Using electrodialysis technology for regeneration of hydrochloric acid from sour pectin extracts

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Abstract. The article focuses on investigation of efficiency of electrodialysis membrane technology for regeneration of hydrochloric acid in pectin extracts. Traditional methods involving using ethanol, encounter various technical problems. Application of electrodialysis membrane technology is considered to be an efficient solution. The study aims at evaluating the capacity of the membrane method in the process of hydrochloric regeneration in apple and beet pectin extracts and the way it affects the characteristics of pectin molecules of both types. The experiments show the possibility of almost full regeneration of hydrochloric acid for a reuse in the process of further extraction of apple and beet pectins. Such approach also enhances an increase in the degree of esterification and molecular mass of pectins, which is especially important in the case of less low-molecular beet pectin. The increase in the esterification degree boosts its jellying effect, but reduces its detoxicant capacity.

1. Introduction

Pectins are the sour polysaccharides, which are widely used in the food industry. Carboxyl groups of pectin molecules are partially methoxylised. The proportion of these groups concerning the total number of carboxyl groups affects the degree of pectin esterification ($E_{\text{met}}$). Highly-esterified pectins ($E_{\text{met}}$ 50%) are used as jellying agents, whereas low esterified ($E_{\text{met}}$ < 50%) are used as detoxicants, removing heavy metals and radionuclides from living organisms [1].

Traditionally, pectins extraction from vegetable raw materials (beet press, apple pomace and other options) is based on using hydrochloric acid with the subsequent sedimentation of it by ethanol. The most common extragent is hydrochloric acid, the concentration of which depends on different parameters of the process, such as: temperature, hydromodule or extraction period. Some authors [2,3] conclude that optimum concentration of acid should be about 0.05 mol/l ($\text{pH} \approx 1.3$). Sedimentation of pectins results into water-ethanol acidulous complexes which prevent the mixture from splitting into acid and ethanol. It causes considerable technological problems connected with corrosion of the rectifying equipment and increase in energy consumption. In the case of the extract neutralization, there is also a risk of the total cease of extragent.

These problems can be solved by applying membrane technology [4]. For example, the method of ultrafiltrational concentration of extracts, followed by diafiltration, allows significantly decreasing the consumption of alcohol for pectin sedimentation and improves its quality due to removal of low-
molecular fractions with low degree of esterification. However, we have to admit that there were observed irrevocable losses of extragent and a dramatic increase in energy consumption to ensure the solution circulation through the membranes. Thus, the most effective and sustainable method of separation of multicomponent mixes into individual components is electrodialysis with ion-exchange membranes. We believe this method proves to be quite effective for processing of pectin extracts and releasing acid and pectin with simultaneous regeneration of hydrochloric acid for its further reuse. Interestingly, the literature survey does not reveal any data about using this method for processing of pectin extracts. The only data found are those about electromembrane water extraction for producing extragent [4,5,6,7] and releasing galacturonic acid from pectin, completely depolimerized by fermentative hydrolysis [1].

In this regard, the study deals with the attempt to understand the capacity of electrodialysis method based on ion-exchange membranes for regeneration of hydrochloric acid from pectin extracts and its potential influence on electromembrane processing of the structure of pectin molecules.

2. Materials and methods

Pectin extracts are produced by processing beet press and apple pomace by hydrochloric acid with concentration of 0.05 mol/l at a temperature of 80 °C, hydromodule 1:12 and mixing the solution during 1.5 hours. After solid-phase extraction, the part of the solution was processed by ethanol for pectin settling. After that, the obtained pectin was dried up and, with help of electrometric titration, analyzed in order to identify carboxyl groups and the esterification degree. In addition to the characteristic viscosity of pectin solutions, we tried to identify its average molecular weight [1,4]. The other part of extract was used for electrodialysis in a special device shown in figure 1.

![Figure 1. Electrodialyzer model. K – a cation exchange membrane, A – an anion exchange membrane, An – acid anion, 1 - 4 – the device sections.](image-url)

We used MA-40 anion-exchange membranes on the basis of the low-basic anion exchange resin EDE-10P and MK-40 cation exchange membrane on the basis of strong-acid cationic-exchange resin, KU-2 [8,9]. The volume of the device sections was 100 cm$^3$ and the intermembrane distance was 2.9 cm with the working area of membranes of 30.8 cm$^2$. The section of a deionization (3) was filled with the analyzed extract, the section of concentration (2) with the distilled water, the cathodic section (4) with NaOH solution (0.01 mol/l) and the anode section (4) with H2SO4 solution (0.01 mol/l).

