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Transforming Salty Whey into Cleaning Chemicals using Electrodialysis with Bipolar Membranes

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***Keywords*:** Salty whey; Electrodialysis with bipolar membrane; Dairy; Acid production; Base Production.

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***Abstract*:**

Large quantities of salty whey are produced during cheese manufacturing, posing an environmental problem. Here the feasibility of electrodialysis with bipolar membranes (EDBM) is evaluated for the first time as a mechanism to transform this saline effluent into sodium hydroxide and hydrochloric acid for reuse within the factory. The work also seeks to find the maximum acid and base concentration that can be achieved. For a pure sodium chloride solution, maximum acid/base concentrations of 3.6 ± 0.2 mol/L and 3.0 ± 0.3 mol/L are achieved using a stack of ten membranes including four bipolar membranes. The effects of proton leakage and water migration limit the generation of higher concentrations. The presence of calcium phosphate also has a negative effect on the EDBM performance, suggesting that pretreatment to remove this impurity is needed. In industrial practice, this pretreatment could be achieved by recycling around 9 % of the base produced to precipitate these salts. The use of a partially cyclic operation allows 99% demineralization of pretreated salty whey, with high purity acid/base solutions of concentration near 3.5 mol/L. This work demonstrates EDBM as an effective process for transforming salty whey into chemicals for clean in place and ion exchange resin regeneration.

1. Introduction

Large quantities of highly saline effluent are generated within dairy manufacturing. In particular, salt (sodium chloride) is added to protein-rich cheese curds to reduce the water activity in the production of semi hard or hard cheese (e.g., Cheddar and Colby). The excess moisture, containing a large amount of the added salt is then expelled during the pressing processes, forming a brine stream called salty whey [1]. When salty whey is discharged from the cheese vat, the typical salt content (mainly NaCl) ranges from approximately 0.7 to 1.7 mol/L (4.1 to 10%) [2]. Similar to the environmental concerns arising from the brines generated from seawater desalination, the disposal of salty whey is subject to increasingly strict regulatory requirements due to the increase in agricultural water usage and local land degradation caused by sodium leaching [3]. As a result, utilization and treatment of salty whey has become a major focus of the sustainability agenda of the dairy industry.

Electrodialysis technology has been applied to the treatment of such high salt wastewaters on an industrial scale since the 1950s [4-6]. Moreover, the use of a bipolar membrane was introduced into the ED process in the 1970s, forming a new technology, electrodialysis with bipolar membranes (EDBM) and expanding the application of this approach [7].

The EDBM technology has been developed as a sustainable approach to split an aqueous saline stream into its corresponding acid and base without any use of chemicals [7-9]. EDBM is configured with a series of ion exchange membranes (IEMs), including anion exchange membranes (AEMs), cation exchange membranes (CEMs) and bipolar membranes (BPMs) between a pair of electrodes (see Fig. 1). The BPM is typically composed of three layers: an anion-exchange layer, a cation-exchange layer, and an intermediate layer which serves to promote the splitting of water into H^+ and OH^- ions via a catalytic mechanism and the second Wien effect [10]. After the application of an electric field, H^+ ions generated from water splitting at the BPM migrate toward the cathode and are trapped in the acid chamber by an AEM. Likewise, OH^- ions migrate toward the anode and are retained in the base chamber by a CEM [9]. Electroneutrality of the acid chamber is maintained by electromigration of anions from the feed solution through the AEM. Charge balance of the base chamber is maintained by cation migration from the feed solution through the CEM. Thus, the high-salinity waste stream

in the feed chamber is desalted to provide a treated water effluent that can be reused or discharged directly. The corresponding acid/base solutions are produced in the acid/base chambers, respectively, which can be readily used for ion exchange regeneration and/or clean in place procedures. It should be noted that electrically driven membrane processes such as EDBM are more capital intensive than pressure driven membrane processes such as reverse osmosis, as the ion exchange membranes are significantly more expensive. In turn, a bipolar membrane is more than twice as expensive as either the CEM or AEM.

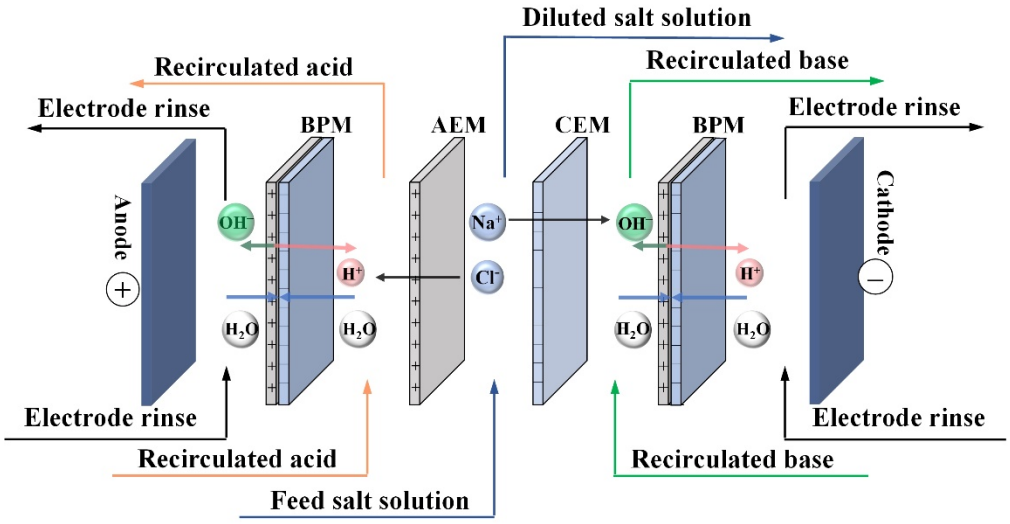

Fig. 1 Schematic diagram of an EDBM stack

A number of papers have already explored the optimum conditions for EDBM efficiency in saline systems [11-13]. In addition, EDBM technology has been used for the production of inorganic acids and bases from industrial wastewater [13, 14], the production of organic acids [15-18], metal recovery [19, 20] and in the food industry [18, 21]. Within the dairy industry, EDBM has been considered for pH correction of whey [22] and for the separation of casein from milk [23-25].

However, relatively little information is available on the maximum acid/base concentration and yield that can be obtained from highly saline waste streams via EDBM technology. Reig et al. [9] showed that acid and base concentrations of 0.7 and 0.6 mol/L respectively could be achieved with a feed concentration of 50 g/L NaCl, but did not investigate the use of higher feed concentrations and ended the experiments when the current density began to fall, rather

than when it reached a zero value. Ghyselbrecht et al. [7] achieved concentrations of 1.2 ± 0.1 and 1.25 ± 0.15 mol/L respectively using a feed solution of 75 g/L.

Furthermore, the application of EDBM to produce acids and bases from saline dairy effluents such as salty whey has not been explored. Salty whey differs substantially from the seawater and wastewater streams that have been the focus of most previous work. Specifically, this dairy effluent contains significant quantities of lactose (~2.5 wt%) [26, 27], and small quantities of divalent ions such as calcium, magnesium and phosphate [26, 27], all of which may interfere with the EDBM process. Further, the dairy industry consumes significant volumes of acids and bases both as clean-in-place chemicals and for ion exchange resin regeneration. If these acids and bases could be generated at sufficient strength in-house from saline effluents there would be obvious cost benefits as well as significant improvements in environmental footprint.

In this study, constant voltage electrodialysis with bipolar membranes was performed to produce sodium hydroxide and hydrochloric acid from salty streams. Pure NaCl solutions were first used to determine the maximum acid/base concentration and to optimize the process conditions. Mixtures of NaCl with calcium phosphate, as well as salty whey samples collected from a dairy factory, were then used as feed to better investigate the technical and economic feasibility for transformation of salty whey. The tolerance of the ion exchange membranes under these extreme conditions, as well as membrane fouling was considered. The work demonstrates that EDBM can be an effective process for transforming salty whey into chemicals of sufficient strength for re-use within the dairy industry.

2. Materials and methods

2.1. Materials

The cation exchange membrane (CEM), anion exchange membrane (AEM) and bipolar membrane (BPM) used were Neosepta CMB/AHA (Tokuyama Co., Japan) and Neosepta BP-1E (Tokuyama Co., Japan) respectively, which are known for their wide pH tolerance and temperature stability (Table 1). Before the experiments, the CEMs and AEMs were immersed in 0.5 mol·L^{-1} NaCl solution for 24 h to ensure that they were in the Na^+ and Cl^- forms.

The salty whey used in the experiments was obtained from a dairy processing company in Victoria, Australia. Ultrafiltration was used to remove most of the protein and it is the ultrafiltration permeate that is used here. This salty whey was kept refrigerated at 2 - 4 ℃. The ionic composition is provided in Table 2.

