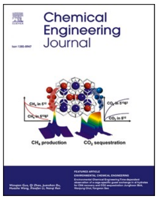
Chemical Engineering Journal 428 (2022) 131082

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej



Redox-mediated electrochemical desalination for waste valorization in dairy production

Nayeong Kim [a,1], Jemin Jeon [a,1], Johannes Elbert [a], Choonsoo Kim [b,*], Xiao Su [a,*]

[a] Department of Chemical and Biomolecular Engineering University of Illinois at Urbana-Champaign, IL 61801, United States
[b] Department of Environmental Engineering and Institute of Energy/Environment Convergence Technologies, Kongju National University, 1223-24, Cheonan-daero, Cheonan-si 31080, Republic of Korea

ARTICLE INFO

Keywords:
Redox electrochemistry
Protein separation
Continuous desalination
Electrodialysis
Whey valorization
Ferricyanide and ferrocyanide

ABSTRACT

With the rapidly growing global population, achieving sustainable food production is a key challenge to mitigate the closely coupled environmental and nutrition crises. As demand for dairy products increases, large volumes of whey are produced – a highly polluting byproduct from food manufacturing, with strict disposal regulations. However, whey has been recognized as an attractive nutrient source; and as such, sustainable separation technologies for demineralizing the highly concentrated salts in whey waste can provide a pathway for the valorization of whey proteins from food processing waste. Herein, we propose a sustainable and energy-efficient strategy to valorize whey waste via a redox-mediated electrodialysis system. As a net-zero waste process, our system leverages reversible redox reaction for continuous desalination and salt concentration for reuse, as well as the simultaneous recovery of highly purified protein contents. The system demonstrates up to 99% salt removal with $>$ 98% of whey proteins retained at various operating parameters: voltages, pHs, and salt concentrations. Remarkably, the performance of protein purification and salt recovery was maintained over multiple cycles, demonstrating outstanding stability and cyclability. Furthermore, a techno-economic analysis confirms the economic potential of our system with 51–73% lower energy consumptions and 51–62% lower operating expenditure than conventional desalination systems. Overall, our redox-electrochemical process offers a sustainable and electrified platform for the recovery of valuable proteins from dairy production waste, with envisioned integration with renewable electricity in the future.

1. Introduction

As the global population is expected to reach 10 billion by 2050, demand for food production is projected to rise 56% between 2010 and 2050 [1]. The lack of sustainable and resource-efficient food production leaves us with the coupled environmental and nutrition crises, due to the large amount of food waste generated from conventional food manufacturing [1–4]. Despite worldwide efforts to achieve sustainable food consumption and production, e.g. highlighted as one of the 17 Sustainable Development Goals of the United Nations, the vast production of animal-based and dairy products are still two major sources of CO_2 emission (up to 13.39 and 1.33 $kg_{CO2}/kg_{product}$, for animal-based and dairy products, respectively) [4–7]. Moreover, dairy products such as cheese are invaluable sources of nutrients. According to the U.S. Department of Agriculture and the OECD-Food and Agriculture Organization [3,8–10], the consumption of cheese in the U.S. has skyrocketed by 27% since 2006 [11], with global production of major dairy items expected to increase continuously; weekly cheese production is expected to exceed 26,800 kt worldwide, with a growth rate of 14% by 2029 [12] (Fig. 1).

During dairy production, large volumes of whey waste are produced, considered one of the most polluting by-products in food manufacturing processes [13,14]. Since whey waste has high chemical oxygen demand (>60,000 ppm), biochemical oxygen demand (>35,000 ppm), and salt concentration, its disposal requires several post-treatment processes [15]. Especially, with the massive production of cheese, whey waste is regarded as a crucial environmental problem because 1 kg of cheese production results in 9 kg of whey waste, accounting for ~ 83% of the total waste stream in the dairy industry [16]. On the bright side, whey is considered a highly attractive source for valorization, due to its range of

---

[*] Corresponding authors.
E-mail addresses: choonsoo@kongju.ac.kr (C. Kim), x2su@illinois.edu (X. Su).
[1] The authors contributed equally to this work.

https://doi.org/10.1016/j.cej.2021.131082
Received 16 May 2021; Received in revised form 24 June 2021; Accepted 26 June 2021

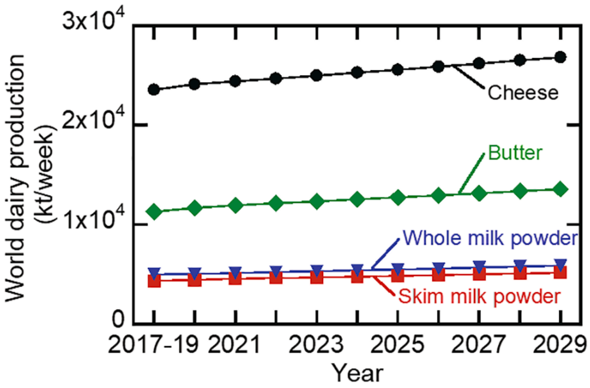


Fig. 1. World dairy productions and prospects (kt/week): average production in 2017–19 and 10-year prospect (2020–2029) analyzed by the OECD-Food and Agriculture Organization [12].

nutrients [15]. Whey contains valuable protein contents such as beta-lactoglobulin (β-LG, 50−55%), alpha-lactalbumin (α-LA, 20−28%), and lactoferrin (7−15%) shown in Table 1 [15].

Studies have confirmed several positive effects of whey proteins for human health such as an improvement of metabolism and a decrease in blood pressure [19–22]. The benefits of these proteins extend from plant-based nutrition to even food texture and color control [23,24]. Furthermore, lactose and its derivatives (4.5−5% of whey waste) have been commercialized in food and pharmaceutical industries [14,25]. Therefore, whey waste could be a secondary nutrient source to meet the growing worldwide demand for food.

However, highly concentrated salts in whey waste remain a major challenge for the valorization of whey proteins. Salt plays an indispensable role in cheese manufacturing, for preservation, flavor, and quality. For instance, salting the cheese contributes to maintaining water activity, osmotic pressure, and even enzymatic activities which, in turn, prevent bacteria growth and degradation of nutrient sources in cheese [26]. In this regard, the salting process is inevitable during cheese manufacturing, leaving a high concentration of salt in the whey waste up to 1 M NaCl (Table 1). Thus, removing this highly concentrated salt content from the proteins is the cornerstone separation challenge in whey protein valorization. Several desalination technologies have been introduced to remove concentrated salts and recover proteins from whey waste, with various specific limitations. Although membrane technologies (e.g. reverse osmosis and nanofiltration) are widely used for whey desalination, they often require additional processes or chemical input for further separation between valuable contents and salts [27,28]. Filtration technologies result in high energy consumption and operating cost for whey separation, due to the high pressure needed across a range of salt and whey concentrations [28,29]. While ion-exchange can also be used for desalination, it requires a large volume of chemicals to regenerate the columns, thus leaving a significant solvent and chemical footprint [30,31].

Recently, electrodialysis (ED) has gained attention as a promising desalination technology due to its environmentally benign operation and tunability [32]. Using electrochemical water splitting reaction, the ED system reduces the energy consumption up to 47−70% compared with the reverse osmosis to perform an equivalent demineralization performance [32,33]. However, water-splitting reaction at the anode results in the decrease of the effluent pH (close to pH 4.0), often causing the aggregation of whey proteins such as β-LG and α-LA whose isoelectric points are around 4.2−5.2 [34], and from an electrochemical perspective, can be quite energy-inefficient due to the relatively high voltages required. Besides, excessive use of membranes (up to 200 membranes [30]) is considered a major bottleneck for the industrialization of the ED system because of the high materials expenditure [32]. Thus, the development of a more energy-efficient and sustainable demineralization technique is critical in the whey valorization process.

