Whey Management for the Dairy Industry: Acid and Salty Whey Treatment and Processing Using Membrane Technology

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Abstract

Acid whey and salty whey have presented a major disposal issue for the dairy industry. The processing of acid whey has proven challenging due to the presence of lactic acid and high levels of minerals, while salty whey is underutilized due to the high levels of salt. The treatment of these two types of whey will allow the production of high value products, including whey powders, lactose powder, and concentrated salt solutions for use in cheese salting or the chlor-alkali industry. The use of membrane technology has been studied for the treatment and processing of these whey streams. Electrodialysis has been shown to be effective for the treatment of acid whey since the process can achieve high removal of lactic acid and minerals when compared to pressure driven membrane processes, such as nanofiltration. However, electrodialysis is not used widely due to the high operating costs associated with membrane replacement and electrical consumption as a result of membrane fouling and poor process performance.

In this thesis, the fouling of ion-exchange membranes during the electrodialysis of fresh sweet and acid whey was investigated. Although the fouling of ion-exchange membrane has been examined by many researchers, the feed solution was generally made using resolubilised powders. It has been demonstrated by other researchers that using fresh solutions provide results and outcomes closer to industrial applications. Furthermore, process optimization is a key parameter to reduce the cost of the treatment process. As a result, the effects of concentrate pH and applied current density were investigated to determine the optimum operating conditions that would minimize membrane fouling and enhance ion removal. Although membrane fouling occurred in all experiments, the effects on system performance were limited. Reductions in the current during pure sodium chloride circulation fell to a minimum of 80% of the original value after 5 hrs of whey processing. The use of an alkaline concentrate resulted in the strongest increase in system resistance, but the mineral deposits formed appeared to detach readily, thereby reducing these effects. The use of an acidic concentrate gave significantly greater rates of lactic acid removal, thus reducing the total membrane area required. A solution of hydrochloric acid with a pH of 1.0 ± 0.15 was effective for in-situ cleaning of the mineral deposits. However, protein deposits were not readily removed when using the recommended base cleaning formula of 3% sodium chloride at a pH of 9.2 ± 0.2.

The concentrate stream in an electrodialysis process is considered a waste stream thus adding to the total volumes of waste generated by the dairy factory. Therefore, the use of salty whey permeate as the concentrate stream was investigated during the electrodialysis of sweet whey. The use of salty whey permeate is expected to reduce freshwater update and the volumes of wastewater generated from the treatment process. The type of concentrate (0.1M sodium chloride or salty whey permeate) did not affect the rate of sweet whey demineralization or the energy consumed per tonne of sweet whey processed, but less sodium and more divalent cations were removed when salty whey permeate was used. In addition, the use of electrodialysis for the demineralization of salty whey permeate was investigated to generate a lactose rich stream as the diluate stream and a concentrated salt solution as the concentrate stream. It was observed that salty whey permeate could be effectively demineralized using either 0.1M sodium chloride or a second stream of salty whey permeate as the concentrate stream. The concentrate purity could be enhanced by using monovalent selective membranes without increasing the energy consumption of the process (3.2 ± 0.3 kWh per kg of sodium chloride removed from the diluate at 15 V across 2 cell pairs).

Furthermore, combining different membrane technologies can assist in enhancing the treatment of acid whey to produce high quality whey powder. Three process combinations were examined at pilot scale, namely, (1) ultrafiltration and electrodialysis; (2) ultrafiltration, nanofiltration, and electrodialysis; and (3) ultrafiltration, dia-nanofiltration, and electrodialysis. Although all three combinations were successful in reducing the levels of lactic acid and minerals in acid whey, the lowest ratio between lactic acid and lactose (0.017 g lactic acid/g of lactose) was obtained with the process that utilized dia-nanofiltration. The energy required for the electrodialysis of the ultrafiltration permeate and dia-nanofiltration retentate were comparable (7.5 and 7.8 kWh/tonne of feed, respectively). However, the dia-nanofiltration retentate was at least 3.5 times more concentrated than the ultrafiltration permeate, thus reducing the annual energy consumption and capital investment of the electrodialysis unit. The product of the nanofiltration and electrodialysis process was successfully dried to produce a powder with an ash and moisture content of 4% and 2.5%, respectively.

To further add value to the acid whey treatment process, the possibility of recovering lactic acid from a salt solution was investigated using either loose reverse osmosis membranes or an electrodialysis process. The recovered lactic acid could be reused in the cheese making process thus reducing fresh acid intake. Partial separation between lactic acid and salts was achieved at low applied pressures and feed pH in the reverse osmosis process, as a greater permeation of salts was observed under these conditions. Furthermore, lactic acid retention was enhanced by operating at room temperature with low feed pH. Partial separation between lactic acid and potassium chloride was also achieved in the electrodialysis process. However, the final concentration of potassium at 70% demineralization of the diluate stream was relatively high resulting in a low purity of lactic acid. Furthermore, the observed losses in lactic acid increased with the addition of sodium chloride to the feed solution. This indicates that the separation becomes more challenging as the complexity of the feed solution increases.

Although electrodialysis has been widely studied for the treatment of sweet and acid whey, other electrically driven membrane processes, such as membrane capacitive deionization, have never been investigated. Three different pre-treated acid whey solutions were processed through a lab scale membrane capacitive deionization unit, namely, ultrafiltration permeate, nanofiltration retentate, and dia-nanofiltration retentate. Although a lowest demineralization rate was calculated for the nanofiltration retentate, a higher removal of lactic acid and cations was achieved when compared to the ultrafiltration permeate. Furthermore, similar molar concentration of ions were removed from the ultrafiltration permeate and dia-nanofiltration retentate (41 mEq/L and 43 mEq/L, respectively), however, the total energy consumption was lower for the dia-nanofiltration retentate (0.0122 Wh/mEq of cations removed Vs 0.0243 Wh/mEq of cations removed from the ultrafiltration permeate). Finally, it was found that the energy consumed for the treatment of acid whey ultrafiltered permeate using membrane capacitive deionization was comparable to the energy reported for the electrodialysis process.

Overall, the results presented in this thesis have demonstrated that both acid whey and salty whey can be treated and transferred into valuable products for the dairy industry. Future work on this topic could include: (1) investigating the feasibility of using electrodialysis reversal for acid whey treatment; (2) performing a pilot scale assessment of the membrane capacitive deionization process; (3) undertaking an economic evaluation to justify using pressure driven membrane process prior to electrodialysis and membrane capacitive deionization processes; and (4) reassessing the possibility of recovering lactic acid from a salt solution by using other available technologies/ processes such as electrodeionization and selective crystallization of lactic acid.

Declaration

This is to declare that

(1) The thesis titled '*Whey Management for the Dairy Industry: Acid and Salty Whey Treatment and Processing Using Membrane Technology*' comprises only of any original work done by me towards the degree of Doctor of Philosophy (PhD).

(2) All other materials used in this thesis have been cited and the contribution of others have been acknowledged.

(3) The thesis is less than 100,000 words in length exclusive of tables, figures, diagrams, bibliographies and appendices.

Sahar Talebi

April 2020

Preface

The results presented in chapters 4, 5, and 6 of this Thesis have been published as below.

1. **Talebi, S**., Chen, G. Q., Freeman, B., Suarez, F., Freckleton, A., Bathurst, K., & Kentish, S. E, *Fouling and in-situ cleaning of ion-exchange membranes during the electrodialysis of fresh acid and sweet whey*. Journal of food engineering, 2019, 246: p. 192-199.
2. **Talebi, S**., Kee, E., Chen, G. Q., Bathurst, K., & Kentish, S. E, *Utilisation of salty whey ultrafiltration permeate with electrodialysis*. International Dairy Journal, 2019, 99: 104549.
3. **Talebi, S**., Suarez, F., Chen, G. Q., Chen, X., Bathurst, K., & Kentish, S. E, *A pilot study on the removal of lactic acid and minerals from acid whey using membrane technology.* ACS Sustainable Chemistry & Engineering, 2020, 8 (7): 2742-2752

Other publications:

1. Hassanvand, A., Wei, K., **Talebi, S**., Chen, G., Kentish, S, *The Role of Ion Exchange Membranes in Membrane Capacitive Deionisation.* Membranes, 2017, 7(3): p. 54.
2. Chen, G. Q., **Talebi, S**., Gras, S. L., Weeks, M., & Kentish, S. E, *A review of salty waste stream management in the Australian dairy industry*. Journal of environmental management, 2018, 224: p.406-413.

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CHAPTER 1. Introduction

The demand for milk and milk products has not only increased the volume of products produced by dairy companies but has also increased the volumes of generated waste. Dairy waste is known for high biological and oxygen demand, high nutrient concentrations, and the presence of organic and inorganic substances [1]. This means that treatment is required before disposal, thus adding additional costs to the dairy industry.

One of these waste streams is whey, which is a by-product of cheese production, as the coagulation of milk proteins leaves behind a stream that contains whey proteins, lactose and minerals [2]. Recent growth in the demand and popularity of cheese has resulted in the generation of large volumes of whey. In 2014, approximately 5.6 million tonnes of whey were transformed into useful products which were traded globally with the majority being in the form of whey powder. It is forecasted that by 2023, more than 25 million tonnes of cheese will be produced worldwide, which would result in the production of even larger volumes of whey [3]. According to Dairy Australia, 381,000 tonnes of cheese were produced in 2018/2019 in Australia [4], indicating that approximately 3 million tonnes of whey were generated simultaneously. These statistics highlight the need for the development of processes and technologies to treat whey.

Whey is divided into three main types based on the manufactured cheese. Sweet whey is produced during the manufacturing of hard cheeses using rennet coagulation of casein. This type of whey is known for its neutral pH and easy processing to powders. Conversely, acid whey is produced as a result of fresh acid coagulation to produce soft cheeses. This type of whey has proven challenging to the dairy industry due to the presence of lactic acid and high levels of minerals that interfere with water evaporation and result in the formation of a sticky powder when dried [5, 6]. Lastly, salty whey is produced as a result of the cheese salting process and is known to contain 50-60% of the salt added to the curd [7]. The large salt content of salty whey limits its utilization.

Membrane technologies are one of the main processes considered for whey treatment. These technologies are widely used in the dairy industry throughout the different manufacturing stages, from concentrating milk on the farm to milk processing in the dairy factory. The membrane processes used in a dairy factory can be divided into two main categories, namely pressure driven membrane and electrically driven membrane processes. The former has been applied in the dairy industry for more than 40 years as a technology for fractionating and concentrating the different functional molecules found in milk and whey (**Figure 1.1**) [8]. The separation in pressure driven membrane processes is based predominantly on the size of the components present in the feed solution. The components smaller than the pore size of the membrane pass through to the permeate side, while the larger components are retained in the retentate stream. However, in nanofiltration (NF) process, the separation is also affected by the charge of the components [9]. This means that multivalent ions, such as calcium and magnesium, can be effectively retained in the retentate stream thus increasing its nutritional value.

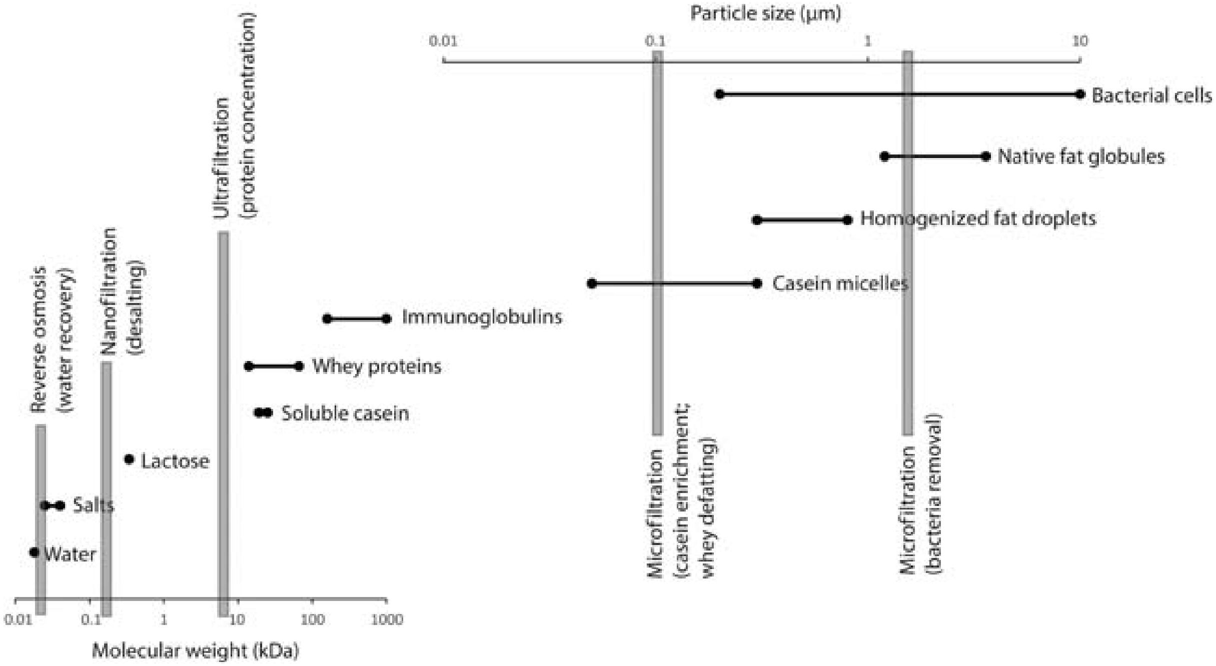


Figure 1.1. Applications of pressure driven membranes in dairy processing (adapted from [8]).

In recent years, electrically driven membrane processes such as electrodialysis (ED) have been utilized for several industrial applications such as water desalination, acid recovery, and heavy metal recovery [10]. The separation is based on the application of an electrical current to separate charged ions from uncharged molecules such as lactose and large charged molecules such as whey proteins [6]. Another well-known electrically driven membrane process that has been developed more recently for water treatment applications is membrane capacitive deionization (MCDI) [11]. Similar to ED, in this process an electrical current is used to remove charged ions from the feed solution, however, in the case of MCDI, the ions are absorbed into the carbon electrodes. Electrically driven membranes are not used widely by the dairy industry due to the high operating costs associated with the high cost of ion-exchange membranes (IEMs) used in the process. Furthermore, high electrical energy consumption cannot be avoided if the process is not operated under the optimal conditions to avoid membrane fouling and water splitting. Nevertheless, membrane fouling is an issue associated also with pressure driven membranes, with the only difference being that pressure driven membrane processes are much more widely researched and optimized to overcome the issues of membrane fouling.

When it comes to whey demineralization and treatment, especially acid whey, the main aim is the removal of lactic acid and minerals to an acceptable level for further processing [12]. Although pressure driven membranes, such as NF, have been validated for the treatment of acid whey, there is a limit to the maximum levels of lactic acid removed. For example, Bédas *et al.* [8] reported 30% lactic acid and 46-60% monovalent ions removal from acid whey when using a semi-industrial scale NF. This indicates that using ED or MCDI processes to achieve higher lactic acid removal is unavoidable, since ED has been proven effective in removing 60% lactic acid when 70% demineralization was achieved [13].

As a result, this thesis aimed at furthering the understanding of the use of ED for acid whey treatment by studying the fouling of IEMs during the treatment of both acid and sweet whey. The operating conditions were optimized to reduce membrane fouling. In-situ cleaning of the membranes was performed using the chemicals recommended by the American Water Works Association. The ED process was also investigated for the treatment of salty whey and the recovery of lactic acid from the waste streams generated from the acid whey treatment process. Although ED has been proven effective for acid whey treatment, MCDI has never been examined for acid whey treatment. Furthermore, since both NF and ED can successfully remove lactic acid to a certain level, combining these two technologies should assist in achieving higher removal of lactic acid and minerals.

CHAPTER 2. Theory and Literature Review

2.1. Introduction

The dairy industry plays an important role in the economy since milk, also known as white gold, can be used to make a variety of food products, such as milk powders, lactoferrin, infant formula, cheese, yogurt, butter, ice cream, etc. The Department of Agriculture in Australia reported that in 2017/2018 the dairy industry contributed $3.5 billion to the agricultural export income. Furthermore, the process of obtaining and processing milk is labour intensive, thus creating many employment opportunities in rural areas [14]. However, the different manufacturing processes used in a dairy factory to convert milk into different products result in the generation of large volumes of waste or by-products. These waste streams require treatment before disposal due to their high biological and chemical oxygen demand, total nitrogen and phosphorous content [1]. The disposal cost is usually determined based on the waste stream characteristics and the ability of the waste treatment facility to cope with the discharged volumes. As a result, many dairy factories tend to recover water for re-use in the manufacturing plant thus reducing wastewater volumes and freshwater intake. In addition, the presence of milk solids in the waste streams is a lost opportunity if not recovered [15]. Therefore, the industry is always exploring opportunities to convert waste streams into high-value products.

In this chapter, one of the main by-products of cheese making is discussed. The possible uses and treatment technologies for this waste are briefly described, and the scope of this thesis is outlined.

2.2. Dairy Waste Streams: Whey

Whey is the term used to describe the excess liquid generated during the conversion of milk to different types of cheese [2]. Whey is known to contain many of the important nutrients found in milk, for example, whey proteins, lactose and water-soluble vitamins [16]. To produce 1 kg of cheese, 10 kg of milk is used with the remaining 9 kg being whey [17]. In 2011, 180-190 million tonnes of whey were produced worldwide with only 50% utilized either as liquid whey or processed to manufacture different powders [18]. The remainder was discarded as waste. Although the solid content of whey is less than 7%, the disposal of whey does not only present a serious environmental issue but a lost opportunity to dairy factories.

A dairy plant manufacturing cheese can produce three types of whey, namely acid whey, sweet whey and salty whey, each having its unique characteristics as a result of the different production method. While sweet whey is produced during rennet coagulation of casein, acid whey is produced during fresh acid coagulation using a starter culture that consumes lactose and produces lactic acid which in turn lowers the milk pH. Salty whey is a by-product of the hard cheese salting process since the addition of salt tends to push more water out of the cheese curd.

When comparing the different types of whey, it is observed that both sweet whey and salty whey are close to neutral in pH while acid whey has an acidic pH (**Table 2.1**). The low pH of acid whey is mainly due to the presence of high concentrations of lactic acid in comparison to sweet and salty whey. Furthermore, as observed in **Table 2.1**, the mineral content of acid whey is much higher than sweet whey but less than salty whey. The high mineral content in acid whey is due to the greater solubility of calcium salts at low pH. On the other hand, the high salinity of salty whey is a result of the cheese salting process where 50-60% of the added salt is removed with the water expelled from the curd [7]. Another important difference is the protein content. The low pH of acid whey results in protein precipitation into the cheese curd thus reducing the protein content of the liquid whey [19]. The low initial protein content of acid whey indicates that the protein content of any dried powder might not be sufficiently high to be of saleable value.

Table 2.1. Comparison of the three major types of whey [13, 19-21].

Type of whey	**Sweet whey**	**Acid whey**	**Salty whey**
Example of cheese	Cheddar	Cream cheese	Salted cheddar
pH	5.9-6.3	4.3-4.6	5.0-5.2
Total solid (%)	6.3-7.7	5.2-6.2	12
Fat (%)	0.50	0.1-0.25	0.60
Protein (%)	0.6-1.0	0.47-0.55	0.60
Lactose (%)	4.6-5.2	4.0-4.3	-
Minerals (%)	0.45-0.50	0.57-0.80	6.9
Lactic acid (%)	0.05-0.20	0.50-0.80	-

2.2.1. Challenges Associated with Processing of Acid Whey

The type of whey to be treated affects greatly the complexity of the treatment process. Although sweet whey is easy to convert into different food ingredients, processing of acid whey is much harder. This is mainly due to the presence of lactic acid and calcium, which are known to affect the crystallization of lactose, resulting in agglomerates and lump formation in the dried powder as demonstrated in **Figure 2.1 (b) and (c)** [12]. Lactic acid forms different complexes with water molecules that bind to the lactose molecules via strong hydrogen bonds. These complexes are further strengthened by the presence of strong ion-dipole interactions with calcium ions [5, 6, 22]. The interactions between calcium and lactic acid can also result in the formation of calcium lactate crystals which can increase the viscosity of the thickened solution [23]. Chandrapala and Vasiljevic [12] reported a yield of 81% when spray drying pure lactose, while the yield dropped to 52% when 1% lactic acid and 0.12% calcium were present. Similar results were obtained by Saffari and Langrish [24], who observed a yield of 60% and an increase in the moisture content to 2.7% when the concentration of lactic acid was 1% in a lactose-lactic acid solution, versus a yield of 71% and a moisture content of 1.3% when lactic acid was not present. These authors also showed that the presence of lactic acid lowered the glass transition temperature of lactose below the dryer temperature (**Figure 2.2**), resulting in the formation of sticky amorphous lactose powder. In addition to the issues faced during the drying process, the low pH of acid whey reduces its value and potential uses in food applications [25]. Nevertheless, several studies have proposed that the partial removal of lactic acid from acid whey can enhance the product taste and dryability [13, 26]. Chandrapala and Vasiljevic [12] demonstrated that the powder structure enhanced as the lactic acid and calcium content were lowered to 0.05% and 0.035%, respectively (**Figure 2.1 (d)**). It is well known that processing of acid whey to a powder will not only reduce the waste volumes but could also add value to a dairy process as the nutrients (i.e. protein and lactose) are readily captured.

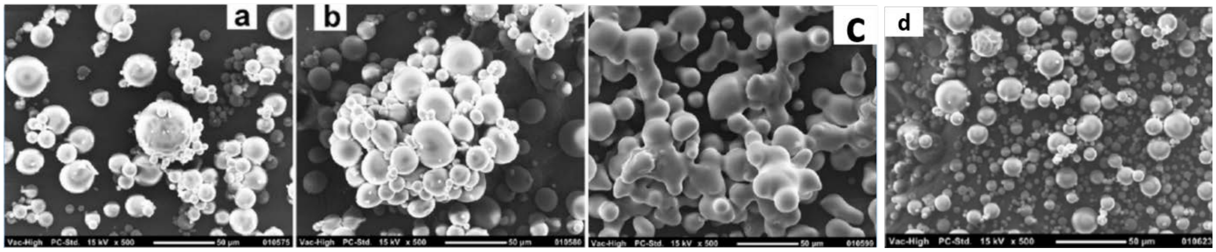


Figure 2.1. Scanning electron microscope images of spray dried lactose powders: (a) pure lactose, (b) lactose + 1% lactic acid, (c) lactose + 1% lactic acid + 0.12% calcium, and (d) lactose + 0.05% lactic acid + 0.035% calcium (reproduced from [12]).

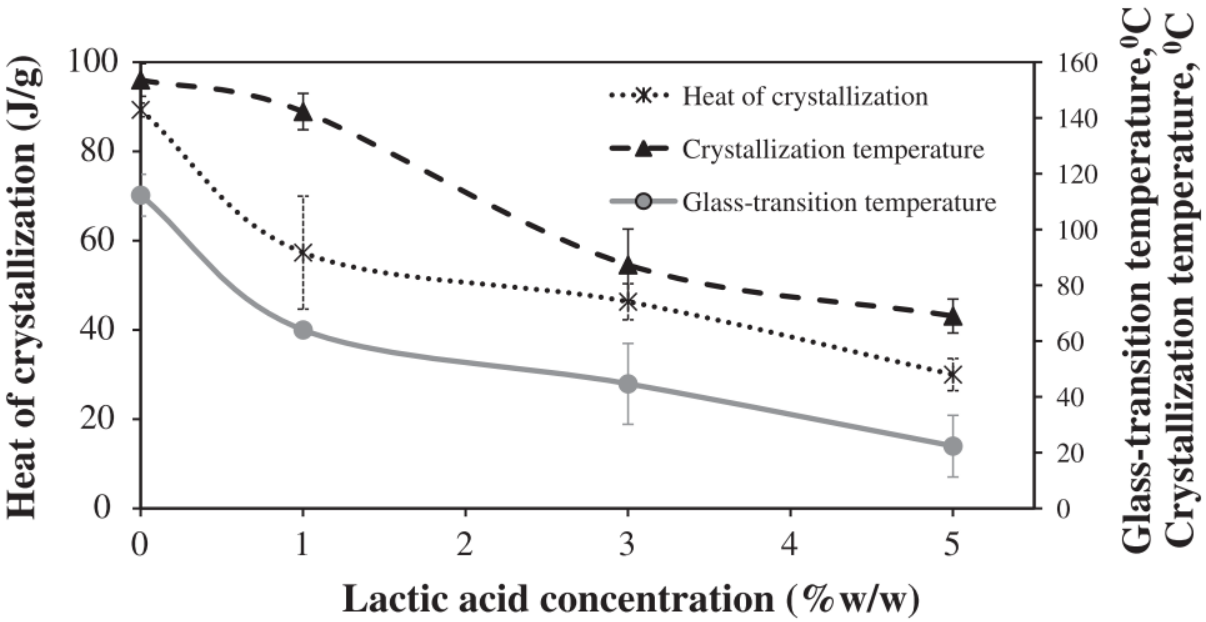


Figure 2.2. Effect of lactic acid concentration on the glass transition temperature of spray dried lactose solution (adapted from [24]).

2.2.2. Possible Uses of Whey

The nutritional properties of whey promote its utilization in many applications. Whey can be utilized to feed cattle and pigs. This means that the milk nutrients found in whey are introduced back into the human food chain. The use of whey as animal feed is cheap, simple and suitable for small farms. However, for the process to be economically feasible, the farm and the dairy production plant need to be located within a short distance to each other to reduce transportation costs of such a dilute product. In addition, costs associated with pre-treatment for the removal of salt and water should be taken into account, as some animals find it difficult to metabolize food with a high salt content [27].

Whey is also known for its land enriching characteristics. In 1974, 40% of liquid whey was sprayed on lands and used as fertilizer in Australia. However, if overdone, it results in the accumulation of salts, that might reduce the land's ability to grow crops [28]. In addition, the application is season-limited, and the high cost of transportation makes the process economically unattractive [29].

The high-water content of whey makes it ideal for beverage production. Gallardo-Escamilla *et al.* [30] performed a sensory test on different types of whey and reported that the flavour is generally affected by the absence or the presence of starter cultures, and the processing conditions during the cheese making processes. Pereira *et al.* [31] developed fermented drinks from the protein rich stream and lactose rich stream produced from the ultrafiltration (UF) of whey. The drinks were made using three different microorganisms and tested by a sensory panel. Unfortunately, not all the drinks were acceptable in taste, indicating that further development and research were needed. In addition, the amount of whey that can be converted into whey drinks is limited, implying the importance of developing other applications for whey [32].

The lactose content of whey can be fermented to different products such as lactic acid and ethanol [3, 32]. Several countries, such as New Zealand, have utilized whey to produce ethanol since 1985, which can be used in food, chemicals, cosmetic and pharmaceutical industries, and as an environmentally friendly fuel source [33]. The organic load of whey can also be used as a feed source for microalgae cultivation media [34] and for the production of different strains of yeast [35].

The main application of sweet whey is the production of different powders since powders have a longer shelf life compared to liquids. Furthermore, whey proteins including β-lactoglobulin, α-lactalbumin, lactoperoxidase, and lactoferrin, are well known for their health-promoting properties [36]. As a result, whey powders are not only used for animal feed, but also in many food applications, such as bakery products, ice-cream, infant formula, and meat products [17]. The use of whey powders as food substitutes does not only have a positive impact on consumer health, but it also reduces the cost of raw materials on the manufacturer [36]. The type of whey powder manufactured depends on the original whey characteristics and the processing steps involved. For example, demineralized whey powder is produced after the removal of salts from the whey. Other examples of whey powders are whey protein concentrate (WPC; 30-60% protein), whey protein isolates (WPI; 90-98% protein) and high purity lactose powder [37, 38]. When manufacturing whey powder for food applications, the following should be taken into consideration [37]: (1) salt content; (2) protein to sugar ratio; (3) sweetening ability; and (4) lactose solubility [19].

2.3. Membrane Technology in the Dairy Industry

The dairy industry was one of the earliest food industries to adopt the use of membrane processes, as a cheaper alternative, for component separation, and for the development of new products [39, 40]. Membrane processes are well known for their low energy requirements and the ability to recover high quality water. These processes are non-thermal thus avoiding or reducing the possibility of protein denaturation [41, 42]. On the other hand, membrane processes are known for their high operating costs associated with the replacement of membranes and the need for pre-treatment to reduce membrane damage and fouling [43, 44]. Furthermore, in most cases, a single membrane process is usually insufficient to obtain the required product, indicating the need to use a combination of membrane processes, thus increasing the capital and operating costs [45].

Membrane processes commonly used in the dairy industry can be divided into two main categories based on the applied driving force, namely pressure driven and electrically driven processes. In pressure driven membrane processes, a semi-permeable membrane is used to separate the feed into two streams, namely permeate and retentate. The former represents the components in the feed solution that permeate through the membrane, while the retentate presents the components in the feed that are rejected by the membrane. Pressure driven membrane processes are characterized based on the applied pressure gradient and the membrane pore size as shown in **Figure 2.3**. Microfiltration (MF) membranes have the largest pore size, therefore they are mainly used to separate bacteria, fat and components with molecular weight cut-off greater than 200 kDa [46]. Ultrafiltration (UF) is capable of retaining molecules with a molecular weight between 1-200 kDa, as a result, the process is used for milk standardization and production of milk protein concentrates [47]. Nanofiltration (NF), with a molecular weight cut-off between 200-1000 Da, is used for demineralization and concentration of whey as discussed in the following sections. Reverse osmosis (RO) is utilized for concentrating lactose and recovering water from waste streams as the process has a molecular weight cut-off of 100 Da [48]. In electrically driven membrane processes, such as electrodialysis (ED) and membrane capacitive deionization (MCDI), an electrical current is used to drive charged ions across ion-exchange membranes (IEMs). ED is mainly used for whey demineralization as discussed in the coming sections.

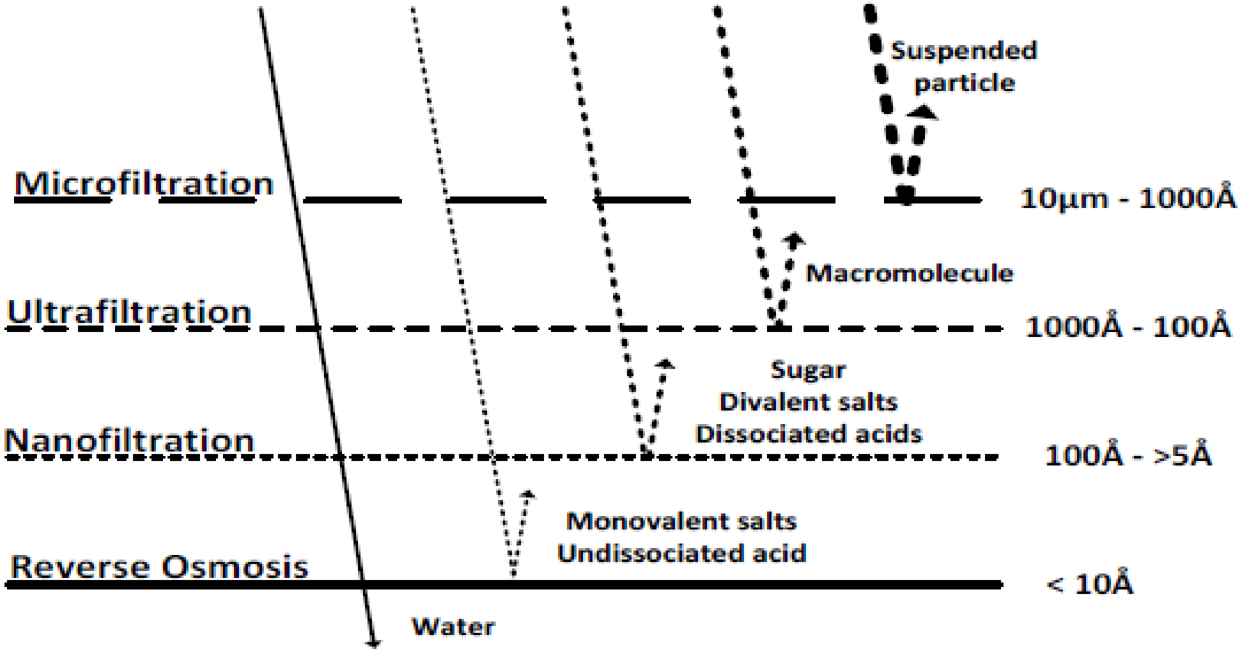


Figure 2.3. Sieving characteristic of pressure driven membranes (adapted from [49]).

2.4. Demineralization Processes

Demineralization is one of the main application of membrane technologies in the dairy industry, especially for processing whey and producing different whey powders [50-52]. Demineralization refers to the process of removing minerals, such as inorganic salts. In some cases, a reduction in the level of organic ions can also be observed. The process aims to produce whey powders that are non-hygroscopic, low in salt content, and are suitable to be used as food ingredients. Demineralization is also known to increase the value of the produced powder. For example, partially demineralized whey (25-30%) can be used in ice-cream and bakery products, while highly demineralized whey (90-95%) can be applied in infant formula. In the following sections, the available demineralization technologies for whey treatment are discussed, with a special focus on acid whey.

2.4.1. Nanofiltration

NF, with a molecular weight cut-off between 200-1000 Da, is one of the widely used pressure driven membrane processes in the dairy industry and especially for whey demineralization and concentration. The separation mechanism in NF is based on both charge and the size distribution among various species, which means that the membranes allow water and monovalent ions to pass through to the permeate side, while the multivalent and disaccharides, such as lactose, remain in the retentate side [9, 45]. It is well known that most of the commercially available NF membranes are negatively charged under neutral and alkaline pH conditions [53]. However, the isoelectric point and surface charge of the membrane can vary based on the solution composition which in turn will result in different separation performance [54].

There are many advantages associated with the use of NF for whey demineralization, for example [55]: (1) low capital cost; (2) 25-55% lower operating cost compared to other demineralization processes; (3) simple installation and operation; (4) elimination of the use of regeneration chemicals or brine solutions; (5) the ability to simultaneously demineralize and concentrate the feed solution; (6) good lactose and protein retention; and (7) selective separation between monovalent and divalent ions. The NF process can typically reduce the feed solution ash content by 35%. Ash removal can be increased to 45% when NF is combined with diafiltration, this process is known as diananofiltration (Dia-NF) [41, 50]. However, greater demineralization rates can be obtained using other available technologies as discussed in the coming sections. Furthermore, the maximum concentration of the retentate stream is limited by the solubility of lactose which is 19.2 grams of lactose per 100 grams of water at room temperature [56]. Another challenge facing the industry is the high total nitrogen in the effluent (even after RO) due to the high urea concentration. UF, NF and RO poorly reject urea which contributes to the effluent wastewater exceeding the discharge guidelines for nitrogen. However, this issue is outside the scope of this thesis.

Conventional whey demineralization and concentration involves the use of evaporators and RO, followed by demineralization using ion-exchange (IE) or ED. This process is known for its high capital and operating costs, making it unattractive to the dairy industry [57]. However, with the development of pressure driven membranes, both concentration and demineralization processes can be performed using a single NF unit [58]. Several researchers have investigated the use of NF for the treatment of sweet whey [59-62]. Greiter *et al.* [63] compared the ionic concentration of sweet whey concentrated three times using NF with the values reported by Chaveron *et al.* [64], who concentrated sweet whey three times using evaporation. Greiter *et al.* [63] found that, in comparison to evaporation, NF was more effective in removing monovalent ions, for example, sodium (Na^{+}) was 35% lower than the product obtained from evaporation, while the levels of potassium (K^{+}), chloride (Cl^{-}), and phosphate (PO_4^{-}) were lower by 42%, 71%, and 16%, respectively [63]. Suarez *et al.* [65] compared the behaviour of NF used for the treatment of sweet whey to when the process was utilized for UF milk permeate. The authors observed a higher flux drop in the case of sweet whey due to the presence of whey protein which tends to form a gel on the membrane surface thus adding to the overall mass transfer resistance. This also resulted in higher retention of ions, nevertheless, the total salt content was reduced by at least 30%. The use of NF for sweet whey demineralization was modelled by Van der Horst *et al.* [66] who concluded that at low permeate flux, diffusive mass transfer allows higher salt removal in comparison to convective mass transport at high flux. NF has also been investigated for salty whey demineralization. For example, Hinkova *et al.* [9] used NF for the treatment of salty whey permeate from UF and reported retention values of 95% for lactose, 5-38% for monovalent ions and 50% for calcium when NTR-7450-S2F membranes from Nitto Denko were used and the feed pH was adjusted to 5-5.7.

NF is also used for the removal of lactic acid from acid whey. The separation is carried out based on the difference in molecular weight of lactic acid and lactose present in acid whey. NF can either be used directly after the removal of fat and bacteria from whey using pre-treatment processes, such as MF, or after the separation of whey proteins using UF (**Figure 2.4**). NF has been successfully validated for lactic acid removal from industrial fermentation broths where the concentration of lactic acid is 10-20 times higher than that found in acid whey [67]. Nanofiltration was examined in 1992 for the treatment of acid whey by Kelly and Kelly [68]. The authors obtained 35% ash removal when the microfiltered acid whey was concentrated by a factor of 4 using NF, the percentage of ash removed increased to 41% when Dia-NF was used. However, the authors did not investigate lactic acid removal in their study. In a recent paper published by Bédas *et al.* [69], a semi-industrial scale NF unit was used to remove both lactic acid and minerals from acid whey. The authors claimed that the powder produced using the NF retentate was not sticky.

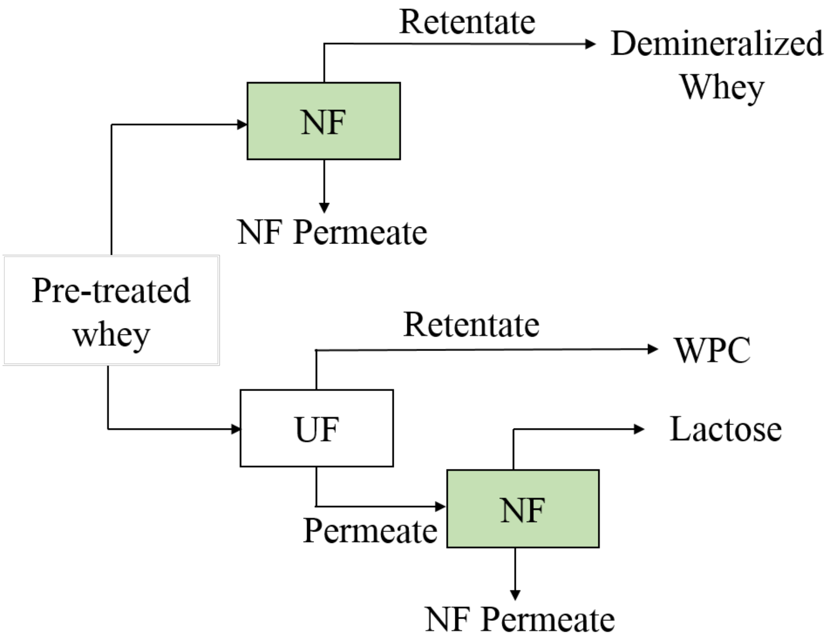


Figure 2.4. The use of nanofiltration process for acid whey treatment (reproduced from [66]).

Several factors affect the degree of lactic acid removal during NF, namely feed solution pH, process temperature, membrane material, the concentration of lactic acid in the feed and mineral solubility. Chandrapala *et al.* [25] concluded that lactose retention is a function of temperature only, as the molecules are uncharged, whereas the permeation of lactic acid depends on the pH, temperature and membrane characteristics. In particular, an important factor that affects the permeability or transmission of lactic acid is the ratio of lactate ions to non-ionized (non-dissociated) lactic acid in the feed stream. This ratio depends strongly on the equilibrium of lactic acid at the operating temperature of the system and can be calculated using the Henderson-Hasselbalch equation (**Eq. 2.1**).

$$pH = pK_a + log\frac{[lactate]}{[lactic\ acid]} \qquad \textbf{Eq. 2.1}$$

where, pK_a is the dissociation constant of lactic acid.

The effect of pH and temperature was further investigated by Chandrapala *et al.* [70]. They showed that at different temperatures and pH, the different components present in acid whey tend to behave differently. The authors predicted that NF would be most efficient for lactic acid removal at lower feed pH. This was further investigated by Chandrapala *et al.* [25] who showed that as the degree of dissociation increases, the retention of lactic acid increases. They found that when the pH of acid whey was adjusted to 3, almost 50% of the lactic acid was removed since only 19% of the lactic acid was dissociated into lactate ions.

Although Kumar *et al.* [50] and Salehi [41] claimed that the use of Dia-NF could increase the removal of ash, this was not the case when it came to lactic acid removal from acid whey. Chandrapala *et al.* [25] illustrated that the use of Dia-NF increased the retention of lactic acid compared to normal NF process under the same feed pH and temperature conditions, as shown in **Table 2.2**. This emphasizes the effect of feed concentration on the separation process, as high feed concentrations result in a better lactic acid removal.

Table 2.2. Effect of operating temperature, membrane type and mode of operation on the removal of lactic acid and ash from micro-filtered acid whey using nanofiltration and diananofiltration processes.

		Nanofiltration [25]	**Diananofiltration** [25]	**Nanofiltration** [67]
Membrane type		Thin film NF- HL	Thin film NF- HL	XN45 Membrane
Operating pH		3	3	3
Temperature (°C)		25	25	5
Lactose retention (%)		95.1	97	97
Lactic acid removal (%)		49	34	60
	Ca^{+2}	39.1	49.9	
Mineral removal (%)	**Mg^{+2}**	31.5	25.1	NaCl rejection of 65%
	Na^{+}	68.5	71.3	
	K^{+}	79.3	84.5	

2.4.2. Electrodialysis

ED refers to the process in which ions are transferred through charged semipermeable non-selective membranes, also known as IEMs, under the application of an electric current, which is generated using a direct current (DC) source [71-74]. An ED unit (**Figure 2.5**) consists of several compartments separated by alternative cation exchange membranes (CEMs) and anion exchange membranes (AEMs). The membranes are separated using spacers that form the main flow channels in the unit [44]. A single ED unit can contain up to 200 cells with the last compartments on each side of the unit containing the electrodes. The applied current will promote the cations and anions to migrate towards the cathode and anode, respectively. Free migration does not take place, as each membrane will prevent the passage of ions having similar charge to the charge of the membrane (**Figure 2.5**).

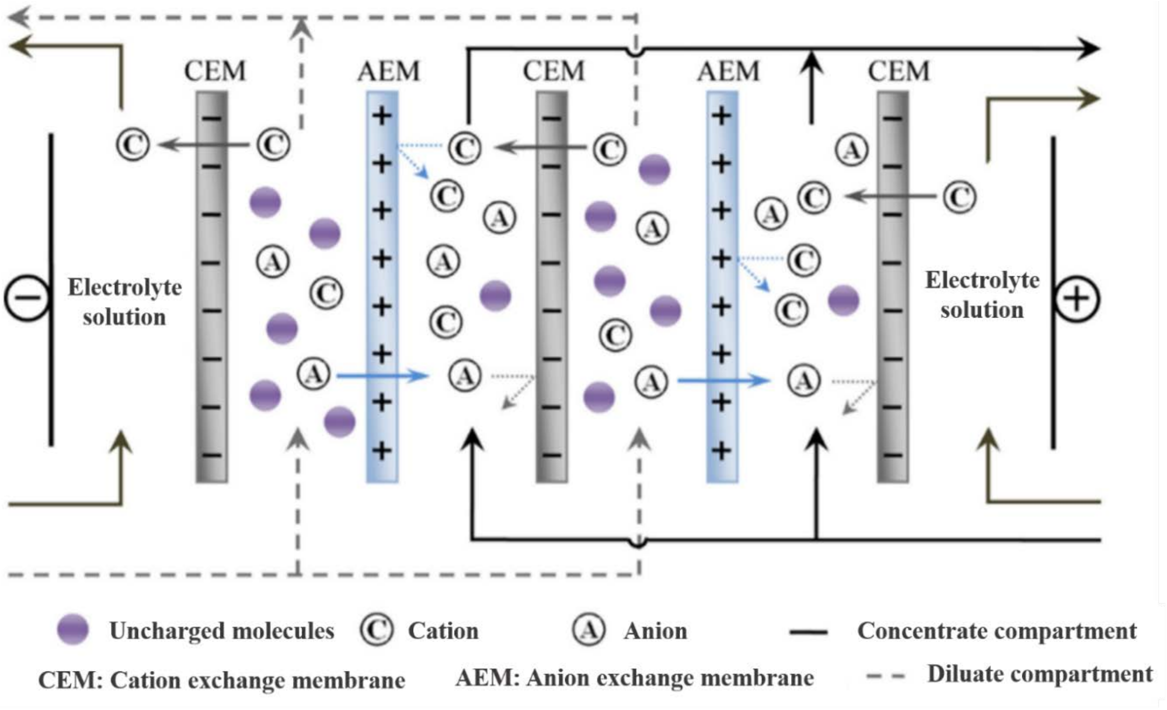


Figure 2.5. Schematic representation of the principle of desalination by electrodialysis stack (reproduced from [75]).

Three main processing streams flow through the unit:

1- An electrolyte solution that flows in the last compartment on each side of the unit. The aqueous electrolyte solution is used to protect the electrodes, facilitate the transfer of the electric current and remove any gases produced as a result of the electrode reactions (**Eq. 2.2** and **Eq. 2.3**) [76, 77]. Since the electrolyte solution is in direct contact with the electrodes, the solution should not react with the electrode nor contribute to the electrode reactions. Although many researchers use sodium chloride (NaCl) as the electrolyte solution, this is not recommended as chlorine gas can be generated which is hazardous to both the electrodes and the operators [78]. Sodium sulphate (Na_2SO_4) is recommended as it does not generate any hazardous substances and allows easy leakage tests by the detection of the total sulfate in the concentrate and diluate streams.

Anode reaction: $$2OH^- - 4e^- \rightarrow O_2 + 2H^+$$ **Eq. 2.2**

Cathode reaction: $$4H^+ + 4e^- \rightarrow 2H_2$$ **Eq. 2.3**

2- A diluate solution which is the main feed stream through the process. The naming diluate indicates that ions are removed from the stream. The characteristics of the diluate stream affect many process parameters. For example, the solution composition and pH can affect membrane fouling as discussed in **section 2.5**. The conductivity of the solution also contributes to the total system resistance and energy consumption. The diluate stream is either passed once through the unit (i.e. continuous process) or recirculated through the process (i.e. batch process) until the required reduction in the concentration of ions is achieved. A continuous ED process uses large membrane areas to reduce the operating time needed to achieve the required demineralization rate [79]. On the other hand, high demineralization rates are economically feasible only in batch processes. The reduction in the concentration of ions in the diluate stream is referred to as the demineralization rate (DR), which is calculated based on the change in the total concentration of ions present in the diluate stream [13]. DR can also be calculated based on the change in the conductivity of the diluate tank using **Eq. 2.4** [80]. The degree of demineralization is dependent on ash content, residence time, current density and flow viscosity [50, 79]. The ionic nature of the solution also affects the rate of demineralization [81]. For example, a solution containing monovalent ions, such as Na^+, will demineralize faster than a solution containing divalent ions, such as calcium ion (Ca^{+2}). This is mainly due to the fact that monovalent ions have higher mobility than divalent ions. In addition, divalent ions are expected to be more strongly retained in the IEM stricture thus slowing their movement from the diluate to the concentrate compartment [82]. Kabay *et al.* [83] also demonstrated that a feed solution containing monovalent ions consumed less energy when compared to a feed solution containing divalent ions.

$$DR(\%) = \frac{x_{initial} - x_{final}}{x_{initial}} \times 100 = \left(1 - \frac{x_{final}}{x_{initial}}\right) \times 100$$ **Eq. 2.4**

where x is either the conductivity of the diluate solution or the concentration of cations in the diluate solution.

3- The concentrate solution is the waste or by-product stream produced during the process. The concentrate solution uptakes the ions lost from the diluate. Similar to the diluate stream, the characteristics of the concentrate stream affects membrane fouling, total system resistance and energy consumption. In industrial applications, water at pH of 2 is used as the concentrate stream [84]. This solution has low conductivity at the start of the process, thus resulting in high system resistance and low current density. However, with time, the solution gains ions which result in increasing its conductivity and reducing the system resistance. When it comes to research work, different concentrate streams are proposed. Some researchers use the feed solution as the concentrate stream. Although this prevents the generation of new waste streams, it is an economical loss especially if the feed solution is valuable. Others use laboratory made salt solutions of potassium chloride (KCl) or NaCl. The concentrate stream is usually operated in a feed and bleed mode, where most the solution is recirculated back to the unit and some is removed and replaced with freshwater to maintain the solution conductivity [85].

The ED process is economically competitive with other processes, such as ion-exchange (IE), for less than 70% demineralization rates regardless of the mode of operation (i.e. batch or continuous) [44]. As a rule of thumb, the operating cost doubles as the demineralization level increases from 50% to 70%, and then, to 90% [79]. Although ED does not require any special cleaning chemicals or mechanical cleaning of the membranes, the replacement cost of the IEMs, spacers and electrodes contribute 35-40% towards the operating cost [44, 79]. Other disadvantages of ED include [73, 86]: (1) the process is capable of removing charged ions only, indicating that neutral components, such as organic materials and microorganisms remain in the diluate stream; (2) high energy consumption during the treatment of concentrated feed solutions; (3) larger equipment is required for highly diluted feed solutions, due to the very low limiting current density (**section 2.4.2.2**); and (4) the need for a brine or concentrate stream, which adds to the volume of wastewater discharged by the factory. Several researchers have demonstrated that electrical driven membrane processes such as ED are economically feasible for salt removal from feed solutions with salinity levels close to brackish water, while for higher salinity feed solution, ED is energetically uncompetitive with RO [87, 88]. Nevertheless, the aim of the treatment process for brackish water is the generation of drinkable water as the permeate, while in dairy applications, the aim is to achieve a high purity retentate, through selective removal of specific salts and organics. Hence for dairy applications, it is not useful to directly compare ED with RO.

2.4.2.1. Ion-Exchange Membranes

IEMs are semi-permeable membranes made of a macromolecular material that contain ionizable groups fixed to the polymetric backbone [89]. In contact with the solution, the fixed ions found in the membrane are electronically neutralized by the oppositely charged counter-ions. These counter-ions are the main charge carriers in the membrane. IEMs are essential to the performance of the ED unit, therefore, the membranes should have high ion permeability, low electrical resistance, high mechanical, chemical, and thermal stability, low production cost, and good retention of uncharged molecules [73, 84, 90]. IEMs are classified according to the following factors [73]:

Membrane charge: IEMs are either CEMs or AEMs depending on the fixed charge group found in the polymer matrix of the membrane. The fixed groups are negatively charged for CEMs, indicating that these membranes only allow the positively charged ions to pass through. On the other hand, AEMs are positively charged and are permeable to anions only. The combination of CEM and AEM forms a third type of IEM known as a bipolar ion-exchange membrane [75].

Charged group type: The degree of charged group dissociation is used to classify the membranes as either strong or weak acid for CEMs and strong or weak base for AEMs. Generally, the charged fixed groups in strong and weak acid CEMs are sulfonic acid and carboxylic acid, respectively. Conversely, the charged groups for strong and weak base AEMs are quaternary and tertiary amines, respectively.

Membrane structure: The structure of the membrane is mainly determined by the membrane production and fabrication methods. Membranes can either be homogenous or heterogeneous. In heterogeneous membranes, the fixed charge groups are clustered, unevenly distributed and physically bonded to the membrane matrix (**Figure 2.6 (b)**). These membranes are formed by physically blending ion exchange resins with the uncharged polymer. This results in high electrical resistance and low permeability. On the other hand, homogenous membranes contain chemically bonded and evenly distributed fixed charge groups across the membrane matrix (**Figure 2.6 (a)**). These membranes are made from a single polymer which is functionalized with the relevant charge groups either before or after membrane formation. Although such membranes have lower electrical resistance and higher permeability, they are more expensive to produce [91]. Another special type of IEMs are the monovalent ion perm-selective membranes, also referred to as monovalent selective membranes. These membranes selectively allow the permeation of monovalent ions while blocking or reducing the passage of divalent ions. The membranes are constructed by either increasing the cross-link density in the membrane matrix; by coating a cross-linked thin layer on the membrane surface; or regulating the composition of the fixed charge groups in the membrane matrix [75]. Monovalent selective membranes have been examined for the demineralization of skimmed milk by Andres *et al.* [92], who noticed that the use of monovalent selective membranes assisted the retention of divalent ions in the diluate solution when compared to non-selective membranes. However, the energy consumption of the process was higher by 27% for the monovalent selective membranes.

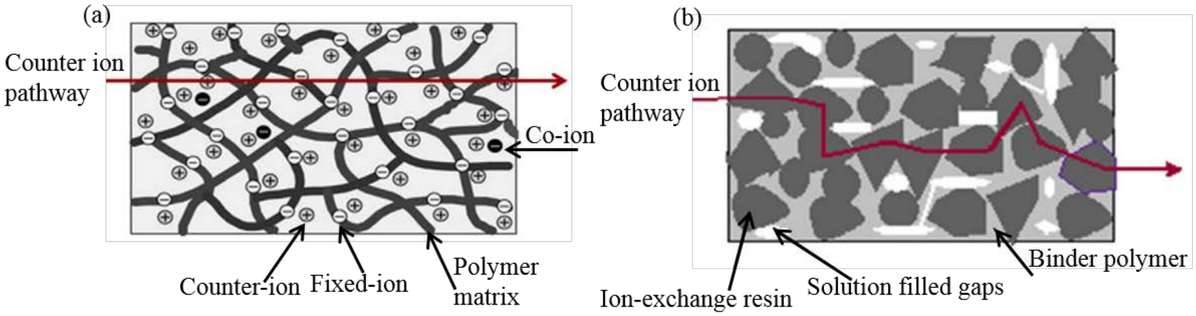


Figure 2.6. Schematic diagram of (a) a homogeneous cation exchange membrane, and (b) a heterogenous ion-exchange membrane (reproduced from [73]).

2.4.2.2. *System Resistance and Limiting Current Density*

The ED unit can be considered as an electrical conductor with a system resistance (R) which represents the sum of the resistance of the individual membranes, the processing solutions and their boundary layers. The total system resistance is calculated using Ohm's law from the voltage and current values obtained directly from the indicator on the power supply as per **Eq. 2.5**. Bazinet and Araya-Farias [93] and Casademont *et al.* [94] explained that the initial resistance in an ED unit is due to the membrane resistance and the conductivity or the composition of the processing solutions. As the demineralization process progresses, an increase in the system resistance is noticed. This is mainly a result of the demineralization of the diluate stream. As the diluate stream loses ions, its conductivity falls and there are fewer ions that can transfer current through the system. Furthermore, membrane fouling contributes to the increase in resistance, as the fouling layer formed on the membrane surface adds an extra layer that the ions need to pass through.

$$R(\Omega) = \frac{V}{I} \qquad \textbf{Eq. 2.5}$$

where, *I* is the current passing through the unit (A) and *V* is the applied voltage (V).

Plotting **Eq. 2.5** results in a straight line with a slope of R. However, at a certain current known as the limiting current (I_{lim}), this linear relationship deviates and results in a sharp increase in the voltage with little corresponding increase in current (**Figure 2.7**). The limiting current density (i_{lim}) is described as the current density at which the system resistance deviates from Ohm's law due to the boundary layer resistance limiting ion movement and is calculated as per **Eq. 2.6** [95]:

$$i_{lim}\left({}^{A}\!/_{m^2}\right) = \frac{I_{lim}}{membrane\ area} = \frac{D \times F \times Z \times C}{(t_m - t_s) \times \delta} \qquad \textbf{Eq. 2.6}$$

where, *D* is the diffusion coefficient, *F* is Faraday's constant, *Z* is the valence, *C* is the concentration, δ is the thickness of the boundary layer, t_m and t_s are the transport number in the membrane and solution, respectively.

It is very difficult to measure the thickness of the boundary layer, therefore, the limiting current density is usually estimated by plotting the applied current density (i) and the applied voltage (**Figure 2.7**). The plot is usually divided into three regions, in the first region, the current density increases linearly with the applied voltage. This region is known as the ohmic region and the applied current is usually maintained in this region in industrial ED units. The second region is the plateau region in which the current density does not change significantly with the increase in voltage due to the boundary layer limitations. This region reflects i_{lim} where the ion concentration at the membrane surface is insufficient to carry a current greater than this limiting value. The increase in the applied voltage causes water to dissociate to H^+ and OH^-, thus increasing the current flow, in what is known as the overlimiting current region (third region in **Figure 2.7**). Water splitting is undesirable as it affects the pH of the processing solution, leading to membrane fouling (as discussed in **section 2.5**). Water splitting also reduces the efficiency of the ED unit and increases the total energy consumed. As the applied voltage increases, an increase in the performance of the ED is usually observed in this region as a result of the formation of electroconvection vortices within the boundary layer that assist the transport of ions towards the membrane surface, thus reducing the resistance of the boundary layer and the extent of water splitting [96].

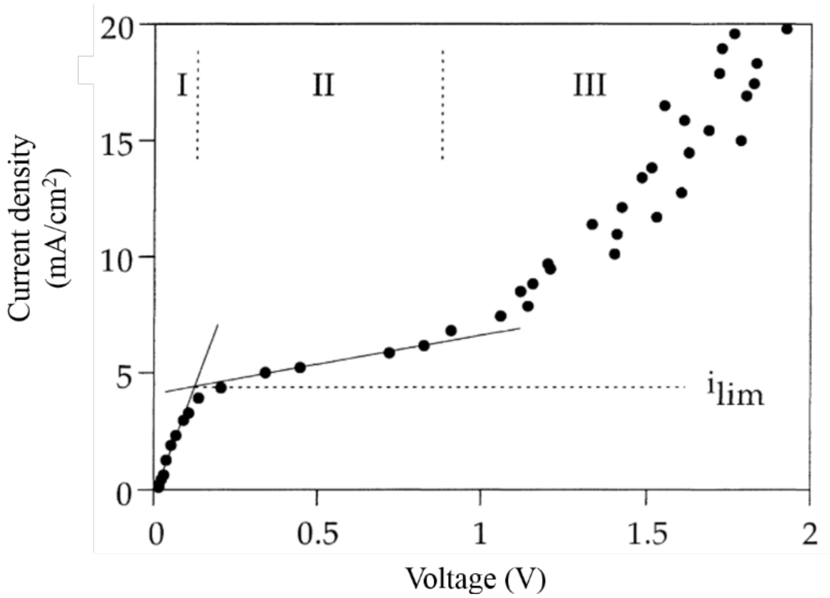


Figure 2.7. Example of a current-voltage curve showing the occurrence of limiting current density and the presence of the three main regions: (I) ohmic region, (II) plateau region, and (III) overlimiting current region (adapted from [97]).

From an operational point of view, it is important to keep the value of the limiting current density high to allow the usage of high operational current densities which will result in a faster demineralization process with smaller membrane area and equipment footprint. Several factors affect the limiting current density of a system, for example, the flowrate or the velocity of the processing streams. It has been demonstrated by Yen and Cheryan [95] that higher flowrates result in a greater value for the limiting current density. This was mainly due to the fact that at high flowrates, the velocity in the compartments increases, thus resulting in a decrease in the thickness of the boundary layer. Increasing the processing temperature also increases the limiting current density due to the change in the diffusion coefficient of the components present in the diluate stream [98]. Another important factor is the concentration of the feed solution. As the concentration of the feed solution increases, the limiting current density value increases [97]. This could be explained by the fact that the current in the bulk solution and the boundary layer is carried by both counter-ions and co-ions, while the current in the membrane is only carried by counter-ions. This forms a concentration gradient in the boundary layers adjacent to the membranes. As the demineralization process continuous, the concentration difference on each side of the membrane becomes greater as the concentration in the diluate solution drops while it increases in the concentrate solution. At the limiting current density, the concentration on the surface of the membrane facing the diluate falls below that required concentration to carry the current thus resulting in water splitting. When the diluate concentration is high, it takes a higher applied current to deplete the ions on the surface of the membrane facing the diluate compartment.

2.4.2.3. *Mode of Power Supply Operation (Constant Current Vs Constant Voltage)*

As per **Eq. 2.5**, an ED unit can either be operated in a constant current mode or a constant voltage mode. When operating in a constant current mode, the voltage will increase in order to keep the applied current constant as the system resistance increases. This results in an increase in the overall electrical consumption [99]. On the other hand, when operating in a constant voltage mode, as the system resistance increases, the current applied through the ED unit will drop down in order to keep the applied voltage constant. Lower applied currents result in a longer processing time required to achieve the desired demineralization rate for an ED process operated in batch mode, while for a continuous ED operation, a greater membrane area is required. Parulekar [100] suggested using a combination of constant current and constant voltage modes. This was demonstrated by Lee *et al.* [101] where the ED unit was initially operated at a constant current mode to speed up the process, once the concentration of the diluate dropped to a certain level (determined by the authors based on the limiting current density of the system), the mode of operation was changed to constant voltage to avoid high energy consumptions and water splitting.

2.4.2.4. *Electrodialysis for Whey Demineralization*

ED has been used for different industrial applications, such as seawater desalination, acid recovery, and heavy metal recovery [10, 102]. The process has been investigated for the demineralization of whey by several researchers. Diblíková *et al.* [84] studied the use of ED for the demineralization of reconstituted whey powder at a constant voltage of 20 V. The authors observed that the concentration of monovalent ions reduced exponentially, while that of the divalent ions reduced linearly. This difference in the removal of monovalent and divalent ions resulted in desirable nutritional value for the treated whey solution. The same results were obtained by Simova *et al.* [2] who used a pilot scale ED unit with 50 cell pairs to demineralize sweet whey at 15°C. They found that monovalent ions were removed more effectively through the process due to their greater mobility and smaller hydration diameters. Furthermore, the authors found that the use of high voltage reduced the total time required for demineralization but resulted in greater energy consumption. Boer and Robbertsen [103] found that maximum demineralization could be obtained at a feed pH close to the isoelectric point of the whey proteins since the uncharged proteins did not respond to the electrical driving force thus allowing better utilization of the electrical current. The effect of whey protein on the demineralization level was further confirmed by Perez *et al.* [104] who noticed a difference between processing UF retentate (protein rich) and UF permeate (lactose rich) through a lab scale ED unit with a total membrane area of 1000 cm^2. The authors explained that whey proteins form a gel layer on the membrane surface which results in increasing the boundary layer thickness thus adding extra resistance to the flow of ions through the membrane.

