Desalination and Water Treatment
www.deswater.com

14 (2010) 208–213
February

1944-3994/1944-3986
doi: 10.5004/dwt.2010.1057

Electrodialysis in whey desalting process

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Received 23 June 2009; accepted 25 November 2009

ABSTRACT

The utilization of whey is limited by its high content of salts. We used electrodialysis unit ED-Z mini (Mega a.s., Stráž pod Ralskem, Czech Republic) to remove ions from sweet whey and whey with added salt (1% w/w of NaCl) and observed conductivity changes during the process. Samples were taken every 10 min and the drop in K^+, Na^+, Ca^{2+}, Mg^{2+} was measured by capillary electrophoresis PrinCE-C 750 (Prince Technologies B.V., Emmen, The Netherlands). Ions were detected with the DAD detector at 206 nm and the quantity was determined according to calibration. The negative detection with imidazole in the basic electrolyte was used. Normal whey was desalted in 50 min from the conductivity of 4.83 mS/cm to 0.32 mS/cm. Concentration of Na^+ decreased from 0.43 g/L to 0.02 g/L, Ca^{2+} from 0.45 g/L to 0.07 g/L. Salted whey was demineralized in 65 min from 18.41 mS/cm to 0.34 mS/cm. The Na^+ concentration decreased from 3.92 g/L to 0.08 g/L, Ca^{2+} from 0.33 g/L to 0.03 g/L. These results demonstrate that electrodialysis is an effective way of elimination of salts from whey.

Keywords: Electrodialysis; Demineralization; Whey; Ion removal; Salts

1. Introduction

Whey is a by-product from cheese and curd production [1]. Depending on the method of recovery, sweet and acid whey can be parted. Sweet (rennet) whey is produced in large amounts worldwide from milk using the enzymatic action of chymosin on the casein fraction [2,3]. Casein represents about 80% of the total milk protein. It looses its colloidal solubility after chymosin treatment. Milk proteins can thus be separated into a coagulum from the casein protein fraction, i.e. the cheese curd, and whey. Whey consists of milk serum, including low molecular weigh solutes such as lactose, milk salts and other minor components, whey proteins and caseinomacropeptide [1–5]. Table 1 shows the average composition of sweet and acid whey.

There is an increased commercial interest in separation and fractionation of whey components, especially whey proteins and lactose [5]. Whey proteins have a high nutritional value and excellent functional properties. Thereby, they are widely used in human and animal nutrition as well as in pharmaceutical and cosmetic industries, namely as food additives (meats, beverages, dairy products, baked foods and infant formula), emulsion stabilizers and as foaming and texturizing agents [5,7]. Their action is more effective when isolated and purified proteins are used instead of the protein concentrate [8]. However, the utilization of whey and whey components is limited by high content of salts. The mineral salts affect the flavour, the functionality, the quality and the value of whey products. The desalination is therefore necessary for many

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Presented at the Fourth Membrane Science and Technology Conference of Visegrad Countries (PERMEA 2009), Prague, 7-11 June, 2009.

Table 1
Average composition of sweet and acid whey [6]

Constituents	Rennet whey	Acid whey
Dry matter (%)	5–7	5–7
Ash (%)	0.5	0.8
Protein (%)	0.5–1.0	0.5–1.0
Fat (%)	0.3	0.1
Lactose (%)	4.9	4.5
Lactic acid (%)	0.05	0.4
Calcium (mg/100 g)	37	93
Sodium (mg/100 g)	46	40
Potassium (mg/100 g)	123	153
Magnesium (mg/100 g)	7	9

technological operations of further manufacturing of whey [2,9]. Typical processes used for demineralization are: nanofiltration (NF), ion exchange (IE) and electrodialysis (ED). These processes differ in their mode and possibilities of operation [2,10].

Electrodialysis with ion-exchange membranes represents one of the most considerable membrane methods. It deals with problems of desalination of salted waters, wastewater minimization, ultra-pure water production, concentration of dilute solutions, separation of electrolytes and non-electrolytes and production of acids and alkalis from their salts. It is also applied for sugar demineralization, amino acid and blood treatment, concentration of mineral acids, preparation of isotonic solutions and wine stabilization [11]. ED is a membrane separation process where electrically charged membranes are used to separate ions from an aqueous solution under the driving force of an electrical potential difference [12]. The electrodialysis stack consists of a series of anion (A) and cation (C) exchange membranes arranged in an alternating pattern between an anode and a cathode to form individual cells. An ionic solution is pumped through these cells and when a direct current potential is applied, positively charged cations migrate toward cathode, pass easily through the negatively charged cation exchange membrane and stay retained by the anion exchange membrane. The contrary situation occurs at the anion selective membranes [6,12]. The overall result is an ion concentration increase in alternate compartments while the other compartments simultaneously become depleted of ions. The depleted solution is generally referred to as the diluate and the concentrated solution as the brine (concentrate) [12]. The principle of electrodialysis is illustrated on Fig. 1.