Table 1
Components of acid [17], sweet and salty whey [18], and whey proteins [15,18].

Component	Acid whey (%)	Sweet whey (%)	Salty whey (%)	Whey protein	%
Water	94–95	90–95	86–92	β-LG	50–55
Salts (mM NaCl)	0.5–0.7 (17–31 mM)	0.2 (35 mM)	2.5–6.9 (400–1,000 mM)	α-LA	20–28
Proteins	0.8–1	0.6–1	0.8	Lactoferrin	7–15
Total solids	5–6.4	6–8	9–12	IgG	3–7
Fat	0.003–0.38	0.2–0.5	0.6–0.8	BSA	2–3

Herein, we demonstrate a sustainable redox-mediated electrodialysis system for energy-efficient desalination from the whey waste and salt concentration for reuse, as well as the simultaneous recovery of protein contents (Fig. 2 and **Fig. S1**). Despite the extensive application of redox couples in energy storage (e.g. batteries) [35–38], we leverage a reversible redox reaction for food manufacturing and waste revalorization for the first time. The system utilizes a reversible redox reaction at lower operation voltage than water-splitting reaction; thus enabling an energy-efficient operation without acidification of whey solution which causes aggregation of whey proteins (Fig. 2**a**). Besides, the redox-mediated electrodialysis system allows recovery of NaCl during the system regeneration step (**Fig. S1b**); therefore, the system could not only reuse the removed salts and redox-involved electrolyte but also dramatically decrease the environmental impact, paving the way to a net-zero waste process of secondary resources in the food industry (Fig. 2**c**). In this paper, we first investigated desalination performance at various operating parameters and whey conditions, including operating voltages, pHs, and salt concentrations, to validate the system feasibility for protein purification from whey waste. Moving towards process sustainability, we demonstrated this net-zero waste at a lab-scale system over multiple cycles. Finally, we provided insights into the larger-scale economic feasibility of the proposed process through a preliminary techno-economic analysis.

2. Experimental section

2.1. Materials

All chemicals were obtained from Sigma Aldrich, VWR, Fisher Scientific or TCI, and used as received.

2.2. Cell assembly

The redox-mediated electrodialysis device is composed of the redox channel (4 × 4 × 0.2 m^3), the whey waste channel (feed channel, 4 × 4 × 0.5 m^3), and cation and anion exchange membranes (CMVN and AMVN, Selemion, Japan). In the redox channel, activated carbon clothes (CH900-20, Kuraray, Japan) were used as electrodes with the size of 4 × 4 cm^2. As depicted in Fig. 2, the feed channel is placed in between the redox channel, and both channels were separated by a pair of ion exchange membranes (5 × 5 cm^2). In the redox channel, 100 mL of 50 mM $K_3Fe(CN)_6$ and 50 mM $Na_4Fe(CN)_6 \cdot 10H_2O$ with 100 mM NaCl was used as an electrolyte for all experiments. In this paper, we typically chose ferricyanide and ferrocyanide as reversible redox species due to their high reversibility and rate capability (**Fig. S2**). The cell was assembled in order of the anodic side of the redox channel, an anion exchange membrane, feed channel, cation exchange membrane, and cathodic side of the redox channel. Then using a peristaltic pump (Langer Instruments Co., USA), flow rates were set to 5 mL/min for both channels.

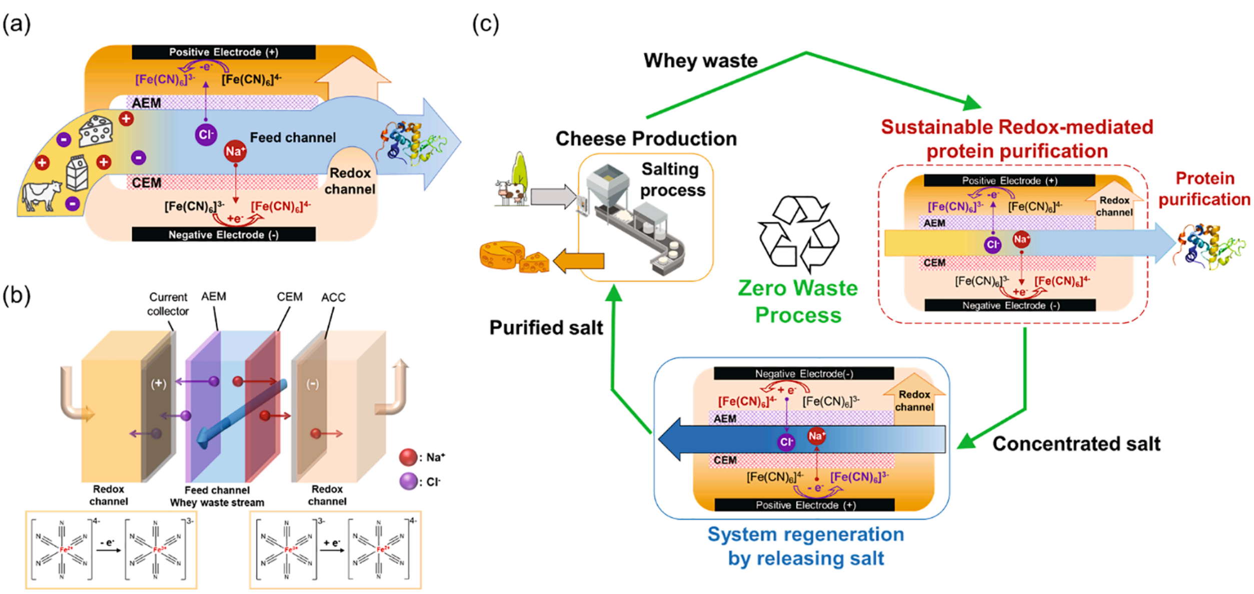


Fig. 2. Proposed whey waste valorization concept: (a) schematic illustration of the redox-mediated electrodialysis system and its mechanism, (b) cell components, and (c) the net-zero waste process. AEM, CEM, and ACC represent anion and cation exchange membranes and activated carbon clothes, respectively.

2.3. Analysis of desalination performance

The desalination performance was analyzed at various operating conditions: operating voltages (0.4–1.2 V), pH of whey solution (pH 4.1–6.4), whey contents (β-LG, α-LA, and lactose), and salt concentration (10–500 mM). In common, the concentration of salt in the feed channel was simultaneously analyzed by a conductivity meter (Horiba, Japan) while the initial and final pH were measured with a pH meter (Horiba, Japan). Our system operated in a two-electrode system at a constant applied voltage using a potentiostat (Admiral Instruments, USA). For various operating voltages (0.4–1.2 V), 30 mL of 100 mM NaCl with 7 ppm β-LG was desalinated. To adjust the pH of the whey solution, 1–10 mM HCl was used. We further investigated the desalination performance at representative whey contents of 7 ppm β-LG, 7 ppm β-LG, or 70 ppm lactose with 100 mM NaCl. Finally, synthetic whey waste was prepared using the commercial whey powder (7 ppm) and various salt concentrations (10, 100, and 500 mM NaCl). The sequential protein purification and regeneration processes were conducted with the reverse-operation voltage mode (1.0 V and −1.0 V for the protein purification and the regeneration steps, respectively). Then with 30 mL of 100 mM NaCl, we investigated the cyclability of the system for the first 10 cycles. For the final cycle (11th cycle), 30 mL of 100 mM NaCl with 7 ppm whey powder was replenished in the feed channel to analyze the protein purification and recovery performance. The desalination performance was evaluated with electrochemical metrics such as charge efficiency and energy consumption. The charge efficiency was calculated by Eq. (1):

$$Charge\ \ efficiency = n_{NaCl}/\left(\int Idt\Big/_{F}\right) \tag{1}$$

where n_{NaCl} is desalinated salt (mole), F is the Faraday constant (96,485 C/mol), and I is the current (A).