ED can be used for whey deacidification which is important for acid whey treatment. The separation between lactose molecules and lactic acid takes place on the basis that lactic acid dissociates into a lactate ion (negatively charged) and a proton (positively charged) under the application of an electrical current. The lactate ions pass through the AEM from the diluate to the concentrate compartments. This idea was patented in 1980 by Williams *et al.* [105]. Since then it has been investigated by several researchers such as Chen *et al*. [13], who found that the rate of lactate ion removal increased with temperature, however, only a slight improvement was observed with increasing the diluate pH. In addition, the authors noticed that at the start of the process, Cl^-competed with other anions, including the lactate ion, to pass through the AEM. As a result, the energy was initially used for the removal of Cl^- ions, which increased the total energy required for the removal of lactate ions. The authors reported that, for a continuous ED process with 70% demineralization, 60% of the lactic acid in the feed solution could be removed with a specific energy of 3.6 kWh per kilogram of lactic acid removed. Furthermore, the authors recommended that the ratio between lactic acid and lactose in acid whey should be lower than 0.04 g/g in order to avoid a sticky powder (**Figure 2.8**). This recommended ratio was estimated based on the concentration of lactic acid and lactose in sweet whey. The configuration used by Chen *et al.* [13] was examined by Dufton *et al.* [106], who obtained 44% lactic acid removal at a DR of 67%. The main difference between the work done by the two researchers is that Dufton *et al.* [106] used raw acid whey, while Chen *et al.* [13] utilized ultrafiltered acid whey.

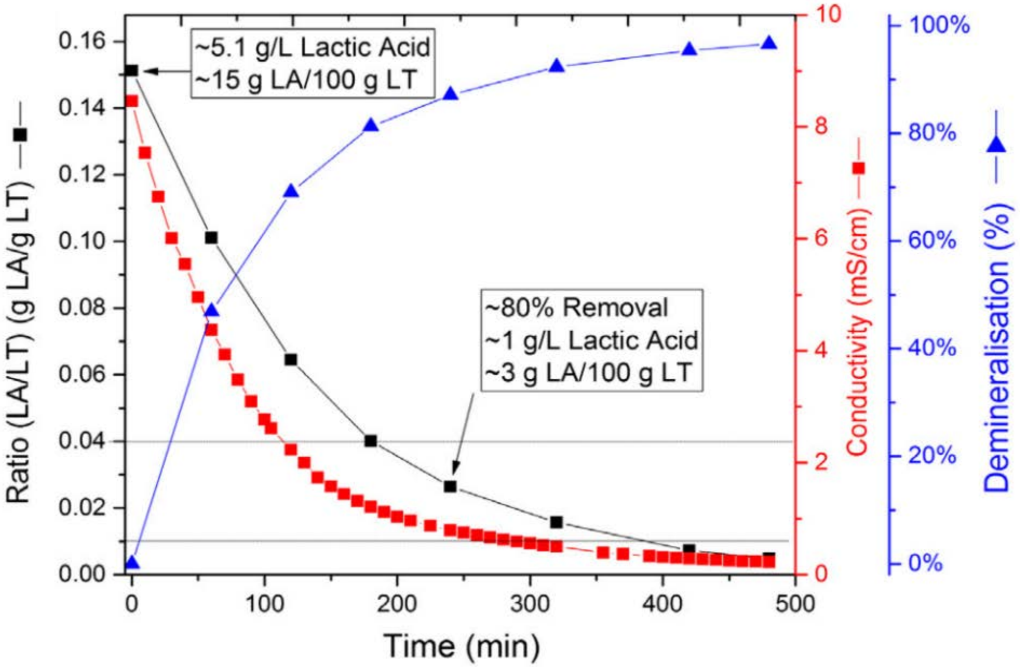


Figure 2.8. Performance of batch electrodialysis process during the treatment of ultrafiltered acid whey at a constant voltage of 7 V and processing temperature of 45°C (adapted from [13]).

In addition to using ED for the removal of lactic acid from acid whey, several researchers have considered the use of electrodialysis with bipolar membranes (EDBM) for adjusting the pH of acid whey [85]. The bipolar membranes generate OH^- ions which will increase the pH of acid whey. Although this method has been demonstrated effective in increasing the pH of acid whey, the process is limited by the increase in membrane fouling and lower removal of lactic acid when compared to conventional ED process. For example, in a recent publication by Kravtsov *et al.* [107] the authors achieved only 25% removal of lactic acid compared to 44% removal obtained by Dufton *et al.* [106].

2.4.2.5. *Electrodialysis for Salty Whey Treatment*

Salty waste streams are produced during day to day operation of a dairy factory (see **Figure 2.9**) and include waste streams from clean in place (CIP) process, the demineralization of sweet whey, and chromatography brines generated from the separation of milk proteins such as lactoferrin [1]. To date, high salinity waste streams from the dairy industry have been disposed of either to trade waste or evaporation ponds. Due to the environmental effects associated with such practices, many water authorities are imposing penalties on the levels of sodium discharged by a dairy factory [7]. As a result, treatment and processing of high salinity waste such as salty whey can not only reduce the sodium levels discharged by a dairy factory but can also result in the production of valuable products that can add to the profit of a dairy plant. Many technologies are available for salty wastewater treatment, such as NF, ED, RO, forward osmosis (FO), membrane distillation (MD), each with its own capabilities and limitations [7]. **Figure 2.10** illustrates the energy consumption of different technologies as a function of feed salinity. It is observed that membrane technology such as NF, ED, and RO are used for relatively low feed salinities (max 50 g/L total dissolved solids) when compared to spray dryers and thermal crystallizers (minimum 300 g/L total dissolved solids). Nevertheless, the higher the feed salinity, the greater the energy required by the process.

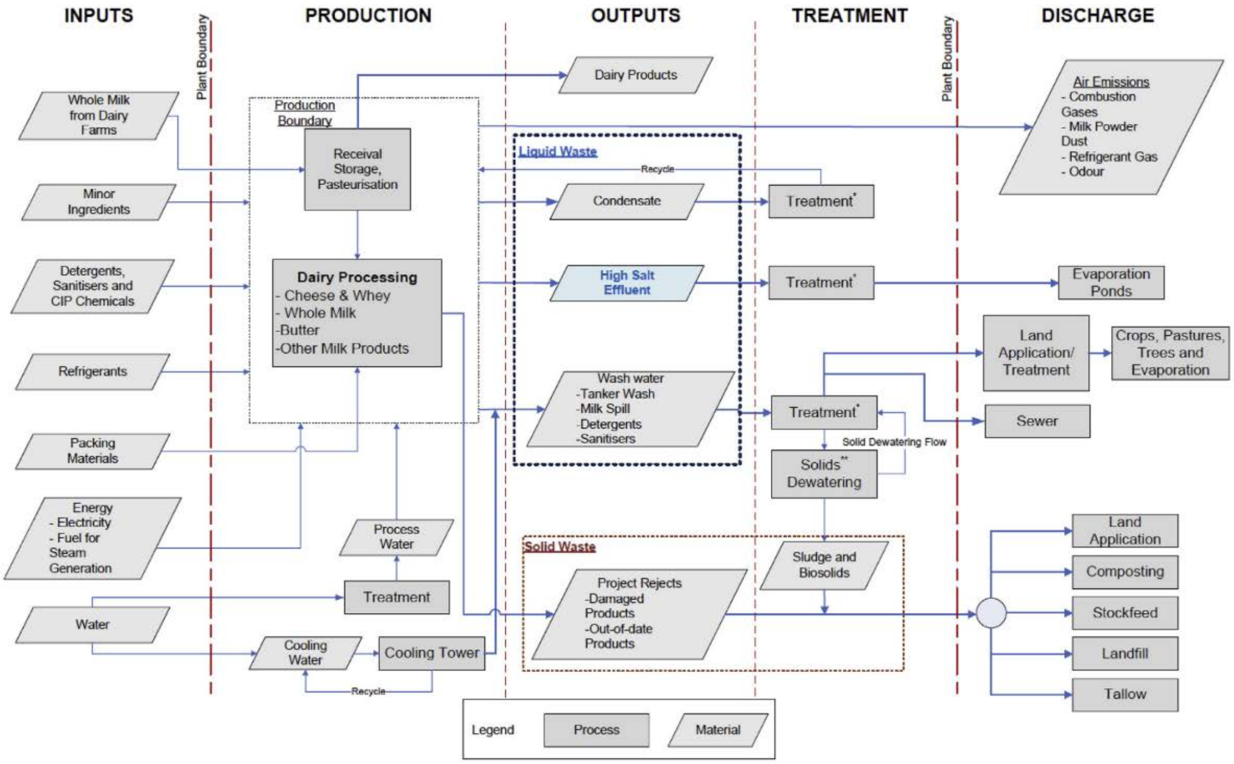


Figure 2.9. A typical approach for dairy waste management used in Australia and New Zealand (adapted from [1]). * Wastewater treatments include various arrangements of standard technologies, which are not shown in detail; ** Sludge and biosolids are generated from biological treatment and wastewater separation processes such as Dissolved Air Flotation.

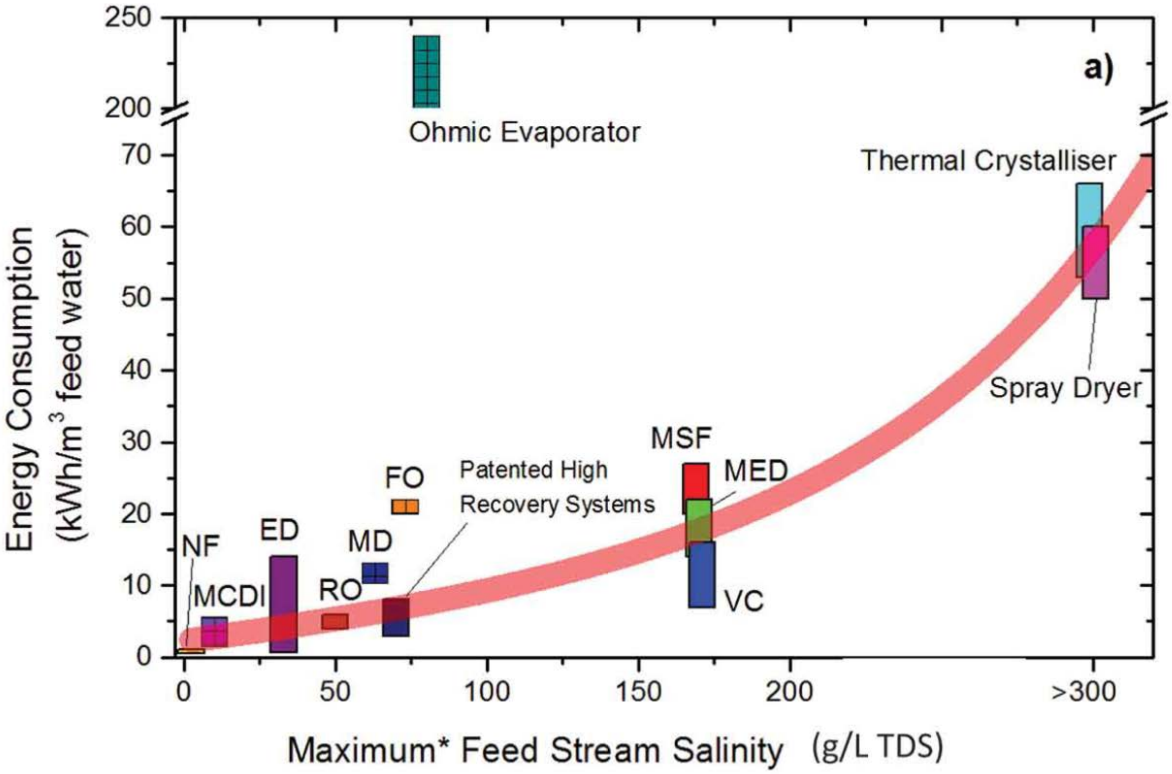


Figure 2.10. Energy consumption of commercial and emerging technologies for processing salty water. Where NF = nanofiltration, MCDI = membrane capacitive deionization, ED= electrodialysis, RO = reverse osmosis, MD = membrane distillation, FO = forward osmosis, MSF = Multi-stage flash distillation, MED = multi-effect distillation, and VC = vapor compression.

When considering the use of ED for salty whey treatment, Diblíková *et al*. [84] studied the use of ED for the demineralization of reconstituted whey powder at a constant voltage of 20 V. The authors investigated the effect of dry matter on the removal of ions by adding NaCl to the whey solution to simulate the salty whey which is produced during the cheese salting process. They found that the addition of NaCl enhanced the demineralization process, however, the time required to achieve the desired final solution conductivity was longer. This was also supported by Ecer *et al*. [108] who found that using a concentrated feed solution enhanced the performance of the ED unit.

ED has been widely investigated for concentrating salty brines produced from seawater desalination. Liu *et al.* [109] investigated the combination of an NF and ED process. The NF process was used to increase the purity of the concentrated NaCl solution by removing divalent ions, such as sulphate, calcium and magnesium from the brine solution. The authors reported a final NaCl concentration of 160 g/L in the concentrate tank at the end of the ED process, with an energy consumption of 1.4 kWh per kilogram of NaCl, when the operating voltage was set to 15 V and the diluate to concentrate volume ratio was 20 to 1. Casas *et al.* [110] used an ED unit assembled with monovalent selective membranes in order to enhance the purity of the concentrated NaCl solution. The authors achieved a maximum concentration of 280 g/L of NaCl at a current density and operating temperature of 0.4 kA/m^2 and 10°C, respectively, with a power consumption of 0.24 kWh per kilogram of NaCl. They noticed that the final concentration of divalent ions in the concentrate stream was much lower due to the transfer of both monovalent ions and water from the diluate to the concentrate stream. The use of monovalent selective membranes was further investigated by Zhang *et al.* [111] who successfully produced coarse salt with a purity of 85%. The authors proposed a three-stage ED process, where monovalent selective IEMs were used in the first stage with a low applied current density which is suspected to enhance the retention of divalent ions in the diluate stream.

The main drawback of using ED to produce a concentrated solution is the fact that there is a limit to the maximum concentration that can be achieved. This is known to be caused by water transport and the back diffusion of ions to the diluate compartment. Liu *et al.* [109] explained that during the ED process, both ions and water migrate from the diluate to the concentrate tank. The authors observed that although the permeation flux for Na^+ and Cl^- was constant throughout the process, an increase in water flux with time was noted as the concentration difference between the diluate and concentrate streams became greater. A similar observation was reported by Reig *et al.* [112], who conducted pilot plant experiments on the electrodialysis of brine concentrate using Neosepta monovalent selective membranes. The authors claim that at the start of the process, two main mass transport phenomena took place, namely the transfer of charged species and the transfer of hydrated water, also known as electro-osmotic flux (**Figure 2.9**). As the concentration process continued and the NaCl concentration gradient increased between the diluate and concentrate streams, two additional mass transfer mechanisms were expected to take place: (a) back diffusion of NaCl from the concentrate to the diluate tank, and (b) osmotic flux of water from the diluate to the concentrate tank. The authors concluded that all these factors affected the NaCl concentration in the concentrate tank. However, Jiang *et al.* [113] argued that the contribution of the osmotic pressure difference to the total water transported is much smaller compared to the water transported due to electro-osmosis. Membrane water uptake is one of the main factors that affect water transfer in an ED unit. Jiang *et al.* [113] demonstrated that Neosepta IEMs were able to produce a better quality concentrate compared to other commercially available IEMs due to the lower water update of Neosepta IEMs.

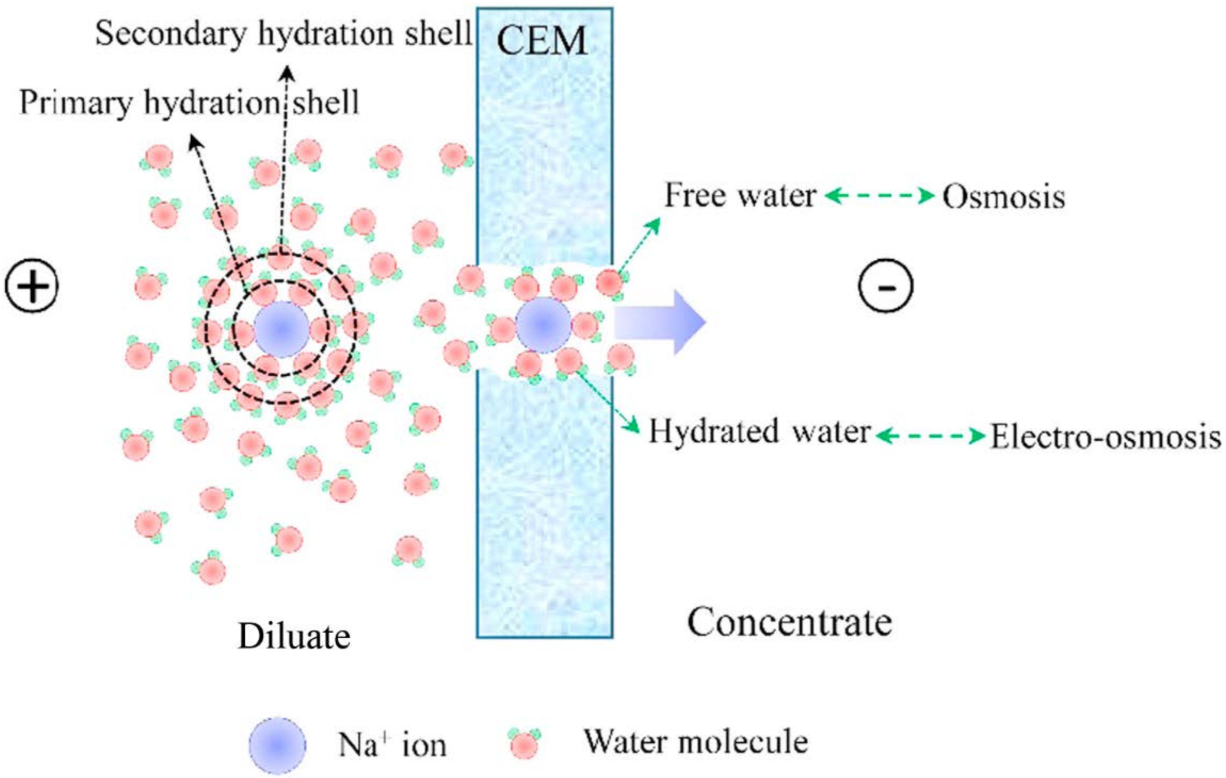


Figure 2.11. The transport of water molecules from the diluate to the concentrate compartment (adapted from [114]).

To overcome the issues associated with the limited concentration that can be achieved in the concentrate tank, Yan *et al.* [114] proposed the use of a multi-batch ED process in which the diluate and concentrate streams flow in a counter-current direction. This means that in any unit the starting concentration of the diluate and concentrate are similar, thus avoiding a high concentration difference between the diluate and concentrate stream. The authors concentrated a solution of NaCl from 3.5 wt% to 17.9 wt% in a two-stage process, and from 3.5 wt% to 20.6 wt% in a three-stage process. They reported a total water transport of 50% for the two-stage process and 42.5% for the three-stage process. Although water transport was lower in the three-stage process, the energy consumption was 1.4 times higher than the two-stage process mainly due to the high concentration of the solutions processed in the third stage.

Lee *et al.* [86] demonstrated that high feed concentrations result in greater energy consumption in an ED process. This explains the high energy cost associated with the use of ED for the treatment of RO brine (**Figure 2.10**). Temperature is another important factor that can affect the performance of an ED process thus affecting the energy consumption. This is mainly due to the fact that temperature affects the transfer of the ionic species, the conductivity of the processing solutions, and the membrane properties. Although higher operating temperatures resulted in lower energy consumption as observed from **Figure 2.10**, the concentration of NaCl in the concentrate stream was lower than the concentration obtained at a lower temperature when similar current densities were used.

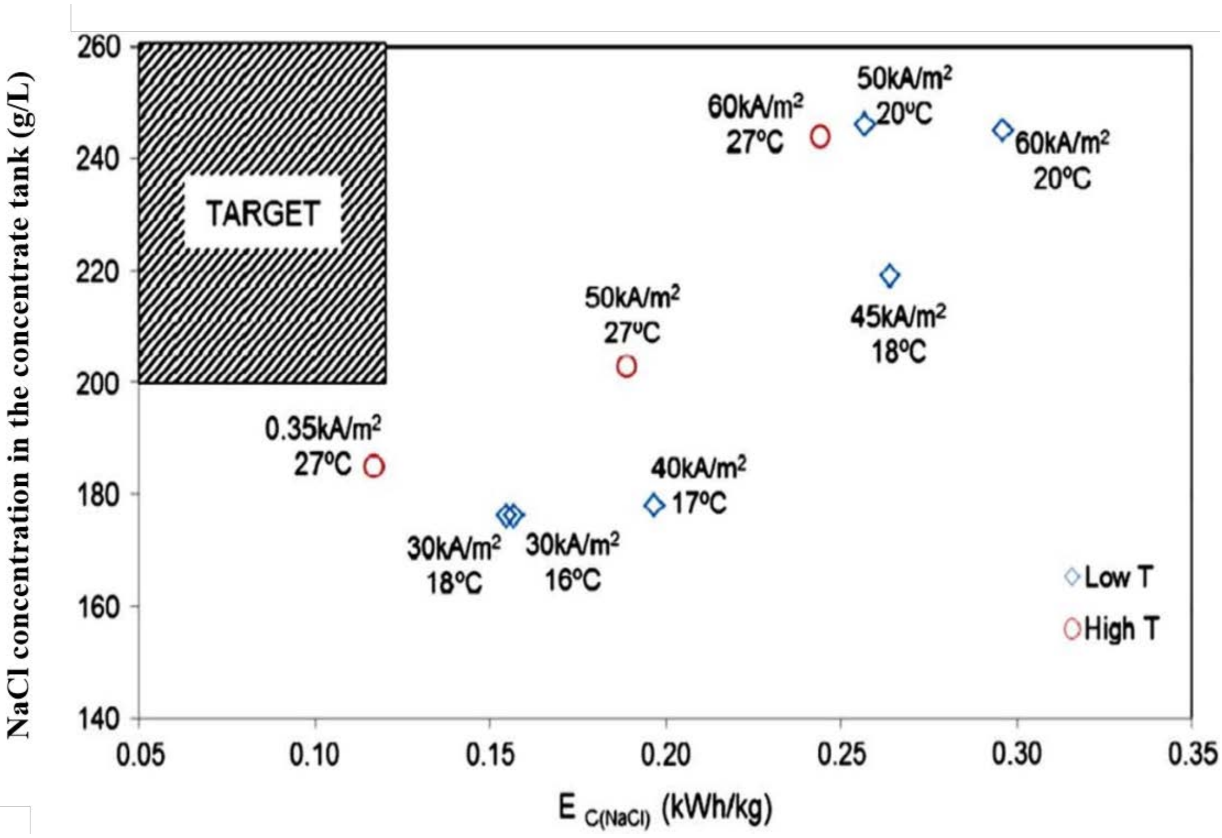


Figure 2.12. Energy consumption of ED used to generate a concentrated NaCl solution from RO brine as a function of operating temperature and applied current density (adapted from [112]).

2.4.3. Membrane Capacitive Deionization

MCDI process is an advanced version of the capacitive deionization (CDI) process. CDI is similar to IE, in which the ions undergo adsorption and desorption processes. The difference is that CDI utilizes porous electrodes and an electrical driving force, while IE utilizes resins and a chemical potential driving force. In CDI, the separation of dissociated ions is achieved by applying an electrical voltage between two porous electrodes. The positively charged ions will adsorb into the cathode, while the negatively charged ions will adsorb into the anode, generating a desalinated stream. Once the electrode capacity is reached, the voltage is dropped to zero, resulting in the desorption of the ions into the waste stream flowing through the unit.

CDI is well known for its low efficiency and high energy consumption due to two main issues [115, 116]: (1) co-ion adsorption into the electrodes; and (2) low salt removal efficiency during the regeneration process as a reversed current cannot be applied since there is no obstacle preventing the adsorption of ions on the oppositely charged electrodes. To avoid these issues, a CEM and an AEM are placed in front of the cathode and anode, respectively, as shown in **Figure 2.11**. This process is known as MCDI. The selectivity of IEMs prevents the movement of co-ions towards the electrodes and allows a negative potential to be applied during the desorption step. In addition, the fouling of carbon electrodes is limited by placing IEMs in front of the electrodes. This was demonstrated by Chen *et al.* [117] who did not observe any physical attachment of organic foulants to the electrodes after 15 days of fouling. Similar results were also obtained by Hassanvand *et al.* [118] who reported insignificant losses in the charge efficiency of the MCDI unit after operating for 6 hours using a feed solution with different concentration of organic foulants. The concept of capacitive deionisation was first proposed around 50 years ago by Blair and Murphy [119], with early studies by Caudle *et al.* [120] and Johnson *et al.* [121]. However, the approach gained momentum after 1996, when Farmer *et al.* [122] showed that carbon materials of high surface area could be used as electrode materials.

Both MCDI and CDI are either operated in a constant current mode where the voltage changes with time, or a constant voltage mode where the current changes with time. Regardless of the mode of operation, the applied voltage is usually limited to a value lower than 1.2 V to avoid water splitting and high energy consumption. The is mainly due to the fact that water electrolysis takes place at 1.23 V. However, in some of the work done on MCDI, the authors either used an applied voltage of 1.5 V during constant voltage mode [123] or allowed the voltage to increase to 1.6 V during constant current mode [124]. This is possible as some of the total electrical potential is consumed in overcoming the resistance of the feed solution and the IEMs, therefore, the net potential available at the electrodes will be below 1.23 V.

This limitation in the applied voltage adds a disadvantage to the MCDI process when compared to ED. MCDI requires a pair of electrodes for each cell, limiting the maximum voltage that can be used to this value. Conversely, an ED process can utilize one pair of electrodes for up to 500 cell pairs allowing the applied voltage to increase by this factor. As the number of membranes in the stack increases, the influence of the redox reactions at the electrodes on the energy consumption also decreases, making ED more attractive than MCDI [87].

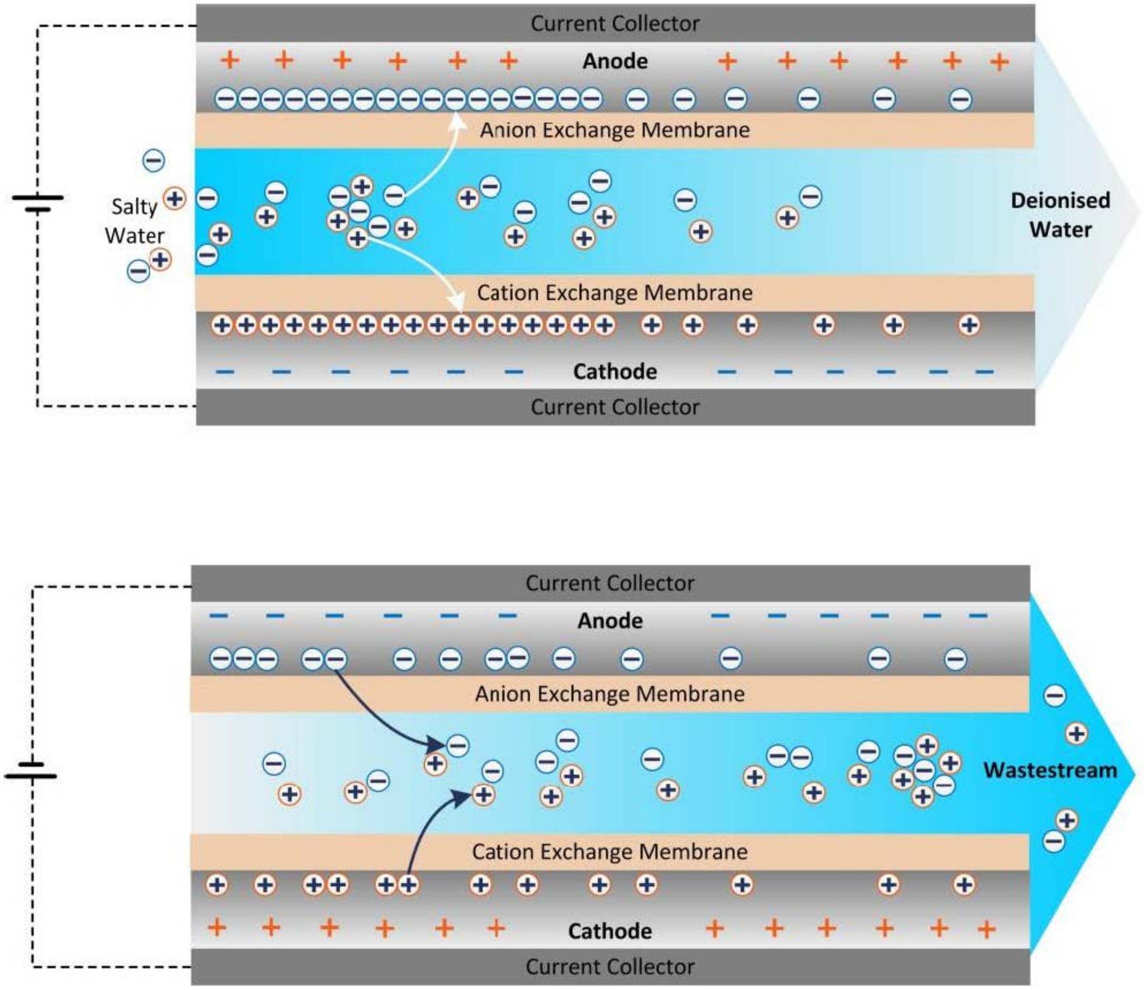


Figure 2.13. Schematic representation showing the adsorption and desorption process during MCDI operation (adapted from [125]).

Most of the research work done on MCDI has been focused on water desalination, the development of electrode materials, and the optimization of system configuration for better process performance [11]. Li and Zou [126] observed that salt removal efficiency decreased with an increase in feed concentration, indicating that MCDI is effective for solutions with low salt concentration due to the limited capacity of the electrodes. Indeed, at feed salt concentration less than 60 mM, MCDI technology has a lower energy consumption when compared to RO, since MCDI separates the minor component, i.e. salt, from the major component, i.e. water [127]. Hassanvand *et al.* [128] studied the competitive sorption of monovalent and divalent ions in both CDI and MCDI for single salt and multiple salt mixtures. In CDI, the hydrated radii govern the mass transfer of different ions, while in MCDI, the IEMs are the controlling factor. When using a mixture of salt solutions, the authors noticed that Ca^{2+} had a higher removal efficiency compared to Na^{+}. This was due to the tendency of Ca^{2+} to replace Na^{+} ions within the membranes. Moreover, it was found that during the desorption step, Ca^{2+} and SO_4^{2-} left the MCDI cell quicker than the other cations and anions, as demonstrated in **Figure 2.12**. The authors explained that this was mainly due to the retention of these ions in the IEMs and not the carbon electrode. It was concluded that when it comes to desorption in MCDI, the ionic charge is the governing factor, followed by the hydrated radii. As a result, ions with smaller hydrated radii and greater ionic charge are desorbed faster.

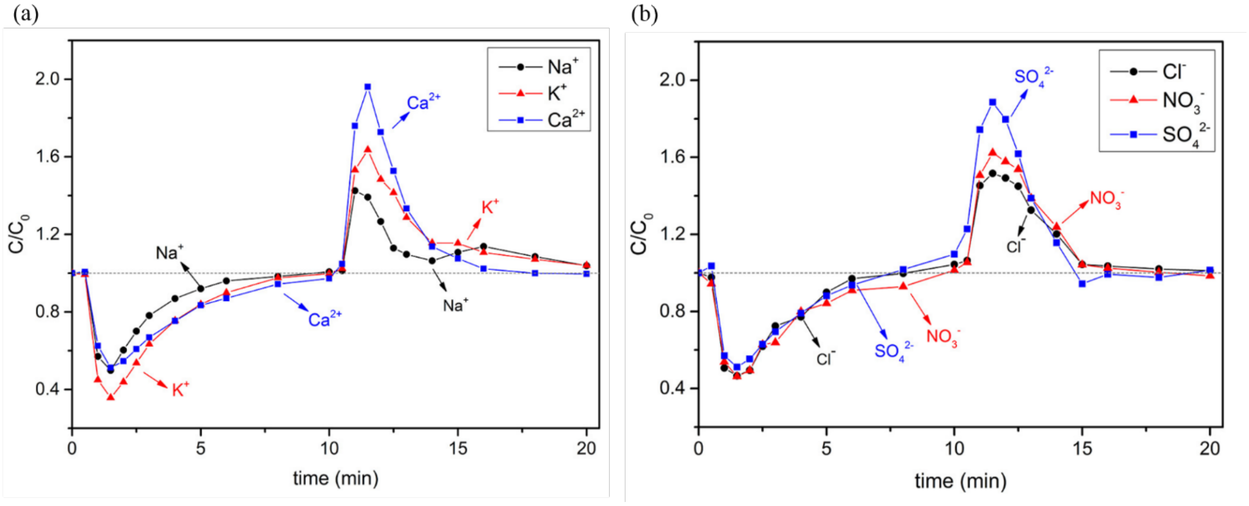


Figure 2.14. Competitive sorption of (a) cations and (b) anions in MCDI operation (adapted from [128]).

When considering the energy consumption, Zhao *et al.* [129] noticed that as the applied voltage increased, the energy consumption increased rapidly for CDI, while the increase was gradual for MCDI (**Figure 2.13 (a)**). Furthermore, the effect of feed concentration on energy consumption was not as significant as the effect of the applied voltage (**Figure 2.13 (b)**). Dlugolecki and van der Wal [130] demonstrated the ability to recover up to 83% of the energy used in the adsorption step when operating under constant current mode, while Chen *et al.* [131] reported a recovery ratio of 30% for an MCDI system operated at 1.2 V during the adsorption step and at a constant current of 0.1 A during the desorption step. This is based on the fact that during the adsorption process, the electrodes store both ions and energy. This energy is released from the electrodes during the desorption step and can be harvested.

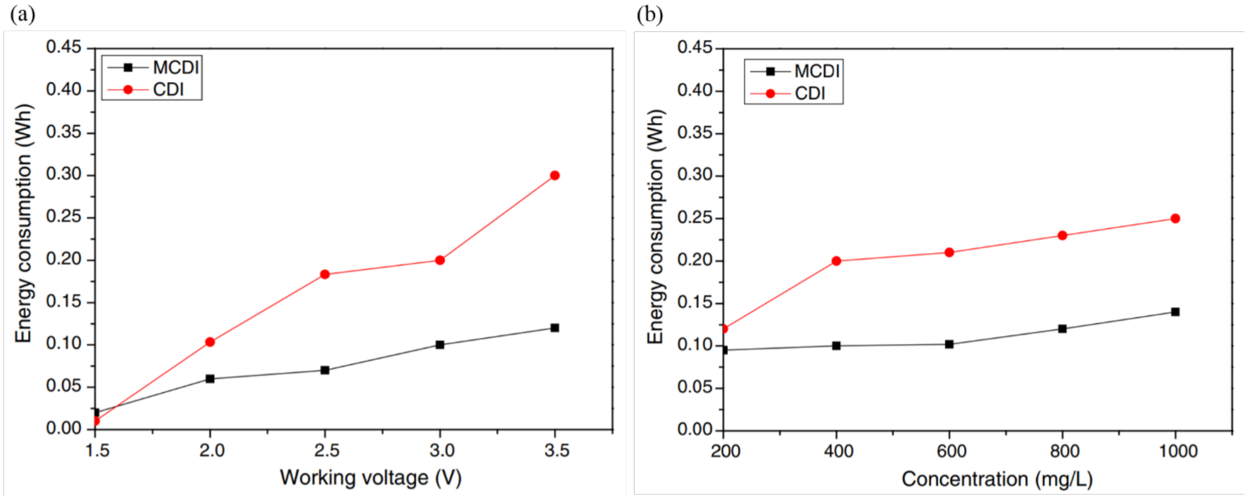


Figure 2.15. Energy consumption during adsorption step in MCDI and CDI at (a) different applied voltages for a feed concentration of 400 mg/L, and (b) different feed concentrations for an applied voltage of 3 V (adapted from [129]).

2.4.4. Ion-Exchange

IE refers to the process in which a feed solution is passed through a fixed-bed column filled with polymeric beads. The beads, also known as ion-exchange resins, are loaded with counter-ions that tend to exchange positions with the counter-ions present in the feed solution. The process has two main steps, namely the equilibrium reaction in which the ions are exchanged between the resins and the feed solution, and the regeneration of the resins once fully loaded [79]. The IE process is usually combined with other demineralization technologies to achieve 90% whey demineralization [44]. Nevertheless, the IE process has several limitations [44, 50]: (1) high selectivity for multivalent ions compared to monovalent ions; (2) two or more beds are required for a continuous process, which will result in high capital cost; (3) short adsorption cycles due to the high ash content of whey; and (4) high consumption of rinse water and chemicals during the regeneration step. As a result, similar to CDI, IE is suitable for feed solutions with low salt concentration to reduce operating cost.

2.4.5. Combination of Different Demineralization Processes

The different demineralization processes are usually combined to enhance process performance and to overcome the limitation of the individual processes.

As described previously, NF allows monovalent ions to pass through the membrane to the permeate side in the form of pairs made up of cations and anions. Although whey is electroneutral, the levels of monovalent cations, $\mathrm{Na^+}$and $\mathrm{K^+}$, present in whey exceeds the amount of the main anion, i.e $\mathrm{Cl^-}$. During the demineralization process, NF will remove almost 100% of $\mathrm{Cl^-}$, while considerable amounts of $\mathrm{Na^+}$and $\mathrm{K^+}$remain in the retentate stream. Okawa *et al.* [55] studied the possibility of enhancing the removal of monovalent cations by increasing the molar ratio of $\mathrm{Cl^-}$ to $\mathrm{Na^+}$+ $\mathrm{K^+}$ in sweet whey from 0.5 to 1. The authors used a Cl-form anion exchange column prior to the NF process to increase the $\mathrm{Cl^-}$ content by replacing other anions present in whey. They noticed that the concentrations of both $\mathrm{Na^+}$and $\mathrm{K^+}$ in the NF retentate were 90% lower in the integrated system (IE+NF) than those in the single NF system where only 60% of $\mathrm{Na^+}$and $\mathrm{K^+}$ were removed. The main drawback of the proposed process is the fact that $\mathrm{Cl^-}$ ions replaced citrate and phosphate ions found in whey, which are known for their important role in the heat stability of whey proteins. Furthermore, NF can be used before IE process to reduce the ionic load on the IE columns by 30% and the size of the columns [79].

Several researchers have also suggested the possibility of combining NF and ED to enhance the quality of the final product. Kelly and Kelly [132] briefly discussed the possibility of combining NF and ED for the treatment of 275 tonnes of acid whey per day. The authors estimated the required membrane area for the ED of acid whey with or without NF pre-treatment. They found that for a final DR of 60%, the membrane area for ED increased from 130 m^2 to 200 m^2 when NF was not used. Nevertheless, the capital cost of the process without the NF process was 20% lower.

However, when the required DR increased to 90%, the cost difference was only 3%. The authors concluded that the best process should be selected taking into consideration the operating cost and the facilities available on the manufacturing site.

2.5. Challenges Associated with the Use of Electrodialysis for Dairy Processing: Fouling of Ion-Exchange Membranes

Membrane fouling is one of the main reasons inhibiting the greater use of membrane technology in the dairy industry. It is well known that dairy products contain colloidal matter and inorganic compounds, such as calcium and proteins [50, 81, 133], which could deposit either on the membrane surface or inside the membrane pores resulting in membrane fouling [134]. For pressure driven membranes, fouling usually results in permeate flux reduction and longer filtration times [135]. In some cases, the applied pressure difference is increased to maintain constant flux, thus resulting in a higher operating cost. In the case of IEMs, fouling causes a reduction in ion migration and an increase in membrane resistance and energy consumption [135, 136].

Since an ED unit utilizes two different types of IEMs, fouling of each membrane is usually observed under different operating conditions. For CEMs, several researchers have reported the formation of mineral scaling made of calcium salts [106, 136, 137], as shown in **Figure 2.14 (a)**. The presence of proteins in the feed stream can also result in protein deposition on the CEMs facing the diluate stream [81]. This usually takes place when: (1) the concentrate solution is maintained at acidic pH; and (2) calcium ions are present in the feed solution that is maintained at acidic pH [138, 139]. For AEMs, protein fouling is usually observed on the membrane surface facing the diluate compartment, as illustrated in **Figure 2.14 (b)**. The main whey proteins, β-lactoglobulin and α-lactalbumin, are negatively charged above their isoelectric points (pH 5.2 and 4.8, respectively). Therefore, whey proteins tend to deposit on the surface of the positively charged AEMs, as these proteins cannot pass through the dense AEMs towards the anode. Furthermore, mineral fouling is also possible on the surface of AEM facing the concentrate compartment under alkaline pH of the concentrate stream [134].

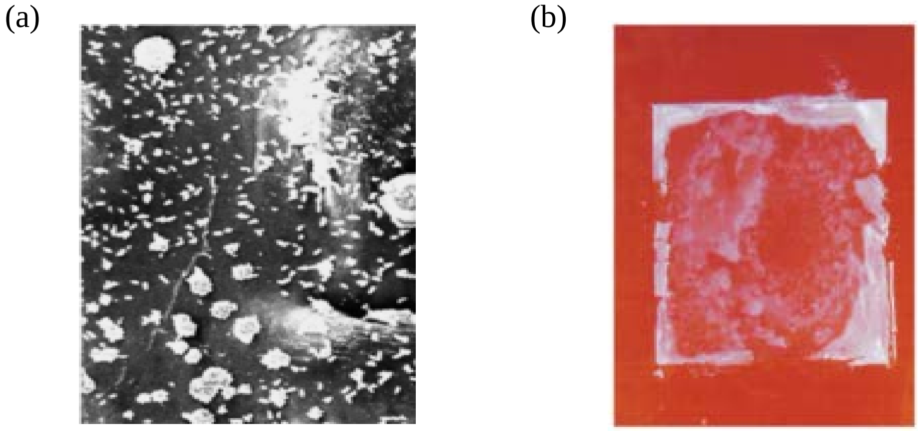


Figure 2.16. Images showing fouling of IEMs by reconstituted whey protein isolate with the presence of 800 mg/L of calcium chloride: (a) calcium deposits on CEM under concentrate pH of 12 (adapted from [139]), and (b) protein deposits on AEM at concentrate pH of 2 (adapted from [81]).

Several factors affect or promote membrane fouling during an ED process. Ayala-Bribiesca *et al.* [139] studied the effect of concentrate solution pH on the fouling of the CEMs. They found that when the concentrate stream was maintained at alkaline pH and the diluate solution contained calcium salts, deposits of calcium hydroxide and calcium carbonate were found on the surface of CEM facing both diluate and concentrate compartments. Furthermore, Ayala-Bribiesca *et al.* [81] noticed that at alkaline concentrate pH no fouling was noticed on the surface of the AEM facing the diluate. However, a gel like protein deposit was observed at concentrate pH values of 2 and 7 [133]. The authors noticed that the deposit easily detached from the membrane surface as they handled the membranes for further analysis. Bleha *et al.* [140] also confirmed that the milk proteins deposited on the surface of the membranes can be removed easily through periodical water rinse, however, whey proteins tended to block the functional groups of the IEMs.

The mineral content of the diluate solution is another factor that impacts the type of deposit noticed on the membranes. Bazinet and Araya-Farias [136] demonstrated that when the feed solution contained calcium chloride and sodium carbonate, a calcium hydroxide deposit formed on the membrane while no calcium carbonate was detected. This was explained by the absence of magnesium in the solution, as magnesium is required to induce the nucleation of calcium carbonate. Casademont *et al.* [141] examined the hypothesis proposed by Bazinet and Araya-Farias [136] and concluded that the presence of magnesium has a great impact on the ED system. For example, calcite ($CaCO_3$) formation increased as the magnesium to calcium ratio increased from 1/20 to 1/5. However, at a ratio of 2/5, the presence of excess magnesium resulted in the formation of amorphous magnesium hydroxide [141]. Ayala-Bribiesca *et al*. [139] observed that some minerals in the solution, especially calcium, tend to replace the counter-ions of the membrane thus changing the membrane's electrical conductivity. It is known that divalent ions have lower mobility compared to monovalent ions, as a result, the electrical conductivity of CEMs drops when calcium ions replace the sodium ions present in the membranes. The tendency for charged ions to replace the counter-ions in the membranes was also observed by other researchers [142]. For example, Lin *et al.* [134], noticed changes in the mineral content of the membrane, although no fouling was observed on the membrane surface.

Furthermore, the mode of operating the concentrate solution (batch or continuous) can affect membrane fouling. Ayala-Bribiesca *et al*. [81, 133] claimed that operating the ED unit in a batch mode, as often is the case in laboratory scale experiments, contributes significantly to the precipitation of calcium salts on AEMs facing the concentrate compartment. The authors explained that as the diluate demineralization progresses, calcium ions will migrate through the CEMs from the diluate to the concentrate stream. When the concentrate stream is recirculated back to the unit, the calcium ions come into contact with phosphorus ions migrating through the AEMs from the diluate stream. This, in turn, results in calcium phosphate formation and precipitation on the AEMs facing the concentrate compartment [94, 133]. The authors argued that in a large-scale continuous ED process this phenomenon will not take place as the concentrate is expected to pass once through the system. However, in industrial scale ED units, the concentrate stream is operated in a feed and bleed mode to reduce the total volumes of waste generated by the process [99]. This means that calcium recirculation and contact with AEMs cannot be avoided.

Membrane fouling in an ED process results in several operational problems. For example, fouling can increase the total resistance of the system. Bazinet and Araya-Farias [93] and Casademont *et al.* [94] agreed that demineralization of the diluate stream and membrane fouling are the two main contributors towards the increase in the resistance of the ED unit. However, Lin *et al.* [134] argued that the contribution of fouling is not as significant as diluate demineralization. Membrane fouling can also affect the integrity of the membrane, as Bazinet and Araya-Farias [136] noticed changes in the electrical conductivity of CEMs in the presence of calcium and carbonate. The authors observed that different concentrations of calcium in the feed solution resulted in equal reductions in the electrical conductivity of the membrane. However, this was not true for carbonate, as different concentrations in the feed solution resulted in varying reductions in membrane electrical conductivity. Moreover, fouling can result in membrane surface deformation. For example, Ayala-Bribiesca *et al.* [139] noticed the deformation of CEM under alkaline concentrate. The authors attributed this to the dehydration of the membranes as a result of calcium salt accumulation. Casademont *et al.* [141] found that the presence of magnesium, especially at high concentrations in the feed solution, could limit the dehydration of the CEM due to the larger hydration shell of magnesium compared to calcium.

2.6. Strategies to Prevent and Control the Fouling of Ion-Exchange Membranes

Different strategies are available to control the fouling of IEMs. For example, feed pre-treatment to remove any particles or components that tend to cause fouling is a commonly practiced strategy when it comes to membrane processes [143]. The flow conditions can also be adjusted to reduce fouling by maintaining turbulent flow in the diluate and concentrate compartments, as very low velocities result in higher concentration polarization and settlement of foulants on the membrane surface. The properties of the membranes can also play an important role, as a result, some researchers have also looked at modifying the membrane surface [144]. Optimizing the concentrate pH can reduce membrane fouling. However, some concentrate pH values can influence and change the diluate pH depending on its buffering capacity. Ayala-Bribiesca *et al*. [81] noticed that at alkaline concentrate pH, significant variation was observed in diluate pH due to the leaching of $\mathrm{OH^-}$ from the concentrate compartment. However, at neutral concentrate pH, the variation was smaller due to less diffusion of $\mathrm{H^+}$ and $\mathrm{OH^-}$. Similar observations were reported by Bazinet and Araya-Farias [93, 136] and Korngold *et al.* [145].

Regardless of how well the operating parameters of the ED process are optimized, the ED unit will still require a clean-in-place (CIP) from time to time to recover process performance. Regular cleaning of the system is one of the main contributors to the operating cost of the process. As a result, researchers have investigated the use of pulsed electrical field (PEF) instead of direct current (DC) to reduce membrane fouling and the frequency of CIP. Furthermore, electrodialysis reversal (EDR) and different cell configurations and stream arrangements have also been proposed.

2.6.1. Clean-in-Place

Membrane fouling is inevitable regardless of the different strategies available to eliminate or control membrane fouling. As a result, many researchers have focused on developing cleaning procedures for membrane processes [146, 147]. Nevertheless, most studies focus on pressure-driven membranes [135, 147], while fewer studies have investigated the cleaning of IEMs in an ED unit [148].

When membrane fouling occurs, the phenomena can either be reversible or irreversible. The former can be treated by water rinse, while the latter can only be removed by chemical cleaning [149]. Membrane cleaning can either be physical or chemical. Physical cleaning involves forward-washing, backwashing, air sparge or vibration. These processes are proven to be effective for pressure driven membranes but not for dense non-porous IEMs [135, 150]. As a result, chemical cleaning is utilized for foulant removal from IEMs. Chemical cleaning utilizes chemical reactions to weaken the foulant-foulant and the foulant-membrane surface bonds [143]. Although chemical cleaning is widely used in different industrial applications, it has several disadvantages, namely membrane damage, consumption of large amounts of chemicals and wastewater generation [149].

Chemical cleaning procedures are classified according to the type of cleaning agent, cleaning solution pH and the dosage. Five groups of chemicals can be used as cleaning agents for membrane processes, namely alkaline solutions, acids, metal chelating agents, surfactants and enzymes, each targeting different types of deposits [146, 151]. Alkaline cleaning agents are known for their ability to remove organic foulants since the functional group of these foulants deprotonate under alkaline conditions. Acids are useful for inorganic foulant removal through solubilization of calcium salts. Acids are also the only cleaning agents that can be used to remove magnesium hydroxide through a neutralization reaction. Enzymes are a complementary cleaning agent used when acids and alkaline agents are not sufficient for removing protein or biofilm fouling [152].

A water rinse is usually the first step in any cleaning protocol. This step aims at removing the weakly bonded foulants before applying cleaning chemicals, this in turn will reduce the required volumes of cleaning agents. A fully automated 100 minute CIP process for ED was suggested by Gernigon *et al.* [79] and consisted of five main steps: (1) water rinse; (2) alkaline solution rinse (maximum pH of 9); (3) water rinse; (4) hydrochloric acid (HCl) solution rinse (pH of 1); and (5) water rinse. The suggested sequence is effective when processing milk products since protein fouling dominates in such systems. However, for whey processing where mineral scaling dominates, it is suggested to start with the acid cleaning step [143]. When it comes to the cleaning agents to be used for ED, the American Water Works Association (AWWA) [153] claims that 2-5% HCl solution, 3-5% NaCl with a pH of 8-10 (adjusted using sodium hydroxide (NaOH)), and 10-50 mg/L chlorine solution are the only chemicals to be considered. The reason behind using an NaCl solution as a base cleaning agent could be explained by the fact that most organic foulants found in food effluents are colloidal particles that bond to the membrane surfaces by Van der Waals forces and electrostatic repulsive forces. The use of saline solutions has been demonstrated to be effective in breaking these forces and releasing the foulants from the surface of UF and RO membranes [154, 155]. However, the pH of this alkaline cleaning step should be limited to 10 to prevent membrane damage through hydrolysis reactions.

Wang *et al.* [135] studied the effect of different cleaning chemicals in removing a fouling layer made of calcium and magnesium hydroxide and carbonates from the surface of CEMs. The membranes were not cleaned directly in the ED unit, rather the unit was dissembled and the membranes were soaked in the cleaning chemicals for a specified period. Soaking in deionized water removed the least amount of foulants, due to the strong adhesion forces between the foulant and membrane surface. When the membranes were soaked in 1% HCl solution for 3 hrs, only some residual fouling was noticed. However, the elemental analysis indicated high levels of oxygen, therefore, ultrasound was introduced to the cleaning procedure. The authors noticed that after the application of ultrasound for 1 min, the used membranes had a clean surface, chemical composition and performance similar to the original membranes. This indicates that using cleaning agents solely might not be enough for extreme cases of fouling. The use of a saline solution for ex-situ cleaning of IEMs used in food application was investigated by Bdiri *et al.* [156]. The authors reported that the use of reconstituted seawater affects the membrane separation capacity as the divalent ions present in seawater tend to occupy the free functional sites of the membranes. On the other hand, the use of 35 g/L of NaCl as a cleaning chemical resulted in higher recovery of the membrane performance when compared to using reconstituted seawater.

Furthermore, the interaction between the counter-ions of the IEM and the cleaning agent should be considered. For example, acid and alkaline cleaning agents tend to replace the counter-ions of the membrane with H^+ and OH^-, respectively. This can cause problems in the next operation cycle as these ions replace other salts in the feed solution. Research has shown that AEMs are more sensitive to cleaning chemicals compared to CEMs. Garcia-Vasquez *et al.* [157] performed an ex-situ CIP cycle on AEMs and CEMs having the same materials as the support and binder, but different ion-exchange groups. They applied a CIP cycle for 400 hrs, consisting of soaking the membranes for 30 min in 0.1M HCl (pH of 1); rinsing with deionized water; soaking for 30 min in 0.1M NaOH (pH of 13); and rinsing with deionized water. The authors noticed an increase in AEM hydrophilicity as a result of shifting the membrane charge group from Cl^- to OH^- during the cleaning sequence. The increase in membrane hydrophilicity resulted in higher water uptake, greater membrane electrical conductivity, the formation of pores and cavities in the membrane, and change in membrane toughness and flexibility. For CEMs, no swelling was observed as the charge group was shifted from Na^+ to H^+, thus resulting in less membrane damage.

2.6.2. Pulsed Electrical Field

The concept of pulsed electrical field (PEF) was first introduced in 1995 by Karlin and Kropotov [158] and involves the application of a constant current density for a fixed period (a pulse) followed by a pause duration where no current is passed through the unit [159]. It is claimed that PEF controls concentration polarization at the membrane interface and reduces the probability of fouling by disturbing the foulants [158, 160]. Casademont *et al.* [80] operated an ED unit as a conventional and pulsed system and noticed a lower degree of fouling when using a pulsed system. However, a longer processing time was required to achieve the desired demineralization rate. Ruiz *et al.* [159] studied the effect of the pulse period on membrane fouling during the electrodialysis of a casein solution. They did not notice any protein fouling on the AEM facing the diluate solution for 10s of pulse followed by a pause of 40s regardless of the applied current density (**Figure 2.15**). However, fouling was noticed for a pause period of 10s when using current densities equal to or higher than 20 mA/cm^2 (**Figure 2.15**). The authors claimed that the relaxation period limits water dissociation and heating of the AEMs thus reducing or eliminating protein fouling. Cifuentes-Araya *et al.* [160] noticed the formation of a deposit layer at 30s pause period while nothing was observed at 10s for an applied current density of 40 mA/cm^2 when the feed solution contained magnesium. On the other hand, Mikhaylin *et al.* [161] proved that decreasing both pulse and pause periods to 2s and 0.5s, respectively, resulted in high demineralization rates and no fouling formation on the AEM. These disagreements found in the literature indicates that for PEF to be effective, it is important to consider the diluate composition and the operating parameters of the ED unit.

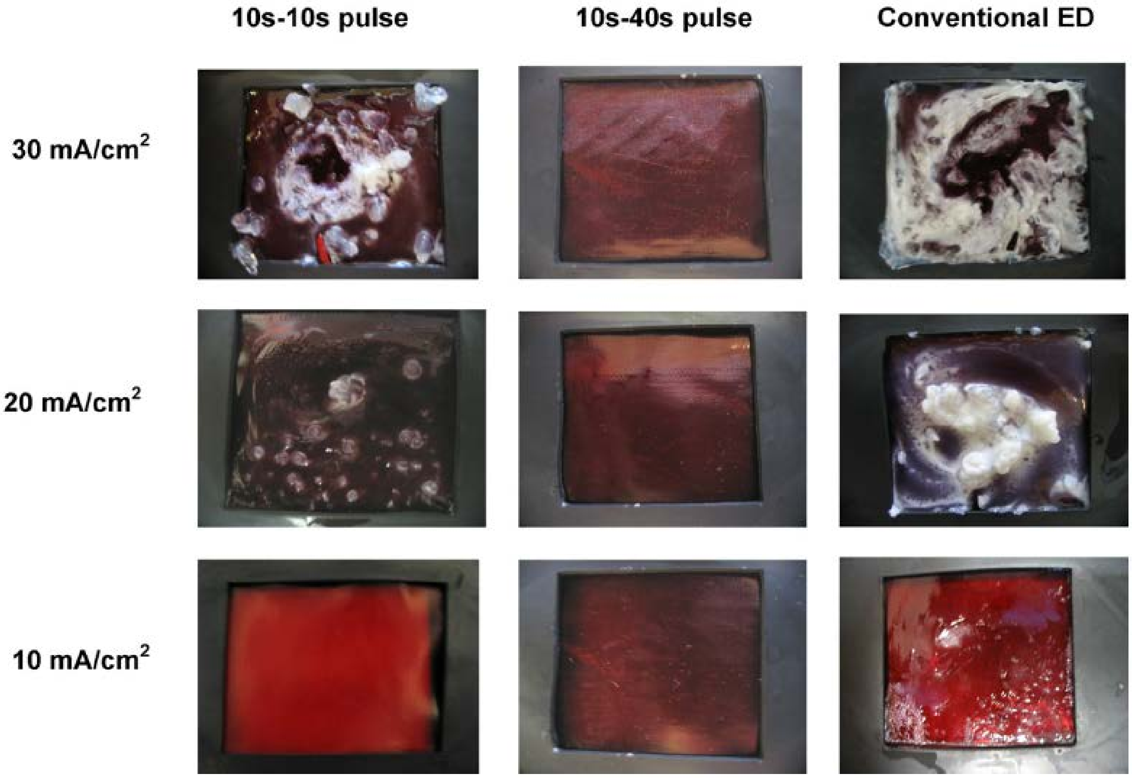


Figure 2.17. Photographs of AEMs facing the diluate compartment during the electrodialysis of a casein solution containing 32 g of protein/L (adapted from [159]).

When it comes to applying PEF to acid whey treatment, Dufton *et al.* [162] used a pulsed/pause period of 25s/ 25s. The authors observed an increase of 16% in the degree of deacidification with a reduction of 33% in the energy consumption of the pulsed system when compared to the conventional ED process. The lower energy consumption was due to the lower fouling noticed in the pulsed system. The authors believed that the use of PEF reduced concentration polarization which in turn reduced water splitting thus affecting the solution pH and membrane fouling. In a recent publication by Dufton *et al.* [163], the authors reported that the total demineralization rate and lactic acid removal were not affected by varying pulsed/pause conditions. However, for the same pause duration, an increase in the pulsed duration resulted in higher system resistance and energy consumption due to greater mineral scaling. In addition, the authors also explained that as the scaling layer developed and its thickness increased, other ions became trapped in the layer and reacted with each other, thus making the removal of this fouling layer harder during the pause period.

2.6.3. Electrodialysis Reversal

Electrodialysis reversal (EDR) operates in the same manner as a conventional ED process, however, the direction of the applied current is reversed periodically thus reversing the direction of ion flow through the unit (**Figure 2.16**). Reversing the polarity will allow fouling removal without the need to terminate the operation for CIP as often as the conventional ED process [73]. Nevertheless, reversing the polarity means that the electrode reactions and the processing streams through the ED unit are also reversed. This, in turn, results in a shorter electrode lifetime, more complicated process design, and the generation of off-specification products at the start of each cycle [153].

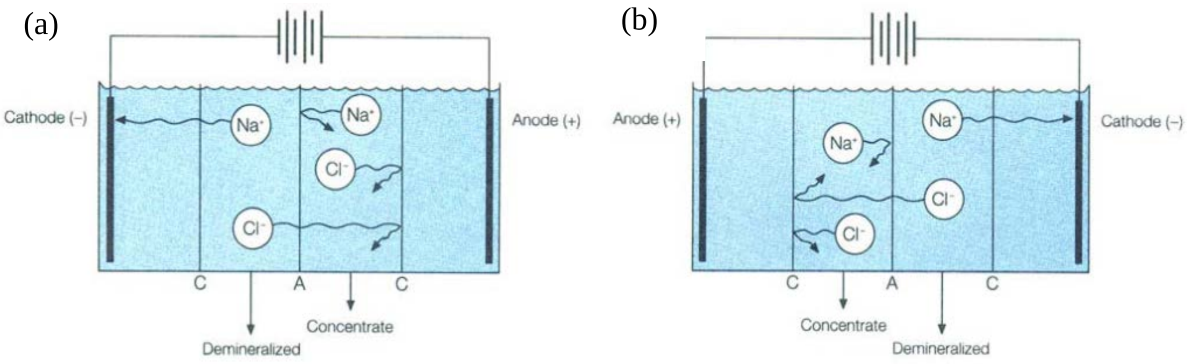


Figure 2.18. Schematic diagram illustrating the operation of electrodialysis reversal: (a) before reversing the polarity, and (b) after reversing the polarity (adapted from [153]).

EDR has been researched for water treatment applications [164-166], but little research work has demonstrated the effectiveness of this process for whey treatment while reducing membrane fouling. Nevertheless, Merkel and Ashrafi [167] recently published a research article examining the effect of combining PEF with EDR for acid whey treatment. The modified process is known as pulsed electrodialysis reversal (PER). It is important to note that the authors only reversed the direction of the applied current and not the processing streams through the unit. Since the processing streams were not reversed, the time required for PER was longer than the conventional ED due to back diffusion of ions to the diluate compartment under the revered current. On the other hand, less fouling was observed on the surface of the membranes when PER was used since the fouling layer was expected to detach from the membrane surface and dissolve back into the processing solutions.

2.6.4. Cell Configuration

In their review paper, Fidaleo and Moresi [99] suggested the configuration illustrated in **Figure 2.17** for acid whey treatment and lactic acid removal. This process utilizes a three-compartment ED unit that is assembled by having two AEM in series followed by a single CEM. The diluate stream, i.e. acid whey, is passed between the two AEMs. The process uses two different concentrate streams, a brine solution and an alkaline solution, that are passed through the two adjusting compartments to the diluate compartment (between the AEM and CEM). The concept of utilizing two different concentrate streams was proposed by Ayala-Bribiesca *et al.* [81] to overcome both protein and mineral deposits on IEMs. The authors suggested that the compartments that will receive cations from the diluate solution should be maintained at neutral pH to prevent mineral fouling of the CEM facing the concentrate compartment. Conversely, the compartments that receive anions from the diluate solution should be maintained at an alkaline pH to prevent protein fouling of the AEM facing the diluate compartment. This configuration was examined by Casademont *et al.* [80] and was proven to be effective in eliminating mineral deposits on the surface of the AEM facing the concentrate compartment. This was mainly due to the fact that the calcium ions removed by the CEM did not encounter the phosphate ions passing through the AEM.