Desalination of whey is an important process in food technology. However, the application of electrodialysis in whey desalting process has been

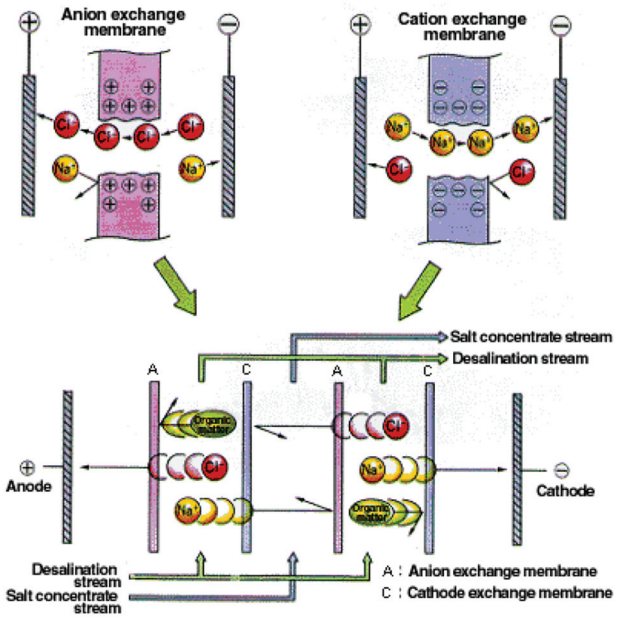

Fig. 1. Separation principle of electrodialysis [13].

investigated for last few years, only. Therefore, further research is needed. There are still many aspects that have not yet been fully assessed and some problems to be solved. In dairy industry electrodialysis has a great potential as an economical and efficient method, that can be used to remove salts even from highly salted wheys such as whey from cheddar or blue-veined cheeses production.

The objective of this paper was to study the electrodialysis in cheese whey processing generally. We also considered the possibility of using the electrodialysis for demineralization of whey with added salt and we compared the efficiency of desalination process of natural sweet whey and salted whey.

2. Materials and methods

2.1. Whey preparation

Pasteurized skimmed cow's milk (5 L) inoculated with 4% w/w of starter culture was warmed to 35°C. Then, 2 mL of $CaCl_2$ and 7 mL of liquid rennet Laktochym (1:5,000, Milcom a.s., Praha, Czech Republic) were added. After 40 min of coagulation, the curd was cut to the adequate grain size and the mixture was gently stirred. Finally, cheese grains were removed and liquid whey was microfiltrated on filtration unit ARNO 700 manufactured by Mikropur a.s., Hradec Králové, Czech Republic (Fig. 2). Tubular three channel ceramic TAMI-Industries membranes (Clover type,

Fig. 2. ARNO 700 lab-scale filtration unit with three channel membrane type Clover.

separative layer of zirconium oxide, length 550 mm, diameter 10 mm, channel diameter 3.5 mm, effective filtration area 0.02 m^2) with the pore size of 1.4 mm, pressure 0.125 MPa and temperature 35°C were applied. Sodium chloride (1% w/w) was then added to a part of whey to obtain salted whey.

2.2. Electrodialysis

Electrodialysis unit ED-Z mini (Fig. 3) was used for demineralization of salted and normal (non-salted) whey after microfiltration. The unit consists of twenty (10 mebrane pairs) heterogeneous ion-exchange RALEX membranes (Mega a.s., Stráž pod Ralskem, Czech Republic) with an effective membrane dimensions 40 × 160 mm, effective surface area 64 cm^2, channel diameter 6 mm and current density 150–160 A/m^2. Anhydrous sodium sulfate (10 g/L, 250 mL) was used as the electrolyte, distilled water acidified with HNO_3 (pH 1.5–2.5, 1,000 mL) as the concentrate. The electrodialysis took approximately 1 h at laboratory temperature and voltage 20.0–20.1 V. Conductivity and pH

