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ATTEMPT TO USE CELLULOSE NITRATE MEMBRANE FOR THE PURIFICATION OF DIFFUSION JUICE*

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Abstract. The aim of the work was to determine the effect of using a cellulose nitrate membrane (CN) for purifying diffusion juice and to compare the content of some components and features of diffusion juice before and after purification. The question was investigated as to whether the membrane filtration process could replace the traditional liming and carbonation methods since the outcome of juice purification depends on its quality. The end result of the purification of good quality diffusion juices when using a cellulose nitrate membrane was 34.8-41.4% and was thus comparable with the traditional method. The application of membrane filtration made it possible to purify juice of bad quality, which could not otherwise be purified under industrial conditions, the purification effect being about 13.1-15.6%. In juices filtered with a cellulose acetate membrane, the content of sucrose and reducing sugars hardly changes. The viscosity of filtered juices decreased by 0.9-1.9 mPas and was close to that of pure sucrose solutions of the same concentration. The content of α-amino-acid nitrogen, after filtering the membrane, decreased by 12% to 34%. The higher the purity and the lower the viscosity of the diffusion juice, the greater was the permeate flux.

Keywords: diffusion juice, membrane filtration, purification effect

INTRODUCTION

Diffusion juice which is obtained from sugar beetroot is a turbid, non-transparent liquid. In addition to sucrose, it contains dissolved substances (mineral salts, simple sugars, nitrogen compounds and others), colloidal substances (mainly proteins and pectins) and root tissue particles (fines). To make the crystallisation of sucrose possible, it is necessary to remove as many substances as possible from the juice with

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the exception of the sucrose. The classical method for purifying diffusion juice is liming and carbonation and filtration of the sediment. As a result, a pure juice (called thin juice) is obtained, which on thickening by evaporation, undergoes crystallisation.

The liming and saturation processes produce great amounts of pollutants (defeco-saturation mud, gases and soot which arise during lime burning) and are very energy consuming. The average Polish sugar plant processes 3000 tons of beetroot daily, consumes 120 tons of limestone and burns 10 tons of coke per day. Chemical reactions occurring in the process of juice purification produce about 180 tons of defeco-saturation mud per day. Thus, during one 70-80 day sugar campaign, one sugar plant of average size consumes, in the production of lime only, about 9 000 tons of limestone and 750 tons of coke, producing 13 500 tons of defeco-saturation mud [12].

An alternative to such dirty and expensive technology could be membrane filtration. One more advantage of such a process in sugar production is the possibility of conducting it at lower temperatures (lower energy consumption) and the relatively low costs of membrane operation.

The traditional membrane processes – micro-filtration, ultra-filtration and reversed osmosis – are already broadly used in food technology. The dairy industry is a good example – the removal of bacteria from milk and whey, the production of lactose, protein preparations and cheeses, juice and fruit pulp condensation and others [11]. Membranes manufactured from new materials that are more durable and resistant to technological processes, as well as the lower costs of manufacture, create new possibilities for applying membranes in other branches of the food industry.

The aim of the work was to determine the effect of using the cellulose nitrate membrane (CN) to purify diffusion juice and to compare the content of some components and features of diffusion juice before and after purification.

MATERIALS AND METHODS

The material used in the investigation was diffusion juice obtained from frozen beetroots. The defrosted beetroots were kept at room temperature for 0, 2 or 4 days. Diffusion was conducted for 30 min at 80°C, and then the supernatant was decanted and filtered [7]. The amount of chips and water was selected so that the filtrate had a 14% dry mass content, measured by refractometric analysis. The juice obtained was centrifuged to obtain an initial removal of the pulp. The diffusion juice was then filtrated by a cellulose nitrate membrane (CN). The process is shown in Appendix 1.

For diffusion juice purified by membrane filtration the following were determined:
- the content of real dry mass by the drier method [1]
- the sucrose content by the polarimetric method and the Lane-Eynon method after acidic hydrolysis by the Clarget-Herzfeld method [6]
- the content of reducing sugars by the Lane-Eynon method [6]
- the content of α-aminoacid nitrogen by the colorimetric method [1]
- viscosity with a Haake RS rotation rheometer, using a DG 41 attachment (coaxial cylinders), at 20°C and constant shear stress $\tau = 1$ [Pa].

The purification effect was calculated using the formula: $E = \frac{10000 \cdot (Cr - Cs)}{Cr \cdot (100 - Cs)}$

Where: E – purification effect, C_r – purity of purified juice in % and C_s – purity of diffusion juice in %

The flux of the permeate was also determined during filtration.

RESULTS AND DISCUSSION

Filtration of eight samples of diffusion juice was conducted in the experiment. The diffusion process was conducted so that the content of dry mass was about 14% – i.e. a value close to that under industrial conditions (13-16% [12]). The juices had different chemical compositions and properties.