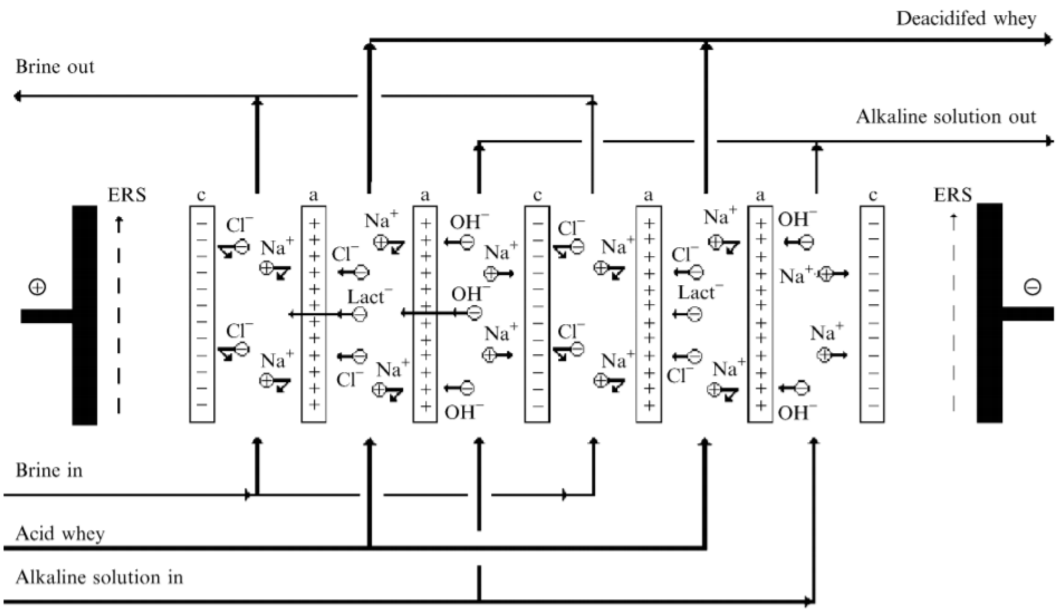


Figure 2.19. The proposed three-compartment ED stack for lactate ion removal from acid whey (adapted from [99]).

2.6.5. Operating in Overlimiting Current Density Region

As discussed in **section 2.4.2.2**, when the applied current exceeds the limiting current density, it leads to the formation of a current induced convection, also known as electroconvection. The vortices formed as a result of electroconvection are predicted to affect membrane fouling. Although operation in overlimiting current density region results in higher energy consumption, higher degrees of demineralization can be achieved with a smaller membrane area. Operation above the limiting current density is applied in the electrodeionization (EDI) process in which the ED compartments are filled with ion-exchange resins. Due to the benefits associated with operating in the over limiting current density region, this practice has been investigated for ED. For example, Bukhovets *et al.* [168] studied the change in voltage as a function of time for an ED unit used to treat phenylalanine-mineral salt solutions. The authors noticed that the increase in voltage with time was insignificant when the system was operated above the limiting current density. This was explained by the lower degree of fouling due to the “wash out” of the amino acids as a result of water splitting.

2.7. Lactic Acid Recovery from a Salt Solution

Lactic acid is an organic acid made of 2-hydroxycarboxylic acid with a chiral carbon atom. Lactic acid is used in food, pharmaceutical, leather, textile, and chemical industries. The industrial demand for lactic acid has increased due to the possibility of producing biodegradable polylactic acid which can be used in plastic production. The worldwide lactic acid demand in 2007 was estimated to be around 150,000 metric tonnes and was forecasted to double in 2015 [169].

Lactic acid is produced either by chemical synthetic hydrolysis of lactonitrile or microbial fermentation. In the former, acetaldehyde is reacted with hydrogen cyanide under high pressure and alkaline conditions to produce lactonitrile which is recovered and purified using distillation. In the next step, lactonitrile is hydrolysed to lactic acid by the addition of hydrochloric acid or sulfuric acid. The lactic acid produced is esterified with methanol to methyl lactate which is recovered and purified using distillation. Finally, the purified methyl lactate is hydrolysed in an acidic aqueous solution to produce lactic acid and methanol.

The production of lactic acid using microbial fermentation is known to be relatively fast with high yields. The process conditions are usually optimized depending on the type of microorganism used [169]. However, the process requires the addition of nutrients, sugars and microorganisms to the reaction media. Nevertheless, there is always the possibility of using low-cost raw materials. One such source is the lactose present in whey. Several researchers have investigated the production of lactic acid using sweet whey UF permeate, as it contains low amounts of protein and high levels of lactose [170]. The main drawback of the process is that the effluent stream from the fermentation process needs to undergo a purification step to separate lactic acid from unconverted lactose and salts.

An unutilized source of lactic acid is acid whey, since lactic acid is removed from acid whey during the demineralization process using either NF or ED. Recovering and re-using the lactic acid found in the NF permeate and ED concentrate can add value to the acid whey treatment process. The NF permeate and ED concentrate will mainly contain water, salts and lactic acid. Water can be removed using evaporation or RO; however, the main challenge is the separation of salts and lactic acid.

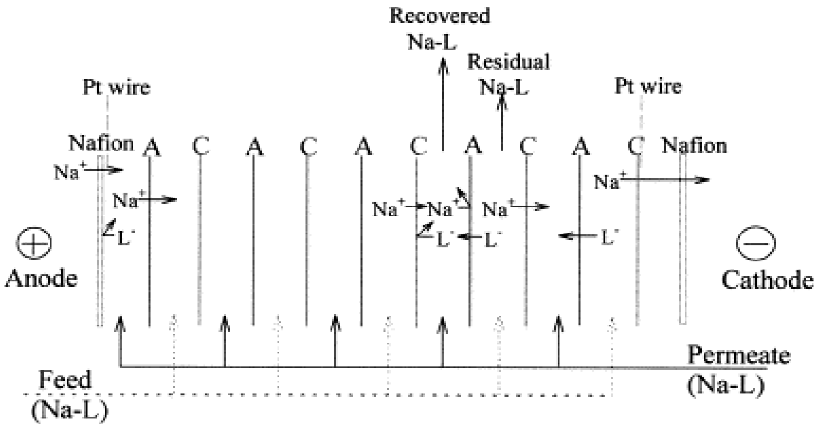
The recovery of lactic acid from NF permeate or ED concentrate has not been studied. The closest concept found in litrature is the recovery of lactic acid from fermentation broths where the solution is made of sodium lactate, glucose and yeast extract [171-174]. Several processes have been identified for the recovery of lactic acid from fermentation broth, including solvent extraction, adsorption and direct distillation. However, each process is associated with many disadvantages. For example, both solvent extraction and adsorption involve the use of other chemicals that require either regeneration or treatment [101]. As a result, researchers have looked into utilizing membrane technology, such as NF or ED, to recover lactic acid from fermentation broths.

Gonzalez *et al.* [175] evaluated the possibility of using NF for separating lactic acid and salts. The authors noticed that lactic acid rejection increased with feed pH and operating pressure. However, the rejection decreased with an increase in initial feed concentration due to Donnan effects. They concluded that separating lactic acid from salts is not feasible using NF, as both components tend to pass through the NF membranes. Similar results were obtained by Freger *et al.* [176] who also noticed a decrease in lactic acid rejection with the increase in the operating temperature as a result of sorption and diffusion mechanisms. Bouchoux *et al.* [177] took advantage of the fact that NF membranes tend to reject divalent ions. The authors used NF as a pre-treatment step before ED to separate divalent ions such as calcium, magnesium, sulfate and phosphate ions. Although the separation of lactic acid from a salt solution using RO membranes has not been investigated, RO membranes have been used widely for the recovery or separation of other organic acids as summarized in **Table 2.3**.

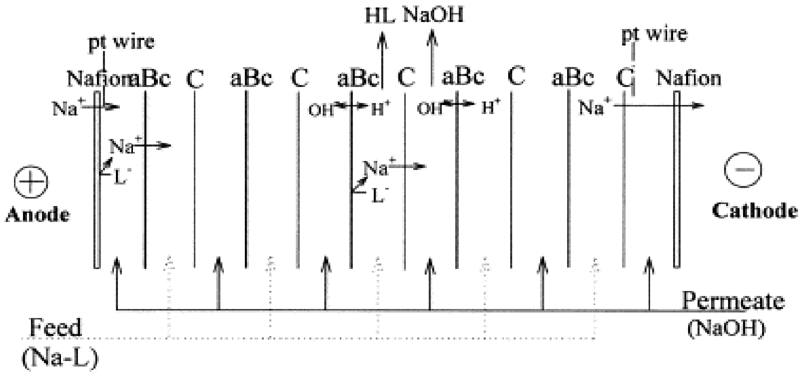
Table 2.3. Separation of different organic acids using reverse osmosis membranes.

Organic acid	**Molecular weight**	**Membrane type/ salt rejection**	**Operating conditions**	**Organic acid rejection**	**Reference**
Acetic acid	60.05	GE Osmonics RO AG (Aromatic polyamide)/ 99.5% NaCl	Feed solution of 7% acetic acid	25% at 26 bars 32% at 40 bars	[178]
			Feed solution of 7% acetic acid and 15% glucose	0% at 26 bars 0% at 40 bars	
Acetic acid	60.05	GE Osmonics RO CE (Cellulose acetate)/ 97% NaCl	Feed solution of 7% acetic acid	-5% at 26 bars 0% at 40 bars	[178]
Boric acid	61.83	BW30LE (polyamide)	Feed solution of 4 mg/L boron and applied pressure of 1200 kPa.	70% rejection at pH = 4 98% rejection at pH = 10.5	[179]
Ethyl acetate	88.10	Poly (ether/amide) membrane	Concentration of ethyl acetate in feed solution: 366 ppm (pH = 6.0)	95.3% rejection at 69 bars	[180]
Phenol	94.11	Poly (ether/amide) membrane	Concentration of Phenol in feed solution: 100 ppm (pH = 4.9)	93% rejection at 69 bars	[180]
			Concentration of Phenol in feed solution: 100 ppm (pH = 12.0)	> 99% rejection at 69 bars	
Benzoic acid	122.12	Cellulose acetate membranes/ 91.7% NaCl	Applied pressure of 10 bar	20% rejection at pH of 3 90% rejection at pH of 7	[181]
Citric acid	192. 12	Poly (ether/amide) membrane	Concentration of citric acid in feed solution: 10,000 ppm (pH = 2.6)	99.9% rejection at 69 bars	[180]

When it comes to the use of ED for the purification of lactic acid, different pathways are proposed in the literature for lactic acid recovery from fermentation broths. Lee *et al.* [101] used a two-stage ED process for the recovery of lactic acid from fermentation broth as shown in **Figure 2.18**. The first step in the proposed process was a desalting electrodialysis step in which the lactate salt was recovered from the fermentation broth (**Figure 2.18 (a)**). Under the application of an electrical current, the sodium ions migrated through the CEM while the lactate ions passed through the AEM from the diluate to the concentrate compartment, leaving behind the uncharged molecules of glucose and yeast extract. The second step in the proposed process was the water-splitting or acidification step (**Figure 2.18 (b)**). The electrodialysis unit in this step was set up with CEM and bipolar membarnes. As a result, lactate ions were retained in the diluate compartment and bonded with the H^+ ions generated by the bipolar membranes, while the Na^+ ions migrated through the CEM towards the concentrate compartment and bonded with the available OH^- ions. Lee *et al.* [101] reported current efficiencies between 86-98% with an energy consumption of 0.25 kWh per kilogram of recovered lactate for the desalting step. The authors also found that the water-splitting electrodialysis step was the main contributor to the total energy consumption as 0.54-0.71 kWh was required to recover one kilogram of lactic acid.



(a) Desalting electrodialysis



(b) Water splitting

Figure 2.20. Proposed two-stage electrodialysis for the recovery of lactic acid from fermentation broth (adapted from [101]). C: cation exchange membrane, A: anion exchange membrane, aBc: bipolar membrane, Na-L: sodium lactate, Na^{+}: sodium ion, L^{-}: lactate ion, HL: lactic acid.

Kim & Moon [171] looked at utilizing a single-stage ED unit with three-compartments to perform both the desalting and acidification steps (**Figure 2.19**). The authors successfully recovered 98% of lactic acid present in the diluate solution with current efficiencies ranging between 77 - 83%. The energy consumed was a function of the initial feed concentration and the type of membranes used in the process. Values as high as 3.8 kWh per kilogram of lactic acid recovered were reported for an initial feed concentration of 58.4 g/L.

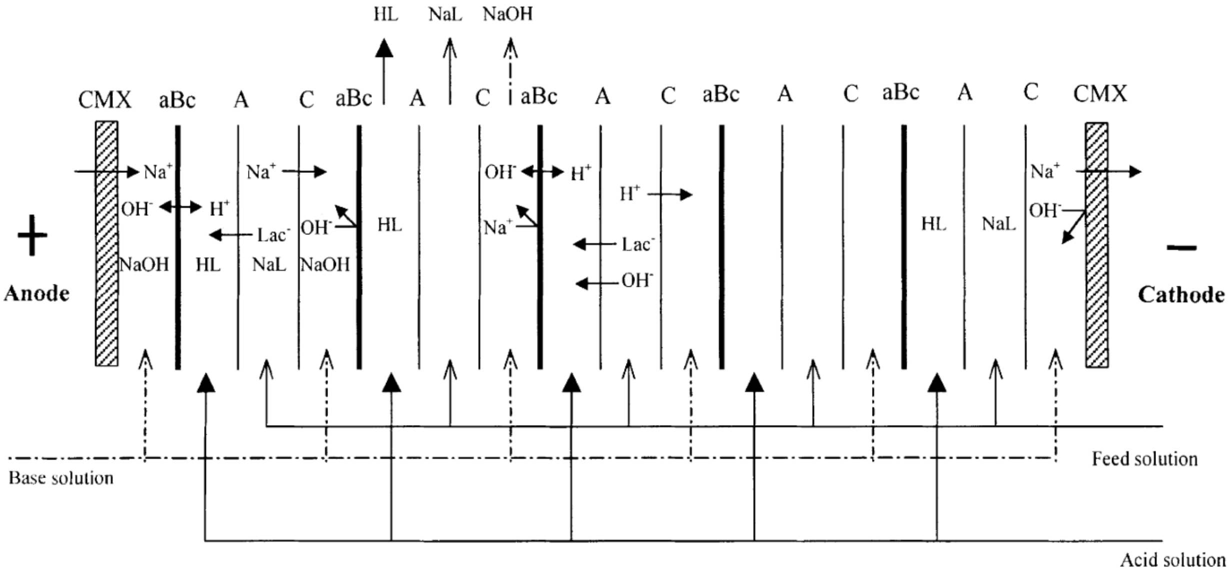


Figure 2.21. Proposed three-compartment water-splitting electrodialysis for the recovery of lactic acid from fermentation broth (adapted from [171]). A: anion-exchange membrane, aBc: bipolar membrane, C: cation-exchange membrane, HL: lactic acid, Lac^{-}: lactate ions, Na^{+}: sodium ions.

Most of the work found in the literature focus on the separation of sodium lactate from the fermentation broth with very low concentrations of other ions. Nevertheless, Thang *et al.* [182] looked at the possibility of recovering lactic acid from grass silage. Grass silage is a complex mixture with a conductivity of 35.8 mS/cm, an acidic pH of 4, 19.28 g/L of cations (mainly K, Na, Ca and Mg), 15.47 g/L of anions (mainly Cl, NO_3, PO_4, and SO_4), 37.54 g/L of lactate, 26.13 g/L of free amino acids, and 38.34 g/L of sugars. The authors used a two-stage ED process, the first stage was operated at a pH of 6.7 where the charged components were separated from uncharged components. The second stage was operated at a pH of 2 to remove salts and retain lactic acid in the diluate stream. The separation process in the second stage was divided into two phases, as demonstrated in **Figure 2.20**. It was found that in the first 80 min of the process, the loss in lactic acid was only 1.1%. This loss increased to 6.6% by the end of the second phase. This was attributed to the pH shift observed in the diluate solution from 2 to 2.9, which is known to affect the ratio between lactic acid and lactate (**Eq. 2.1**). The authors did not comment on the purity of the generated lactic acid, however, the reported results demonstrated the presence of sulfate and divalent cations in the final diluate solution.

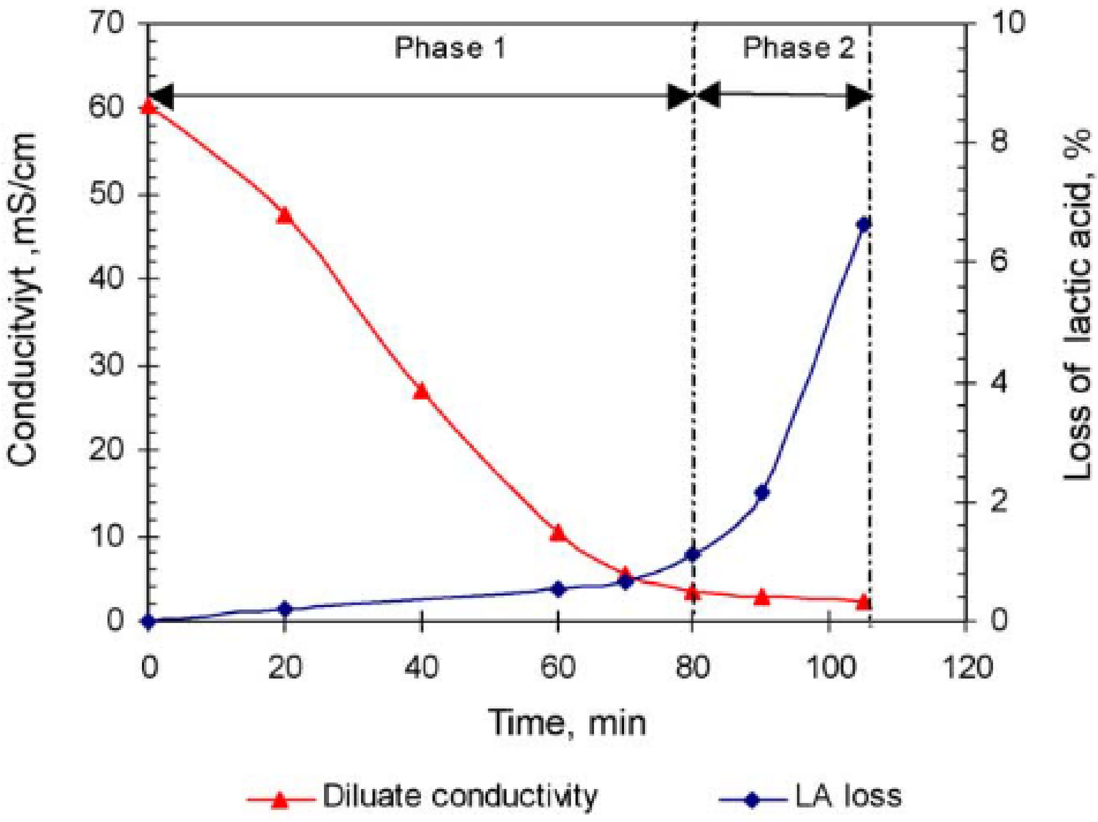


Figure 2.22. Change in conductivity of the diluate stream and the loss in lactic acid from the diluate for an ED unit operated at 290 A/m^2 (adapted from [182]).

2.8. Scope of the Thesis

Although the use of membrane technologies have been proven effective for the treatment of acid whey, large scale applications are still limited in the dairy industry in Australia due to the uncertainties associated with the proposed technologies, especially ED which is known for its high operating cost associated with the cost of replacing IEMs and high electrical consumption. Therefore, this thesis aimed at furthering the understanding of the treatment of acid whey using ED by addressing the following.

- *Understanding the fouling of IEMs during the electrodialysis of industrial samples of sweet and acid whey (**Chapter 4**).* Although several researchers have studied the fouling of IEMs during the electrodialysis of reconstituted whey powders, it has been illustrated by Rice *et al.* [183] that real solutions behave differently than reconstituted solutions. The experiments were performed using both sweet and acid whey to allow direct comparison since sweet whey is well known to the dairy industry and is easily processed.

- *Process optimization for the reduction of membrane fouling (**Chapter 4**).* The effect of concentrate pH has been studied widely for the fouling of IEMs, however, this factor has not investigated in conjunction with concentrate conductivity and mode of power supply operation (i.e. constant current Vs constant voltage).

- *In-situ cleaning of IEMs using the cleaning agents recommended by the American Water Works Association (**Chapter 4**).* Soaking of IEMs in cleaning solutions is a common practice followed by many researchers [147, 157]. However, from the perspective of mass transfer, circulating the cleaning chemicals in the ED stack is more efficient [148, 184]. Furthermore, for the implementation of any process in an industrial scale, it is important to develop and validate the CIP process.

- *Process optimization for reduction of the volumes of waste generated as the concentrate stream (**Chapter 5**).* Salty whey permeate (a by-product of cheddar salting process) is readily available in many dairy factories. The use of this by-product as the concentrate stream during the electrodialysis of sweet or acid whey could reduce the total volumes of waste generated by the dairy factory. In addition, the use of salty whey permeate could eliminate the need for a concentrate stream prepared from freshwater and salt, thus reducing the overall water consumption and effluent salt load on the dairy factory.

- *Effectiveness of combining several membrane technologies for acid whey treatment using a pilot scale setting (**Chapter 6**).* The use of other membrane technologies, such as UF and NF, as a pre-treatment step prior to ED is expected to reduce the fouling of IEM and the load on the ED process thus enhancing the removal of lactic acid and minerals.

- *Adding value to the treatment process by recovering lactic acid from the concentrate stream (**Chapter 7**).* During the treatment of acid whey, lactic acid is removed in the waste streams (NF permeate and ED concentrate). Recovering lactic acid from the waste streams could add value to the treatment process as the recovered lactic acid could be utilized in the cheese making process thus reducing the intake of fresh stock.

In addition to the focus of this work on the treatment of acid whey using ED, the below was also investigated as value adding alternatives for the dairy industry:

- *Treatment of salty whey permeate using ED (**Chapter 5**).* Salty whey permeate is known to contain high levels of lactose that can be recovered and dried to produce lactose powder. In addition, it is also possible to produce a concentrated salt solution that could either be used for the chlor-alkali industry [110] or used in process cheese production [185].

- *Evaluation of other electrically driven membrane processes for acid whey treatment (**Chapter 8**).* MCDI has been mainly investigated for the water treatment and no work has demonstrated the use of this technology for acid whey demineralization. Due to the mode of operation in an MCDI process (i.e. periodic reverse in polarity), it is expected that membrane fouling will be less thus affecting the overall energy consumption of the process.

CHAPTER 3. Materials and Methods

3.1. Introduction

This chapter details the materials and methods used to generate the data and results presented in this thesis. Since some of the experiments were performed in both lab scale and pilot scale, detailed description of both are provided here.

3.2. Chemical Reagents and Fresh Whey Samples

Fresh whey samples, namely raw acid whey, salty whey permeate, and skimmed sweet whey were provided by Bega Cheese Limited from three main factories. All samples were refrigerated at 4 ± 1°C and used within two weeks, except for salty whey permeate samples which were used over a longer period since the high salt content prevents the growth of bacteria. The raw acid whey was skimmed in the laboratory using a centrifuge separator (Milky cream separator; Model FJ 130 ERR; MilkyDay, Czech Republic) to remove fat and whey cream.

All solutions used in this work were prepared using purified water (>8.6 MΩ cm; Merck Millipore KGaA, Germany), except for the pilot plant trials conducted on-site, where tap water was used to make some of the solutions as specified in **Chapter 6**. Sodium sulphate (Na_2SO_4; >99%; Thermo Fisher Scientific Australia Pty., Ltd., Australia) and sodium chloride (NaCl; >99.5%; Merck KGaA, Germany) were used to prepare the electrolyte and the concentrate solutions, respectively, for the ED experiments unless specified otherwise. For pH adjustment, 5M hydrochloric acid (HCl; 36%; Thermo Fisher Scientific Australia Pty., Ltd., Australia), and 5M sodium hydroxide (NaOH; chem-supply Pty., Ltd., Australia) were used. Lactic acid (85-90%; Thermo Fisher Scientific Australia Pty., Ltd., Australia) and potassium chloride (KCl; >99.0%; Chem-supply Pty., Ltd., Australia) were used to prepare the feed solution for the lactic acid and salt separation experiments.

IEM cleaning was done by using HCl solution with a pH of 1.0 ± 0.15 and a solution of 3% NaCl adjusted to a pH of 9.15 ± 0.15 using 5M NaOH. While for the pilot scale experiments, P3-Ultrasil 69 (Ecolab, Australia) was used as the cleaning agent.

A multi-element standard solution (Fluke Analytical; Signa Aldrich Co. LLC) was used to prepare standard solutions for ion detection. Lactose (Analytical grade; Thermo Fisher Scientific

Australia Pty., Ltd., Australia) was used to prepare the standards for lactose detection. Lactic acid and NaCl were used to prepare the standards for lactate and chloride (Cl), respectively.

For the preparation of carbon electrodes, activated carbon (AC Norit SA 4, D50 = 30 µm, Cabot Norit Activated Carbon, USA), Polyvinylidene fluoride (PVDF, MW ~530,000 g/mol, Sigma-Aldrich), and N-N dimethylformamide (DMF, 99.8%, Merck Millipore), and titanium plates (TA2 titanium, Shenzhen Hongwang Mould Co., Ltd., China) were used.

3.3. Commercial membranes

Different commercial electrically driven and pressure driven membranes were used in this work as detailed below.

3.3.1. Ion-Exchange Membranes

Two main types of IEMs were used, non-selective IEMs (CMB and AHA) and monoselective IEMs (CIMS and ACS). All IEMs were purchased from Astom Co., Ltd., Japan and their characteristics are summarized in **Table 3.1**. The membranes were soaked in 3% NaCl solution to remove any preserving agents and to allow for membrane hydration and expansion prior to use in all experiments.

Table 3.1. Properties of Neosepta ion-exchange membranes used in this work (provided by the manufacturer).

Property	**Unit**	**Cation exchange membrane**		**Anion exchange membranes**	
		CMB	**CIMS**	**AHA**	**ACS**
Type	-	Strong acid (Na type)		Strong base (Cl type)	
Characteristics	-	Alkaline resistance	Monovalent cation selective	Alkaline resistance	Monovalent anion selective
Thickness	mm	0.21	0.15	0.22	0.13
Temperature range	°C	≤ 60	≤ 40	≤ 60	≤ 40
pH range	-	0-14	0-10	0-14	0-8
Electrical resistance	Ω. cm^2	4.5	1.8	4.1	3.8

3.3.2. Pressure Driven Membranes

Proprietary semi-permeable polyethersulfone UF membranes with a molecular weight cut-off of 10 kDa was used for the pilot scale UF experiments (Lenntech, Netherlands). The NF and Dia-NF processes were performed using a thin-film NF spiral wound module (Suez, USA) with clean water flux of 24 L/h, molecular weight cut-off of 150-300 Da for uncharged molecules, and a minimum rejection of 98% for 2,000 ppm magnesium sulfate at 25°C and 110 psi. For the lactic acid separation from a salt solution, two commercial polyamide thin-film composite low energy RO membranes were used, namely LE-4040 and XLE-2521 (Filmtec, USA). In addition, a loose RO membrane sample was provided by GE (USA). Both the Filmtec LE-4040 and XLE-2521 membranes are specified to have a salt rejection of 99% but the former is for a feed solution of 2,000 ppm NaCl at an applied pressure of 10.3 bar; while the latter is for a feed solution of 500 ppm NaCl at an applied pressure of 6.9 bar.

3.4. Experimental Rigs

3.4.1. Lab Scale Units

The lab scale experiments were performed at the University of Melbourne and the details are described below.

3.4.1.1. *Electrodialysis Unit*

The electrodialysis experiments were conducted using an FTED-40 module manufactured by FuMA-Tech GmbH (Bietigheim-Bissingen, Germany). The ED unit consisted of two titanium-iridium plasma coated stainless steel electrodes. The module was arranged with three CEMs separated by two AEMs and alternating diluate and concentrate spacers. A CEM was placed in front of the electrodes to prevent the migration of anions into the electrode compartment (See **Figure 3.1**) The effective area per IEM was 36 cm^2. The potential difference was generated using a DC power supply (Agilent DC Modular Power System N6764A) with an output voltage range between 0-60 V and an output current range between 0-20 A. Three peristaltic pumps (Masterflex L/S digital drive 600 RPM with Masterflex L/S high performance pump head) were used to circulate the electrolyte, concentrate and diluate solution through the ED unit. For all the lab scale ED experiments, the diluate and concentrate flowrates were maintained at 500 mL/min, while the electrolyte flowrate was kept at 1000 mL/min as recommended by the manufacturer to minimize concentration polarization effects. The flowrate was increased to 750 mL/min during cleaning. The solutions were stirred continuously throughout the experiments. A water bath was used to maintain the temperature of the solutions.

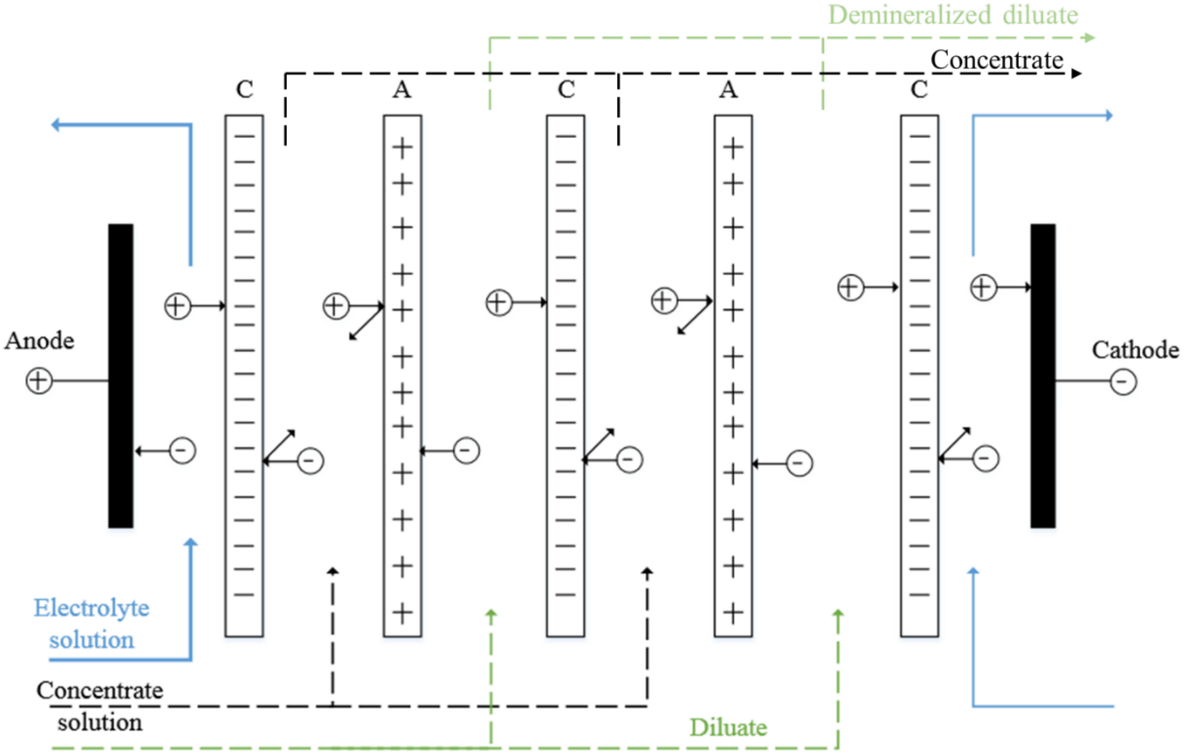


Figure 3.1. The arrangement of ion-exchange membranes and processing solutions in the lab scale electrodialysis unit.

3.4.1.2. *Membrane Capacitive Deionization Unit*

The MCDI rig consisted of a single cell unit made of two parallel electrodes separated by an anion and cation exchange membrane. The membranes were separated by a non-conductive spacer (Low foulant spacer 34 mil, Sterlitech). The spacer prevents the direct contact of the membranes, electrical short circuiting, and provides a pathway for the feed solution. All the elements were housed in a polycarbonate housing. The membrane active area was 20 cm in length and 10 cm in width. However, to prevent leakage, the membranes were cut 1 cm larger than the electrodes. The feed channel was located 9 mm from the edge of the membrane and was 3 mm wide and 20 mm long. **Figure 3.2** shows the setup of the lab scale MCDI unit. A DC power supply (Agilent DC Modular Power System N6731B) was used to provide the potential difference. The DC power supply had an output voltage range between 0-5 V and an output current range between 0-10 A. A peristaltic pump (NEMA 4×, Watson Marlow, Australia) was used to pump the feed solution. Mettler-Toledo conductivity and pH meters (Greifensee, Switzerland) were used to measure the changes in the conductivity and pH of the feed solution.

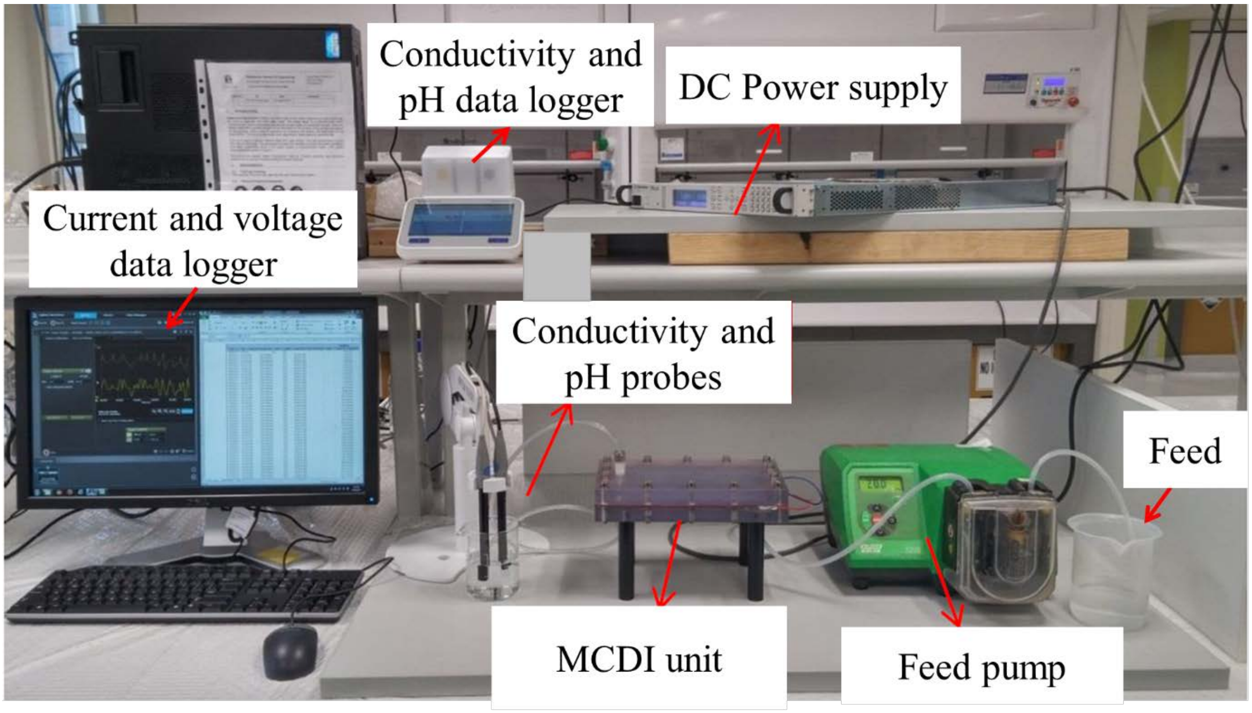


Figure 3.2. Membrane capacitive deionization unit set up (adapted from [186]).

3.4.1.3. *Pressure Driven Membrane Unit*

The experiments for lactic acid and salt separation were carried out in a crossflow configuration using two parallel flat sheet membrane modules (CF042 Sterlitech Corporation). The membrane active dimension per cell was 4.6 cm X 9.2 cm. The unit consisted of (**Figure 3.3**): (1) a 50 L feed tank; (2) Hydra cell G10 positive displacement pump (Wanner Engineering, Australia); (3) a guard filter (5 µm carbon filter, Puretec, Australia) in the retentate line to eliminate any contaminants from re-entering the system; (4) water bath to maintain the temperature; (5) a digital pressure indicator (C62 series, Hydra-cell, Wanner Engineering, Australia) was used to monitor the feed pressure; and (6) back pressure regulators (BP-60 Series, Swagelok, USA), flow meters (Blue-White Industry, USA), and an analogue pressure gauge (Floyd, Australia) were installed on the retentate line from each membrane cell.

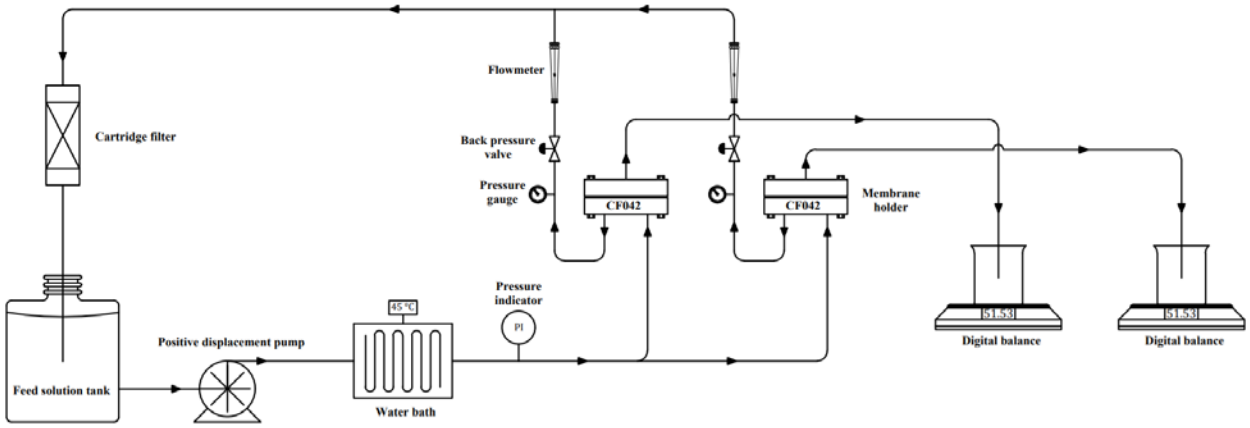


Figure 3.3. Reverse osmosis rig set up.

3.4.2. Pilot Scale Units

The pilot scale experiments were performed at Tatura Milk Industries and the detailed description of the equipment are as below.

3.4.2.1. *Electrodialysis Unit*

The ED experiments were conducted using an FT-TS40 module manufactured by FuMA-Tech GmbH (Bietigheim-Bissingen, Germany). Titanium-iridium coated plasma and stainless steel were used as the anode and the cathode, respectively. Starting with a CMB, a total of ten membrane cell pairs (10 CMB and 10 AHA) were installed between the two electrodes with alternating spacers to form the diluate and concentrate compartments. An eleventh CMB was used in front of the electrode compartment to prevent anion migration. The effective area per ion exchange membrane was 100 cm^2. The pilot plant was fitted with three centrifugal pumps (MD 70 RZM, IWAKI Europe GmbH, Germany) and three cylindrical polyethylene tanks of 6 L each (**Figure 3.4**). A direct current power supply (Voltage regulator Type 3257.3, Statron Geratetechnik GmbH, Germany) was used to generate the potential difference across the membrane cell pairs. The DC power supply had an output voltage range between 0-72 V while the current ranged between 0-20 A.

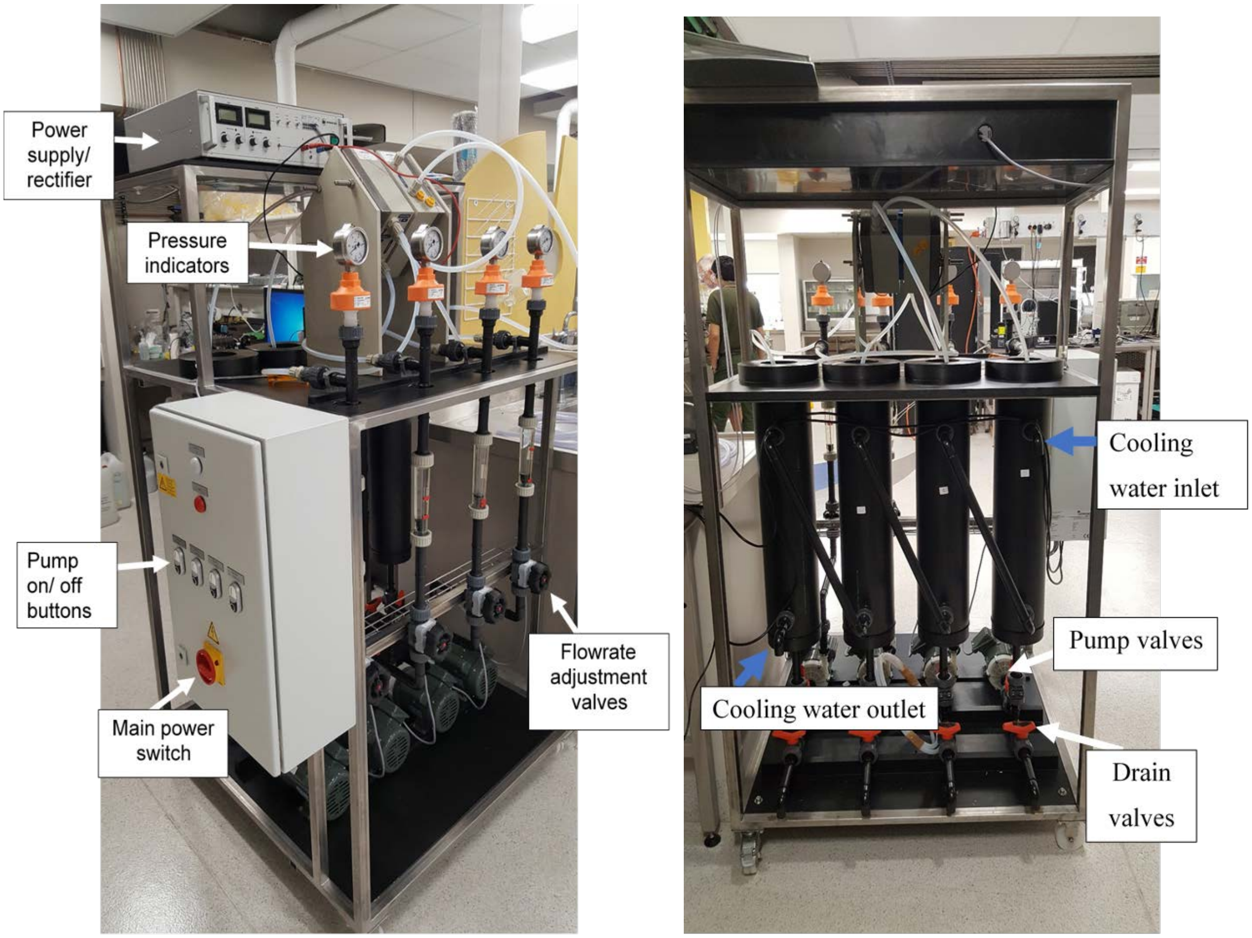


Figure 3.4. Pilot scale electrodialysis unit.

3.4.2.2. *Pressure Driven Membrane Unit*

The UF and NF pilot plant, model R, was purchased from GEA, Australia. The pilot plant can operate up to 40 bar feed pressure with a total membrane area of 14 m^2. **Figure 3.5** shows the pilot plant general arrangement. The unit was equipped with a 60 L balance tank and the feed was pumped using a Hydra cell pump type DG10 (Wanner Engineering, Australia). A centrifugal pump (type WHP +30/80, SPX Flow Technology, Poland) was used to achieve the required recirculation flowrate.

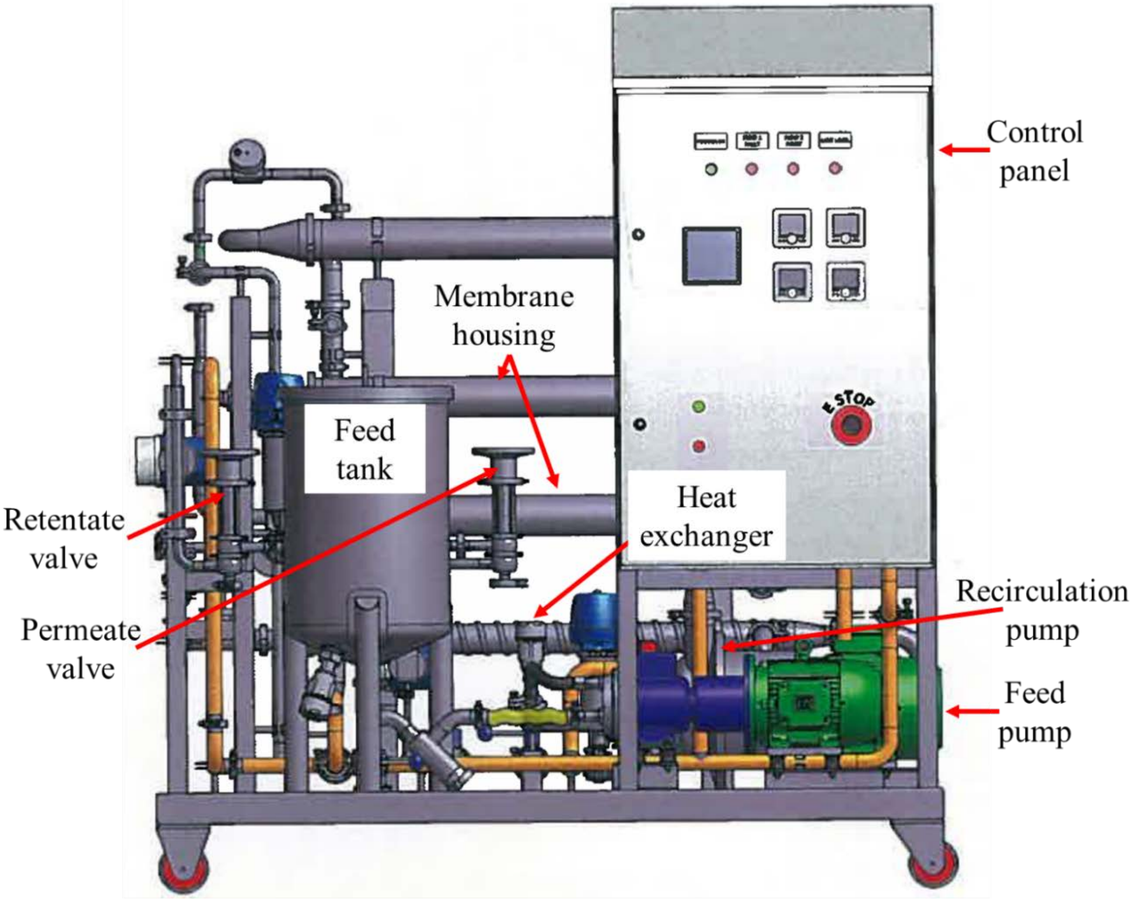


Figure 3.5. Membrane filtration pilot plant model R (adapted from GEA operating manual).

3.5. Sample Analysis

3.5.1. Inductively Coupled Plasma Optical Emission Spectroscopy

Inductively coupled plasma optical emission spectroscopy (ICP-OES 720ES, Varian, USA) was used to measure the concentration of calcium (Ca), sodium (Na), magnesium (Mg), potassium (K) and phosphorus (P) at wavelengths of 317.933, 568.821, 279.800, 766.491, and 213.618 nm, respectively. The samples were diluted to appropriate dilution levels and whey samples were filtered to ensure the removal of proteins. The calibration curves were generated in the range of 0-50 mg/L for Ca, 0-20 mg/L for K, 0-40 mg/L for Mg, 0-100 mg/L for Na, and 0-70 mg/L for P. The analysis was performed in axial view using a robust 40 MHz plasma system. Argon gas was utilized to purge the system with plasma and auxiliary flowrates of 15 and 1.5 L/min, respectively. The ion concentrations were used to calculate the percentage ion removal in an individual process according to **Eq. 3.1**.

$$Ion\ removal(\%) = \frac{C_{j,initial} - C_{j,final}}{C_{j,initial}} \times 100 = \left(1 - \frac{C_{j,final}}{C_{j,initial}}\right) \times 100 \qquad \textbf{Eq. 3.1}$$

where, C_j is the concentration of ion j (mg/L).

When combining NF/ Dia-NF (Step 1) and ED (Step 2), the overall ion removal with respect to the initial feed was calculated using **Eq. 3.2**

$$Ion\ removal(\%) = \frac{\left(C_{j,initial} \cdot v_{initial} - C_{j,step\ 1} \cdot v_{Step\ 1\ end}\right) + \left(C_{j,step\ 1} - C_{j,step\ 2}\right) \cdot v_{Step\ 2\ end}}{C_{j,initial} \cdot v_{initial}}\ x\ 100 \qquad \textbf{Eq. 3.2}$$

where, v is the volume (L).

3.5.2. High-Performance Liquid Chromatography

High-performance liquid chromatography (HPLC, Shimadzu, Japan) was used to measure lactate and lactose concentrations. The HPLC unit was fitted with an Aminex HPX-87H ion exclusion column (Particle size 9 µm, BIO-RAD) operated using a mobile phase of 0.009N sulfuric acid at 0.6 mL/min and 60°C. A UV-Vis detector (Wavelength of 220 and 285 nm, Shimadzu, SDP-20A) was used to detect lactate ions, while Refractive Index Detector (RID-10A, Shimadzu) was used to detect lactose. The calibration curve for lactate was generated in the range of 0.5-10 g/L, while for lactose a range between 8-55 g/L was selected.

3.5.3. Ion-Chromatography

Ion-chromatography (IC-Dionex, ICS-1000, Thermo Fisher Scientific Australia Pty. Ltd., Australia) was used to measure the concentration of chloride (Cl). A Dionex IONPAC AS-14 (Thermo Fisher Scientific Australia Pty. Ltd., Australia) column was utilized with a retention time of 15 min at an applied constant suppressor current of 35 mA. The mobile phase was made of 8 mM of sodium carbonate and 1mM of sodium bicarbonate. The mobile phase was pumped through the unit at 1 mL/min and room temperature (25°C). The calibration curve for Cl was constructed in the range between 7.5 and 121 mg/L.

3.5.4. Membrane Characterization

3.5.4.1. *Fourier Transform Infrared Spectroscopy*

Fourier Transform Infrared Spectroscopy (FT-IR, PerkinElmer Spectrum 100, North America) was used to detect any alteration to the chemical structure and the surface groups found in the used IEMs. Eight scans for wavelength between 800-2000 nm were completed per sample.

3.5.4.2. *Thickness Measurements*

The thickness of the IEMs was measured using a Digimatic Micrometer (Mitutoyo, Japan). The membranes were first padded dry using Kimwipe tissues (Kimtech, Australia). Multiple measurements were taken at different locations and the average value is presented.

3.5.4.3. *Scanning Electron Microscope*

Membrane surface images were captured using a Scanning Electron Microscope (SEM, FEI Quanta 200 ESEM FEG, Thermo Fisher Scientific, USA) operated at an accelerating voltage of 10 kV. The membrane samples were dried and sputtered with a thin layer of gold using a Dynavac Mini Sputter Coater (Dynavac, USA).

3.5.4.4. *Contact Angle Measurements*

The contact angle for the loose RO membranes were measured using First Ten Angstroms 200 (FTA200, USA). An image was captured using a digital recorder (Sanyo Electric VCB-3512) and analysed using instrument software.

3.6. Experimental Procedures

3.6.1. Fouling Experiments Reported in Chapter 4.

The fouling study was done using both acid and sweet whey as their different characteristics resulted in different types and extent of membrane fouling. The study aimed at examining the in-situ cleaning of the IEMs. The ED unit was only dissembled after base cleaning was performed. Therefore, membrane performance was determined by circulating a solution of 5.5 g/L NaCl with a pH of 5.5 ± 0.5 through both the diluate and concentrate compartments in a batch mode from a single 20 L tank. This step was carried out for 30 min under a content voltage of 7 V until the current passing through the unit was stable. A single experiment was divided into 5 main steps:

1. Initial membrane performance as described above;
2. Membrane fouling using either acid or sweet whey for 300 min;
3. Membrane performance after fouling as described above;
4. Membrane cleaning using HCl (pH 1.0 ± 0.15) for 30 min, followed by a 10 min rinse using 5.5 g/L NaCl solution, then membrane performance evaluation as described above;
5. Membrane cleaning using 3% NaCl (pH 9.2 ± 0.2) for 30 min, followed by a 10 min rinse using 5.5 g/L NaCl solution, then membrane performance evaluation as described above.

Step 2 was carried out in both constant voltage mode (7 V) and constant current mode (166 A/m^2, 305 A/m^2 or 444 A/m^2) in separate experiments. In-situ cleaning was carried out by passing the cleaning solution once through the unit to prevent solution contamination. The flowrates were increased from 500 mL/min to 750 mL/min during the cleaning and rinsing steps. Although the membranes were cleaned in-situ after each trial, the membranes were also cleaned ex-situ before re-use. This was done by soaking in an HCl solution (pH 1.0 ± 0.15) for two days, followed by 3% NaCl at pH values of 9.2 ± 0.2 and 5.5 ± 0.5 for two days each.

3.6.2. Salty Whey Permeate Experiments Reported in Chapter 5

The salty whey permeate experiments were divided into two sections. The first set of experiments aimed at investigating the possibility of using salty whey permeate as the concentrate stream in electrodialysis for the demineralization of sweet whey. These experiments were carried out in a constant voltage mode (7 V), using sweet whey as diluate and salty whey permeate or 0.1M NaCl as the concentrate stream.

In the second set of experiments, salty whey permeate was used as the diluate solution and salty whey permeate or 0.1M NaCl as the concentrate stream in an electrodialysis process. The experiments were carried out for 8 hrs at room temperature either in a constant current mode (55 mA/cm^2) or a constant voltage mode (5 V, 10 V, and 15 V). The starting volume ratio between the concentrate and diluate tanks was 1:4.

3.6.3. Pilot Scale Experiments Reported in Chapter 6

The UF and NF experiments were performed at room temperature. The permeate was removed continuously, while the retentate was redirected back to the feed tank. The feed pressure was maintained at 6 bar for UF, while the pressure was increased to 20 bar for NF. The total recirculation flowrate was set at 15,000 L/hr to ensure steady performance of the centrifugal pump. The raw acid whey was initially processed to a concentration factor of 4-5 using UF membranes to generate a protein rich stream as retentate and a lactose stream as permeate. The UF permeate was further processed through the NF membranes to produce a lactose rich stream (14-16% TS) as retentate. The UF permeate stream was also diafiltrated using the NF membranes with a diafiltration factor of 1 (for every 100 L of UF permeate, 100 L of water was used). The diafiltration water was added once the UF permeate was processed through NF to 15% total solids. Due to the limited capacity of the feed tank, the diafiltration water was added gradually to avoid overflow. During the diafiltration process, the permeate stream was removed continuously while the retentate stream was recycled back to the feed tank. The process was terminated when the total solid of the retentate reached 15%.

The ED experiments were conducted at 35 ± 4°C at a constant voltage mode of operation with the voltage set at 24 V. 5 L of three different streams were processed through the ED unit in a batch mode: (1) UF permeate; (2) NF retentate; (3) Dia-NF retentate. The demineralization process was terminated when the final diluate conductivity was 0.7 mS/cm for UF permeate and 2.6 mS/cm for the NF and Dia-NF retentate. It is important to note that the NF and Dia-NF retentate were at least 3.5 times more concentrated than the UF permeate, therefore the selected final conductivity of these solutions was 3.5 times higher than the UF permeate. The flowrates of the diluate, concentrate and electrolyte solutions were set at 200 L/hr during the demineralization experiments and 300 L/hr during cleaning.

3.6.4. Lactic Acid Recovery Experiments Reported in Chapter 7

This chapter aimed at recovering lactic acid from the waste streams generated from the acid whey treatment process (i.e. NF permeate and ED concentrate). As a result, lab made solutions with different lactic acid and KCl mass ratio were prepared. KCl was selected as the main salt due to the higher concentration of K in acid whey when compared to Na.

To investigate the separation of lactic acid and salt solutions, two membrane processes were evaluated, namely RO using low energy membranes and ED. The RO experiments aimed at collecting lactic acid in the permeate stream while retaining the salts. Before conducting the experiments, the membranes were soaked in water to allow membrane hydration. Once the membranes were placed inside the membrane cell, the membranes were compacted under 30 bar feed pressure. The experiments were performed at 25 ± 1°C, using feed solutions with different concentration of KCl and lactic acid with or without pH adjustment. The applied pressure during the experiments was 6-30 bar. The permeate was collected over a fixed period once the system had reached steady state under the applied pressure. For each experiment, 40 L of feed solution was used to minimise fluctuations in feed conditions. Samples were taken continuously from the feed tank and analysed for lactic acid concentration, pH and conductivity to ensure uniform feed conditions throughout the run. Permeate samples were collected twice for each applied pressure to ensure data reproducibility.

The ED experiments aimed at removing the salts from the feed solution while retaining lactic acid in the diluate stream. One litre of solution was used for the diluate and concentrate streams. The composition of the concentrate solution was similar to the diluate solution to minimize mass transfer by diffusion between the two streams. The experiments were performed at room temperature under a constant voltage of 2.4 V. This was based on the limiting current density of the membranes which was determined using Haber-Luggin capillaries in a six-compartment cell at RWTH University, with a solution of 1 g/L lactic acid. For further details on this method see Luo *et al.* [187].

3.6.5. Membrane Capacitive Deionization Experiments Reported in Chapter 8

The activated carbon electrodes were prepared by firstly weighing and dissolving approximately 0.170 ± 0.01 grams of PVDF in 30 mL of DMF at 100°C. After that, activated carbon powder was weighed and added gradually. The mass ratio of PVDF to AC was 1:10. The carbon slurry was stirred for 1 hr, the top of the beaker was covered to prevent the escape of DMF. Once the slurry was well mixed, the cover was removed and DMF was evaporated at 150°C. The dense carbon slurry was casted on the current collector (i.e. titanium plate). To cast two electrodes, two beakers of the above was prepared. The coated electrodes were dried in a fan-forced oven at 110°C overnight and then in a vacuum oven at 80°C for 2 hr to ensure that the organic solvent has been fully removed.

The MCDI experiments were carried out at 30 ± 4°C using 100 mL of three different feed solutions: (1) UF permeate; (2) NF retentate; (3) Dia-NF retentate. The experiments were divided into two main parts, namely the unit stabilization cycles and the acid whey treatment cycles. Each set of experiment was performed over 2 days, with 9 cycles in the first day (4 cycles of system stabilization + 5 cycles of acid whey treatment) and 12 cycles in the second day (4 cycles of system stabilization + 7 cycles of acid whey treatment).

The stabilization cycles were performed to reduce the effect of storing the membranes and the electrodes in a concentrated NaCl solution. At the start of each experiment, the unit was rinsed with water for 30 min followed by a desorption cycle using purified water at -1.2 V and flowrate of 30 mL/min. This was followed by 4 adsorption and desorption cycles.

For the acid whey treatment cycles, the adsorption step was performed in a batch mode where the feed was recycled back to the feed tank. The adsorption step was carried out under a constant voltage of 1.2 V and a flowrate of 20 mL/min for 5 min. The feed solution was weighed at the start of each adsorption cycle to account for the volume lost at the end of the pervious adsorption cycle. The desorption step was performed using purified water as the feed solution. The mode of operation during desorption was changed to single-pass mode. The voltage was maintained at -1.2 V and the flowrate was increased to 30 mL/min to allow fast removal of ions from the system and to promote fouling removal from the membrane surface. The desorption step was terminated when the conductivity of the effluent was less than 30 µS/cm. The tubing and the unit were purged with air for 10 min after the desorption cycle. This was followed by passing a fresh feed solution through the unit to remove any residual water from the system before the next adsorption cycle. The fresh feed solution used for this removal step was different from the feed solution processed during the adsorption steps.

At the end of each experiment, the system was rinsed using purified water, followed by a 20 min rinse using HCl solution (pH of 1.0 ± 0.15), 10 min water rinse, and 3% NaCl solution (pH of 9.15 ± 0.15). The cleaning sequence was finished with a water rinse and recirculation of 3% NaCl solution (pH of 5.5 ± 0.5).

3.7. Performance Metrics

Below is a summary of the parameters used to evaluate the success of the experiments.

3.7.1. Electrodialysis Performance Evaluation

The conductivity of the diluate stream was continuously measured to allow the calculation of the demineralization rate, also known as percentage removal in conductivity, as per **Eq. 2.4**. The total system resistance was calculated using Ohm's law (**Eq. 2.5**) from the voltage and current values obtained directly from the indicator on the power supply. System resistance directly affects the total energy consumed by the unit. The higher the system resistance, the greater the energy required to achieve the targeted demineralization rate. The energy consumed during constant voltage electrodialysis can be calculated according to **Eq. 3.3**.

$$E\left({}^{kWh}/_{tonne\ of\ feed}\right) = \frac{V_{cell}\int I dt}{m_{diluate}} \qquad \textbf{Eq. 3.3}$$

where, V_{cell} is the voltage (V), I is the current (A), t is the time (s), and $m_{diluate}$ is the mass of the diluate stream.

The energy consumption in **CHAPTER 5** was calculated per kg of NaCl removed from the diluate compartment as per equation **Eq. 3.4**.

$$E\left({}^{kWh}/_{kg\ of\ NaCl\ removed}\right) = \frac{V_{cell}\int I dt}{\left(v_{D,initial} \times C_{Na,initial} - v_{D,final} \times C_{Na,final}\right) \times \left({}^{MW_{NaCl}}/_{MW_{Na}}\right)} \qquad \textbf{Eq. 3.4}$$

where, the subscript *D* refers to the diluate stream.

The current efficiency is another parameter used to evaluate the performance of an ED unit. The current efficiency refers to the ratio between the number of ions transferred and the total number of charge applied to the unit (**Eq. 3.5**) [13].

$$\eta(\%) = \frac{F \times v_D\left(\sum z_j \times C_{Dj,initial} - \sum z_j \times C_{Dj,final}\right)}{n\int I dt} \times 100 \qquad \textbf{Eq. 3.5}$$

where, z_j is the valence of ion j, n is the number of cell pairs, F is the Faraday constant (96,486 C/mol).

The current efficiency is used to assess process efficiency under the selected operating conditions. Although values of less than 100% would be expected, several researchers have reported values greater than 100% for ED process used for different applications [10, 188]. Such an observation was attributed to either molecular diffusion or conductive transport through the membranes.

3.7.2. Membrane Capacitive Deionization Performance Evaluation

The charge consumption (σ) during either adsorption or desorption steps for constant voltage operation is calculated by integrating the electrical current over the applied time period (**Eq. 3.6**).

$$\sigma\ (A.s) = \int_{0}^{t_{ads/des}} I dt \qquad \textbf{Eq. 3.6}$$

The energy consumption during adsorption and desorption steps for constant voltage operation is calculated using **Eq. 3.7**. The total energy is the sum of energy required during the adsorption and desorption steps as per **Eq. 3.8**. However, Several researchers have shown that energy can be recovered during the desorption step, for example, Chen *et al.* [131] reported a recovery ratio of 30% for an MCDI system operated at 1.2 V during the adsorption step and at a constant current of 0.1 A during the desorption step. Therefore, the total energy was also estimated as per **Eq. 3.9** considering the possibility of recovering energy during the desorption step.

$$E_{ads/des}\ (kWh/kg\ of\ feed) = \frac{V_{cell} \int_{0}^{t_{ads/des}} I dt}{m_{feed}} \qquad \textbf{Eq. 3.7}$$

$$E_{Total}\ \left({}^{kWh}/_{kg\ of\ feed}\right) = E_{ads} + E_{des} \qquad \textbf{Eq. 3.8}$$

$$E_{Total\ with\ recovery}\ \left({}^{kWh}/_{kg\ of\ feed}\right) = 0.7E_{ads} \qquad \textbf{Eq. 3.9}$$

3.7.3. Pressure Driven Membrane Performance Evaluation

3.7.3.1. *Ultrafiltration and Nanofiltration*

The energy consumption of the pilot plant UN and NF were calculated as per **Eq. 3.10**

$$E\left({}^{kWh}/_{tonne\ of\ feed}\right) = \frac{P_e \times t}{m_{feed}}$$ **Eq. 3.10**

where P_e is the electric power determined using pump curves (kW).

