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GALACTURONIC ACID RECOVERY FROM PECTIN RICH AGRO-WASTES BY ELECTRODIALYSIS WITH BIPOLAR MEMRANES

E. MOLNÁR✉, N. NEMESTÓTHY, K. BÉLAFI-BAKÓ

[1]University of Pannonia, Research Institute of Chemical and Process Engineering
Egyetem u. 10., 8200 Veszprém, HUNGARY
✉E-mail: emolnar@mukki.richem.hu

Pectin rich agro wastes can be utilised for manufacture of galacturonic acid. Pectin is a complex polysaccharide found in the primary cell walls and intercellular regions of higher plants. Backbone of pectin molecules is composed of galacturonic acid as a monomer. Galacturonic acid and derivates are valuable raw materials in food and cosmetic industries as acidic agents and for production of vitamin C.

In this work the aim was to produce galacturonic acid from citrus pectin and sugar beet pulp. The hydrolysate of pectin contains mainly carbohydrates (oligo- and monosaccharides) and galacturonic acid. Electrodialysis with bipolar membranes (EDBM) represents an efficient technology to separate charged compounds from a solution. To remove galacturonic acid, EDBM seems a suitable process, because galacturonic acid is present as a charged compound in the solution. To obtain galacturonic acid from hydrolysate of pectin laboratory experiments were performed, similar to the system applied by Novalic et al. for recovery of other organic acids. An ED stack containing anion and cation selective and bipolar membranes was applied to obtain GA from hydrolysate.

Keywords: agro wastes, galacturonic acid, electrodialysis, bipolar membrane

Introduction

Pectin rich agro-wastes are available to manufacture galacturonic acid (GA). Pectin is a complex polysaccharide found in the primary cell walls of higher plants. Function of pectin is formation of bond in cells and between cell wall substances. The strength and structure of plants texture are determined also by this polysaccharide. The main component of pectin is backbone of α-1,4-linked galacturonic acid residues. Galacturonic acid and derivates can be utilised in food industry (as acidic agents), chemical industry (as washing powder agent and nonionic or anionic biodegradable surfactants) and pharmaceutic of industry (for production of vitamin C) [1].

Sugar beet pulp, apple pomace and other wastes (e.g. press cakes) from fruit juice industry are pectin rich raw materials. To obtain galacturonic acid, pectin is extracted from raw resources then its enzymatic hydrolysis results in galacturonic acid in diluted aqueous solution.

In this work the plan was to produce galacturonic acid from citrus pectin and sugar beet pulp. For this purpose firstly pectin was extracted with hot water from sugar beet pulp then enzymatic hydrolysis was carried out using Pectinex 100L enzyme preparation. The hydrolysate contains mainly carbohydrates (oligo- and monosaccharides) and galacturonic acid. To recover galacturonic acid, electrodialysis with bipolar membranes (EDBM) [2-4] seems to be a suitable process, because only galacturonic acid is present as a charged compound in the solution.

Electrodialysis with bipolar membranes (EDBM) is an electromembrane process to separate ions and produce acids and basis. Under electrical potential difference, charged compounds move in the direction of the oppositely charged electrode. Anion- (A) and cation-selective (C) membranes let counter-ions cross and exclude co-ions. The function of bipolar membrane (BM) is to generate protons and hydroxyl ions which are removed from interphase of the membrane to outside phases. Base is formed by hydroxyl ions and cations, acid is formed by protons and anions. Uncharged components of salt solution are retained by bipolar membrane.

To obtain galacturonic acid from hydrolysate electrodialysis with bipolar membranes was used [5]. Galacturonic acid was separated and concentrated by EDBM. The principle of our EDBM shows *Fig. 1*. When an electric field is applied, galacturonate ions migrate towards the anode. Galacturonate ions leave the diluate solution and move through anion-selective membrane into acid compartment where galacturonic acid are formed by galacturonate ions and protons. Sodium ions pass through cation-selective membranes and NaOH is formed by generated hydroxyl and sodium ions. Uncharged saccharide components are retained in the diluted solution.