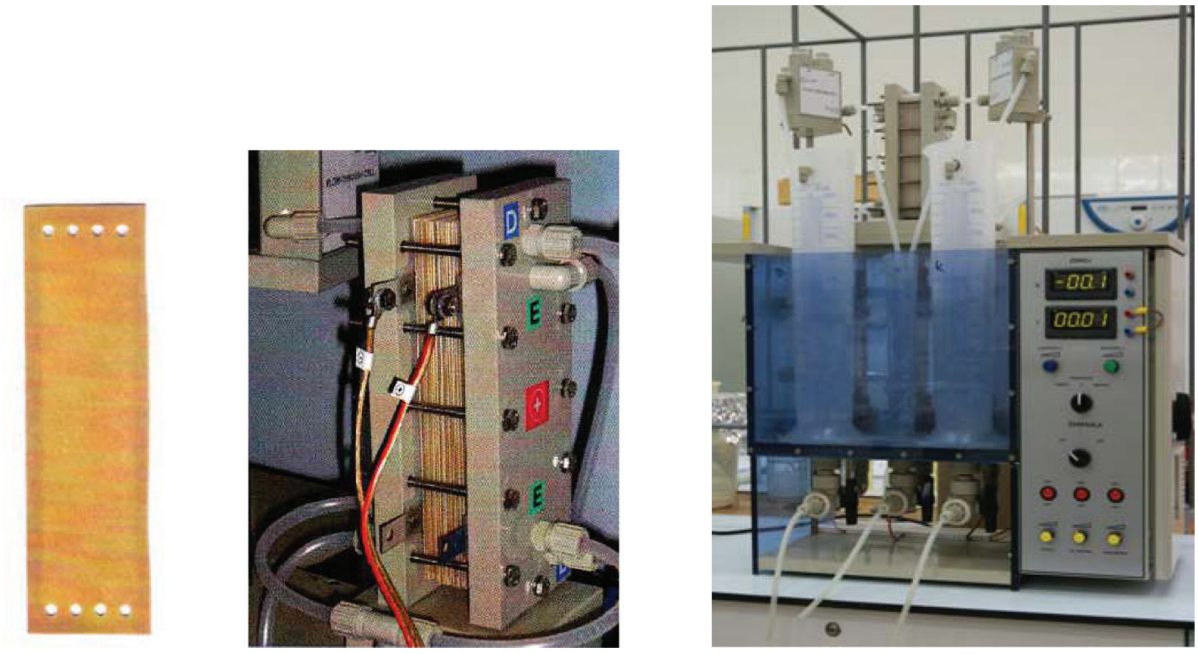

Fig. 3. Electrodialysis unit ED-Z mini with RALEX membranes.

Table 2
Composition of fresh and microfiltrated whey

Constituents	W1[a]	PMF1[a]	W2[b]	PMF2[b]
Dry matter (%)	6.95	6.08	6.93	6.17
Protein (%)	0.979	0.874	0.969	0.884
Fat (%)	0.2	0.0	0.3	0.0
Ash (%)	0.59	0.54	0.58	0.54
pH	6.1	6.1	6.3	6.3
Freezing point (°C)	−0.553	−0.505	−0.564	−0.505
Conductivity (mS/cm)	6.37	5.88	6.26	5.75

[a]Raw material before electrodialysis; [b]Raw material before adding salt and further electrodialysis

changes were observed during the process. Moreover, the samples were taken every 10 min and the drop in four main cations of milk–K^+, Na^+, Ca^{2+}, Mg^{2+} was measured by capillary electrophoresis. Anions were not determined.

2.3. Capillary electrophoresis

Electrophoresis unit PrinCE-C 750 (Prince Technologies B.V., Emmen, The Netherlands) was used to analyze samples of the diluate according to method described by Suaréz-Luque et al. [14]. Silica capillary with the length of 60 cm and inside diameter 75 μm was applied at 25°C. Ions were detected with the DAD detector at 206 nm and the quantity was determined according to calibration. The negative detection with imidazole (10 mmol/L) in the basic electrolyte, hydrodynamic injection at 34 Pa, 0.4 min was used. Each analysis took 4 min and was repeated at least twice.

3. Results and discussion

3.1. Whey characterization

Fresh cheese whey, obtained after rennet coagulation, was microfiltrated in order to prevent microbial growth, to remove residual fat and fine particles. A ceramic membrane (TAMI-Industries, Hermsdorf, Germany) with the pore size of 1.4 mm, pressure 0.125 MPa and temperature 35°C were applied. Average composition of sweet whey (W) and permeate after filtration (PMF) is presented in Table 2. At least two different wheys from lab-scale cheese production were used for constituent analysis and following desalination process.