3.7.3.2. *Reverse Osmosis*

The water flux through the system is measured experimentally as a function of pressure. The flux through RO membranes is usually defined as per **Eq. 3.11**.

$$J_v(LMH) = L_p\ (\Delta P - \Delta\pi_m)$$ **Eq. 3.11**

where, L_p is the permeability constant, ΔP is the applied pressure (kPa), and $\Delta\pi_m$ is the osmotic pressure (kPa).

The solute rejection (R_j) refers to the percentage of compounds that do not pass through the membrane and is calculated based on equation **Eq. 3.12**.

$$R_j(\%) = 1 - \frac{C_{j,P}}{C_{j,F}} \times 100$$ **Eq. 3.12**

where, $C_{j,P}$ and $C_{j,F}$ refer to the concentration of ion j in the permeate and feed, respectively.

CHAPTER 4. Fouling and In-Situ Cleaning of Ion-Exchange Membranes During the Electrodialysis of Fresh Acid and Sweet Whey

The use of electrodialysis (ED) for acid whey (AW) treatment is limited due to the pre-conceived ideas of the difficulties associated with the treatment of AW, while sweet whey (SW) has been widely researched and promoted as a less challenging solution to process. Therefore, it is important to compare the processing of these two solutions using ED considering operating parameters such as the applied current density and the concentrate solution pH and conductivity.

4.1. Introduction

Sweet whey (SW) is readily processed within dairy operations through membrane concentration, evaporation and spray drying. However, the processing of acid whey (AW) is much more difficult due to the high mineral content and the presence of lactic acid (LA) [5, 6]. Acid whey is lower in pH than sweet whey, and it contains greater amounts of calcium phosphate due to its greater solubility at low pH conditions [105]. Furthermore, the low pH promotes protein precipitation [189], which reduces the protein content to almost half of the amount found in sweet whey. In a recent publication by Chen *et al.* [13], we proposed that acid whey processing could be enhanced by partial removal of minerals and lactic acid using electrodialysis (ED) equipped with ion-exchange membranes (IEMs).

Dairy products such as acid whey contain colloidal matter and inorganic compounds, including calcium, carbonate, phosphate, and protein [50], which can deposit either on the surface or inside a membrane, resulting in membrane fouling [134]. In ED, fouling can compromise the membrane integrity, cause a reduction in ion migration and result in an increase in energy consumption [135, 136]. Several factors affect or promote membrane fouling in an ED unit including the mineral content of the feed solution [133, 136, 141], the mode of operation (batch or continuous) [94, 133, 134], and the concentrate pH [81, 133, 139, 141].

Protein fouling is expected to dominate on the diluate side of anion exchange membranes (AEMs) in dairy applications [133]. The main whey proteins, β-lactoglobulin and α-lactalbumin, are negatively charged above their isoelectric points (pH 5.2 and 4.8, respectively) and so deposit on the positively charged surface of the AEM membrane. Mineral fouling is also possible on the side of the AEM facing the concentrate compartment as phosphates migrate into this channel [94, 133]. For similar reasons, mineral scales, consisting mainly of calcium salts, have been observed on cation exchange membranes (CEMs) facing the concentrate compartment, particularly under alkaline concentrate pH [136, 137]. However, the presence of proteins in the feed stream can also result in CEM fouling facing the diluate compartment, when the concentrate is maintained at acidic pH [81]. Leakage of H^+ ions from the concentrate compartment through the CEM reduces the pH on the diluate side of the CEM membrane surface, thus decreasing protein solubility and promoting its precipitation [84, 138, 139].

The literature lacks consensus on the type and sequence of acid and base agents used for cleaning these IEMs after fouling [44, 135, 147, 149, 156, 157]. However, the American Water Works Association (AWWA) claims that a 2-5% HCl solution for acid cleaning, a 3-5% NaCl solution adjusted to a pH of 8-10 using NaOH for alkali cleaning, and a 10-50 mg/L chlorine solution are the only chemicals that should be used [153].

In this work, the extent of membrane fouling is studied during the electrodialysis of fresh acid and sweet whey obtained from a dairy plant in Victoria, Australia. It has been demonstrated in comparable work with nanofiltration that this approach gives significantly different results than the use of re-solubilised powders as commonly used in the scientific literature [183]. Furthermore, the effectiveness of the cleaning agents suggested by AWWA during *in-situ* cleaning of the fouled membranes is examined. Finally, since the ED unit is not dissembled after each cleaning step, a new method is proposed to monitor membrane performance. In this method, the current in a pure NaCl solution is recorded after each step. This is similar to the approach used to assess the performance of pressure-driven membranes using a clean water flux.

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4.2. Methods and Materials

4.2.1. Materials

Raw acid whey and skimmed sweet whey samples were obtained from Bega Cheese Pty. Ltd. (Victoria, Australia). The acid whey samples were skimmed in the laboratory using a centrifuge separator (Milky cream separator; Model FJ 130 ERR; MilkyDay, Czech Republic) to remove fat and whey cream. All the whey samples were refrigerated at 4 ± 1 °C and used within two weeks. The sample compositions (**Table 4.1**) were consistent with the values reported by Chen *et al.* [13].

Table 4.1. The composition of skimmed sweet and acid whey used in this work.

Component	Unit	Sweet whey	Acid whey
pH	-	6.1 ± 0.2	4.4 ± 0.3
Conductivity	mS/cm	6.1 ± 0.3	7.8 ± 0.3
Total protein*	% (m/v)	0.85 ± 0.05	0.36 ± 0.01
K	mg/100mL	114 ± 7	125 ± 8
Na	mg/100mL	38 ± 4	47 ± 4
Ca	mg/100 mL	34 ± 8	121 ± 8
Mg	mg/100 mL	8.3 ± 0.6	13 ± 1
P	mg/100 mL	43 ± 4	71 ± 2
LA	mg/100 mL	86 ± 2	570 ± 3

* Total protein = Total nitrogen × 6.38

Purified water (>8.6 MΩ cm; Merck Millipore KGaA, Germany) was used to prepare solutions of 20 g/L sodium sulphate (Na_2SO_4; >99%; Thermo Fisher Scientific Australia Pty., Ltd., Australia) and 5.5 g/L sodium chloride (NaCl; >99.5%; Merck KGaA, Germany) as the electrolyte and the concentrate solutions, respectively. The pH adjustment of the concentrate was performed using appropriate amounts of 5M hydrochloric acid (36% HCl; Thermo Fisher Scientific Australia Pty., Ltd., Australia) and 5M sodium hydroxide (NaOH; chem-supply Pvt., Ltd., Australia), while the conductivity was adjusted using high purity water (18.2 MΩ cm; Merck Millipore KGaA, Germany). Acid and base cleaning steps were performed using an HCl solution with a pH of 1.0 ± 0.15 and a solution of 3% NaCl adjusted to a pH of 9.15 ± 0.15 using NaOH, respectively. Although 2-5% HCl is recommended by AWWA, a less concentrated HCl solution was used to ensure operation was well within the pH tolerance range specified by the membrane manufacturer (0-14).

4.2.2. Electrodialysis Unit

The electrodialysis experiments were conducted using an FTED-40 module manufactured by FuMA-Tech GmbH (Germany) as described by Chen *et al.* [13]. Cation exchange membranes (Neosepta CMB) and anion exchange membranes (Neosepta AHA) were purchased from Astom Co., Ltd., Japan. These membranes are well known for their wide pH tolerance and thermal stability. Information on the membrane characteristics can be found elsewhere [13]. All membranes were pre-conditioned by soaking in 3% NaCl solution to allow for membrane hydration and expansion. After each trial the membranes were soaked in HCl (pH 1.0 ± 0.15) for two days, followed by subsequent soaking in 3% NaCl at pH values of 9.2 ± 0.2 and 5.5 ± 0.5 for two days each. This protocol ensured that the membranes were fully clean before re-use and had returned to their original ionic state.

4.2.3. Experimental Protocol

Through all the steps, the temperature was maintained at 45 ± 2°C, since dairy streams are operated either below 10°C or above 45°C to minimize microbial growth [190].

Experiments were conducted in both constant voltage and constant current modes of operation. For the constant voltage experiments, the operation was divided into five main steps as summarized in **Table 4.2**. The performance tests (Steps 1, 3, 4c and 5c) were conducted by circulating a solution of 5.5 g/L NaCl with a pH of 5.5 ± 0.5 through both diluate and concentrate channels in a batch mode from a single 20 L tank. Membrane fouling (Step 2) used sweet or acid whey circulating through the diluate channels from one 20 L tank, while 5.5 g/L NaCl at pH 5.5 ± 0.5 was circulated through the concentrate channels from a second 20 L tank. The diluate and concentrate flowrates were maintained at 500 mL/min, while the electrolyte flowrate was retained at 1000 mL/min as recommended by the manufacturer to minimize concentration polarization effects in the ED unit.

The concentrate and diluate were passed only once through the unit during cleaning and rinsing steps to prevent solution contamination. The flowrates of both the diluate and concentrate streams were increased to 750 mL/min during these two steps. It is a common practice that cleaning is performed at higher flowrates, since under such conditions, the relaxed fouling layer is more susceptible to shear stress [143].

In the constant current experiments, Step 2 was performed at a constant current (166 A/m^2, 305 A/m^2 or 444 A/m^2) and variable voltage. In this case, the diluate and concentrate flowrates were maintained at either 300 mL/min or 500 mL/min to study the relationship between shear force and electrostatic interactions.

To provide an estimate of experimental error, the constant voltage experiment for acid whey at pH 9.25 was repeated twice and these replicates used to estimate error margins. Access to further quantities of sweet and acid whey limited our ability to conduct further replicate runs.

Table 4.2. Details of the main steps for constant voltage experiments.

Step	Step length (min)	Diluate	Concentrate	Voltage (V)	Aim	Mode of operation
1	30	NaCl	NaCl	7	Initial membrane performance	Batch, single tank
2	300	Acid or sweet whey (no pH adjustment)	Concentrate (pH = 2.25, 6.25 and 9.25 ± 0.25)	7	Membrane fouling	Batch
3	30	NaCl	NaCl	7	Performance after fouling	Batch, single tank
4a	30	HCl (pH 1.0 ± 0.15)	HCl (pH 1.0 ± 0.15)	0	Acid cleaning	Continuous
4b	10	NaCl	NaCl	0	Rinse	Continuous
4c	30	NaCl	NaCl	7	Performance after acid clean	Batch, single tank
5a	30	3% NaCl (pH 9.15 ± 0.15)	3% NaCl (pH 9.15 ± 0.15)	0	Base cleaning	Continuous
5b	10	NaCl	NaCl	0	Rinse	Continuous
5c	30	NaCl	NaCl	7	Performance after base clean	Batch, single tank

4.2.4. Analysis Methods

The pH and conductivity of the concentrate tank were measured continuously during the fouling run (Step 2) using a pH (Mettler-Toledo Ltd., Switzerland) and conductivity meter (Crison, Switzerland). When the conductivity value of the concentrate tank increased by 10% of its initial value, the conductivity was adjusted by adding 1.7 ± 0.3 L of high purity water and removing an identical volume of concentrate solution. The adjustment of concentrate conductivity in this manner is a common practice used in the industry [99]. Similarly, the pH of the concentrate tank was adjusted if it deviated by more than 0.25 pH units from the target value, through addition of NaOH or HCl. The conductivity of the diluate stream was measured using a second conductivity meter (Mettler-Toledo Ltd., Switzerland), which allowed the calculation of the demineralization rate (DR) according to **Eq. 2.4** (refer to **section 2.4.2**) [191].

$$DR(\%) = \frac{x_{initial} - x_{final}}{x_{initial}} \times 100 = \left(1 - \frac{x_{final}}{x_{initial}}\right) \times 100 \qquad \textbf{Eq. 2.4}$$

The total system resistance was calculated using Ohm’s law from the voltage and current values obtained directly from the indicator on the power supply. The performance of the membranes was evaluated by averaging the last 20 min of the current data collected during Steps 1, 3, 4c and 5c. Each value was then normalized with respect to the initial current (value obtained in Step 1).

Samples were taken on an hourly basis from both the diluate tank and outlet pipe and analysed using inductively coupled plasma optical emission spectroscopy (ICP-OES 720ES, Varian, USA) to measure the concentration of calcium (Ca), sodium (Na), magnesium (Mg), potassium (K) and phosphorus (P). High-performance liquid chromatography (HPLC, Shimadzu, Japan) was used to measure lactic acid concentrations in samples collected hourly from the diluate output. The samples were filtered to remove proteins but were not diluted. Information on the operating parameters of the ICP-OES and HPLC can be found in **section 3.5**.

4.3. Results and Discussion

4.3.1. Effect of Concentrate pH and Feed Composition on Fouling Rates

The resistance in the ED unit is initially due to the membranes [93] and the solutions [94]. For the system reported in this chapter, the resistance of the concentrate, electrolyte solution, and membranes should be consistent for all experiments, thus making the diluate solution the main differentiating resistance. As shown in **Figure 4.1**, acid whey has a lower initial resistance compared to sweet whey. This is due to the higher conductivity of the former. The increase observed in the resistance with time is either due to whey demineralization and/or membrane fouling [93, 94, 134]. The extent of fouling was evaluated based upon this increase in resistance with time as well as the drop in the current while using pure 5.5 g/L NaCl solution in both the compartments after Step 2 (see **Figure 4.2**).

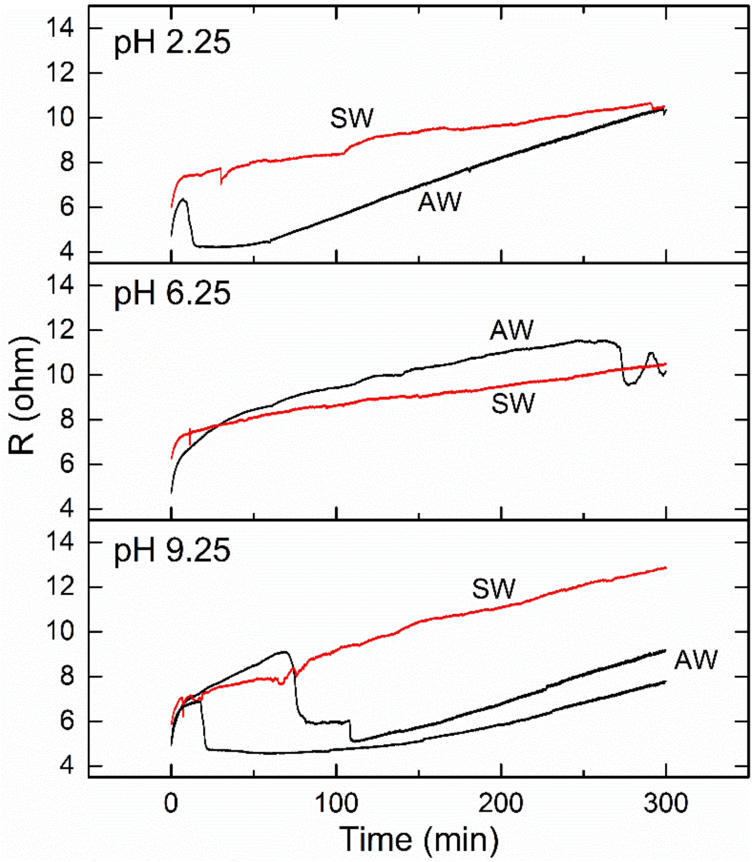

Figure 4.1. Changes in the resistance of ED unit as a function of time during whey demineralization (Step 2, refer to **Table 4.2**). The pH value refers to the pH of the concentrate solution. AW and SW are acid and sweet whey, respectively. Replicate experiments were conducted for acid whey at concentrate pH of 9.25.

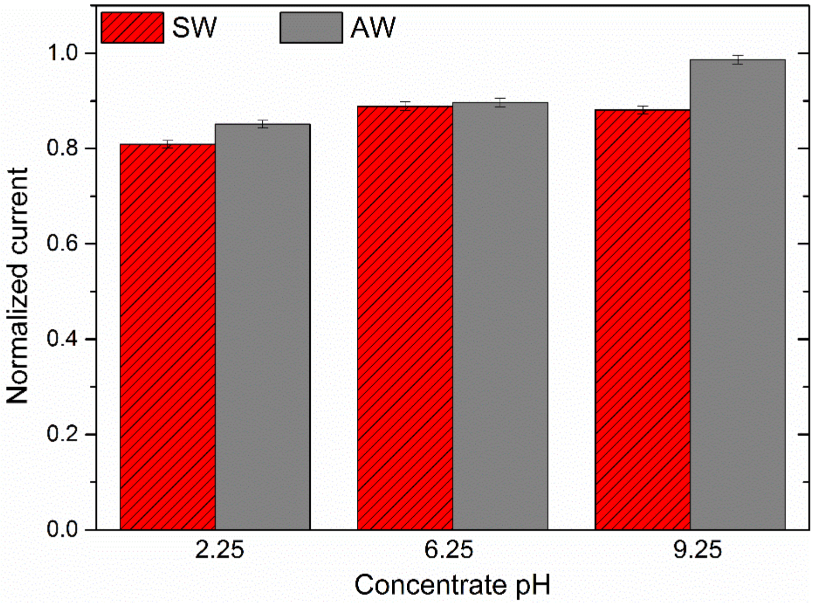

Figure 4.2. The current observed in an NaCl solution after membrane fouling (Step 3, refer to **Table 4.2**), normalized to the initial value (Step1). AW and SW are acid and sweet whey, respectively.

In all experiments, the extent of fouling is relatively low, with the current remaining above 80% of the initial value after 5 hours of fouling (**Figure 4.2**). When an acidic concentrate was used, protein fouling was expected [84, 138, 139]. Indeed, protein deposits were observed on the AEM membranes facing the diluate compartment after disassembling the ED unit at the end of Step 5. However, the extent of protein fouling for both acid and sweet whey is relatively small, as the rate of increase in resistance is lower than at other pH values (**Figure 4.1**). A greater difference in both the normalized current and the system resistance was expected for sweet whey compared to acid whey, since the protein content in sweet whey is almost double the amount in acid whey. However, the greater proportions of calcium in acid whey also appeared to promote protein precipitation, as there is only a small difference in current drop (**Figure 4.2**), as well as in the final system resistance (**Figure 4.1**) or demineralization rate (**Figure 4.3**). Casademont *et al.* [94] observed a greater demineralization rate when using acidic concentrate rather than that at higher pH values, but within experimental error this trend is not observed here (**Figure 4.3**).

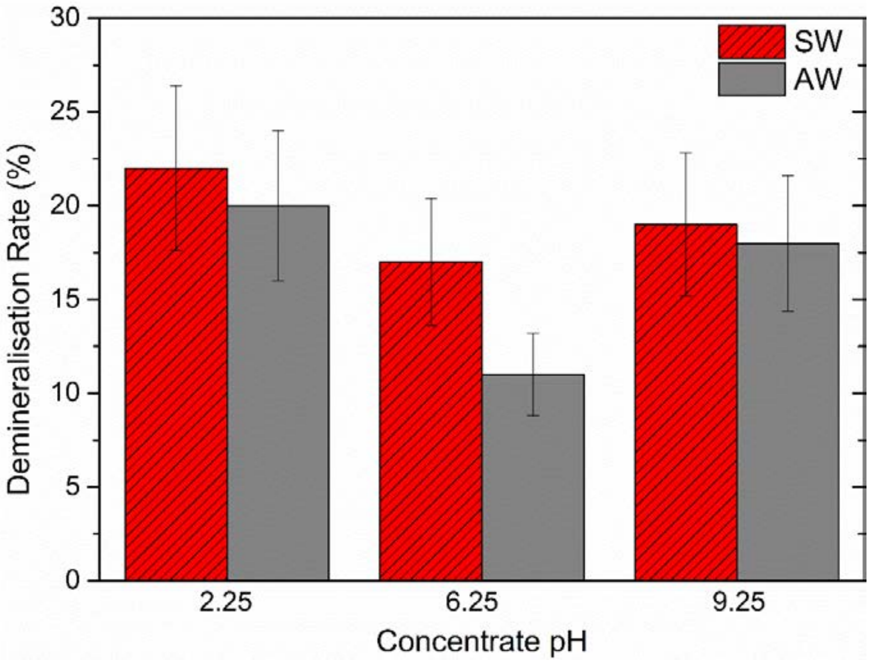

Figure 4.3. Overall demineralization rate (DR) calculated using **Eq. 2.4**. AW and SW are acid and sweet whey, respectively.

When the concentrate pH was maintained at 6.25 ± 0.25, only small overall levels of fouling were observed, with the current in pure NaCl remaining at around 90% of its original value for both acid and sweet whey (**Figure 4.2**). Under such pH conditions, both mineral and protein fouling were expected to take place as reported by the literature [81]. The increase in resistance as a function of time was much greater for acid whey (**Figure 4.1**), which might be related to a greater extent of mineral fouling due to the higher concentrations of calcium and phosphate in these samples. This is also suggested by the lower overall demineralization rate for acid whey determined from diluate conductivity measurements (**Figure 4.3**). In the last 50 minutes of the run, fluctuations in the resistance are observed for acid whey (**Figure 4.1**). Such fluctuations might arise from the displacement or partial removal of the fouling layer as the electrostatic interaction between the mineral fouling layer and the membranes becomes weaker than the shear force exerted by the fluid. This hypothesis is discussed further in **section 4.3.5**.

At alkaline pH and a processing temperature of 45 ± 2°C, mineral deposits of calcium salts dominated due to the reduction in solubility. For the sweet whey, there was a steady increase in the system resistance. The final value was significantly higher than that for the other sweet whey experiments. The final salt concentration in the diluate was not particularly low, indicating that mineral fouling was the main source of this increased system resistance. In the initial minutes of the fouling step, the system resistance increased even faster for the acid whey, again probably reflecting greater mineral scaling. However, as observed in **Figure 4.1**, this resistance dropped dramatically at the 70-minute mark (first run) and 17-minute mark (replicate run), which was possibly due to the dislodgement of the fouling layer. The second linear increase in resistance could be due to the demineralization of the diluate stream and/or the development of a fouling layer on the surface of the membranes as discussed above. The removal of this fouling layer led to a net increase in the current flow for acid whey relative to that for the sweet whey at Step 3 (**Figure 4.2**). The overall rates of demineralization were comparable (**Figure 4.3**) for both whey types and similar to that at pH 2.25 ± 0.25, again suggesting that while fouling occurred, the overall effect on performance was not severe.

4.3.2. Ion Migration

In most experiments, the cation migration (**Figure 4.4**) reflected that reported previously in the literature, as the monovalent ions migrated faster than the divalent ions following an descending order: $K^+ > Na^+ > Ca^{2+} > Mg^{2+}$ [81, 84, 192]. The percentage of phosphorus removed over a period of 5 hours is generally greater than that of lactic acid, which differs from our prior work where these percentage removals were comparable [13].

The Na^+ and K^+ migration was generally higher for acid whey compared to sweet whey (**Figure 4.4** and **Figure 4.5**), which could be due to the high initial concentration of minerals and lower solution pH (see **Table 4.1**). Higher initial concentration results in a greater concentration difference between the diluate and concentrate streams, thus allowing ion transport through diffusion. Furthermore, the major proteins will be uncharged at the acid whey pH [99], thus enhancing cation and anion transport. On the other hand, significantly greater lactic acid removal was achieved at acidic concentrate pH (**Figure 4.4** and **Figure 4.5**) for both types of whey. This may be because lactate ions crossing from the diluate to the concentrate channel immediately combine with hydrogen ions, thus reducing the lactate concentration in this channel. In turn, this maintains a strong diffusional driving force for more lactate to cross the AEM. This is useful for acid whey treatment where the removal of lactate is known to enhance downstream processing [26]. No obvious difference was noted in the lactic acid removal at other pH conditions.

The trends in calcium and phosphate migration are difficult to explain and probably reflect a complex interplay between the speciation of calcium as well as fouling effects. The calcium in the acid whey diluate (pH 4.4 ± 0.3) will be present entirely as Ca^{2+}. Conversely, the calcium in the sweet whey diluate at pH 6.1 ± 0.2 could be present partly as a monovalent anion complex of calcium citrate and possibly as neutral colloidal calcium phosphate [54]. Upon crossing into the concentrate channel at pH 9.25 ± 0.25, more neutral calcium phosphate species will form, as well as monovalent $CaPO_4^-$. These changes in speciation can affect migration rates.

For the acid whey run at a concentrate pH of 6.25 ± 0.25, the calcium and phosphate migration appear particularly high and the corresponding Na^+ and K^+ migration appear low (**Figure 4.4** and **Figure 4.5**). These changes in ion migrations possibly also reflect mineral fouling. That is, the ion migration is determined from the loss of these species from the diluate, rather than the gain in the concentrate. As the pH on the membrane surface increases, phosphate will transition from neutral H_3PO_4 to $H_2PO_4^-$ and HPO_4^{2-}, which are less soluble ions and hence more likely to precipitate. If these calcium phosphate complexes precipitate on the membrane surface, then this loss will appear larger. Conversely, potassium and sodium migration may be reduced by the presence of this fouling, which results in an overall lower demineralization rate (**Figure 4.3**). Similar effects may have occurred at a concentrate pH of 9.25 ± 0.25 in the first minutes of the run, but the apparent release of the calcium phosphate back into the diluate tank as this dislodgement occurred may also have explained the reduced removal of the calcium ions from the acid whey, relative to the case at pH 6.5 ± 0.25.

Migration of H^+ and OH^- possibly also occurred during these experiments. As the whey solutions are naturally buffered, it is not possible to determine these migration rates from changes in the diluate pH, which remained constant during all experiments. The concentrate pH did vary but was adjusted throughout the experiment to maintain a value within 0.25 pH units of the target value. The number of times an adjustment was required gives an approximation of the pH changes that occurred (**Table 4.3**).

At the concentrate pH of 2.25 ± 0.25, uncharged lactic acid and phosphoric acid are favoured over phosphate and lactate ions. The addition of HCl for the two runs at pH 2.25 thus probably reflects the combination of H^+ ions with lactate and phosphate as they cross from the less acidic diluate. Conversely, as phosphate crosses the membranes into a concentrate at pH 9.25 ± 0.25, it will change speciation from $H_2PO_4^-$ to HPO_4^{2-} and PO_4^{3-} thus releasing H^+, leading to the need for NaOH addition.

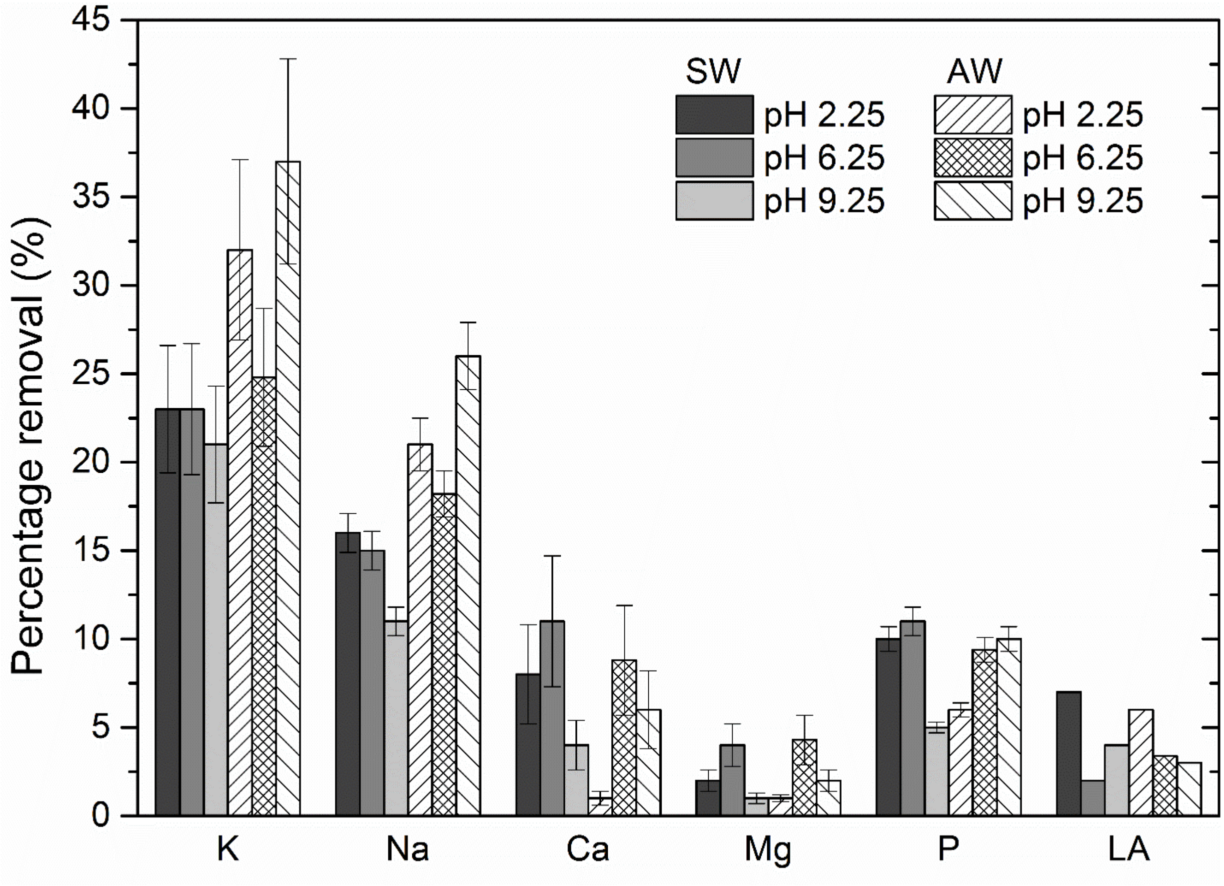

Figure 4.4. Percentage removal of the major ions as a function of whey type and concentrate pH. AW and SW are acid and sweet whey, respectively.

Table 4.3. Concentrate pH adjustment frequency during membrane fouling run (Step 2, refer to **Table 4.2**).

Whey type	Concentrate pH target range	No. of pH adjustments	
		NaOH addition	HCl addition
SW	2.25 ± 0.25	-	1
	6.25 ± 0.25	-	7
	9.25 ± 0.25	1	-
AW	2.25 ± 0.25	-	2
	6.25 ± 0.25	4	-
	9.25 ± 0.25	6, 23*	-

* This run was repeated twice, with 6 adjustments in the first trial and 23 adjustments in the second.

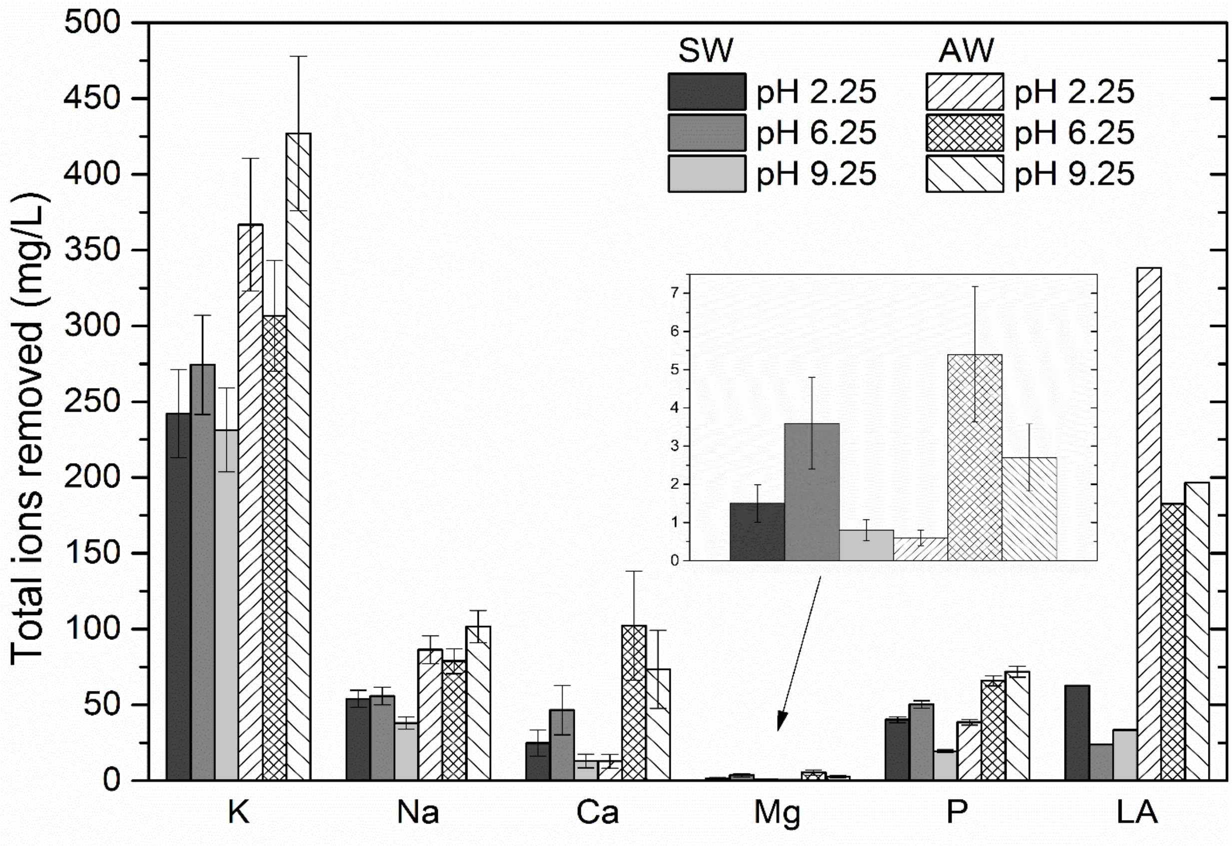

Figure 4.5. Total ions removed from the diluate over a period of 5 hours (Step 2, refer to **Table 4.2**) under the application of a constant voltage. AW and SW are acid and sweet whey, respectively.

4.3.3. Effect of Mode of Operation

The mode, in which the ED unit is operated (batch or semi-continuous), also affects the membrane fouling. Ayala-Bribiesca *et al.* [81, 133] claimed that operating the ED unit in batch mode, as often is the case in laboratory scale experiments, contributes significantly to the precipitation of calcium salts. These authors found calcium phosphate deposits on the AEMs facing the concentrate compartment, while calcium hydroxide and calcium carbonate were found on the CEM facing the concentrate compartment. The authors [81, 133] explained that during the demineralization step, Ca^{2+} ions will migrate through the CEMs from the diluate to the concentrate stream. When the concentrate is recycled back to the ED unit, the Ca^{2+} ions come into contact with phosphorus ions migrating through the AEMs from the diluate stream, resulting in the formation and precipitation of calcium phosphate under alkaline conditions [94, 133]. They argued that this phenomenon will not take place if the concentrate stream is passed only once through the unit.

However, according to Fidaleo and Moresi [99], most industrial ED units are operated in a semi-continuous mode, in which the diluate stream flows continuously, while the concentrate stream is operated in a feed and bleed mode. This means that Ca^{2+} recirculation and contact with AEM cannot be avoided. Conversely speaking, adjusting the conductivity of concentrate stream to a standard value is a common practice in industrial ED units. We believe that adjusting the concentrate conductivity during the performed experiments diluted the Ca^{2+} ion concentration, which was recycled back to the unit, and hence, reduced the potential for this effect to occur. To investigate this issue, a separate experiment was conducted with sweet whey at the pH of 9.25 ± 0.25, where the concentrate conductivity was not adjusted, and hence, increased during the fouling run (Step 2) from 10.2 to 12.5 mS/cm. Under these conditions, fouling was observed on the AEM after cleaning the unit (see supplementary material **Figure S4.1**), while no deposits were observed when the concentrate conductivity was adjusted throughout the experiment.

4.3.4. Cleaning Efficiency

For experiments where the concentrate conductivity was adjusted, no mineral deposits were observed on the members after cleaning, indicating that the acid cleaning was effective in removing the mineral deposits. Furthermore, protein deposits were only observed after cleaning for the experiment with sweet whey under acidic concentrate conditions. Whey protein precipitation is expected to be reversible, if it is sorbed on the membrane either by relatively weak dipole-dipole interactions or by hydrogen bonding. However, the sites, where electrostatic bonds have formed between the charged sites on the protein and the functional groups on the membrane [140], require chemical cleaning under high ionic strength and high pH conditions. In the present case, the use of an alkaline solution of 3% NaCl (pH of 9.2 ± 0.2) for 30 minutes was insufficient to remove the protein deposits formed when sweet whey was processed under acidic concentrate conditions. Organic fouling is usually avoided in such cases by modifying the mode of current supply to the ED unit. This is commonly achieved by using either a pulsed electrical field or electrodialysis reversal.

As noted from the results reported in **Figure 4.6**, it is difficult to assess the effectiveness of chemical cleaning by monitoring the current in a pure NaCl solution. From the acid whey replicate experiment, the recorded current values after fouling of the unit are in close proximity to each other, while the measured values after both the acid and base cleaning deviate in both experiments, and do not exhibit a clear trend.

Such behaviour is probably a result of the contact of membranes with different solutions during the five steps in each experiment. IEMs contain high concentrations of counter-ions to balance the fixed charges. The CEMs and AEMs were pre-soaked before use to ensure that these counter-ions are Na^+ and Cl^-, respectively. However, during the cleaning step, these counter-ions would be replaced with H^+ (during the acid cleaning) and OH^- (during the alkali cleaning). We aimed to return these counter ions to Na^+ and Cl^- by a 10-minute NaCl rinse prior to the current measurements. However, we believe that the high mobility of residual H^+ and OH^- ions led to the variability in the observed current after acid and base cleaning, affecting the results seen in **Figure 4.6**. A longer period of operation would be required to obtain the true current under these conditions.

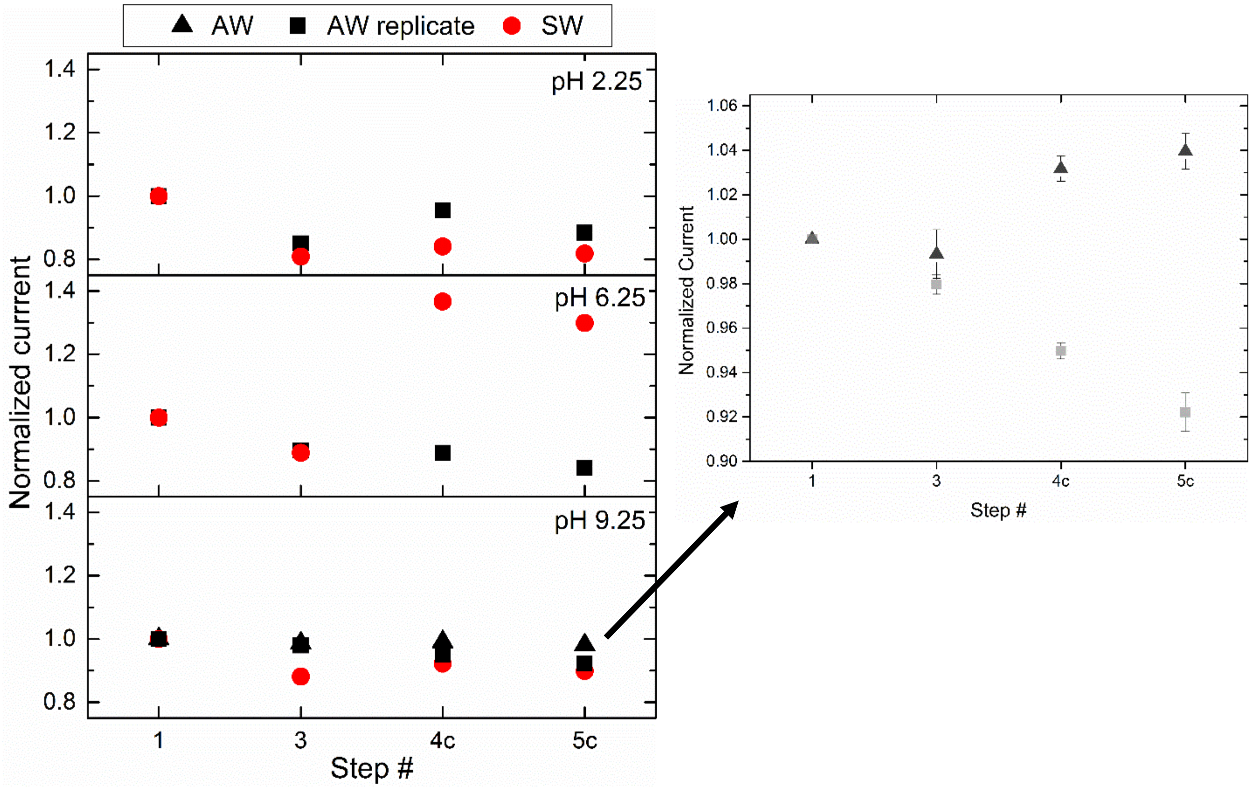

Figure 4.6. Membrane performance check using NaCl solution (Steps 1, 3, 4c and 5c, refer to **Table 4.2**). The pH value refers to the pH of the concentrate solution. AW and SW are acid and sweet whey, respectively.

4.3.5. Constant Current Mode

We believe that the fluctuations observed in the resistance during whey processing (**Figure 4.1**) are related to the shear stress exhibited by the flow and electrostatic interactions between the membrane surface and foulant. As the current falls during the demineralization process, the electrostatic interactions reduce until they are less than the shear forces exerted by the liquid flow. This allows partial or even total removal of the fouling layer from the membrane surface. This in turn reduces the contribution of membrane fouling to the total resistance of the unit. To test this hypothesis, a series of fouling runs were performed using acid whey and alkaline concentrate at constant current (166, 305, 444 A/m^2) and varying voltage. The use of constant current is more likely to be the mode of operation in an industrial environment.

As expected, a higher applied current resulted in greater demineralization and greater removal of monovalent ions (**Figure 4.7**). Although a DR close to 30% was achieved for 444 A/m^2 at a fluid flowrate of 500 mL/min, the concentrations of Ca and P removed were comparable to the amount removed at the applied current of 305 A/m^2 (DR of 20%). However, the extent of fouling observed on the membrane surface was much lower at 444 A/m^2 (see Supplementary Material, **Figure S4.2**) than at 305 A/m^2. During the fouling run at 444 A/m^2, the frequency at which the concentrate pH was adjusted using NaOH was greater than at 305 A/m^2. This suggests that more H^+ is migrating from the diluate, through both an increased migration rate and greater water splitting. When operating at this highest current density, the limiting current condition was probably exceeded, as noted by a significant increase in the system resistance in these experiments. The voltage was also observed to fluctuate in time at this highest current density, indicative of electroconvection occurring [193]. The greater H^+ concentrations at the membrane surface that arise from water splitting reduce the potential for calcium scaling due to localised lower pH values thus decreasing precipitation of calcium phosphate [154, 191]. The electroconvection can also cause the fouling layer to be disrupted. Although Ayala-Bribiesca *et al.* [81] reported that water splitting could contribute to protein and mineral fouling in the diluate compartment, this was not observed in the system under investigation.

When the applied current was limited to 166 A/m^2 at a flowrate of 500 mL/min, no scaling was observed, although a reasonable amount of Ca was removed from the diluate compartment (**Figure**

4.7). However, when the flowrates of both the diluate and concentrate streams were dropped to 300 mL/min, fouling was observed in the concentrate compartment (see Supplementary Material **Figure S4.3**). This fouling resistance was also reflected in lower migration rates for all ions (**Figure 4.7**). We believe that the increased fouling at lower flowrates reflects the reduced fluid shear stress that assists in foulant removal. The concentrate pH was adjusted 19 times for both 500 mL/min and 300 mL/min flowrates, indicating that only minimal water splitting occurred as the flowrate fell. However, the electrical resistance increased in a manner similar to that observed at 444 A/m^2 and voltage fluctuations were again observed, suggesting that water splitting was occurring to some extent.

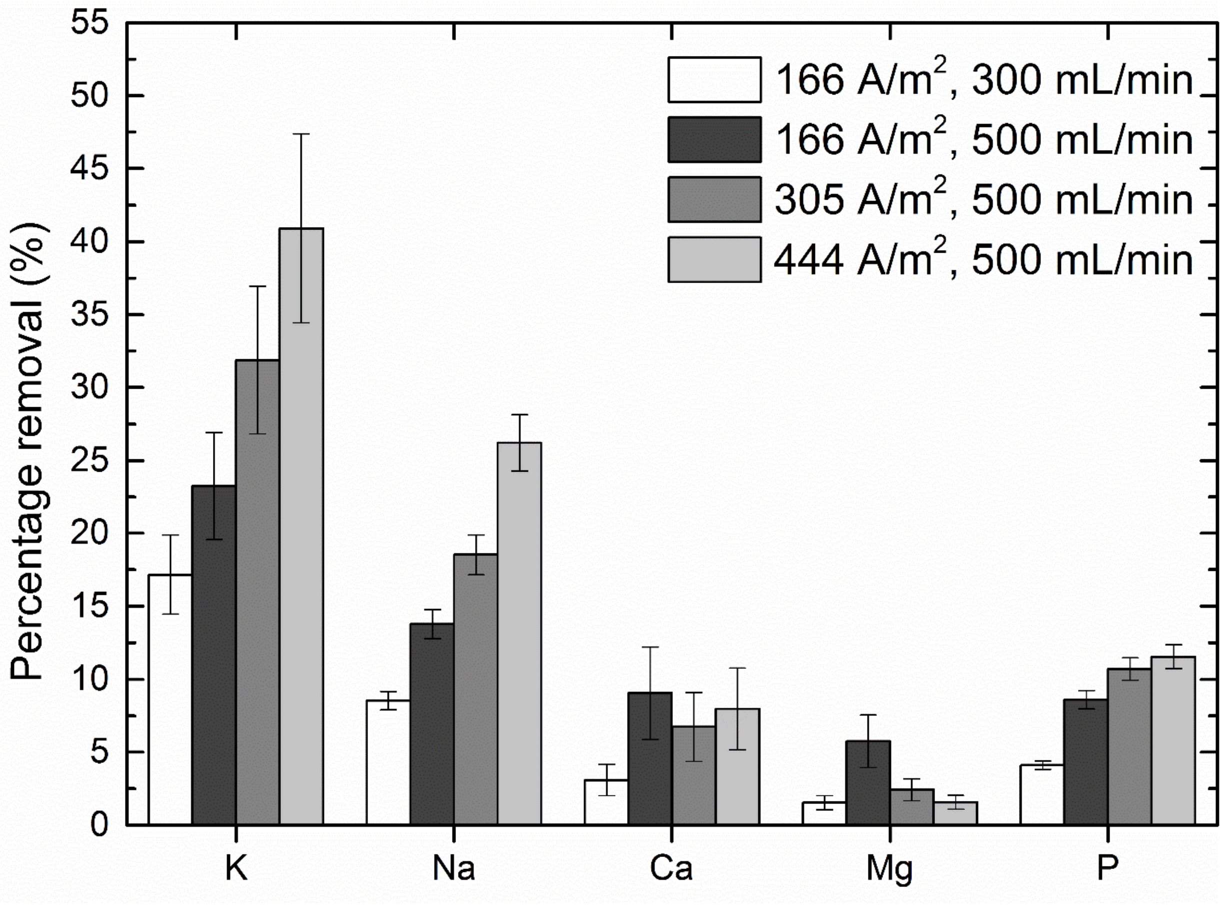

Figure 4.7. Percentage of ions removed from the diluate tank under constant current operation over a period of 5 hours (Acid whey; concentrate pH of 9.25 ± 0.25).

4.4. Conclusions

Fouling rates during electrodialysis of acid and sweet whey are generally low and comparable to each other. The current in 5.5 g/L NaCl retained over 80% of its initial value after a 5 hour fouling run under all conditions. Although, the protein content of acid whey is lower than that of sweet whey, protein precipitation in the diluate compartment was comparable for both solutions when operating with an acidic concentrate. When operating with an alkaline concentrate, greater increases in system resistance were observed with time due to mineral fouling. However, this mineral fouling was readily dislodged, leading to variability in the demineralization performance. Furthermore, the use of higher flowrates and lower current densities also proved effective in reducing mineral fouling. Maintaining a constant concentration of the concentrate stream through dilution of multivalent ions, especially calcium within the concentrate compartment, reduced the extent of mineral fouling on this side of the membranes. Cleaning with HCl solution at pH of 1.0 ± 0.15 was effective in removing mineral deposits. However, cleaning with 3% NaCl (pH of 9.2 ± 0.2) was ineffective in removing the strongly bound protein deposits that were formed when acidic concentrate was utilized.

When it comes to acid whey treatment using electrodialysis, the greatest migration rates for lactate anions were observed when an acidic concentrate was used. It is thus recommended to operate the concentrate stream at an acidic pH to avoid calcium phosphate precipitation and to achieve strong removal of lactate ions. The use of electrodialysis reversal, or a pulsed electric field, could be used in combination with this pH to reduce protein fouling that might occur under these conditions.

4.5. Acknowledgments

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4.6. Supplementary Material

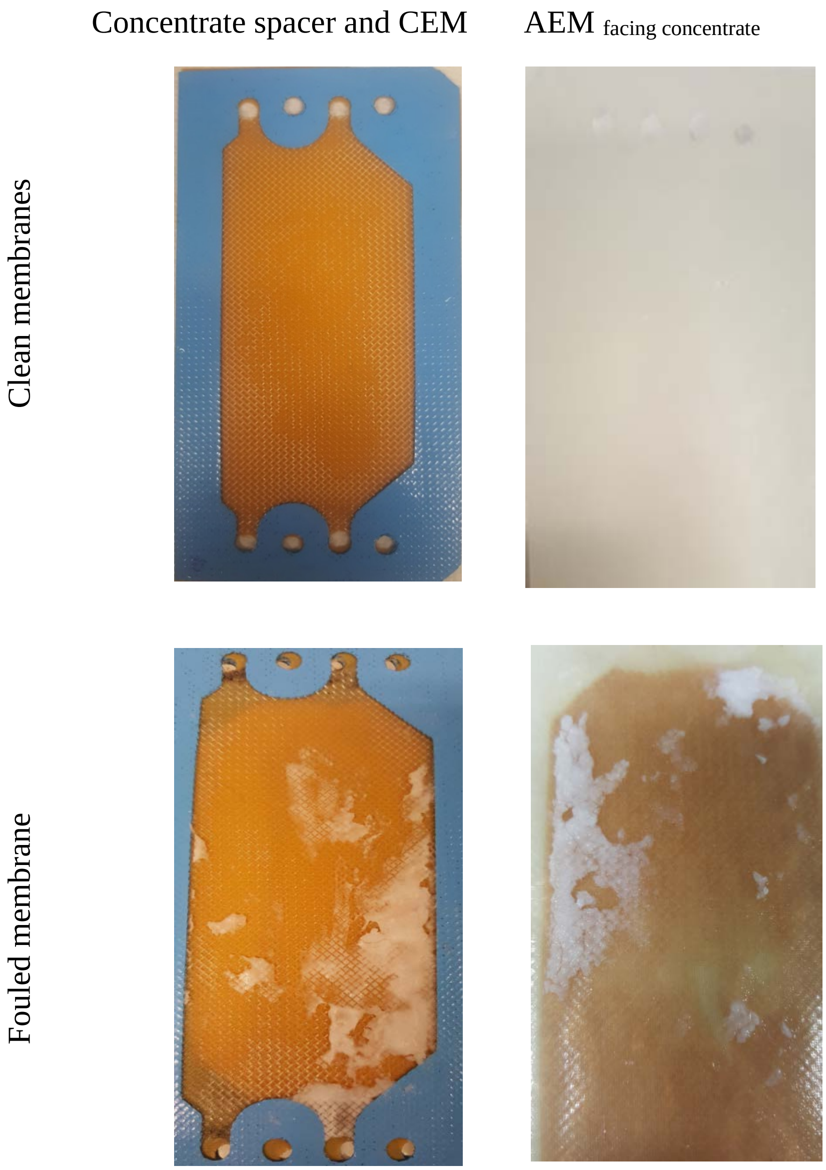

Figure S4.1. Traces of mineral fouling noted in the concentrate compartment after both acid and base cleaning. Operating conditions: sweet whey, concentrate pH of 9.25 ± 0.25, no concentrate conductivity adjustment. The clean membranes are presented for comparison.

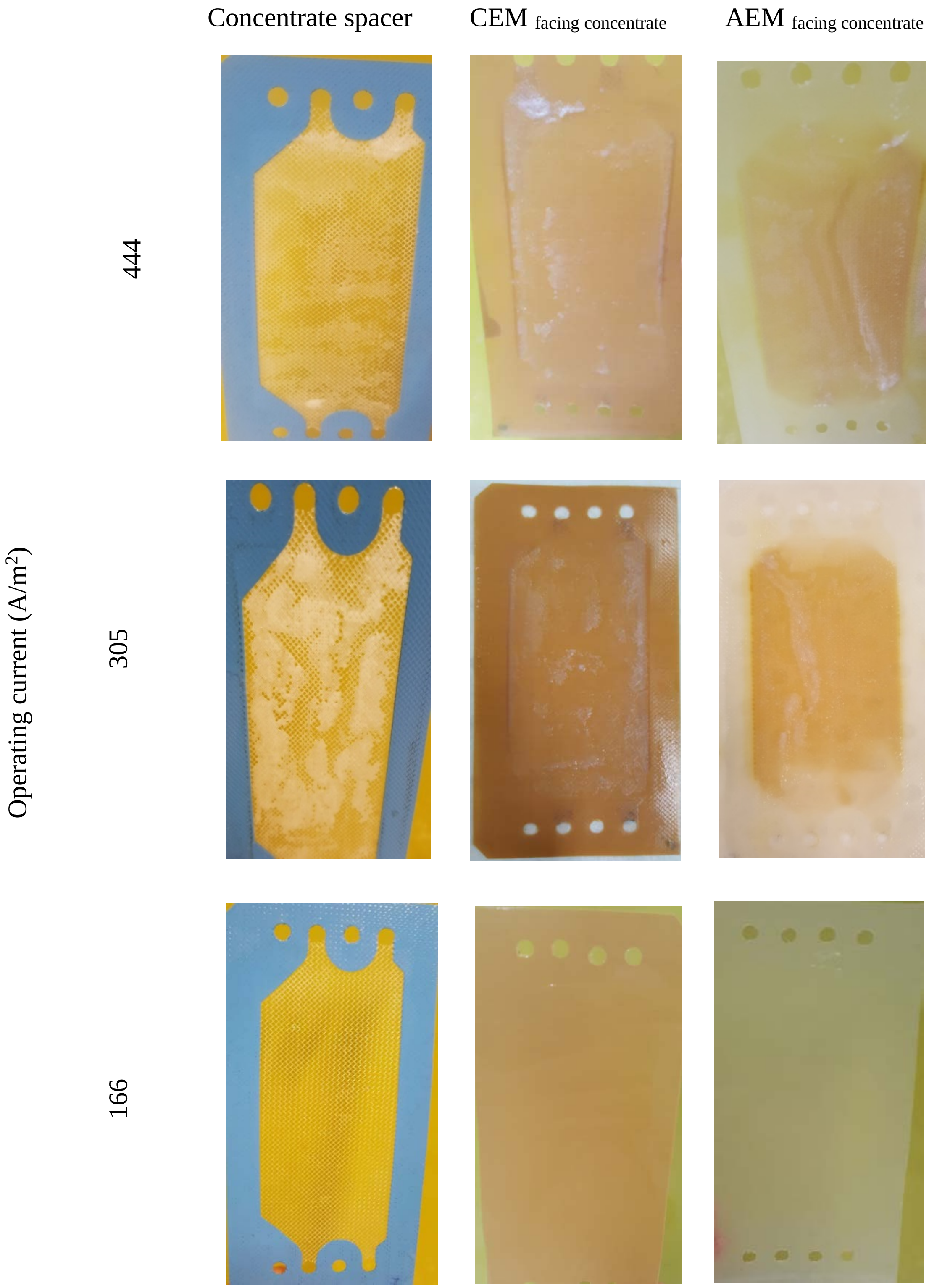

Figure S4.2. Membrane images after 300 min demineralization under constant current mode (Acid whey; concentrate pH of 9.25 ± 0.25, flow rate of 500 mL/min).

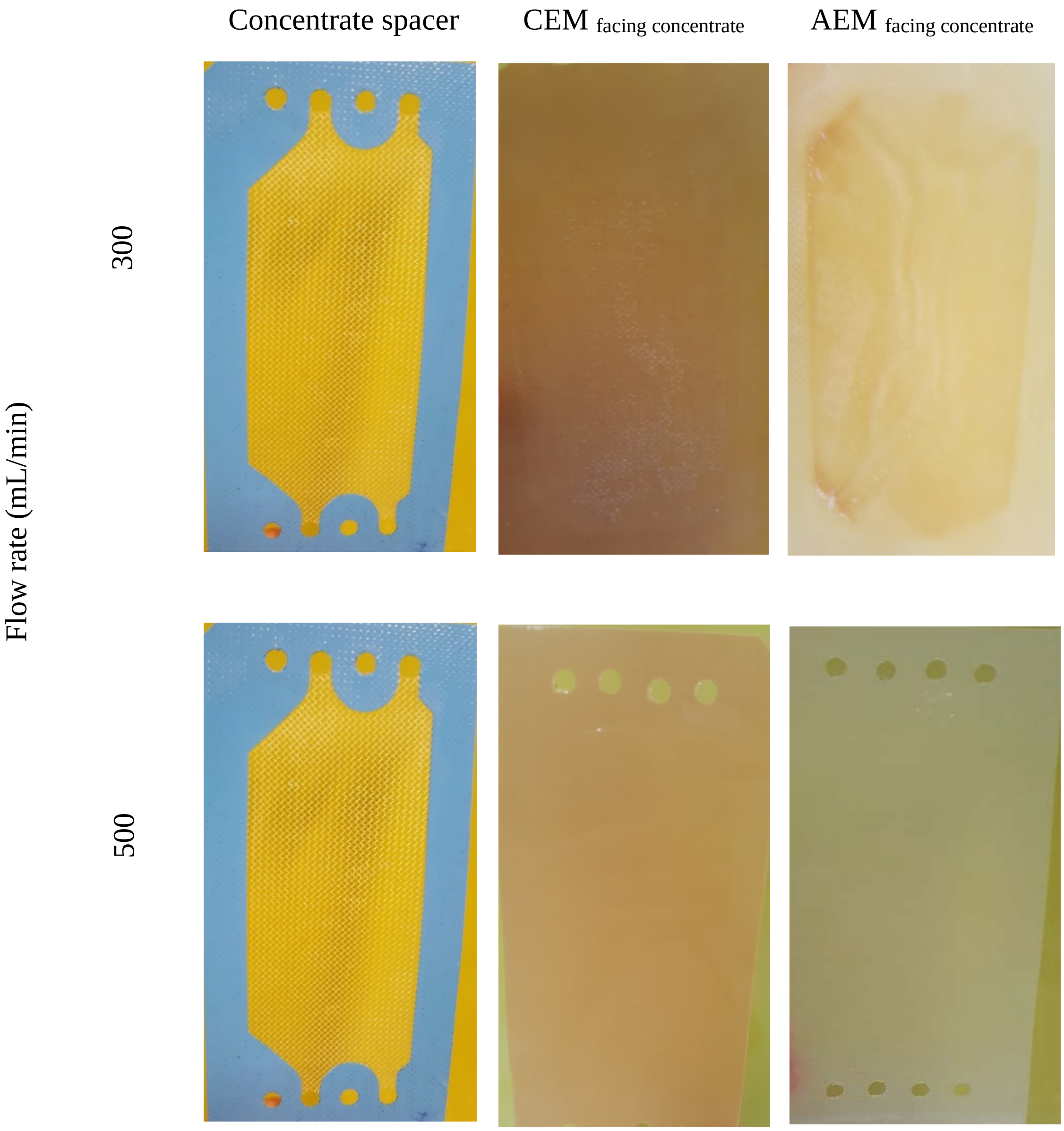

Figure S4.3. Membrane images after 300 min demineralization under constant current mode of 166 A/m^2 (Acid whey; concentrate pH of 9.25 ± 0.25).

CHAPTER 5. Utilisation of Salty Whey Ultrafiltration Permeate with Electrodialysis

Salty whey is a by-product of hard cheese production and is underutilized by the dairy industry. However, this stream is known for its high conductivity due to the presence of salts such as sodium chloride (NaCl), making it a potential concentrate stream for the electrodialysis of whey. In addition, the different components present in salty whey, such as lactose and NaCl, might be recoverable as value adding by-products.

5.1. Introduction

Salty whey is produced during the cheese salting process, with 50-60% of the added salt ending up in this stream [7]. The protein content of this stream can be recovered through an ultrafiltration (UF) step. However, the high mineral content of the permeate stream from the UF process limits its utilization in human and animal feed [84] and presents a major environmental concern if disposed of without treatment [194]. As the costs of salt disposal to the sewer are increasing in Australia, this is also becoming an economic burden to the dairy industry. Hence this chapter examines different applications for salty whey permeate that might add value to dairy processing.

Firstly, the use of salty whey permeate as the concentrate stream during the electrodialysis (ED) of sweet whey (see **Figure 5.1 (a)**) is examined. ED refers to the process in which ions are transferred through ion-exchange membranes (IEMs) under the application of an electric field. An ED module contains three major processing streams: (1) a diluate stream that is demineralized; (2) a concentrate stream that uptakes the ions that are removed from the diluate stream; and (3) an electrolyte solution that conducts the current through the system and protects the electrodes. The process has been commercialised for mineral removal from sweet whey prior to whey powder production. The use of salty whey permeate as the concentrate stream in such a process could eliminate the use of a concentrate stream prepared from fresh water and salt, thus reducing the overall water consumption and effluent salt load for the dairy factory.

Secondly, the potential to use salty whey permeate as the feed to the ED process (**Figure 5.1 (b)**) is considered. This allows the recovery of a demineralized lactose rich stream that can be utilized for the production of lactose powders, while also producing a concentrated salt solution that could be either processed to produce salts for the chlor-alkali industry [109, 112] or re-used in the cheese salting process. Using ED for salty whey processing has been investigated by Diblíková *et al.* [84]. In this work the authors used fresh whey and reconstituted cheese whey with different dry matter and sodium chloride concentrations to simulate salty whey. ED has also been studied widely for concentrating salty brines produced from seawater desalination using reverse osmosis (RO). Such solutions are known for their high conductivity and sodium content [109, 112]. However, the sodium levels found in salty whey permeate are almost double the levels reported for these salty brines.

Furthermore, the use of monovalent selective IEMs in this application is investigated. These membranes can selectively pass sodium and chloride generating a purer salt concentrate, while retaining the more nutritionally useful calcium within the lactose rich stream. However, they tend to have a more limited pH and temperature tolerance range thus making them more challenging to clean in a dairy processing environment. Andrés *et al.* [92] examined the use of these membranes in the electrodialysis of skimmed milk intended for infant formula. The work presented in this manuscript is believed to be one of the first that examines the use of monovalent selective membranes in whey treatment.