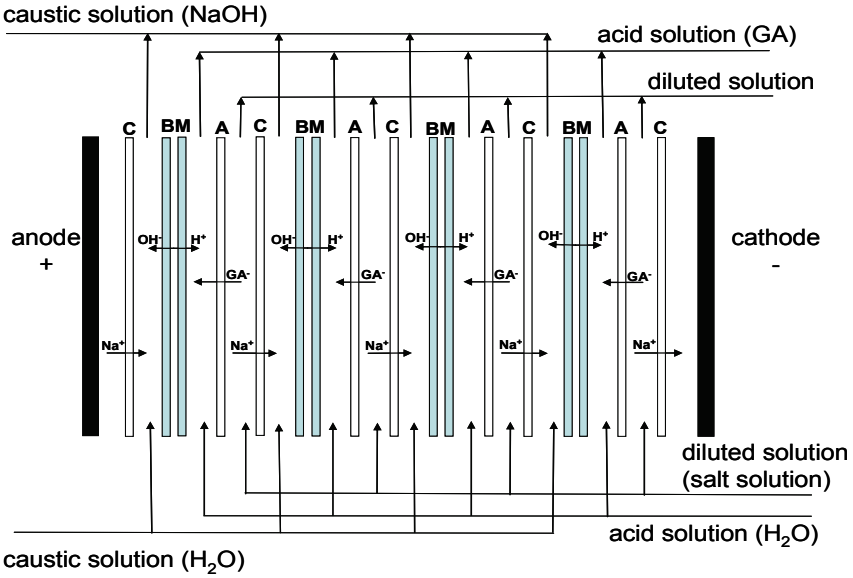

Figure 1: The principle of recovery galacturonic acid

Materials and methods

The experimental set-up was purchased from Fumatech (FT-ED-4-100-10 module). The electrodes were made of stainless steel.

Fumasep FKB, Fumasep FAB and Fumasep FBM membranes, which are commercially available from Fumatech GmbH (Germany), were used. Characteristics of membranes are shown *Table 1.* The set-up composed of 10 anion-, 11 cation and 10 bipolar membranes. The effective membrane area was 0.31 m^2.

Galacturonic acid applied as a standard and for model solution was purchased from Sigma-Aldrich, while sodium sulphate (electrolyte solution) from Spectrum (Hungary).

Firstly experiments were carried out with sodium-galacturonate model solution, then secondly hydrolysate of sugar beet pulp was used to investigate removal of galacturonate.

Hydrolysis of pectin solution obtained from sugar beet pulp and citrus pectin was carried out by pectinase enzymes (Pectinex 100L enzyme preparation) in a shaking incubator. The operation conditions were: 500 µl enzyme/ dm^3 solution, 40 °C and 120 rpm. Degradation of pectin was followed by acid titration (0.5 M NaOH) and HPLC, using Perkin-Elmer LC200 HPLC.

In order to recover GA, pretreatment of hydrolysate could be needed, because the membrane fouling is one of the main limiting factor of the process. Large molecules can be removed by ultrafiltration or centrifugation.

Concentration of galacturonic acid in acid and diluted solutions was measured by colorimetrically with the dinitrosalicylic acid test (DNA) method [6].In the acid solution, pH was followed by WTW Microprocessor pH-meter.

The data of conductivity in diluted, acid and base solutions, the electric current and voltage between electrodes was collected by data acquisition device (National Instruments USB-6008/6009). The data were recorded by the program LabVIEW.

Table 1: Main characteristics of membranes

membrane	characteristic	
Fumasep FKB	cation-exchange membrane PEEK-reinforced	
	selectivity	>98%
	electric resistance	<4 Ω*cm^2
	stability	acid and caustic stable
	thickness	0,08–0,10 mm
	specific conductance	>2 mS/cm
	ion exchange capacity	0,9–1,0 meq/g
	swelling	15%
Fumasep FAB	anion-exchange membrane PEEK reinforced	
	selectivity	>0,96%
	electric resistance	<1 Ω*cm^2
	stability	0–13 pH
	thickness	0,10–0,13 mm
	specific conductance	>6 mS/cm
	ion exchange capacity	>1,3 meq/g
	swelling	20%
Fumasep FBM	bipolar membrane PEEK reinforced	
	electric resistance	<3 Ω*cm^2
	thickness	0,2–0,25 mm
	thermal stability	max 60 °C
	efficiency of water splitting	>98%

Experiments were carried out at room temperature.