Juices A, B, C, D were obtained from beetroots directly after defrosting. The properties and chemical composition of the juices did not differ from those obtained in the sugar factories. The content of dry mass in the juices ranged from 12.90-14.26%; the sucrose content determined by the polarimetric method was 11.5-13.3% and that by the reduction method 11.5-12.5% (see table 1). The purity of the juices was from 87.8% to 91.9% - practically the same as the juices obtained under industrial conditions (88-92% [12]). The content of other components in these juices, i.e. reducing sugar (0.3%) and alfa-amino-acid nitrogen (0.20-0.30%), was also close to that of industrial juices. Juice E was obtained from beetroots kept for 2 days after defrosting, juices F, G and H – from beetroots kept for 4 days. Their composition and properties corresponded to diffusion juices that sugar factories obtain from roots damaged by frost, which often happens under Polish conditions. The results obtained by the polarimetric method indicate 11-13% sucrose in the juice, whereas the actual content in these juices was 4.7-10,0% (tab. 1). Determination of the sucrose content in such roots by the polarimetric method, which is a standard in sugar factories, leads to large errors [9]. Therefore, calculations of juice purity and the purifying effect were made on the basis of the results obtained by the Lane-Eynon method.

Table 1. Content of some components in diffusion juice before (D) and after (O) purification

Juice	Dry mass (%)		Sucrose polarimetric method (%)		Sucrose by reduction (%)		Reducing sugars (%)		α-aminoacid nitrogen (%)	
	D	O	D	O	D	O	D	O	D	O
A	12.90	12.32	11.5	11.6	11.5	11.5	0.3	0.3	0.020	0.015
B	14.24	13.53	13.3	13.4	12.5	12.5	0.3	0.3	0.029	0.020
C	13.85	13.38	12.9	12.6	12.5	12.5	0.3	0.3	0.030	0.022
D	13.60	13.20	12.7	12.5	12.5	12.5	0.3	0.3	0.033	0.028
E	14.17	13.52	13.2	12.9	10.0	10.0	3.5	3.5	0.037	0.030
F	13.31	12.18	12.2	12.1	4.7	4.7	3.9	3.9	0.042	0.034
G	13.39	12.49	12.5	12.5	7.2	7.2	3.9	3.9	0.044	0.032
H	13.09	12.14	11.3	11.1	7.0	7.0	4.0	4.0	0.046	0.041

Diffusion juices (E, F, G, H) obtained from beetroots of worse technological quality had about double the content of α-amino-acid nitrogen (0.37-0.46%) and a ten times greater content of reducing sugars (3.5%-4.0%) than those obtained from beetroots of good technological quality. In spite of the close content of dry mass, these juices exhibited considerable viscosity (tab. 2). Beetroots whose technological value decreased as a result of frost or other factors contain less sucrose but have more reducing sugars, α-aminoacid nitrogen, colloids and other substances and increased juice viscosity [8,9]. This causes many difficulties in the technological process of juice purification [2].

Since the membrane cut-off was larger than the molar mass of the sucrose, the content of the sucrose and reducing sugars did not change after juice filtration.

The content of the other components assayed decreased to varying degrees. The filtration caused a decrease in the dry substance content in juices of worse quality (F, G, H) by ca. 1% (tab. 1) and by ca. 0.5% in juices A, C, D, attributable most probably, to the large content of colloids and the low molecular suspensions in these juices. In juices B and E the dry substance content decreased by ca. 0.7%; indicating that the juices had an increased content of colloids and suspended matter compared with juices A, C and D.

Table 2. The viscosity and purity of diffusion juice before (D) and after (O) purification with elimination efficiency

Juice	Viscosity (m Pa s)		Purity (%)		Elimination efficiency (%)
	D	O	D	O	
A	2.40	1.53	89.1	93.3	41.4
B	2.53	1.60	87.8	92.4	40.8
C	2.29	1.59	90.3	93.4	34.8
D	2.16	1.53	91.9	94.7	36.4
E	2.50	1.54	70.6	74.0	15.6
F	2.75	1.62	35.3	38.6	13.1
G	2.53	1.58	53.8	57.6	14.5
H	3.36	1.58	53.5	57.7	15.6

As a result of filtration, the content of α-amino-acid nitrogen – known also as harmful nitrogen – decreased; the changes were very low however (0.005-0.012%) (tab.1). In view of the low molecular mass of amino-acids, it is to be expected that they are practically all in the permeate. These compounds can be assayed with a method based on a reaction with copper, resulting in an overall content of amino-acids, amides and betaine [5]. Some of the compounds having large molecular sizes could be retained by the membrane, resulting in a lower content of harmful nitrogen after filtration.

Independently of the initial value (2.16-3.36 mPas), the viscosity of diffusion juices after filtration was from 1.53 to 1.62 mPas (tab. 2) and close to that of a pure sucrose solution with a concentration of 15% and 1.59 mPas viscosity [13]. This indicates that the juice is free of any colloidal substances. In studies conducted by Siediakina [10] membranes made of cellulose acetate, polysulfonamide and polyquatrofluoroethylene were applied in the filtration of juices with a purity of 85.5-92.4%. The membranes reduced the protein content by 50% while the pectins of the molecular mass $(50\text{-}100)x10^3$ were removed totally.