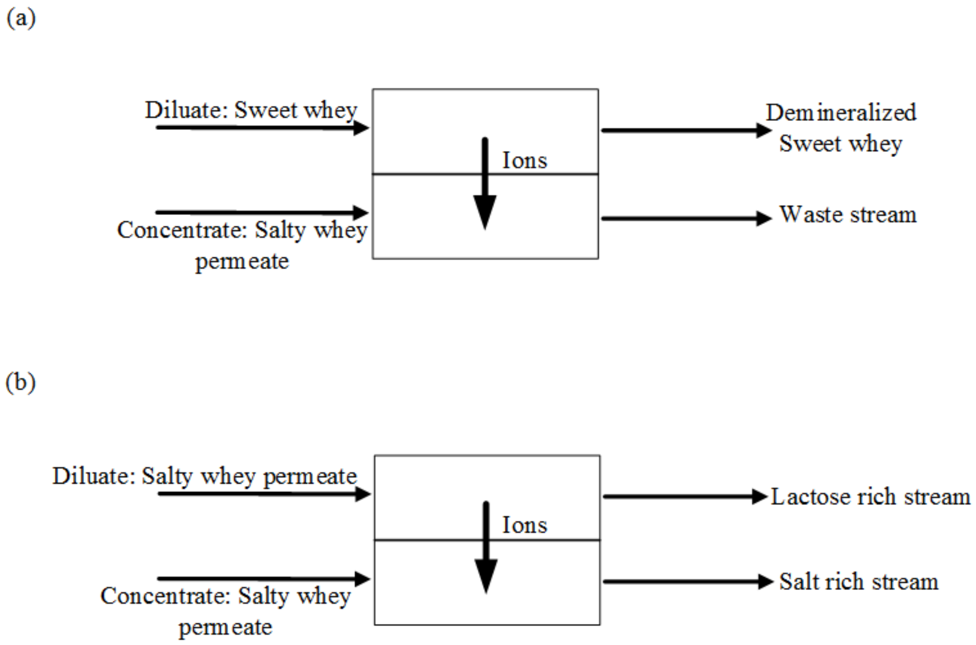

Figure 5.1. Proposed applications for salty whey permeate: ED process with (a) sweet whey as the diluate stream and salty whey permeate as the concentrate stream and (b) salty whey permeate as both diluate and concentrate streams.

5.2. Methods and Materials

5.2.1. Materials

Skimmed sweet and salty whey permeate were obtained from dairy companies in Victoria, Australia. The salty whey permeate samples were produced using ultrafiltration to remove whey protein. The composition of the solutions is given in **Table 5.1**. The samples were stored at 4 ± 1°C. Purified water (>8.6 MΩ cm; Merck Millipore KGaA, Darmstadt Germany) was used in the preparation of all laboratory made solutions. Sodium sulphate (Na_2SO_4; >99%; Thermo Fisher Scientific Australia Pty., Ltd., Scoresby, Australia) with a concentration of 20 g L^{-1} was used as the electrolyte solution. Cleaning chemicals were prepared from hydrochloric acid (HCl; 36%; Thermo Fisher Scientific Australia, Scoresby, Australia), sodium chloride (NaCl; >99.5%; Merck KGaA, Darmstadt Germany) and 5M sodium hydroxide (NaOH; Chem-Supply, Port Adelaide, Australia).

Table 5.1. The composition of skimmed sweet and salty whey permeate used in this work.

Component	Unit	Sweet whey	Salty whey permeate
pH	-	6.3 ± 0.05	5.3 ± 0.1
Conductivity	mS cm^{-1}	6.4 ± 1	130 ± 4
Total solids	% (m/v)	6.5 ± 0.3	14.5 ± 0.5
Total protein [1]	% (m/v)	1.04 ± 0.05	0.3 ± 0.05
K	mg $100mL^{-1}$	82.5 ± 4	160 ± 33
Na	mg $100mL^{-1}$	32 ± 1	5000 ± 500 (2.2M)
Ca	mg $100mL^{-1}$	39 ± 7	130 ± 8
Mg	mg $100mL^{-1}$	9 ± 1	20 ± 2
Lactose	mg $100mL^{-1}$	Not measured	2600 ± 200
Lactic acid	mg $100mL^{-1}$	Not measured	0.72 ± 0.2

[1] Total Protein = Total nitrogen × 6.38

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5.2.2. Electrodialysis Unit

The experiments were carried out using an FTED-40 unit manufactured by FuMA-Tech GmbH (Bietigheim-Bissingen, Germany). Detailed information of the unit can be found in **section 3.4.1.1**. The module was arranged with three cation exchange membranes (CEMs) separated by two anion exchange membrane (AEMs) purchased from Astom (Tokyo, Japan) (see **Table 3.1**) and alternating diluate and concentrate spacers. The effective area per IEM was 36 cm^2. All membranes were preconditioned by soaking in 5% NaCl solution to allow for membrane hydration and expansion. After each trial the CMB and AHA membranes were removed from the ED unit and cleaned by soaking in HCl (pH 1.0 ± 0.15), followed by 3% NaCl (pH 9.2 ± 0.15) and then 5% NaCl (neutral pH) for two days each. This was done to ensure that the membranes were clean and had returned to their original ionic state. The alkali soaking step was eliminated for the monovalent selective membranes due to the low pH tolerance of the ACS membrane (**Table 3.1**).

5.2.3. Experimental Protocol

The experiments were carried out in batch mode, with all solutions continuously recycled to their supply tanks. The diluate and concentrate flowrates were maintained at 500 mL min^{-1}, while the electrolyte flowrate was kept at 1000 mL min^{-1} as recommended by the manufacturer to minimize concentration polarization effects. Samples were collected (5-10 ml) on an hourly basis from the diluate and concentrate tanks for analysis. To provide an estimate of experimental error, some of the experiments were repeated twice.

For the demineralization of sweet whey, a total volume of 2 L was used for both diluate and concentrate streams and the experiments were terminated when 75% sweet whey demineralization was achieved. Both salty whey permeate and 0.1M NaCl solution were used as the concentrate solution. These experiments were performed at 44 ± 2°C to minimize microbial growth.

For the demineralization of salty whey permeate, experiments were run for 8 hours using either salty whey permeate or 0.1M NaCl as the concentrate solution. The unit was operated either at a constant current density of 55 mA cm^{-2}; or a constant voltage of 5, 10 or 15 V. The experiments were performed at 26 ± 2°C. Ambient temperatures can be used with salty whey, since the high salinity limits bacterial growth. The volume ratio between the concentrate and diluate tanks was maintained at 1:4 (actual volumes were 1 L and 4 L for concentrate and diluate tanks, respectively).

While it was not possible to experimentally determine the limiting current density of this system, operation was likely to be below this value for the salty whey permeate/salty whey permeate system, based on measurements in comparable systems [195]. The initial current density was 56, 167, and 278 mA cm^{-2} at 5, 10 and 15 V, respectively. Conversely, for the salty whey permeate/ 0.1M NaCl system, the initial current density was 41, 125, and 194 mA cm^{-2} at 5, 10 and 15 V, respectively, which is likely to be above the limiting current density at the two higher voltages, given the lower ionic strength of the concentrate solution.

5.2.4. Analysis Methods

Inductively coupled plasma optical emission spectroscopy (ICP-OES 720ES, Varian, Santa Clara, CA, USA) was used to measure the concentration of sodium (Na), potassium (K), calcium (Ca), and magnesium (Mg) in both the diluate and concentrate tanks. Total solid analysis was performed by weighing 2 ml of samples before drying under vacuum at 100°C for more than 20 hours in a fan forced oven to evaporate all the moisture.

During each experiment, the conductivity and pH of the concentrate tank were measured continuously using a pH probe (Mettler-Toledo, Greifensee, Switzerland) and a conductivity probe (Crison Instruments, Greifensee, Switzerland), while the diluate conductivity was measured using a second conductivity probe (Mettler-Toledo, Greifensee, Switzerland). At the start and end of each experiment, the conductivity and pH of the electrode solution was also recorded. The recorded conductivity value can be used to calculate the diluate demineralization rate (DR) according to **Eq. 2.4** [113, 191].

$$DR(\%) = \frac{x_{initial} - x_{final}}{x_{initial}} \times 100 = \left(1 - \frac{x_{final}}{x_{initial}}\right) \times 100 \qquad \textbf{Eq. 2.4}$$

The current and voltage were read directly from the current supply and used to calculate the system resistance using Ohm's law. The energy consumed (kWh kg^{-1} of NaCl) during the batch process can be estimated using **Eq. 3.4** [112]. The diluate concentration was used as the calculation basis. The sodium chloride concentration was estimated from the sodium concentration, assuming that chloride is the dominant anion present in this system.

$$E\left({}^{kWh}/_{kg\ of\ NaCl\ removed}\right) = \frac{V_{cell}\int Idt}{\left(v_{D,initial}\times C_{Na,initial} - v_{D,final}\times C_{Na,final}\right)\times\left({}^{MW_{NaCl}}/_{MW_{Na}}\right)} \quad \textbf{Eq.3.4}$$

Purity was defined by Zhang *et al.* [111] as the NaCl concentration in the final concentrate solution according to **Eq. 5.1**.

$$P_{NaCl}(\%) = \frac{\left(v_{C,initial}\times C_{Na,final}\right)\times\left({}^{MW_{NaCl}}/_{MW_{Na}}\right)}{m_{c,dry}}\times 100 \quad \textbf{Eq. 5.1}$$

Where $c_{Na,f}$ is the final concentration of Na ion in the concentrate tank (g L^{-1}), and $m_{C,dry}$ is the final solid weight in the concentrate tank (g). However, using this equation in the present work resulted in values greater than 100% as the salty whey permeate contains anions other than chloride. Therefore, purity in this work is used only as a qualitative parameter.

5.3. Results and Discussion

5.3.1. Use of Salty Whey as Concentrate Stream for Sweet Whey Demineralization

Initial experiments used a constant voltage of 7 V with fresh sweet whey as the diluate stream and either salty whey permeate (2.2M Na) or 0.1M NaCl as the concentrate. The reduction in diluate conductivity was identical for both types of concentrate solutions, as illustrated in **Figure 5.2 (a)**. However, the concentrate conductivity only increased by 1 mS cm^{-1} for salty whey permeate while it increased by 5 mS cm^{-1} for the 0.1M NaCl solution. This more limited change in conductivity partly reflects the nonlinear relationship between conductivity and salt concentration, but also probably reflects an osmotic flow of water from the diluate to the salty whey permeate (concentrate tank), given their very different concentrations [109, 112, 113]. Analysis of ion concentrations (**Figure 5.2 (b)**), shows that fewer Na ions were removed from the sweet whey when salty whey permeate was used as the concentrate stream. Conversely, a greater quantity of all other ions (K, Ca and Mg ions) were removed. Such a behaviour is a result of the high concentration of Na in the salty whey permeate thus resulting in diffusional backflow of Na from the concentrate to the diluate. However, the final Na concentration in the diluate tank (2.8 ± 0.3 g Na per kg of dry mass) falls in the reported range for demineralised whey powders.

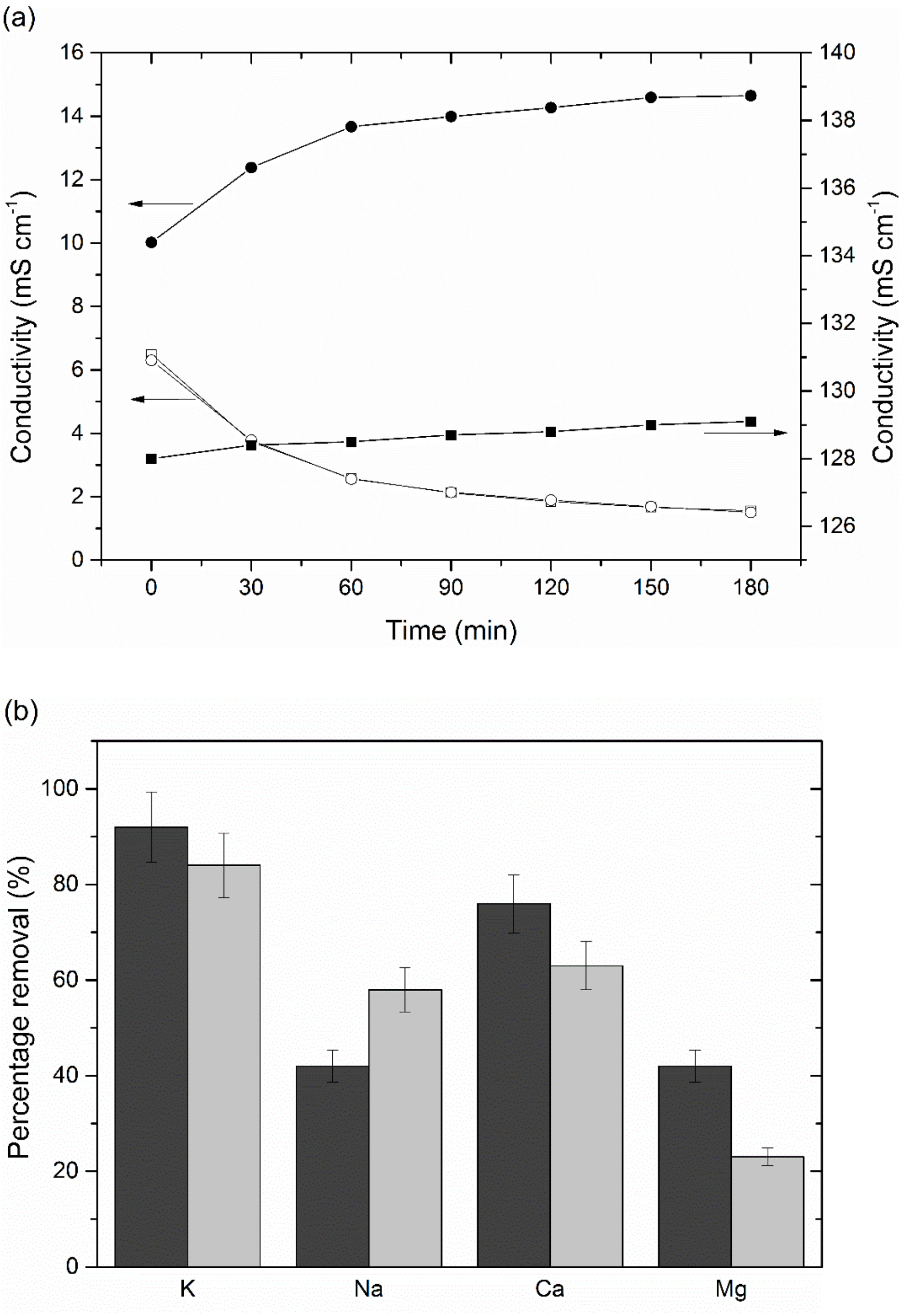

Figure 5.2. Demineralization of sweet whey under a constant voltage of 7 V using two different concentrate streams: (a) change in the conductivity of the diluate (□, sweet whey/salty whey permeate; ○, sweet whey/0.1M NaCl) and concentrate (■, sweet whey/salty whey permeate; ●, sweet whey/0.1M NaCl) and (b) percentage removal of cations from sweet whey (■, salty whey permeate; ▨, 0.1M NaCl).

The initial system resistance for the sweet whey/ salty whey permeate system was lower compared to the sweet whey/ 0.1M NaCl system (see **Figure 5.3**), due to the higher conductivity of the salty whey. The resistance increased with time for both systems due to diluate demineralization and possibly membrane fouling [93, 94]. Since both systems achieved 75% demineralization in 3 hours, the greater increase in resistance for the sweet whey/ 0.1M NaCl system suggests that membrane fouling was greater comparing to the sweet whey/ salty whey permeate system. There was indeed some visual evidence of greater scaling for this system on the sides of the membranes facing the concentrate (see supplementary information **Figures S5.1** and **Figures S5.2**). Although salty whey permeate contains more salts that might cause membrane scaling, the solution pH played a significant role. As observed from **Figure 5.4**, the pH increased for both concentrate solutions, however, the increase was greater for the 0.1M NaCl solution due to its lower buffering capacity which is a function of the charge number and charge properties of the salts present in the solution [196] (see supplementary information **Figures S5.3**). It is well known that the solubility of calcium salts reduces with an increase in pH, thus resulting in their precipitation on the membrane surface. When 0.1M NaCl solution is used as the concentrate stream, membrane fouling could be avoided or reduced by adjusting the pH of the solution as demonstrated in **Chapter 4**. However, adjusting the pH for salty whey permeate is less readily achieved because of the system buffering (see supplementary information **Figures S5.3**). Fouling in such systems could be avoided or minimized by using a pulsed electrical field, electrodialysis reversal, using higher liquid flowrates or by acid cleaning. Finally, the dip observed in **Figure 5.3** (at 45 min for sweet whey/ 0.1M NaCl and at 165 min for sweet whey/ salty whey permeate system) indicates a point in the experiment when the concentrate feed pipe raptured, due to the high pressures developed in the ED unit as a result of membrane fouling (see supplementary information **Figure S5.1** and **Figure S5.2**). Termination of the power supply to the unit in order to fix the pipe resulted in the relaxation of the fouling layer which could have either dissolved back into the solution or been dislodged when the process was restarted. This may explain the lower total system resistance after the observed dip.

The use of the salty whey permeate as the concentrate may lead to lower power consumption, because of the lower resistance as shown in **Figure 5.3**. However as noted, more energy is wasted in this system due to the diffusional backflow of sodium and the greater transfer of ions such as calcium and magnesium, so the total energy consumption per kg of NaCl removed, is indeed higher when this stream is used (**Table 5.3**). However, sodium ions are not the dominant ions in sweet whey (**Table 5.1**), therefore calculating the energy per kg of NaCl is overestimating the energy cost of the process. The energy consumed per tonne of sweet whey is more comparable for both systems (**Table 5.3**) and falls within the range reported by Chen *et al.* [13] for 75% demineralization.

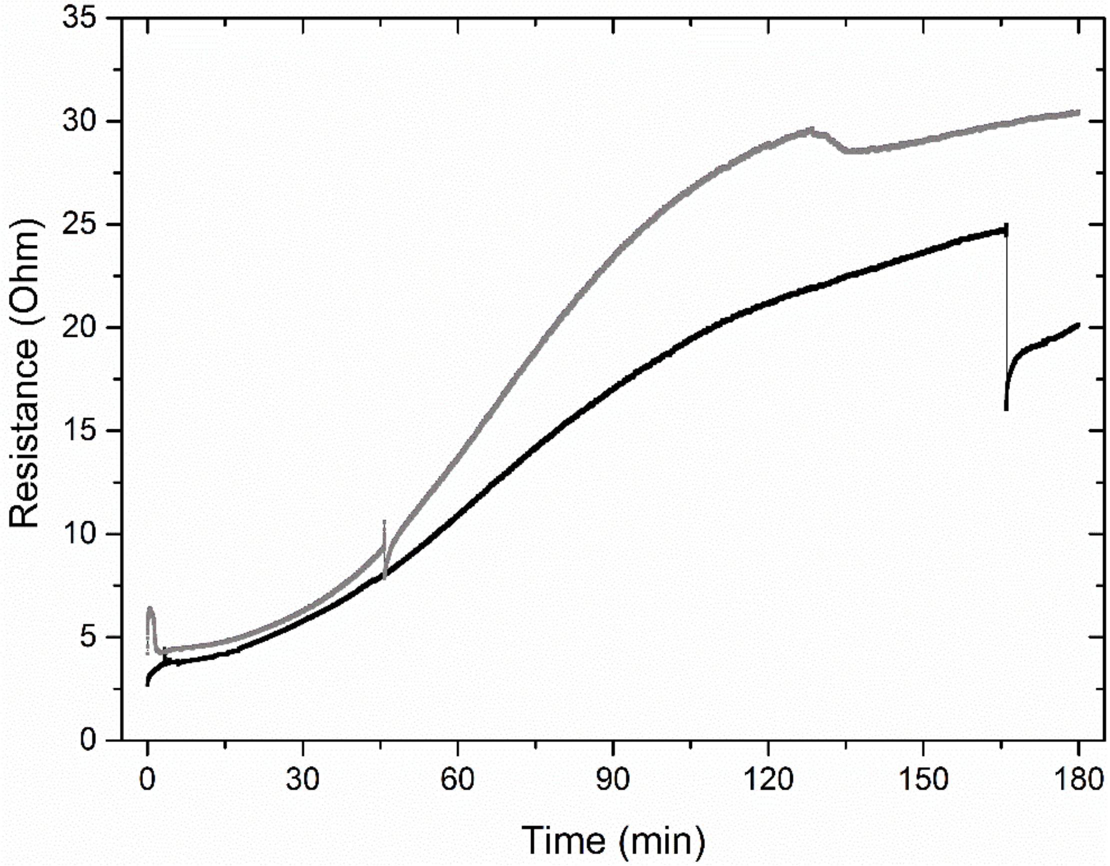

Figure 5.3. Change in system resistance during the demineralization of sweet whey under a constant voltage of 7 V using two different concentrate streams: sweet whey/salty whey permeate system (dark grey trace) and sweet whey/0.1M NaCl system (pale grey trace).

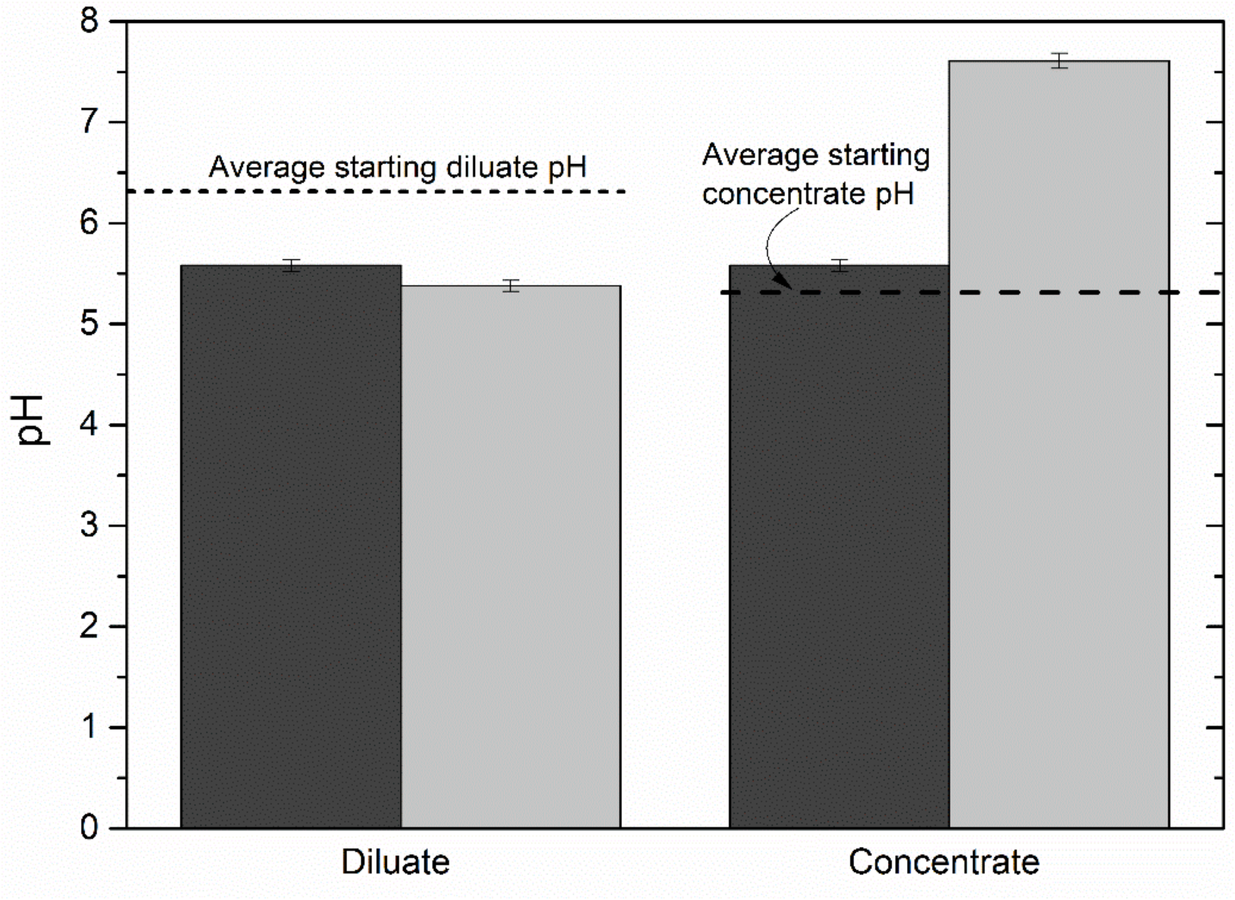

Figure 5.4. pH of the diluate and concentrate tanks after 75% demineralization of sweet whey under a constant voltage of 7 V using two different concentrate streams: salty whey permeate (■) and 0.1M NaCl (■).

Table 5.2. Energy consumption for 75% demineralization of sweet whey at 7 V and using a concentrate of either 0.1M NaCl or salty whey permeate (2.2M Na).

Energy calculation basis	Salty whey permeate	0.1M NaCl
Removal of sodium (kWh kg^{-1} of NaCl)	18 ± 0.5	11.4 ± 0.5
Removal of Monovalent cations (kWh kg^{-1} of NaCl and KCl)	3.7 ± 0.5	3.2 ± 0.5
Whey treated (kWh ton^{-1} of whey)	7.4 ± 0.5	5.9 ± 0. 5

5.3.2. Demineralization of Salty Whey Using ED

5.3.2.1. *Constant Current Mode*

The use of salty whey permeate as the diluate was next examined, with the objective of creating a purified lactose stream and a salt stream suitable for re-use. Initial experiments were run in constant current mode with salty whey permeate acting as diluate, and either salty whey permeate or 0.1M NaCl as the concentrate.

As observed for the sweet whey case, the change in diluate conductivity over a period of 8 hours was identical regardless of the salinity of the concentrate solution (**Figure 5.5 (a)**). This was consistent with the measured change in concentrations of the major ions in the diluate stream, with the sodium ion concentration falling by 6.5 ± 0.5 g L^{-1} regardless of the concentrate type. Again, the change in concentrate conductivity was lower for the salty whey permeate, reflecting the osmotic flows of water from diluate to concentrate. The concentrate solution volume changed by 160 ± 10 mL when 0.1M NaCl was used versus 195 ± 10 mL when salty whey permeate was used. The higher salt concentrations in the salty whey permeate concentrate again resulted in a reduction in the system resistance (**Figure 5.5 (b)**).

During the 8 hours operation, changes in the concentration of the divalent ions in the diluate tank were within the experimental error margins. The main reason behind such an observation is the high concentration of monovalent ions found in salty whey permeate (**Table 5.1**). No significant changes were noticed in the diluate pH but the concentrate pH fell from 5.5 ± 0.25 to 3.4 ± 0.1 for 0.1M NaCl solution and to 5.1 ± 0.1 for salty whey permeate. The more limited drop in the salty whey permeate pH was again a result of the greater buffering capacity of this system (Supplementary Information **Figures S5.3**). This is in contrast to the sweet whey system, where the pH increased in the concentrate (**Figure 5.4**).

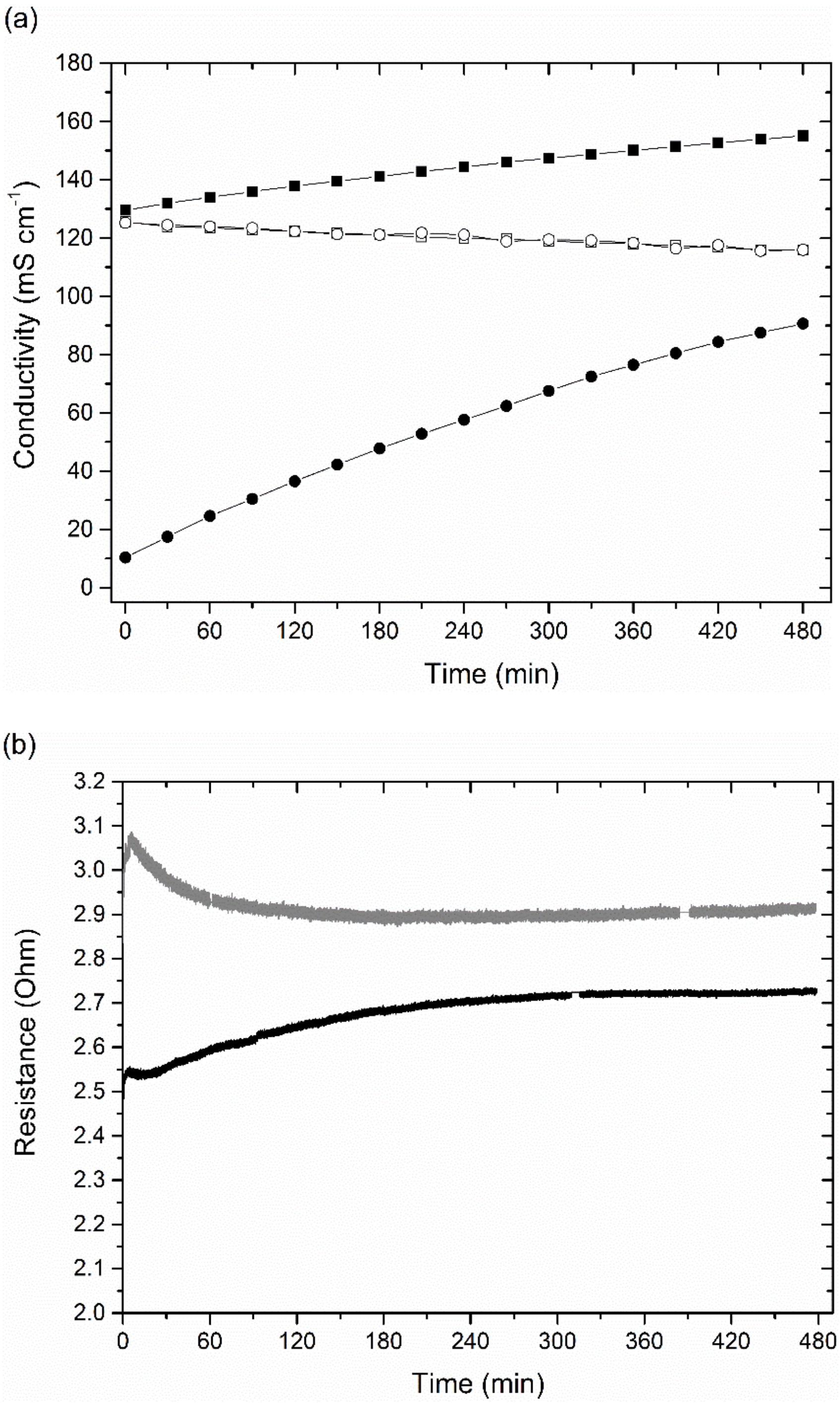

Figure 5.5. Demineralization of salty whey over a period of 8 hours under a constant current density of 55 A m^{-2}: (a) change in the conductivity of the diluate (□, salty whey permeate/salty whey permeate system; ○, salty whey permeate/0.1M NaCl system) and concentrate (■, salty whey permeate/salty whey permeate system; ●, salty whey permeate/0.1M NaCl system) and (b) system resistance (dark grey trace, salty whey permeate/salty whey permeate system; pale grey trace, salty whey permeate/0.1M NaCl system).

5.3.2.2. *Constant Voltage Mode*

Similar to constant current experiments, no major differences were observed in the final diluate conductivity or monovalent ion removal rates between the salty whey permeate and 0.1M NaCl concentrates at applied voltages of 5 V and 10 V (see **Table 5.3**, **Figure 5.6** and **Figure 5.7**). However, when the applied voltage was increased to 15 V, more sodium was removed when the 0.1M NaCl solution was used (**Figure 5.7**). This was again the result of less back diffusion in this concentrate, relative to that of salty whey permeate. Due to the absence of other ions or lactose in the starting 0.1M NaCl solution, the final NaCl purity in this concentrate will be higher. The energy consumption (**Figure 5.8**) is less than that obtained for the sweet whey system due to the lower solution resistance as salty whey permeate has a much higher conductivity than sweet whey. These energy consumptions (**Figure 5.8**) are still relatively high compared to the values reported for RO brine by Reig *et al.* [112] (<1.2 kWh kg^{-1} of NaCl) and Liu *et al.* [109] (1.4 kWh kg^{-1} of NaCl at 15V). However, such values reflect the complexity of the whey solution due to the presence of lactose, residual protein and larger ions. Furthermore, the consumed energy is overestimated as all Na will not be present as NaCl.

Table 5.3. Process outcomes for constant voltage experiments conducted over 8 hours with salty whey permeate as the diluate and either salty whey permeate or 0.1M NaCl as concentrate.

Concentrate type	Salty whey permeate			0.1M NaCl		
System voltage (V)	5	10	15	5	10	15
Change in concentrate volume (mL)	140 ± 5	540 ± 30	650 ± 30	100 ± 5	480 ± 30	750 ± 40
Demineralization rate (DR)	6.5	22	33	6.5	22	38

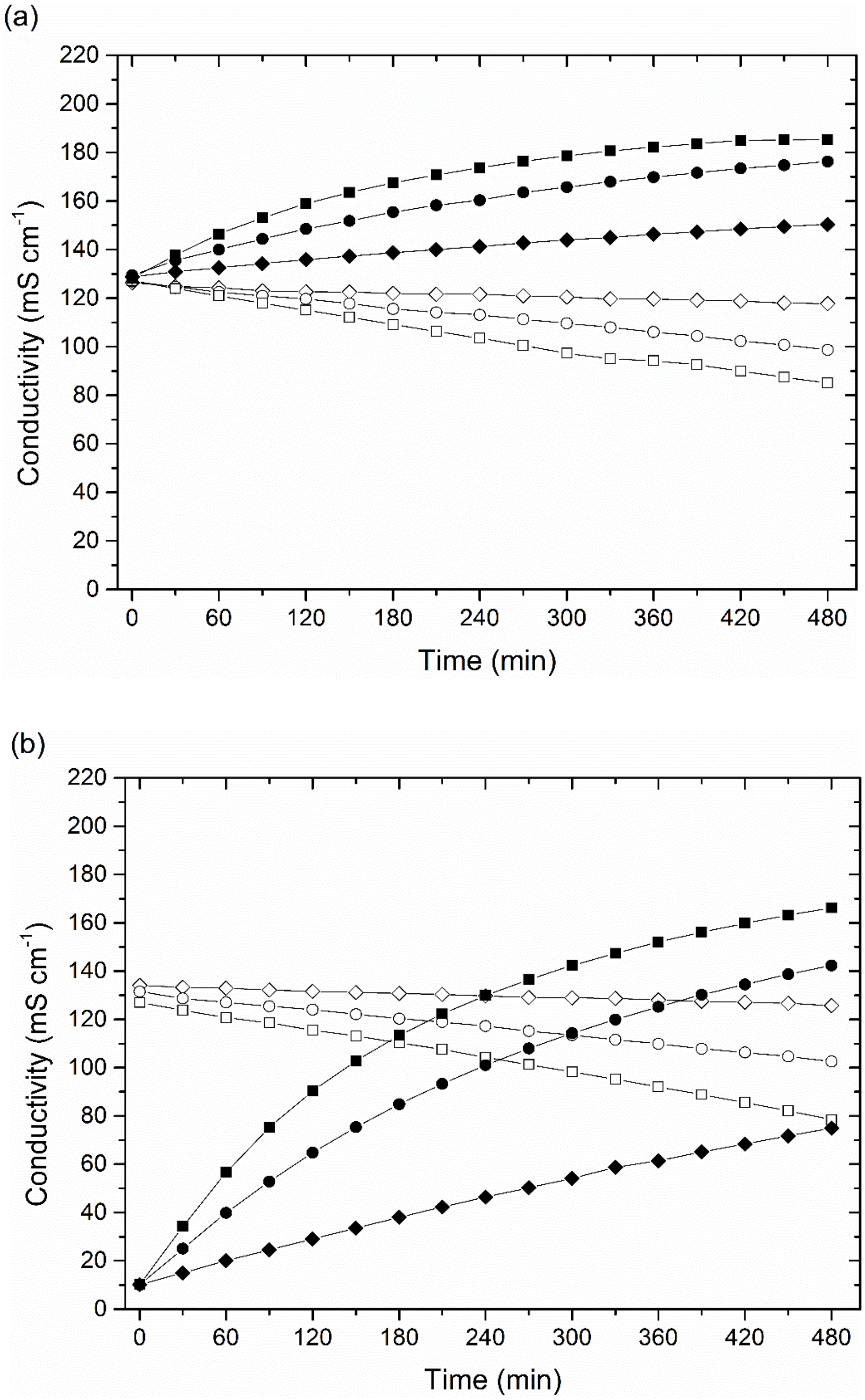

Figure 5.6. Demineralization of salty whey permeate over a period of 8 hours under different applied voltages showing the change in the conductivity of the diluate at 5 V (◇), 10 V (○) and 15 V (□) and concentrate at 5 V (◆), 10 V (●) and 15 V (■) for (a) salty whey permeate and (b) 0.1M NaCl as the concentrate solution.

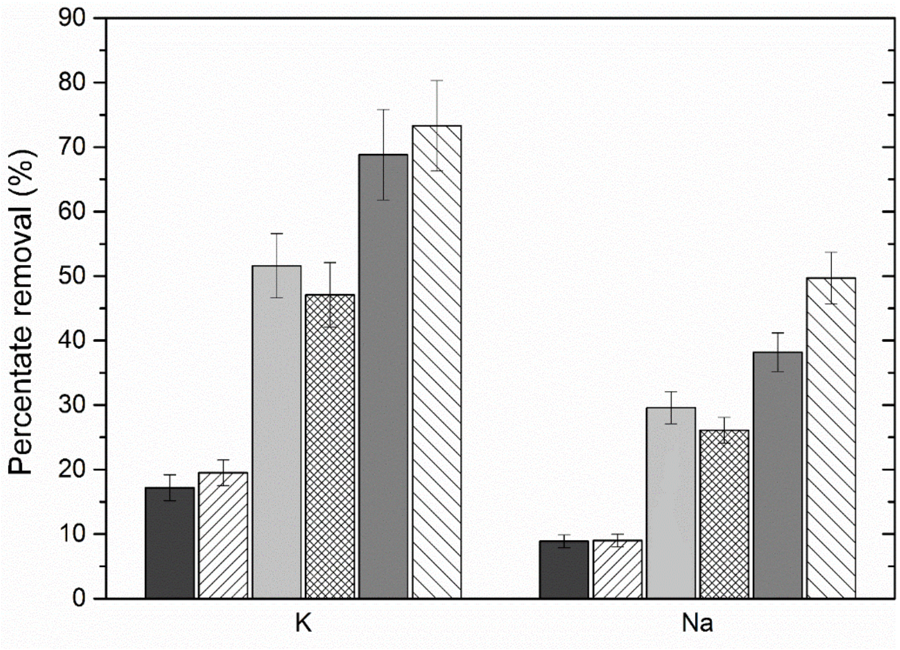

Figure 5.7. Percentage removal of monovalent ions from salty whey permeate during demineralization over an 8 hour period with the concentrate solution being either salty whey permeate at an applied voltage of 5 V (■),10 V (■) and 15 V (■) or 0.1M NaCl at an applied voltage of 5 V (▨),10 V (▩) and 15 V (▧).

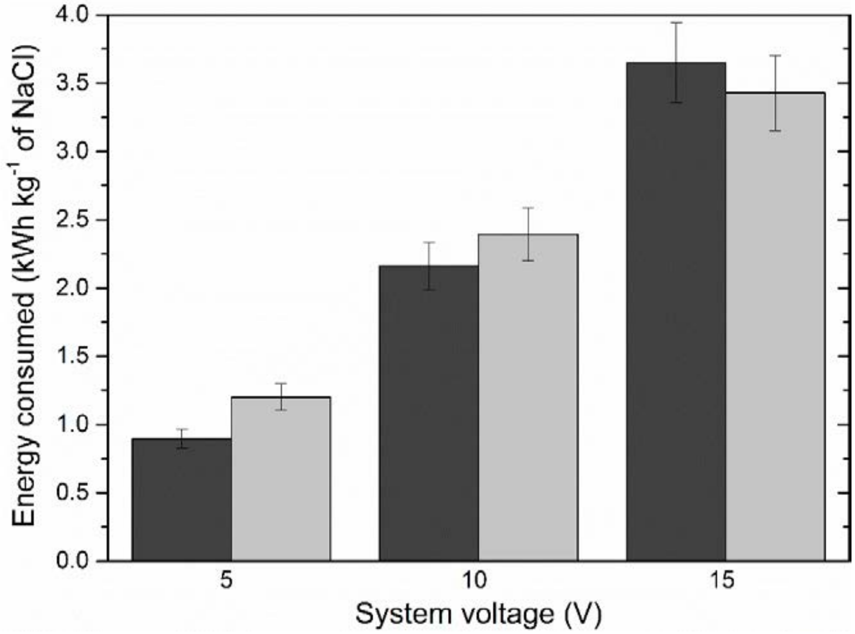

Figure 5.8. Energy consumption during demineralization of salty whey permeate over an 8 hour period with either salty whey permeate (■) or 0.1M NaCl (■) as the concentrate solution, as a function of the applied voltage.

5.3.2.3. *Monovalent Selective Membranes*

Experiments were finally conducted to determine whether monovalent selective IEMs (CIMS/ACS) could be used to improve the quality of the final concentrate stream so that it can more readily be re-used; and to retain nutritionally important calcium in the final diluate. These experiments were conducted at a constant voltage of 15V using 0.1M NaCl as the concentrate stream.

The concentrate conductivity increased further for the monovalent selective IEMs (CIMS/ACS) compared to the non-selective IEMs (CMB/AHA) (**Figure 5.9 (a)**). However, this only reflects the fact that the conductivity of monovalent ions is greater than that of divalent ions. As shown in **Figure 5.10**, the monovalent selective IEMs allow less divalent ions to pass through the membranes and hence more monovalent ions are transferred (see Supplementary Information **Figure S5.4**). The lower the concentration of multivalent ions in the concentrate stream, the higher will be the purity of the NaCl produced [111]. The energy consumed per kg of NaCl removed from the diluate tank was comparable for both types of membranes (3.2 ± 0.3 kWh kg^{-1} of NaCl for CIMS/ACS, and 3.4 ± 0.3 kWh kg^{-1} of NaCl for CMB/AHA). While these results would tend to suggest that these monovalent selective IEMs can indeed produce a cleaner salt solution for the same energy demand, this needs to be balanced against the greater cost of these membranes and their more limited tolerance of both process temperature and pH (**Table 5.2**), making them less attractive for industrial applications.

Regardless of the type of ions transferred to the concentrate tank, the change in tank volume was 700 ± 35 ml for both cases. The monovalent selective membranes are known to have lower electrical resistance (**Table 3.1**) and this was reflected in a lower system resistance calculated for these experiments (see Supplementary Information **Figure S5.5**). The lower resistance of monovalent selective membranes should have reduced the overall resistance of the system (13 $Ohm.cm^2$ for CIMS/ACS Vs 22 $Ohm.cm^2$ for CMB/AHA). However, the difference in the resistance between both systems is less than 0.5 Ohms, thus suggesting the presence of greater water splitting for the CIMS/ACS system. This is further observed in the lower pH of the concentrate stream for the monovalent selective IEMs as shown in **Figure 5.9 (b)**. In addition, no fouling was observed on either membrane pairs (CIMS/ACS or CMB/AHA) at the end of the experiments. This indicates that membrane fouling is not a contributor to the difference observed in the total system resistance for each membrane pair. The drop in the concentrate pH (**Figure 5.9 (b)**) increases the solubility of calcium salts thus reducing the possibility of mineral scaling.

The low pH values obtained for both concentrates after eight hours of processing at 15 V could limit the usefulness of these streams for re-use in cheese making. However, the pH fall is likely due to water splitting as a result of the low ionic strength of the concentrate solution and high voltage used in these experiments. This could be eliminated at industrial scale by operating with a lower voltage per membrane pair or using a concentrate of higher ionic strength.

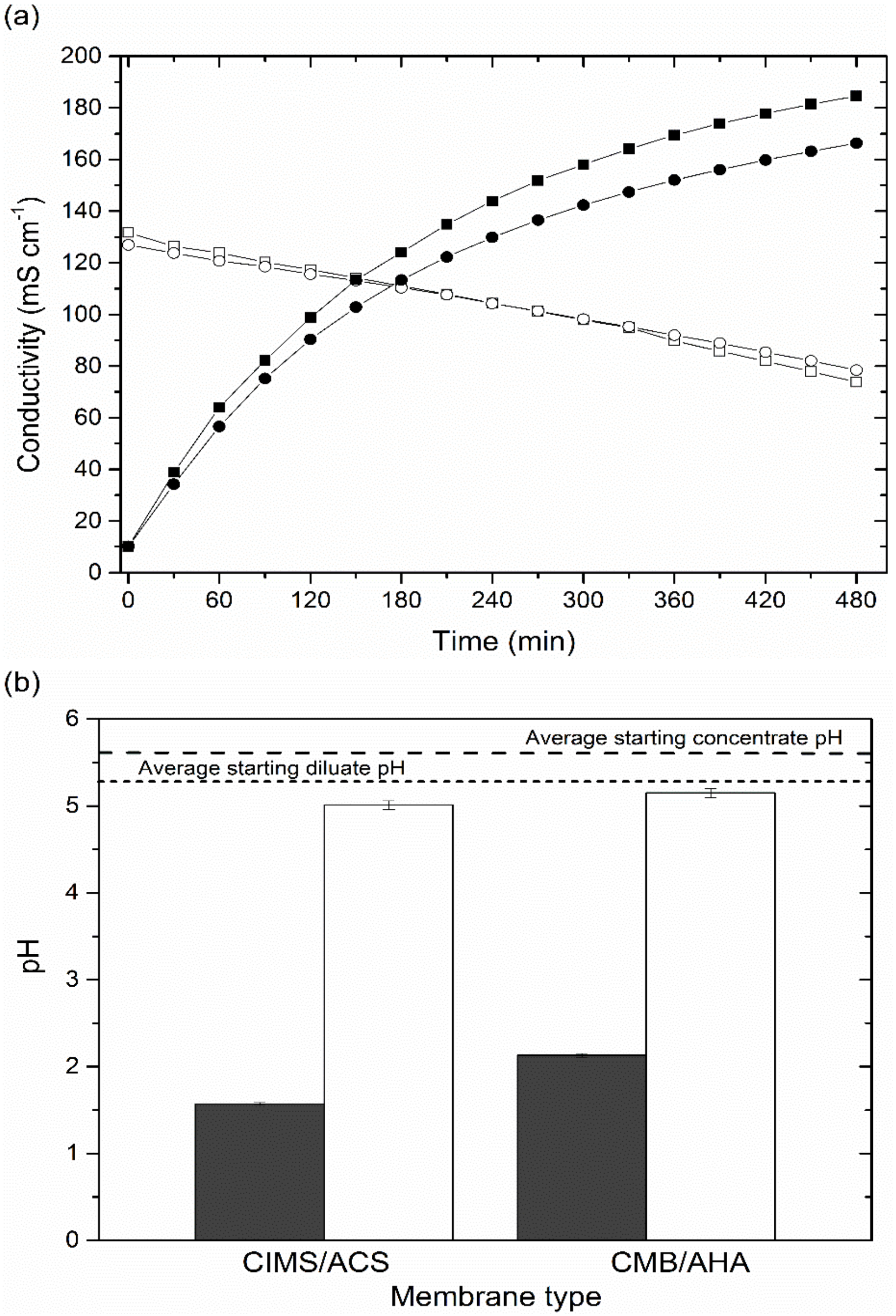

Figure 5.9. Demineralization of salty whey permeate over a period of 8 hours under a constant voltage of 15 V with 0.1M NaCl as concentrate: (a) the change in conductivity of the diluate (□) and concentrate (■) using monovalent selective (CIMS/ACS) membranes; and change in conductivity of the diluate (○) and concentrate (●) using non-selective (CMB/AHA) membranes; and (b) the final pH of the diluate (□) and concentrate (■).

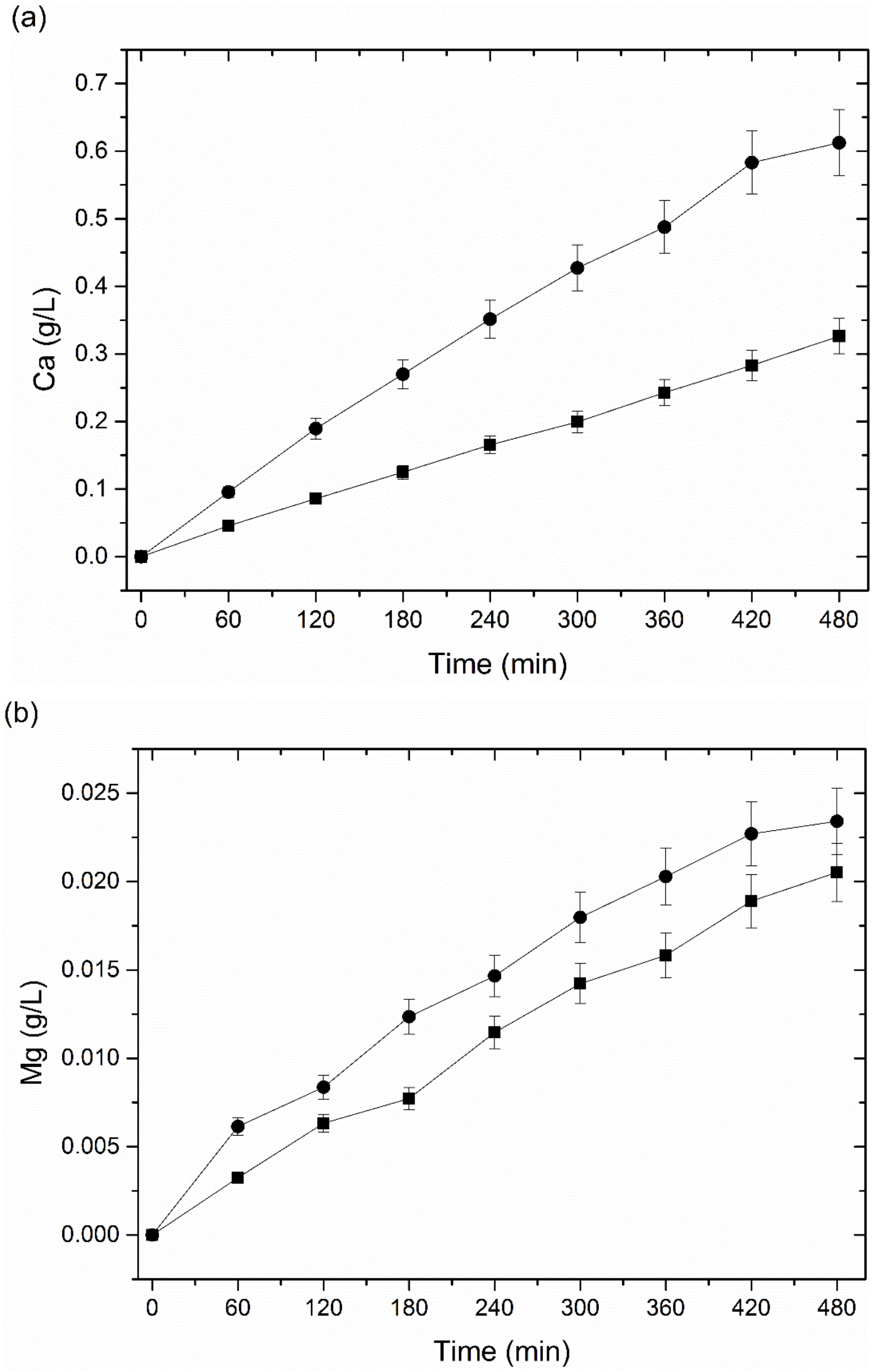

Figure 5.10. Concentration of divalent ions in the concentrate compartment over 8 hours of demineralization of salty whey permeate with 0.1M NaCl as concentrate at a system voltage of 15 V using monovalent selective (CIMS/ACS) (■) or non-selective (CMB/AHA) (●) membrane pairs: (a) calcium; and (b) magnesium.

5.4. Conclusions

This work has shown that salty whey permeate can be used as the concentrate stream for sweet whey demineralization, with 75% demineralization achieved within 3 hours at 7V with two membrane pairs of 36 cm^2 each in size. This time could be reduced at industrial scale by increasing the membrane area. Furthermore, membrane fouling was less extensive when a salty whey concentrate was used. However, while the overall demineralization rates were comparable, the levels of sodium removed were lower with this concentrate (43% Vs 58% for 0.1M NaCl). While the energy demand was higher per kg of sodium removed from the diluate tank, this demand was comparable to that for a sweet whey/ 0.1M NaCl system when the energy demand was calculated per tonne of treated whey. The quality of the concentrated salt solution produced from salty whey permeate demineralization can be improved by utilizing monovalent selective IEMs. The concentration of calcium in the concentrate solution dropped to half of the amount found when using non-selective IEMs. This, in turn, results in a concentrate of greater purity. The energy consumption is comparable for both types of membranes. However, the non-selective IEMs have a higher pH tolerance range thus allowing the use of base cleaning agents within the dairy factory environment.

5.5. Acknowledgments

This research was supported under Australian Research Council’s Industrial Transformation Research Program (ITRP) funding scheme (Project Number IH120100005). The ARC Dairy Innovation Hub is a collaboration between The University of Melbourne, The University of Queensland and Dairy Innovation Australia Ltd.

5.6. Supplementary Material

5.6.1. Salty Whey as Concentrate Stream for Sweet Whey Demineralization

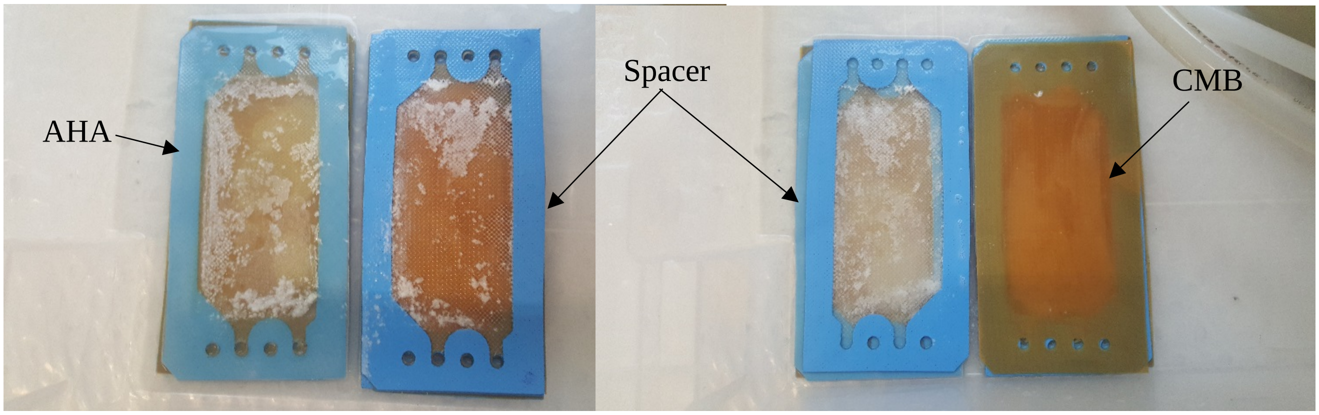

Figure S5.1. The fouling of membranes for the sweet whey/ salty whey permeate system. Fouling was noted on the sides of both the cation and anion membranes facing the concentrate compartment. However, the extent of fouling was higher for the anion exchange membrane (AHA).

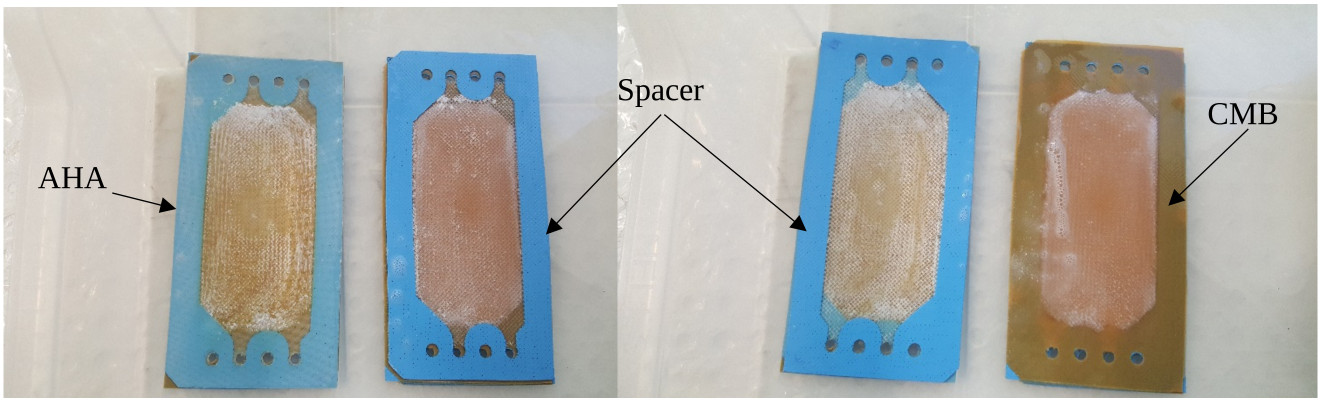

Figure S5.2. The fouling of membranes for the sweet whey/ 0.1M NaCl system. Fouling was noticed on the sides of both the cation and anion membranes facing the concentrate compartment.

5.6.2. Buffering Capacity

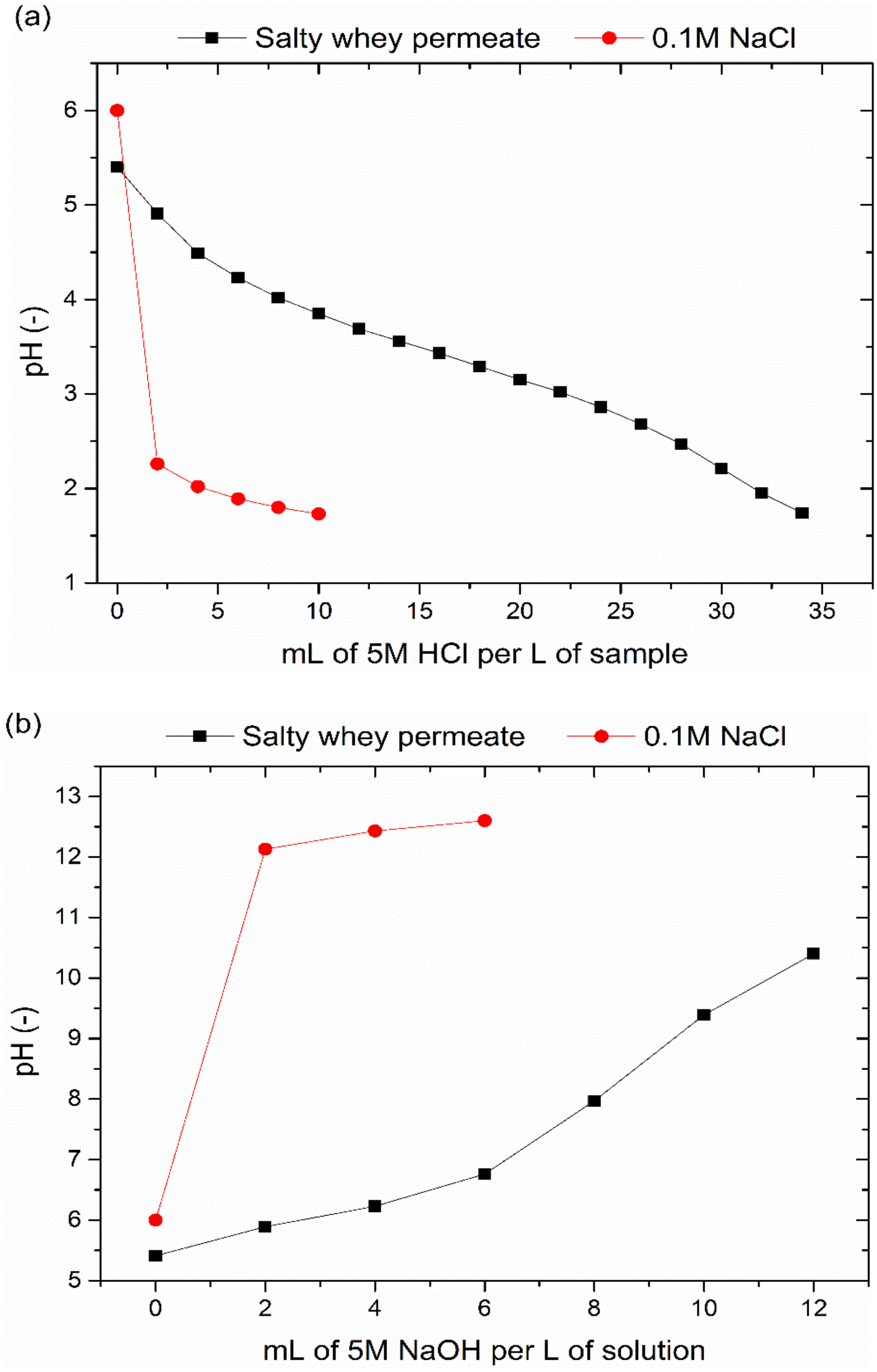

Figure S5.3. Buffering capacity of salty whey permeate and 0.1M NaCl: (a) volume of 5M HCl required to reduce solution pH; and (b) volume of 5M NaOH required to reduce the solution pH.

