

Application of ultrafiltration and electro dialysis techniques in lactic acid removal from whey solutions

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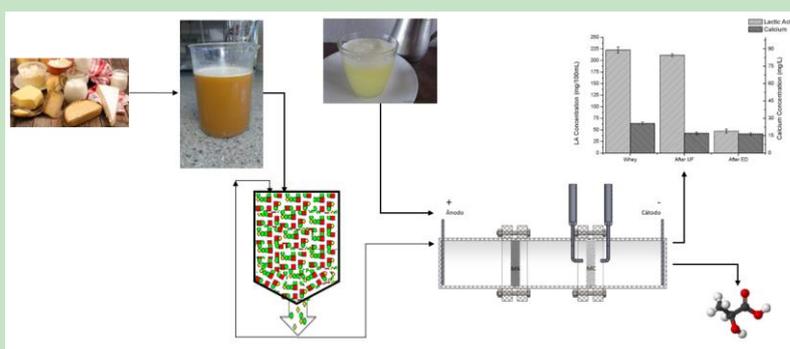
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ABSTRACT: Due to the biotechnological value of whey, this work aims at applying the ultrafiltration (UF) and subsequently the electro dialysis (ED) techniques in pilot scale plant. Whey (5% concentration) was treated twice by the UF technique, with a pressure of 4 bar (flow mode 20 L h⁻¹). The permeate obtained was submitted to the ED process, in which 12 V were applied for 4 h. In order to evaluate the UF, parameters as turbidity, color, TOC and pH were measured. Regarding the ED technique, parameters as pH, conductivity, calcium, sodium and lactic acid concentration were evaluated. The electro dialysis unit was operated on a constant voltage, and tested the range was from 3 to 12 V. After the UF and ED processes, the pH remained unchanged. Thereafter the UF treatment, the initial turbidity was reduced by 99.9%. In terms of parameter reduction after ED, the calcium concentration was decreased in 36.0% soon after UF and ED treatments, and the lactic acid concentration in 80.0%. These results point to the possible combination of UF and ED to treat the whey and signals the potential of further using the resulting solutions as inputs in new applications in the food industry such as lactose.



1. Introduction

Whey is one of the by-products of high added value in the dairy industry, by the expressive volume generated as well as by its composition, containing important nutrients. In this process¹, there is no total feedstock conversion in final product, hence, for each kilogram of cheese produced, an average of 10 liters of whey is generated. The milk whey consists, basically, of 94 to 95% water, 3.8 to 4.9% lactose, 0.8 to 1.0% protein and 0.7 to 0.8% of minerals². In terms of Chemical Oxygen Demand (COD), the content of organic compounds is around 60,000 mg L⁻¹³.

According to some authors⁴⁻⁶, there are numerous current alternatives for the use of fresh milk whey and its components. Among the

alternatives, it can be mentioned, for example, animal feed, production of ricotta, dairy drink, whey powder production, which can be also used in the pharmaceutical industry.

One of the main stages to produce biotechnological products is drying out the whey using a spray dryer equipment. The presence of lactic acid in whey (containing lactate ions) promotes products that are more susceptible to moisture absorption⁷, because of the hygroscopic behavior. This phenomenon allows the formation of powdered agglomerates that cannot be tolerated in this process.

The membrane separation processes (MSP) go through clean technology which play an important role in the separation of whey components⁸, such as proteins and lactose with subsequent drying.

Such components both contribute to the environment improvement and provide gains to industries. In addition, they are more valued when segregated.

Ultrafiltration (UF) is an alternative and attractive method, since it does not use heat as well as a phase change. This technique is usually applied to retain macromolecules and has been widely used in the dairy industry for the recovery of important components and compounds^{9,10}. The UF allows the concentration variance among different compounds, due to the protein retention and selective permeation of lactose, minerals, water and compounds of low molar mass.

Electrodialysis (ED) is an electrochemical technique and shows benefits when compared to traditional processes, since it does not require phase change or addition of chemical reagent, as well as its operational cycle is continuous. It has been widely used in water and wastewater treatment for the removal of ions, for example, ionic species in solution are transported in

compartments of a cell through ion-selective, anionic and cationic membranes by the action of an electric field. In addition to this, electro dialysis is an alternative^{11,12}, method of lactose separation and concentration, when whey solutions are used.

In this context, the aim of this study is to investigate the potential applicability of combining ultrafiltration and ED techniques (in a pilot scale system), in order to remove lactic acid (LA) and other ions from whey, focusing on biotechnological applications.