The reagents used in the study were all AR grade and deionized water (> 18.2 MΩ cm; Merck Millipore KGaA, Germany) was used throughout the experiments. Solutions of mixed salts were prepared by mixing 1.95M sodium chloride (NaCl, >99.5%, Chem-supply Pty. Ltd., Australia) with 0.04M dihydrate calcium chloride ($CaCl_2 \cdot 2H_2O$, >99.5%, Merck Pty. Limited, Australia) with 0.025 M di-sodium hydrogen orthophosphate (Na_2HPO_4, >99.0%, Chem-supply Pty. Ltd., Australia) to mimic the concentration of ions in salty whey (see Table 2). Hydrochloric acid (HCl, 36%, Thermo Fisher Scientific Australia Pty., Ltd., Australia) was added to ensure the complete dissolution of the phosphate salts.

In other experiments, sodium hydroxide (NaOH. pellets, Chem-Supply Pty. Ltd., Australia) was used to adjust the pH to 11 to precipitate calcium and magnesium phosphates, as these multivalent salts are known to increase the electrical resistance in electrodialysis systems. After vacuum filtration through a 0.22 micron polyethersulfone filter (Stericup, Corning Incorporated, USA), the solution retained only 5% of the original calcium, 45% of the Magnesium and 15% of the phosphate content and is referred to as pre-treated salty whey (Table 2).

Solutions of 20 g/L sodium sulphate (Na_2SO_4, >99%; Thermo Fisher Scientific Australia Pty., Ltd., Australia) were prepared as the electrode rinse solutions used throughout the experiments.

149 Table 1 Relevant properties of the membranes used in the unit*

Properties	Unit	Membranes		
		AHA	CMB	BP-1E
type	-	Strong base (Cl type)	Strong acid (Na type)	-
Electric resistance	$\Omega \cdot cm^2$	4.1	4.5	-
Thickness	mm	0.22	0.21	0.22
Temperature tolerance	℃	0-60	0-60	-
pH tolerance	-	0-14	0-14	-
Water splitting voltage [a]	V	-	-	1.2
Water splitting efficiency [b]	-	-	-	⩾0.98

150 **The data were obtained from the product brochure provided by manufacturers.*

151 *[a] 1 N NaOH / 1 N HCl, 10 A/dm^2, 30 ℃*

152 *[b] potential difference measured between silver-silver chloride electrodes.*

153

154 Table 2 The concentration of key ions in salty whey, pretreated salty whey and the salt mixtures

155 used in this work**

Component (g/L)	Salty whey	Pretreated salty whey[c]	Salt mixtures	
			NaCl+HCl	NaCl+$CaCl_2$+Na_2HPO_4+HCl
Sodium	51.9 ± 2.6	50.9 ± 3.5	46.0 ± 1.5	51.2 ± 2.4
Potassium	2.1 ± 0.2	1.77 ± 0.2	/	/
Calcium	1.5 ± 0.03	0.07 ± 0.01	/	1.6 ± 0.03
Phosphorus [d]	0.7 ± 0.1	0.1 ± 0.02	/	0.8 ± 0.1
Magnesium	0.2 ± 0.01	0.09 ±0.004	/	/
pH	5.1 ± 0.4	11.0 ± 0.2	1.6 ± 0.08	2.3 ± 0.2

156 ***Data obtained from ICP analysis.*

157 *[c] pretreated by increasing pH to 11 by the addition of 2.6 g sodium hydroxide pellets into each litre of the*

158 *salty whey.*

159 *[d] Phosphorus (P) is present as phosphate ions in salty whey. Chloride ions (not determined) are the primary*

160 *anions in the sample with a similar molar concentration to that of sodium[28].*

161

162

2.2. EDBM Setup and operation

EDBM was conducted using an FT-TS3 module manufactured by FuMA-Tech GmbH (Germany). Four pieces of BP-1E, three pieces of AHA and three pieces of CMB were installed in the BPM-AEM-CEM-BPM configuration in this study, as shown in Fig. 1. The effective area for each membrane was 100 cm^2 (10 cm × 10 cm). The anode was titanium coated with ruthenium and iridium, and the cathode was composed of stainless steel. Membranes were separated by a silicone spacer with a thickness of 0.50 mm.

Sodium chloride solutions, their mixtures with calcium phosphate and hydrochloric acid and salty whey (Table 2) were used as feed solutions. Deionized water was used as initial solution in the acid and base compartments. Unless otherwise noted, the initial volume of feed, acid and base solutions were 1 L. Four adjustable peristaltic pumps (Masterflex L/S digital drive 600 RPM with Masterflex L/S high performance pump head, Cole-Parmer, USA) were separately used to pump feed, acid, base and electrode solutions through the corresponding compartments. All experiments were conducted in batch operation, with solutions circulated via four separate tanks (feed, acid, base and electrode solution) each kept in a water bath for temperature control. Through all the experiments, the temperature was maintained at 30 ± 2 ℃. A magnetic stirrer was used in each tank to ensure homogeneous solutions. All of the solutions were circulated at 800 mL/min as recommended by the manufacturer, to eliminate the effect of concentration polarization as far as possible [29]. The experiments were operated under constant voltage (CV) mode with a regulated power supply (Agilent DC Modular Power System N6700B). Operating in CV mode is preferred in batch operation because it can reduce the possibility of the system operating beyond the limiting current density [29]. Before the supply of power, the solutions were circulated for 15 min to eliminate air bubbles. Unless otherwise specified, each experiment ended with a 99% desalination rate in the feed chamber. Most experiments were completed in triplicate to confirm reproducibility.

After each experiment, the EDBM stack was cleaned-in-place by flushing the units with deionized water for 30 min, followed by circulating HCl solution (pH of 1.0 ± 0.15) and NaOH solution (3% NaCl adjusted to a pH of 9.15 ± 0.15 using NaOH) for 30 min in sequence and then flushing with deionized water for 30 min. Finally, the membrane stack was soaked in 2 %

NaCl for more than 12 hours. This protocol ensured that the membranes were fully clean before re-use and had returned to their original ionic state [30].

2.3. Analytical methods

Samples (approximately 10 mL each) from feed, acid and base streams were collected at intervals for analysis. The concentrations of the samples in the acid and base compartments were detected by acid/base titration (905 Titrando, coupled with 814 USB Sample Processor and 800 Dosing Unit, Metrohm, Switzerland). The concentrations of sodium, calcium, potassium, magnesium and phosphorus were measured using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP–OES 720ES, Varian). All samples were filtered and diluted to meet the equipment detection limits. The conductivity and pH variations of the solutions were monitored by a pH/conductivity multi-parameter (S470-SevenExcellence, Mettler-Toledo Ltd., Switzerland). Fourier Transform Infrared spectroscopy (FT-IR, PerkinElmer Spectrum 100, North America) was used to compare the chemical structure and the surface groups of the fresh and used membranes. Eight scans for wavelengths between 650-4000 nm were completed per sample.

2.4. Performance evaluation

The desalination rate (DR) was calculated according to following equation.

$$DR=\frac{(C_0-C_t)}{C_0}\times 100\% \quad (1)$$

where C_t and C_0 (mol/L) are the concentration of acid (or base) at time t and 0 respectively.

The current efficiency and energy consumption were calculated based on the concentrations of the final acid or base. Current efficiency η (%) is calculated by Equation 2 [31]:

$$\eta=\frac{z\cdot(C_t-C_0)\cdot V\cdot F}{N\cdot I\cdot t} \quad (2)$$

where η (%) is current efficiency; z is the absolute valence of the ion; V (L) is the volume of the acid (or base) compartment; F is the Faraday constant (96500 C); N is the number of repeat cells, which was three in the present case; I (A) is the current applied in the stack; t (s) is the

test time.

The energy consumption per kg of acid or base, E (kWh/kg) was calculated as the following equation [31]:

$$E = \int_0^t \frac{U \cdot I \cdot dt}{(C_t - C_0) \cdot V \cdot M} \quad (3)$$

where E (kWh/kg) is energy consumption; U (V) is the voltage drop across the EDBM stack and M is the molar mass of the acid (or base).

3. Results and discussion

3.1. NaCl as feed solution

3.1.1 The effect of applied voltage

When treating a pure solution of 50 g/L NaCl (0.86 M), an increase in the applied voltage from 11 to 21V leads to a higher acid and base production rate (Fig. 2). The greater applied voltage accelerates the transmembrane migration of ions and increases the rate of water dissociation at the BM due to the second Wien effect [10]. The maximum acid and base concentrations are similar regardless of the voltage, at approximately 0.77 mol/L HCl and 0.82 mol/L NaOH. These values are very similar to those reported by Reig et al. [9] working at the same feed concentration and 9 V. The final acid concentration is slightly lower than the base concentration here, due to a greater leakage of protons through the anion-exchange membrane into the feed chamber than the leakage of hydroxide ions through the cation-exchange membrane. This reflects the smaller hydrodynamic radius of protons. Such proton leakage has been observed by many other researchers [7, 32-34].

