water to be reused, desalination by DCMD could provide a viable means to recover fresh water using waste heat.

Two waste streams were tested;

- Combined dairy effluent before anaerobic digestion (Pre-AD)
- Combined dairy effluent after anaerobic digestion (Post-AD)

These two streams were first tested for their composition in order to identify the chemical nature of these waste streams, especially in terms of organic matter present which could affect the DCMD process as experienced in the previous chapters. The streams were first processed by DCMD using the conventional hydrophobic PTFE (HP) membrane. The membrane performance was determined by different parameters such as permeate flux, concentration factor/water recovery, solute rejection and permeate quality. The issues like fouling and wetting were also explored. Considering the potential of wetting from fats in the waste water, a different membrane having a different chemistry which is hydrophobic and oleophobic acrylic copolymer (HOA-0.8) membrane was also considered for the tests. Fouling and wetting were identified by analysis of the components attached to the membrane and present in the feed stream.

Overall, this chapter investigates the viability of DCMD to treat dairy waste waters to recover high quality potable water for reuse.

7.2. Composition of combined dairy effluent

7.2.1. Total solids of combined dairy effluent

Table 7.1 outlines the total solids (TS) of the two waste streams measured by the dry sand method described in section 3.2.1.1 in Chapter 3. TS of Pre-AD (12,000 mg/L) is higher than that of Post-AD (3,000 mg/L). This is because of the AD process where most of the organic matter contributing to total solid are broken down into methane gas [87]. The components mainly contributing to this total solids are identified in the following sections.

Table 7.1 TS of combined dairy effluent

Combined dairy effluent stream	Total solids (mg/L)
Pre-AD	12,000
Post-AD	3,000

7.2.2. Chemical oxygen demand of combined dairy effluent

The COD is an important parameter measured in dairy waste characterisation [87, 123]and COD is the amount of oxygen required to completely oxidise organic carbon to CO_2 [124, 125]. Therefore, COD in these dairy waste stream indicate how much organic matter present in there.

Table 7.2 shows the average COD level in each stream. Pre-AD shows the higher value for COD (34,800 mg/L) than Post-AD (4,100 mg/L)as AD process breaks down most of the organic matter. This COD level in Pre-AD is much higher than that of SWROR (19,200 mg/L) explained Chapter 4 and SUFP (15,170 mg/L) in Chapter 5. Variations in COD depend on the organic load present and it can vary according to the product stream and the process line. Most of the organic matter contributing to COD in milk are lactose, protein and fat [127]. Therefore, the high COD level in Pre-AD indicates that it contains more organic load than SWROR and SUFP. This is possible as the tested Pre-AD stream was the combined waste line which contains all the waste in the dairy plant including process lines and also waste from cleaning. Contribution of several organic compounds will be discussed in the next section.

Table 7.2 COD of combined dairy effluent

Combined dairy effluent stream	COD (mg/L)
Pre-AD	34,800 ± 3.5%
Post-AD	4,100 ± 10.4%

Standard error of the mean is reported based on 95% confidence interval calculated from three samples

7.2.3. Organic composition of combined dairy effluent

Table 7.3 summarises the average concentration of TOC, TN and organic compounds like proteins, lactose and fat in each waste stream.

Table 7.3 Organic composition of combined dairy effluent

Component	Concentration in Pre-AD (mg/L)	Concentration in Post-AD (mg/L)
TOC	3,022 ± 11.0%	220 ± 10.1%
TN	218 ± 7.3%	203 ± 2.3%
Protein	2,100	400
Lactose	3,400	< 100
Fat	1,269	152

Standard error of the mean is reported based on 95% confidence interval calculated from three samples

There is a significant difference in the organic load between Pre-AD and Post-AD as indicated by COD measurement. TOC, protein, lactose and fat in Pre-AD are much higher than that of Post-AD. Thus, it is confirmed that AD process has broken down most of the organic compounds in the Pre-AD. Nevertheless, TN values look almost the same in both streams as due to ammonia production during AD process which can be present in Post-AD [15]. Therefore, although proteins are broken down, ammonia can still contribute to the TN in Post-AD. Another critical feature is the high level of fat present in Pre-AD which is much higher than in SUFP (268 mg/L).

7.2.4. Mineral analysis of combined dairy effluent

Table 7.4 summarises the mineral composition of both Pre-AD and Post-AD.

Table 7.4 Mineral analysis of combined dairy effluent

Component	Concentration in Pre-AD (mg/L)	Relative Amount in Pre-AD	Concentration in Post-AD (mg/L)	Relative Amount in Post-AD
K^+	241 ± 7.2%	7%	134 ± 6.8%	10%
Na^+	963 ± 7.1%	29%	671 ± 4.5%	49%
P	17 ± 6.7%	0.5%	2 ± 0.0%	0.1%
Ca^{2+}	109 ± 12.8%	3%	43 ± 10.6%	3%
Mg^{2+}	10 ± 6.3%	0.3%	3 ± 0.0%	0.2%
S	12 ± 9.4%	0.4%	3 ± 24.5%	0.2%
Cl^-	2,000	60%	500	37%

Standard error of the mean is reported based on 95% confidence interval calculated from three samples

All the minerals present in the Pre-AD are higher than Post-AD. This could be due to the deposition of these minerals in the sludge produced in the AD process and which does not entering the Post-AD stream. Na^+ and Cl^- are the two main minerals present in Pre-AD which is about 89% of the total minerals measured. These ions are largely present in milk itself and can also be added to the waste streams during the cleaning process where NaOH and HCl are mostly used.

7.2.5. Conductivity and pH of combined dairy effluent

Table 7.5 outlines the pH and the conductivity of Pre-AD and Post-AD.

Table 7.5 pH and conductivity of combined dairy effluent

Parameter	Pre-AD	Post-AD
pH	5.3	7.4
Conductivity (μS/cm)	6,150	4,010

The reason for the lower pH of Pre-AD may be due to acids (HCl) present in the stream as there was relatively high amount of Cl^- present in Pre-AD. The acidity has reduced in Post-AD and it tends to be basic as ammonia is present in AD process. The higher conductivity in Pre-AD than Post-AD can be because of the relatively higher concentration of ions in Pre-AD than Post-AD as observed in the mineral analysis in Table 7.4.