2. Materials and methods

The research consisted in the recovery of whey (5% concentration) and the purification treatment was carried out twice by the UF technique, in a pilot scale plant (flow mode 20 L h⁻¹), and the permeate obtained was submitted to the ED process in a prototype pilot scale (Fig. 1).

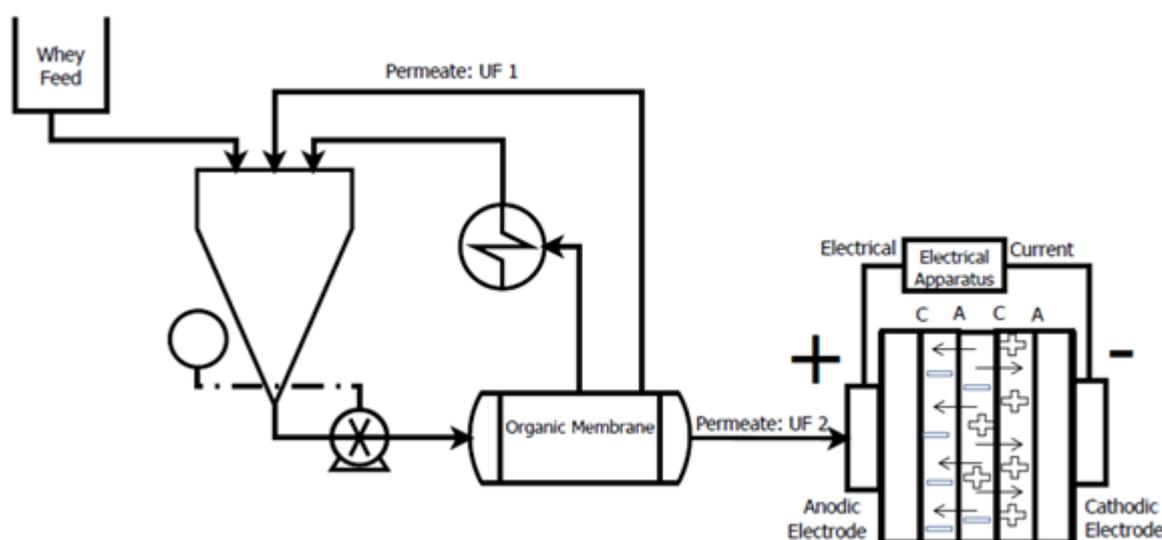


Figure 1. Schematic diagram of ultrafiltration and electro dialysis treatments.

In the ultrafiltration experiments, the volume of permeate was evaluated, and it was collected to determine the flux. In addition, the whey was ultrafiltered under varied conditions, i.e., pH ranging from 5.9 to 7.0 and transmembrane pressure (TMP) ranging between 3.5 and 5.0 bar. After this evaluation, the TMP was maintained at 4 bar and pH 5.9. The UF membrane was AG1812, made of polyethersulfone, manufactured by GE Water. The molar weight cut-off was 200 kDa, and permeation area was 0.37 m². The UF experiments

were conducted in batch processing. In this process, the concentrate stream return to the begin, like total recirculation mode. The whey was ultrafiltered two times.

After UF treatments, the permeate obtained was submitted to the ED process, in which 12 V were applied for 1 h (for evaluation) and 4 h (total treatment time), in an acrylic cell containing five compartments (total volume of 7 L). In this system, the cathode was a titanium plate and the anode, a 70TiO₂/30RuO₂ plate (189 cm²). The

electrodialysis cell was operated on a constant electrochemical potential, and the potential range was 3 to 12 V. The area per ion exchange membrane (AMV and CMV Selemion) was 63.61 cm².

2.1 Analysis of limiting current in ED process

Initially, the limiting current in ED process has been determined using a CaCl₂ solution for comparison with the results of Na⁺ ions, according to the Tanaka¹⁴, in a cation-exchange membrane, to simulate Ca²⁺ ions present in whey. In this evaluation, a constant current source ICEL PS-7000 was used to apply successive increments of electrical current each two-minute intervals, in a cell containing 0.1 mol L⁻¹ CaCl₂ solution. The cationic membrane potentials were measured (multimeter MINIPA ET-2081) using a multimeter connected to two reference electrodes (Ag/AgCl/KCl(sat) with Luggin capillary placed at the membrane's interfaces (in a three-compartment acrylic cell). In this experiment, the cathode was a titanium plate and the anode a 70TiO₂/30RuO₂ plate (8.9 cm²). At the end of each interval data of applied current, potential of the system and membrane were recorded.