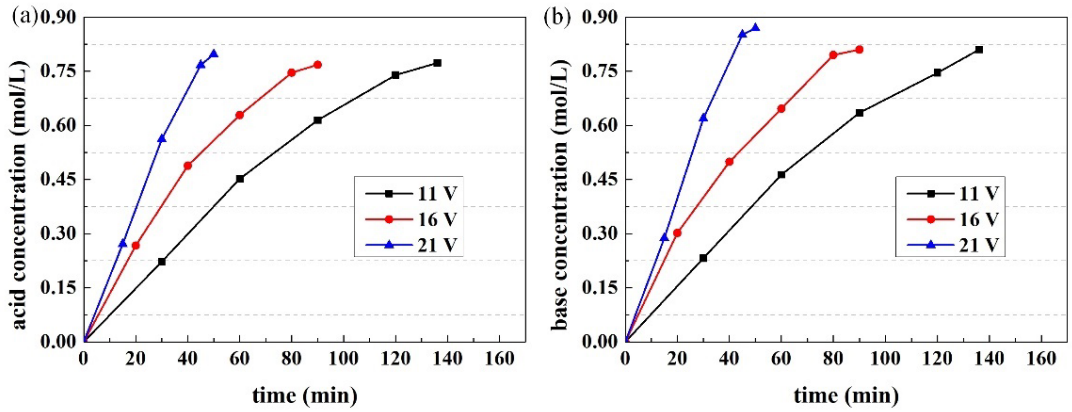

Fig. 2 The concentration of acid and base produced from 50 g/L NaCl at different applied voltages.

The unit energy consumption increases when the applied voltage increases due to the greater current (Fig. S1). The current efficiency falls as the product sodium and chloride concentrations begin to exceed that in the feed chambers, due to back diffusion of these ions and osmotic water flows coming into play. The current efficiency at 16 V is generally higher than that at 11 V or 21 V, particularly at lower product concentrations (Fig. S1). This is attributed to the competing effects of increased water dissociation at the BPM at higher applied voltage, but greater water dissociation at the electrodes and IEMs, which is less effective in building the acid and base concentrations in the product compartments. As 16 V is identified as an optimal voltage for this system, this voltage is used for the following experiments.

3.1.2 The effect of initial feed concentration

When the initial feed solution concentration increases at constant voltage, the current increases due to the lower solution resistance (Fig. 3a). The current and the feed conductivity (Fig. 3b) decrease more slowly when the initial feed concentration is high. This is firstly because the rate of transfer of sodium and chloride, as given by the current, does not increase in proportion to the feed solution concentration and hence it takes longer to fall. Secondly, as time progresses, protons and hydroxide ions migrate from the acid and base chambers back into the feed chamber and these add to the feed conductivity. Finally, osmotic water flows from the feed chamber limit the reduction in the salt concentrations in this chamber. Specifically,

when the initial concentration increases from 50 g/L to 150 g/L, the feed volume decreases from an initial 1 L to a final 0.86 L and 0.56 L, respectively (Table S1). As noted in the work by Jiang et al. [35], this net water migration occurs predominantly due to the hydration shell that surrounds each ion as it migrates, rather than from differences in osmotic pressure.

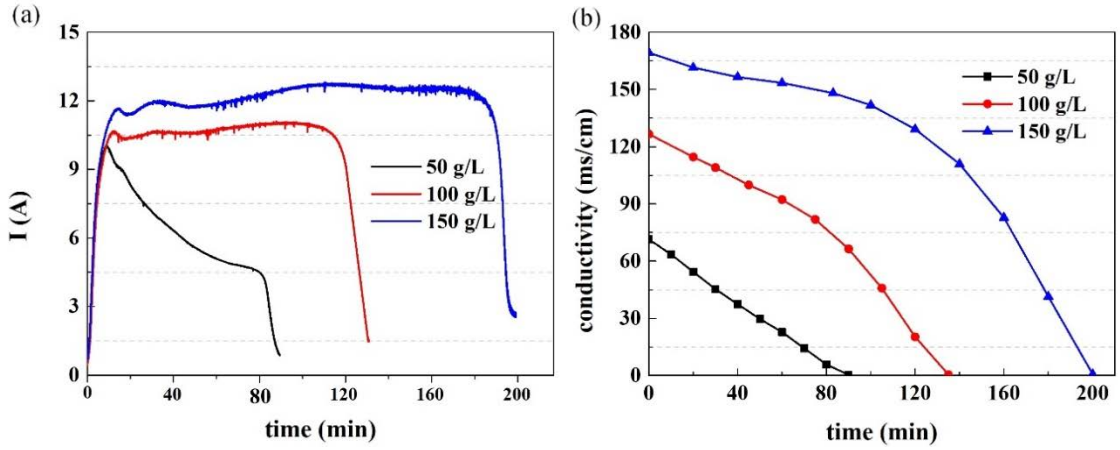

Fig. 3 (a) The current and (b) desalination rate in the feed chamber with different feed concentrations of NaCl.

The production rate of acid and base increase with the initial feed concentration (Fig. 4a), reflecting the increases in current. The acid and base concentrations increase more rapidly at the beginning, as there is no competing proton or hydroxide leakage and less osmotic water flows. Moreover, the concentration of NaOH is also slightly higher than that of HCl due to the preference for proton over hydroxide transfer. Ghyselbrecht et al. achieve comparable results with their feed solution of 75 g/L [7].

The final concentration of acid and base increases with the feed solution concentration (Fig. 4b), which is expected as each experiment concluded only when the DR reached 99%. However, as also identified by Li et al.[8], all values are below the ideal concentration calculated by dividing the moles of sodium and chloride ions transferred from the feed chamber by the initial solution volume of the acid and base chambers. The greater the initial feed concentration, the greater the discrepancy. This is partly due to back diffusion of the sodium ions through the anion exchange membranes and bipolar membrane; and chloride ions through the cation exchange membranes to form sodium chloride, rather than acid or base. It is also due to the net water migration described above.

A higher acid and base concentration leads to a decrease in current efficiency and increase in the unit energy consumption, regardless of the initial feed concentration (Fig. S2). This again reflects greater back diffusion of all ions and water transfer at the higher concentrations.

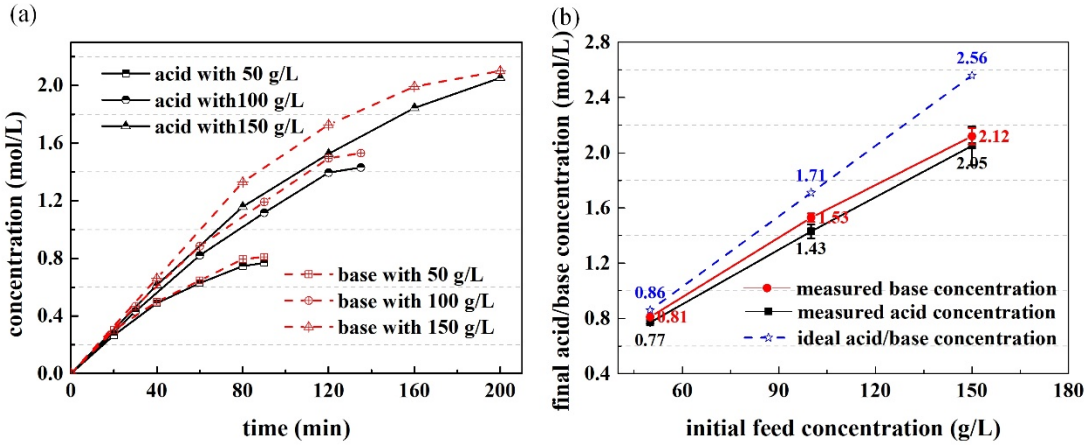

Fig. 4 The effect of initial feed concentration on (a) acid/base production rate, (b) final acid/base concentration.

3.1.3 The effect of initial volume ratio

A multistage-batch or feed and bleed operation may be used in industry [36, 37] to reduce capital costs. These arrangements can be mimicked at the lab scale by changing the volume ratio of diluate to concentrated solution. The experiments in this section were performed at 16 V with 50 g/L (0.86M) NaCl feed concentration. The volumes of acid and base solutions were 1 L, while the volume of feed solution was increased from 1 L to 6 L ($V_{acid\ and\ base}$: V_{feed}= 1:1, 1:3 and 1:6).

The rate of increase in acid and base concentrations are essentially unaffected by the feed volume in the early stage of each experiment, as the concentrations on both sides of the membrane are similar (Fig. 5a). However, the increased feed volume allows higher concentrations to be obtained. The rate of increase slows at higher concentrations, as back diffusion of protons and hydroxide ions, and osmotic flows of water becomes greater. Reig et al. [9] found that increasing the initial acid and base concentration had a diminishing impact on the final concentrations for similar reasons. When the volume ratio is 1 to 6, the acid and

base concentrations stabilize at around 540 min, even though the feed solution still contains salt. At this point, the number of protons transferred from the acid chamber to feed chamber by diffusion is equal to that generated by water dissociation at the BPM. This represents the maximum acid (3.6 ± 0.2 mol/L) and base (3.2 ± 0.3 mol/L) concentration that can be achieved, regardless of feed volume (Fig. 5b).

