Membranes for the Downstreaming of Lactic Acid from Grain

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In addition to lactic acid, which is present as sodium lactate, the reaction mixture which results from the production of lactic acid from grain hydrolysates through fermentation contains impurities which must be removed depending on the kind of product and the purity requirements it must fulfill. Membrane techniques are increasingly being used as an alternative to conventional methods. Nanofiltration in the form of diafiltration and electrodialysis count among these techniques. They not only allow uncharged components, such as sugar and proteins, but also foreign ions, such as chloride ions, to be removed from the target product.

Keywords

Lactic acid, down streaming, nanofiltration, electrodialysis

Introduction

The process steps which are required for the gaining of the final product after fermentation are termed downstreaming. Depending upon the kind of product and the purity requirements it must meet, several process steps are combined, which exert a significant influence on the costs. The expenses for the downstreaming of a bioproduct, for example, amount to up to 90 % of the entire production costs depending on the value of the product [1]. Therefore, the downstreaming of fermentation has particular media importance. Membrane techniques in the form of micro-, ultra-, and nanofiltration, as well as reverse osmosis and electrodialysis are increasingly being used as an alternative to conventional methods, such as filtering, separating, crystallizing, vaporization, drying, and ion exchange [2]. These methods provide gentle product treatment and are costeffective, energetically and safetytechnologically attractive, as well as environmentally friendly technologies [3, 4]. Their modular design allows them to be adapted to any capacity. As compared with thermal techniques, the energy costs are lower [5].

In some cases, the lactic acid, which is gained through ultrafiltration after continuous fermentation [6], also contains the solved substances used for fermentation, which constitute impurities and must be removed depending upon the application of the lactic acid.

Conventionally, this is done using ion exchange resins and activated carbon. However, this method consumes large amounts of regeneration agents (acid, lye, and activated carbon) and produces large quantities of wastewater. Pre-cleaning of the product with the aid of membrane techniques may ease the problems caused by conventional techniques.

For the combined salvaging of recoverable substances and wastewater cleaning during lactic acid production from whey permeate, which is used an example, BÖRGARDTS et al. [7] employ membrane techniques for the downstreaming of lactic acid. In this case, however, this method does not focus on the cleaning, but rather on the production of lactic acid.

MADZINGAIDZO [8] and DANNER et al. [9] examine electrodialysis with monoand bipolar membranes for the cleaning of sodium lactate after the fermentation of solutions of glucose and lactic acid from silage press liquid following ultrafiltration. This study in particular

focuses on the decoloration of the lactic acid and the retention of non-transformed glucose and certain minerals. LEE et al. [10] also examine the desalination of lactic acid through electrodialysis and model this process using experimental data

Initial results of the author's own studies on downstreaming steps using the aid of membrane techniques for biomass separation, the decoloration of the culture filtrate solution, as well as the concentrating, cleaning, and conversion of sodium lactate into free lactic acid have already been described in references [11] and [12]. In these publications, the properties, the areas of application, and the fermentation of lactic acid from grain hydrolysates have also been covered extensively.

The present contribution presents new results gained during the application of membrane techniques for the cleaning of the product from model- and practical experimental solutions used for laboratory trials. These results in particular concern the permeability and the transport speeds of chloride-, sulphate-, and lactate ions.

Material and Methods

The nanofiltration experiments were carried out in a laboratory plant with exchangeable membranes. When the diafiltration technique was employed, the drained quantity of permeate was replaced with distilled water, and the original medium was cooled in a double-jacketed container (figure 1). The temperature, the pressure in front of and behind the membrane, as well as the permeate flow were registered regularly during the experiments.