The device was switched to the direct-current network, and at the density of current of 5 mA/cm$^2$, within an hour, the electrodialysis was carried out. Under the influence of a gradient of electric potential, chloride ions were transferred from section 3 to section 2 through an anion exchange membrane. It resulted in producing hydrochloric acid with ions of hydrogen, generated on the anode and then transferred through a cation exchange membrane. Simultaneously, hydroxyl ions generated...
on the cathode were transferred from section 4 to section 3 through the other anion exchange membrane, where the extract was neutralized. After the transfer process was finished, the obtained solutions (in sections 2 and 3) were analyzed for the content of chloride ions matching the hydrochloric acid concentration. And the solution from section 3 was used for pectin extraction. The results of the analysis were used to estimate the current output \( B_T \) (formula 1):

\[
B_T = \frac{(C_0 - C) \cdot F}{i \cdot S \cdot \tau}
\]  

(1)

where \( C_0 \) and \( C \) – refer to concentration of chloride ions in deionization section, \( F \) – Faraday’s number, \( S \) – the area of a membrane, \( i \)-current density, \( \tau \)-experience time.

The degree of extract demineralization (\( R \)) was estimated on the basis of the following formula 2:

\[
R = \left(1 - \frac{C_0}{C}\right) \cdot 100\%
\]  

(2)

and the degree of acid regeneration (in %) as the correlation of its contents in the concentration section with the initial content in the extract.

Previously, besides using anion-exchange film MA-40 there had been an attempt to experiment on using an option of MA-41. However, it did not demonstrate its due efficiency. The process took place in four-section apparatus according to the scheme: anode – anode section – cation-exchange film MK-40 – concentration section – anion-exchange film MA-40 or MA-41 – deionization section – anion-exchange film MA-40 or MA-41 – catelectrode section – catelectrode, during an hour with the current density 1-6 mA/cm². The initial solution was placed in the deionization section. During the electrodialysis there was formed hydrochloric acid as the result of chlorine ions transition through anion-exchange film, and hydrogene ions, generated on the anode, through cation-exchange film. In

Figure 2. Dependence of concentration of hydrochloric acid (C) on current density (i) in the concentration section (1, 2) and chloride-ions in the deionisation section (3, 4) during electrodialysis with membranes MA-40 (1, 3) and MA-41 (2, 4)
the deionization section there was deacidification process due to hydroxide ions, generated on the catelectrode and transferred through another anion-exchange film. The results of alkalimetric potentiometric titration of the composition of concentration and deionization sections were used for estimation of acid extract, the degree of its regeneration as well as the degree of deionization of the initial solution. Figure 2 shows profiles of process performance concerning current density. The amount of acid in the concentration section as well as its regeneration degree grow along with growing current density up to 4 mA/cm² in case of using membranes MA-40 and 3 mA/cm² – membranes MA-41. Similarly, the amount of the acid decreases in the deionization section, which means the degree of deionization of the solution increases. With higher current density the profiles growth slows down, which means super maximum performance.

The results demonstrate the lower limiting current density if we use membranes MA-41 in contrast to MA-40. If we use membranes MA-41, the performance is high with relatively low current density, and in case of MA-40 the performance is high with high current density (Table 1).

**Table 1.** The amount of extracted hydrochloric acid (\(\eta\)) in the case of various current density in the concentration section.

| Membrane | \(i\), mA/cm² | \(\eta\) | Membrane | \(i\), mA/cm² | \(\eta\) |
|----------|---------------|-------|----------|---------------|-------|
| MA-40    | 1.10          | 0.759 | MA-40    | 1.11          | 0.799 |
|          | 2.14          | 0.805 |          | 2.16          | 0.822 |
|          | 3.09          | 0.812 |          | 3.09          | 0.812 |
|          | 4.17          | 0.768 |          | 4.11          | 0.692 |
|          | 5.19          | 0.697 |          | 5.13          | 0.619 |
|          | 6.14          | 0.608 |          | 6.15          | 0.523 |

Difference in the dialysis profiles when using various chemical membranes is due to a number of reasons. It is known that the number of counter-ions transference in membranes MA-40 and MA-41 differs slightly [8]. However, there is pectin involved in the process. Functioning as electrolyte it can become absorbed on membranes. Also, the aliphatic character of the matrix of the membrane MA-40 and location on it of groups with similar polarity, unlike hydrophobic aroma matrix of MA-41, increases pectin sorption. It is commonly known [10,11] that during electrodialysis on receiving side of the anion-exchange film there appears a dipolar layer between positively charged fixed ions and the pectin polyanion, in which there is a process of additional water dissociation inducted by the electric field [12,13]. As a result, there is not only useful transference of chloride-ions, but also that of hydroxide-ions, which deacidify acid in the concentration section. This in its turn leads to lower current profile (chart 1) in comparison with traditional profiles concerning chloride-ions in the systems with no pectin involved. Since the dipolar layer at the membrane surface (MA-40) is stronger, with low current density the profiles are lower than in cases with the membranes MA-41. Higher deionization of the solution with membrane MA-41 will very soon bring about maximum current. Yet, as we think, there is another, more important reason for that. Fig. 3 shows the photos of the anion-exchange membranes involved in the research. The considerable part of MA-41 is occupied with current-proof lavsan reinforcement thread, so the real surface size occupied for transference is much less than that of MA-40. Hence, the maximum current density for MA-41.