When the volume ratio is 1:6, the maximum acid concentration is greater than the alkali concentration, which is the opposite of the effects observed when the volume ratio was 1:1 (see Section 3.1.1). At the larger feed volumes, the water transferred from the feed chamber to the base chamber (0.97 L) is significantly larger than that transferred to the acid chamber (0.3 L). These volume changes are much higher than the volume change of acid (0.08 L) and base (0.05 L) when the volume ratio was 1:1 (Table S1), due to the much higher acid and base concentrations achieved. As the concentration difference between feed solution and acid/base solution increases, the forward osmosis of water from the feed chamber increases, as does the water carried by the hydration sheath of each ion. The hydration number for sodium entering the base chamber (5-8), is higher than that for chloride entering the acid chamber (4) [38]. Similarly, more water leaves the acid chamber due to the greater proton leakage, relative to hydroxide leakage. This explains the greater net water transfer for the base chamber.

As expected, with an increase in the maximum acid and base concentration (the volume ratio from 1:1 to 1:6), the current efficiency decreases due to the increasing back diffusion, unwanted water dissociation and water osmosis, while the energy consumption increases (Fig. S4).

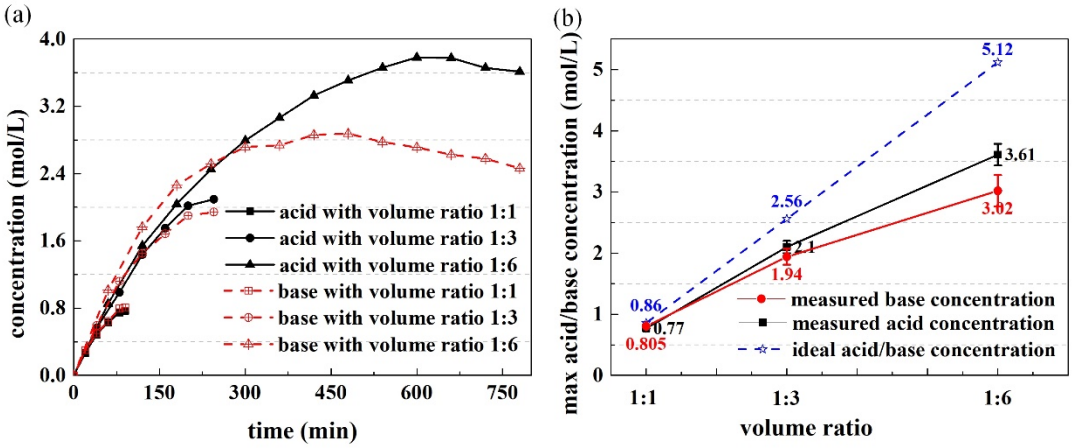

Fig. 5 The effect of volume ratio ($V_{acid\ and\ base}$: V_{feed}) on (a) acid/base production rate, (b) maximum acid/base concentration. The volumes of acid and base solutions were 1 L, while the volume of feed solution was increased from 1 L to 6 L.

The properties of the membranes after 25 h of operation in these high acid/base concentration environments were also investigated (Fig. S5). Fig. S5 d indicates the infrared spectra of different BP-1E detected from the cation exchange side. The peaks at 1015 cm^{-1} and 1175 cm^{-1} confirmed the presence of SO_3 and SO_2 respectively, due to sulfonation [39]. There is clear evidence of the change of the BP-1E near the cathode, with these SO_3 and SO_2 peaks weakening, indicating that the sulfonic acid groups in the cation exchange layer of the BP-1E have decomposed. This may be attributed to the strong oxidation of the sulfuric acid groups by the combination of the proton produced by the bipolar membrane near the cathode and the sulfate ion in the electrolyte.

3.2. The effect of Calcium Phosphate

The species Na^+ and Cl^- have the largest concentrations in salty whey solution (Table 2). Nevertheless, the presence of multivalent ions (principally as calcium phosphate) might significantly affect the performance of the EDBM system. To test these impacts, experiments were performed by mixing 114 g/L NaCl (1.95 mol/L) with 0.04 mol/L $CaCl_2$ and 0.025 mol/L Na_2HPO_4 and HCl to a pH of 2.3 (see Table 2). These experiments were conducted at an applied voltage of 16 V and a volume ratio of 1:3. As a comparison, solutions of 117 g/L NaCl (2

mol/L), both at neutral pH and also adjusted to a low pH with HCl, were tested at an applied voltage of 16 V and a volume ratio of 1:2.

The current decreases significantly when calcium and phosphate are added into the feed solution, which indicates a significant increase in stack resistance (Fig. 6a). As noted by Firdaous et al. [40], multivalent ions preferentially pair with the fixed charge groups in the IEM due to Donnan exclusion, reducing the available sites for monovalent transfer. This reduces the flux of monovalent ions such as sodium, and therefore the current [41]. Further, calcium salts such as calcium hydroxide and calcium phosphate can precipitate in the base chamber, leading to membrane fouling that also increases system resistance. Such membrane fouling under alkaline conditions has been observed in previous studies using dairy whey in EDBM by Merkel et al. [22] and Bazinet et al.[42] and in ED by Talebi et al.[30]. The lower current leads to a lower acid-base production rate (Fig. 6b).

It is worth noting that the feed pH in these experiments was low (pH= 2.3) in order to ensure complete dissolution of all salts. However, adjustment of the pH of the pure NaCl solution with HCl (to pH =1.6) did not cause any comparable loss in current or acid/base production, indicating that this low pH was not the cause of the observed effects.

The current efficiency and energy consumption based on unit acid and base production with the different solutions are shown in Fig. S6. The presence of the calcium and phosphate ions causes a small reduction in current efficiency and an increase in unit energy consumption of acid. The current efficiency of the solution containing calcium phosphate at the acid concentration of 2 mol/L was 51 ± 5 %, which is lower than the value of 60 ± 2 % for the NaCl solution. Similarly, the energy consumption was 7.2 ± 0.3 kWh/kg versus 6.4 ± 0.3 kWh/kg for the NaCl solution.

To evaluate the quality of the acid and base generated from the solution containing calcium and phosphate, the concentrations of relevant ions were analyzed as a function of time in experiments at a volume ratio of 1:3 (Fig. 7). During the EDBM process, sodium transfers from the feed chamber and accumulates in the base chamber. A small quantity of sodium also migrates through the anion exchange membrane into the acid compartment, due to the high feed concentrations. Daniliidis et al.[43] found that membrane permselectivity falls below 90%

384 when the concentration exceeds 2M. Calcium initially transfers to the base chamber, but the
385 concentration in this chamber then falls, probably due to precipitation of calcium hydroxide as
386 the pH in this chamber increases. Phosphate migrates to the acid chamber, although the
387 migration rate is low due to the very low feed concentrations.
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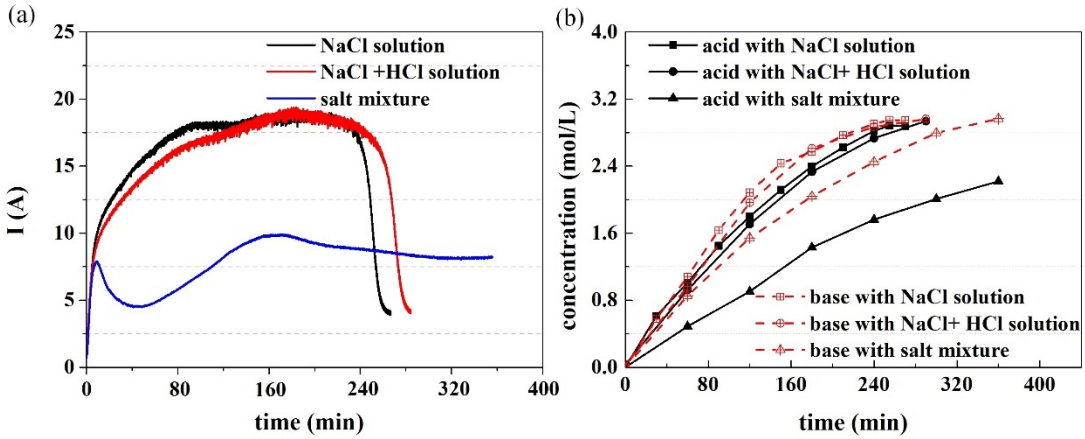

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390 Fig. 6 (a) The current across the stack and (b) acid/base production rate with different
391 solution types (117 g/L NaCl (2M); 117 g/L NaCl (2M) adjusted to pH 1.6 with HCl; 114 g/L
392 NaCl (1.95M) with 0.04 M $CaCl_2$ and 0.025M Na_2HPO_4 and HCl to a pH of 2.3)