7.3. DCMD of Pre-AD

In this section, DCMD of Pre-AD will be reported and results discussed in terms of membrane performance (permeate flux, concentration factor/water recovery, solute rejection, permeate quality). In addition, any issues such as fouling and wetting will be identified and investigated.

7.3.1. Membrane performance of Pre-AD

A volume of 8 L from Pre-AD was taken as the initial feed and tested by the DCMD equipment in batch mode using the HP membrane. Figure 7.1 shows the DCMD performance of Pre-AD on the HP membrane in terms of permeate flux and the concentration factor (F_T).

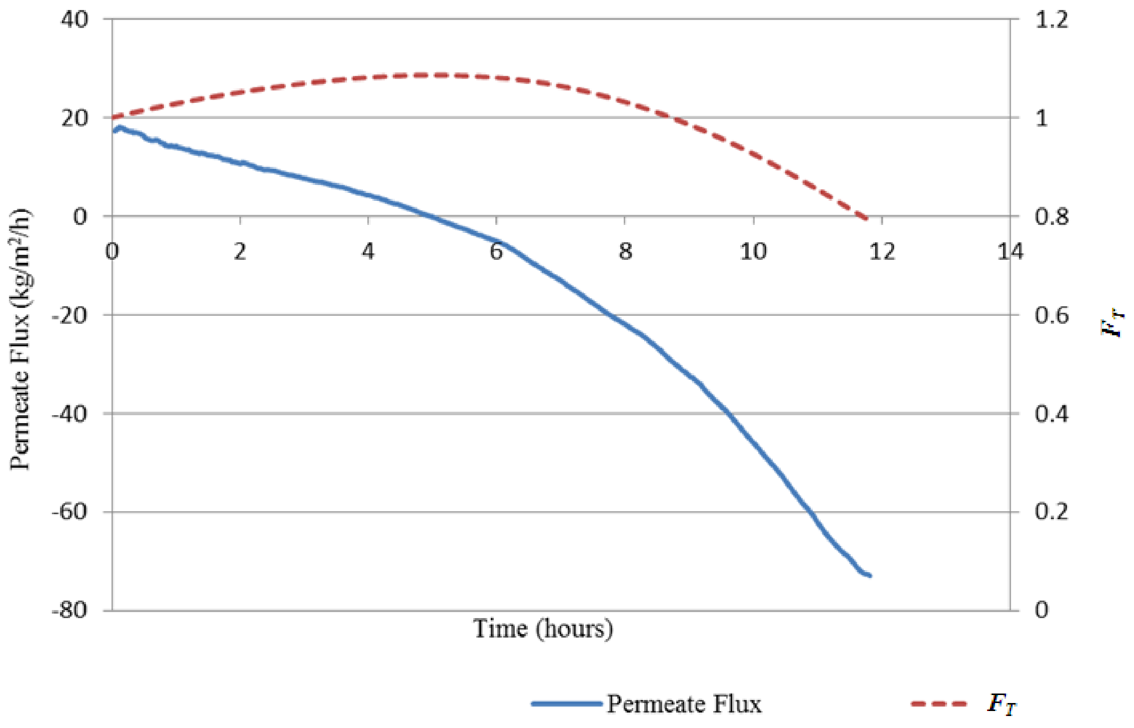
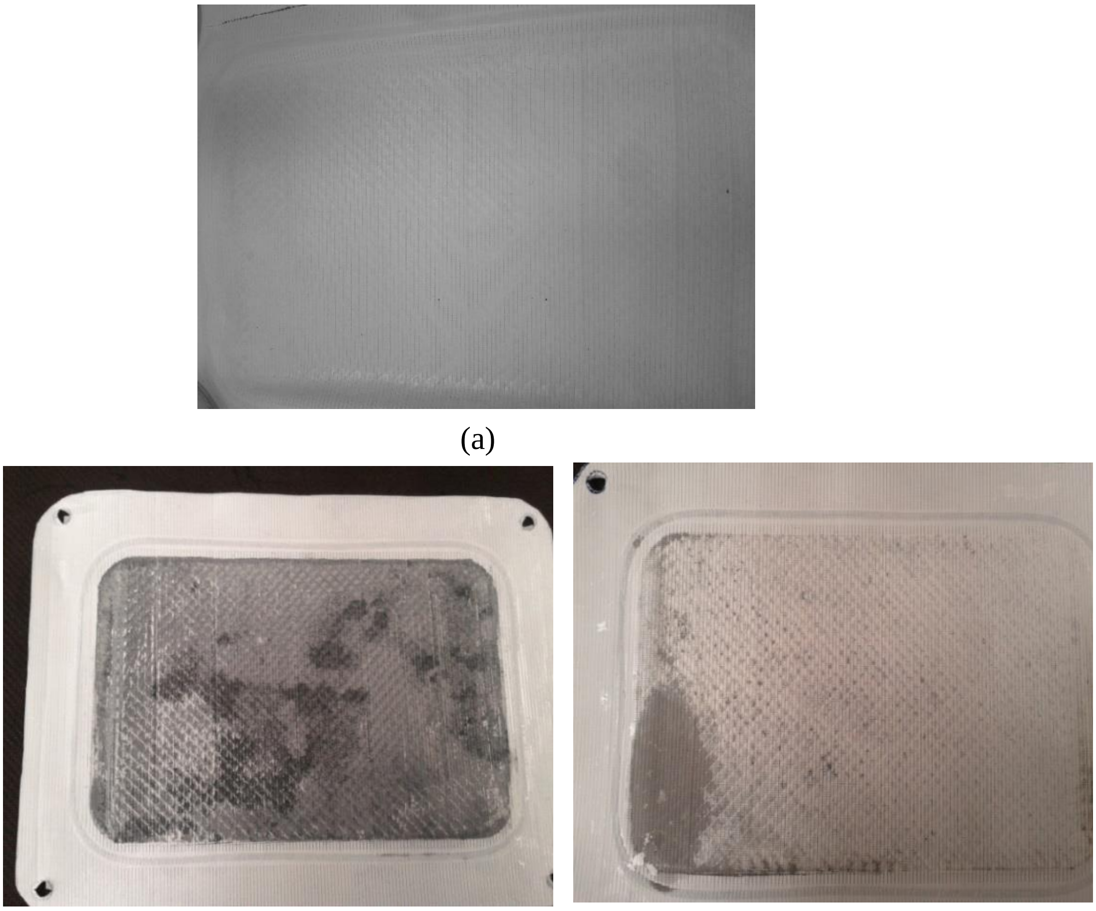