The energy consumption per mole of salt removed was evaluated using Eq. (2), for a constant voltage operation process:

$$Energy\ \ consumption(J/mol) = \frac{V}{n_{NaCl}}\int Idt \tag{2}$$

where V is the applied voltage (V).

2.4. Electrochemical analysis

Cyclic voltammetry was conducted to investigate the peak potential and the reversibility of the ferricyanide and ferrocyanide at various scan rates (1–100 mV/s). A three-electrode system was used with Pt wires as working and counter electrodes and Ag/AgCl (3 M KCl) as a reference electrode. A solution containing 5 mL of 100 mM NaCl and 100 mM sodium ferrocyanide was used as the electrolyte. To investigate the faradaic reactivity, peak current was analyzed with respect to the square root of scan rate.

Electrochemical Impedance Spectroscopy (EIS) was measured to calculate the solution resistances at various operating voltages over the desalination test. The EIS of the redox-mediated electrodialysis system was analyzed at various operating voltages (0.4 –1.2 V) with an amplitude of 50 mV in the frequency range of 0.01–10,000 Hz at the initial and in the frequency range of 0.1 – 10,000 Hz after 99% salt removal. The solution resistance value was calculated based on an equivalent circuit of R(Q(RW))(QR) with ZsimpWin (AMETEK, Inc., USA).

2.5. Analysis of various whey contents (β-LG, α-LA, and lactose)

The concentrations of β-LG and α-LA in the feed and redox channels were measured by using reversed-phase high-performance liquid chromatography (RP-HPLC) (Agilent 1260 Infinity II, Agilent Technologies, USA). Using the C_3 column (75 mm× 2.1 mm × 5 µm, Agilent POROSHELL 300SB), we could detect both β-LG and α-LA separately with gradient elution between two solvents: Phase A, 0.1% (V/V) trifluoroacetic acid (TFA) in DI water and Phase B, 0.1% TFA in acetonitrile. The elution gradient with respect to phase A was set as follows: 0–5 min, 70–45%; 5–10 min, 45–40%; 10–12 min, 40–70%; 12–16 min, 70%. The sample volume of 40 µL was injected with a flow rate of 1.0 mL/min and the column temperature at 50°C. The injection sample was prepared after a 1:5 dilution of samples with phase A. The injection volume was 40 µL after 1:5 dilution with Phase A. The concentrations were determined from the absorbance at a wavelength of 280 nm for β-LG and 215 nm for α-LA. Since β-LG and α-LA are two major whey proteins (70–80% of whey proteins in whey waste), we analyzed percent of the whey protein recovery based on changes in both concentrations.

The CD spectra of β-LG were measured over the wavelength range of

190–260 nm by using a circular dichroism spectrometer (Cary-16 , OLIS, USA). A quartz cuvette with 1 mm of path length and 190–2500 nm of wavelength range (Azota Co., USA) was used as a sample holder and the temperature of the sample chamber was maintained at 20℃ by a temperature controller (TC 125, Quantum Northwest, USA). The concentrations of lactose were determined by using a UV–vis spectrophotometer (Cary 60, Agilent Technologies, USA) after the post-treatment with EnzyChrom™ Lactose Assay Kit (BioAssay Systems, USA). During the post-treatment, enzyme-coupled reactions cleaved lactose into galactose which of the calibration was made at 570 nm.

2.6. Techno-economic analysis (TEA)

The TEA of the redox-mediated electrodialysis system and conventional ED systems was carried out with the following assumptions: an equal volume of 600 L whey waste is treated per operation, with the system operated twice a day, 7 days per week, and 52 weeks a year. The size and composition of a scale-up system are estimated based on the desalination performance at our bench scale. Along with our system, we conducted the TEA of the ED system with system composition, operation, and demineralization performance based on data from previous studies [17,30]. A summary of capital cost, yearly operating expenditures, and yearly revenue for each process is described in **Supplementary** along with the detailed procedures for the technoeconomic analysis.

3. Results and discussion

3.1. The redox-mediated electrodialysis system and its mechanism

The redox-mediated electrodialysis system was composed of two-independently controllable channels for the whey waste (feed channel) and the electrodes (redox channel), separated by a pair of cation and anion exchange membranes (Fig. 2**b**). A reversible redox couple of ferricyanide $[Fe(CN)_6]^{3-}$ and ferrocyanide $[Fe(CN)_6]^{4-}$ in the redox channel allowed continuous demineralization via its reversible redox reaction (Fig. 2**a** and **Fig. S1a**). In general, ferri-/ferrocyanide is widely used in redox flow batteries [35,36] and reverse electrodialysis [39,40] due to its high stability and reversibility. Recently, the reversible redox couple, including ferri-/ferrocyanide, has garnered significant attention in the desalination and ion separation field [41–44]. In our system, applying ferri-/ferrocyanide allows continuous desalination below the potable water range, 100 µS/cm, without any additional process. During the protein purification process, positive ions such as Na^+ moved from the feed to the redox channel when ferricyanide was reduced to ferrocyanide at the negative electrode, while negative ions such as Cl^- moved to the redox channel when ferrocyanide was oxidized back to ferricyanide at the positive electrode, resulting in a sustainable regeneration of the redox couple (Fig. 2**a**). By releasing the removed ions to the feed channel, the redox channel can maintain its electrolyte concentration, and recovered NaCl can be reused in the cheese production, suggesting a net-zero waste process (**Fig. c** and **Fig. S1b**).

3.2. Investigation of protein purification performance at various operating voltages

The performance of the protein purification from the whey waste was evaluated at the operating voltage range from 0.4 to 1.2 V (Fig. 3). The redox-mediated electrodialysis system successfully demineralized 99% of salt from the whey solution within a single step (Fig. 3**a** and **Fig. S3a**). Considering 6% salt removal in the absence of the redox couple at 1.0 V, demineralization up to 99% was mostly attributed to the continuous redox reaction between ferri- and ferrocyanide. Notably, the time required for protein purification highly depended on the operating voltages. For instance, 99% of the salt removal took only 4 h at the operating voltage of 1.2 V, while requiring>11 h at the operating voltage of 0.4 V. The use of two ion-exchange membranes and two independent channels increased the resistance, requiring higher operating voltage to fully trigger the redox reaction. Therefore, a sufficiently high operating voltage (over 0.6 V) is required to reach 99% salt removal with effective utilization of the redox couple in the redox channel.

Moreover, several operational features such as desalination rate and pH changes were also analyzed. The rate of desalination (slope of Fig. 3**a**; unit of %/h) was 17–66%/h up to 50% salt removal and then significantly decreased to 2–5%/h for 90–99% salt removal. The nonlinear salt removal rate could be attributed to the increased solution resistance from the feed channel. The electrochemical impedance spectroscopy demonstrated that the solution resistance of the system