Diluted, acid, caustic and electrode solution were circulated by peristaltic pumps. The flow rate of diluted, acid and caustic solution was 51 dm^3/h, 44 dm^3/h and 46 dm^3/h.

Results

Voltage- current curves

The voltage vs. current curves (U-I) were measured across the 31 compartment cell under different concentrations of Na_2SO_4 in electrode solution. The concentration of electrode solutions was 0.05/ 0.1/ 0.5/ 1 mol Na_2SO_4/dm^3-solution. The results are plotted in *Fig. 2.* Three regions are observed on the experimental U-I curves: at low value of voltage, the increase of potential voltage does not cause electric current increase, because the electric field turns to generate protons and hydroxide ions by bipolar membrane. In second region, rise of voltage causes rising current, nearly linear relationship exist between applied voltage and electric current. At high voltage, the resistance increases drastically when a certain current is reached. The amount of protons and hydroxyl ions produced at the transition region becomes a limiting factor. During experiments the current should not exceed this certain value (limiting current) otherwise membranes will be destroyed.

The limiting value of electric current increases with increasing concentration of electrode solution. Although at high concentration of electrolyte, lower limiting current was measured because of evolved concentration polarization.

By the grounds of experiments electrode solution of concentration 0.1 mol Na_2SO_4/dm^3 was chosen, because the curve did not show limiting current in the voltage range studied.

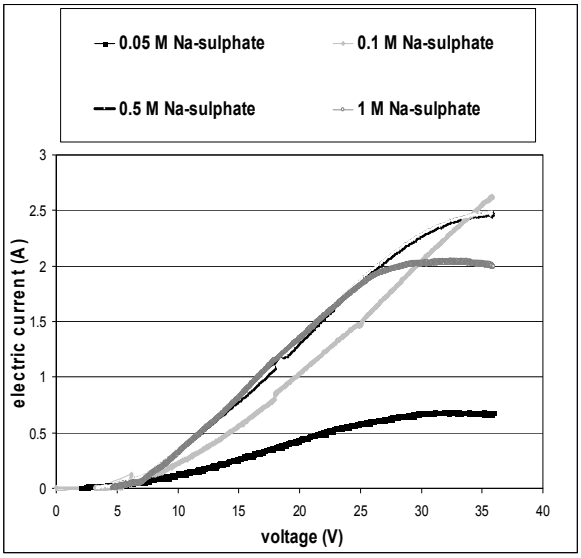

Figure 2: Potential drop as a function of electric current

Comparison of measurements at constant voltage with model solution

The experiments with model solutions were carried out with constant voltage namely at 12 V, 24 V and 36 V. The diluate concentration was initially 20 g Na-galacturonate/dm^3. The volume of circulated diluted, acid and caustic solution was 0.4 dm^3, 0.4 dm^3 and 0.45 dm^3.

The driving force for the transport of ions is the electrical potential difference. Increasing voltage obviously enhances the ion transport through the membrane. The current in the stack as a function of time are plotted in Fig. 2. Due to Ohm's law, at he beginning of experiments higher electric current was measured at higher constant voltage. As ions were transported from diluate solution, the concentration of ions and conductivity in diluate solution decreases, the resistance of diluate increases therefore electric current drops.

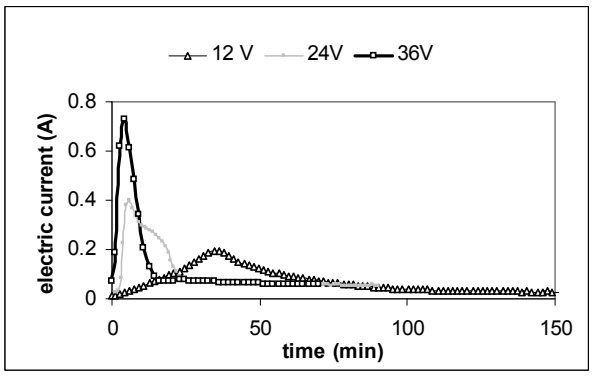

Figure 3: Electric current in the EDBM cell

Due to the transport of galacturonate ions and protons, galacturonic acid is formed in acid solution. The concentration of galacturonic acid *(Fig. 4)* tends to a limiting value, independently of the value of voltage, as a function of time.