2.2 Sample analysis

The parameters evaluated for the UF treatments were: turbidity (Digimed DM TU), Total Organic Carbon – TOC (Shimadzu TOC-V_{CPH}), Total Nitrogen (Shimadzu TNM-1), Color (Co-Pt), conductivity (856 Metrohm Module) and pH

(827 pH Lab Metrohm). For the ED technique, the parameters evaluated were pH and conductivity. A HPLC Shimadzu, LC-20AT, detector DAD: SPD M20A, Autosampler: SIL-20A HT with Supelcogel C-610H; 0.8 mL min⁻¹ H₂SO₄ 0.05 mol L⁻¹, temperature = 50 °C, λ = 207 nm, retention time = 9.90 min, was used to detect lactate ions⁶. Calcium ions were detected by an Atomic Absorption Spectrometer (Perkin Elmer PinAAcle 900T), λ = 422.67 nm.

3. Results and discussion

3.1 Evaluation of ultrafiltration and ED treatments

To evaluate the efficiency of UF and ED techniques, some initial parameters were analyzed.

3.1.1 Evaluation of ultrafiltration conditions

The results of water and whey flux vs. transmembrane pressure are shown in Fig. 2. It is possible to observe that the water flow increased linearly in function of the TMP ($r^2 = 0.9229$), and for whey solutions the behavior was linear with different slope. The same behavior was found in another study¹³.

The transmembrane pressure during Ultrafiltration process was optimal at 4.0 bar. Lower pressure resulted in a decreased flow, in function of lower driving¹⁵. Also, previous studies showed that higher values of pressure promote an irreversible fouling¹⁶.

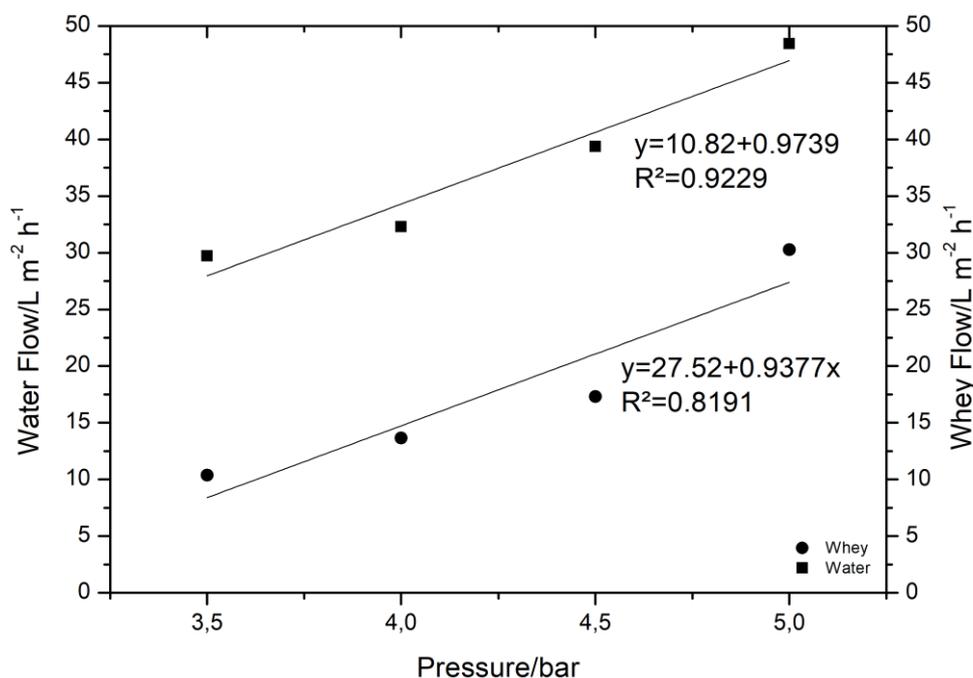


Figure 2. Water and whey flux vs transmembrane pressure. Membrane AG1812, T=25 °C, feed flow rate= 20 L h⁻¹. Legend: (■) water, (●) whey.

The evaluation of the ultrafiltration technique was performed by monitoring the turbidity and reduction of color (Co-Pt). In **Table 1**, results of whey flux (L m⁻² h⁻¹), reduction of turbidity and

color are shown, and in this ultrafiltration system, the best results were obtained using pressure at 4 bar and pH 5.9.