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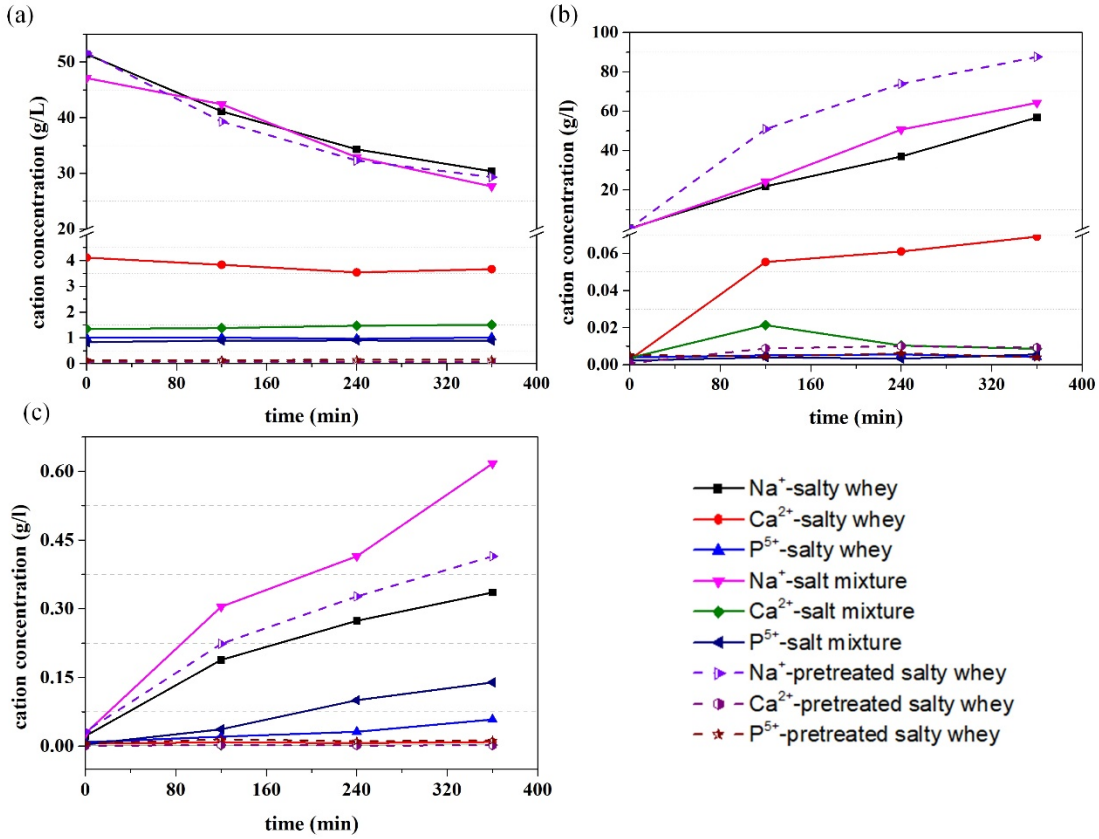

Fig. 7 The cation concentrations with time in (a) feed, (b) base and (c) acid chambers with feed solutions of a salt mixture (1.95 mol/L NaCl with 0.04 mol/L $CaCl_2$ and 0.025 mol/L Na_2HPO_4 and HCl to a pH of 2.3); salty whey; and salty whey pre-treated to remove divalent salts, with a volume ratio of 1:3

3.3 Salty whey as a feed solution

3.3.1 The feasibility for salty whey treatment

Salty whey was next tested at an applied voltage of 16 V and a volume ratio of 1:3, to investigate the technical and economic feasibility for EDBM of this effluent. As a comparison, a salty whey sample pre-treated to remove the divalent calcium and magnesium phosphate salts was also tested. While these multivalent salts might be removed at scale using an ion exchange process, in the present case, these salts were removed by pH adjustment with sodium hydroxide to pH 11 (as shown in Table 2), followed by vacuum filtration.

It is clearly shown that EDBM can be used for the treatment of the salty whey and the simultaneous production of acid and base. However, the presence of impurities (such as calcium phosphate salts and organic compounds) leads to a decrease in current (Fig. S7) and

production rate of acid/base (Fig. 8). Importantly, pre-treatment of the salty whey to remove the multivalent salts significantly improves the production rate.

As shown in Fig. 9a, using this pretreated salty whey, the current efficiency to achieve an acid concentration of 2 mol/L is 59 ± 1 %, which is comparable to that of pure NaCl (60 ± 2 %) and higher than that for either the salt mixture (51 ± 5 %) or the salty whey (54 ± 3 %). The energy requirements to produce 2 mol/L acid varies from 7.5 ± 0.6 kWh/kg for the salt solution to 7.2± 0.3 kWh/kg for salty whey and 6.6 ± 0.1 kWh/kg for pretreated salty whey. Again, the results for the pretreated whey are identical within error to that of a pure NaCl solution (6.7 kWh/kg). The trends of current efficiency and energy consumption for base production are similar to those for acid production (Fig. 8b).

The pretreatment of the salty whey required around 65 mmol of NaOH per liter to adjust the pH to 11. This is equivalent to 32 mL of the final alkali product, if this is 2 mol/L in concentration. Hence in the commercial application, around 8.7 % of the final base product would be recycled for the pretreatment application.

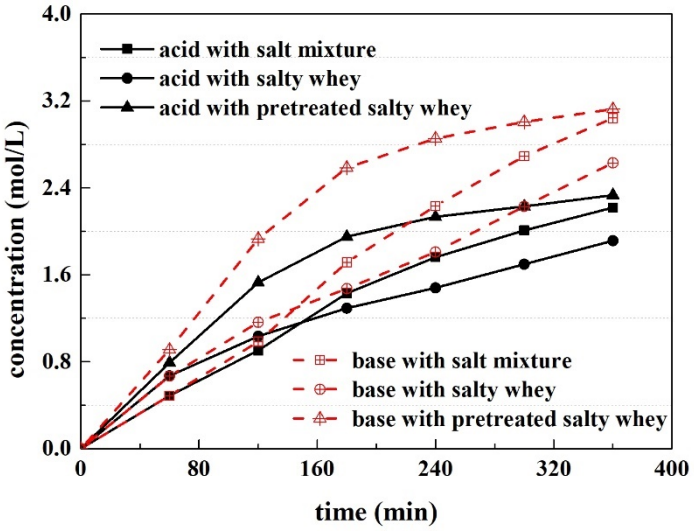

Fig. 8 The acid/base production rate with different salty whey types at an applied voltage of 16 V and a volume ratio of 1:3.

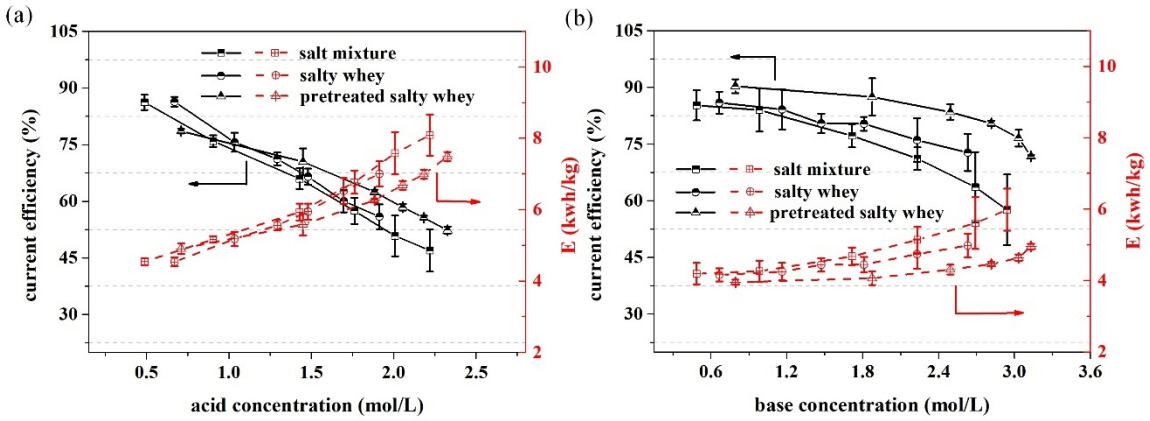

Fig. 9 The current efficiency and unit energy consumption of (a) acid and (b) base with different salty whey types at an applied voltage of 16 V and a volume ratio of 1:3.

3.3.2 Extended experiment with pretreated salty whey

As the pretreatment of salty whey to remove calcium phosphate was effective, EDBM of this feed stream was further investigated to determine the maximum acid/base concentration that could be achieved over a longer time period and whether the feed stream could be de-mineralised to a level suitable for discharge. The experimental conditions were the same as the experiment in section 3.3.1 with an applied voltage of 16V and a volume ratio of 1:3. The pretreated salty whey with pH of 11 was used as the feed solution. Fig. 10a demonstrates that the concentration of acid and base first increased with time, but then stabilized and even slightly decreased as the process continued. The maximum concentrations of acid and base were 3.5 ± 0.2 mol/L and 3.9 ± 0.3 mol/L, which are similar to that for a pure sodium chloride feed solution although they took longer to achieve (19 and 14 hours versus 10 and 6 hours for pure NaCl). The concentrations are sufficient to meet the requirements for chemical cleaning agents in dairy industry applications [44].