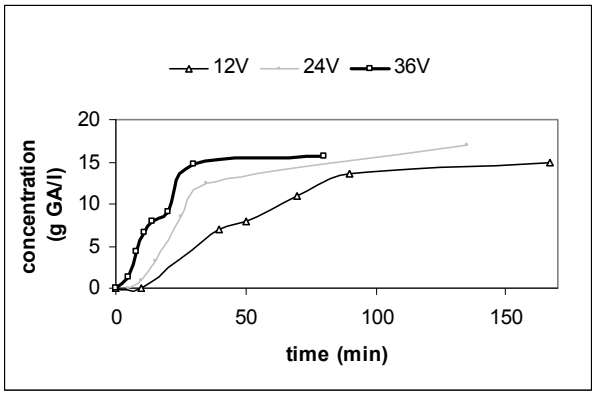

Figure 4: Concentration of galacturonic acid in acid compartment

In acid solution the pH value rapidly decreases at beginning then it slightly increases *(Fig. 5).* The pH drop depends generated protons and formed galacturonic

acid. Protons are transported faster from interphase than galacturonate ions from diluate solution. At the beginning protons cause rapid pH drop. Increase of pH shows galacturonic acid formation in acid solution. At lower applied voltage, pH has lower value because the transport of galacturonate ions is slower.

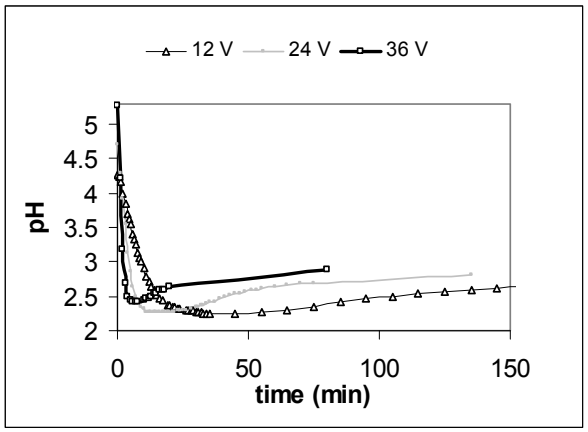

Figure 5: pH vs. time in acid solution

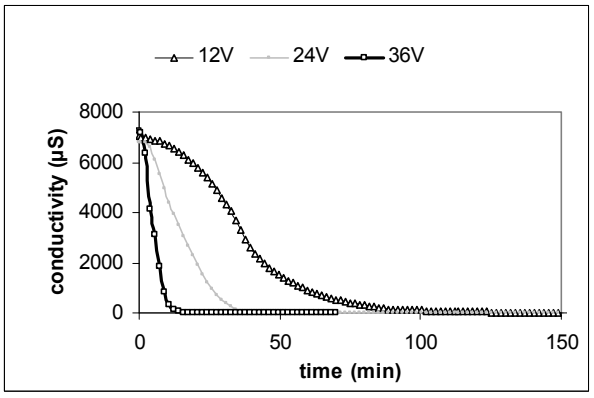

Figure 6/a: Conductivity of the diluate solution as a function of time

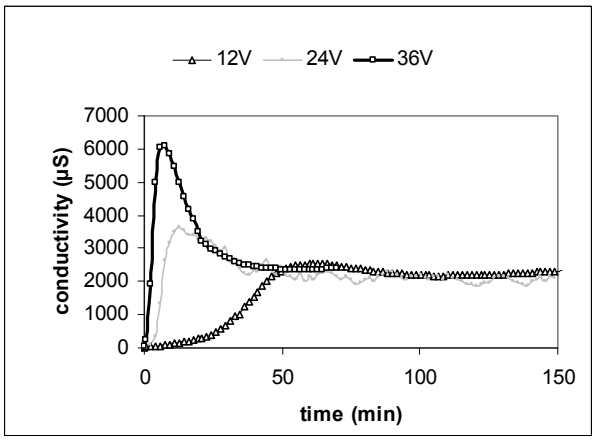

Figure 6/b: Conductivity of the acid solution as a function of time

Conductivity of diluate solution *(Fig. 6/a)* decreases as a function of time due to the carried galacturonate and sodium ions.