Table 1. Results of experimental conditions and turbidity and color removed after ultrafiltration process

Conditions (pressure and pH)	Whey flux/L m ⁻² h ⁻¹	Reduction of turbidity/%	Reduction of color/%
4.0 bar - pH 5.9	15.69	94.81	73.81
4.0 bar – pH 7.0	16.60	92.72	70.54
4;5 bar – pH 5.9	18.83	99.23	67.33

The pH is an important parameter to show the behavior of whey in the ultrafiltration plant. It is a precautionary measure with respect to the range of pH allowed to the membrane. The turbidity and measure of color are quality indicators of solution. The first one is linked to the concentration in colloidal substance in suspension present in the sample and the second one, as well as turbidity also is the result of the light scattering, relatively. The increase of the pressure, hence increase the removal rate of turbidity and decrease the removal rate of color.

These turbidity results are in line with other studies^{17,18}, when evaluate the ultrafiltration performance for the same endpoint, also find high removal rate. Though, the same does not occur to the measure of color. This parameter is related to the quality of the treatment, according to another study¹³, higher pressure decreases the quality of the permeate.

3.1.2 Evaluation of electro dialysis conditions

A typical current-potential of the membrane (U_m) curve observed in working ED unit is depicted in Fig. 3, for the electro dialysis of a 0.1 mol L^{-1} CaCl_2 solution. For the cationic membranes evaluation, the second region (plateau) in the graphic of Fig. 3 determines a limiting current between 1.79 and 2.02 mA cm^{-2} with cell potential (E_{cell}) around 13 V . After this evaluation, the limiting current was also determined using the work solution (whey), and the results were comparable.

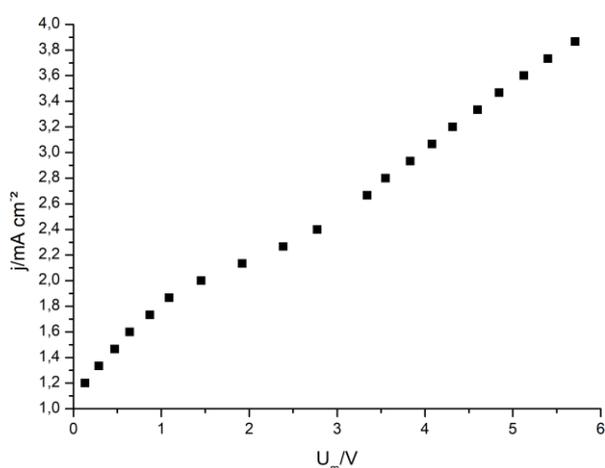


Figure 3. Current-potential of the membrane (U_m) curve observed in working ED unit, for the electro dialysis of a 0.1 mol L^{-1} CaCl_2 solution.

In terms of the removal rate of the of Ca^{2+} and Na^+ cations, applying ED treatment for 1 h (for evaluation this treatment), the results are in Table 2, and, in this evaluation, the best results were obtained using a voltage of 12 V . Also, after the ED treatment (operated with a constant 12 V), the initial concentration of lactate ions was reduced in 36.31% . The conductivity of the whey solution (after UF) was around 17.4 mS cm^{-1} .

Table 2. Percentage of ions removed from whey solutions after 60 min of a batch electro dialysis process.

Cell voltage/ V	Removal of Na^+ ions/ %	Removal of Ca^{2+} ions/ %
3	5.91	4.34
6	2.16	9.68
12	13.00	14.63

3.2 Purification and demineralization of whey by UF combined with ED

After the initial evaluation of some parameters in the UF and ED techniques, the purification and demineralization of whey by UF combined with ED were investigated. Fig. 4 shows that the initial flow decays to approximately constant values, from $15.63 \text{ L m}^{-2} \text{ h}^{-1}$ (initially), to $9.5 \text{ L m}^{-2} \text{ h}^{-1}$ (after 80 min), similar results were shown in previous study^{19,20}.