Similarly, membranes MA-41 demonstrate lower profiles with the current density over 3 mA/cm² (Fig. 1), due to the fact that real current density is higher than established and the negative process of water decomposition on the pre-membrane layer is more intensive than in case of MA-40. Yet, we should take into account the fact that with the maximum current density the generated hydroxide-ions
can react with methyl group of fixed ion of benzyltriethylammonium chloride of MA-41 with formation of methanol and tertiary amine group. The latter functions as catholytes during the process of water dissociation, which also causes the low profiles.

![Figure 3. The surface of anion-exchange membranes: 1 – MA-40, 2 – MA-41.](image)

The above mentioned shows that if use the profiles shown in Fig. 1, the degree of deionization of the solutions with current density of 5 mA/cm² is 84-88 % for the membranes MA-40 and 74-79 % for the membranes MA-41. The degree of the acid regeneration is correspondingly 83-86 and 73-74 % with the current profiles of 0.70-0.61 and 0.62-0.52.

### 3. Results and discussion

The results of the electrodialysis process are presented in Table 2.

**Table 2. Concentration of hydrochloric acid after the electrodialysis process.**

| Pectin | Sc     | Sd       | Co       | R       | R       |
|--------|--------|----------|----------|---------|---------|
| beet   | 0.0485±0.0035 | 0.0059±0.0016 | 0.826±0.052 | 97.0±7.0 | 88.2±3.2 |
| apple  | 0.0492±0.0038 | 0.0068±0.0003 | 0.831±0.064 | 98.4±7.6 | 86.4±0.6 |

Concentration of hydrochloric acid after electrodialysis in sections of concentration (Sc) and a deionization (Sd), mmol/l, the current output (Sd), degree of acid regeneration (R, %) and extract demineralization (R, %).

The obtained data show that the content of hydrochloric acid in the concentration section (Sc) recovers almost to the concentration used for acid extraction of pectin (0.05 mol/l), and the degree of its regeneration approaches 100%. The current outputs are slightly lower than those usually obtained during the transfer of chloride-ions in MA-40 membrane (0.94). It is due to the fact that pectin molecules in the sections of deionization, occluded on the membrane dividing sections 2 and 3 of the electrodialyzer, form a bipolar layer in which we could observe additional dissociation of water. The hydroxyl ions, formed as a result of this, are transferred through the membrane, thus reducing the useful mass transfer of chloride ions [14,15]. The bipolar layer creates a potential barrier preventing the migration of chloride ions, which leads to lower values of the demineralization degree of the extract in comparison with degree of acid regeneration.

Characteristics of pectins are shown in Table 2 before and after electromembrane processing of the extracts. After the electrodialysis, the molecules of both types of pectin show a decrease in the number of free carboxyl groups and an increase in the esterified ones. It is especially vivid in the case of beet pectin, which, unlike apple pectin, has smaller molecular weight. Apparently, during the electrodialysis the low-molecular fractions of beet pectin join free carboxyl groups. Alternatively, it could be due to the fact that the molecules of galacturonic acid, formed as the result of the extraction,
are transferred through MA-40 membrane, and therefore pectin is enriched with molecules having more ester linkage and bigger molecular weight. Table 3 demonstrates the conversion of low esterified beet pectin into high-esterified option.

Table 3. The content of free carboxyl groups (C_{fc}), esterified carboxyl groups (C_{ec}), their total content (C_t) (mmol/l) and the degree of esterification (E_{met}) in pectin. Characteristic viscosity [η] at 293 K and the molecular mass (M) of pectins.

| Pectin | C_{fc} | C_{ec} | C_t | E_{met} | [η] | M, kDa |
|--------|--------|--------|-----|---------|-----|-------|
| beet   |        |        |     |         |     |       |
| a)     | before the | 1.95   | 1.56| 3.51    | 0.44| 0.96  | 11.2  |
|        | electrodialysis | 1.46   | 2.42| 3.88    | 0.62| 1.14  | 12.9  |
| b) after the electrodialysis | | | | | | |
| apple  |        |        |     |         |     |       |
| a)     | before the | 1.66   | 2.49| 4.15    | 0.60| 2.31  | 23.0  |
|        | electrodialysis | 1.52   | 2.72| 4.24    | 0.64| 2.33  | 23.2  |
| b) after the electrodialysis | | | | | | |

Electromembrane processing of extracts only slightly affects the molecular mass of apple pectin, causing minor changes in its esterification degree (Tab. 3). At the same time, the removal of low-molecular fractions of beet pectin results in the increase of its average molecular weight by 15%.

The study clearly demonstrates that the electromembrane technology used for processing the pectin extracts, especially in the case of beet pectin, can eventually change the scope of the final product application. It is also important to note that the increase in pectin’s esterification degree boosts its jellying effect, but at the same time reduces its complexity power and therefore its ability to remove ions of heavy metals [1].

4. Conclusion
The results of the study show the advantage of using the membrane technology for almost full regeneration of hydrochloric acid and its further reuse during electrodialysis with ion-exchange membranes of sour pectin extracts.

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