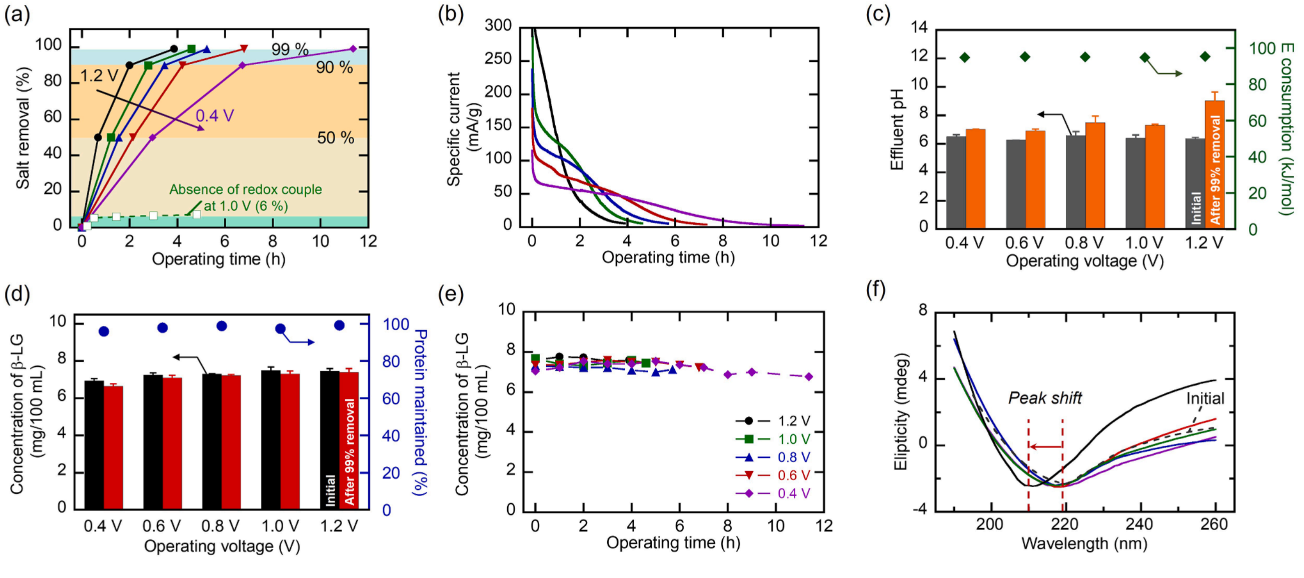


Fig. 3. Performance of the protein purification at various operating voltages from 0.4 to 1.2 V: (a) salt removal %, (b) specific current profiles, (c) changes in pH and energy consumptions after 99% salt removal (d) concentration and percent changes in whey protein of β-LG after 99% salt removal, (e) profiles of whey protein concentration, and (f) circular dichroism spectra of β-LG. The experiments were performed with 100 mM NaCl and 7 ppm β-LG as treating water and 100 mM NaCl with 50 mM ferri- and ferrocyanide as a redox electrolyte. The redox-mediated electrodialysis system was operated until 99% salt removal with flow rates of 5 mL/min for both channels. Label coloring of panels (b), (e), and (f) is equivalent.

increased over 56 times after 99% salt removal due to the low ionic concentration in the feed channel, resulting in a much slower salt removal rate (**Fig. S4**). In this regard, applying conductive resins in the feed channel would allow a consistent desalination rate over the purification process by maintaining the ionic concentration in the feed channel [45]. Considering the increase in the effluent pH at the voltage between 0.4 and 1.0 V (Fig. 1**c**), the system was operated with the presence of minor side reactions such as the production of hydrogen peroxide [46]. At most, the effluent pH changed from 6.4 to 9.0 at the operating voltage of 1.2 V. Along with the pH change, the relatively high current flow at 1.2 V indicated the presence of the side reaction (Fig. 3**b** and **Fig. S3b**). However, based on the pH change in the feed channel and the electron balance, the charge used for the water-splitting reaction was less than 0.01% (Table S1). Regardless of the presence of side reactions, this calculation demonstrates that protein purification was mostly attributed to the continuous redox reaction, not the side reaction. Then, the energy consumption was maintained at around 95 kJ/mol$_{NaCl}$ (2.50 kWh/m^3) as shown in Fig. 3**c**. Assuming the side reaction is mostly the water-splitting reaction, it might also promote the salt removal from the feed channel with the analogous mechanism to the conventional electrodialysis system. Consequently, the charge efficiency was close to unity over the investigated range of the operating voltages, indicating that the applied charge was extensively used for protein purification.

Furthermore, Fig. 3**d** and **e** highlight that the representative whey protein, β-LG, was retained in the feed channel throughout the desalination with an average of 2% loss, possibly due to the adhesion to the membranes or tubes. Undetected protein in the redox channel also proved that the protein is excluded by the ion exchange membranes due to its high molecular mass. Besides, undetected iron concentration in the feed channel confirmed that the redox couple would not contaminate the whey protein in the feed solution (Table S2). To confirm the stability and conformational change of the purified protein, circular dichroism (CD) spectra were measured. As shown in Fig. 3**f**, insignificant changes in the CD spectra were observed over the range of 0.4–1.0 V. The spectrum of β-LG after the operation at 1.2 V was shifted to the left because the pH increase changed the conformational distribution between α-helix and β-sheet [47]. However, the protein was not denatured permanently, proved by adjusting the pH back to its starting value (**Fig. S5**); rather, as the pH increased, the protein might become a deprotonated form [48,49]. Considering desalination performance as well as the whey protein condition, 1.0 V was thought to be the optimal operating voltage in this lab-scale system and used for the rest of the experiments.

3.3. Investigation of protein purification performance at various whey conditions

As shown in Fig. 4**a-d**, effective protein purification at various whey solution pH demonstrates that our redox-mediated electrodialysis system can compatibly treat various whey solutions such as acidic, sweet, and salty whey wastes. The desalination rates were independent of the feed pH condition (Fig. 4**a**), with the average energy consumption of 95 kJ/mol$_{NaCl}$ (2.61 kWh/m^3) shown in Fig. 4**b**. Besides, 98% of β-LG was preserved over the experiments (Fig. 4**c**). The effluent pH after 99% of salt removal slightly increased to around pH 6 and pH 7.3, but the protein maintained its stability (Fig. 3**d**). In fact, the increase in pH from acidic to neutral can help to reduce the probability of the aggregation or denaturation of whey proteins [48–50]. At the isoelectric point, the net charge of a protein becomes zero, which significantly reduces the repulsive electrostatic forces between protein molecules, resulting in the aggregation and denaturation of proteins [48]. Considering the isoelectric points of major whey protein contents (e.g., β-LG and α-LA around 4.2–5.2) [49,50], a minor increase of pH to neutral would effectively avoid precipitation and degradation which was recognized as a major limitation of conventional ED systems. Given that the majority of acid whey, which contains as much protein as sweet whey, is still discarded due to its low pH [51,52], pH control by electrochemistry would extend the application of acid whey.

Moreover, the system successfully purified each of the valuable whey contents such as β-LG, α-LA, and lactose respectively. Note that β-LG and α-LA are the two major protein contents in the whey waste (70–80% of total protein content; Table 1) while whey waste usually contains