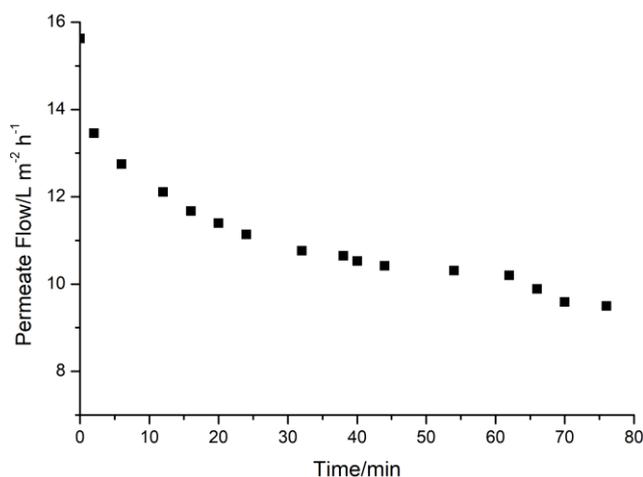


Figure 4. Average flux as a function of time for whey solutions at 4 bar .

The phenomenon of permeation flux reduction must be evaluated to avoid compromising the application of ultrafiltration technique in real systems (scale up). In this study, the whey solution has a pH of 6.2 , soluble total organic carbon (TOC) of 8.1 g L^{-1} and total nitrogen of 3.5 g L^{-1} .

The results of concentration in terms of anions (lactate ions) and cations (Ca^{2+}), after ultrafiltration (twice) and electro dialysis treatment (4 h – total time), are shown in Fig. 5. After the electro dialysis process, the conductivity of the treated solution was around 15.69 mS cm^{-1} this result demonstrates the demineralization after ED⁶.

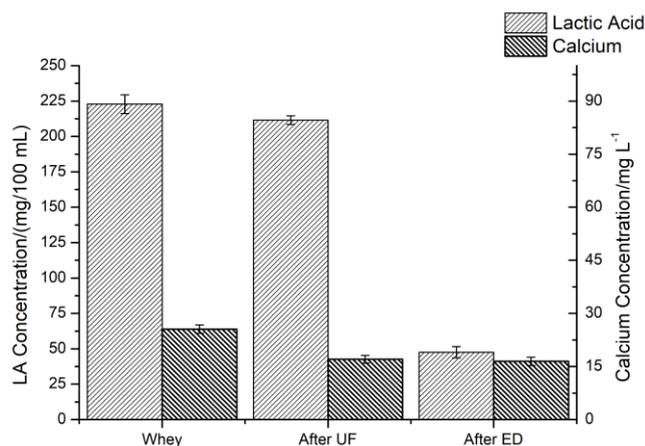


Figure 5. Lactic acid and ion calcium concentration before and after ultrafiltration and ED (4 h).

After the UF and ED processes, the pH remained unchanged, and the initial turbidity was reduced by 99.93%. The calcium concentration was decreased in 36% in the permeate solution, the lactic acid concentration in 80% (after UF + ED), and the TOC was reduced in 56%.

The removal of lactate ions occurs at a slower rate compared to other ions present in whey (when applied ED technique during 1 and 4 h), due to the more complex nature^{8,19}. Furthermore, the final calcium concentration (after 4 h) was 41.13 mg L⁻¹ and in terms of acid lactic, the final concentration was 43.65 mg/100 mL; and the final acid lactic concentration was 43.65 mg/100 mL; and the decrease of electrical conductivity of the permeate solution is function of time and indicates the efficiency of the ED treatment²¹.

These result points to the possible combination of UF and ED to treat the whey and signal the potential of further using the resulting solutions as inputs in new applications in the food industry, such as lactose. In addition, for the whey to be adequately treated by the spray dryer technique, a reduction of the lactic acid concentration is required, being an important step in the milk industry (specially to increase the shelf life).

4. Conclusions

The combination of both methods ultrafiltration (UF) and electro dialysis (ED) is useful to remove the lactic acid and calcium ions from whey, through UF (twice steps) to concentrate and purify lactate, before submitting the permeate in ED treatment (4 h). After the treatments, the initial turbidity was reduced by 99.93%. The calcium concentration was decreased in 36% in the permeate solution, and the lactic acid concentration in 80% (after UF + ED). In UF was observed the membrane fouling phenomenon. This phenomenon occurred because have been colloidal material and macromolecules have been depositing at the membrane surface area promoting a low permeate flux. All these in UF system have been totally depended of pH and transmembrane pressure. In the first minutes of the pilot scale operation, the permeate flow decreased by around 14%. In ED processes, it was also observed this phenomenon. In the same sense of UF, this phenomenon increases the resistance, reducing the efficiency of ED system, and, for this reason, removal rate of the ions from the studied system was modified. These results point to the possible combination of UF and ED to treat the whey and the using of resulting solutions as inputs in new applications, such as lactose.

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