The cation purity of the final base solution was over 97% wt % NaOH (Table 3), with the most significant impurity being potassium (about 3 wt %). The calcium ion concentration was negligible. The main impurity in the acid solution was sodium at 2.5 g/L (0.11 mol/L) when the concentration of hydrochloric acid is 3.5 mol/L.

The conductivity of the feed solution remains at a relatively high level throughout the operation and finishes even higher than that of the initial feed solution (Fig. 10b). This is despite

the sodium ion concentration declining continuously (Fig S8). Rather, the increase relates to proton migration, which is high due to the high initial pH of the feed (Fig. 10b). Bunani et al. [33] similarly observe a decrease in feed pH due to such proton leakage.

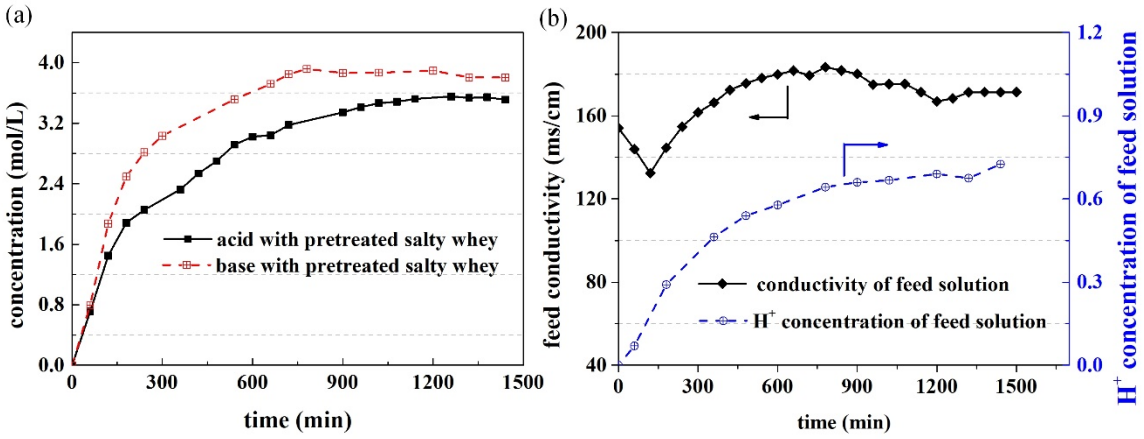

Fig. 10 (a) The concentration of acid/base solutions and (b) the conductivity and proton concentration of the feed solution in an extended experiment with pretreated salty whey at an applied voltage of 16 V and a volume ratio of 1:3.

Table 3 Quality of the acid and base produced from the pretreated salty whey solution after 25 h operation time

Compositions	Pretreated salty whey		
	Acid	Diluate	Base
Sodium (g/L)	2.5 ± 0.4	6.4 ± 0.5	98.1± 9
Calcium (g/L)	0.007 ±0.001	0.035 ± 0.008	0.009 ± 0.002
Potassium (g/L)	/	0.46 ± 0.06	3.8 ± 0.5
Phosphorus (g/L)	0.017 ± 0.002	0.18 ± 0.02	0.01 ± 0.001
H^+ concentration (mol/L)	3.5 ± 0.2	0.7 ± 0.05	/
OH^- concentration (mol/L)	/	/	3.9 ± 0.3

The acidity and residual sodium of this final diluate is too high for direct discharge to sewer. Hence a partially cyclic operation mode was tested, based on the approach used by Yan et al. [36]. That is, a feed solution of 3L was continuously re-circulated throughout the experiment. Conversely, the acid and base solutions, initially of 1L, were replaced by a fresh water of volume 1L after 1500 min (25 h). The replacement of the acid and base with fresh water reduced the proton leakage into the feed chamber and allowed more sodium and chloride ions to be transferred into the fresh solutions.

Fig. 11 shows that the conductivity and HCl concentration of the feed solution could be reduced to 1 mS/cm and 0.02 mol/L, respectively in this second step. Meanwhile, the concentrations of the second batches of acid and base increase gradually to 1.3 mol/L and 0.4 mol/L, respectively. A large number of protons in the feed chamber migrated to the alkali chamber, which resulted in the base concentration being much lower than that of acid here. Without doubt, the operation parameters of such a partially cyclic operation mode could be optimized further. In sum, these results indicate that salty whey can be demineralized by over 99% and thus could be directly discharged or re-used in the dairy factory. The second batch of acid and alkali, which is less concentrated, might still be viable in some cleaning operations, or could be blended with the first batch to provide acids and bases of intermediate concentration.

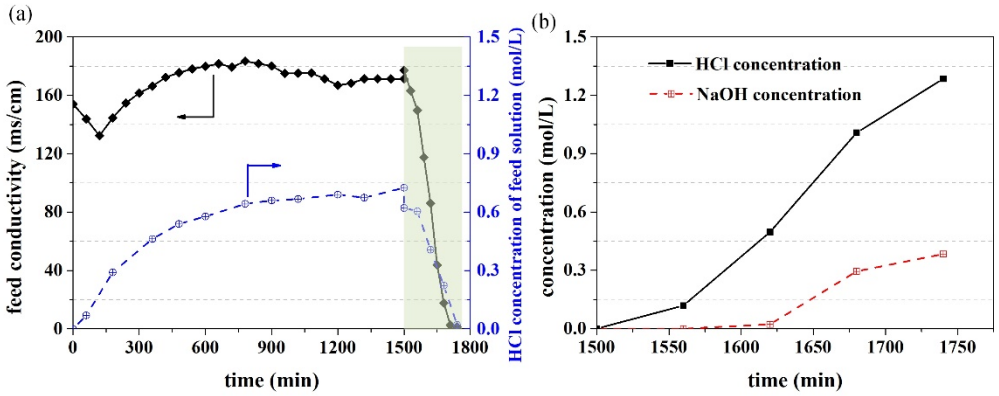

Fig. 11 (a) The conductivity and acid concentration of the feed solution and (b) the concentration of the acid/base solutions with further desalination.

4. Conclusion

Electrodialysis with bipolar membranes was successfully applied for the treatment of salty whey to generate high purity HCl and NaOH. Maximum acid and base concentrations of 3.6 ± 0.2 mol/L and 3.0 ± 0.3 mol/L could be produced, regardless of the operating conditions. Specifically, the final acid and base concentrations are similar regardless of the applied voltage (from 11 V to 21 V). The final concentration of acid and base increases with the feed solution concentration, but the rate of increase slows at higher concentrations. When the amount of NaCl in the feed solution is further increased (the volume ratio reaches 1:6), the acid and base concentrations stabilize, even though the feed solution still contains salt. The effects of proton leakage and water migration limit the generation of higher concentrations. These effects lead to reductions in current efficiency and corresponding increases in energy consumption. It should be noted that this conclusion is based on the membrane materials used in this study. If different membrane materials are used, the permeability of the membrane, the proton leakage and water migration may change.

The presence of calcium phosphate ions had a negative effect on the EDBM system performance, resulting in a decrease in current and hence acid/base production rate. However, the pretreatment of the salty whey to remove these impurity ions was effective. At industrial scale, this pretreatment step could be achieved by recycling 9 % of the final base produced. When the pretreated salty whey was used as feed solution in a partially cyclic mode, over 99% desalination could be achieved and high purity acid/base solutions were generated with a

concentration of almost 3.5 mol/L.

Acknowledgments

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Supporting information

The supporting information is to be made available to the readers of the published work.

Nomenclature

Latin letters	
C_0, C_t,	concentration of acid (or base) at time t and 0 respectively (mol/L)
E	energy consumption (kWh/kg)
F	Faraday constant (96485 $C \cdot mol^{-1}$)
I	current (A)
i	current density ($A \cdot m^{-2}$)
M	the molar mass of the acid (or base)
N	repeating unit number
t	the operation time (s)
U	constant applied voltage (V)
V	volume of feed/acid/base compartment (L)
z	absolute valence of the ion
Greek letters	
η	current efficiency (%)
Acronyms	
AEM	anion-exchange membrane
BPM	bipolar membrane
CEM	cation-exchange membrane
CV	constant voltage
DR	desalination rate
EDBM	electrodialysis with bipolar membranes
IEM	ion exchange membrane

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Supporting information

Transforming Salty Dairy Wastewater into Cleaning Chemicals using Electrodialysis with Bipolar Membranes

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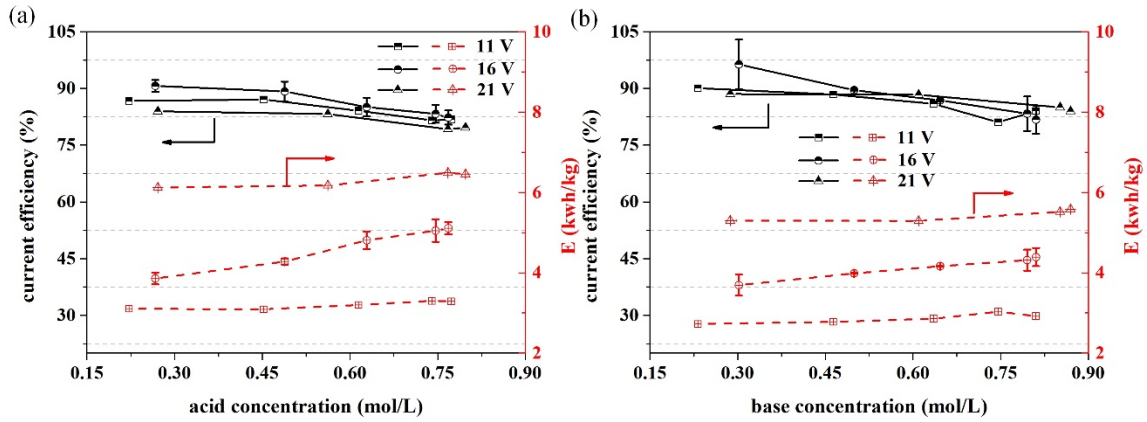

Fig. S1 The current efficiency and unit energy consumption of acid and base produced from 50 g/L NaCl at different applied voltage.

