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professional paper

Separation and Concentration of Citric Acid by Means of Electrodialytic Bipolar Membrane Technology

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Summary

Especially from an ecological point of view, it would be desirable to replace the conventional separation method (calcium-citrate precipitation) of citric acid from fermentation broths with new technology. One possibility is to use electrodialysis with bipolar membranes, which is a process using only an electrical potential and special ion exchange membranes. Beside the separation the citric acid is simultaneously concentrated, and concentrations close to the saturation point are achievable. In order to isolate and concentrate one kg of the acid around 9 MJ of electrical energy are required. The measured conversion rate is in average $6 \cdot 10^{-5}$ kg m^{-2} s^{-1} whereby the efficiency of the process lies around 70%.

Keywords: citric acid, separation, membrane technology, electrodialysis, bipolar membranes

Introduction

Electrodialysis is a recognised membrane tehnology which can be used to separate and concentrate ionogenic and organic substances from a solution *(1,2)*. Bipolar membranes are special ion exchange membranes which, in an electrical field, enable the splitting of water into H^+ and OH^- *(2,3)*. By integrating such bipolar membranes into electrodialysis, salts (*e.g.* NaCl) can be separated from a solution and simultaneously converted into their corresponding acids and bases (*e.g.* HCl and NaOH). The principle of the process is shown in Fig. 1.

As well as inorganic salts, organic salts can also be converted into their corresponding acids and bases. The fact that when converting organic salts, high acid concentrations are achievable *(4)* (as opposed to mineral salts) makes the process in this application especially advantageous, as the evaporation step normally required can be omitted. However, organic salts such as sodium citrate often have a relatively large molecular mass and the solutions also show relatively low conductivities. These properties usually make the separation more difficult and lead to higher energy consumption, as is the case with inorganic compounds.

The behaviour of citric acid (Na_3Cit) during electrodialysis as well as electrodialysis with bipolar membranes has previously been studied and investigated using model solutions *(5,6)*. The experiments showed for example that in the salt circuit a pH value of around 7.0 is favourable for the process. At significantly lower pH

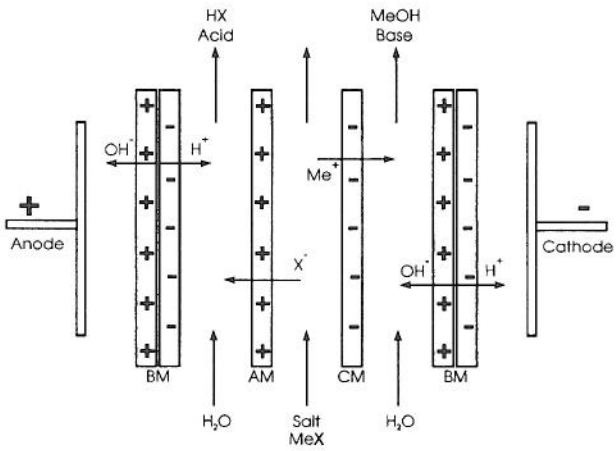

Fig. 1. The principle of electrodialysis with bipolar membranes. BM...bipolar membrane, AM...anion exchange membrane, CM...cation exchange membrane

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values the conversion rates are very small, rendering the process uneconomical. The investigations also showed that, with increasing current density the consumption of energy increases significantly. However, the process can be optimized and is of great interest for the present application. Contrary to previous investigations with model solutions, in this work an original fermentation broth was treated.

Materials and Methods

Before electrodialysis, a pretreatment consisting of an ultrafiltration with cut-off M_r=10 000 (Dalton) and an ion exchange (strongly acidic) step was carried out. The electrodialysis was carried out using an EDB setup consisting of 5 circuits (salt, base, acid and two separate electrode rinse) including an (TDS 2) ED stack made by Tokuyama Co. (Tokyo, Japan). Spacers having a thickness of 0.75 mm defined the distance between the membranes, whereby the effective area per membrane was 0.02 m^2. Four three-compartment cells consisting of CMH (cationic exchange membrane), AMX (anionic exchange membrane) and BP-1 (bipolar membrane), all commercially available from Tokuyama Co., were arranged in the stack. The flow rate per cell was 6 cm^3/s. The separation was carried out at 303 K. A 0.25 M Na_2SO_4 solution was used for the electrode rinsing. The acid concentrations were analysed by HPLC using Aminex HPX-87H column (Bio-Rad Labs, Richmond, California, USA).

Technological and experimental aspects of the process

A schema of the major process steps for the separation and concentration of citric acid using electrodialysis with bipolar membranes is shown in Fig. 2.

Before the fermenter solution comes to the electrodialysis, normally some pre-treatment steps are necessary. Firstly a filtration of the broth (*e.g.* using ultrafiltration) is required. After that a removal of ionogenic substances, especially Ca^{+2} and Mg^{+2} ensues. The citric acid solution thus obtained is neutralized using for example NaOH. In the subsequent electrodialytic step the Na_3Cit solution is converted into NaOH and citric acid, which is simultaneously concentrated and for the most part purified. As Fig. 2. shows the produced NaOH is reused for neutralization. Finally, the citric acid obtained has to be treated by conventional methods in order to obtain the quality required.

Fig. 3. shows how such complete electrodialytic batch process looks in terms of the current density and acid concentration (Na_3Cit concentration) in the salt stream. While the electrical potential was held constant, the current density decreased with decreasing Na_3Cit concentration. It is important to reach a low concentration in order to reduce the acid loss, since the salt solution is discharged after the process.