5.6.3. Monovalent Selective Membranes

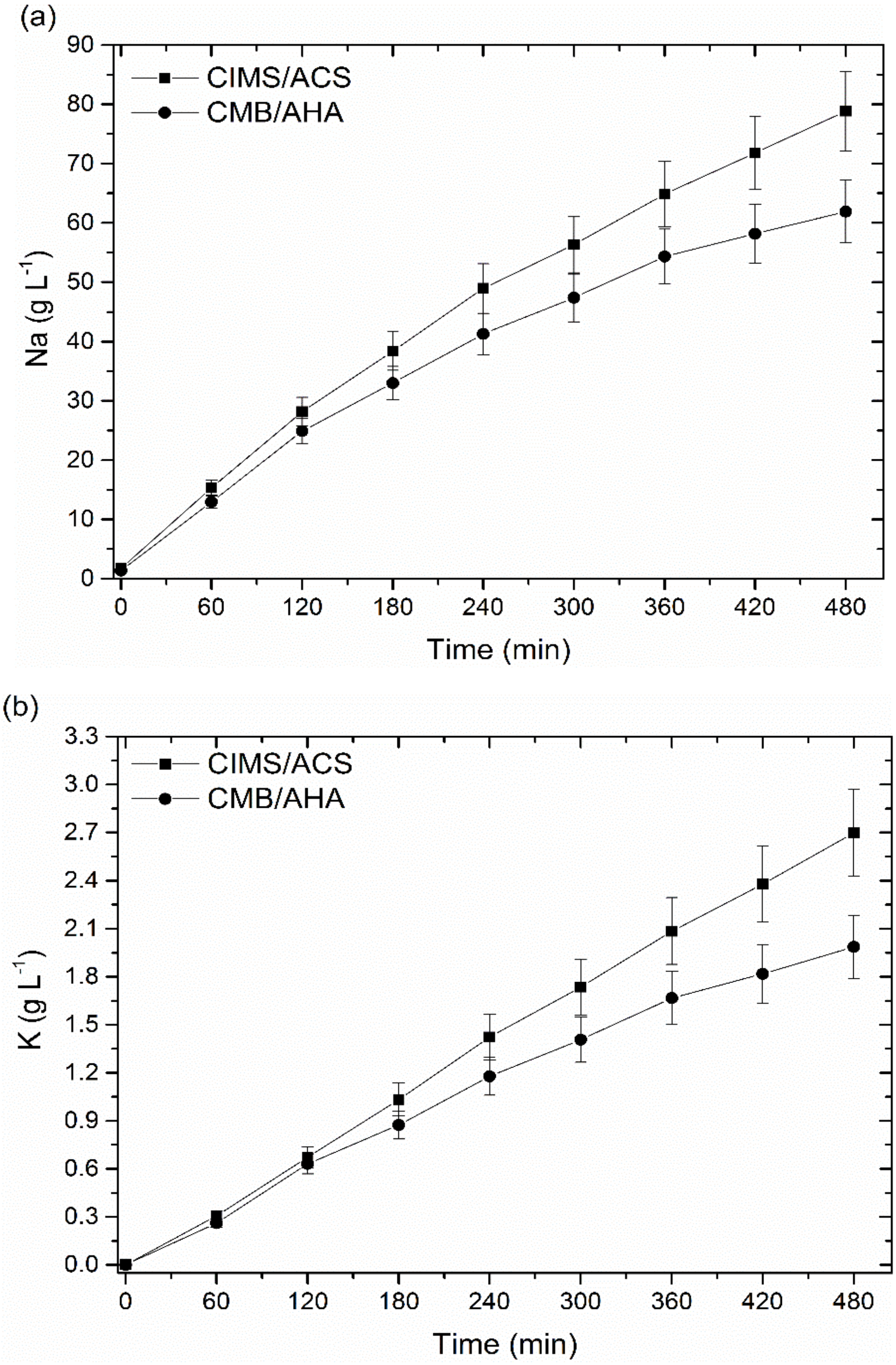

Figure S5.4. Concentration of monovalent ions in the concentrate compartment over 8 hours of demineralization of salty whey permeate with 0.1M NaCl as concentrate at a system voltage of 15 V using two different IEMs: (a) sodium; and (b) potassium.

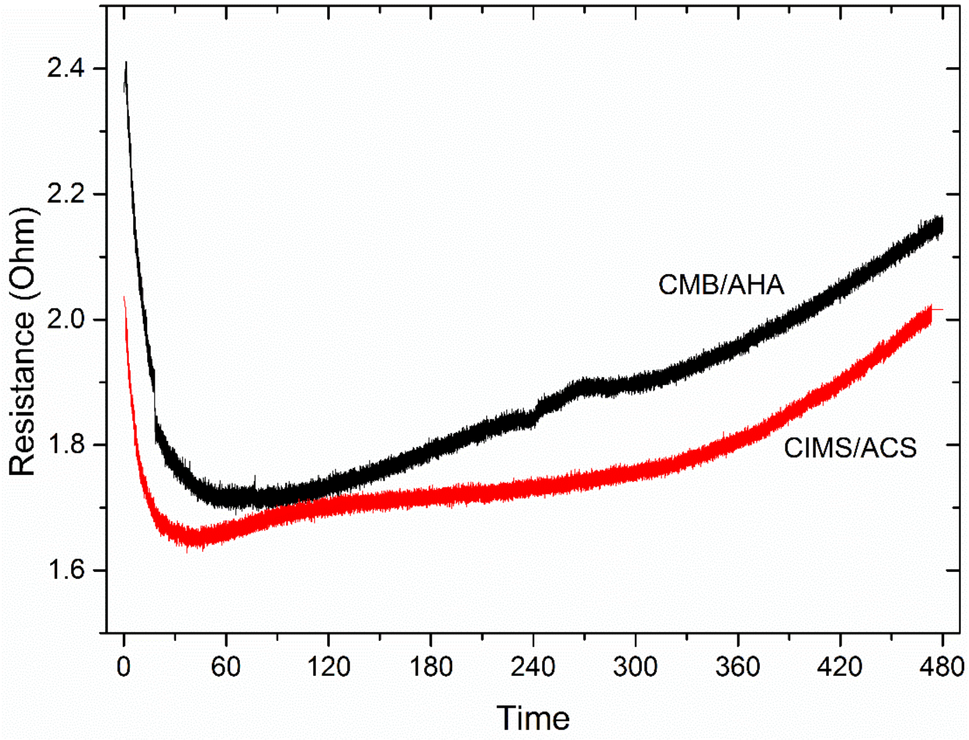

Figure S5.5. Change in the system resistance for monovalent selective (CIMS/ACS) and non-selective (CMB/AHA) membrane pairs over 8 hours of demineralization of salty whey permeate with 0.1M NaCl as concentrate at a system voltage of 15 V.

CHAPTER 6. Pilot Study on the Removal of Lactic Acid and Minerals from Acid Whey Using Membrane Technology

The results of **Chapter 4** successfully demonstrated the ability to minimize the fouling of ion-exchange membranes during the electrodialysis (ED) of acid whey. However, several membrane processes are often combined in industrial applications to either reduce the required membrane area, remove components that can cause fouling, or to reduce the total energy consumption. This chapter explores the possibility of combining pressure driven membranes with ED for the treatment of acid whey.

6.1. Introduction

Acid whey, the by-product of cream cheese and yogurt manufacturing, presents a major disposal issue for the dairy industry. Unlike sweet whey, which is produced during rennet coagulation, acid whey is challenging to dry to powder due to the presence of lactic acid (LA) and high levels of calcium [6]. The lactic acid imparts a sour taste to the final product and also lowers the glass transition temperature of the lactose, which can result in a sticky powder that renders spray drying impossible [6]. Knipschildt & Andersen [197] showed that it was possible to increase the glass transition temperature of acid whey from ~70°C to 95°C, by decreasing the mass ratio of lactic acid to lactose from 0.2 g LA/g lactose to 0.04 g LA/g lactose. Currently, acid whey is concentrated and used as cattle feed, however, this practice is not sustainable as the demand on cream cheese and yogurt keeps increasing. As a result, producing whey powder from acid whey does not only add value to dairy operations by capturing the nutrients present in acid whey (i.e. protein and lactose), it will also provide a more suitable approach to manage the increasing volumes of acid whey.

Both pressure and electrically driven membrane technologies are widely used by the dairy industry due to their ability to fractionate milk and dairy products. In pressure driven membrane processes, a pressure difference is applied to separate high molecular weight components into the retentate and low molecular weight components into the permeate stream. As an example, ultrafiltration (UF) is used to separate milk into proteins and lactose [198]. In addition to separation by size, the separation mechanism in nanofiltration (NF) is also related to electrical charge. For example, NF membranes are able to achieve a greater removal of monovalent anions while retaining divalent anions due to the greater repulsion between the divalent anions and the negatively charged membrane [9]. NF membranes have proven successful for several dairy applications and are widely used in the treatment and concentration of sweet whey to produce whey powder [44]. The removal of ions from the NF retentate can be future increased by utilizing diananofiltration (Dia-NF), where water is added to the feed stream to flush more ions through to the permeate.

In electrically driven membrane processes, such as electrodialysis (ED), an electrical current is used to separate charged ions from uncharged molecules such as lactose and large charged molecules such as whey proteins [99]. The process uses two different types of ion-exchange membranes (IEMs), known as cation exchange membranes (CEM) and anion exchange membranes (AEM). These membranes are arranged alternatively in the ED unit to prevent free migration of ions throughout the process. Arranging the membranes in such a manner creates the three main processing streams, namely: (1) the diluate stream that is demineralized and deacidified; (2) the concentrate stream that accumulates the ions lost by the diluate stream; and (3) the electrolyte stream that carries the electrical current through the electrolyte compartments and protects the electrodes.

Several researchers have proposed the use of membrane technology for acid whey treatment. For example, NF has been investigated at laboratory and pilot scale for separating LA and minerals from acid whey before drying and crystallization. Chandrapala and Chen *et al.* [67] found that at the natural pH of acid whey (4.2-4.5), only 30% of lactate was removed from the acid whey when NF was used. Similar results were observed by Bédas *et al.* [69], who used a semi-industrial scale NF unit to remove 30% lactic acid and 46-60% of the monovalent ions from acid whey. The authors claimed that the dryability of acid whey increased after treatment. Chandrapala *et al.* [25] were unable to improve the lactic acid removal when using diananofiltration (diafiltration factor of 1.5). Chen *et al.* [13] used ED with two cell pairs and a membrane area of 72 cm^2 to treat acid whey permeate. ED is usually terminated at 70% demineralization of the diluate stream to avoid high energy costs [44] and in the work by Chen *et al.* [13], 50% of the lactic acid had been removed from the feed solution at this demineralization level.

In this work, we combine NF and ED to overcome the individual process limitations associated with lactic acid and mineral removal. UF is also used upstream to remove protein from the feed solution which might otherwise foul the downstream NF and ED processes. Kelly and Kelly [132] briefly discuss the possibility of combining these technologies for acid whey treatment. In a recent publication, Markel *et al.* [85] processed nanofiltered acid whey through ED to obtain 70% and 90% demineralized solutions that were used in a bipolar-electrodialysis process for the purpose of adjusting the pH of acid whey. In the work presented here, three different process combinations were examined in a pilot scale setting (See **Figure 6.1**), namely (1) UF+ ED; (2) UF+ NF+ ED; and (3) UF+ Dia-NF+ ED. The use of UF will allow the removal of protein and fat from the feed solution to the NF process thus avoiding membrane fouling and blockage. The experiments were performed in a pilot scale setting. This ensured that outcomes were close to that of a full-scale operation since the acid whey, cleaning chemicals and water supply were taken directly from the full-scale dairy operations. Further, full size spiral wound modules were used for the UF and NF operations.

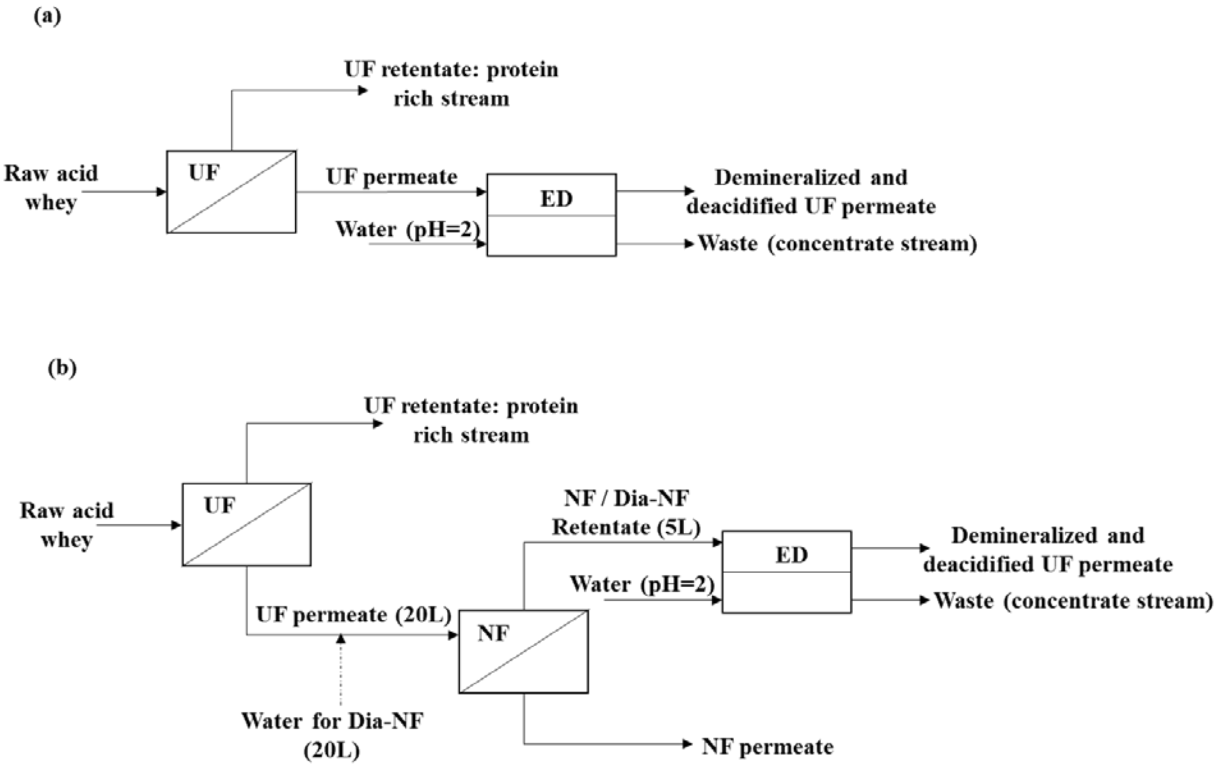

Figure 6.1. Proposed process flow diagrams for (a) ultrafiltration and electrodialysis and (b) ultrafiltration, nanofiltration or nanodiafiltration and electrodialysis. UF = ultrafiltration, NF = nanofiltration, Dia-NF = diananofiltration, and ED = electrodialysis.

6.2. Methods and Materials

6.2.1. Materials

Fresh raw acid whey (**Table 6.1**) was obtained from Tatura Milk Industries Pty. Ltd. (Victoria, Australia). Spiral wound polyethersulfone UF membranes with a molecular weight cut-off of 10kDa were used for the UF process. The NF and Dia-NF processes were performed using a thin-film composite NF spiral wound membrane, with a molecular weight cut-off of 150-300Da for uncharged molecules and a minimum rejection of 98% for 2,000 ppm $MgSO_4$ at 25°C and 7.6 Bar. For the ED process, cation exchange membranes (Neosepta CMB) and anion exchange membranes (Neosepta AHA) were purchased from Astom Co., Ltd. (Tokyo, Japan). These membranes have a wide pH tolerance and thermal stability. An electrolyte solution of 20 g/L sodium sulphate (Na_2SO_4; >99%; Thermo Fisher Scientific Australia Pty. Ltd., Australia) was prepared using purified water (>8.6 MΩ cm; Merck Millipore KGaA, Germany), while mains supply tap water was used as the concentrate stream. The pH adjustment of the concentrate was performed using appropriate amounts of hydrochloric acid (36% HCl; Thermo Fisher Scientific Australia Pty. Ltd., Australia), while the conductivity was adjusted using tap water. For all three processes, an alkaline cleaning step was performed using an industrial cleaning agent (P3-Ultrasil 69, Ecolab, Australia). The cleaning solution was prepared by adding appropriate amounts of the cleaning agent to tap water to achieve a pH of 10.5 ± 0.5.

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6.2.2. Ultrafiltration and Nanofiltration Pilot Scale Unit

The UF and NF pilot plant, model R, was purchased from GEA, Australia. The pilot plant can operate up to 40 bar feed pressure. The feed solution was fed to the recirculation loop through a 60 L balance tank using a Hydra Cell pump type DG10 (Wanner Engineering, Australia). The UF and NF experiments were carried out at room temperature in a mode where the permeate was removed continuously while the retentate was redirected back to the feed tank. A double pipe heat exchanger supplied with cooling water was used to maintain the temperature. The feed pressure was maintained at 6 bar for UF, while the pressure was increased to 20 bar for NF. These values were selected based on the pressure ranges recommended by the pilot plant manufacturer. The total recirculation flowrate was set at 15,000 L/hr to ensure steady performance of the centrifugal pump (type WHP +30/80, SPX Flow Technology, Poland) as the maximum capacity of this pump was 20,000 L/hr.

The raw acid whey was initially processed using UF membranes to generate a protein rich stream as retentate of around fivefold concentration and a lactose stream as permeate (**Table 6.1** and **Figure 6.1**). The UF permeate was further processed through the NF membranes to produce a lactose rich stream (14-16% TS) as retentate (**Table 6.1**). The UF permeate stream was also diafiltrated using the NF membranes. A diafiltration factor of 1 was used, indicating that for every 100L of UF permeate, 100L of water was used. The diafiltration water was added once the UF permeate was processed through NF to 15% total solid. Due to the limited capacity of the feed tank, the diafiltration water was added gradually to avoid overflow. The permeate stream was removed continuously while the retentate stream was recycled back to the feed tank. The process was terminated when the total solids again reached 15%.

6.2.3. Electrodialysis Pilot Scale Unit

The ED experiments were conducted using an FT-TS40 module manufactured by FuMA-Tech GmbH (Bietigheim-Bissingen, Germany). Titanium-iridium coated plasma and stainless steel was used as the anode and the cathode, respectively. Starting with a CMB, a total of ten membrane cell pairs (10 CMB and 10 AHA) were installed between the two electrodes with alternating spacers to form the diluate and concentrate compartments. An eleventh CMB was used in front of the electrode compartment to prevent anion migration towards the electrodes. More information on the disposition of the IEMs could be found elsewhere [105]. The effective area per ion exchange membrane was 100 cm^2. The pilot plant rig was fitted with three centrifugal pumps (MD 70 RZM, IWAKI Europe GmbH, Germany) and three cylindrical polyethylene tanks of 6L each (See **Figure 6.2**). A direct current power supply (Voltage regulator Type 3257.3, Statron Geratetechnik GmbH, Germany) was used to generate the potential difference across the membrane cell pairs. The output voltage ranged between 0-72 V while the current ranged between 0-20 A.

Table 6.1. The composition of raw acid whey and the three different types of solutions fed to the ED unit.

Component	Unit	Raw acid whey	UF permeate	NF retentate (CF=3.5-4)[a]	Dia-NF retentate (CF=3.5-4)[a]
pH	-	4.8 ± 0.2	4.4 ± 0.2	4.5 ± 0.1	4.3 ± 0.2
Conductivity	mS/cm	7.2 ± 0.2	6.9 ± 0.2	8.7 ± 0.4	5.0 ± 0.1
Total Solids[b]	% (m/v)	5.5 ± 0.1	4.0 ± 0.3	15 ± 1	15 ± 1
Total Protein[b]	% (m/v)	0.46 ± 0.05	0.17 ± 0.01	0.38 ± 0.02	0.27± 0.02
Ash[b]	% (m/v)	0.7 ± 0.06	0.55 ± 0.07	1.4 ± 0.05	1.1 ± 0.05
Fat[b]	% (m/v)	0.11 ± 0.01	Undetectable	Undetectable	Undetectable
K	mg/100mL	109 ± 6	104± 7	130 ± 16	11 ± 2
Na	mg/100mL	43 ± 8	43 ± 2	52 ± 9	20 ± 2
Ca	mg/100 mL	114 ± 5	107 ± 7	400 ± 39	413 ± 2
Mg	mg/100 mL	12 ± 0.5	11 ± 0.6	41 ± 5	52 ± 1
P	mg/100 mL	63 ± 2	59 ± 4	198 ± 13	196 ± 3
Cl	mg/100 mL	80 ± 8	75 ± 2	108 ± 8	30 ± 2
Lactate	g/L	6 ± 0.6	5.7 ± 0.3	12 ± 0.6	6 ± 0.5
Lactose	g/L	44 ± 2	35 ± 2	132 ± 9	150 ± 3

[a] CF= concentration factor. [b] Measured in the laboratory of Tatura Milk Industries Pty. Ltd.

The ED experiments were conducted in a constant voltage mode of operation with the voltage set at 24 V. The selected voltage was calculated based on the value used by Chen *et al*. [13] who used similar IEMs for a similar application. 5 L of three different streams were processed through the ED unit in a batch mode: (1) UF permeate; (2) NF retentate; (3) Dia-NF retentate (see **Table 6.1**). The demineralization process was terminated when the final diluate conductivity was 0.7

mS/cm for UF permeate and 2.6 mS/cm for the NF and Dia-NF retentate, which corresponds to a 90% reduction in feed conductivity. It is important to note that the NF and Dia-NF retentate were at least 3.5 times more concentrated than the UF permeate, therefore the selected final conductivity of these solutions were 3.5 times higher than the UF permeate.

The flowrates of the diluate, concentrate and electrolyte solution were set at 200 L/hr as recommended by the manufacturer to minimize concentration polarization effects in the ED unit. The flowrates of all streams were increased to 300 L/hr during the cleaning steps, as this is a common practice used in industry [143]. During the ED experiments the temperature of all streams was maintained at 35 ± 4°C. At the end of the trials, the unit was disassembled and the membranes were stored in purified water (>8.6 MΩ cm; Merck Millipore KGaA, Germany) before membrane characterization was carried out.

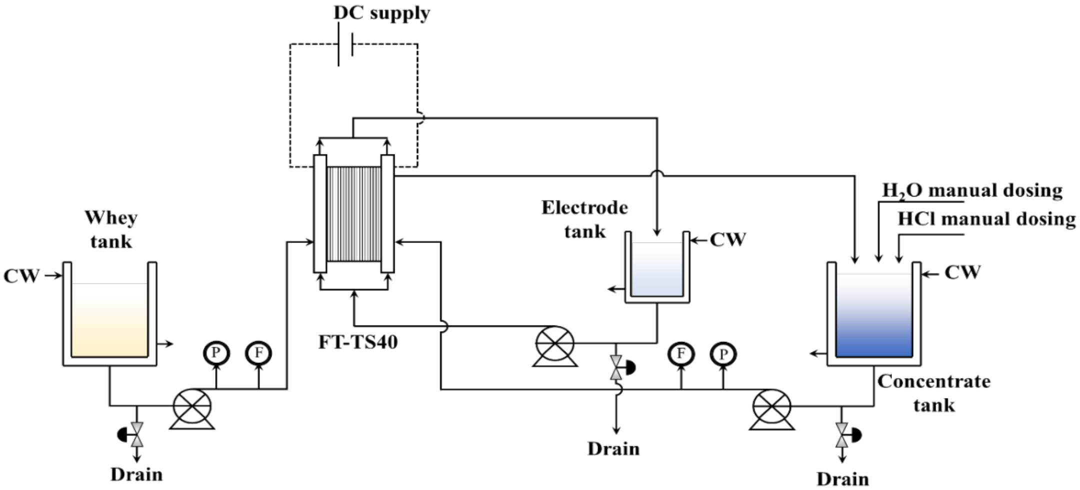


Figure 6.2. A schematic diagram of the electrodialysis pilot plant where CW = cooling water; P = pressure gauge; DC = direct current; and F = flowmeter.

6.2.4. Evaporator and Dryer

The lactose rich stream from the NF+ED process was remixed with the protein-rich retentate stream collected from the UF process to create a solution with 8% protein content. This solution and the original raw acid whey were then processed by evaporation and drying at the CSIRO Food Innovation Centre (Werribee, Australia) to produce powdered products. A two-effect falling film evaporator operating under vacuum was used with the first and second effects operating at 76°C and 62°C, respectively. The combined UF retentate/NF+ED solution was concentrated to 55%

total solid (TS), while the raw acid whey was concentrated to 45% TS. Rotary dryers supplied with hot air at 180°C were used to produce the powders, with outlet air temperature set at 80°C.

6.2.5. Analysis Methods

The pH and conductivity of the ED concentrate tank were measured continuously using a pH and conductivity meter (Mettler-Toledo, Greifensee, Switzerland). The conductivity of the concentrate tank was always maintained below 15 mS/cm by adding a total of 2.5 L of tap water and draining a total of 2.5 L of the concentrate tank content using the drain valve on the tank (see **Figure 6.2**). The adjustment of concentrate conductivity in this manner is a common practice [99] which can reduce the possibility of mineral scaling as demonstrated in **section 4.2.3**. In a similar manner, the pH of the concentrate was maintained below 3 to reduce the possibility of mineral scaling [81]. The conductivity and pH of the diluate stream were measured using a second conductivity meter (Crison Instruments, Greifensee, Switzerland) and pH meter. The demineralization rate (DR), also known as percentage change in conductivity, was calculated based on the conductivity of the diluate tank according to **Eq. 2.4** [191].

$$DR(\%) = \frac{x_{initial} - x_{final}}{x_{initial}} \times 100 = \left(1 - \frac{x_{final}}{x_{initial}}\right) \times 100 \qquad \textbf{Eq. 2.4}$$

The energy consumed during ED was calculated according to **Eq. 3.3**, while the specific energy consumption of the NF and Dia-NF process was calculated using **Eq. 3.10**.

$$E\left({}^{kWh}/_{tonne\ of\ feed}\right) = \frac{V_{cell} \int I dt}{m_{diluate}} \qquad \textbf{Eq. 3.3}$$

$$E\left({}^{kWh}/_{tonne\ of\ feed}\right) = \frac{P_e \times t}{m_{feed}} \qquad \textbf{Eq. 3.10}$$

To calculate the annual energy consumption of NF, Dia-NF and ED, the annual volume of feed supplied to each process was multiplied by the energy required to treat one tonne of feed (calculated using **Eq. 3.3** and **Eq. 3.10**). Taking a basis of 200 tonnes of acid whey per year and considering the concentration factors of UF and NF/Dia-NF processes, 160 tonnes of UF permeate and 40 tonnes of NF and Dia-NF is expected annually.

In the ED process, the current efficiency refers to the ratio between the number of ions transferred and the total charge supplied (**Eq. 3.5**). This parameter is important to assess process efficiency at the selected operating conditions. The current efficiency was calculated using the concentration of the four main cations found in acid whey (sodium, potassium, calcium, magnesium) due to the complexity of the anions present in acid whey [13].

$$\eta(\%) = \frac{F \times v_D\left(\sum z_j \times C_{Dj,initial} - \sum z_j \times C_{Dj,final}\right)}{n \int I dt} \times 100 \qquad \textbf{Eq. 3.5}$$

Samples were taken every 10-15 min from the ED diluate tank and analysed using inductively coupled plasma optical emission spectroscopy (ICP-OES 720ES, Varian, USA) to measure the concentration of calcium (Ca), sodium (Na), magnesium (Mg), potassium (K) and phosphorus (P). High-performance liquid chromatography (HPLC, Shimadzu, Japan) was used to measure lactic acid and lactose concentrations in the collected samples. Ion chromatography (IC-Dionex, ICS-1000, Thermo Fisher Scientific Australia Pty. Ltd., Australia) was used to measure the concentration of chloride (Cl). All samples were filtered and diluted according to the equipment detection limits. Information on the operating parameters of the ICP-OES, HPLC and IC can be found in **Chapter 3**. The ion concentrations were used to calculate the percentage ion removal during NF, Dia-NF and ED processes according to **Eq. 3.2**.

$$Ion\ removal(\%) = \frac{\left(C_{j,initial} \cdot v_{initial} - C_{j,step\ 1} . v_{Step\ 1\ end}\right) + \left(C_{j,step\ 1} - C_{j,step\ 2}\right) . v_{Step\ 2\ end}}{C_{j,initial} \cdot v_{initial}}\ x\ 100 \qquad \textbf{Eq. 3.2}$$

The thickness of the IEMs was measured using a Digimatic Micrometer (Mitutoyo, Japan). The membranes were first wiped dry using Kimwipe tissues (Kimtech, Australia). Nine random measurements were taken for selected membranes and the average thickness values are reported. Fourier Transform Infrared (FT-IR, PerkinElmer Spectrum 100, North America) was used to compare the chemical structure and the surface groups of the used and fresh IEMs. Eight scans for wavelengths between 800-2000 nm were completed per sample and the averaged value is presented here. Membrane surface images were captured using Scanning Electron Microscope (SEM, FEI Quanta 200 ESEM FEG, Thermo Fisher Scientific, USA). Information on membrane preparation for FTIR and SEM could be found in **Chapter 3**. Images of the dried powder was taken using an optical microscope (Prism Optical, SciTech, Australia).

The UF, NF and Dia-NF experiments were repeated at least 5 times while the ED experiments were repeated at least twice. The data is presented in this study as the average value ± standard deviation.

6.3. Results and Discussion

6.3.1. Demineralization and Deacidification of Acid Whey

The concentration of lactic acid in the UF permeate was similar to the raw acid whey (**Table 6.1**), as expected due to the difference between the UF pore size and the lactate anion. However, a significant difference in the lactic acid concentration was noticed between the NF and Dia-NF retentates. The Dia-NF process assisted in removing more lactic acid and monovalent cations. As shown in **Figure 6.3**, 71% and 48% of the lactic acid and total cations were removed in the Dia-NF process, while only 42% and 36% were removed using the NF process, respectively. Nevertheless, the degree of lactic acid removal in both processes is higher than the values reported by both Chandrapala & Chen *et al.* [67] and Chandrapala *et al.* [25]. This may have related to the use of spiral wound membranes rather than flat sheet laboratory coupons, which could have led to differences in bulk concentration and in concentration polarisation along the module length. Furthermore, the combination of Dia-NF and ED resulted in the greatest removal of lactic acid (**Figure 6.3**). The lactic acid to lactose ratio (**Table 6.2**) in all three products of the ED process was below 0.04 g LA/ g Lactose, indicating that the solution should not produce a sticky powder [197].

The percentage change in conductivity for all three different feeds processed through the ED unit is shown in **Figure 6.4**. The Dia-NF retentate required the shortest time to obtain the target final conductivity (0.7 mS/cm (UF permeate) and 2.6 mS/cm (NF and Dia-NF retentate)), reflecting the lower initial conductivity. Although the percentage removal of monovalent ions in both UF+NF+ED and UF+Dia-NF+ED was above 90%, the percentage removal of divalent ions was lower due to their larger hydraulic diameter which results in lower diffusion/migration rates in both pressure and electrically driven membrane processes [81, 199]. Interestingly, no Mg was removed within experimental error when Dia-NF was used. Furthermore, the total removal of calcium was lower for the UF+Dia-NF+ED process compared to the two other processes. This can be a result of the short processing time during the ED step for the UF+Dia-NF+ED process thus not allowing enough time for Ca and Mg migration. Furthermore, since the NF and Dia-NF retentates were 3.5-4 times higher in concentration compared to UF permeate, concentration polarization on the IEM surfaces can result in lower divalent ion removal. Nevertheless, retaining greater amounts of Ca and Mg in the diluate stream has nutritional benefits in comparison to Na [84].

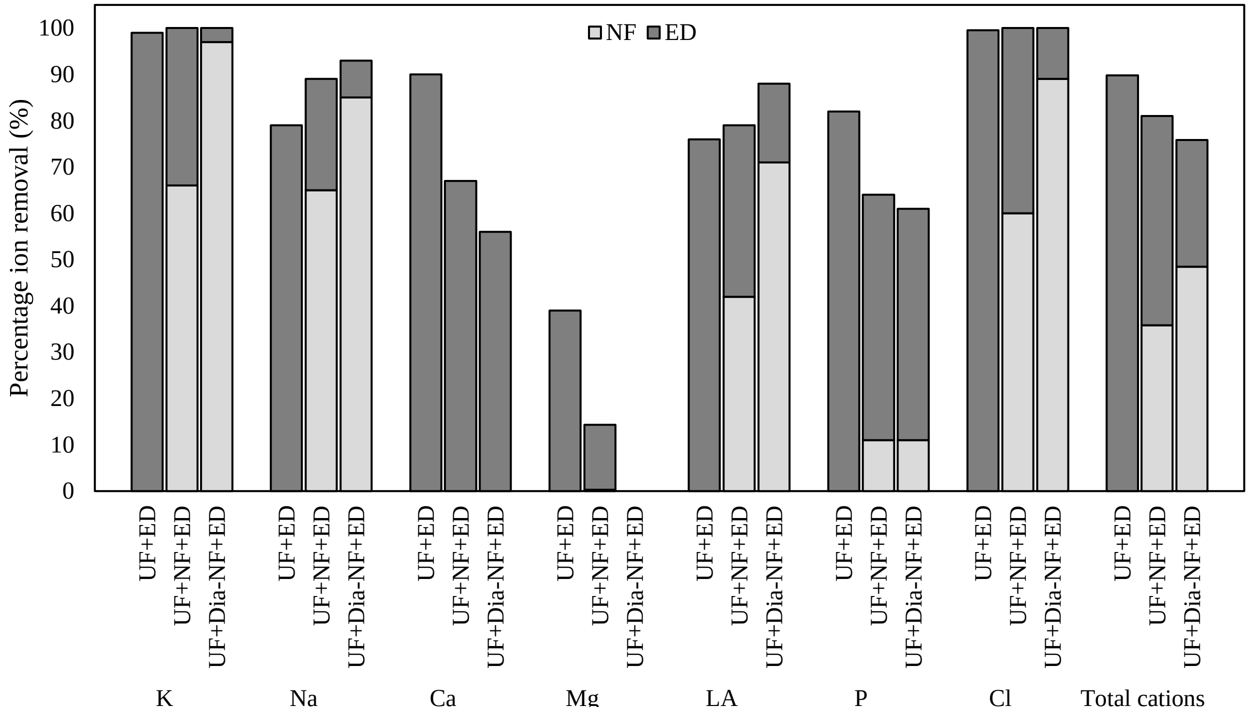


Figure 6.3. Percentage removal of different components of acid whey. The total cations were calculated based on both monovalent (K and Na) and divalent (Ca, Mg) cations.

The pH of the diluate dropped during the ED process (**Figure 6.4**); such a behaviour was also noticed by Dufton *et al.* [106]. This is predicted to be the result of several phenomena. Under the application of an electrical current, the lactate ions will migrate to the concentrate compartment and pair with the available protons (the concentrate pH is always maintained below 3). The migration of lactate reduces the lactate concentration in the diluate stream, favouring the dissociation reaction of lactic acid to generate more lactate and protons and thus reducing the pH of this stream [13]. Further, since the concentrate compartment was always maintained at a pH below 3 by the addition of HCl, the difference in proton concentration between concentrate and diluate can also result in Fickian diffusion of protons from the concentrate stream to the diluate stream. This hypothesis can be supported by the fact that the concentrate pH always increased during experiments indicating loss of H^+. Finally, the shift in diluate pH could also be a result of water splitting during the experiments [13, 106]. While the applied current density was below the estimated limiting current density at the commencement of each experiment, the value of the limiting current density is expected to fall during the experiment as demineralization takes place.

The current efficiency in the ED processes using UF permeate and NF retentate were around 81% (See **Table 6.2**), comparable to the values reported by Chen *et al.* [13]. This indicates a good system performance with little water splitting. However, a current efficiency of 103 ± 1% was obtained for the Dia-NF retentate. Values larger than 100% have been reported by several researchers such as Alhéritière *et al.* [188] and were explained to be a result of either Fickian diffusion or convective transport through the membranes.

Table 6.2. Final diluate compositions following electrodialysis.

Component	Unit	Demineralized and deacidified UF+ED	Demineralized, deacidified and concentrated (CF=3.5-4) [(a)]	
			UF+NF+ED	UF +Dia-NF+ED
pH	-	3.9 ± 0.1	3.8 ± 0.1	4.2 ± 0.1
Conductivity	mS/cm	0.71 ± 0.03	2.63 ± 0.03	2.6 ± 0.05
K	mg/100mL	0.9 ± 0.7	1.9 ± 0.4	1.2 ± 2
Na	mg/100mL	9 ± 4	16 ± 2	10 ± 2
Ca	mg/100 mL	12 ± 0.5	132 ± 7	177 ± 5
Mg	mg/100 mL	7 ± 0.3	35 ± 2	45 ± 3
P	mg/100 mL	11 ± 1	70 ± 6	92 ± 5
Cl	mg/100 mL	Not measured	1.2 ± 0.7	0.5 ± 0.2
Lactate	g/L	1.4 ± 0.1	4.3 ± 1	2.6 ± 0.5
Lactose	g/L	36 ± 3	134 ± 5	150 ± 3
Lactic acid/ lactose ratio	g/g	0.038 ± 0.003	0.032 ± 0.002	0.017 ± 0.002
ED Current efficiency	%	82 ± 1	81 ± 2	103 ± 1

[a] CF= concentration factor

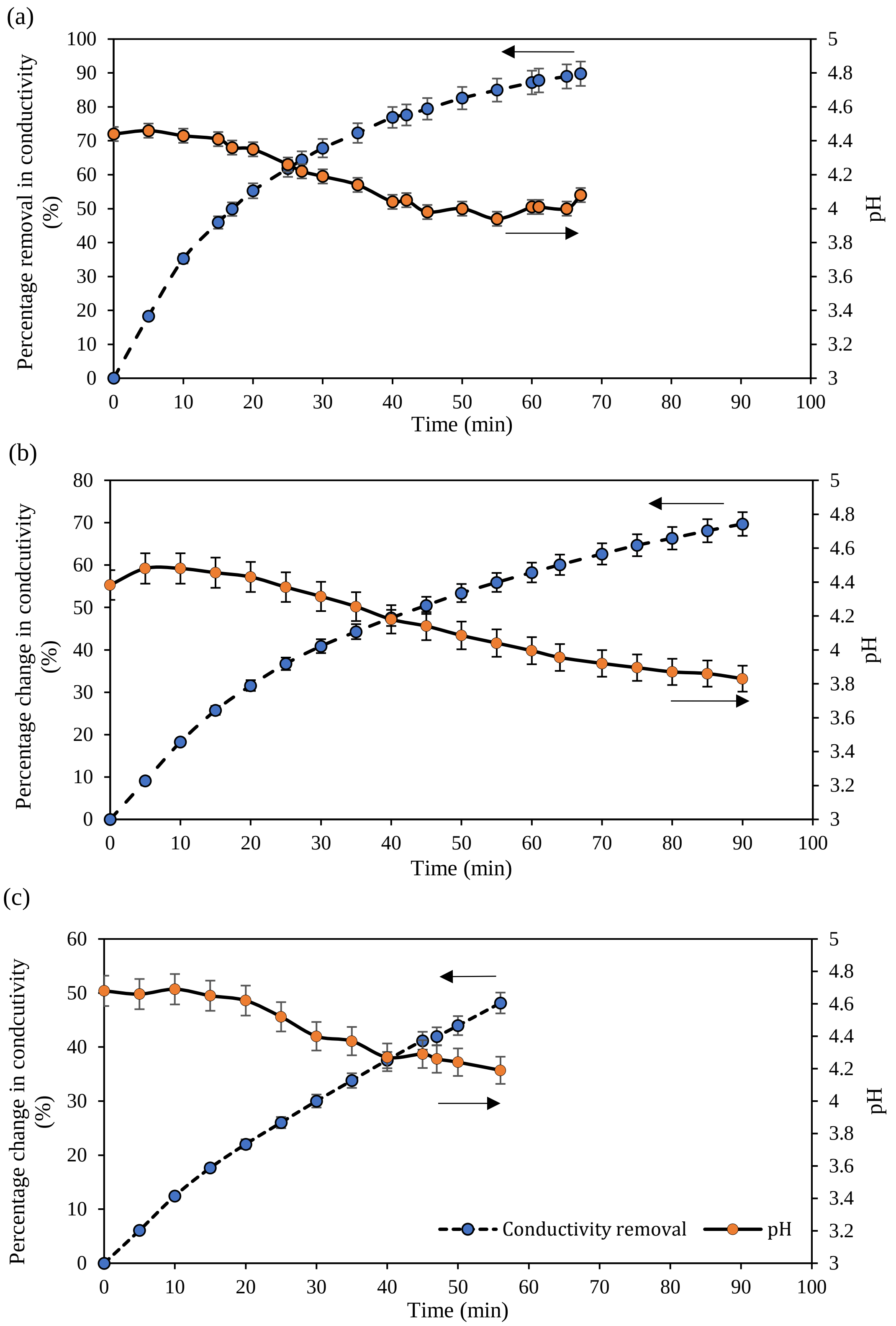


Figure 6.4. Change in diluate conductivity and pH as a function of time during electrodialysis of (a) UF permeate, (b) NF retentate, and (c) Dia-NF retentate.

6.3.2. Energy Consumption

The energy required for the ED step of the UF permeate (7.5 kWh/ tonne of feed) was lower than the energy required for the NF retentate (14.5 kWh/ tonne of feed), see **Figure 6.5 (a)**. The higher feed concentrations result in higher energy consumption due to the greater number of ions that must be moved per tonne of feed [86]. Diafiltration reduces the ionic concentrations, thus reducing this energy demand. Thus, the energy consumption for ED of this stream was lower (7.8 kWh/tonne of feed).

Figure 6.5 (b) shows the energy costs for the three processes, based on the processing of 200 tonnes per annum of acid whey. The energy cost of the UF process is not included as this step is common between all three proposed processes. The energy consumption of the NF step is calculated to be 10 kWh/tonne of feed processed through the unit (**Eq. 3.10**) which equates to 1600 kWh/year. This energy cost doubles to 3200 kWh/year for the Dia-NF, as double the volume is processed. Similarly, the annual energy consumed for the UF permeate through the ED unit is higher than the NF and Dia-NF retentate due to its greater volume, while this energy demand is smallest for Dia-NF due to the small volume and low ionic concentration. For the process involving UF and ED only, the final product is 3.5 to 4 times more dilute than the NF and Dia-NF retentate, so there is an additional energy cost for concentrating this product stream prior to evaporation. The expected cost for this concentration step is also shown in **Figure 6.5 (b)** (calculated using **Eq. 3.10**, assuming that the same NF unit is used for this purpose). In addition to the lower annual energy demand of the NF and Dia-NF retentate, the area of the IEMs required to achieve the desired levels of demineralization will be significantly smaller for these processes compared to the UF permeate. Considering that the price of ED membranes is significantly higher than that of pressure driven membranes, this will lead to lower capital costs. When looking at the total energy consumed, NF retentate has the lowest total energy consumption comparing to the other two types of feed (**Figure 6.5 (b)**). Dia-NF is advised if high levels of lactic acid removal is necessary, however, due to the large volumes of permeate, it may be useful to consider the use of reverse osmosis (RO) to recover high purity water that can be re-used in the Dia-NF process.

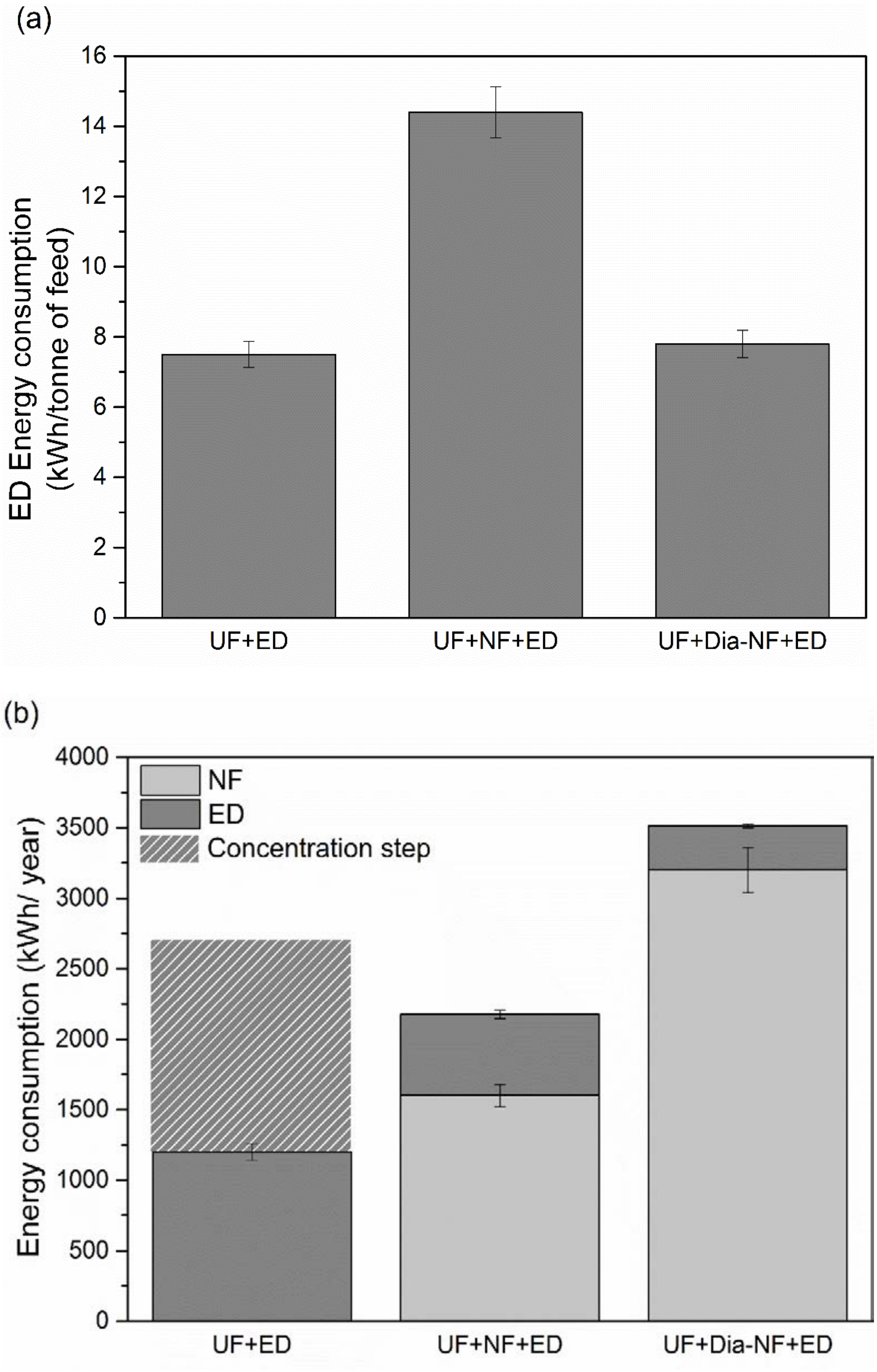


Figure 6.5. Energy consumption of the three proposed processes. (a) Energy consumption of the ED process per tonne of feed. (b) Annual energy consumption base on 200 tonnes of acid whey per year.

6.3.3. Ion-Exchange Membrane Analysis

No visual fouling was observed on the surface of the membranes when the ED unit was disassembled at the end of the trials. This was somewhat expected as the protein content of the feed solutions was low and the concentrate solution was maintained at a pH below 3 thus eliminating mineral scaling as observed in **Chapter 4.**

The average thicknesses of the used CMB membranes were similar to the fresh membrane (**Figure 6.6 (a)**), expect for the CMB membrane facing the cathode compartment. When FTIR analysis was performed on these membranes, it was found that the absorbance spectrum for the cathode CMB was also different when compared to the other used membranes and the fresh membrane (**Figure 6.7 (a)**). Furthermore, SEM imagines (**Figure 6.8 (c & d)**) showed cracks and deformation on the surface of the cathode CMB. This suggests that damaging electrode reactions may have occurred. An alternate electrode material to the stainless steel used here may alleviate this issue.

The AHA membranes neighbouring the anode and cathode electrode were slightly thicker than the fresh membranes and the other AHA membranes after use (**Figure 6.6 (b)**). Further, all used AHA membranes were darker in color than the fresh materials (**Figure 6.7 (b)**). AHA membranes are known to incorporate charged amine and/or amide groups, such as $-NH_3^+$, $-NRH_2^+$, NR_2H^+, and $-NR_3^+$. Maillard reactions may take place between these fixed charges and the lactose present in acid whey, producing N-containing polymers known as melanoidins, which are brown in color [200]. While Maillard reactions are usually favoured above 140°C, the reaction can still take place at temperatures as low as 0°C but at a slower rate [201]. In addition, Choi and Moon [202] suggest that the temperature of the IEMs may be higher than the bulk solutions when subjected to electrical fields and this may have accelerated the reaction rate. Maillard reactions can be observed by the formation of new peaks in the FTIR spectrum between 1630 and 1650 cm^{-1} (C=N stretching) [203] as is indeed observed for the used membranes in **Figure 6.7 (b)**. However, the increased absorbance in this region could also occur through adsorption of proteins within the membrane, which would increase the Amide I (1600 -1700 cm^{-1}) and Amide II peaks (1500 -1600 cm^{-1}). Choi and Moon [202] and Zabolotskii *et al*. [204] indicate that under the application of strong electrical fields, the quaternary ammonium groups in anion exchange membranes can react with OH^- ions produced as a result of water splitting to form weakly basic (secondary and ternary) amino groups.

This can be observed by the introduction of a new peak in the region 1020-1200 cm^{-1} as is indeed observed in **Figure 6.7 (b)**. Regardless of these physical and chemical changes, SEM images (**Figure 6.8 (f)**) did not show any structural damage.

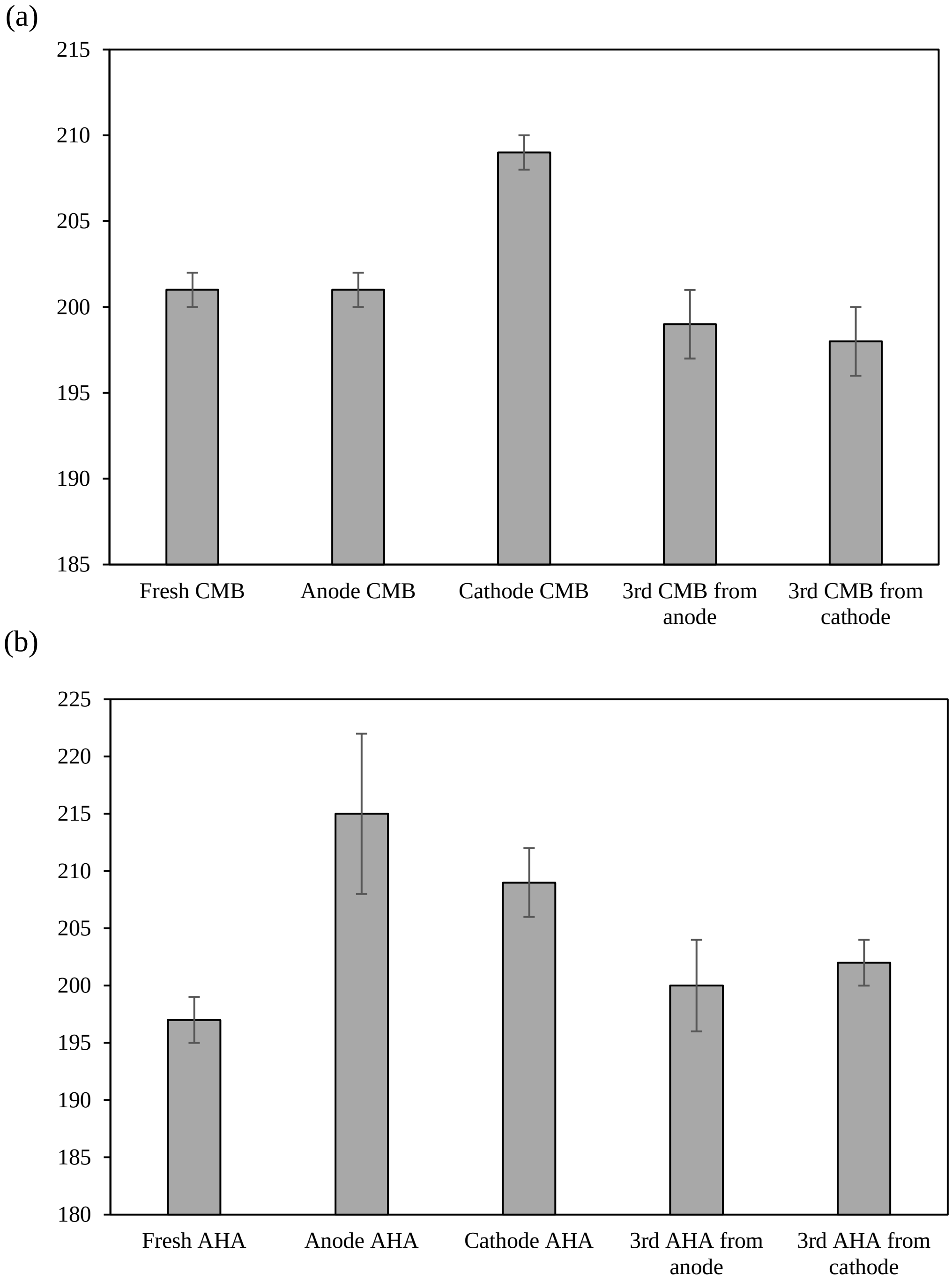


Figure 6.6. Average membrane thickness for randomly selected: (a) CMB membranes and (b) AHA membranes.

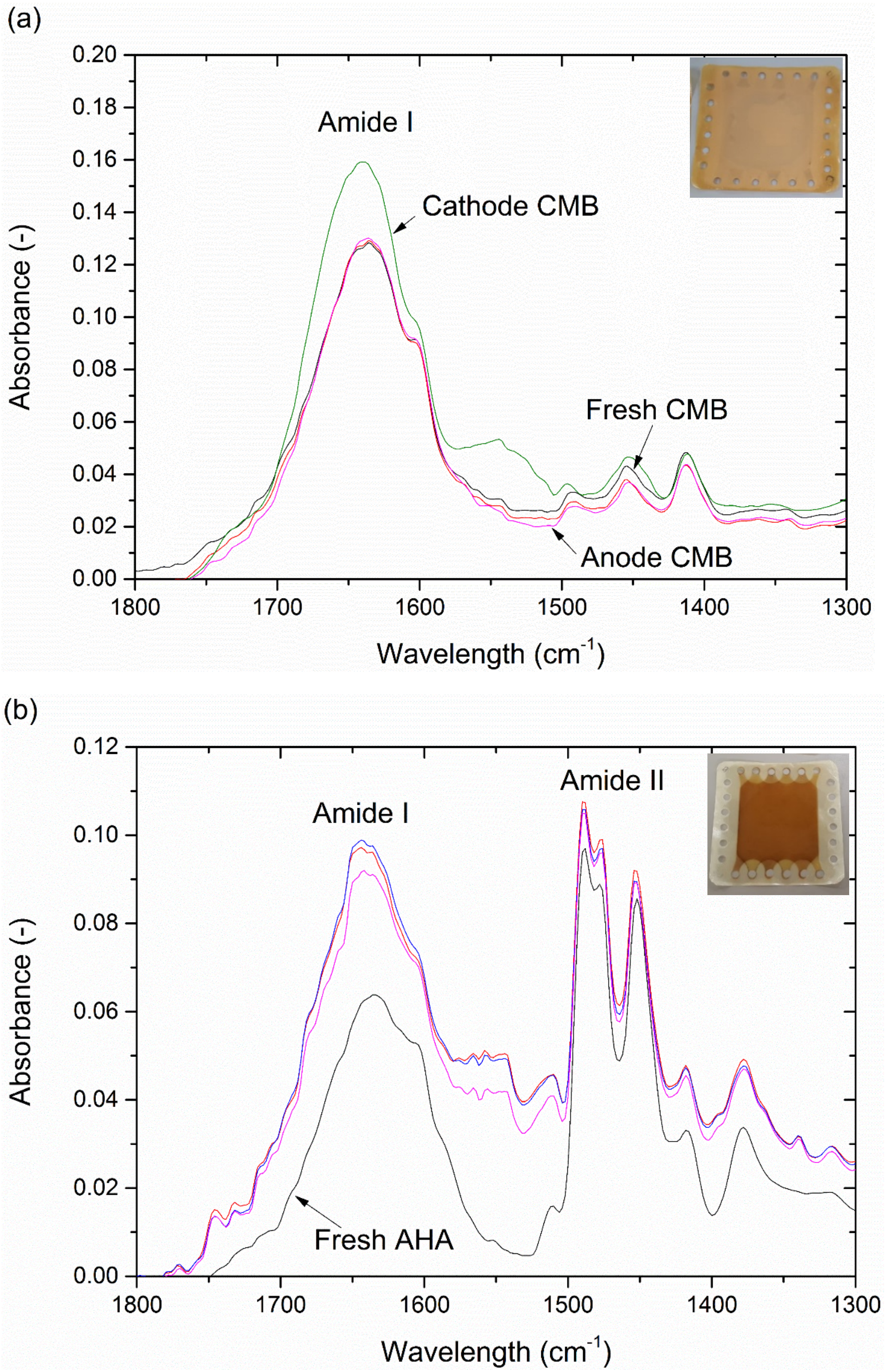


Figure 6.7. FTIR analysis for (a) CMB and (b) AHA membranes used in the electrodialysis trials.

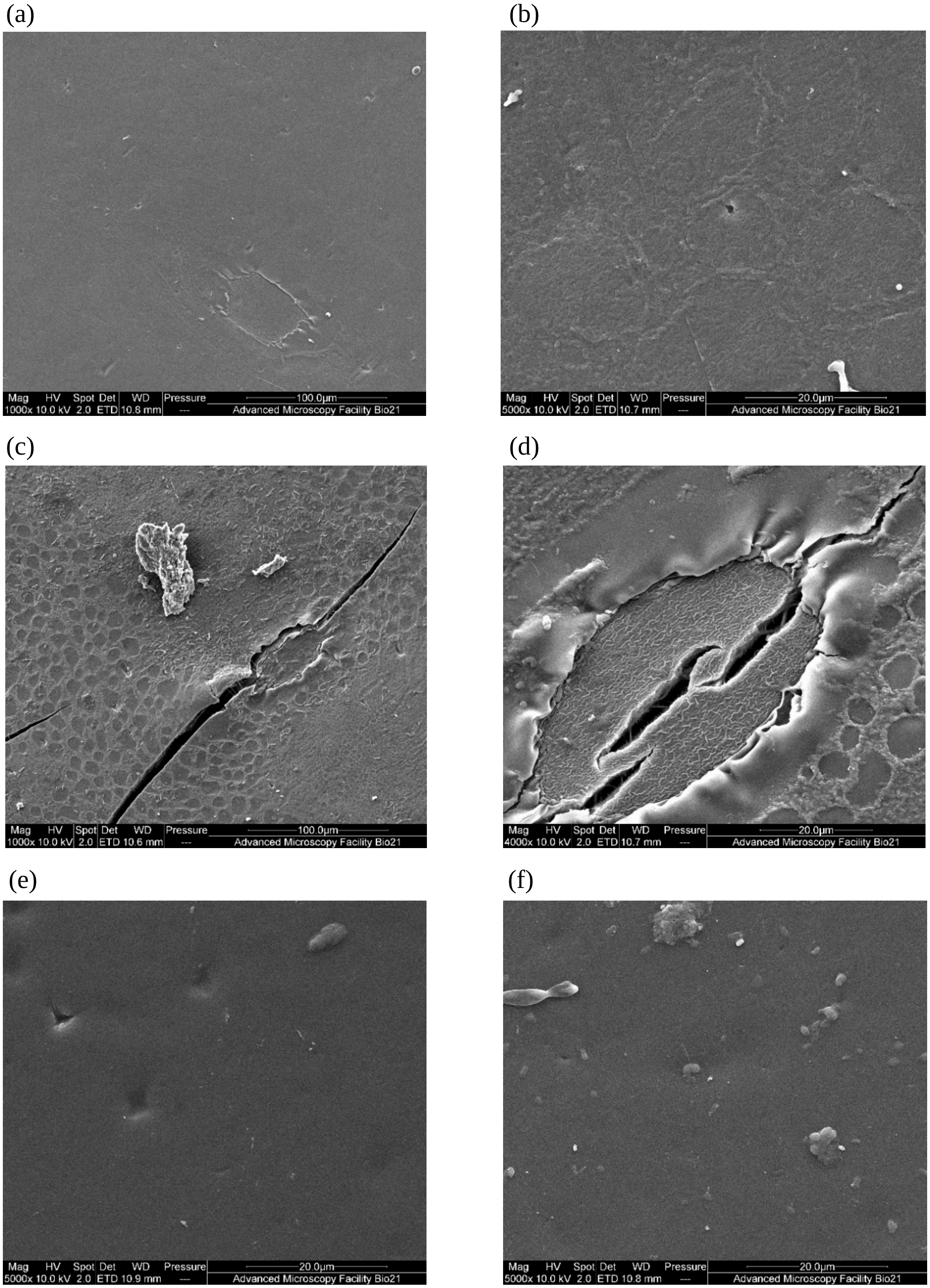


Figure 6.8. SEM images of the membrane surface for (a) fresh CBM, (b) used CMB, (c & d) CMB facing cathode, (e) fresh AHA, and (f) used AHA.

6.3.4. Acid Whey Powder Characterization

When the raw acid whey was dried, it stuck to the surface of the dryer (**Figure 6.9 (b)**) as anticipated due to the low glass transition temperature of the lactose causing an amorphous crystal phase to form (**Figure 6.10 (b)**). The high levels of lactic acid and calcium are also known to restrict water mobility and removal [6] resulting in a powder of high moisture content (**Table 6.3**).

The lactose rich stream from NF+ED process was remixed with the rich UF protein retentate to create a solution with 8% protein content, which is similar to the protein content of the raw acid whey. This solution could readily be dried without the formation of sticky deposits (**Figure 6.9 (a)**) and with a lower moisture content (**Table 6.3**). Furthermore, the optical microscope photos (**Figure 6.10 (a)**) show clear tomahawk-like lactose crystals in the powder produced from NF+ED processes [205]. The final ash content of the NF+ED powder was three times lower than the raw acid whey, providing a product that could meet specifications for 70% demineralised powder, referred to as D70.

Table 6.3. Characteristics of the produced acid whey powders.

Component	Unit	Raw acid whey powder	NF+ED treated powder
Moisture content [a]	%	4	2.5
Ash content [a]	%	12	4
Lactic acid [a]	g/g of powder	Unmeasured	0.026

[a] Analysis performed by an external laboratory

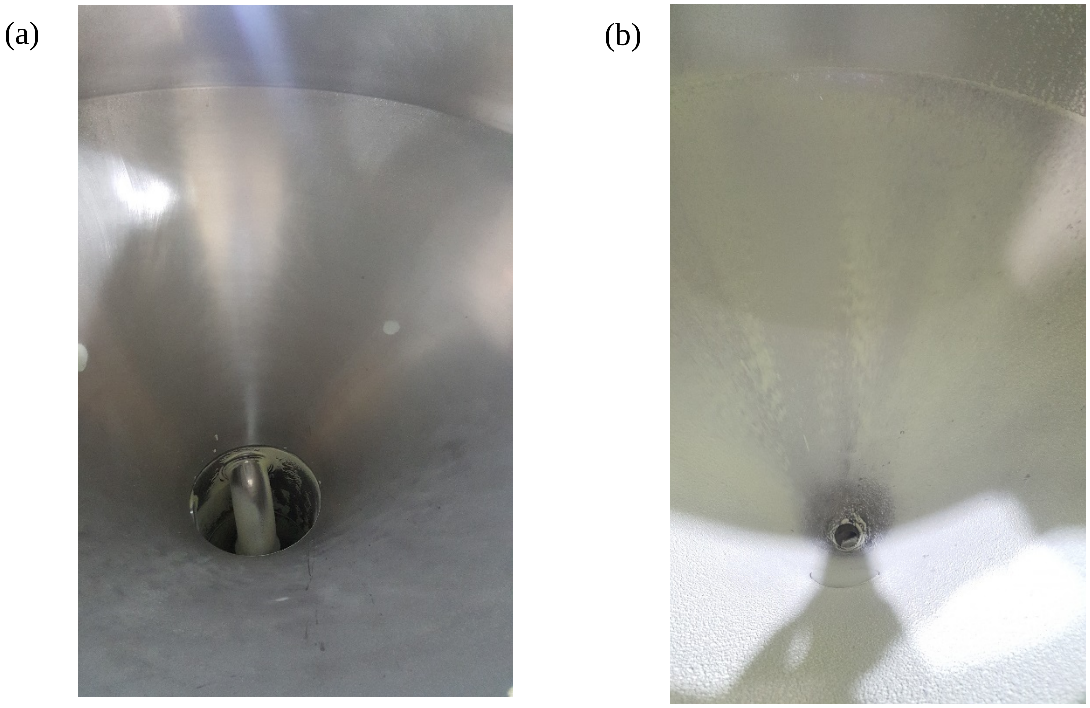


Figure 6.9. Dryer walls after the production of (a) UF retentate and NF+ED treated powder and (b) raw acid whey powder.

