**University of Pannonia**
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# Preparation of Itaconic acid. Application of electrodialysis for the recovery of Itaconic acid

**Ph.D. Theses**

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## INTRODUCTION

The itaconic acid is a dicarboxylic acid, containing one double bond, too. It can be polymerized by esterification or can also participate in polymerization as a copolymer when linked to other compounds. The itaconic acid has a wide range of applications: Beyond the application in traditional polymer industry, it is also widely used in healthcare and medicine as a biocompatible plastic. In the long term, the aim is to replace petrochemical-based plastics, which can be achieved by further reducing the cost of producing itaconic acid.

Nowadays, itaconic acid is produced by fermentation, followed by a multi-step purification and crystallization process. Accordingly, research to reduce costs is focused on two main areas: developing and applying more efficient and cheaper fermentation techniques on an industrial scale and reducing and simplifying the product extraction and purification steps following fermentation.

Main area of my research is related to the fermented broth processing and product recovery stage. My goal was to study a separation method that would replace the commonly used multistep crystallization-purification with an efficient, environmentally friendly process. Electrodialysis is a membrane technique that uses electric field to separate the differently charged components of a solution, leaving behind the neutral components. Thus, the itaconic acid containing solution can be separated from the fermentation broth in one step, without generating waste streams.

During the electrodialysis study, I determined the optimum setting for itaconic acid separation while varying the parameters. Since itaconic acid fermentation is a product-inhibited process, the purpose of the electrodialysis is twofold: in addition to the product solution separated, I also obtained an itaconic acid-free solution that can be recycled back to further fermentation. Thus, the main consideration in the evaluation of the experiments was the optimization of the electrodialysis, but I also considered the possibility of an integrated fermentor/electrodialysis system. As a final step of my study, I crystallized the itaconic acid from the dialyzed solution, thus completing the process for the itaconic acid production.

## EXPERIMENTAL METHODS

In the experiments, an electrodialyser was used that contained a bipolar membrane in addition to the anion- and cation-exchange membrane. In this apparatus, I investigated the effect of the main parameters on the separation of itaconic acid. In the composition of the solutions, I step by step moved from a model solution with pure itaconic acid to the electrodialysis of the real fermentation broth. From the measured data, I calculated the current efficiency related to the itaconic acid at each set-up and based on this, I determined the optimum electrodialysis within the operating range of the system. The results of the electrodialysis with the real fermentation solution were compared with those of the model solutions, considering the fermentation parameters.

## NOVEL SCIENTIFIC ACHIEVEMENTS

In my Ph.D. work the following scientific results have been achieved:

1. Studying bipolar electrodialysis of model solutions containing itaconic acid it was found, that

   – the effect of three parameters investigated – initial itaconic acid content of the diluate, initial pH of diluate and the cell voltage of the electrodialysis device – on the current efficiency of the itaconic acid could not be described by a linear model.
   – a highest current efficiency value – 91.9-99.2 % - was reached in the middle range of the parameters investigated: 33 g/L initial itaconic acid content, pH = 5 initial value, 20 V cell voltage.

   In the experiments where the initial pH of the diluate was kept constant and varying the cell voltage of the ED device and the initial itaconic acid content of the diluate, the current efficiency related to the itaconic acid ED was determined under the circumstances and parameters applied. Using variance analysis, it was found that in the range studied the initial itaconic acid content and the cell voltage has significant effect on the current efficiency, using quadratic model. The optimal input parameters were determined from the surface maximum adjusted to the figure of current efficiency as functions of initial diluate itaconic acid concentration and cell voltage. The optimal values of the initial diluate itaconic acid concentration and the cell voltage of the ED were found as 32.81g/L and 17.84 V, respectively. A two-parameters, quadratic equation was adjusted on the experimental data, its standard deviation was $R^2$ =0.95. The fitted surface is valid only for the points within the range under consideration [I].

**2.** Based on the results of the bipolar electrodialysis experiments with the complex model solutions it was found, that

- the salt components of the model solutions decreased the current efficiency (related to the itaconic acid) with more than 25 %, since as ionic constituents they passed together with the itaconic acid due to the electric driving force.
- glucose content did not influence the current efficiency, because it is a neutral molecule, thus it does not migrate due to the electric force.
- the initial itaconic acid content of the diluate had strong effect on the current efficiency and the time necessary for the separation. Increasing the initial itaconic acid content from 5 g/L to 15 g/L, the value of the current efficiency has grown from 78.3 % to 98.5 %, while the time of the separation has risen from 5 hours to 9 hours [II].

**3.** Based on the results of electrodialysis measurements with real fermentation broths it was found, that

- as an effect of higher pH, the separation became more complete and faster, however the current efficiency obtained was lower: increasing the initial pH of the diluate from 3.04 to 7.4, the current efficiency related to the itaconic acid has reduced from 56.1 % to 37.8 %, while the product recovery has increased from 67.3 % to 74.7 % [III].
- reducing the number of membrane triplets of the bipolar membrane electrodialyser, at same voltage switched on the device, the voltage of one triplet unit has doubled, thus the current passing through one unit has doubled, too. In addition, the current efficiency increased from 37.8 % to 63.2% [IV].

**4.** Electrodialysis was carried out in a way where the low itaconic acid content diluate was changed to fresh itaconic acid content at the end of the ED process. Thus, the level of the acidic concentrate was increased up to the saturation limit.