The electrodialysis experiments were carried out in a laboratory plant with 4 cycles and exchangeable membrane stacks (type: OS-ED-100) and OS-EDwith 100 Quadro) monopolar (AMX/CMX) and bipolar membranes (figure 2). Each cycle was equipped with a pump and measuring equipment for flow, pressure, temperature, pH-value, and conductivity. The receivers were thermostatted. The membrane stack was supplied with electricity by a direct current supply unit with an adjustable current of 0 to 5 A, which was designed for both current- and tension-constant operation. The membrane stack is designed for an effective membrane surface of 100 cm². Cell frame size amounted to 15 x 15 cm with a cell frame thickness of 0.5 mm. 10 AMX membranes, 11 CMX membranes, and 10 bipolar membranes each were used.

Anions and cations were determined under the following conditions using the ion chromatograph DX-120 from the Dionex company, Idstein: column: IonPac AS14 (4 mm) with precolumn (anions); Ion-Pac CS12A (4 mm) with precolumn (cations): eluent: 3.5 mM disodium carbonate. 1 mM sodium hvdrogen carbonate (anions), 22 mM sulphuric acid (cations); flow rate: 1.12 ml/min (anions), 11 ml/min (cations): detection: conductivity with autosuppression; suppressor: ASRS in the recycle mode (anions), CSRS in the recycle mode (cations); injection volume 25 µl; elution duration: 12 min (anions), 14 min (cations).

Results and Discussion

Nanofiltration

Nanofiltration membranes exhibit pronounced ion selectivity for mono- and polyvalent ions. In some cases, polyvalent ions are retained, while monovalent ions can pass the membrane [13-18]. On this basis, experiments regarding the washing out of chloride ions in the diafiltration technique were carried out.

The membranes used are listed in **Table 1**.

Preliminary experiments with model solutions of sodium lactate and lactic acid have shown that the selectivity of the membranes for lactate ions and lactic acid exhibits significant differences due to different dissociation in these two solutions. Independent of the kind of membrane, significantly more lactic acid passes the membrane as compared with the lactate ion of the salt, whereas if sodium lactate is used the permeation of



lactate ions is largely determined by the kind of membrane (**figures 3** and **4**). The poorest results were achieved with the membrane NF 90. Therefore, this membrane was excluded from further experiments.

When removing chloride ions from a cellfree sodium lactate solution. the membrane OS-50 allowed the best results to be achieved (figure 5). A washing liquid quantity of 140 % of the amount of sodium lactate solution used enabled 99.7 % of the chloride ions to be washed out. During this process, the loss of lactate ions reached up to 26 %. The permeability of the membrane for potassium ions, lactate ions, phosphate ions, and sulphate ions varies depending upon the their molecular weight (figure 6).

Electrodialysis

General

Electrodialysis is a membrane technique for the removal, separation, and concentrating of ions from watery solutions. With the aid of semipermeable membranes and electrical current, ions pass from a less concentrated solution to a more concentrated one. Ion separation is caused by the different retaining ability of the ion exchange membrane for ions with different charge. The basic functional diagram of electrodialysis is shown in **Figure 7**. The anions (negatively charged ions) travel from the dilute solution cell in the direction of the anode through an anion exchange membrane into the neighbouring concentrate cell. In the direction of the anode, this cell is limited by a cation exchange membrane, which prevents further travelling of the anions. In an analogue manner, the same applies to the cations (positively charged ions). Within the cells, electricity always flows in the form of ion transport. This substance transport begins at the electrodes, where water is split up into protons and hydroxyl ions. This process is always combined with the production of gas, which is washed away from the electrodes through permanent rinsing of the cells. This rinsing solution consists of an electrolyte (e.g. Na₂SO₄), which has sufficient conductivity and does not lead to undesirable electrode reactions.

Electrodialysis stacks are so-called flat membrane modules. As in a filter press, membranes and spacers, which are also termed cell frames, are alternatingly placed behind each other and pressed together by a tensioning device. The supply- and draining lines in the stacks as well as the electrodes are housed in the end plates.