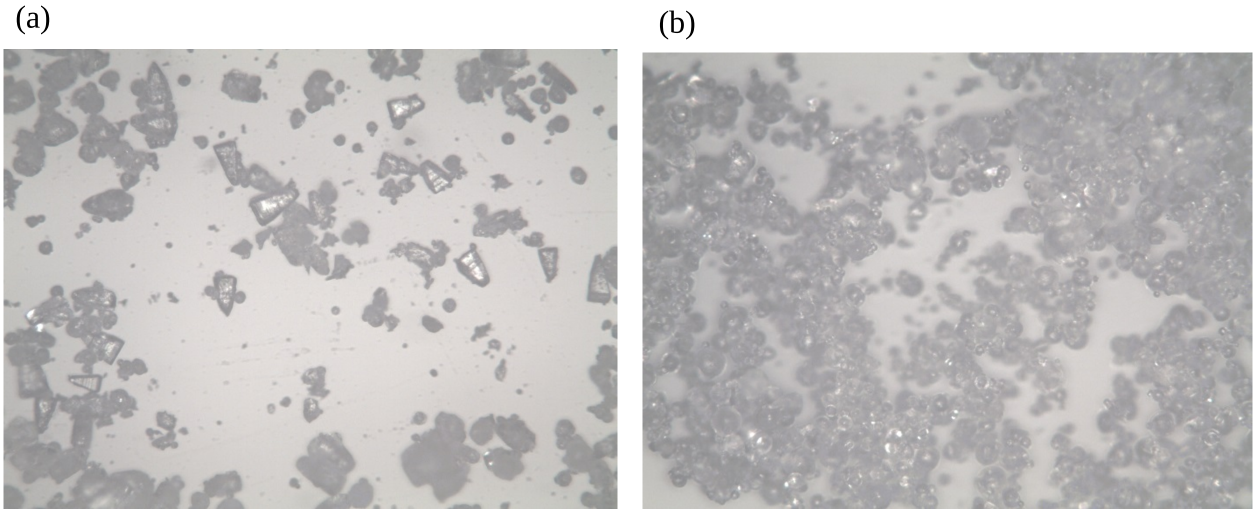


Figure 6.10. Optical microscope photographs (10x) of (a) UF retentate and NF+ED treated powder and (b) raw acid whey powder.

6.4. Conclusions

This work has shown the feasibility of combining different membrane processes to produce demineralized whey powders from acid whey, with a special focus on the ED process. The ability to produce consumable products from acid whey not only increases profitability but also reduces waste, leading to a more sustainable dairy industry. A pilot scale ED with a total membrane area of 0.1 m^2 was successfully used to reduce the conductivity and lactic acid levels of UF permeate, NF retentate and Dia-NF retentate. The concentrate compartment was maintained at a pH below 3 to control mineral scaling and to increase the lactic acid transfer. While this addition of acid might be considered as unsustainable, the amount used was negligible when compared to the cleaning chemicals that would be required to remove the mineral scaling if this practice had not been used. Similarly, the use of a relatively mild alkaline cleaning step (pH 10.5) minimised the use of sodium hydroxide, which has a significant embodied energy demand.

The maximum levels of lactic acid removal, 88%, was achieved when Dia-NF was combined with ED. However, the energy cost of the Dia-NF step was double the cost of standard NF. The annual energy consumed during ED was the greatest for the UF permeate due to the large feed volume (1200 kWh/year for an annual volume of 200 tonnes of acid whey). This large feed volume would also result in a significantly larger capital cost, given the high cost of ion-exchange membranes, relative to pressure driven membranes. The powder produced from combining the NF+ED lactose rich stream with the rich UF protein retentate was non-sticky, with a moisture content of 2.5%. Although, the combination of UF+NF+ED was successful in reducing the levels of lactic acid and had the lowest annual energy consumption, the best process combination should be selected taking into consideration the capital investment, the operating cost and the facilities available on the manufacturing site.

6.5. Acknowledgments

This research was supported under Australian Research Council’s Industrial Transformation Research Program (ITRP) funding scheme (Project Number IH120100005). The ARC Dairy Innovation Hub is a collaboration between The University of Melbourne, The University of Queensland and Dairy Innovation Australia Ltd. Funding support and provision of acid whey by Bega Cheese Limited is also gratefully acknowledged.

CHAPTER 7. Recovery of Lactic Acid from a Salt Solution

The treatment of acid whey using membrane technology, as described in the previous chapters, generates waste streams that contain lactic acid which has value as a food preservative and in the production of biodegradable plastics. Recovering lactic acid from the waste streams can thus add more value to the acid whey treatment process.

7.1. Introduction

Lactic acid is an organic acid made of 2-hydroxycarboxylic acid with a chiral carbon atom. It is used in the food, pharmaceutical, leather, textile, and chemical industries. Lactic acid is commercially produced using two available methods, namely hydrolysis of lactonitrile or microbial fermentation. The chemical synthesis pathway is costly as several distillation steps are used. On the other hand, the production of lactic acid from microbial fermentation is economically attractive due to the possibility of using low-cost raw materials.

An unutilized source of lactic acid is the waste stream (nanofiltration permeate or electrodilaysis concentrate) generated from the treatment of acid whey. In addition to lactic acid, this waste stream contains large amounts of minerals found originally in acid whey. The purity of lactic acid is reduced by the presence of these minerals, thus limiting its applications. The recovery of lactic acid from acid whey is not studied or found in the literature. The closest concept is the recovery of lactic acid from fermentation broths where the solution is made of sodium lactate, glucose and yeast extract with low concentration of other charged ions [171-174].

Pressure driven membranes, such as nanofiltration (NF), are known for their ability to separate components based on size and charge. As a result, several researchers have investigated the use of NF membranes for the separation of lactic acid and salt [175, 176]. However, both lactic acid and salt tend to pass through the membranes, since NF membranes have a cut-off between 200-1000 Da. When considering the use of reverse osmosis (RO) membranes, different researchers have investigated the use of these membrane for organic acid separation as presented in **Table 2.3**.

Electrically driven membranes, such as electrodialysis (ED), have also been investigated for the purification of lactic acid from fermentation broths [101, 171, 206, 207]. Thang *et al.* [182] are one of the few researchers that investigated the recovery of lactic acid from a complex solution containing high concentrations of charged components. The authors showed that operating the ED unit at low pH assisted in retaining the lactic acid in the diluate stream in the first 80 min of the process. Although the authors did not report the purity of the lactic acid, their results demonstrated that sulfate and divalent cations were not fully removed from the diluate stream.

This chapter aimed at recovering lactic acid from the waste streams generated from the acid whey treatment process (i.e. NF permeate and ED concentrate) using either loose RO membranes or an ED process. KCl was selected as the main salt due to the higher concentration of K in acid whey when compared to Na. The aim of the RO experiments was to permeate the lactic acid through the membrane while retaining the salts. Therefore, different factors affecting the permeation of lactic acid through the loose RO membranes were investigated. On the other hand, the ED experiments used a solution containing KCl and aimed at retaining the lactic acid in the diluate stream. The effect of different mass ratios between lactic acid and KCl were examined. In addition, the effect of the presence of other salts on the retention of lactic acid was evaluated by the addition of NaCl to the diluate stream.

7.2. Results and Discussion

7.2.1. Loose Reverse Osmosis Membranes

Three loose RO membranes, namely LE-4040 (Filmtec, USA), XLE-2521 (Filmtec, USA) and a sample provided by GE (USA) were used in this study. All three membranes were hydrophilic, with contact angles lying within the range of 48°-76° (**Figure 7.1**).

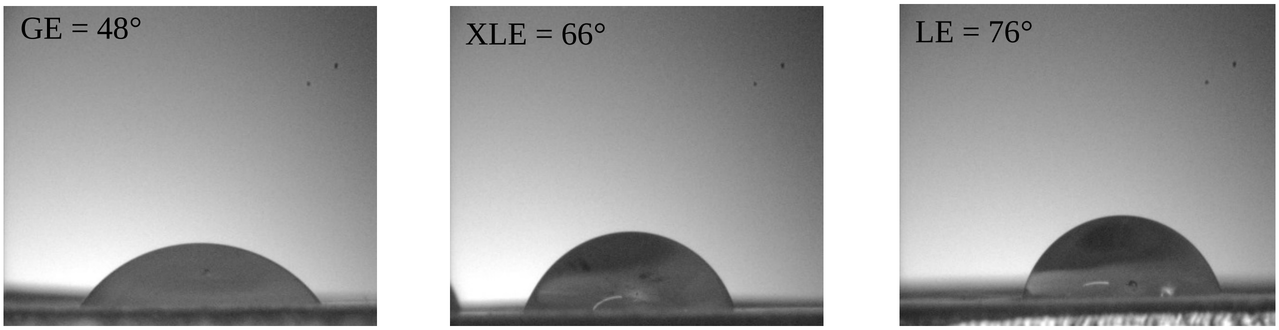


Figure 7.1. Contact angle of the loose RO membranes used in this study.

To ensure that concentration polarization did not contribute to the results reported in the coming sections, the feed pump was operated at 20 Hz and 25 Hz which is equal to a cross flow velocity (CFV) of 10.6 m/s and 12.8 m/s, respectively. The permeate flux was measured at different applied pressures for a solution of 0.9 ± 0.1 g/L of lactic acid with no added KCl (**Figure 7.2**). No significant difference was observed for the permeate flux obtained at the two different CFVs, indicating that concentration polarization did not affect the system. It is observed that the flux of XLE membrane was lower than the GE membrane (**Figure 7.2**). This could be partially due to the greater hydrophilicity of the GE membrane (**Figure 7.1**) thus allowing more water to pass through the membranes. It may also reflect a 'looser' structure, leading to lower salt rejection. Unfortunately, insufficient information was provided by GE to make such a conclusion.

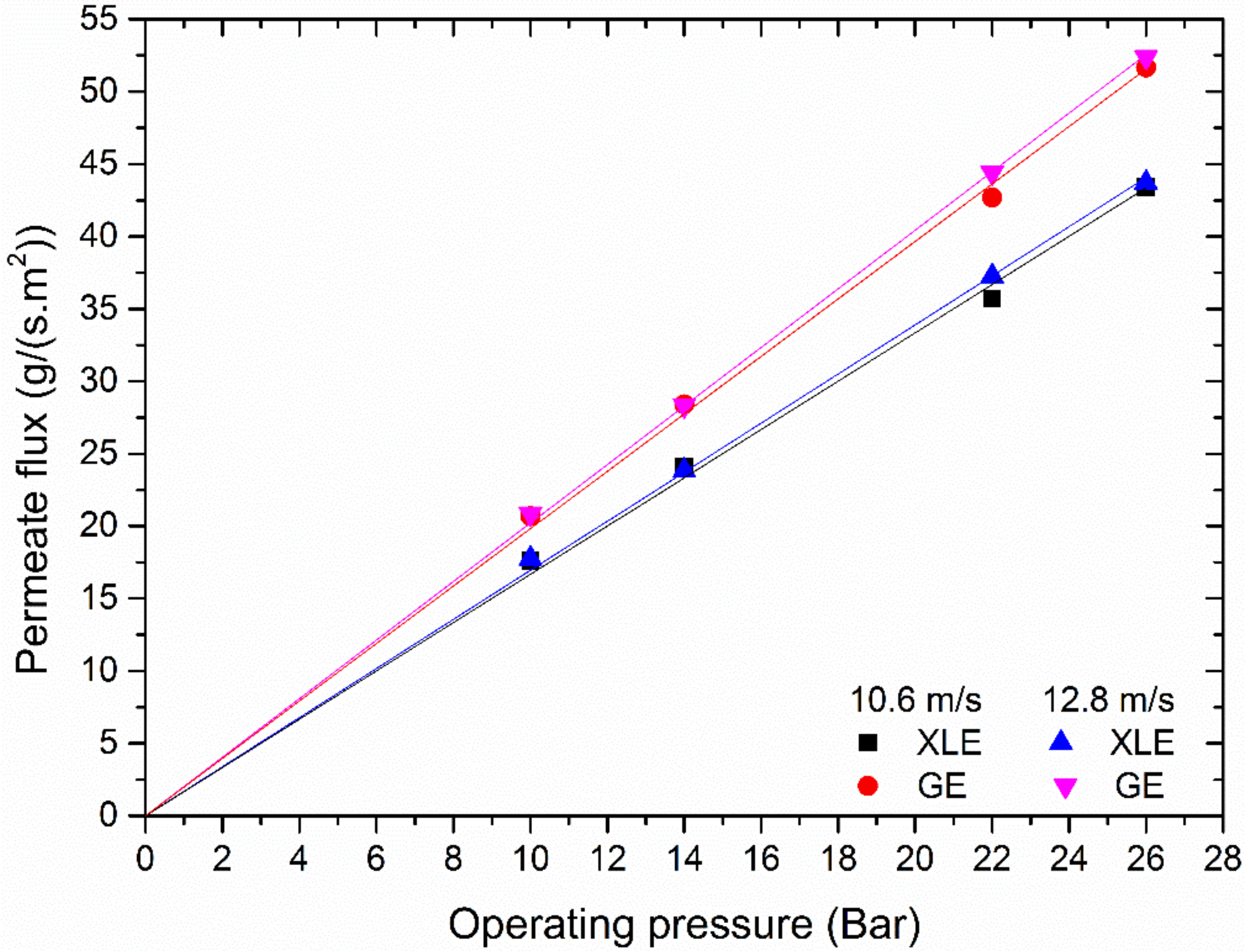


Figure 7.2. Permeate flux at two different cross flow velocities for a feed solution of 0.9 ± 0.1 g/L of lactic acid with no added KCl.

7.2.1.1. *Effect of Operating Pressure on Lactic Acid Rejection*

The effect of operating pressure was evaluated using a feed solution made of 2.5 g/L of KCl and 650 ± 50 mg/ L of lactic acid. The water and permeate flux are illustrated in **Figure 7.3 (a)** for LE and XLE membranes. Higher flux values were observed for the XLE membrane due to its greater hydrophilicity when compared to LE membrane (**Figure 7.1**). Furthermore, it was observed that as the applied pressure increased, the rejection of lactic acid and KCl increased (**Figure 7.3 (b)**) from 85 to 98% and 54 to 75%, respectively. This is a very common phenomena and results from the fact that salt flux is independent of pressure, while water flux increases with pressure. This is a very common phenomena and results from the fact that salt flux is independent of pressure, while water flux increases with pressure. Thus, the concentration of salt decreases in the permeate with an increase in pressure, in turn increasing rejection. The rejection of lactic acid was always higher than the salt present in the feed solution. This is mainly due to the larger molecular weight of lactic acid (90 g/mol) when compared to K (39.0 g/mol) and Cl (35.4 g/mol). These results are in agreement with the results reported for other organic acids in **Table 2.3**, where acids with MW equal or greater than 88 are highly retained by RO membranes, while acids with smaller molecular weight (such as boric acid and acetic acid) tend to pass through. Moreover, lactic acid has a radius of 3.13°A [208] and contains only two OH^- groups in its structure. This reduces the number of hydrogen bonds that can be formed with the water permeating through the membranes in comparison with, for example, boric acid which has three OH^- groups. The high rejection of lactic acid may provide an opportunity to separate the lactic acid from the salt in the reverse manner to that anticipated. That is by removing the salts in the permeate stream while retaining lactic acid in the retentate stream. Since both the LE and XLE membranes behaved similarly, the remaining experiments used XLE membranes only.

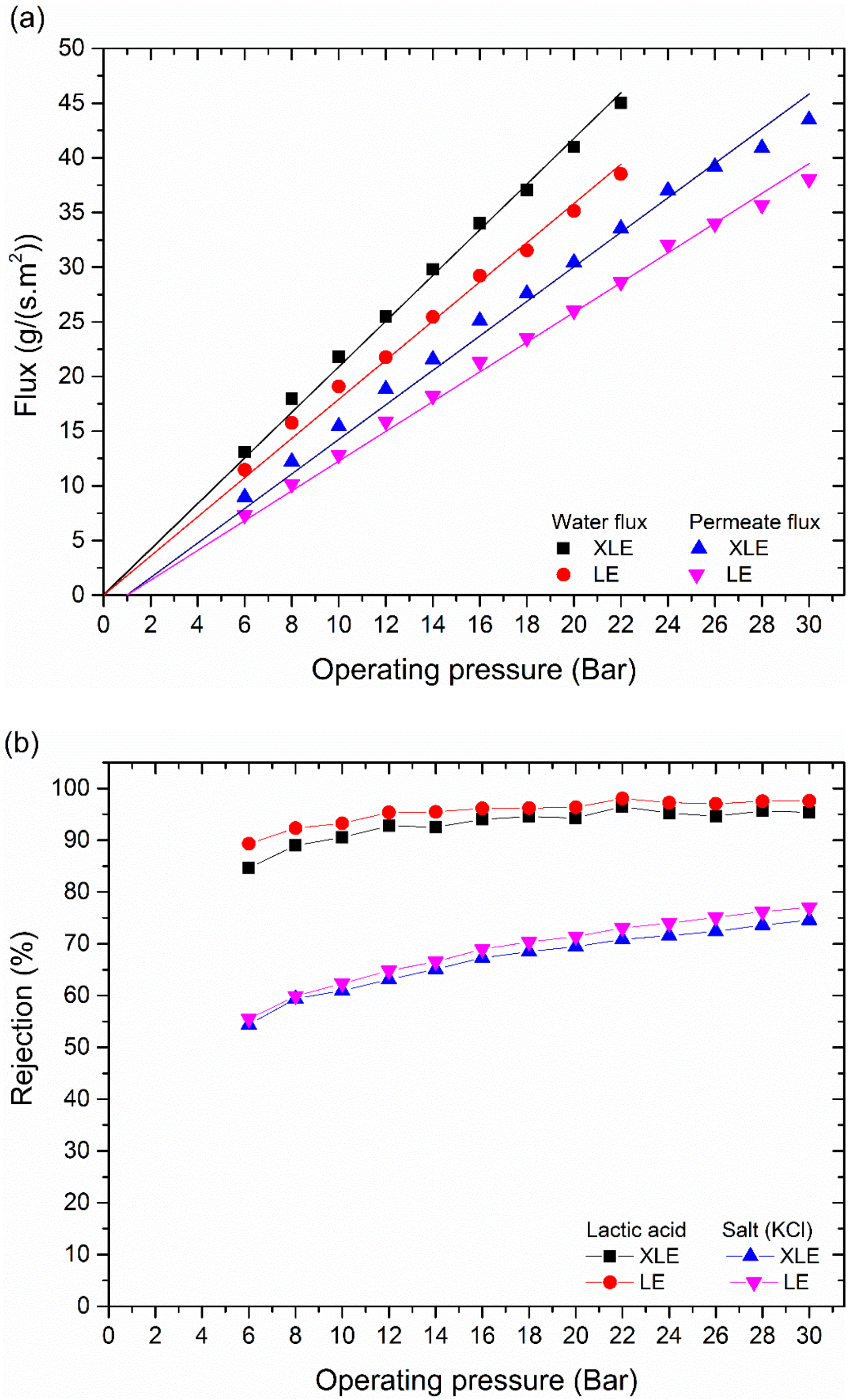


Figure 7.3. Results of experiments with Filmtec low energy membranes and a feed solution of 2.5 g of KCl and 650 ± 50 mg lactic acid per litre, pH of 3.5, conductivity of 4.8 mS/cm, and operating temperature of 25°C: (a) pure water and permeate flux, and (b) lactic acid and KCl rejections.

7.2.1.2. *Effect of Potassium Chloride on Lactic Acid Rejection*

The high ionic strength induced by the presence of KCl could be a factor contributing to the high rejection of lactic acid. As a result, a feed solution made of 0.9 ± 0.1 g/L of lactic acid with no added KCl was investigated. It can be observed that the absence of KCl did not significantly alter the high rejection of lactic acid, as shown in **Figure 7.4**.

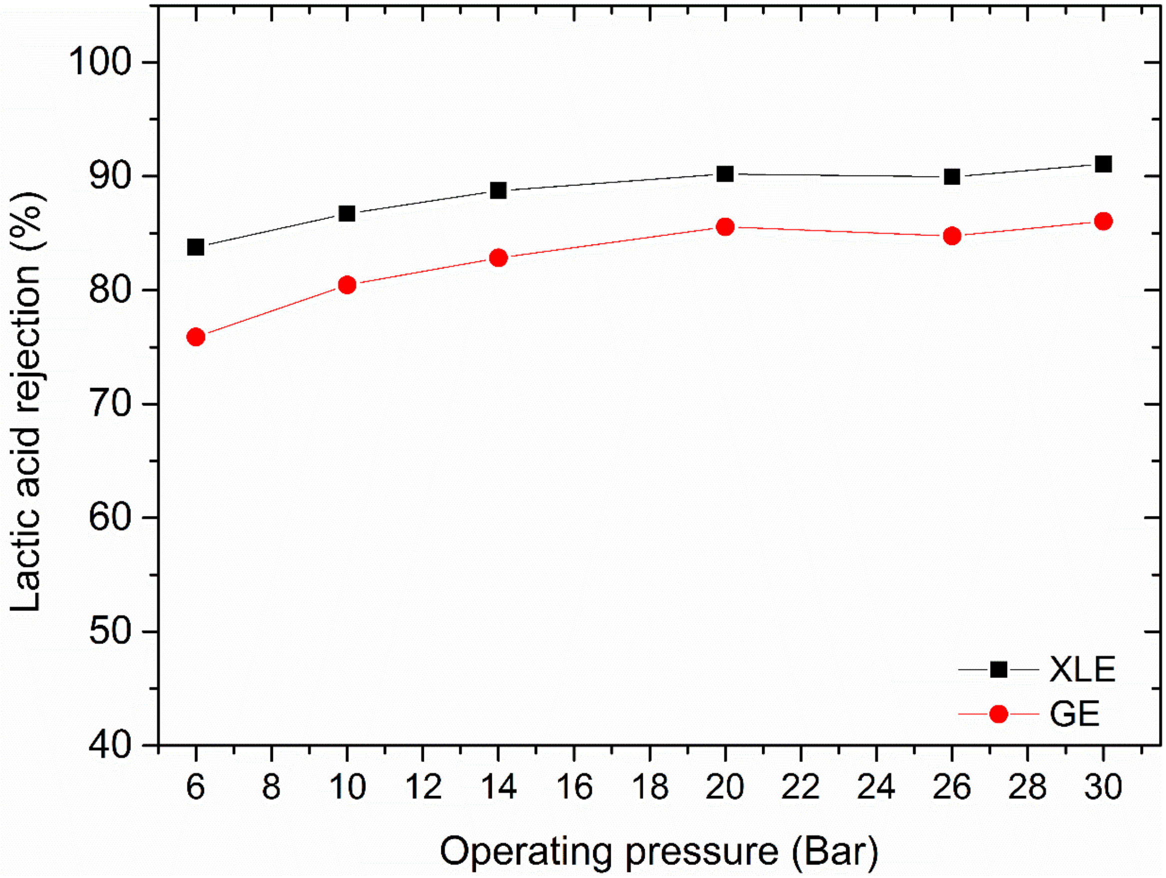


Figure 7.4. Effect of the absence of KCl on lactic acid rejection. Feed solution 0.9 ± 0.1 g/L of lactic acid, pH of 2.85 and operating temperature of 25°C.

7.2.1.3. *Effect of Operating Temperature on Lactic Acid Rejection*

To study the effect of system temperature on lactic acid rejection, experiments were conducted at 25°C and 35°C using a feed solution of 0.9 ± 0.1 g/L lactic acid with no added KCl. The increase in temperature from 25°C to 35°C is expected to decrease the pKa value for lactic acid from 3.873 to 3.4 (reported at 37°C by Thylin *et al.* [209]). This indicates that at higher temperatures and at the same pH, higher dissociation of lactic acid is achieved. It is apparent that an increase in temperature reduces the lactic acid rejection (**Figure 7.5**). It is reported that the isoelectric pH of the XLE membrane is between 3.2-3.9 [122, 210], indicating that at a feed pH of 2.85, the membrane is positively charged thus allowing the dissociated lactate ion (negatively charged) to flow through while retaining the neutrally charged lactic acid.

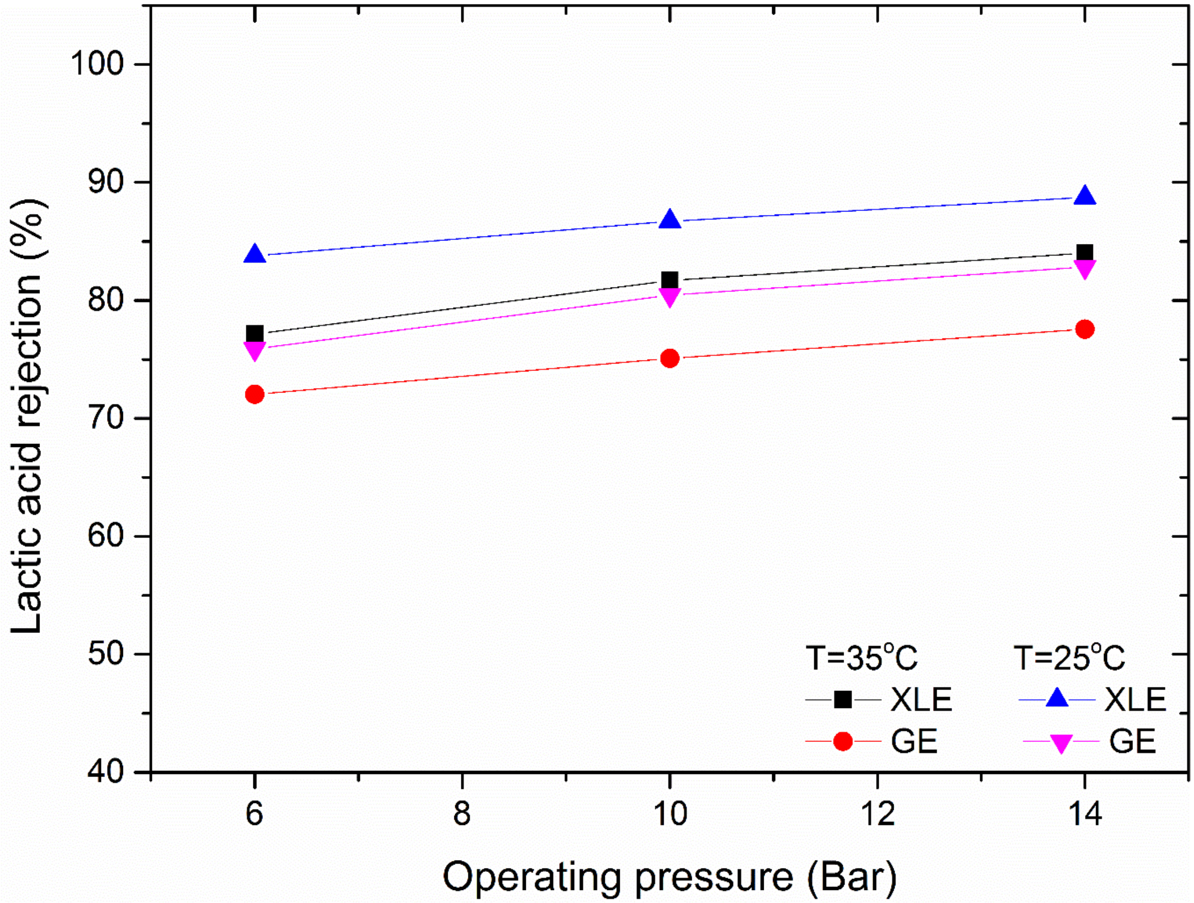


Figure 7.5. Effect of operating temperature on lactic acid rejection. Feed solution 0.9 ± 0.1 g/L of lactic acid and pH of 2.85.

7.2.1.4. *Effect of Feed pH on Lactic Acid Rejection*

It is well known that negatively charged anions such as lactate and chloride will be repelled by a negatively charged membrane such as the polyamide membranes used here at neutral pH. Therefore, the rejection of lactic acid can be increased by maintaining lactic acid in a non-ionized form. The pH of the feed solution was decreased to 2.3 using 5M HCl solution, to reduce lactic acid dissociation (**Eq. 2.1**). The addition of HCl resulted in increasing the feed conductivity from 4.8 to 14 mS/cm. It is noticed from **Figure 7.6**, that the rejection of lactic acid did not change significantly with the change in feed solution pH. Conversely, as the acidity of the feed solution increased, it is expected that the zeta potential of the membranes will also increase resulting in a positively charged membranes (isoelectric pH of XLE is reported to be between 3.2-3.9 [122, 210]). This leads to a lower rejection of salt (HCl + KCl), as the chloride ion can now pass freely. Again, this may provide an opportunity to separate the lactic acid from the salt in the reverse manner to that anticipated. That is, at 6 bars, 80% of the salt (HCl + KCl) is permeating, whereas 80% of the lactic acid is being retained. With an 80% stage cut, the retentate composition would change to 4.2 g/L lactic acid and 0.5 g/L salt (HCl + KCl); after a second stage, this would be 17.6 g/L lactic acid and 0.9 g/L salt (HCl + KCl).

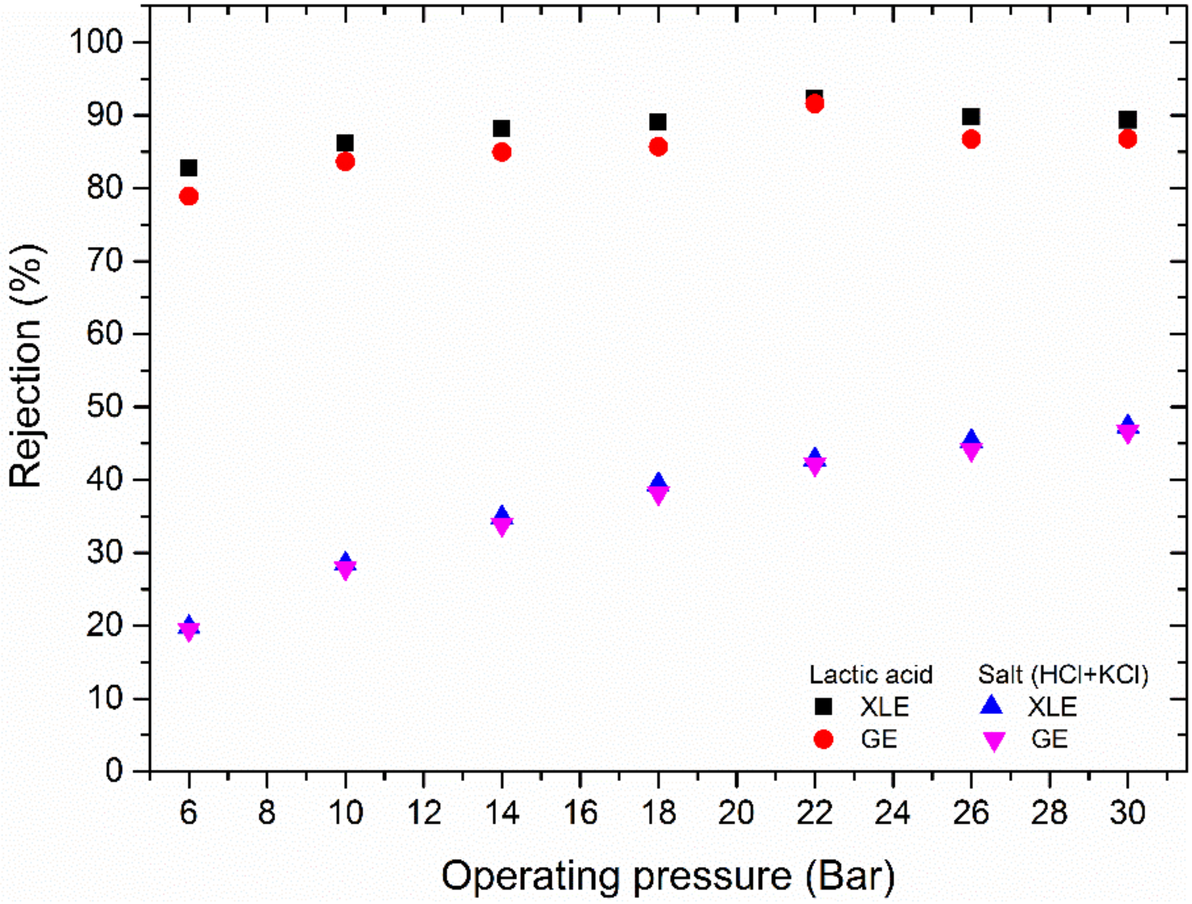


Figure 7.6. Effect of feed solution pH on lactic acid and salt rejection (feed solution pH of 2.3, operating temperature of 25°C, conductivity of 14 mS/cm and estimated composition of 11 mM of lactate, 38 mM of Cl^-, 33 mM of K^+, and 5 mM H^+).

7.2.2. Electrodialysis

An electrodialysis process was used with the aim to retain lactic acid in the diluate stream while removing the salts from the diluate to the concentrate stream. Identical solutions were used for both the diluate and concentrate streams to reduce the impact of diffusive mass transfer. In addition, ED is usually terminated at 70% demineralization of the diluate stream to avoid high energy costs [5], therefore, the results are evaluated at 70% removal of conductivity (70% demineralzation rate (DR)).

7.2.2.1. *Limiting Current Density Determination*

The limiting current density for the proposed experiments was determined using a feed solution made of 1 g/L of lactic acid as this is the lowest ion concentration likely to be encountered. The three different regions described in **section 2.4.2.2** are not observed clearly for the selected feed solution, as the Ohmic region merges with the limiting current region (**Figure 7.7**). This is mainly due to the low concentration or conductivity of the feed solution, thus resulting in low limiting current density. A value of 6 and 7 mA/cm^2 was calculated for AHA and CMB membranes, respectively, from the intersection of the linearized ohmic and plateau regions of the I-V curve (see Luo *et al.* [187]). For the lab-scale ED unit used, the membrane area was 36 cm^2 per membrane pair. Therefore, the limiting current for the system would be 216-252 mA. All experiments were performed at a constant voltage of 2.4 V where the starting current was always below 216 mA.

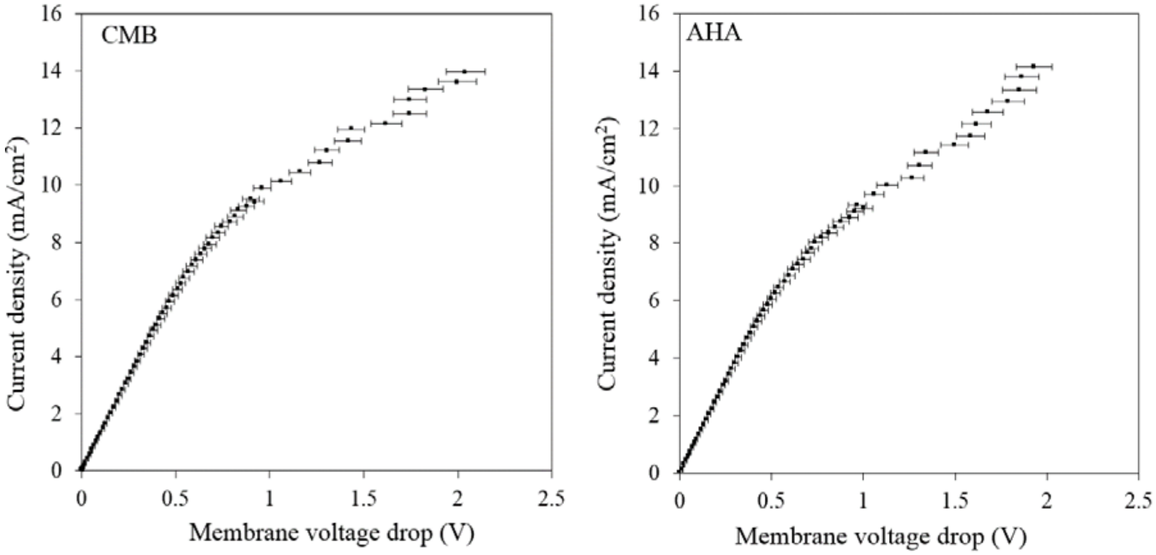


Figure 7.7. The current-voltage curve for a solution of 1 g/L lactic acid.

7.2.2.2. *Effect of Lactic Acid Concentration on the Retention of Lactic Acid*

Three feed solutions with different ratios of lactic acid and KCl were examined under the same operating conditions of constant voltage. In all experiments, the concentration of KCl was kept constant while the concentration of lactic acid was changed. It was observed that as the demineralization rate increased, more lactic acid was lost from the diluate (**Figure 7.8**). Cl^- ions act as the main competitor to the lactate ion in carrying the electrical charge. The electrical potential is used initially to remove the majority of Cl^- ions from the solution. Once most of the Cl^- ions are removed, this driving force becomes available for the removal of lactate ions.

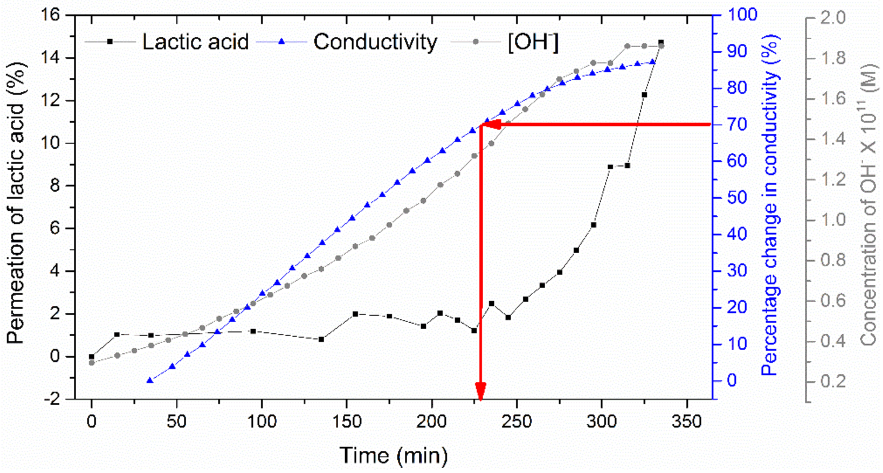
Interestingly all three feed solutions reached the 70% removal in conductivity around the 225 min mark (**Figure 7.8**). The experiment with the highest or equal concentration of lactic acid to KCl in the feed solution, resulted in the smallest percentage loss of lactic acid into the concentrate stream. This could be attributed to the smaller change noted in the diluate pH. This change in pH is a result of water splitting or the migration of lactate ions and protons from the diluate to the concentrate stream [13, 106]. It is well known that as the feed solution becomes less acidic, the dissociation of lactic acid to lactate increases (see **Table 7.1**). This means that the electrical current is not used anymore to split the lactic acid into lactate, but solely used to transfer the lactate ion from the diluate to the concentrate tank. This argument can be supported by considering the case where the concentration of KCl was twice that of lactic acid. The highest concentration of OH^- is observed in the diluate stream (**Figure 7.8 (c)**) which in turn resulted in the highest ratio between lactate to lactic acid (0.32 as per **Table 7.1**) and the highest loss of lactic acid.

The lactic acid to K^+ molar ratio improved around fourfold for all starting feed concentrations (**Table 7.1**). Nevertheless, food-grade lactic acid contains minerals at the ppm level, indicating the further treatment is required to remove the remaining traces of potassium and chloride ions.

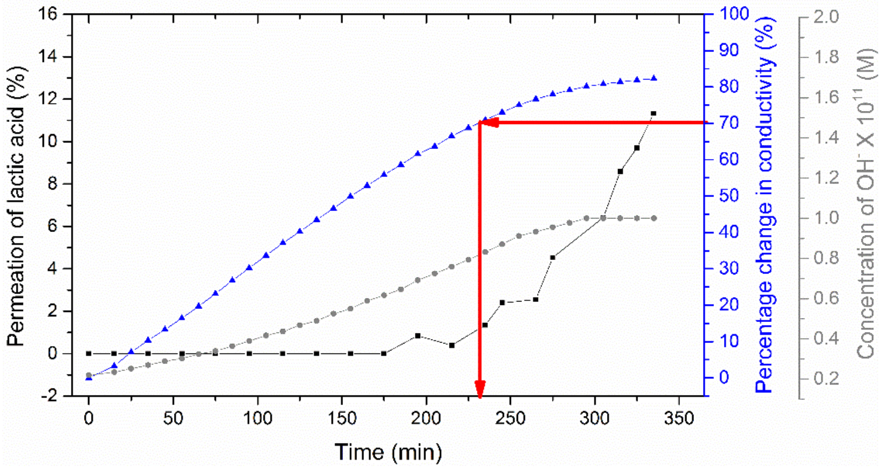
Table 7.1. Experimental results at 70% DR for a feed solution of lactic acid and KCl.

Initial lactic acid to KCl mass ratio		**0.5:1**	**1:1**	**2:1**
Initial concentration in the diluate (g/L)	**K**	0.99	1.01	1.01
	Lactic acid	1.25	2.42	4.92
Concentration at 70% DR (g/L)	**K**	0.21	0.24	0.23
	Lactic acid	1.19	2.38	4.84
Lactic acid to K^+ molar ratio	**Initial**	0.55	1.0	2.1
	70% DR	2.5	4.3	9.1
Lactate to lactic acid ratio	**Initial**	0.07	0.04	0.03
	70% DR	0.32	0.18	0.11
Percentage loss in lactic acid (%)		4.8	1.7	1.6

(a) Lactic acid: KCl = 1:1



(b) Lactic acid: KCl = 2:1



(c) Lactic acid: KCl = 1:2

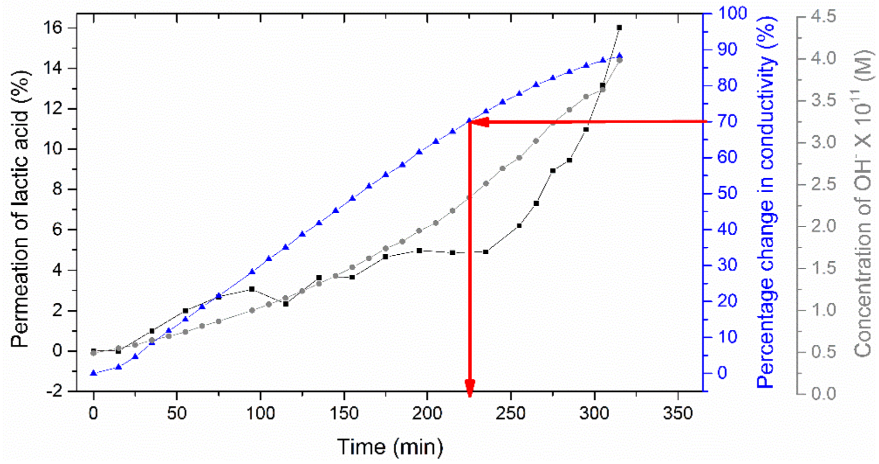


Figure 7.8. Process evaluation for three different feed compositions treated at a constant voltage of 2.4 V. The red arrows indicate the point corresponding to 70% demineralization, as measured by the diluate conductivity.

7.2.2.3. *Effect of NaCl Addition on the Retention of Lactic Acid*

It is known that the waste streams generated from acid whey treatment will contain different types of cations and anions. Previous work has demonstrated that ions tend to compete in electrodialysis, for example, monovalent ions have a faster migration rate when compared to divalent ions [81]. To demonstrate the effect of multiple cations on lactic acid retention, a solution was made with 1:1 mass ratio between lactic acid and total salts. The salt mixture used was 70 wt% KCl and 30 wt% NaCl. It is noticed that the addition of NaCl increase the time required to achieve 70% DR from 225 min (**Figure 7.8 (a)**) to 285 min (**Figure 7.9**). Furthermore, the addition of NaCl resulted in 6% loss of lactic acid at 70% DR (**Figure 7.9**) in comparison to less than 2% lost when only KCl was added to the feed solution (**Figure 7.8 (a)**). Interestingly, although the total concentration of salts was kept constant, a greater increase in diluate pH was observed when NaCl was added to the solution, which in turn resulted in a greater loss of lactic acid. This can be attributed to the longer time required to achieve 70% removal in conductivity, which in turn could promote more water splitting to take place. The molar ratio of lactic acid to cations in the diluate also dropped from 4.3% (**Table 7.1**) to 1.8% (**Table 7.2**) as NaCl was added. These results reflect the lower mobility of the sodium ion relative to the smaller potassium ion and demonstrate that the recovery of lactic acid becomes challenging when the feed solution contains multiple ions.

Table 7.2. Experimental results at 70% DR for a feed solution of lactic acid, KCl and NaCl.

Initial lactic acid to salt mass ratio		**1:1**
Initial concentration in the diluate (g/L)	**Na**	0.27
	K	0.77
	Lactic acid	2.46
Concentration at 70% DR (g/L)	**Na**	0.24
	K	0.15
	Lactic acid	2.31
Lactic acid to cations molar ratio	**Initial**	0.87
	70% DR	1.8
Lactate to lactic acid ratio	**Initial**	0.05
	70% DR	0.26
Percentage loss in lactic acid (%)		6

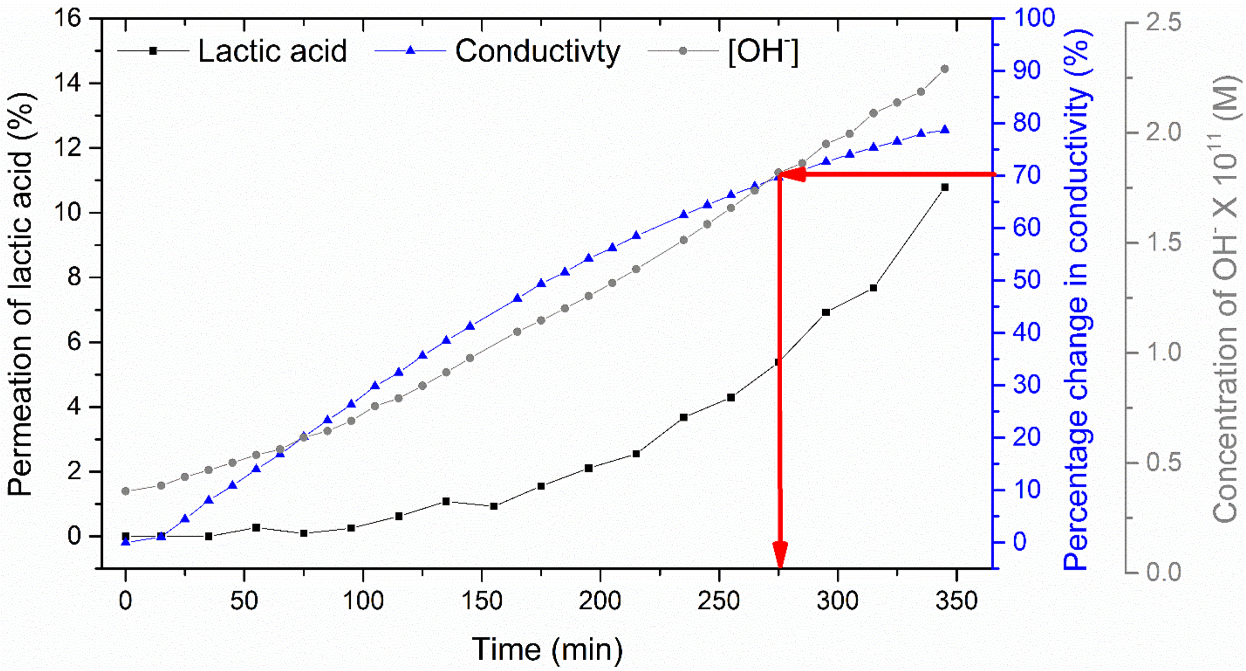


Figure 7.9. Effect of NaCl addition on lactic acid permeation at a constant voltage of 2.4 V. The red arrows indicate the point corresponding to 70% demineralization, as measured by the diluate conductivity.

7.3. Conclusion

Although the waste streams generated from acid whey treatment are a valuable source of lactic acid, these streams are known to contain many other minerals that reduce the purity and final use of this potentially valuable ingredient. In this chapter, the use of loose RO membranes and ED were investigated using a simple system made of lactic acid and KCl. It was found that while it was not possible to permeate the lactate ion as originally intended, operation at low pH and room temperature allowed for partial separation of lactic acid from KCl as the lactic acid was retained in the retentate stream with the salts permeating. The use of ED also showed some positive results as 70% DR was achieved with retaining most of the lactic acid in the feed solution. However, when NaCl was added to the system, the permeation of lactic acid increased and purity of the remaining lactic acid in the diluate declined. This indicates that as the complexity of the feed solution increases, the ED process becomes less effective. This is mainly due to the difference in the migration rate observed for different ions. As a result, either the ED or RO process could be used to achieve a certain level of demineralization after which the solution might be further treated using other demineralization technologies such as an ion-exchange process.

CHAPTER 8. Membrane Capacitive Deionization for Acid whey Treatment.

Although the results presented in the previous chapters have successfully demonstrated the feasibility of using electrodialysis (ED) for the treatment of acid whey, it is important to study the capability of other electrically driven membrane processes. Such studies will provide more options for the dairy industry regarding the available technologies that can be utilized. In addition, this chapter provides a comparison between the different available options in regard to process requirements, energy consumption and treatment capabilities.

8.1. Introduction

Whey is the industrial term used to describe the liquid waste generated during the conversion of milk to different types of cheese. Whey is known to contain many of the important nutrients found in milk, for example, whey proteins, lactose and water-soluble vitamins [16]. Based on the manufactured cheese, a dairy plant can produce two main types of whey, namely acid whey and sweet whey, each having its unique characteristics as a result of the cheese production method. Sweet whey is produced during rennet coagulation of casein, while acid whey is produced during fresh acid coagulation using a starter culture that converts lactose into lactic acid which in turn lowers the milk pH.

Although sweet whey is readily converted into different food ingredients, processing of acid whey has proven to be difficult. This is mainly due to the high levels of lactic acid and calcium found in acid whey. These components are known to affect the crystallization of lactose and result in agglomerate formation during the drying process [5, 6]. Nevertheless, several studies have suggested that the partial removal of lactic acid from acid whey can enhance dryability [24]. Bédas *et al.* [69], used a semi-industrial scale nanofiltration (NF) unit to remove 30% lactic acid and 46-60% monovalent ions from acid whey. Chen *et al.* [13] were able to treat acid whey ultrafiltration (UF) permeate using a batch electrodialysis (ED) unit to remove 80% of lactate and 90% of minerals. Furthermore, in **Chapter 6** of this thesis, it was demonstrated that pressure driven membranes, such as UF and NF, and electrically driven membranes, such as ED, could be combined to enhance the treatment process and produce a powder with an ash content of 4% and moisture content of 2.4%.

Membrane capacitive deionization (MCDI) is an emerging electrically driven membrane process where the separation of dissociated ions is achieved by passing the feed solution between two porous carbon electrodes. When an electrical potential is applied, the positively charged ions are adsorbed into the cathode, while the negatively charged ions are adsorbed into the anode, generating a desalinated feed stream. Once the electrode capacity is reached, the voltage is reversed, resulting in the desorption of the ions into a waste stream flowing through the unit. A cation exchange membrane (CEM) and an anion exchange membrane (AEM) are placed in front of the cathode and anode respectively, to allow the application of reverse voltage during the desorption step. The use of these membranes also prevents the fouling of the carbon electrodes [118].

The concept of capacitive deionisation was first proposed around 50 years ago by Blair and Murphy [119], with early studies by Caudle *et al.* [120] and Johnson *et al.* [121]. However, the approach gained momentum after 1996, when Farmer *et al.* [122] showed that carbon materials of high surface area could be used as electrode materials. Many researchers have since investigated this technology for applications such as brackish water desalination [126], wastewater treatment [211], generation of ultrapure water [212], and selective removal of nitrate ions [213].

There is currently disagreement in the literature as to the relative energy efficiency of MCDI versus ED. Zhao *et al.* [214] conclude that MCDI can be more energy efficient than ED for feed waters of salinity less than 60 mM (3.5 g/litre NaCl). This analysis assumed that the energy from the absorption step can be partly recovered during the desorption step. Conversely, Patel *et al.* [87] indicate that for a feed salinity of 3 g/litre NaCl, the specific energy consumption of MCDI is 0.12 kWh/m^3 for 20% salt removal, 5.6 times that calculated for ED, if energy recovery is not incorporated. With the inclusion of energy recovery, the systems are more comparable but MCDI still consumed 172% more energy than that for ED. These differences in energy demand were attributed predominantly to the limitation of MCDI to a single feed channel, whereas ED allows for many membrane pairs and thus multiple feed channels. Nevertheless, these studies did not consider the fouling of the membranes and its effect of energy consumption. Furthermore, developments such as flow-electrode CDI [215, 216] and the radial deionisation approach being commercialised by Atlantis Technologies [217] can overcome these issues, which can again lead to more comparable energy demand.

In this work and for the first time, a lab scale MCDI unit was used to evaluate the feasibility of this approach for acid whey treatment. The processing of three different types of pre-treated acid whey, namely UF permeate, NF retentate and dia-nanofiltration (Dia-NF) retentate were compared to determine if pre-treatment using pressure driven membrane technologies could assist in enhancing the performance of the MCDI unit. Finally, the energy demand of the MCDI process was compared to the more traditional ED approach.

8.2. Materials and Methods

8.2.1. Materials

Raw acid whey was obtained from Tatura Milk Industries Pty. Ltd. (Victoria, Australia) and processed at the manufacturing site through UF membranes to separate proteins and fat as the retentate stream. The permeate stream (UF permeate) was further treated through nanofiltration or dia-nanofiltration processes to produce a demineralized, deacidified and concentrated retentate (NF retentate or Dia-NF retentate). More information on the above processes are presented in **Chapter 6** of this thesis. The samples were stored at 4 ± 1°C and used within 3 weeks. It is important to note that the lactic acid content for the Dia-NF retentate reported here (**Table 8.1**) is double that reported in **Chapter 6**. This is believed to be due to microbial conversion of lactose to lactic acid in the sample during storage.

All chemicals used in this work were analytical grade. Purified water (>8.6 MΩ cm; Merck Millipore KGaA, Germany) was used for the preparation of all solutions. Activated carbon (AC Norit SA 4, Cabot Norit Activated Carbon, USA), polyvinylidene fluoride (PVDF, Mw~530,000, Sigma-Aldrich), N-N dimethylformamide (DMF, 99.8%, Merck Millipore) and titanium plates (TA2 titanium, Shenzhen Hongwang Mould Co., Ltd., China) were used for the fabrication of the carbon electrodes. Acid and base cleaning steps were performed using a hydrochloric acid solution (HCl; 36%; Thermo Fisher Scientific Australia Pty., Ltd., Australia) with a pH of 1.0 ± 0.15 and a solution of 3% sodium chloride (NaCl; >99.5%; Merck KGaA, Germany) adjusted to a pH of 9.15 ± 0.15 using sodium hydroxide (NaOH; Chem-Supply, Australia), respectively. The cation exchange membrane (Neosepta CMB) and anion exchange membrane (Neosepta AHA) were purchased from Astom Co., Ltd. (Tokyo, Japan). These membranes have a wide pH tolerance and thermal stability. Information on the IEM characteristics can be found in **section 3.3.1**.

Table 8.1. The composition of the three solutions processed through the MCDI unit.

Description	Unit	UF permeate	NF retentate[a]	Dia-NF retentate[a]
pH	-	4.5 ± 0.2	4.4 ± 0.1	4.4 ± 0.2
Conductivity	mS/cm	6.5 ± 0.2	8.3 ± 0.4	5 ± 0.1
Total Solids[b]	% (m/v)	4.0 ± 0.3	15 ± 1	15 ± 1
K	mg/100mL	111 ± 7	130 ± 16	9.2 ± 2
Na	mg/100mL	43 ± 2	57 ± 5	19 ± 2
Ca	mg/100 mL	103 ± 7	350 ± 50	360 ± 30
Mg	mg/100 mL	10 ± 0.6	41 ± 2	52 ± 1
Cl	mg/100 mL	36.7 ± 1	90 ± 20	26 ± 3
Lactate	g/L	6.00 ± 0.15	12.2 ± 0.3	12.8 ± 0.1

[a] Concentration factor of 3.5-4. [b] Measured in the laboratory of Tatura Milk Industries Pty. Ltd.

8.2.2. MCDI Setup

The MCDI rig consisted of a single cell unit made of two parallel electrodes separated by an AEM and CEM. The membranes were separated by a non-conductive spacer (Low foulant spacer 34 mil, Sterlitech). The spacer prevents the direct contact of the membranes, electrical short-circuiting and provides a pathway for the feed solution. All the elements were housed in polycarbonate housing. The membrane active area was 20 cm in length and 10 cm in width. The feed channel was located 9 mm from the edge of the membrane and was 3 mm wide and 20 mm long. A DC power supply (Agilent DC Modular Power System N6731B) was used to generate the potential difference through the unit. The DC power supply had an output voltage range of 0-5 V and an output current range of 0-10 A. The feed was supplied at a constant flowrate using a peristaltic pump (NEMA 4×, Watson Marlow). A magnetic stirrer was used to ensure that the feed to the unit was homogenous and the temperature was maintained at 30 ± 4°C using a water bath.

The carbon electrodes were prepared using the procedure reported by Hassanvand *et.al* [123], with the only difference being that the carbon was cast onto titanium plates rather than a graphite sheet. The average carbon mass of the electrodes was 2.9 ± 0.1 g.

8.2.3. Experimental Protocol

The MCDI experiments were carried out at 30 ± 4°C using 100 mL of three different feed solutions: (1) UF permeate; (2) NF retentate; (3) Dia-NF retentate. The experiments were divided into two main parts, namely the unit stabilization cycles and the acid whey treatment cycles. Each set of experiment was performed over 2 days, with 9 cycles on the first day (4 cycles of system stabilization + 5 cycles of acid whey treatment) and 12 cycles on the second day (4 cycles of system stabilization + 7 cycles of acid whey treatment).

The stabilization cycles were performed to reduce the effect of storing the membranes and the electrodes in a concentrated NaCl solution. At the start of each experiment, the unit was rinsed with water for 30 min followed by a desorption cycle using purified water at -1.2 V and flowrate of 30 mL/min. This was followed by 4 adsorption and desorption cycles.

For the acid whey treatment cycles, the adsorption step was performed in a batch mode where the feed was recycled back to the feed beaker. The adsorption step was carried out under a constant voltage of 1.2 V and a flowrate of 20 mL/min for 5 min. The feed solution was weighed at the start of each adsorption cycle to account for the volume lost at the end of the pervious adsorption cycle. The desorption step was performed using purified water as the feed solution. The mode of operation during desorption was changed to single-pass mode. The voltage was maintained at -1.2 V and the flowrate was increased to 30 mL/min to allow fast removal of ions from the system and fouling removal from the membrane surface. The desorption step was terminated when the conductivity of the effluent was less than 30 µS/cm. The tubing and the unit were purged with air for 10 min after the desorption cycle. This was followed by passing a feed solution through the unit to remove any residual water from the system before the next adsorption cycle. The feed solution used for this removal step was different from the feed processed during the adsorption step.

At the end of each experiment, the system was rinsed using purified water, followed by a 20 min acid cleaning using HCl solution (pH of 1.0 ± 0.15), 10 min of water rinse, and a 20 min of alkaline cleaning using 3% NaCl (pH of 9.15 ± 0.15). The cleaning sequence was finished with a water rinse and recirculation of 3% NaCl solution. Preliminary experiments were completed three times to establish the reproducibility of the data, with other experiments conducted only once.

8.2.4. Analytical Methods

Changes in the conductivity and pH of the feed solution during the adsorption step was measured continuously using a conductivity and pH meters (Mettler-Toledo, Greifensee, Switzerland), while a secondary conductivity meter (Crison, Switzerland) was used to measure the conductivity of the effluent during the desorption step. The change in the conductivity of the feed solution is defined as the demineralization rate (DR) and is calculated as per **Eq. 2.4**. The DR can also be calculated based on the total concentration of cations and anions removed from the diluate solution. However, due to the complexity of the whey solutions, only the concentration of the four major cations, i.e calcium (Ca), sodium (Na), magnesium (Mg), and potassium (K), were used to evaluate the DR as per **Eq. 2.4** (refer to **section 2.4.2**).

$$DR(\%) = \frac{x_{initial} - x_{final}}{x_{initial}} \times 100 = \left(1 - \frac{x_{final}}{x_{initial}}\right) \times 100 \qquad \textbf{Eq. 2.4}$$

Samples of 2 mL were taken from the feed beaker at the end of each cycle. High-performance liquid chromatography (HPLC, Shimadzu, Japan) was used to measure lactate concentration, while inductively coupled plasma optical emission spectroscopy (ICP-OES 720ES, Varian, USA) was used to measure the concentration of K, Na, Ca, and Mg. The samples were filtered and diluted to appropriate dilution levels. For more information refer to **section 3.5**.

The energy consumption during adsorption and desorption steps for constant voltage operation is calculated using **Eq. 3.7**. The total energy is the sum of energy required during the adsorption and desorption steps as per **Eq. 3.8**. However, Several researchers have shown that energy can be recovered during the desorption step, for example, Chen *et al.* [131] reported a recovery ratio of 30% for an MCDI system operated at 1.2 V during the adsorption step, therefore, the total energy was also estimated as per **Eq. 3.9** considering the possibility of recovering energy during the desorption step.

$$E_{ads/des}\,(kWh/kg\ of\ feed) = \frac{V_{cell}\int_0^{t_{ads/des}} I dt}{m_{feed}} \qquad \textbf{Eq. 3.1}$$

$$E_{Total}\,\left({}^{kWh}/_{kg\ of\ feed}\right) = E_{ads} + E_{des} \qquad \textbf{Eq. 3.2}$$

$$E_{Total\ with\ recovery}\left({}^{kWh}/_{kg\ of\ feed}\right) = 0.7E_{ads} \qquad \textbf{Eq. 3.3}$$

8.3. Results and Discussion

8.3.1. Demineralization and Deacidification of Acid Whey

Calculating the DR based on either the conductivity or the concentration of the four main cations resulted in slightly different values (**Table 8.2**). This can be contributed to several factors, such as the non-linear relationship between concentration and conductivity, and the fact that only the concentrations of the four main cations were used. As per **Table 8.2**, a greater demineralization rate was calculated for the UF permeate compared to the retentate steams. However, when considering the total concentration of cations removed from the feed solution over 12 cycles, it was found that more cations were removed from the NF retentate compared to the other two feed solutions (**Figure 8.1**). This is because the NF retentate was of greater ionic concentration than either the UF permeate or the dia-NF retentate (**Table 8.1**). Although the mass concentration of cations removed from the UF permeate was higher than that removed from the Dia-NF retentate (**Figure 8.1 (a)**), the values were comparable when considering the concentration of cations in molar equivalent (**Figure 8.1 (b)**). This is due to the higher removal of divalent ions from the NF retentate streams, as a result of the lower initial concentrations of monovalent ions.