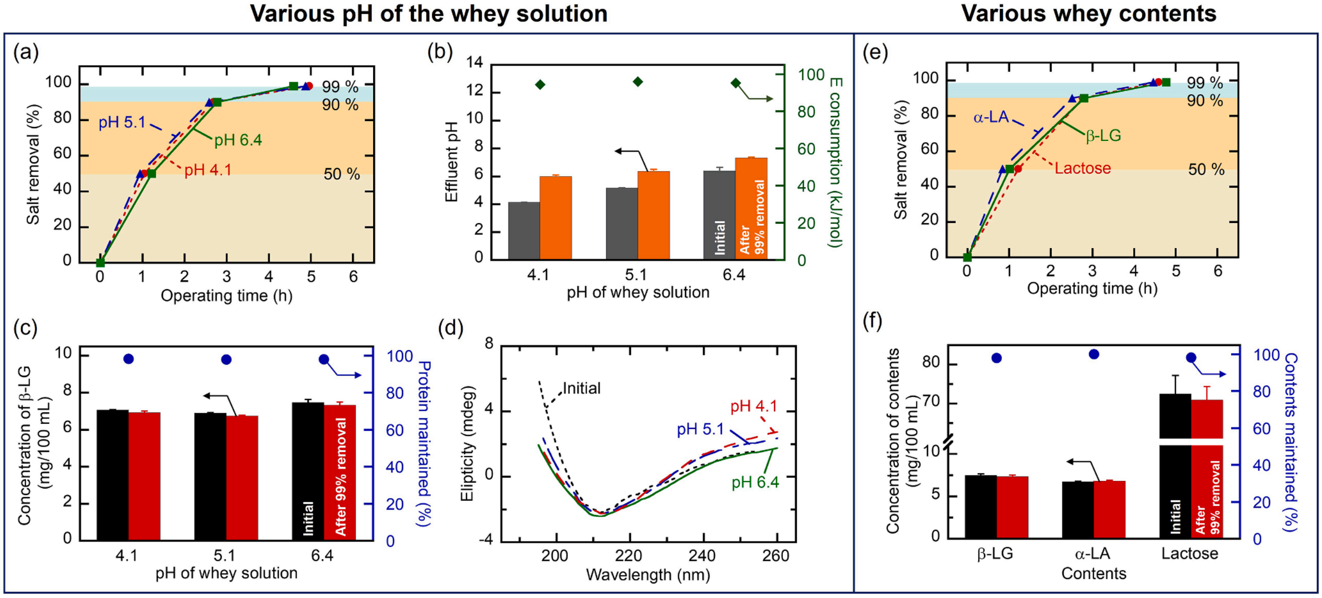


Fig. 4. Protein purification performance at various pH of the whey solution and representative whey contents: (a) salt removal %, (b) changes in pH and energy consumptions, (c) concentration and percent changes in whey protein of β-LG after 99% salt removal, and (d) circular dichroism spectra of β-LG. Each pH represents the acidic whey waste (pH 4.1), the sweet and salty whey waste (pH 5.1), and without any pH adjustment (pH 6.4). (e) salt removal % and (f) concentration and percent changes in whey protein of β-LG, α-LA, and Lactose after 99% salt removal. The experiments were performed with 100 mM NaCl and representative whey waste contents such as 7 ppm of β-LG and α-LA and 70 ppm of Lactose as treating water, while 100 mM NaCl with 50 mM ferri- and ferrocyanide was used as a redox electrolyte. The system was operated until 99% salt removal with flow rates of 5 mL/min for both channels at the operating voltage of 1.0 V.

4.5–5% lactose [14]. The results show that within an average of 4.6 h, the system could achieve 99% salt removal (Fig. 4**e**) with an energy consumption around 94–96 kJ/mol$_{NaCl}$ (2.59–2.63 kWh/m^3). We also observed an insignificant increase of pH from 6.3–6.5 to 7.3–7.7 (**Fig. S6**) with > 98% contents maintained (Fig. 4**f**). Since the size of valuable whey proteins and whey contents are considerably larger than Na$^+$ and Cl$^-$, they cannot cross-over the ion exchange membranes. In the future, by taking advantage of the characteristic molecular size and isoelectric point of each whey content, the system has the potential to valorize whey wastes by further separating protein contents between themselves. For instance, there is room for further improvement to achieve even molecular selectivity by tuning the membrane pore size [53,54], incorporating selective protein adsorbents [55], or leveraging controllable affinity in metallopolymer electrodes [56,57][61,62].

3.4. *Whey valorization in a net-zero waste process*

The redox-mediated electrodialysis system exhibited remarkable desalination performance in whey waste solutions, from 10 mM NaCl (simulating acidic whey waste) to 500 mM NaCl (simulating salty whey waste) in Fig. 5**a**. The operating time to desalinate to a potable water range varied based on the salt concentrations from 0.92 h for 10 mM to 9.76 h for 500 mM NaCl. Besides, the overall desalination rate was dependent on the feed concentration. By reducing the systematic resistance, faster desalination was achieved as the feed concentration increased (10 mM/h, 22 mM/h, and 52 mM/h for 10 mM, 100 mM, and 500 mM, respectively). Importantly, analysis of the two major proteins in the whey powder (β-LG and α-LA) indicated that over 98% of whey proteins were preserved in various synthetic conditions. Because of the osmotic effect, the protein concentrations increased by 2–5% in the synthetic salty whey solution (500 mM NaCl) (Fig. 5**b**). A high salt concentration gradient between the redox and feed channels resulted in the diffusion of water from the feed due to high osmotic pressure, increasing the protein concentrations [58]. This implies that the system condition might need to be adjusted depending on the conditions of the treated whey. For instance, the system could reduce the osmotic effect by simply using a lower salt concentration or a larger volume of the redox channel with comparable desalination performance.

With a view towards a fully sustainable and circular process, the redox-mediated electrodialysis system can be designed as a net-zero waste process for waste valorization as depicted in Fig. 2**c**. Subsequent to the protein purification process, the removed salt was released in the feed channel to test the feasibility of recycling whey salts for the salting process in cheese production (Fig. 2, **Fig. S1**). Releasing concentrated salts from the redox channel also allows for the sustainable use of the redox couple, by maintaining a high concentration of the electrolyte. Therefore, recycling the removed salt would not only be cost-effective but allow sustainable system operation. Cyclability test was conducted