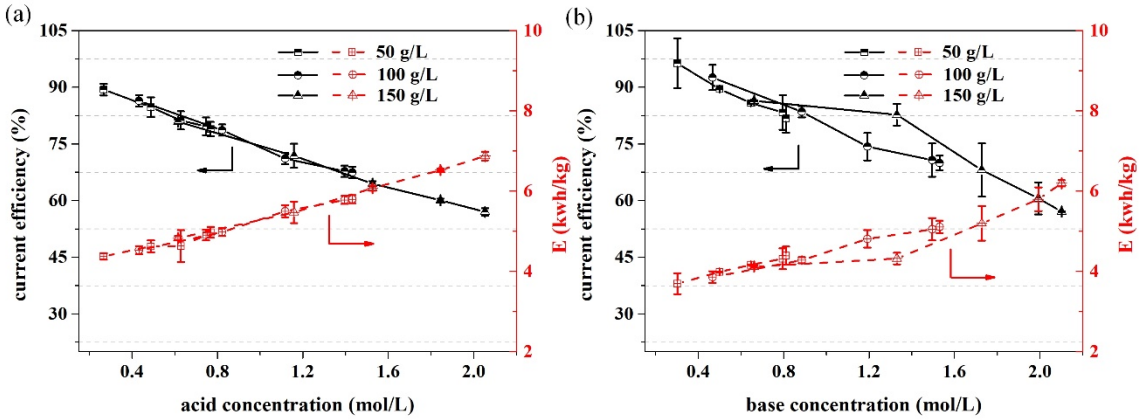

Fig. S2 The current efficiency and unit energy consumption of (a) acid and (b) base with different initial feed concentration.

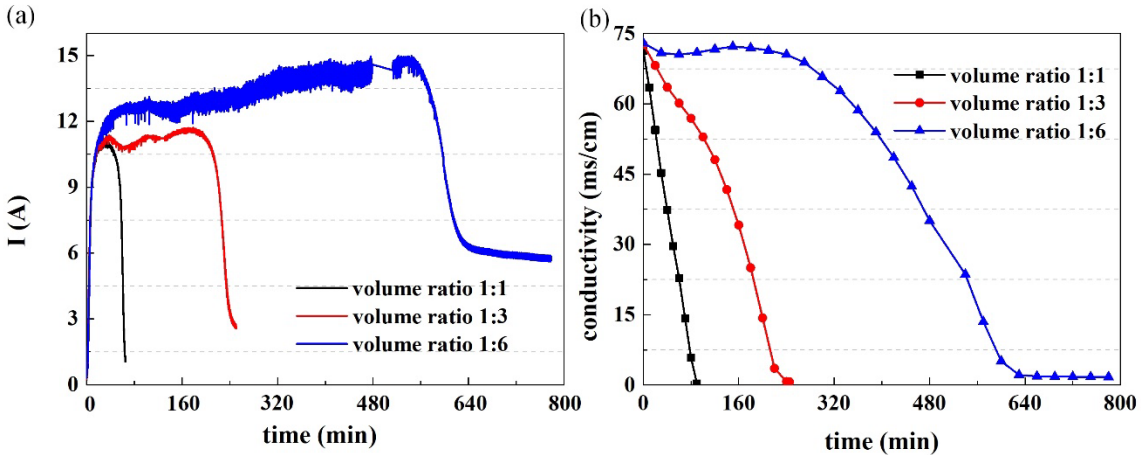

Fig. S3 (a) The current and (b) desalination rate in the feed chamber with different volume ratios ($V_{acid\ and\ base}$: V_{feed}). The volumes of acid and base solutions were 1 L, while the volume of feed solution was increased from 1 L to 6 L.

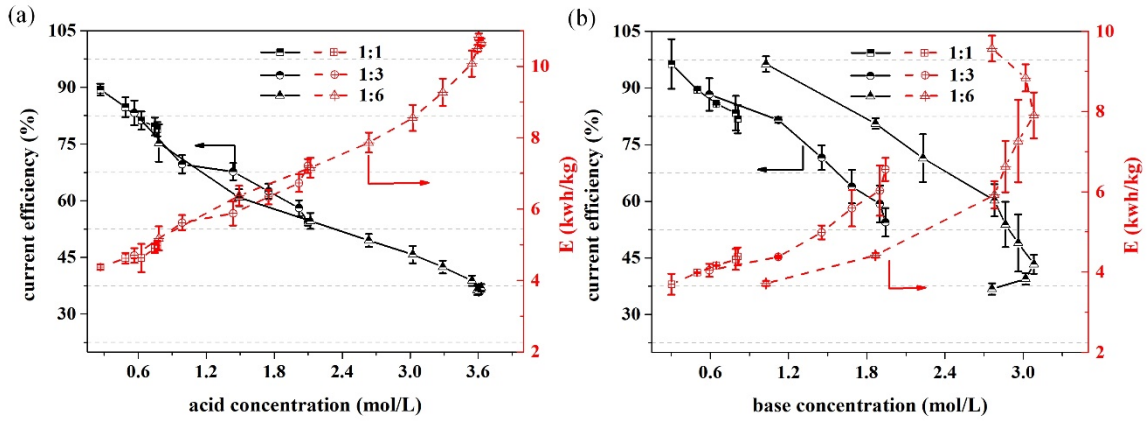

Fig. S4. The current efficiency and unit energy consumption of (a) acid and (b) base chambers with different volume ratios ($V_{acid\ and\ base}$: V_{feed}). The volumes of acid and base solutions were 1 L, while the volume of feed solution was increased from 1 L to 6 L

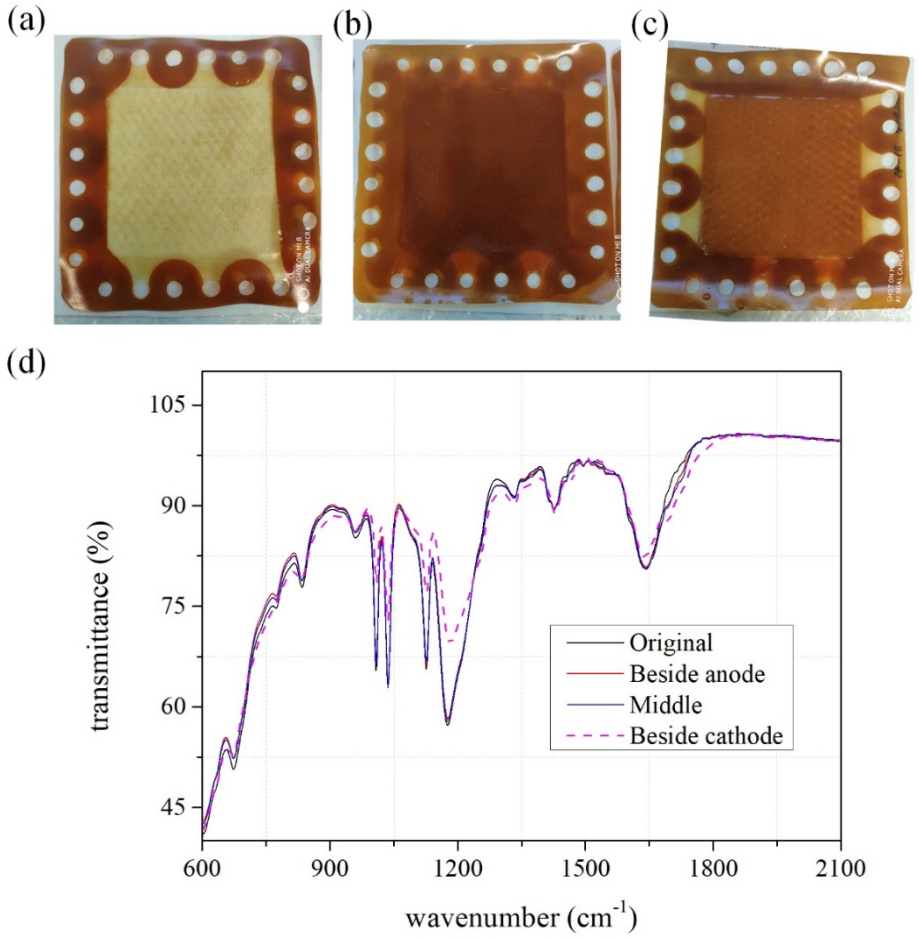

Fig. S5 the changes in the BP-1E membrane from use in experiments with NaCl feed solutions (a) an image of the BP-1E beside the cathode, (b) an image of the BP-1E in the middle of stack (c) an image of BP-1E beside the anode, (d) FTIR spectra of different BP-1E.