A greater removal of Na was expected due to its small hydration diameter and greater migration rate compared to divalent ions. The low removal rate, demonstrated in **Figure 8.1**, may have been because the four stabilization cycles performed before each experiment were insufficient to remove the residual Na ions from the system. Such an observation could also be due to the tendency of Ca ions to replace Na in the membranes as demonstrated by Hassanvand *et al.* [128] and Chen *et al.* [142], therefore, the concentration of Na in the feed solution does not drop significantly.

The main aim in treating acid whey is the removal of lactic acid and cations, especially calcium. It is observed from **Table 8.2** that more lactic acid was removed from the dia-NF retentate when compared the NF retentate. This could be due to the lower levels of chloride found initially in the Dia-NF retentate, since lactic acid competes against other anions present in whey [13]. A higher percentage of lactic acid was removed from the UF permeate but this solution is at least 3.5 times less concentrated than the two retentate streams. This means that if the treated UF permeate was concentrated without further lactic acid removal, the concentration would increase from 4 g/L to 14 g/L which is greater than that in the treated NF retentate (9.5 g/L) and Dia-NF retentate (9 g/L). The lower lactic acid concentration in the retentate streams is due to the partial removal of lactic acid in the pre-treatment steps, i.e. NF and Dia-NF processes. Pre-treatment of acid whey is expected to reduce the membrane area required for electrically driven membrane processes [132]. However, capital and operating costs need to be considered to justify the pre-treatment of acid whey before MCDI.

Chandrapala and Vasiljevic [12] demonstrated that the lactic acid and calcium content in a lactose solution should be below 0.05% and 0.035%, respectively, to produce a dryable powder. Due to the limitation associated with the lab scale MCDI unit, only 12 adsorption cycles were performed. The percentage of lactic acid and calcium removed are not sufficient to produce a non-sticky powder, therefore more adsorption cycles or a larger membrane area will be required to achieve the desired removal of lactic acid and calcium.

Table 8.2. Demineralization rate and percentage of lactic acid removed at the end of 12 adsorption cycles.

		UF permeate	NF retentate [a]	Dia-NF retentate [a]
DR (%)	Based on conductivity	48 ± 2	23 ± 1	25 ± 1
	Based on concentration of cations	40 ± 3	26 ± 5	22 ± 2
Final lactic acid concentration (g/L)		4 ± 0.1	9.5 ± 0.1	9 ± 0.05
Percentage lactic acid removal (%)		34.5 ± 0.3	23.8 ± 0.6	30.4 ± 0.8

[a] Concentration factor of 3.5-4

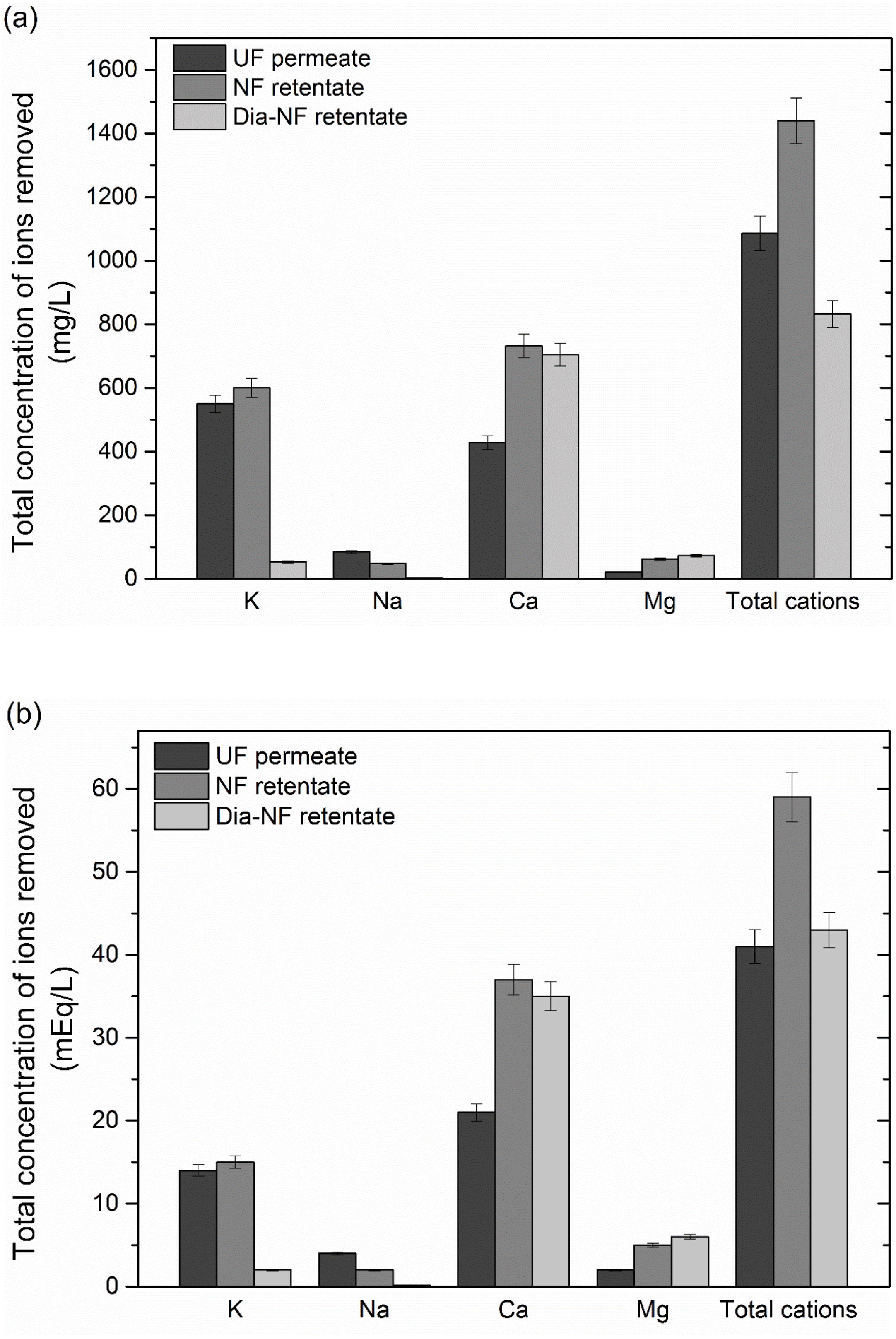


Figure 8.1. Total concentrations of cations removed at the end of 12 cycles: (a) concentration in mg/L, and (b) concentration in mEq/L.

8.3.2. Energy Consumption

The total energy consumed per kg of feed over 12 cycles did not change significantly with the type of feed (**Table 8.3**). This is in accordance with the results reported by Zhao *et al.* [129], who noticed that the effect of feed concentration on energy consumption was not as significant as the applied voltage. On one hand, it can be argued that a higher DR was achieved for UF permeate with the same amount of energy when compared to the two retentate streams thus supporting the fact that MCDI performs better for lower feed concentration [126]. On the other hand, a higher concentration of cations was removed (1440 g/L or 59 mEq/L) for the NF retentate with the same amount of energy per kg of feed (**Table 8.3**) . As a result, the energy was also estimated per molar equivalent of cations removed. It was observed that the retentate streams required half of the energy used by the UF permeate. These results demonstrate that MCDI is more energy efficient when using concentrated feed solution containing more divalent ions then monovalent ions.

Table 8.3. Total Energy consumption for 12 adsorption and desorption cycles.

	UF permeate	NF retentate[a]	Dia-NF retentate[a]
DR based on concentration of cations (%)	40	26	22
Total cation removed (mg/L)	1086	1440	832
E_{ads} (kWh/ kg of feed)	0.0017	0.0019	0.0018
E_{des} (kWh/ kg of feed)	0.0014	0.0016	0.0015
E_{Total} (kWh/ kg of feed)	**0.0031**	**0.0035**	**0.0033**
$E_{Total\ with\ recovery}$ (kWh/ kg of feed)	**0.0011**	**0.0013**	**0.0013**
E_{ads} (Wh/ mEq of cations removed)	0.0198	0.0093	0.0098
E_{des} (Wh/ mEq of cations removed)	0.0164	0.0077	0.0083
E_{Total} (Wh/ mEq of cations removed)	**0.0362**	**0.017**	**0.0181**
$E_{Total\ with\ recovery}$ (Wh/ mEq of cations removed)	**0.0139**	**0.0065**	**0.0069**

[a] Concentration factor of 3.5-4.0.

The results for MCDI of the UF permeate was compared to the work done by Chen *et al.* [13] who used a lab scale ED unit to treat acid whey UF permeate. The ED process was operated at 45°C while the MCDI unit in this study was operated at 30 ± 4°C. The higher operating temperature in ED should result in a better separation performance [13], therefore, a lower energy consumption.

Nevertheless, the total energy (calculated using **Eq. 3.8**) consumed for MCDI was comparable to the energy reported for the ED process. This might be attributed to the fact that lower fouling would be expected in MCDI as a result of the periodic reverse in the electrode polarity during the adsorption and desorption steps. In ED this fouling layer remains on the surface of the membrane and adds extra resistance to the current flowing through the unit, unless the unit is operated as electrodialysis reversal (EDR) or the pH and conductivity of the concentrate stream are optimized to prevent membrane fouling as demonstrated in **Chapter 4**. However, it should be noted that these results are not reflective of systems that have been optimised in either case. The energy demand for ED could be reduced significantly if more cell pairs were used and the operating parameters were optimized to avoid membrane fouling. Similarly, the energy for MCDI could be reduced significantly if the system is designed to recover the energy released during the desorption step (without energy recovery system: 0.0031 kWh/ kg of feed Vs with energy recovery system: 0.0011 kWh/ kg of feed), or by moving to a flow-electrode CDI approach.

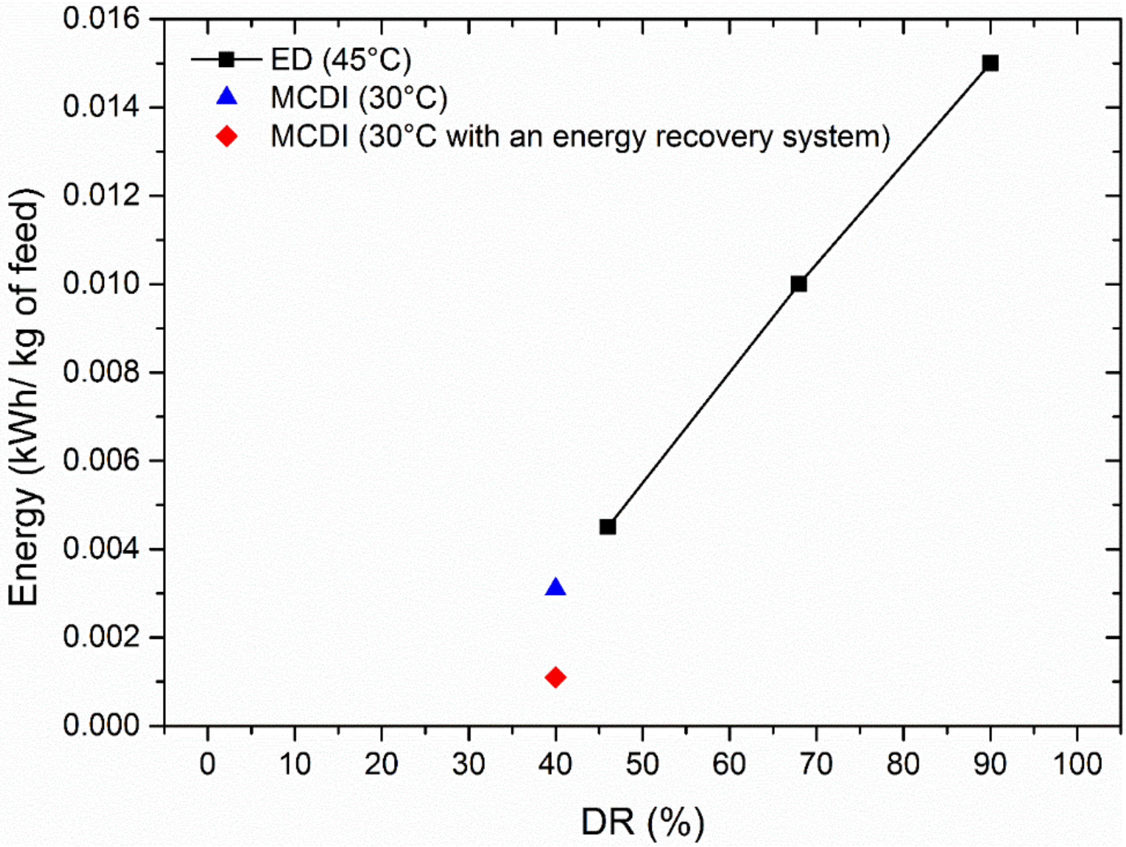


Figure 8.2. Comparison between the energy consumed during the treatment of acid whey UF permeate using MCDI and ED (ED results adapted from Chen *et al.* [13]).

8.4. Conclusion

This work has shown the possibility of using MCDI for the treatment of acid whey. A lab scale MCDI unit with a total membrane area of 200 cm^2 was used to process three pre-treated acid whey solutions, namely, UF permeate, NF retentate and Dia-NF retentate. Although no major differences were noticed between the three different feeds when it came to the overall energy consumed (kWh/kg of feed) over the 12 cycles, the total demineralization rate was 40% for ultrafiltered permeate while it was less than 30% for the two retentates. Nevertheless, pre-treatment using NF or Dia-NF assisted in increasing the removal of divalent ions and lactate ion due to the lower concentration of monovalent ions in these streams when compared to the UF permeate. Finally, the energy consumed during the treatment of UF permeate using MCDI at 30 ± 4°C was comparable to an ED process operated at 45°C, possibly due to the lower extent of fouling in MCDI as a result of the periodic reverse in polarity.

8.5. Acknowledgments

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CHAPTER 9. Conclusion and Future Prospective

9.1. Conclusion

In recent decades, the volumes of dairy products produced have increased significantly, resulting in the generation of waste/ by-products that require treatment and processing. One such by-product is whey which is produced as a result of cheese making processes and is known to contain whey proteins, lactose, and many of the nutrients found initially in milk. This indicates that whey is valuable to the dairy industry if treated and used either in liquid form or dried to powders. A dairy plant can produce three main types of whey depending on the manufactured cheese, namely sweet whey, acid whey, and salty whey. Sweet whey is easily processed to different types of powder; however, the processing of acid whey has proven challenging due to the presence of lactic acid and high levels of minerals. In addition, salty whey is underutilized due to the high levels of salt.

This thesis aimed at furthering the understanding of the use of membrane technology, with a special focus on electrodialysis, for acid and salty whey treatment. The use of new membrane processes was also explored. The main outcomes of each chapter are summarized below.

- **Fouling and in-situ cleaning of ion-exchange membranes during the electrodialysis of fresh acid and sweet whey.**

In this chapter, the fouling of ion-exchange membranes was evaluated under three different concentrate pH (acidic, neutral, and alkaline) since different types of fouling would be expected. For example, under acidic concentrate pH, protein fouling is expected on the membranes facing the diluate stream, while under alkaline concentrate pH, mineral fouling would be expected in the concentrate compartment. Interestingly, it was observed that the concentrate pH could also affect the removal of lactic acid as a higher percentage removal was obtained for an acidic concentrate (pH of 2.25 ± 0.5). In addition, the concentrate conductivity was maintained below 10 mS/cm to dilute the concentration of divalent ions especially calcium and phosphate which tend to deposit on the surface of the membranes.

In this work, sweet whey was also processed under the same operating conditions to allow direct comparison to acid whey. Interestingly, no significant difference was observed for the current measured through a standard NaCl solution after processing either sweet whey or acid whey for 5 hrs. Based on the measured increase in system resistance over time, protein precipitation in the diluate stream was comparable for both solutions when operating with an acidic concentrate. However, the change in system resistance under alkaline concentrate pH demonstrated higher mineral fouling for sweet whey when compared to acid whey. When considering in-situ cleaning of the membranes, cleaning with HCl solution at pH of 1.0 ± 0.15 was effective in removing mineral deposits. However, cleaning with 3% NaCl (pH of 9.2 ± 0.2) was ineffective in removing the strongly bound protein deposits that were formed when an acidic concentrate was utilized.

In summary, the results obtained demonstrate that both acid whey and sweet whey behave similarly during the ED process. The ED process can be optimized by using a concentrate stream at acidic pH to remove more lactic acid and reduce the mineral scaling on the IEMs. However, pre-treatments to remove protein from the whey solution is required to avoid protein precipitation.

- **Utilization of salty whey ultrafiltration permeate with electrodialysis.**

In this chapter, salty whey permeate was used as the concentrate stream for sweet whey demineralization. The results were compared to using 0.1M NaCl solution as the concentrate stream. Interestingly, the time required to achieve 75% removal in the conductivity of sweet whey was achieved within 3 hrs for both concentrate streams. However, less sodium was removed when using salty whey permeate due to the back diffusion of sodium from the concentrate stream towards the diluate stream as a result of concentration difference. The mineral scaling on the surface of the membranes facing the concentrate compartment was more significant for 0.1M NaCl solution when compared to salty whey permeate. In summary, it has been demonstrated that salty whey permeate could be used as the concentrate stream during the demineralization of whey, thus reducing freshwater intake by the dairy factory and the total volumes of wastewater generated by the ED treatment process.

In addition, salty whey permeate is rich in lactose which could be recovered to produce lactose powders, while the salt could be concentrated for the potential use in the chlor-alkali industry. The demineralization of salty whey permeate was carried out for 8 hrs, however, only up to 38% demineralization was achieved; therefore, it was not possible to evaluate the properties of the final lactose solution. Nevertheless, the quality of the concentrated salt solution produced from the demineralization process was improved by utilizing monovalent selective IEMs. The concentration of calcium in the concentrate solution dropped to half of the amount found when using non-selective IEMs.

- **Pilot study on the removal of lactic acid and minerals from acid whey using membrane technology.**

Literature has demonstrated the feasibility of both NF and ED in treating acid whey. However, each has its limitation. For example, there is a limit to the percentage of lactic acid that can be removed during NF, while the diluate stream in the ED process cannot be concentrated. Therefore, as part of this thesis, the feasibility of combining different membrane processes to produce demineralized whey powders from acid whey was demonstrated. A pilot scale UF process was used to separate protein and fat from acid whey as retentate. The UF permeate was processed through NF or Dia-NF to achieve partial removal of lactic acid and minerals. A total of 40% and 70% lactic acid removal was achieved using NF and Dia-NF, respectively, while the total cation removal was 35% and 48%, respectively.

A pilot scale ED with a total of 10 pairs and an area of 100 cm^2 per pair was used to remove lactic acid and minerals from UF permeate, NF retentate, and Dia-NF retentate. The concentrate compartment was maintained at a pH below 3 to control mineral scaling and to increase the lactic acid transfer. The maximum level of lactic acid removal, 88%, was achieved when Dia-NF was combined with ED. However, the energy cost of the Dia-NF step was double the energy cost of standard NF. The powder produced from combining the NF+ED lactose rich stream with the rich UF protein retentate was nonsticky, with a moisture content of 2.5%. No change was observed in the chemical structure of cation-exchange membranes, except for the membrane facing the cathode. However, changes were observed in the chemical structure of the anion exchange membranes which resulted in a change in the color of the membranes from white to brown. Nevertheless, these changes did not have any significant impact on the separation performance of the membranes over the duration of the pilot plant trials.

In summary, the combination of pressure driven and electrically driven membrane processes allows the conversion of acid whey from a dairy waste stream to a high value powder.

- **Recovery of lactic acid from a salt solution.**

Lactic acid is a valuable component which is removed from acid whey during the treatment process. The waste stream does not only contain lactic acid, but different cations and anions found originally in acid whey. The separation of these species was evaluated using a model solution prepared from lactic acid and KCl. Three hydrophilic loose RO membranes were used with the aim to permeate lactic acid and retain KCl. However, the membranes demonstrated high rejection of lactic acid while permeating KCl to some extent, this could be attributed to the large molecular weight and molecular radius of lactic acid in comparison to other ions. ED was partially successful in separating the majority of the KCl from lactic acid. Minor losses were observed in lactic acid when the process was terminated at 70% removal in the feed conductivity. When NaCl was added to the feed solution, it was observed that the loss in lactic acid increased from 2 to 6%. This indicates that the separation process becomes challenging as the feed solution becomes complex.

- **Membrane capacitive deionization for acid whey treatment.**

Although ED has been researched and established for the treatment of acid whey, the use of MCDI has never been investigated. A lab scale MCDI was successfully used to treat three different pre-treated acid whey solutions, namely, UF permeate, NF retentate and Dia-NF retentate. A total of 12 adsorption cycles were performed to successfully reduce the conductivity of the UF permeate by 40% and by less than 30% for the retentate streams. Nevertheless, a greater removal in divalent ions and lactic acid was observed for the retentate streams due to the absence of monovalent ions from this stream. A greater percentage of lactic acid was removed from the Dia-NF retentate (30%) compared to 24% removal from the NF retentate, due to the lower levels of Cl^- ions found initially in Dia-NF retentate. When comparing the energy consumption of MCDI and ED for the treatment of UF permeate, it was observed that energy consumption for both systems was comparable. However, the energy consumption for the MCDI process could be reduced by recovering the energy released from the electrodes during the desorption step. In summary, this chapter provides other alternatives to ED process for the treatment of acid whey thus adding extra flexibility to the process design and optimization.

9.2. Future Perspectives

Although the results obtained in this thesis would assist in industrializing the use of membrane technology, especially ED, for the treatment of acid whey, the following is recommended for future work:

- Investigate the use of electrodialysis reversal (EDR) for acid whey treatment. EDR has been used for water treatment applications [218], however, it has not been demonstrated for whey treatment. In EDR the polarity is periodically reversed, therefore, less fouling would be expected. However, in addition to reversing the polarity of the electrodes, the direction of the process streams is also reversed thus requiring complex valving and piping arrangements. Therefore, it is recommended to compare the results obtained for EDR with ED in terms of process performance, capital cost and operating costs.

- Economic evaluation of using a combination of membrane processes for the treatment of acid whey. Given the costs associated with the installation and maintenance of each process, it will be valuable to combine the results reported in **Chapter 6** of this thesis with an economic analysis including the cost of evaporation and drying.

- The recovery of lactic acid from a salt solution can be reassessed considering other available technologies such as electrodeionization (EDI) and selective crystallization of lactate. EDI is a hybrid technology that combines electrodialysis and ion-exchange process. This process has shown the ability to treat low ionic strength solutions much more efficiently than using the individual processes [219]. The selective crystallization of lactate using zinc oxide was studied by Cheryan and Parckh [220] who reported an overall lactic acid recovery of 85%.

- Further the understanding on the ion migration during MCDI. Although Hassanvand *et al.* [128] have demonstrated the kinetic behavior of major cations during the adsorption and desorption of a mixture of salts, the authors did not investigate the effect of organic acids such as lactic acid.

- Pilot scale assessment of MCDI. Although the lab scale MCDI unit has proven to consume less energy when compared to ED, it is recommended to investigate the technology in a pilot scale and assess the health of the membranes by the end of the trials.

CHAPTER 10. References

1. Chen, G., et al., *A review of salty waste stream management in the Australian dairy industry*. 2018. **224**: p. 406-413.
2. Šímová, H., V. Kysela, and A. Černín, *Demineralization of natural sweet whey by electrodialysis at pilot-plant scale*. Desalination and Water Treatment, 2010. **14**(1-3): p. 170-173.
3. Archana, P., et al., *Incorporation of whey permeate, a dairy effluent, in ethanol fermentation to provide a zero waste solution for the dairy industry*. Journal of Dairy Science, 2016. **99**(3): p. 1859-1867.
4. Dairy-Australia. *In focus report 2019*. 2019; Available from: https://www.dairyaustralia.com.au/about-dairy-australia/about-the-industry/in-focus.
5. Chandrapala, J., R. Wijayasinghe, and T. Vasiljevic, *Lactose crystallization as affected by presence of lactic acid and calcium in model lactose systems*. Journal of Food Engineering, 2016. **178**: p. 181-189.
6. Wijayasinghe, R., T. Vasiljevic, and J. Chandrapala, *Lactose behaviour in the presence of lactic acid and calcium*. Journal of Dairy Research, 2016. **83**(3): p. 395-401.
7. Chen, G., S. Gras, and S. Kentish, *Separation Technologies for Salty Wastewater Reduction in the Dairy Industry*. Separation & Purification Reviews, 2018: p. 1-29.
8. Galanakis, C.M., *Separation of Functional Molecules in Food by Membrane Technology*. 2018: Academic Press.
9. Hinkova, A., et al., *Potential of Membrane Separation Processes in Cheese Whey Fractionation and Separation*. Procedia Engineering, 2012. **42**: p. 1425-1436.
10. Luo, G., S. Pan, and J. Liu, *Use of the electrodialysis process to concentrate a formic acid solution*. Desalination, 2002. **150**(3): p. 227-234.
11. Kim, C., et al., *Semi-continuous capacitive deionization using multi-channel flow stream and ion exchange membranes*. Desalination, 2018. **425**: p. 104-110.
12. Chandrapala, J. and T. Vasiljevic, *Properties of spray dried lactose powders influenced by presence of lactic acid and calcium*. Journal of Food Engineering, 2016.
13. Chen, G.Q., et al., *Removal of lactic acid from acid whey using electrodialysis*. Separation and Purification Technology, 2016. **158**: p. 230-237.
14. Falvey, L., *Smallholder dairying in the tropics*. 1999: ILRI (aka ILCA and ILRAD).
15. Baskaran, K., L. Palmowski, and B. Watson, *Wastewater reuse and treatment options for the dairy industry*. 2003. **3**(3): p. 85-91.
16. Mollea, C., L. Marmo, and F. Bosco, *Valorisation of cheese whey, a by-product from the dairy industry*, in *Food industry*. 2013, IntechOpen.
17. Božanić, R., I. Barukčić, and K. Lisak, *Possibilities of whey utilisation*. 2014. **2**(7): p. 1036.
18. Baldasso, C., T. Barros, and I. Tessaro, *Concentration and purification of whey proteins by ultrafiltration*. 2011. **278**(1-3): p. 381-386.
19. Jelen, P., *WHEY PROCESSING*. Encyclopedia of Dairy Sciences, 2011. **4**.
20. Blaschek, K., W. Wendorff, and S. Rankin, *Survey of salty and sweet whey composition from various cheese plants in Wisconsin*. Journal of dairy science, 2007. **90**(4): p. 2029-2034.
21. Riera Rodríguez, F.A., A. Fernández Martínez, and C. Muro Urista, *Cheese whey as a source of active peptides: Production, analysis, purification and animal and human trials*. Agricultural Research Updates, 2014.

22. Wijayasinghe, R., T. Vasiljevic, and J. Chandrapala, *Water-lactose behavior as a function of concentration and presence of lactic acid in lactose model systems.* Journal of dairy science, 2015. **98**(12): p. 8505-8514.
23. Mimouni, A., et al., *The formation of calcium lactate crystals is responsible for concentrated acid whey thickening.* Journal of dairy science, 2007. **90**(1): p. 57-65.
24. Saffari, M. and T. Langrish, *Effect of lactic acid in-process crystallization of lactose/protein powders during spray drying.* Journal of Food Engineering, 2014. **137**: p. 88-94.
25. Chandrapala, J., et al., *Nanofiltration and nanodiafiltration of acid whey as a function of pH and temperature.* Separation and Purification Technology, 2016. **160**: p. 18-27.
26. Chandrapala, J., et al., *Strategies for maximizing removal of lactic acid from acid whey–Addressing the un-processability issue.* Separation and Purification Technology, 2017. **172**: p. 489-497.
27. Palmieri, N., M.B. Forleo, and E. Salimei, *Environmental impacts of a dairy cheese chain including whey feeding: An Italian case study.* Journal of Cleaner Production, 2016.
28. Kosikowski, F.v., *Whey Utilization and Whey Products I.* Journal of Dairy Science, 1979. **62**(7): p. 1149-1160.
29. Prazeres, A.R., F. Carvalho, and J. Rivas, *Cheese whey management: A review.* Journal of Environmental Management, 2012. **110**: p. 48-68.
30. Gallardo-Escamilla, F., A. Kelly, and C. Delahunty, *Sensory characteristics and related volatile flavor compound profiles of different types of whey.* 2005. **88**(8): p. 2689-2699.
31. Pereira, C., et al., *Novel Functional Whey-Based Drinks with Great Potential in the Dairy Industry.* Food Technology & Biotechnology, 2015. **53**(3): p. 307-314.
32. Das, M., A. Raychaudhuri, and S.K. Ghosh, *Supply Chain of Bioethanol Production from Whey: A Review.* Procedia Environmental Sciences, 2016. **35**: p. 833-846.
33. Alvarez, V.B., M. Eastridge, and T. Ji, *Utilities and Effluent Treatment | Reducing the Negative Impact of the Dairy Industry on the Environment.* Encyclopedia of Dairy Sciences, 2011: p. 631-635.
34. Tsolcha, O.N., et al., *Treatment of second cheese whey effluents using a Choricystis-based system with simultaneous lipid production.* Journal of Chemical Technology & Biotechnology, 2016. **91**(8): p. 2349-2359.
35. Maullu, C., et al., *Production of lysozyme-enriched biomass from cheese industry by-products.* Journal of Applied Microbiology, 1999. **86**(2): p. 182-186.
36. Krolczyk, J.B., et al., *Use of whey and whey preparations in the food industry - a review.* Polish Journal of Food and Nutrition Sciences, 2016. **66**(3): p. 157-165.
37. Siso, M.G., *The biotechnological utilization of cheese whey: a review.* Bioresource Technology, 1996. **57**(1): p. 1-11.
38. de Souza, R.R., et al., *Recovery and purification of lactose from whey.* Chemical Engineering and Processing: Process Intensification, 2010. **49**(11): p. 1137-1143.
39. Pouliot, Y., *Membrane processes in dairy technology—From a simple idea to worldwide panacea.* International Dairy Journal, 2008. **18**(7): p. 735-740.
40. Rosenberg, M., *Current and future application for membrane processes in the dairy industry.* Trends in Food Science & Technology, 1995. **6**.
41. Salehi, F., *Current and future applications for nanofiltration technology in the food processing.* Food and Bioproducts Processing, 2014. **92**(2): p. 161-177.

42. Rektor, A. and G. Vatai, *Membrane filtration of Mozzarella whey.* Desalination, 2004. **162**: p. 279-286.
43. Sarkar, B., et al., *Wastewater treatment in dairy industries — possibility of reuse.* Desalination, 2006. **195**(1-3): p. 141-152.
44. Bylund, G., *Dairy processing handbook*. 2003: Tetra Pak Processing Systems AB.
45. Balannec, B., et al., *Treatment of dairy process waters by membrane operations for water reuse and milk constituents concentration.* Desalination, 2002. **147**(1): p. 89-94.
46. Daufin, G., et al., *Recent and emerging applications of membrane processes in the food and dairy industry.* Food and Bioproducts Processing, 2001. **79**(2): p. 89-102.
47. Harper, W.J. *Factors affecting the application of ultrafiltration membranes in the dairy food industry*. 1980. Dep. of Food Sci. & Nutr., Ohio State Univ., Columbus, Ohio 43210, USA.
48. Hiddink, J., R. De Boer, and P. Nooy, *Reverse osmosis of dairy liquids.* Journal of Dairy Science, 1980. **63**(2): p. 204-214.
49. Kezia, K., *Toward zero liquid discharge: membrane technology for concentration and crystallisation of dairy minerals*. 2016.
50. Kumar, P., et al., *Perspective of Membrane Technology in Dairy Industry: A Review.* Asian-Australasian Journal of Animal Sciences, 2013. **26**(9): p. 1347-1358.
51. Onwulata, C. and P. Huth, *Whey processing, functionality and health benefits*. Vol. 82. 2009: John Wiley & Sons.
52. Di Giacomo, G., G. Del Re, and D. Spera, *Milk whey treatment with recovery of valuable products.* Desalination, 1997. **108**(1): p. 273-276.
53. Rice, G., et al., *Membrane‐Based Dairy Separation: A Comparison of Nanofiltration and Electrodialysis.* Developments in Chemical Engineering and Mineral Processing, 2005. **13**(1‐2): p. 43-54.
54. Rice, G., et al., *The influence of dairy salts on nanofiltration membrane charge.* Journal of food engineering, 2011. **107**(2): p. 164-172.
55. Okawa, T., et al., *Demineralisation of whey by a combination of nanofiltration and anion-exchange treatment: a preliminary study.* International Journal of Dairy Technology, 2015. **68**(4): p. 478-485.
56. Kyrychuk, I., et al., *Two-stage whey treatment by nanofiltration and reverse osmosis.* Ukrainian food journal, 2015(4, Issue 4): p. 638-647.
57. Cuartas-Uribe, B., et al., *A study of the separation of lactose from whey ultrafiltration permeate using nanofiltration.* Desalination, 2009. **241**(1): p. 244-255.
58. Alkhatim, H.S., et al., *Treatment of whey effluents from dairy industries by nanofiltration membranes.* Desalination, 1998. **119**(1--3): p. 177-184.
59. Das, B., et al., *Recovery of whey proteins and lactose from dairy waste: A step towards green waste management.* Process Safety and Environmental Protection, 2016. **101**: p. 27-33.
60. Pan, K., et al., *A study of demineralization of whey by nanofiltration membrane.* Desalination, 2011. **267**(2): p. 217-221.
61. Cuartas-Uribe, B., et al., *Application of nanofiltration models for the prediction of lactose retention using three modes of operation.* Journal of food engineering, 2010. **99**(3): p. 373-376.

62. Cuartas-Uribe, B., et al., *Nanofiltration of sweet whey and prediction of lactose retention as a function of permeate flux using the Kedem–Spiegler and Donnan Steric Partioning models.* Separation and purification technology, 2007. **56**(1): p. 38-46.
63. Greiter, M., et al., *Desalination of whey by electrodialysis and ion exchange resins: analysis of both processes with regard to sustainability by calculating their cumulative energy demand.* Journal of Membrane Science, 2002. **210**(1): p. 91-102.
64. Chaveron, M., J.-J. Sihver, and H. Duperrex, *Demineralization of whey*. 1979, Google Patents.
65. Suárez, E., et al., *Partial demineralization of whey and milk ultrafiltration permeate by nanofiltration at pilot-plant scale.* Desalination, 2006. **198**(1): p. 274-281.
66. Van der Horst, H., et al., *Use of nanofiltration for concentration and demineralization in the dairy industry: model for mass transport.* Journal of Membrane Science, 1995. **104**(3): p. 205-218.
67. Chandrapala, J., et al., *Removal of lactate from acid whey using nanofiltration.* Journal of Food Engineering, 2016. **177**: p. 59-64.
68. Kelly, J. and P. Kelly, *Desalination of acid casein whey by nanofiltration.* International Dairy Journal, 1995. **5**(3): p. 291-303.
69. Bédas, M., et al., *Nanofiltration of lactic acid whey prior to spray drying: Scaling up to a semi-industrial scale.* LWT-Food Science and Technology, 2017. **79**: p. 355-360.
70. Chandrapala, J., et al., *Properties of acid whey as a function of pH and temperature.* Journal of dairy science, 2015. **98**(7): p. 4352-4363.
71. Greiter, M., et al., *Electrodialysis versus ion exchange: comparison of the cumulative energy demand by means of two applications.* Journal of membrane science, 2004. **233**(1): p. 11-19.
72. Xu, T. and C. Huang, *Electrodialysis ‐based separation technologies: A critical review.* AIChE journal, 2008. **54**(12): p. 3147-3159.
73. Strathmann, H., *Electrodialysis, a mature technology with a multitude of new applications.* Desalination, 2010. **264**(3): p. 268-288.
74. Kánavová, N. and L. Machuca, *A novel method for limiting current calculation in electrodialysis modules.* Periodica Polytechnica. Chemical Engineering, 2014. **58**(2): p. 125.
75. Ran, J., et al., *Ion exchange membranes: New developments and applications.* 2017. **522**: p. 267-291.
76. Madzingaidzo, L., H. Danner, and R. Braun, *Process development and optimisation of lactic acid purification using electrodialysis.* Journal of Biotechnology, 2002. **96**(3): p. 223-239.
77. Zhang, Y., et al., *RO concentrate minimization by electrodialysis: techno-economic analysis and environmental concerns.* Journal of environmental management, 2012. **107**: p. 28-36.
78. Banasiak, L.J., T.W. Kruttschnitt, and A.I. Schäfer, *Desalination using electrodialysis as a function of voltage and salt concentration.* Desalination, 2007. **205**(1): p. 38-46.
79. Gernigon, G., et al., *Whey processing| demineralization.* Encyclopedia of dairy sciences, 2nd edn. Academic, San Diego, 2011: p. 738-743.
80. Casademont, C., et al., *Electrodialysis of model salt solution containing whey proteins: Enhancement by pulsed electric field and modified cell configuration.* Journal of Membrane Science, 2009. **328**(1): p. 238-245.

81. Ayala-Bribiesca, E., et al., *Effect of concentrate solution pH and mineral composition of a whey protein diluate solution on membrane fouling formation during conventional electrodialysis.* Journal of Membrane Science, 2006. **280**(1): p. 790-801.
82. Kabay, N., et al., *Effect of salt combination on separation of monovalent and divalent salts by electrodialysis.* Desalination, 2006. **198**(1-3): p. 84-91.
83. Kabay, N., et al., *Effect of feed characteristics on the separation performances of monovalent and divalent salts by electrodialysis.* Desalination, 2003. **158**(1-3): p. 95-100.
84. Diblíková, L., L. Čurda, and J. Kinčl, *The effect of dry matter and salt addition on cheese whey demineralisation.* International Dairy Journal, 2013. **31**(1): p. 29-33.
85. Merkel, A., A.M. Ashrafi, and J. Ečer, *Bipolar membrane electrodialysis assisted pH correction of milk whey.* Journal of Membrane Science, 2018. **555**: p. 185-196.
86. Lee, H.-J., et al., *Designing of an electrodialysis desalination plant.* Desalination, 2002. **142**(3): p. 267-286.
87. Patel, S.K., et al., *Energy Efficiency of Electro-Driven Brackish Water Desalination: Electrodialysis Significantly Outperforms Membrane Capacitive Deionization.* Environmental Science & Technology, 2020. **54**(6): p. 3663-3677.
88. Qin, M., et al., *Comparison of energy consumption in desalination by capacitive deionization and reverse osmosis.* Desalination, 2019. **455**: p. 100-114.
89. Bazinet, L., *Electrodialytic phenomena and their applications in the dairy industry: a review.* BFSN, 2005. **44**(7-8): p. 525-544.
90. Ho, W. and K. Sirkar, *Membrane handbook.* 2012: Springer Science & Business Media.
91. Valero, F., A. Barceló, and R. Arbós, *Electrodialysis technology-theory and applications.* Desalination, trends and technologies, 2011. **28**: p. 3-20.
92. Andrés, L., F. Riera, and R. Alvarez, *Skimmed milk demineralization by electrodialysis: conventional versus selective membranes.* Journal of food engineering, 1995. **26**(1): p. 57-66.
93. Bazinet, L. and M. Araya-Farias, *Electrodialysis of calcium and carbonate high concentration solutions and impact on composition in cations of membrane fouling.* Journal of colloid and interface science, 2005. **286**(2): p. 639-646.
94. Casademont, C., et al., *Impact of electrodialytic parameters on cation migration kinetics and fouling nature of ion-exchange membranes during treatment of solutions with different magnesium/calcium ratios.* Journal of membrane Science, 2008. **325**(2): p. 570-579.
95. Yen, Y.-H. and M. Cheryan, *Electrodialysis of model lactic acid solutions.* Journal of food engineering, 1993. **20**(3): p. 267-282.
96. Nikonenko, V.V., et al., *Desalination at overlimiting currents: State-of-the-art and perspectives.* Desalination, 2014. **342**: p. 85-106.
97. Krol, J., M. Wessling, and H. Strathmann, *Concentration polarization with monopolar ion exchange membranes: current–voltage curves and water dissociation.* Journal of Membrane Science, 1999. **162**(1): p. 145-154.
98. Hwang, J.Y. and J.Y. Lai, *The effect of temperature on limiting current density and mass transfer in electrodialysis.* Journal of Chemical Technology & Biotechnology, 1987. **37**(2): p. 123-132.
99. Fidaleo, M. and M. Moresi, *Electrodialysis applications in the food industry.* Advances in food and nutrition research, 2006. **51**: p. 265-360.
100. Parulekar, S.J., *Optimal current and voltage trajectories for minimum energy consumption in batch electrodialysis.* Journal of membrane science, 1998. **148**(1): p. 91-103.

101. Lee, E.G., et al., *Lactic acid recovery using two-stage electrodialysis and its modelling.* Journal of Membrane Science, 1998. **145**(1): p. 53-66.
102. Sadrzadeh, M. and T. Mohammadi, *Sea water desalination using electrodialysis.* Desalination, 2008. **221**(1-3): p. 440-447.
103. de Boer, R. and T. Robbertsen, *Electrodialysis and ion-exchange processes: The case of milk whey*. Progress in food engineering, 1983.
104. Pérez, A., et al., *Electrodialysis of whey permeates and retentates obtained by ultrafiltration.* Journal of food process engineering, 1994. **17**(2): p. 177-190.
105. Williams, A.W. and H.A. Kline, *Electrodialysis of acid whey*. 1980, Google Patents.
106. Dufton, G., et al., *How electrodialysis configuration influences acid whey deacidification and membrane scaling.* Journal of dairy science, 2018. **101**(9): p. 7833-7850.
107. Kravtsov, V., et al., *Alkalinization of acid whey by means of electrodialysis with bipolar membranes and analysis of induced membrane fouling.* Journal of Food Engineering, 2020. **277**: p. 109891.
108. Ečer, J., J. Kinčl, and L. Čurda, *Using foil membranes for demineralization of whey by electrodialysis.* Desalination and Water Treatment, 2015. **56**(12): p. 3273-3277.
109. Liu, J., et al., *Concentrating brine from seawater desalination process by nanofiltration–electrodialysis integrated membrane technology.* Desalination, 2016. **390**: p. 53-61.
110. Casas, S., et al., *Seawater reverse osmosis brines as a new salt source for the chlor-alkali industry: integration of NaCl concentration by electrodialysis.* Solvent Extraction and Ion Exchange, 2012. **30**(4): p. 322-332.
111. Zhang, W., et al., *Separation of divalent ions from seawater concentrate to enhance the purity of coarse salt by electrodialysis with monovalent-selective membranes.* Desalination, 2017. **411**: p. 28-37.
112. Reig, M., et al., *Concentration of NaCl from seawater reverse osmosis brines for the chlor-alkali industry by electrodialysis.* Desalination, 2014. **342**: p. 107-117.
113. Jiang, C., et al., *Electrodialysis of concentrated brine from RO plant to produce coarse salt and freshwater.* Journal of Membrane Science, 2014. **450**: p. 323-330.
114. Yan, H., et al., *Multistage-batch electrodialysis to concentrate high-salinity solutions: Process optimisation, water transport, and energy consumption.* Journal of Membrane Science, 2019. **570**: p. 245-257.
115. Biesheuvel, P. and A. Van der Wal, *Membrane capacitive deionization.* Journal of Membrane Science, 2010. **346**(2): p. 256-262.
116. Moon, S.-H. and S.-H. Yun, *Process integration of electrodialysis for a cleaner environment.* Current Opinion in Chemical Engineering, 2014. **4**: p. 25-31.
117. Chen, L., et al., *Investigation of the long-term desalination performance of membrane capacitive deionization at the presence of organic foulants.* Chemosphere, 2018. **193**: p. 989-997.
118. Hassanvand, A., et al., *An investigation of the impact of fouling agents in capacitive and membrane capacitive deionisation.* Desalination, 2019. **457**: p. 96-102.
119. Blair, J.W. and G.W. Murphy, *Electrochemical demineralization of water with porous electrodes of large surface area*. 1960, ACS Publications.
120. Caudle, D., et al., *Electrochemical demineralization of water with carbon electrodes: research and development progress.* United States Department of the Interior, 1966: p. 190.

121. Johnson, A. and J. Newman, *Desalting by means of porous carbon electrodes.* Journal of the Electrochemical Society, 1971. **118**(3): p. 510.
122. Farmer, J.C., et al., *Capacitive deionization of NaCl and NaNO3 solutions with carbon aerogel electrodes.* Journal of the Electrochemical Society, 1996. **143**(1): p. 159-169.
123. Hassanvand, A., et al., *Improvement of MCDI operation and design through experiment and modelling: Regeneration with brine and optimum residence time.* Desalination, 2017. **417**: p. 36-51.
124. Zhao, R., et al., *Optimization of salt adsorption rate in membrane capacitive deionization.* Water research, 2013. **47**(5): p. 1941-1952.
125. Hassanvand, A., et al., *The role of ion exchange membranes in membrane capacitive deionisation.* Membranes, 2017. **7**(3): p. 54.
126. Li, H. and L. Zou, *Ion-exchange membrane capacitive deionization: a new strategy for brackish water desalination.* Desalination, 2011. **275**(1): p. 62-66.
127. Zhao, R., et al., *Energy consumption in membrane capacitive deionization for different water recoveries and flow rates, and comparison with reverse osmosis.* Desalination, 2013. **330**: p. 35-41.
128. Hassanvand, A., et al., *A comparison of multicomponent electrosorption in capacitive deionization and membrane capacitive deionization.* Water research, 2018. **131**: p. 100-109.
129. Zhao, Y., et al., *Performance comparison and energy consumption analysis of capacitive deionization and membrane capacitive deionization processes.* Desalination, 2013. **324**: p. 127-133.
130. Długołęcki, P. and A. van der Wal, *Energy recovery in membrane capacitive deionization.* Environmental science & technology, 2013. **47**(9): p. 4904-4910.
131. Chen, L., et al., *Energy recovery and electrode regeneration under different charge/discharge conditions in membrane capacitive deionization.* Desalination, 2018. **439**: p. 93-101.
132. KELLY, J. and P. KELLY, *Nanofiltration of whey: Quality, environmental and economic aspects.* International Journal of Dairy Technology, 1995. **48**(1): p. 20-24.
133. Ayala-Bribiesca, E., G. Pourcelly, and L. Bazinet, *Nature identification and morphology characterization of anion-exchange membrane fouling during conventional electrodialysis.* J. Colloid Interface Sci., 2007. **308**(1): p. 182-190.
134. Lin, T.S.F., P. Angers, and L. Bazinet, *Microscopic approach for the identification of cationic membrane fouling during cheddar cheese whey electroacidification.* J Colloid Interface Sci, 2008. **322**(2): p. 551-7.
135. Wang, Q., P. Yang, and W. Cong, *Cation-exchange membrane fouling and cleaning in bipolar membrane electrodialysis of industrial glutamate production wastewater.* Separation and purification technology, 2011. **79**(1): p. 103-113.
136. Bazinet, L. and M. Araya-Farias, *Effect of calcium and carbonate concentrations on cationic membrane fouling during electrodialysis.* Journal of colloid and interface science, 2005. **281**(1): p. 188-196.
137. Bazinet, L., et al., *Identification of skim milk electroacidification fouling: a microscopic approach.* Journal of colloid and interface science, 2001. **237**(1): p. 62-69.
138. Bazinet, L., et al., *Neutralization of hydroxide generated during skim milk electroacidification and its effect on bipolar and cationic membrane integrity.* Journal of membrane science, 2003. **216**(1): p. 229-239.

139. Ayala-Bribiesca, E., G. Pourcelly, and L. Bazinet, *Nature identification and morphology characterization of cation-exchange membrane fouling during conventional electrodialysis.* Journal of colloid and interface science, 2006. **300**(2): p. 663-672.
140. Bleha, M., et al., *Characteristic of the critical state of membranes in ED-desalination of milk whey.* Desalination, 1992. **86**(2): p. 173-186.
141. Casademont, C., G. Pourcelly, and L. Bazinet, *Effect of magnesium/calcium ratio in solutions subjected to electrodialysis: Characterization of cation-exchange membrane fouling.* Journal of colloid and interface science, 2007. **315**(2): p. 544-554.
142. Chen, G., et al., *Single and binary ion sorption equilibria of monovalent and divalent ions in commercial ion exchange membranes.* Water Research, 2020: p. 115681.
143. Trägårdh, G., *Membrane cleaning.* Desalination, 1989. **71**(3): p. 325-335.
144. Andreeva, M., et al., *Mitigation of membrane scaling in electrodialysis by electroconvection enhancement, pH adjustment and pulsed electric field application.* Journal of Membrane Science, 2018. **549**: p. 129-140.
145. Korngold, E., et al., *Fouling of anionselective membranes in electrodialysis.* Desalination, 1970. **8**(2): p. 195-220.
146. Ang, W.S., S. Lee, and M. Elimelech, *Chemical and physical aspects of cleaning of organic-fouled reverse osmosis membranes.* Journal of Membrane Science, 2006. **272**(1): p. 198-210.
147. Guo, H., et al., *Mechanisms of chemical cleaning of ion exchange membranes: a case study of plant-scale electrodialysis for oily wastewater treatment.* Journal of Membrane Science, 2015. **496**: p. 310-317.
148. Haddad, M., et al., *Electrochemical acidification of kraft black liquor: effect of fouling and chemical cleaning on ion exchange membrane integrity.* ACS Sustainable Chemistry & Engineering, 2016. **5**(1): p. 168-178.
149. Lujan-Facundo, M.J., et al., *Cleaning efficiency enhancement by ultrasounds for membranes used in dairy industries.* Ultrason Sonochem, 2016. **33**: p. 18-25.
150. Ebrahim, S., *Cleaning and regeneration of membranes in desalination and wastewater applications: state-of-the-art.* Desalination, 1994. **96**(1-3): p. 225-238.
151. Mohammadi, T., S. Madaeni, and M. Moghadam, *Investigation of membrane fouling.* Desalination, 2003. **153**(1): p. 155-160.
152. Tang, X., et al., *The efficacy of different cleaners and sanitisers in cleaning biofilms on UF membranes used in the dairy industry.* Journal of Membrane Science, 2010. **352**: p. 71-75.
153. American-Water-Works-Association, *Electrodialysis and electrodialysis reversal: M38.* Vol. 38. 1995: American Water Works Association.
154. Mikhaylin, S. and L. Bazinet, *Fouling on ion-exchange membranes: Classification, characterization and strategies of prevention and control.* Advances in colloid and interface science, 2016. **229**: p. 34-56.
155. Matzinos, P. and R. Álvarez, *Effect of ionic strength on rinsing and alkaline cleaning of ultrafiltration inorganic membranes fouled with whey proteins.* Journal of Membrane Science, 2002. **208**(1): p. 23-30.
156. Bdiri, M., et al., *Cleaning of cation-exchange membranes used in electrodialysis for food industry by chemical solutions.* Separation and Purification Technology, 2018. **199**: p. 114-123.

157. Garcia-Vasquez, W., et al., *Effects of acid–base cleaning procedure on structure and properties of anion-exchange membranes used in electrodialysis.* Journal of Membrane Science, 2016. **507**: p. 12-23.
158. Karlin, Y.V. and V. Kropotov, *Electrodialysis separation of Na+ and Ca2+ in a pulsed current mode.* Russian journal of electrochemistry, 1995. **31**(5): p. 472-476.
159. Ruiz, B., et al., *Application of relaxation periods during electrodialysis of a casein solution: Impact on anion-exchange membrane fouling.* Journal of membrane science, 2007. **287**(1): p. 41-50.
160. Cifuentes-Araya, N., G. Pourcelly, and L. Bazinet, *Impact of pulsed electric field on electrodialysis process performance and membrane fouling during consecutive demineralization of a model salt solution containing a high magnesium/calcium ratio.* Journal of colloid and interface science, 2011. **361**(1): p. 79-89.
161. Mikhaylin, S., et al., *Intensification of demineralization process and decrease in scaling by application of pulsed electric field with short pulse/pause conditions.* Journal of Membrane Science, 2014. **468**: p. 389-399.
162. Dufton, G., et al., *Positive Impact of Pulsed Electric Field on Lactic Acid Removal, Demineralization and Membrane Scaling during Acid Whey Electrodialysis.* International Journal of Molecular Sciences, 2019. **20**(4): p. 797.
163. Dufton, G., et al., *Systematic study of the impact of pulsed electric field parameters (pulse/pause duration and frequency) on ED performances during acid whey treatment.* Membranes, 2020. **10**(1): p. 14.
164. Yang, G., Y. Zhang, and S. Guan, *Study on the desalination of high hardness water by electrodeionization reversal.* Desalination and Water Treatment, 2016. **57**(18): p. 8127-8138.
165. Allison, R.P., *Electrodialysis reversal in water reuse applications.* Desalination, 1995. **103**(1): p. 11-18.
166. Katz, W.E., *The electrodialysis reversal (EDR) process.* Desalination, 1979. **28**(1): p. 31-40.
167. Merkel, A. and A.M. Ashrafi, *An Investigation on the Application of Pulsed Electrodialysis Reversal in Whey Desalination.* International journal of molecular sciences, 2019. **20**(8): p. 1918.
168. Bukhovets, A., et al., *The influence of current density on the electrochemical properties of anion-exchange membranes in electrodialysis of phenylalanine solution.* Electrochimica Acta, 2011. **56**(27): p. 10283-10287.
169. Martinez, F.A.C., et al., *Lactic acid properties, applications and production: a review.* Trends in food science & technology, 2013. **30**(1): p. 70-83.
170. Boyaval, P., C. Corre, and S. Terre, *Continuous lactic acid fermentation with concentrated product recovery by ultrafiltration and electrodialysis.* Biotechnology letters, 1987. **9**(3): p. 207-212.
171. Kim, Y.H. and S.H. Moon, *Lactic acid recovery from fermentation broth using one‐stage electrodialysis.* Journal of Chemical Technology & Biotechnology: International Research in Process, Environmental & Clean Technology, 2001. **76**(2): p. 169-178.
172. Handojo, L., et al., *Electro-membrane processes for organic acid recovery.* RSC Advances, 2019. **9**(14): p. 7854-7869.

173. Choi, J.-H., S.-H. Kim, and S.-H. Moon, *Recovery of lactic acid from sodium lactate by ion substitution using ion-exchange membrane.* Separation and purification technology, 2002. **28**(1): p. 69-79.
174. Li, Y., et al., *Separate and concentrate lactic acid using combination of nanofiltration and reverse osmosis membranes.* Applied biochemistry and biotechnology, 2008. **147**(1-3): p. 1-9.
175. Gonzalez, M.I., et al., *Lactic acid recovery from whey ultrafiltrate fermentation broths and artificial solutions by nanofiltration.* Desalination, 2008. **228**(1): p. 84-96.
176. Freger, V., T. Arnot, and J.A. Howell, *Separation of concentrated organic/inorganic salt mixtures by nanofiltration.* Journal of Membrane Science, 2000. **178**(1): p. 185-193.
177. Bouchoux, A., H. Roux-de Balmann, and F. Lutin, *Investigation of nanofiltration as a purification step for lactic acid production processes based on conventional and bipolar electrodialysis operations.* Separation and purification technology, 2006. **52**(2): p. 266-273.
178. Teella, A., G.W. Huber, and D.M. Ford, *Separation of acetic acid from the aqueous fraction of fast pyrolysis bio-oils using nanofiltration and reverse osmosis membranes.* Journal of Membrane Science, 2011. **378**(1-2): p. 495-502.
179. Kezia, K., et al., *Convective transport of boron through a brackish water reverse osmosis membrane.* Journal of membrane science, 2013. **445**: p. 160-169.
180. Merson, R., G. Paredes, and D. Hosaka, *Concentrating fruit juices by reverse osmosis*, in *Ultrafiltration membranes and applications*. 1980, Springer. p. 405-413.
181. Malaiyandi, M., S. Shah, and V. Sastri, *Reverse osmosis separation of some organic acids from their aqueous solutions.* Separation Science and Technology, 1982. **17**(8): p. 1065-1074.
182. Thang, V.H., et al., *Detailed investigation of an electrodialytic process during the separation of lactic acid from a complex mixture.* Journal of membrane science, 2005. **249**(1): p. 173-182.
183. Rice, G., et al., *Fouling of NF membranes by dairy ultrafiltration permeates.* Journal of Membrane Science, 2009. **330**(1-2): p. 117-126.
184. Liu, C., et al., *Membrane chemical cleaning: from art to science.* Pall Corporation, Port Washington, NY, 2001. **11050**.
185. Kapoor, R. and L. Metzger, *Evaluation of salt whey as an ingredient in processed cheese.* Journal of dairy science, 2004. **87**(5): p. 1143-1150.
186. Hassanvand, A., *Membrane capacitive deionisation as a novel approach to wastewater treatment*. 2018.
187. Luo, T., F. Roghmans, and M. Wessling, *Ion mobility and partition determine the counter-ion selectivity of ion exchange membranes.* Journal of Membrane Science, 2019: p. 117645.
188. Alhéritière, C., W.R. Ernst, and T.A. Davis, *Metathesis of magnesium and sodium salt systems by electrodialysis.* Desalination, 1998. **115**(2): p. 189-198.
189. Jelen, P., *Whey Processing| Utilization and Products.* 2011.
190. Beaton, N.C., *Ultrafiltration and reverse osmosis in the dairy industry-An introduction to sanitary considerations.* Journal of Food Protection®, 1979. **42**(7): p. 584-590.
191. Cifuentes-Araya, N., G. Pourcelly, and L. Bazinet, *Water splitting proton-barriers for mineral membrane fouling control and their optimization by accurate pulsed modes of electrodialysis.* Journal of membrane science, 2013. **447**: p. 433-441.

192. Simova, H., V. Kysela, and A. Cernin, *Demineralization of natural sweet whey by electrodialysis at pilot-plant scale.* Desalination and Water Treatment, 2010. **14**(1-3): p. 170-173.
193. Krol, J., M. Wessling, and H. Strathmann, *Chronopotentiometry and overlimiting ion transport through monopolar ion exchange membranes.* Journal of membrane science, 1999. **162**(1): p. 155-164.
194. Nishanthi, M., J. Chandrapala, and T. Vasiljevic, *Compositional and structural properties of whey proteins of sweet, acid and salty whey concentrates and their respective spray dried powders.* International Dairy Journal, 2017.
195. Długołęcki, P., et al., *Transport limitations in ion exchange membranes at low salt concentrations.* Journal of Membrane Science, 2010. **346**(1): p. 163-171.
196. Shu, L., et al., *Why does pH increase with CaCl2 as draw solution during forward osmosis filtration.* Process Safety and Environmental Protection, 2016. **104**: p. 465-471.
197. Knipschildt, M. and G. Andersen, *Drying of milk and milk products*, in *Robinson: Modern Dairy Technology*. 1994, Springer. p. 159-254.
198. Buhler, M., H.-U. Bohren, and T. Hodel, *Ultrafiltration process for the recovery of proteins from milk*. 1977, Google Patents.
199. Schaep, J., et al., *Removal of hardness from groundwater by nanofiltration.* Desalination, 1998. **119**(1-3): p. 295-301.
200. Rongsirikul, N. and P. Hongsprabhas, *Brown pigment formation in heated sugar–protein mixed suspensions containing unmodified and peptically modified whey protein concentrates.* Journal of food science and technology, 2016. **53**(1): p. 800-807.
201. Croguennec, T., *Non‐enzymatic browning.* Handbook of Food Science and Technology 1: Food Alteration and Food Quality, 2016: p. 133-157.
202. Choi, J.-H. and S.-H. Moon, *Structural change of ion-exchange membrane surfaces under high electric fields and its effects on membrane properties.* Journal of colloid and interface science, 2003. **265**(1): p. 93-100.
203. Monajjemzadeh, F., et al., *Assessment of feasibility of Maillard reaction between baclofen and lactose by liquid chromatography and tandem mass spectrometry, application to pre formulation studies.* AAPS PharmSciTech, 2009. **10**(2): p. 649-659.
204. Zabolotskii, V., R.K. Chermit, and M. Sharafan, *Mass transfer mechanism and chemical stability of strongly basic anion-exchange membranes under overlimiting current conditions.* Russian Journal of Electrochemistry, 2014. **50**(1): p. 38-45.
205. Saito, Z., *Lactose crystallization in commercial whey powders and in spray-dried lactose.* Food Structure, 1988. **7**(1): p. 9.
206. Hábová, V., et al., *Electrodialysis as a useful technique for lactic acid separation from a model solution and a fermentation broth.* Desalination, 2004. **162**: p. 361-372.
207. Lee, E.G., et al., *Recovery of lactic acid from fermentation broth by the two-stage process of nanofiltration and water-splitting electrodialysis.* Biotechnology and Bioprocess Engineering, 2006. **11**(4): p. 313-318.
208. Knipp, G.T., et al., *Paracellular diffusion in Caco-2 cell monolayers: Effect of perturbation on the transport of hydrophilic compounds that vary in charge and size.* Journal of Pharmaceutical Sciences, 1997. **86**(10): p. 1105-1110.
209. Thylin, I., et al., *Influence of pH and lactic acid concentration on Clostridium tyrobutyricum during continuous growth in a pH‐auxostat.* Journal of applied bacteriology, 1995. **79**(6): p. 663-670.

210. Meng, J., et al., *A novel salt-responsive TFC RO membrane having superior antifouling and easy-cleaning properties.* Journal of Membrane Science, 2014. **461**: p. 123-129.
211. Lee, J.-B., et al., *Desalination of a thermal power plant wastewater by membrane capacitive deionization.* Desalination, 2006. **196**(1-3): p. 125-134.
212. Lee, J.-H. and J.-H. Choi, *The production of ultrapure water by membrane capacitive deionization (MCDI) technology.* Journal of membrane science, 2012. **409**: p. 251-256.
213. Kim, Y.-J., J.-H. Kim, and J.-H. Choi, *Selective removal of nitrate ions by controlling the applied current in membrane capacitive deionization (MCDI).* Journal of membrane science, 2013. **429**: p. 52-57.
214. Zhao, R., et al., *Energy consumption in membrane capacitive deionization for different water recoveries and flow rates, and comparison with reverse osmosis.* Desalination, 2013. **330**: p. 35-41.
215. Zhang, C., et al., *Integrated flow-electrode capacitive deionization and microfiltration system for continuous and energy-efficient brackish water desalination.* Environmental Science & Technology, 2019. **53**(22): p. 13364-13373.
216. Ma, J., et al., *Flow-electrode capacitive deionization (FCDI) scale-up using a membrane stack configuration.* Water research, 2020. **168**: p. 115186.
217. AtlantisTechnologies. *Radial Deionization.* [cited 2020; Available from: atlantis-water.com/technoloogy/.
218. Valero, F. and R. Arbós, *Desalination of brackish river water using Electrodialysis Reversal (EDR).* Desalination, 2010. **253**(1): p. 170-174.
219. Alvarado, L. and A. Chen, *Electrodeionization: principles, strategies and applications.* Electrochimica Acta, 2014. **132**: p. 583-597.
220. Cheryan, M. and S.R. Parekh, *Separation of glycerol and organic acids in model ethanol stillage by electrodialysis and precipitation.* Process biochemistry, 1995. **30**(1): p. 17-23.