Figure 7.1 Performance of Pre-AD on HP membrane

As shown in the Figure 7.1, the initial flux was around 17 kg/m^2/h which declined rapidly to 0 kg/m^2/h within 5 hours due to fouling where the F_T was 1.1. The permeate conductivity increased from 0.8 µS/cm to 80.7 µS/cm during this period. After 5 hours, a negative flux could be observed which is not desirable. Instead of concentrating the feed, from this point onwards the feed started to become diluted because of the reversing of flux and migration of permeate to the retentate. This was a clear indication of membrane wetting which was confirmed by the appearance of the final membrane. Flow can reverse because the membrane is no operating in filtration mode and the pressure of the permeate side was likely higher than the feed. The final membrane appeared completely wetted and there were fat-like spots even after the membrane was dried. Figure 7.2 presents the appearance of this wetted PTFE membrane and fat-like spots on it.

As identified in the organic composition analysis the reason for this fast wetting may be possibly due to high amount of organic matter present in pre-AD specially very high amount of fat. This is a similar observation as in SUFP where the HP membrane was wetted as a result of high organic matter. This organic matter can show a great affinity to the hydrophobic PTFE material and cause fouling which ultimately will lead to wetting [41, 100]. The fouling analysis on the membrane will be discussed in the following section 7.3.2.



(a)

(b) (c)

Figure 7.2 Wetted HP membrane by pre-AD (a) original membrane (b) completely wetted membrane (c) fat-like spots on the wetted membrane after drying

As HP membrane did not appear to be suitable for Pre-AD treatment, a new membrane having a different chemistry was tested. That was hydrophobic and oleophobic acrylic copolymer (HOA-0.8) membrane which has a pore size of 0.8 µm. This was also tested under the same conditions like HP membrane and Figure 7.3 shows the performance of DCMD of Pre-AD on HOA membrane.

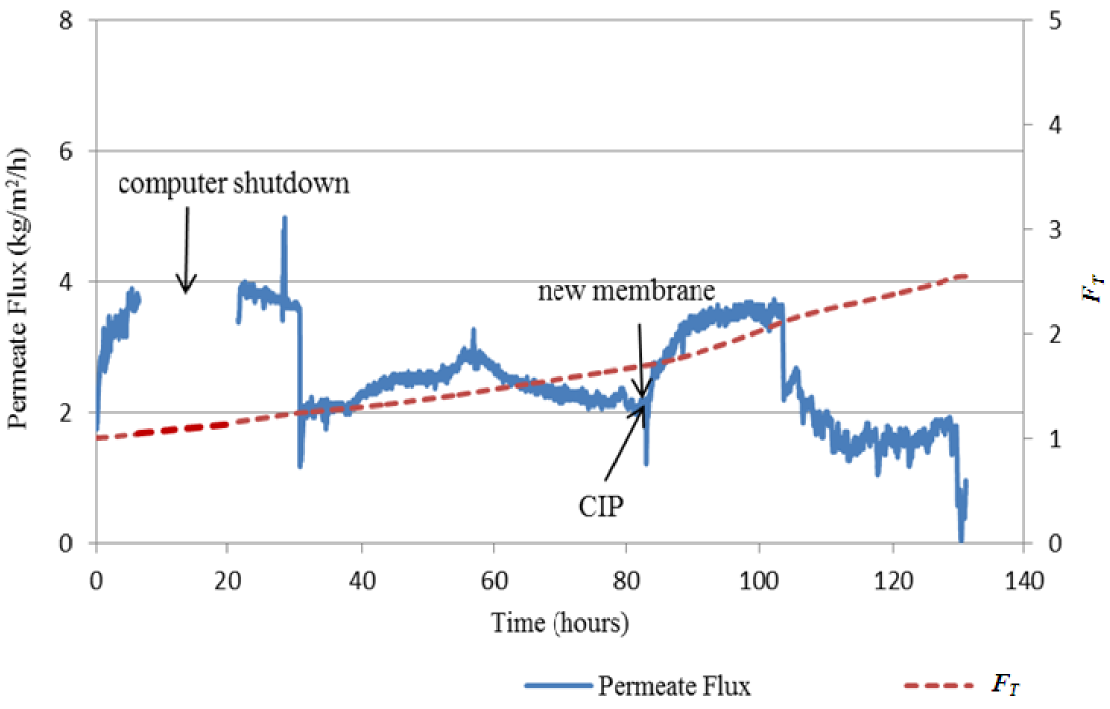


Figure 7.3 MD performance of treating Pre-AD on HOA membrane

The initial flux started from about 2 kg/m^2/h and this increased gradually within few minutes to up to 3.8 kg/m^2/h. The data loss between 5 – 22 hours due to computer shut down due to a failure. However, the flux showed a declining trend from this point onwards possibly due to fouling. The sudden flux drop at 30 hours may be related to the increased fouling on the membrane caused by the stopping of the run where more deposition can happen due to the stop of the cross flow velocity. When the run was started again after the shutdown period the flux could not get recovered to the original state, however, showed some increase which may be due to dissolving of the foulants on the membrane during the run. After that, the flux dropped up to 2 kg/m^2/h within about 83 hours where F_T had reached 1.7. After this point a dairy CIP was performed (with 1.5% w/w NaOH and 0.8% w/w HNO_3) in order to clean the membrane to remove the fouling. However, CIP appeared to cause wetting which was confirmed by a subsequent 1% NaCl test which gave a negative flux. The final membrane also appeared wetted.