Sodium chloride (1% w/w) was then added to PMF2 to obtain salted whey and both microfiltration permeates were demineralized.

3.2. The electrodialysis process

The lab-scale electrodialysis unit ED-Z mini (Mega a.s., Stráž pod Ralskem, Czech Republic) with the capacity of 2L of the diluate and concentrate was used to remove ions from cheese whey. During electrodialysis conductivity and pH changes were observed. Initial and final values are given in Table 3.

Initial values were measured when the unit pump was already working and this is the reason, why pH and conductivity values are lower in Table 3 than in Table 2. Normal whey was desalted in 50 min from the initial conductivity of 4.83 to 0.32 mS/cm. Whey with added salt was desalted in 65 min from 18.41–0.34 mS/cm. Conductivity changes of the diluate during the process are demonstrated on Fig. 4. As the consequence of ion transport through membranes, conductivity of concentrates increased to 16.26 mS/cm and 33.60 mS/cm for normal whey and salted

Table 3
Initial and final values of conductivity and pH of diluates and concentrates

Variable	Normal whey (diluate)		Salted whey (diluate)		Normal whey (concentrate)		Salted whey (concentrate)	
	Initial value[a]	Final value[b]	Initial value	Final value	Initial value	Final value	Initial value	Final value
Conductivity (mS/cm)	4.83	0.32	18.41	0.34	7.73	16.26	11.63	33.60
pH	4.85	4.25	4.44	4.17	1.82	1.61	1.72	1.59

[a]Before ED; [b]After ED

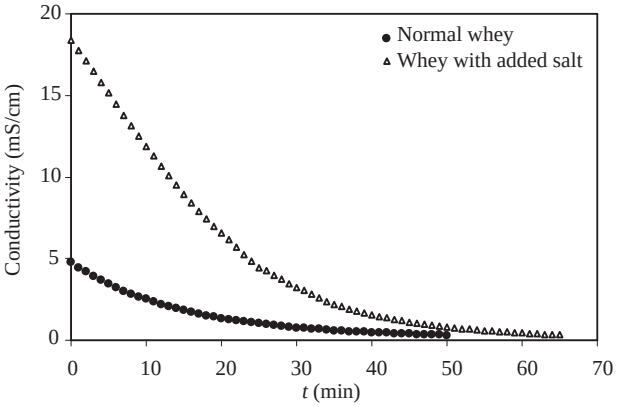

Fig. 4. Conductivity changes during demineralization of whey.

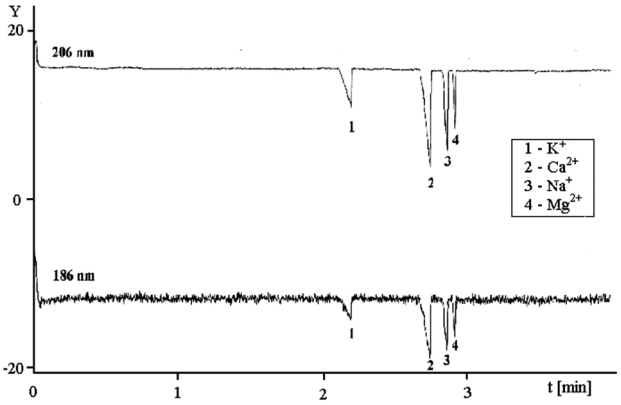

Fig. 5. Electrophoretogram of standard mixture solution of cations.

whey, respectively. During electrodialysis pH values decreased. We assume that a part of cations was replaced by H^+ ions.

Fig. 4 shows that the most significant decrease of conductivity appeared until 20 min of dialysis, when ion transports are the fastest. Till 40 min of electrodialysis more than 90% of all salts were removed in both types of whey and conductivity decreased under 0.5 mS/cm and 1.5 mS/cm in normal whey and salted whey, respectively. Average composition of ED products is presented in Table 4 (data after electrodialysis). Ions migration to the concentrate resulted in a significant decrease of ash content, dry matter and also influenced the freezing point.

3.3 Analysis of salt content

Samples of the diluate were taken every 10 min and analyzed by capillary electrophoresis. Results obtained from the electrophoretic measurements were evaluated according to Fig. 5. Four main cations of milk were measured: K^+, Na^+, Mg^{2+} and Ca^{2+}. The first peak corresponds to K^+ ion, the following are Ca^{2+}, Na^+, Mg^{2+} ions, respectively. Cations were detected with the DAD detector at 206 nm, because of less signal noise in comparison with wavelength 186 nm originally used by Suaréz-Luque et al. [14].