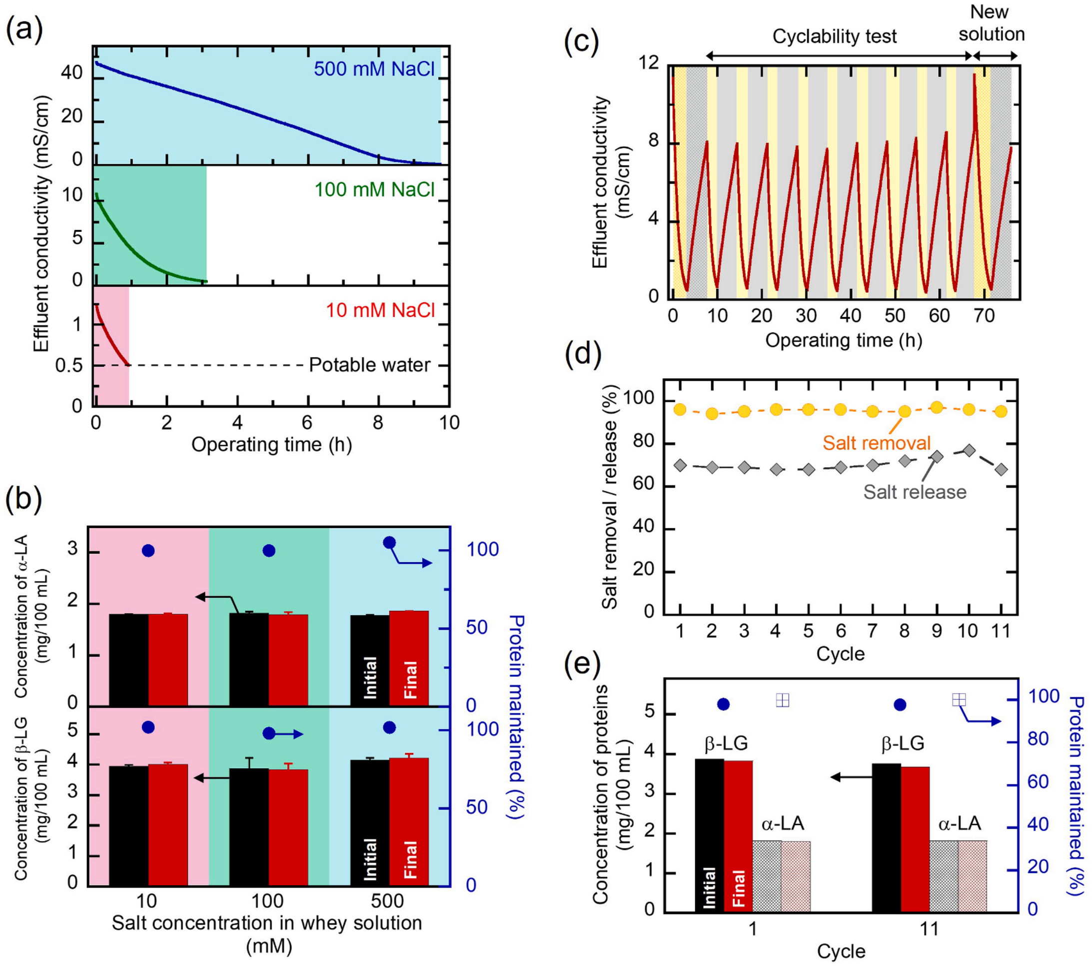


Fig. 5. Protein purification from whey solution: (a) profiles of effluent conductivity and (b) concentration of β-LG and α-LA in various synthetic whey waste solutions. Whey waste solutions were synthesized with 10 mM, 100 mM, and 500 mM NaCl which represent salt concentrations of acidic, sweet, and salty whey waste, respectively. The system demineralized the whey solution up to 95% salt removal (0.5 mS/cm) which is within the potable water range. Long-term stability tests for 11 sequential protein purification and system regeneration processes: (c) profiles of effluent conductivity, (d) percent of salt removal and releasing, and (e) concentration of β-LG and α-LA during 1st and 11th cycle.

over 11 cycles between salt removal (1.0 V) and releasing processes (-1.0 V). As a lab-scale proof of concept, we chose judicious voltages and time to achieve 95% salt removal and 70% salt recovery. The result confirmed a steady protein purification performance over 11 cycles (Fig. 5**d and e**). Notably, 98% and 100% of β-LG and α-LA were preserved at the 11th protein purification process (Fig. 5**f**). As demonstrated, our system can be feasible in cyclable operation, both for the valorization of the whey protein and the recovery of the separated salts.

3.5. Techno-economic analysis

To provide insights into practical feasibility, a techno-economic analysis (TEA) of the redox-mediated electrochemical system (95% salt removal) was carried out in comparison with conventional ED systems (90% salt removal) (Fig. 6). For simplification, we analyzed the capital and operating cost required to treat the equal volume of whey waste (1,200 L per day) and considered the major components required to build up and operate the system (refer to **Supplementary** for more details). As depicted in Fig. 6**a**, the capital expenses of the redox-mediated electrodialysis system are composed of equipment, current collectors, membranes, and electrodes. Our system requires 59% of capital expenses to purchase peripheral equipment such as tubing, pumps, and system design, highlighting the decreased expenditures in essential systems compartments. Followed by the equipment expenditure, current collectors are 24% of the capital cost. As current collectors could be used over the system lifetime (about 10 years [59]), the cost of current collectors is a reasonable proportion of the capital cost. Notably, the cost of membranes and electrodes accounts for only 17% of capital cost. The operating cost of our system is divided into 5 components: electricity, chemicals, replacements for membranes, electrodes, and equipment (Fig. 6**b**). Although the energy consumption was lower than conventional systems (51−72% lower than the conventional ED systems), 55% of the yearly operating cost comes from electricity. This cost could be potentially reduced by harvesting energy during the regeneration process. Analogous to the redox flow battery [35,36], the system could utilize two different redox reactions in the cathode and anode chambers; thereby, it recovers not only removed salts but also the electrical energy during the regeneration process, possibly decreasing the electricity cost. Still, using the redox couple, membranes, and carbon electrodes requires replacement costs (34% of operating cost). For industrial application, advancement in energy harvesting strategy and developing economical membranes would be the most essential aspects to reduce overall expenditure going forward.

The result of the TEA indicates that our system can be operated with lower capital and operating costs than reported ED systems (Fig. 6**c**). To treat a large volume of water, ED systems need to be scaled-up by stacking up the membranes [30], which become the major expenditure in the capital and operating costs (up to 54% and 39% in capital and operating cost, respectively). On the other hand, our system could be scaled-up more conveniently by stacking up the electrodes and the current collectors in the redox channel [60], effectively lowering the capital costs and membrane replacement cost. Besides, operated at relatively high voltage (e.g., 7 V [17]), conventional ED systems consumed 25−275% more energy than our system where the reversible redox reactions could effectively desalinate ions at a low operating voltage under 1.0 V (Tables S4, S7, and S10). Note that the electricity cost was compared between 95% salt removal for our system and 90% salt removal for conventional ED systems; thus, we believe that our system requires even less electricity cost than ED systems for equal salt removal. In fact, as the number of stacked membranes increases [30], the capital cost of conventional ED systems significantly increases. On the other hand, lowering the number of stacked membranes in the ED system (G. Chen (2016) [17]) results in higher operating costs due to the high energy consumption to treat the equal volume of solution. For our system, integration of low-voltage-driven redox reaction and uncomplicated scale-up strategy enhances the economic feasibility, reducing 51–62% operating cost and up to 22% capital cost compared with conventional ED systems. Moreover, recycling the removed salts could reduce our systematic costs in several aspects. First, it would valorize the wasted salts and reduce the cost of the cheese production process. Second, the recycling process maintains the salt concentration in the redox channel, lowering the replacement cost of the electrolyte. Finally, this net-zero waste process significantly reduces the cost for the post-treatment or the disposal of the concentrated solution compared with conventional techniques. It is noteworthy that the yearly revenue of our system would exceed the capital and operating costs by $61,500/yr in the first operating year. Overall, this study demonstrated a sustainable net-zero waste process for valorizing the whey wastes via the redox-mediated electrodialysis system. Still, the major fundamental challenge remains in investigating environmentally benign and innocuous redox materials and preventing any cross-over. Therefore, with the development of more reliable redox materials, we envision our system to eventually translate to industrial practice as an economically-viable and greener platform for desalination in food manufacturing, and to promote waste valorization.

4. Conclusions

A redox-mediated electrodialysis system successfully demonstrated an energy-efficient and sustainable desalination of whey waste streams, and tandem purification of valuable whey proteins. Leveraging the reversible redox reaction between ferri- and ferrocyanide, concentrated salts in the whey solution were desalinated to valorize whey proteins (during the protein purification process), while the removed salts could be recovered and recycled back to the cheese production (during the electrochemical regeneration process). A sustainable redox reaction resulted in 99% salt removal from the whey solutions at operating voltages ranging from 0.4 V to 1.2 V. We comprehensively investigated

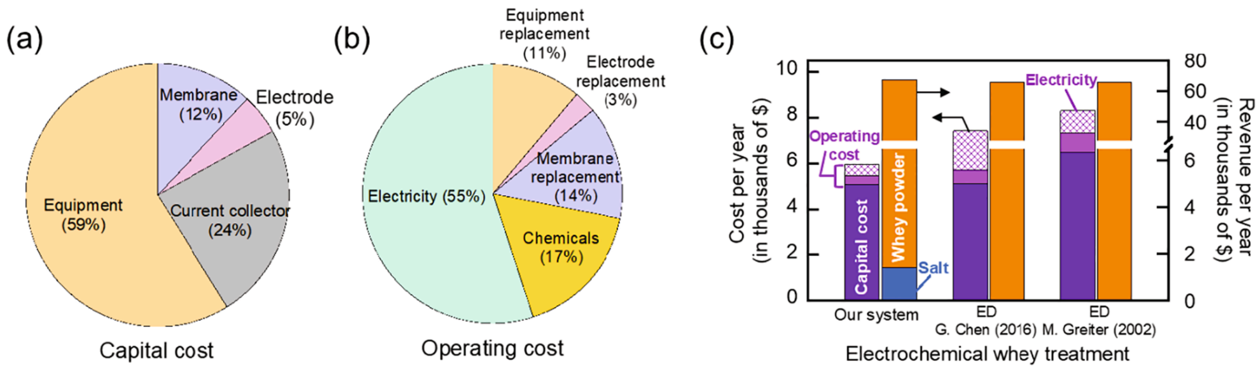


Fig. 6. Techno-economic analysis: (a) capital cost and (b) operating cost for the redox-mediated electrodialysis system and (c) comparison of the yearly payment and the product revenue between our system and the representative electrodialysis systems.