As the HOA-0.8 membrane was wetted by the CIP, a new HOA membrane having a pore size of 1.2 µm (HOA-1.2) was installed and the test was carried out further with the remaining retentate. This membrane could concentrate the retentate from $F_T \approx 1.7$ to $F_T \approx 2.6$ and did not show any wetting issues at this point. Therefore, it can be stated that the HOA-1.2 membrane worked well for the Pre-AD without CIP to concentrate the Pre-AD up to about $F_T \approx 2.6$. However conventional dairy CIP will wet the membrane. This may be due to the production of surfactant by-products, for example reaction of NaOH with fats fouled on the membrane. They may have wetted the surface of the hydrophobic and oleophobic membrane which compromised its essential hydrophobicity.

Table 7.6 shows the rejection of some tested solutes of the HOA-1.2 membrane at the end of the test. The rejection was above 99% for all the solutes tested and thus it can be confirmed that Pre-AD treatment by HOA-1.2 membrane is viable as it can be operated to a reasonable concentration factors ($F_T > 2.5$) and can produce high quality permeate. The final membrane also did not show any wetted spots as shown in the Figure 7.4. However, there can be wetting issues associated with conventional CIP as observed for HOA-0.8 membrane and therefore a revised cleaning method must be explored for sustained operation of the membrane. The membrane appeared to have been altered during the exposure to the water solution, expanding and giving it a wrinkled appearance. This may be due to heat exposure, or some effect during operation as a membrane which has been observed for PTFE membranes, where some stabilisation period occurs under pure water [143].

Table 7.6 Solute rejection – Pre-AD on HOA-1.2 membrane

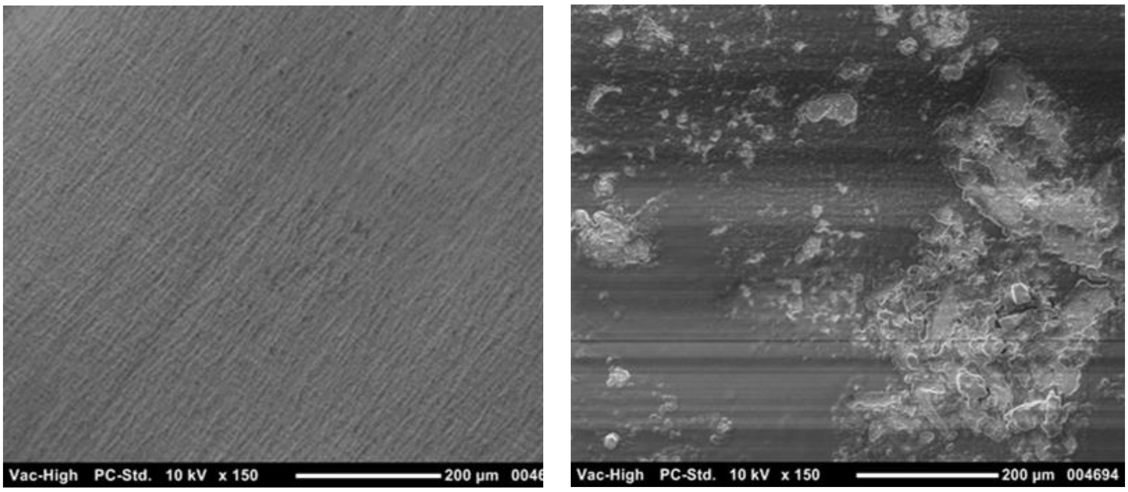
Component	Final retentate concentration (mg/L)	Final permeate concentration (mg/L)	Rejection (%)
TOC	6,290 ± 9.7%	12 ± 8.4%	99.81
TN	561 ± 8.8%	0.1 ± 10.3%	99.98
K^+	541 ± 10.1%	0.1 ± 12.3%	99.98
Na^+	2,480 ± 3.8%	0.5 ± 4.8%	99.98
P	41 ± 11.1%	0.1 ± 0.0%	99.76
Ca^{2+}	451 ± 8.8%	0.5 ± 1.3%	99.89
Mg^{2+}	21 ± 13.3%	0.1 ± 10.3%	99.52
S	28 ± 12.2%	0.2 ± 8.8%	99.29

Standard error of the mean is reported based on 95% confidence interval calculated from three samples

Figure 7.4 Pre-AD fouled HOA-1.2 membrane

7.3.2. Fouling analysis of wetted membrane

Figure 7.5 show the SEM images of the HP membrane wetted by Pre-AD water.



(a) (b)

Figure 7.5 SEM of wetted HP membrane (a) original HP membrane (b) wetted HP membrane

There is a clear difference between the original HP membrane and the wetted HP membrane. The wetted membrane appeared to be wetted by fats as there were fat-like spots on the wetted HP membrane even after drying. The SEM images show some layer on the wetted membrane, however, the nature of the compound was not identified by the SEM images.

Figure 7.6 shows the FTIR graph obtained for the wetted HP membrane by Pre-AD. The two peaks for wavenumbers at 1205 cm^{-1} and 1151 cm^{-1} are for C─F stretching in PTFE [138] from the membrane material. Apart from these two common peaks there are clear additional peaks for the wetted HP membrane specially for fats. The significant peaks for wavenumbers at 2916 cm^{-1} and 2841 cm^{-1} can be related to $-CH_2$ stretching of fats whereas 1734 $cm^{-1}$is for C=O stretching of fat [140]. Therefore, it can be clearly seen that fat has contributed to wetting of PTFE membrane.

The several peaks in the area between 1300 cm^{-1} to 1600 cm^{-1} could be most probably due to the presence of Amide I, Amide and Amide III in proteins [136, 137, 139, 140]. The additional peaks in the area between 700 cm^{-1} to 1020 cm^{-1} can be related for lactose and crystallised lactose [139, 140]. Although it shows some indicative peaks for proteins and lactose as well, the FTIR results indicate that fat is dominating the wetted membrane as there are very clear peaks for fats. This is possible as discussed in previous sections as Pre-AD contains a significant amount of fat which can cause membrane wetting [67].