When well soluble substances, such as common salt, mineral acids, lyes, etc. are concentrated, maximum concentration is limited by water transport, which is coupled with ion transport in the form of a

Table 1: Parameters of different nanofiltration membranes for the purification of a cell-free solution of sodium lactate

| Parameters | Membrane designation | | | | |
|----------------------------|----------------------|-----------|-----------|---------|---------|
| | NF 45 | NF 70 | NF 90 | OS-15 | OS-50 |
| Material | Polyamide | Polyamide | Polyamide | Polymer | Polymer |
| NaCl retention % | - | 60 | - | 15 | 50 |
| Filter area m ² | 2.1 | 1.4 | 2.1 | 2.4 | 1.4 |
| Pressure bar | 30 | 14 | 15 | 30 | 30 |
| Permeate flow I/m2*h | 32 | 18 | 1.1 | 8.3 | 5.4 |



hydrate envelope. In addition, the membrane modules are not 100 % hydraulically leak-free.

Bipolar membranes are used to transform anorganic and organic salts into their corresponding acids and bases. A biopolar membrane consists of an anion- and cation-selective layer. Both layers are separated by a thin water film and arranged between two electrodes such that the cation exchange membrane is situated on the side of the cathode, while the anion exchange membrane is located on the side which faces the anode. If an electric potential difference is given between the two electrodes, all ionogenic components on the water film between the ion exchange membranes are removed. If the layer between the membranes exclusively contains water, protons and hydroxyl ions, which can even be found in pure water at a concentration of 10^{-7} mole/l, are transported. The H⁺ and OH⁻ ions carried away by the electric field are supplied again due to water dissociation leading to balance. Thus, water is split а continuously. This happens significantly faster than in a free solution due to the catalytic effect of charge carriers in the laver of the intermediate bipolar membrane, which are uncompensated for. The advantage over electrolytic water dissociation resides in the fact that, as in the case of electrodialysis, serveral bipolar membranes can be arranged between a pair of electrodes. Hence, the production of oxygen and hydrogen at the electrodes takes place only once. For this theoretical reason. the energy requirements for water dissociation with bipolar membranes are only slightly less than 50 % of those for comparable electrolysis [19]. Without the addition of chemicals, the protons and hydroxyl ions form the corresponding acid and base with the ions of the salt so that there are no other waste products.

Electrodialysis with Monopolar Membranes

According reference [20], to demineralization processes of whey through electrodialysis cause а disproportioning of the composition of the salts remaining in the whey. This is caused by different transport speeds of monovalent and polyvalent ions, among other factors.

In reference [21], these effects, which are intended to be used for the cleaning of sodium lactate, are described as well.

Initial experiments with a model solution of sodium lactate at a concentration of 51 g/l and a current density of 50 mA/cm² showed a chloride ion transport of 86 % after an experimental time of just 60 min. The percentage of sulphate- and lactate ions transported after this time amounted to 63 % and 34 % respectively (figure 8). Depending on the time, the transport of chloride and sulphate ions exhibits a development, degressive while the transport of lactate ions is linear to progressive. Although, as compared with monovalent chloride ions, the transport rate of sulphate ions is higher due to their divalence, the permeability of the chloride ions is higher due to their lower molecular weight.

The comparison of former results with a cell-free sodium lactate solution after fermentation allowed the temporal course of transport in the model solution shown in Figure 8 to be confirmed.

According to Faraday's law, ion transport increases with growing current density diagram of electro-

Figure 8: Temporal

volume: 1 I of salt solution)

Figure 9: Temporal

current densities

concentrating of a

current density = 50

mA/cm²)

model solution of

51 g/l)

dialysis

(figure 9). As compared with lactate ions, chloride ions exhibit a greater increase and, hence, higher transport speed at the same current density. In the case of lactate ions, the influence of current density on ion transport only becomes significant at a current density of 50 and 25 mA/cm² after an experimental time of 60 min.