The drop in K^+, Na^+, Mg^{2+} and Ca^{2+} concentrations as a function of demineralization time is illustrated on Figs. 6 and 7.

As follows from Figs. 6 and 7, during electrodialysis priority is given to monovalent ions removal. Concentrations of K^+ and Na^+ ions decreased by 99–95% of the initial values in both types of whey. Many factors, such as an individual ion concentrations in the solution, ion mobility, membrane selectivity etc., might be responsible for this preference [15,16]. Ca^{2+} and Mg^{2+} ions were removed in the range of 80–91%. Worse calcium separation can be caused by its stabilizing role in whey proteins structures [17].

In about 1 h of electrodialysis process, nearly 95% of all salts were shifted away from normal sweet whey and more than 97% of all minerals were removed from salted cheese whey. Cations were separated in the range of 80–99%. Similar data we obtained for normal whey and whey with added salt. Some differences in removed salt percentage

Table 4
Composition of ED diluates and concentrates of normal and salted whey

Constituents	Normal whey (diluate)	Salted whey (diluate)	Normal whey (concentrate)	Salted whey (concentrate)
Dry matter (%)	5.26	5.43	–	–
Protein (%)	0.778	0.834	0.011	0.014
Fat (%)	0.0	0.0	0.0	0.0
Ash (%)	0.065	0.065	0.36	1.46
pH	4.3	4.2	1.6	1.6
Freezing point (°C)	−0.275	−0.307	−0.294	−0.934
Conductivity (mS/cm)	0.32	0.34	16.26	33.60

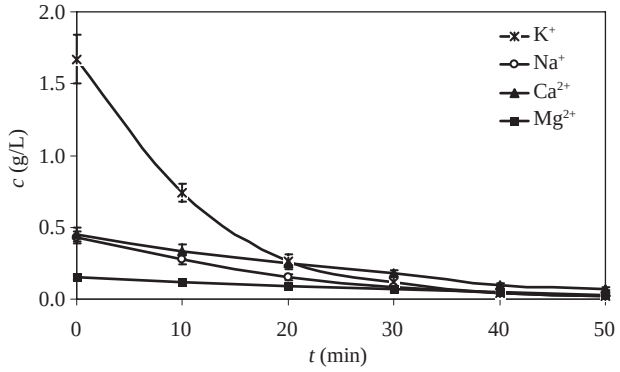

Fig. 6. Removal of cations from normal whey.

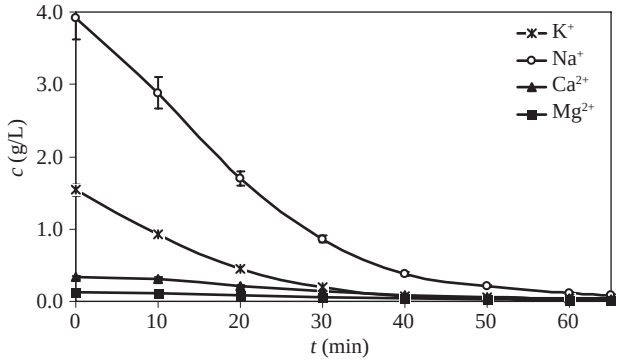

Fig. 7. Removal of cations from whey with added salt.

might be caused by longer time of desalination of salted whey and different initial concentrations of minerals. Overall, these results demonstrate that electrodialysis is an effective way of eliminating salts from whey even when salted.

4. Conclusions

The separation of monovalent (K^+, Na^+) and divalent (Ca^{2+}, Mg^{2+}) ions from sweet whey and whey with added salt was investigated using a laboratory scale electrodialysis cell. Normal whey was desalted in 50 min, salted whey in 65 min. The degree of mineral salt removal was higher than 95% in both types of whey. ED was observed to be an effective, modern, fast, energy saving method to perform demineralization of whey, which is nowadays one of the main products in dairy industry. Desalination is necessary for further use of whey as a raw material for other valuable products such as infant formula or animal feed or for the recovery of proteins, that are widely used not only in food industry. Thereby, electrodialysis is one of the most important membrane method with a great potential in the future.

Acknowledgments

This work was supported by Ministry of Education, Youth and Sports of Czech Republic (MSM 6046137305) and by Mega a.s., Czech Republic.

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