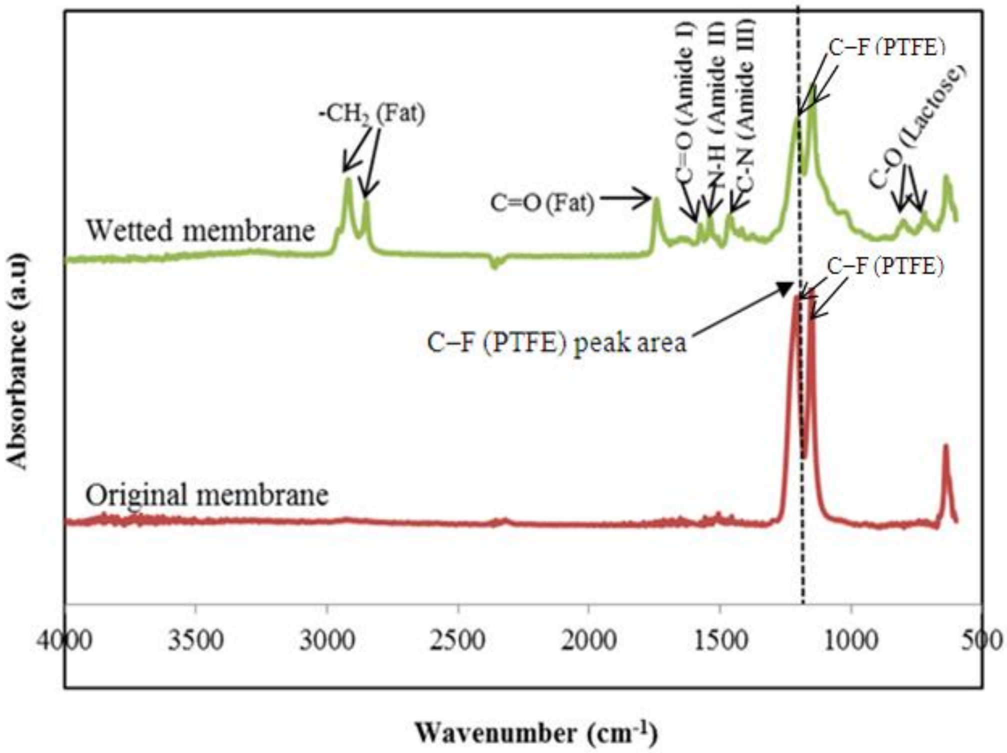


Figure 7.6 FTIR of Wetted HP membrane by Pre-AD

7.4. DCMD of Post-AD

In this section, the DCMD performance of Post-AD will be presented in terms of membrane performance (permeate flux, concentration factor/water recovery, solute rejection, permeate quality). In addition, any issues such as fouling and wetting will be identified and investigated.

7.4.1. Membrane performance of Post-AD

A volume of 8 L from Post-AD was taken as the initial feed and tested by the DCMD equipment in batch mode using the HP membrane. Figure 7.7 shows the DCMD performance of Post-AD on the HP membrane in terms of permeate flux and the F_T.

The initial flux started from 14 kg/m^2/h and increased after few hours due to stabilisation of the DCMD process. After that the flux again dropped slowly to 14 kg/m^2/h within 30 hours which could be due to fouling [67]. At this point the F_T was approximately 5. The permeate conductivity rose from 1.5 µS/cm to 95.6 µS/cm during the test. The increase in the permeate conductivity could be possibly due to penetration of ammonia in the retentate as there was an increase in permeate pH from 8.4 to 9.5. The rise in pH causes a shift in the equilibrium of ammonia and ammonium, where more volatile ammonia becomes available and can penetrate into the permeate. The ammonia taken up by the clean permeate can solubilize again into ammonium form which will lead to the observed increase in permeate conductivity.

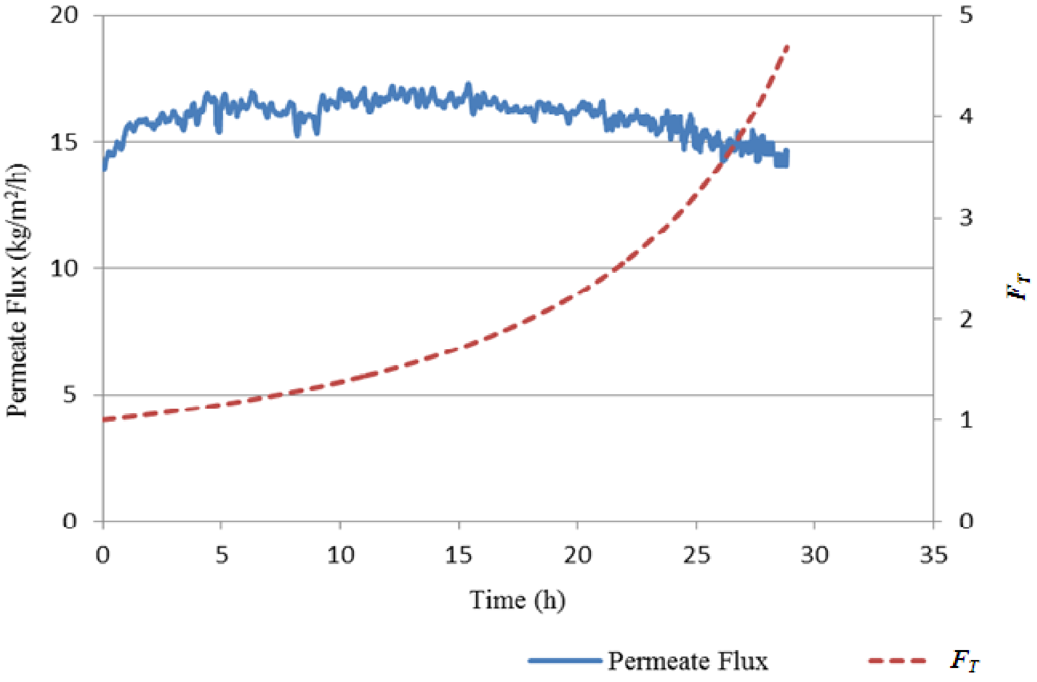


Figure 7.7 Performance of Post-AD on HP membrane

Table 7.7 shows the rejection of solutes tested at the end of the test.