– During the ED, it was achieved such a way that the rate of itaconic acid transport has not decreased using this technique in spite of the fact that the difference of itaconic acid concentration was higher between the two sides of the membrane.
– The current efficiency was 71.4 %, which was the highest among the electrodialysis experiments of real fermentation broths.

– During the crystallization measurements itaconic acid with 99.5 % purity was produced. The product yield regarding the whole crystallization process was 78 – 80 % [IV].

## LIST OF PUBLICATIONS

I. **Péter Komáromy**, Tamás Rózsenberszki, Péter Bakonyi, Nándor Nemestóthy, Katalin Bélafi-Bakó: Statistical analysis on the variables affecting itaconic acid separation by bipolar membrane electrodialysis. *Desalination and Water Treatment* (2020), **192**, 408-414. DOI 10.5004/dwt.2020.25899. Impact factor: **1,254**.

II. Tamás Rózsenberszki, **Péter Komáromy,** Enikő Kőrösi, Péter Bakonyi, Nándor Nemestóthy, Katalin Bélafi-Bakó: Investigation of Itaconic Acid separation by Operating a Commercialized Electrodialysis Unit with Bipolar Membranes. *Processes* (2020), **8**, 1031. doi:10.3390/pr8091031. Impact factor: **2,847**.

III. Tamás Rózsenberszki, **Péter Komáromy**, Éva Hülber-Beyer, Péter Bakonyi, Nándor Nemestóthy, Katalin Bélafi-Bakó: Demonstration of bipolar membrane electrodialysis technique for itaconic acid recovery from real fermentation effluent of *Aspergillus terreus*. *Chemical Engineering Research and Design* (2021), 175, *pp.* 348-357. doi:10.1016/j.cherd.2021.09.022. Impact factor (2020): **3,739**.

IV. Tamás Rózsenberszki, **Péter Komáromy**, Éva Hülber-Beyer, Andrea Pesti, László Koók, Péter Bakonyi, Katalin Bélafi-Bakó, Nándor Nemestóthy: Bipolar membrane electrodialysis integration into the biological production of itaconic acid: A proof-of-concept. (under acceptance)

V. **Péter Komáromy**, Péter Bakonyi, Adrienn Kucska, Gábor Tóth, László Gubicza, Katalin Bélafi-Bakó, Nándor Nemestóthy: Optimized pH and Its Control Strategy Lead to Enhanced Itaconic Acid Fermentation by *Aspergillus terreus* on Glucose Substrate. *Fermentation* (2019), **5**, 31; doi:10.3390/fermentation5020031. Impact factor: **2,964.**

VI. Nándor Nemestóthy, **Péter Komáromy**, Péter Bakonyi, András Levente Tóth, Gábor Tóth, László Gubicza, Katalin Bélafi-Bakó: Carbohydrate to itaconic acid conversion by *Aspergillus terreus* and the evaluation of process monitoring based on the measurement of $CO_2$. *Waste and Biomass Valorization* (2020), 11, 1069-1075. doi.org/10.1007/s12649-019-00729-3. Impact factor: **3,703.**

VII. Nándor Nemestóthy, Péter Bakonyi, **Péter Komáromy**, Katalin Bélafi-Bakó: Evaluating aeration and stirring effects to improve itaconic acid production from glucose using *Aspergillus terreus*. *Biotechnol Lett* (2019), **41,** 1383-1389. doi: 10.1007/s10529-019-02742-x. Impact factor: **1,977**.

VIII. **Péter Komáromy,** Katalin Bélafi-Bakó, Éva Hülber-Beyer, Nándor Nemestóthy: Enhancement of oxygen transfer through membranes in bioprocesses. *Hungarian Journal of Industry and Chemistry (2020), **48(2)**, pp.5-8.* doi:10.33927/hjic-2020-21

IX. Rózsenberszki Tamás, **Komáromy Péter**, Hülber-Beyer Éva, Koók László, Bakonyi Péter, Bélafi-Bakó Katalin**,** Nemestóthy Nándor: Biológiai hulladékkezelés támogatása fermentáció-elektrodialízis integrált rendszer fejlesztésével. *Membrántechnika és ipari biotechnológia* (2021), XII (4) pp 38-42.

X. **Komáromy Péter**, Nemestóthy Nándor, Bélafi-Bakó Katalin: Ionos folyadék tartalmú szennyvizek kezelése. *Membrántechnika és ipari biotechnológia* (2022), XIII (3) pp 26-31.

**Oral presentation:**

- Tamás Rózsenberszki, Enikő Kőrösi, **Péter Komáromy**, Nándor Nemestóthy: Itaconic acid separation by bipolar membrane. PERMEA 2019. Membrane Conference of Visegrád Countries. 26-29 August 2019 Budapest.
- **Komáromy Péter**, Rózsenberszki Tamás, Bakonyi Péter, Nemestóthy Nándor, Bélafiné Bakó Katalin: Itakonsav kinyerése valós fermentléből, elektrodialízissel és kristályosítással. 50. Műszaki Kémiai Napok, Veszprém, 2022. április 26-28.
- Rózsenberszki, Tamás; **Komáromy, Péter**; Hülberné-Beyer, Éva, Anna; Nemestóthy, Nándor: Bipolar electrodialysis as a promising approach for the manufacturing of itaconic acid. PERMEA 2022. Membrane Conference, SOREA HUTNIK I, Tatranské Matliare, High Tatras, Slovakia, 23-26 May 2022.