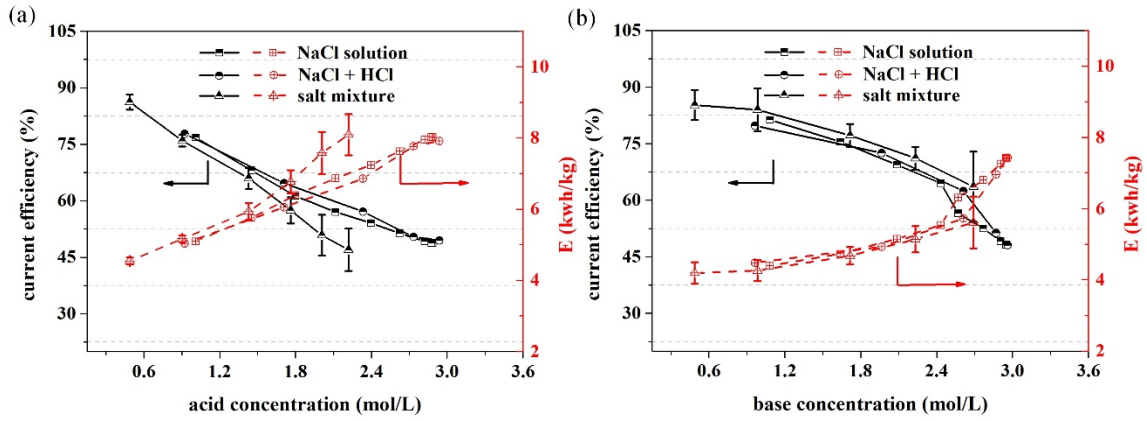

Fig. S6 The current efficiency and unit energy consumption of (a) acid and (b) base with different salt mixtures.

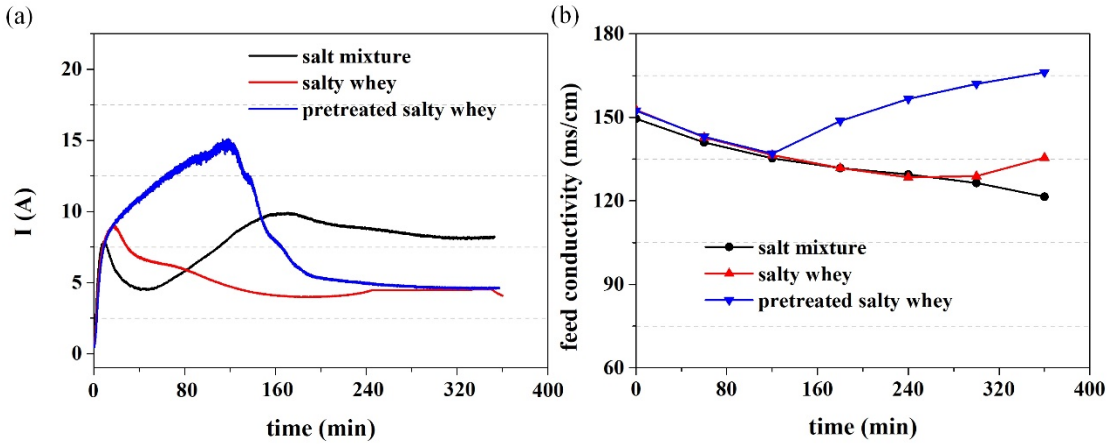

Fig. S7 (a) The current across the stack and (b) the feed conductivity with different salty whey types

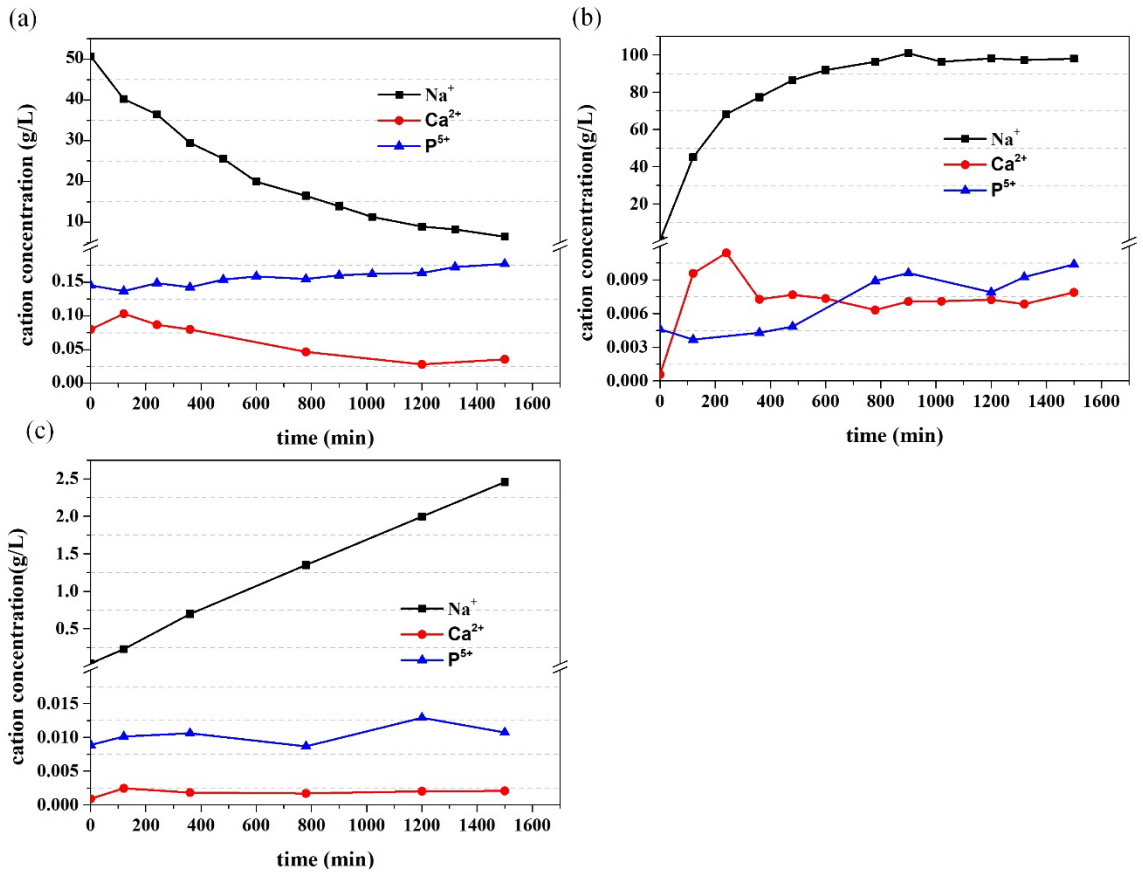

Fig. S8 The cation concentration with long time in (a) feed, (b)base and (c) acid chambers with pretreated salty whey

Table S1 The changes in chamber volume resulting from water transport with NaCl feed solutions under different operation conditions

	conditions	Acid chamber volume		Feed chamber volume		Base chamber volume	
		initial (L)	final (L)	initial (L)	final (L)	initial (L)	final (L)
Effect of applied voltage	11 V	1	1.06	1	0.87	1	1.04
	16 V	1	1.08	1	0.86	1	1.05
	21 V	1	1.08	1	0.86	1	1.04
Effect of initial feed concentration	50 g/L	1	1.08	1	0.86	1	1.05
	100 g/L	1	1.15	1	0.72	1	1.11
	150 g/L	1	1.18	1	0.56	1	1.18
Effect of volume ratio	1:1	1	1.08	1	0.86	1	1.05
	1:3	1	1.23	3	2.48	1	1.33
	1:6	1	1.30	6	4.62	1	1.97

Table S2 The changes in chamber volume resulting from water transport with different salt solutions and salty whey types as the feed.

conditions	Operation time(h)	Acid chamber volume		Feed chamber volume		Base chamber volume	
		initial (L)	final (L)	initial (L)	final (L)	initial (L)	final (L)
Na^++HCl	4.6 （DR>99%）	1	1.39	2	1.28	1	1.35
salt mixture	6	1	1.21	3	2.61	1	1.15
Pretreated salty whey	6	1	1.20	3	2.42	1	1.22
Pretreated salty whey	25	1	1.40	3	1.97	1	1.61
Salty whey	6	1	1.08	3	2.85	1	1.05