Table 7.7 Solute rejection- Post-AD on HP membrane

Component	Final retentate concentration (mg/L)	Final permeate concentration (mg/L)	Rejection (%)
TOC	960 ± 7.7%	3 ± 2.4%	99.69
TN	715 ± 10.2%	90 ± 1.3%	87.41
K^+	548 ± 1.1%	0.1 ± 10.3%	99.98
Na^+	2,917 ± 3.1%	0.1 ± 6.3%	99.99
P	6 ± 11.5%	0.1 ± 7.0%	98.33
Ca^{2+}	177 ± 7.1%	1 ± 7.0%	99.62
Mg^{2+}	12 ± 5.6%	0.1 ± 0.0%	99.16
S	11 ± 5.8%	0.1 ± 12.6%	99.09

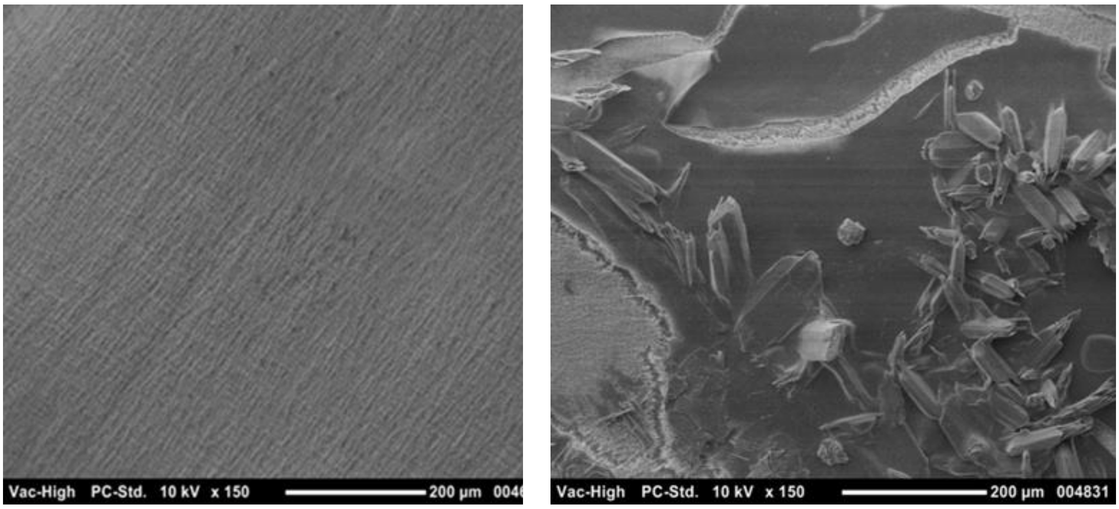
Standard error of the mean is reported based on 95% confidence interval calculated from three samples

According to solute rejection data, all the other solutes show a rejection above 98% which indicates that these components have not penetrated through the membrane in significant amounts. However, TN shows the lowest rejection of 87.4% which is clear indication of nitrogen penetration through the membrane. As observed by the pH increase of the permeate, this low TN rejection could be ammonia gas penetration through the membrane which is produced during the AD process and can be present in the Post-AD. Ammonia is well known to transport through MD membranes due to its volatility [145]. Therefore in our case for removing clean water from the waste water, ammonia penetration can be a problem if it is largely present in the permeate. However the concept for instead stripping ammonia from the waste water is also possible from this result, and has been explored for water treatment applications [146]. Except ammonia penetration, other solutes are well retained and therefore they do not affect the permeate quality. There was no indication of membrane wetting as there were no wetted spots on the final membrane as shown in the Figure 7.8. MD is thus a viable technique to concentration the Post-AD of combined dairy effluent using PTFE membrane. However managing ammonia transport to the permeate must be taken into account.

Figure 7.8 Post-AD fouled HP membrane

7.4.2. Fouling analysis of Post-AD fouled membranes

Figure 7.9 shows the SEM images of the fouled HP membrane by Post-AD where there is a thick fouling layer and some rod shaped fouling materials on the membrane. The chemical nature of the fouling layer will be discussed below.



(a) (b)

Figure 7.9 Post-AD fouled HP membrane (a) original membrane (b) Post-AD fouled membrane

FTIR graphs outlined in Figure 7.10 shows some indicative peaks for proteins and possibly lactose. The two common peaks for wavenumbers at 1195 cm^{-1} and 1045 cm^{-1} are for C─F stretching in PTFE [138] from the membrane material. Apart from these two common peaks there are clear additional peaks in the fouled membrane. These peaks are 1514 cm^{-1} and 1633 cm^{-1} which can be related to Amide I and Amide II indicating proteins as observed in Pre-AD as well. Although lactose was relatively lower in Post-AD, there are some peaks shown in the range of lactose which is 1010 cm^{-1} – 1045 cm^{-1}. This is however could also be calcium phosphate as this is also in the range of 800 cm^{-1} – 1050 cm^{-1}.The peaks observed for fats (2916 cm^{-1}, 2841 cm^{-1}, 1734cm^{-1}) in Figure 7.6 for the HP membrane wetted by Pre-AD could not be seen. This indicates that there was no considerable amount of fat present in the Post-AD, thus no membrane wetting caused by fat.

Table 7.8 summarises the chemical analysis of the fouling layer on HP membrane by Post-AD. This chemical analysis shows that there are some organic compounds in the fouling layer which could be mostly proteins as the relative composition of proteins in the feed is high compared to lactose and fat as shown in Table 7.3. However, deposition of inorganic materials has become more significant according to Table 7.8.

Similarly to the relative mineral composition of the feed shown in the Table 7.4, Na^+ is the most abundant cation followed Ca^{2+} and K^+. Na^+ and K^+ could exist either as free ions or could be bound with the membrane or proteins by charge interaction [69]. In terms of Ca^{2+}, it represents relatively high amount in fouling material compared to its relative composition in the feed indicating Ca^{2+} is a major contributor in fouling. Ca^{2+} is likely to adhere on the PTFE membrane with whey proteins [68, 69]. Ca^{2+} coupled with protein was also found to be a main contributor in fouling on polypropylene capillary membranes in DCMD of wastewater studied by Gryta (2008) [90]. Therefore, it can be assumed that Ca^{2+} has also played a similar role here with proteins, thus has contributed to fouling. In the same study , $CaSO_4$ crystallisation inside membrane pores was found to cause wetting of the membrane. Although, a membrane wetting could not be observed, $CaSO_4$ might have also contributed for fouling as relative composition of S is high in the fouling solution compared to the relative composition in the feed. Although the exact chemistry cannot be confirmed here, the most suitable cleaning method for Post-AD would be a combination of alkaline and acid as there is a combined organic and inorganic fouling.