the desalination performance at various pH, whey contents, and salt concentrations, confirming the system could be utilized in diverse whey sources such as acidic, sweet, and salty whey wastes. Throughout our experiments, over 98% of whey proteins were preserved without any observable denaturation or aggregation, by maintaining the pH above the isoelectric points of whey protein contents; thus, we overcome a major bottleneck of conventional electrodialysis systems. The redox-mediated electrodialysis system exhibited consistent desalination and salt recovery performance (95% salt removal and 70% salt recovery) over multiple cycles of protein purification and system regeneration, validating the sustainable revalorization cycle with the net-zero waste. Besides, our techno-economic assessment supports the economic feasibility of the proposed process, showing lower energy consumptions and expenditures than conventional electrodialysis systems. Integration of a reversible redox reaction and desalination process provides a sustainable and energy-efficient avenue for desalination and protein separation in dairy processing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

X. Su would like to thank startup support by the University of Ilinois Urbana-Champaign (UIUC) and the School of Chemical Sciences (SCS), seed funding by the Institute for Sustainability, Energy, and Environment (iSEE) at UIUC, and funding support from the NSF under CBET Award #1942971. This research was also supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (NRF-2021R1I1A3040360)

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2021.131082.

References

[1] J. Ranganathan, R. Waite, T. Searchinger, C. Hanson, How to sustainably feed 10 billion people by 2050, in 21 charts, World Resources Institute, 2018.
[2] D.B. Lobell, W. Schlenker, J. Costa-Roberts, Climate trends and global crop production since 1980, Science 333 (6042) (2011) 616–620.
[3] L. Reisch, U. Eberle, S. Lorek, Sustainable food consumption: an overview of contemporary issues and policies, Sustainability: Sci. Practice Policy 9 (2) (2013) 7–25.
[4] D. Griggs, M. Stafford-Smith, O. Gaffney, J. Rockström, M.C. Öhman, P. Shyamsundar, W. Steffen, G. Glaser, N. Kanie, I. Noble, Sustainable development goals for people and planet, Nature 495 (7441) (2013) 305–307.
[5] A. Chaudhary, D. Gustafson, A. Mathys, Multi-indicator sustainability assessment of global food systems, Nat. Commun. 9 (1) (2018) 1–13.
[6] Y. Du, Y. Ge, Y. Ren, X. Fan, K. Pan, L. Lin, X.u. Wu, Y. Min, L.A. Meyerson, M. Heino, S.X. Chang, X. Liu, F. Mao, G. Yang, C. Peng, Z. Qu, J. Chang, R. K. Didham, A global strategy to mitigate the environmental impact of China's ruminant consumption boom, Nat. Commun. 9 (1) (2018), https://doi.org/10.1038/s41467-018-06381-0.
[7] M. Pieper, A. Michalke, T. Gaugler, Calculation of external climate costs for food highlights inadequate pricing of animal products, Nat. Commun. 11 (1) (2020) 1–13.
[8] A.M. Prentice, Dairy products in global public health, Am. J. Clin. Nutri. 99 (5) (2014) 1212S–1216S.
[9] H. Hartwell, A. Perez-Cueto, I. Mavridis, A. Giboreau, M. Ronge, Shaping smarter consumer behaviour and food choice, CAUTHE 2016: the changing landscape of tourism and hospitality: the impact of emerging markets and emerging destinations, 2016, 668.
[10] M. Morales-de la Peña, J. Welti-Chanes, O. Martín-Belloso, Novel technologies to improve food safety and quality, Curr. Opin. Food Sci. 30 (2019) 1–7.
[11] USDA, Dairy products: per capita consumption, United States (Annual), 2019.
[12] OECD/FAO, OECD-FAO Agricultural Outlook 2020-2029, FAO/OECD Publishing Rome/Paris, 2020.
[13] S. Marwaha, J. Kennedy, Whey—pollution problem and potential utilization, Int. J. Food Sci. Technol. 23 (4) (1988) 323–336.
[14] B. Das, S. Sarkar, A. Sarkar, S. Bhattacharjee, C. Bhattacharjee, Recovery of whey proteins and lactose from dairy waste: a step towards green waste management, Process Saf. Environ. Prot. 101 (2016) 27–33.
[15] G.W. Smithers, Whey and whey proteins—from 'gutter-to-gold', Int. Dairy J. 18 (7) (2008) 695–704.
[16] A.R. Prazeres, F. Carvalho, J. Rivas, Cheese whey management: a review, J. Environ. Manage. 110 (2012) 48–68.
[17] G.Q. Chen, F.I.I. Eschbach, M. Weeks, S.L. Gras, S.E. Kentish, Removal of lactic acid from acid whey using electrodialysis, Sep. Purif. Technol. 158 (2016) 230–237.
[18] K.M. Blaschek, W.L. Wendorff, S.A. Rankin, Survey of salty and sweet whey composition from various cheese plants in Wisconsin, J. Dairy Sci. 90 (4) (2007) 2029–2034.
[19] Á.A. Fekete, C. Giromini, Y. Chatzidiakou, D.I. Givens, J.A. Lovegrove, Whey protein lowers systolic blood pressure and Ca-caseinate reduces serum TAG after a high-fat meal in mildly hypertensive adults, Sci. Rep. 8 (1) (2018) 1–9.
[20] G. Frühbeck, Slow and fast dietary proteins, Nature 391 (6670) (1998) 843–845.
[21] A.M. Jastreboff, Demystifying the "magical cure" for diabetes, Science Translational Medicine 5(184), 2013, 184ec76-184ec76.
[22] R.C. Zapata, A. Singh, A. Pezeshki, T. Nibber, P.K. Chelikani, Whey protein components-lactalbumin and lactoferrin-improve energy balance and metabolism, Sci. Rep. 7 (1) (2017) 1–14.
[23] J. Aschemann-Witzel, R.F. Gantriis, P. Fraga, F.J.A. Perez-Cueto, Plant-based food and protein trend from a business perspective: markets, consumers, and the challenges and opportunities in the future, Crit. Rev. Food Sci. Nutr. (2020) 1–10.
[24] S.M. Loveday, Food proteins: technological, nutritional, and sustainability attributes of traditional and emerging proteins, Ann. Rev. Food Sci Tech. 10 (2019) 311–339.
[25] M.G. Gänzle, G. Haase, P. Jelen, Lactose: crystallization, hydrolysis and value-added derivatives, Int. Dairy J. 18 (7) (2008) 685–694.
[26] P.L.H. McSweeney, Salt in cheese, cheese problems solved, Woodhead Publishing 2007, pp. 80-99.
[27] A. Román, J. Wang, J. Csanádi, C. Hodúr, G. Vatai, Partial demineralization and concentration of acid whey by nanofiltration combined with diafiltration, Desalination 241 (1-3) (2009) 288–295.
[28] K. Pan, Q.i. Song, L. Wang, B. Cao, A study of demineralization of whey by nanofiltration membrane, Desalination 267 (2-3) (2011) 217–221.
[29] H. Rabiee, K.R. Khalilpour, J.M. Betts, N. Tapper, Chapter 13 - Energy-water nexus: renewable-integrated hybridized desalination systems, in: K.R. Khalilpour (Ed.), Polygeneration with Polystorage for Chemical and Energy Hubs, Academic Press, 2019, pp. 409–458.
[30] M. Greiter, S. Novalin, M. Wendland, K.-D. Kulbe, J. Fischer, Desalination of whey by electrodialysis and ion exchange resins: analysis of both processes with regard to sustainability by calculating their cumulative energy demand, J. Membr. Sci. 210 (1) (2002) 91–102.
[31] N. Miladinovic, L.R. Weatherley, Intensification of ammonia removal in a combined ion-exchange and nitrification column, Chem. Eng. J. 135 (1-2) (2008) 15–24.
[32] K. Walha, R.B. Amar, L. Firdaous, F. Quéméneur, P. Jaouen, Brackish groundwater treatment by nanofiltration, reverse osmosis and electrodialysis in Tunisia: performance and cost comparison, Desalination 207 (1–3) (2007) 95–106.
[33] J. Tate, P. Harleysville, EDR case study, IWC 17 35.
[34] L. Diblíková, L. Čurda, J. Kinčl, The effect of dry matter and salt addition on cheese whey demineralisation, Int. Dairy J. 31 (1) (2013) 29–33.
[35] K. Lin, Q. Chen, M.R. Gerhardt, L. Tong, S.B. Kim, L. Eisenach, A.W. Valle, D. Hardee, R.G. Gordon, M.J. Aziz, M.P. Marshak, Alkaline quinone flow battery, Science 349 (6255) (2015) 1529–1532.
[36] K. Lin, R. Gómez-Bombarelli, E.S. Beh, L. Tong, Q. Chen, A. Valle, A. Aspuru-Guzik, M.J. Aziz, R.G. Gordon, A redox-flow battery with an alloxazine-based organic electrolyte, Nat. Energy 1 (9) (2016) 1–8.
[37] Y. Zhao, L. Wang, H.R. Byon, High-performance rechargeable lithium-iodine batteries using triiodide/iodide redox couples in an aqueous cathode, Nat. Commun. 4 (1) (2013) 1–7.
[38] B. Dunn, H. Kamath, J.-M. Tarascon, Electrical energy storage for the grid: a battery of choices, Science 334 (6058) (2011) 928–935.
[39] O.S. Burheim, F. Seland, J.G. Pharoah, S. Kjelstrup, Improved electrode systems for reverse electro-dialysis and electro-dialysis, Desalination 285 (2012) 147–152.
[40] D.A. Vermaas, E. Guler, M. Saakes, K. Nijmeijer, Theoretical power density from salinity gradients using reverse electrodialysis, Energy Procedia 20 (2012) 170–184.
[41] E.S. Beh, M.A. Benedict, D. Desai, J.B. Rivest, A redox-shuttled electrochemical method for energy-efficient separation of salt from water, ACS Sustainable Chem. Eng. 7 (15) (2019) 13411–13417.
[42] N. Kim, S.P. Hong, J. Lee, C. Kim, J. Yoon, High-desalination performance via redox couple reaction in the multichannel capacitive deionization system, ACS Sustainable Chem. Eng. 7 (19) (2019) 16182–16189.
[43] N. Kim, X. Su, C. Kim, Electrochemical lithium recovery system through the simultaneous lithium enrichment via sustainable redox reaction, Chem. Eng. J. 420 (2021) 127715, https://doi.org/10.1016/j.cej.2020.127715.
[44] J. Ma, D.i. He, W. Tang, P. Kovalsky, C. He, C. Zhang, T.D. Waite, Development of redox-active flow electrodes for high-performance capacitive deionization, Environ. Sci. Technol. 50 (24) (2016) 13495–13501.
[45] B. Zhang, H. Gao, Y. Chen, Enhanced ionic conductivity and power generation using ion-exchange resin beads in a reverse-electrodialysis stack, Environ. Sci. Technol. 49 (24) (2015) 14717–14724.