At the beginning conductivity in acid solution *(Fig. 6/b)* increases rapidly at higher value of voltage (36 V). This increase is caused by protons, after 7.5 minutes the produced galacturonic acid decreases the conductivity. At lower value of voltage the water dissociation is slower, that causes less conductivity increase.

Our results shows measurements can be efficiently performed at voltage of 36 V.

Experiment with citrus pectin hydrolysate

EDBM with citrus pectin was carried out at 36V. The volume of citrus pectin hydrolisate was 2.95 dm^3, the concentration of hydrolysate was 35.4 g Na-galacturonate/dm^3. The volume of acid and caustic solution was 1 dm^3. Results were agreement with results of model solutions. The concentration of GA in acid and diluate solution are shown in *Fig. 7.*

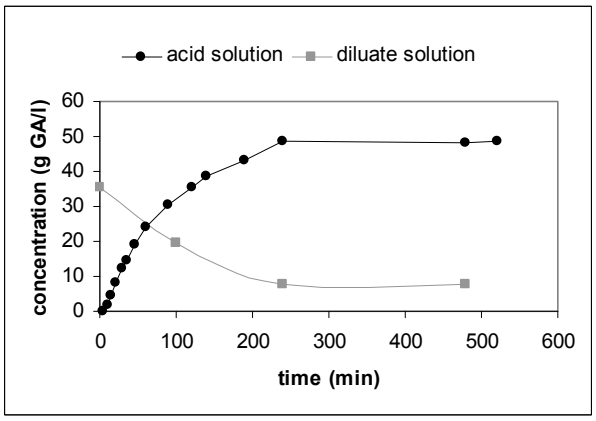

Figure 7: Concentration of galacturonic acid in the acid and the diluate solution

In an electrodialysis process not all of the current flowing through the stack can be utilized. Average current efficiency [7] for galacturonic acid can be calculated as

$$\eta = \frac{QF\Delta C}{NI}$$

where Q is volume flux of acid solution, F is the Faraday constant, ΔC is the concentration difference between acid solution in the feed of the entrance and that in the exit, N is the number of the cell units, and I is the average current.

The change of current efficiency shows *Fig. 8* in the course of experiment with citrus pectin hydrolisate.

As shown in Fig. 8, the average current efficiency decreases with time therefore restricts the possibility of obtaining higher concentration of GA in acid solution.

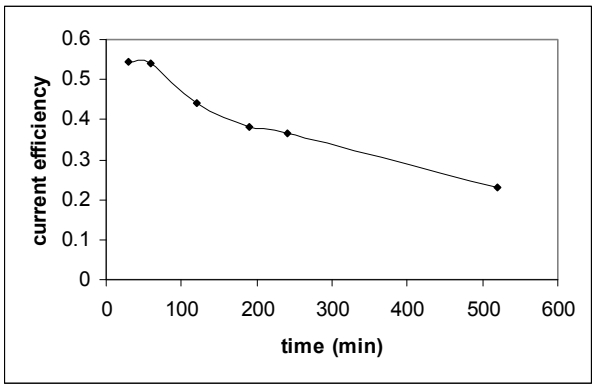

Figure 8: The change of current efficiency as a function of time

Recovery of galacturonic acid from acid solution

The saccharide composition (determined by HPLC) of hydrolysate is 76% galacturonic acid, 3% partly hydrolysed pectin, 2.4% pectin, 8.2% glucose and 10.4% other monosaccharide, while acid solution is composed of 97.97% galacturonic acid and 2.03% partly hydrolysed pectin.

To obtain galacturonic acid from the acid solution it was crystallised with methanol, then water and methanol were eliminated by vacuum filtration and vacuum drying.

Conclusion

Bipolar membrane electrodialysis can be applied for separation galacturonic acid. Crystallised galacturonic acid has purity of 98%.

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