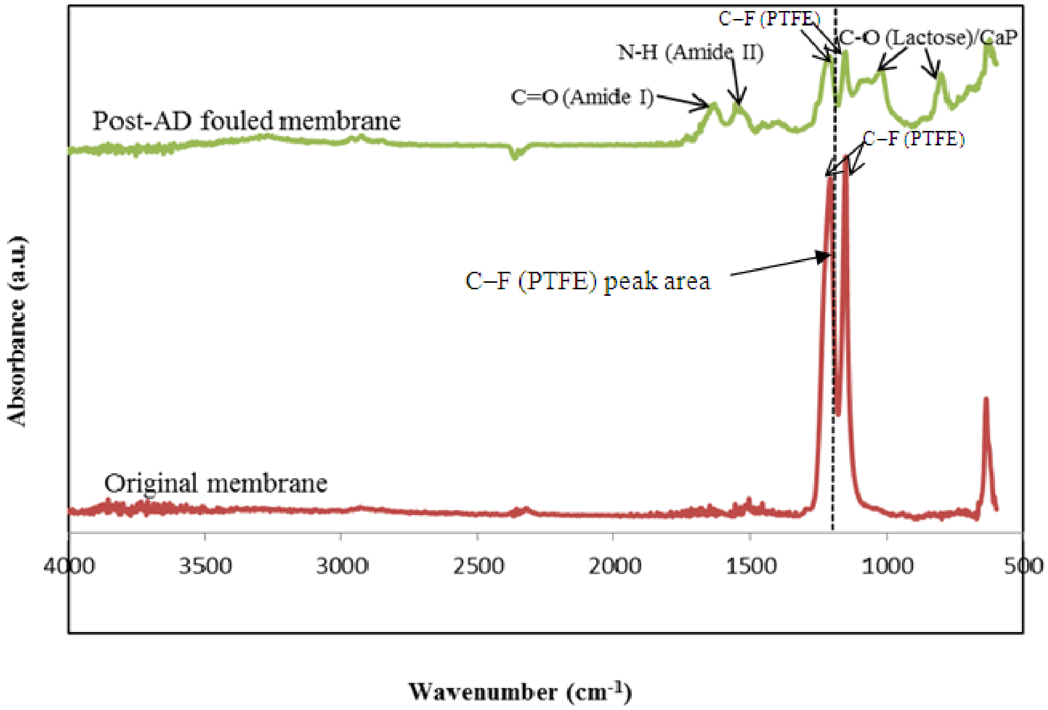


Figure 7.10 FTIR of Post-AD fouled HP membrane

Table 7.8 Chemical analysis of fouling on the HP membrane fouled by Post-AD

Component	Average fouling on membrane strip ($\mu g/cm^2$)	Relative amount of minerals in the feed
TOC	110 ± 10.1%	N/A
TN	38 ± 6.1%	N/A
K^+	310 ± 9.1%	10%
Na^+	1,057 ± 1.5%	49%
P	52 ± 9.4%	0.1%
Ca^{2+}	1,033 ± 3.7%	3%
Mg^{2+}	68 ± 10.2%	0.2%
S	111 ± 6.2%	0.2%

Standard error of the mean is reported based on 95% confidence interval calculated from three samples

7.5. Conclusions

DCMD is a viable membrane process for the treatment of combined dairy effluent stream with a membrane having suitable chemistry depending on the effluent stream, i.e. Pre-AD and Post-AD.

Use of conventional HP membrane for DCMD of Pre-AD was ineffective due to high amount of organic matter, particularly fats, which lead to membrane wetting. The permeate flux was observed to decrease from the beginning and then showed negative values after few minutes where the retentate was diluted. Wetting was confirmed by the appearance of the final membrane where it appeared transparent and the FTIR results showed some significant peaks related to fats and proteins, however, peaks for fats were more significant.

As the HP membrane was not suitable for Pre-AD treatment, the possibility of using the hydrophobic and oleophobic acrylic copolymer (HOA) was investigated with Pre-AD. The outcome was more promising. The maximum flux achieved with HOA membrane was 4 kg/m^2/h and it could reach up to F_T about 1.7 after 83 hours where the flux decreased to 2 kg/m^2/h. As the fouling was significant, a conventional CIP was performed to see try and restore flux by removing the fouling. However, a clean NaCl solution test performed after CIP showed negative flux and the membrane appeared to be wetted during the CIP. Thus, it can be stated that conventional CIP could lead to wetting in DCMD of Pre-AD. Nevertheless, after replacing with a new HOA membrane to further concentrate the retentate , a F_T of up to 2.6 was achieved with no observed wetting. For all solutes tested, rejection was above 99%. However, a revised cleaning routine was proposed, possibly avoiding NaOH which may have produced surfactants upon reaction of the fats on the membrane surface.

DCMD by Post-AD was also tested under the same conditions as Pre-AD with HP membrane. The initial flux started from 14 kg/m^2/h and increased after few hours due to stabilisation and then again dropped slowly to 14 kg/m^2/h within 30 hours where the F_T was approximately 5. The permeate conductivity rose from 1.5 µS/cm to 95.6 µS/cm during the test. The increase in the permeate conductivity could be possibly due to penetration of ammonia in the retentate as there was an increase in permeate pH from 8.4 to 9.5 and also TN rejection was 87%. Apart from ammonia penetration, all the other solutes showed a rejection above 98% and the final membrane did not appear wetted. If ammonia penetration can be minimised probably by a proper pre-treatment method, the use of HP membrane for DCMD of the Post-AD would be viable as all the other performance parameters (permeate flux, F_T, permeate quality in terms of other solutes except TN) ensure an efficient performance. However, if ammonia stripping is of use, MD could be applied to instead remove ammonia from the waste water for more suitable disposal or reuse of the waste water.