Sufficient initial conductivity of the original concentrate is required for a high current yield to be obtained. This is usually achieved by adding sodium lactate to distilled water so that a certain conductivity (5-10 mS/cm) is reached. Since this salt is a waste product of cleaning processes, the direct use of pure tap- and distilled water as concentrate was examined. Figure 10 shows that if distilled water was used to which sodium added lactate was to reach set conductivity, the largest amount of chloride ions was transported, as expected. If the initial conductivity of the concentrate diminishes, as in the case of pure tap water (0.8 mS/cm) or distilled water (0.015 mS/cm), chloride ion transport decreases. Lactate ion transport, however, is influenced only after an experimental time of 60 min.

Electrodialysis with Bipolar Membranes

As in the case of electrodialysis with monopolar membranes, the use of bipolar membranes also results in а disproportioning of ion composition due different transport speeds to and permeabilities.

Experiments with a model solution of concentrated sodium lactate having a concentration of 209 g/l, to which defined quantities of sodium chloride and sodium sulphate were added show that, as compared with the sulphate- and lactate ions, the chloride ions exhibit a significantly stronger time-dependent increase and, hence, higher transport speed during the first 30 min at a current density of 50 mA/cm² (figure 11). After 30 min and 120 min, a respective percentage of 63.5 % and 98.4 % of all chloride ions have been transported into the acid cycle. As compared with the divalent sulphate ions, the monovalent chloride ions exhibit greater permeability. Former experiments regarding the conversion of concentrated sodium lactate produced through fermentation confirm the results shown in Figure 11 with the model solution.

Depending upon current density, chloride ion transport increases with growing current density according to Faraday's law (figure 12). For lactate ions, the difference is less clear at a current density of 25 and 10 mA/cm².



Figure 13 shows the influence of acid conductivity on ion transport. For this purpose, different media were tested. In addition to distilled water, to which lactic acid was added to reach a conductivity of 2.75 mS/cm at a lactic acid concentration of 13 g/l, both pure tap water having a conductivity of 0.8 mS/cm and distilled water having a conductivity of 0.015 mS/cm were examined. Among these, tap water showed the highest ion

transport values. Thus, acid cleaning provides the possibility of minimizing lactic acid losses caused by the replacing of the acid after a short running time of electrodialysis.

Conclusions

For the cleaning of lactic acid gained through fermentation. costand

%

ransported ions

Ionentransport %

%

100

80

60

40

20

0

100

80

0

20

40

wastewater-intensive ion exchange resins are primarily The presented used. experimental results showed that fermentation media can also be cleaned with the aid of membrane techniques. For this purpose, nanofiltration in the form of diafiltration was employed. Since chloride ions have greater permeability than lactate ions, the latter can be washed out, which allows the quantity of washing water to be minimized.

Electrodialysis with mono- and bipolar membranes provides the possibility of separating chloride- from lactate ions using the different permeabilities and transport speeds of the ions. Optimally adjusted current density as well as appropriate initial conductivity of the concentrate- or acid media allow for maximum chloride ion transport while reducing lactate ion losses. This enables cleaning during effects the downstreaming of sodium lactate and lactic acid to be achieved.

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Figure 11: Temporal course of the transport of ions during the conversion of a concentrated model solution of sodium lactate (NaL) into lactic acid through electrodialysis with bipolar membranes (NaL = 209 g/l; current density = 50 mA/cm²)

Figure 12: Temporal course of the transport of ions (chloride Cl and lactate Lac) during the conversion of a concentrated model solution of sodium lactate (NaL) into lactic acid through electrodialysis with bipolar membranes at different current densities (NaL = 209 g/l)

Figure 13: Temporal course of the transport of ions (chloride Cl; lactate Lac) during the conversion of a concentrated model solution of sodium lactate (NaL) into lactic acid through electrodialysis with bipolar membranes and different kinds of acid media (acid, tap water, and distilled water; NaL = 209 g/l; current density = 50 mA/cm²)

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100

Lactat

120

---Sulfat

80

Chlorid

60

Zeit min

Time min

Author

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