[46] P. Srimuk, X. Su, J. Yoon, D. Aurbach, V. Presser, Charge-transfer materials for electrochemical water desalination, ion separation and the recovery of elements, Nat. Rev. Mater. 5 (7) (2020) 517–538.

[47] M. Nishanthi, J. Chandrapala, T. Vasiljevic, Compositional and structural properties of whey proteins of sweet, acid and salty whey concentrates and their respective spray dried powders, Int. Dairy J. 74 (2017) 49–56.

[48] P. Novák, V. Havlíček, Protein extraction and precipitation, Proteomic profiling and analytical chemistry, Elsevier2016, pp. 51-62.

[49] L. Wang, Y. Ma, J. Cui, S. He, J. Cheng, Effect of pH and heat-induced on the yak Β-lactoglobulin denaturation and aggregation, J. Adv. Dairy Res. 5 (168) (2017) 2.

[50] K.K.J. Burrington, Whey protein heat stability, 2011, pp. 1-8.

[51] N. Huma, I. Pasha, M. Sarwar, S. Ahmad, F.-u.-H. Shah, Effect of different filtration membranes on composition of sweet and acid whey protein, Pak. J. Food Sci 25(2), 2015, 79-85.

[52] C. Baldasso, T.C. Barros, I.C. Tessaro, Concentration and purification of whey proteins by ultrafiltration, Desalination 278 (1-3) (2011) 381–386.

[53] N. Adrus, M. Ulbricht, Novel hydrogel pore-filled composite membranes with tunable and temperature-responsive size-selectivity, J. Mater. Chem. 22 (7) (2012) 3088–3098.

[54] H. Fan, M. Peng, I. Strauss, A. Mundstock, H. Meng, J. Caro, MOF-in-COF molecular sieving membrane for selective hydrogen separation, Nat. Commun. 12 (1) (2021) 1–10.

[55] E. Casal, A. Montilla, F.J. Moreno, A. Olano, N. Corzo, Use of chitosan for selective removal of β-lactoglobulin from whey, J. Dairy Sci. 89 (5) (2006) 1384–1389.

[56] X. Su, A. Kushima, C. Halliday, J. Zhou, J. Li, T.A. Hatton, Electrochemically-mediated selective capture of heavy metal chromium and arsenic oxyanions from water, Nat. Commun. 9 (1) (2018) 1–9.

[57] X. Su, K.-J. Tan, J. Elbert, C. Rüttiger, M. Gallei, T.F. Jamison, T.A. Hatton, Asymmetric Faradaic systems for selective electrochemical separations, Energy Environ. Sci. 10 (5) (2017) 1272–1283.

[58] C. Kim, J. Lee, P. Srimuk, M. Aslan, V. Presser, Concentration-gradient multichannel flow-stream membrane capacitive deionization cell for high desalination capacity of carbon electrodes, ChemSusChem 10 (24) (2017) 4914–4920.

[59] J. Shen, J. Huang, H. Ruan, J. Wang, B. Van der Bruggen, Techno-economic analysis of resource recovery of glyphosate liquor by membrane technology, Desalination 342 (2014) 118–125.

[60] N. Kim, J. Lee, S.P. Hong, C. Lee, C. Kim, J. Yoon, Performance analysis of the multi-channel membrane capacitive deionization with porous carbon electrode stacks, Desalination 479 (2020), 114315.

[61] Xiao Su, Electrochemical interfaces for chemical and biomolecular separations, Current Opinion in Colloid & Interface Science 46 (2020) 77–93.

[62] Xiao Su, Jonas Hübner, Monique J. Kauke, Luiza Dalbosco, Jonathan Thomas, Christopher C. Gonzalez, Eric Zhu, Matthias Franzreb, Timothy F. Jamison, T. Alan Hatton, Redox Interfaces for Electrochemically Controlled Protein–Surface Interactions: Bioseparations and Heterogeneous Enzyme Catalysis, Chemistry of Materials 29 (13) (2017) 5702–5712.