Chapter 8. Conclusions and Recommendations

8.1. Conclusions

The main objective of this research was to investigate the feasibility of MD to concentrate dairy waste streams and recover potable water. Sweet whey RO retentate (SWROR), Salty whey UF permeate (SUFP), Ion exchange regeneration stream and combined dairy effluent (Pre anaerobic digestion and Post anaerobic digestion stream) were tested using membranes with one or more of the following chemistries:. hydrophobic PTFE (HP), hydrophobic and oleophobic acrylic copolymer (HOA) and hydrophilic coated PTFE (HCP). The performance of the tested membranes was assessed on the basis of the permeate flux, achievable concentration factors, membrane rejection, membrane fouling and incidence of wetting.

Overall, MD was found to be a promising technique for the concentration of all the tested dairy streams and the recovery of high quality potable water. For SWROR, all three membranes gave high solute rejection (> 99%) with no signs of membrane wetting. The HP was selected for this process stream due to its highest permeate flux (17 kg/m^2/h).

The HP membrane was not found to be suitable for SUFP as the membrane wetting appeared to be a major issue, resulting in the increase in permeate conductivity and low solute rejection. This was attributed to hydrophobic interactions of the PTFE and organic compounds, which was accelerated by the increasing concentration of organic matter in the retentate with time. This was confirmed by the analysis of the foulants on the wetted membrane. There were relatively higher concentration of organic matter like fat, protein and lactose. The use of the HCP membrane was found to avoid the wetting problems and could be a suitable membrane for SUFP. Due to the hydrophilic chemistry, it reduced the interactions with the organic matter in the feed and minimise fouling and subsequent wetting.

The IX regeneration acid stream is another possible opportunity for the dairy industry to apply MD to concentrate the stream and recovery good quality potable water. The chemistry of the conventional hydrophobic PTFE membrane looked suitable to process this stream as there was no significant fouling or any wetting issues were observed.

MD is also a promising membrane process for the treatment of combined dairy effluent stream, i.e. Pre-AD and Post-And wastewater, provided a membrane having suitable chemistry is chosen. Use of conventional HP membrane for MD of Pre-AD was ineffective due to high amount of organic matter, particularly fats, which lead to membrane wetting as result of interactions between organic matter and the membrane leading membrane to lose its hydrophobicity . However, HOA membrane appeared to be suitable due to its hydrophobic and oleophobic properties. In contrast to the Pre-AD, Post-AD performed well with HP membrane which showed an effective flux, high water recovery and efficient solute rejection. The reason is the lower organic composition of Post-AD compared to Pre-AD. However, ammonia penetration was an issue confirmed by the low TN rejection. The HOA membrane, however, was found to be wetted by conventional CIP procedures. Further research is required to address this difficulty.

8.2. Recommendations

As recommendation for further studies in future, further research is required on the fouling of different feed streams in terms interactions between membranes and feed components. In depth analysis of fouling mechanism using advanced methods will help in order to select suitable membrane and develop new MD membranes with the desired characteristics. Also, membrane cleaning methods (enzymatic) other than conventional dairy CIP methods used in these experiments could be tested as conventional dairy CIP method may not work for all cases (i.e. HOA membrane was wetted by conventional CIP in Pre-AD treatment).

In addition, as observed in the SUFP treatment on HP membrane, high organic matter present in the feed could lead to membrane wetting and make some membranes not suitable for MD. Therefore, it is worth investigating possible pre-treatment methods before MD such as coagulant ion, antiscalant uses (to reduce the effect of $CaSO_4$) and adsorption methods (activated carbon) in order to remove organic matter from the feed.

Also, more effective filters prior to MD, biological degradation process or advanced methods like ultraviolet treatments can also be in interest. The use of these methods may, however, depend on different factors like nature of feed, feasibility and cost. For Post-AD treatment, it is important to use a suitable method of removing ammonia from the feed before MD as ammonia penetration was an issue and affects the quality of the permeate/water produced. Similarly, HCl gas penetration in the IX regeneration solution was also an issue that has to be prevented which affects the quality of water produced although in both cases HP membrane performed well with an efficient flux and no sign of wetting. However, with the help of further methods MD could be used as a technique to recover HCl and ammonia by IX regeneration and Post-AD treatment respectively.

As the methods discussed here are labour and time intensive, it is worth implementing automated, near real-time methods in membrane processes. These can be linked to robotic liquid handling systems which monitor and analyse membrane processes of complex feed streams generated in food and other industries which has higher sensitivity and accuracy [76, 123].

The scope of this study was to see the viability of MD for the selected dairy streams and to assess the overall level of fouling. It is recommended that high resolution SEM be used as a next step in future studies to more closely look at fouling of selected dairy streams on different membranes.

The use of hydrophilic coated PTFE membrane has been shown to give rise to less wetting by organic components than the use of a conventional PTFE membrane. The starting permeate flux of hydrophilic coated PTFE is, however, lower compared to the PTFE membrane. More work is required to relate these flux changes with theoretical models of mass transfer to better understand the MD performance of hydrophilic coated membranes.

Modelling of fouling is very difficult in MD of dairy streams due to the simultaneous heat and mass transfer that relies on too many uncertain parameters. These need to be modelled and assessed reliably in a good amount of time which is difficult in this study as the main focus was to experiment industry opportunities instead of focussing on fundamental aspects. A thorough study of fouling mechanism and relationship to fouling models in literature is an interesting area that could be pursued in future studies. The extension of these studies to novel membranes to elucidate the mechanisms of interactions of different components with the membrane would also be useful, especially for the hydrophilic coated membrane which minimises the wetting. Techniques such as lactose HPLC and reflectometry can be used along with techniques used in this study such as SEM, ICP and carbon and nitrogen analyser. SEM can be used at a range of resolutions to closely look at fouling. Reflectometry can be used to study component adhesion on membrane surface. These techniques were used by Hausmann et al. (2013) to study fundamental interactions of dairy components with PTFE membrane [67-69].

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