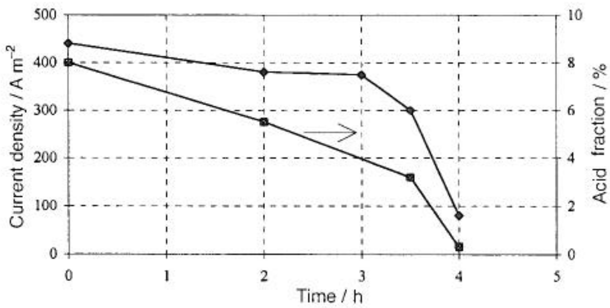

Fig. 3. Behaviour of current density and acid concentration (Na_3Cit concentration) at constant potential during a conversion batch process (fermentation broth)

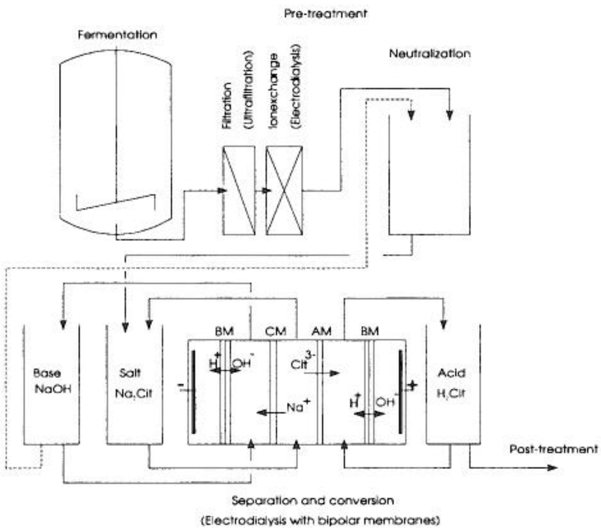

Fig. 2. Schema of a possible process for separation and concentration of citric acid by means of electrodialysis with bipolar membranes including pretreatment steps

The most interesting process data are illustrated in Table 1.

In a further experiment the influence of the acid concentration (in the acid stream) on the efficiency and conversion rate was investigated. The results are shown in Fig. 4.

Table 1. Major process data for the electrodialytic separation of citric acid during a batch process

Conversion rate	Process efficiency	Specific energy consumption	Conversion efficiency
$6 \cdot 10^{-5}$ kg $m^{-2}s^{-1}$	69%	9 MJ / kg acid	96%

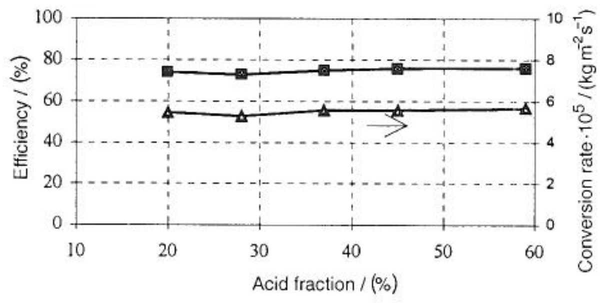

Fig. 4. Effect of acid concentration (in acid circuit) on process efficiency and conversion rate (model solution, current density = 330 A/m^2)

As can be seen above, practically no influence was observed, which is of great advantage for the technology because high acid concentrations are achievable in opposition to inorganic acids like HCl.

Conclusion

The present technology appears to be of a great value for the separation and concentration of citric acid (and also for other organic acids) since the acid is isolated, purified and simultaneously concentrated without producing any byproduct. Lower energy consumption would make the process more attractive. For this reason it is the aim of further investigations to reduce the energy consumption. This should be possible *e.g.* by using monopolar membranes with higher permeability for Na_3Cit.

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References

1. Y. Nomura, M. Iwahara, M. Hongo, *Appl. Environ. Microbiol. 54* (1988) 137.
2. P. Boyaval, J. Seta, C. Gavach, *Enzyme Microb. Technol. 15* (1993) 683.
3. H. Strathmann, H. J. Rapp, B. Bauer, C. H. Bell, *Desalination, 90* (1993) 303.
4. T. Kobayashi, T. Tomita, F. Hanada, *Presentation at ICOM '93*, Heidelberg, Germany (1993).
5. B. Bauer, H. Chmiel, Th. Menzel, H. Strathmann: Internal Report *»Separation of Bioreactor Constituents by Electrodialysis Using Bipolar Membranes«*, Fraunhofer-Institut für Grenzflächen- und Bioverfahrenstechnik, Stuttgart, Germany (1992).
6. S. Novalic, F. Jagschitz, J. Okwor, K. D. Kulbe, *J. Membrane Sci. 108* (1995) 201.
7. S. Novalic, J. Okwor, K. D. Kulbe: *Desalination, 105* (1996) 277.

Separiranje i koncentriranje limunske kiseline elektrodijalizom s bipolarnim membranama

Sažetak

S ekološkoga gledišta povoljno je da se konvencionalni postupak odvajanja (taloženje kalcijevog citrata) limunske kiseline iz fermentacijske podloge zamijeni novim postupkom. Jedna od mogućnosti je primjena elektrodijalize s bipolarnim membranama, što je postupak u kojem se koristi samo električni potencijal i specijalne membrane za ionsku izmjenu. Osim što se izdvaja, limunska se kiselina istodobno koncentrira, i to približno do točke zasićenja. Za izolaciju i koncentraciju 1 kg limunske kiseline potrebno je otprilike 9 MJ električne energije. Izmjerena je brzina konverzije približno $6 \cdot 10^{-5}$ $kg\ m^{-2}\ s^{-1}$, *pri čemu je uspješnost postupka oko 70%.*