The efficiency of membrane processes is determined by the flux of permeate. Figure 1 shows permeate flux as a function of the time of membrane filtration for all juices. In the initial stages of filtration the permeate flux decreased at a relatively fast rate. The material the membrane was made of (cellulose nitrate) and the applied dead-end system led one to suppose that a blockage had occurred in the pores of the plug mechanism. This mechanism contained many juices of low purity, which in turn contained many high-molecular compounds (pectins, dextran, levan) [8].

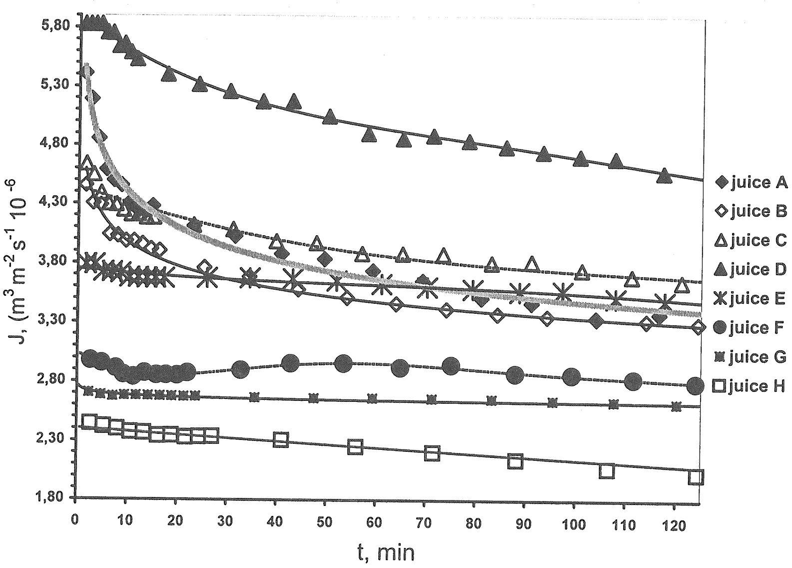

Fig. 1. Time dependence of permeate flux during membrane filtration

After the initial time, the flux for juices A, B and C was about 3.5 x 10^{-6} $m^3 m^{-2} s^{-1}$, while that of D was about 4.5 x 10^{-6} m^3 m^{-2} s^{-1}; the latter juice being of the highest purity (92.2% before and 95% after filtration) and the lowest viscosity (2.16 before and 1.53 m Pa s after). Juice F, G and H of high viscosity had a significantly lower permeate flux – ca. 2.5x 10^{-6} m^3 m^{-2} s^{-1}. This confirms the tremendous influence of viscosity on filtration efficiency, which was almost two times smaller when filtering juices of high viscosity.

One of the most significant parameters in the juice purification process – in the sugar production - is 'elimination efficiency', which describes the amount of non-sugars removed from the juice. When purifying juices obtained from beetroots of good technological value, the efficiency is 28-35%, rarely over 40%. This depends on many factors, such as the chemical composition of the beetroots, the calcium dose, and the method and parameters of the technological processes. In the investigations, the efficiency of elimination obtained for juices of good quality was at the level of 35-41%. It could be said therefore that the membrane applied allows a satisfactory purification to be obtained which is even better than is obtainable by the traditional method. The effect for juices of very low technological quality was considerably lower and was about 15%. Such juices contained so little sucrose and so many simple sugars, which were also present in the permeate that their purity could not be significantly increased by filtration. In sugar factories, such purification is obtained for juices of ca. 80% purity [3], and is thus much lower than for the juices studied (35-70%). It is worth stressing that the problems with purifying juices taken from beetroots of low technological value often lead to a total stoppage of the technological process [2].

Thus, the application of membrane techniques for the purification of diffusion juice enables an elimination efficiency of over 40% to be obtained; it also makes the technological production cycle considerably shorter and solves the problem of how to use the waste produced – i.e. the defeco-carbonation mud.

At present, this is inhibited by the high costs of installation and the necessity of insuring continuously good process efficiency throughout the entire sugar processing procedure.

CONCLUSIONS

1. The membrane filtration process could replace traditional liming and carbonation methods, the juice purification effect depends on its quality.
2. The effect of the purification of good quality diffusion juices when using a cellulose nitrate membrane was 34.8-41.4% and was thus comparable with the traditional method.
3. The application of membrane filtration made it possible to purify juice of bad quality which otherwise could not be purified under industrial conditions, the purification effect being about 13.1-15.6%.
4. In juices filtered with the cellulose acetate membrane, the content of sucrose and reducing sugars hardly ever changes.
5. The viscosity of the filtered juices decreased by 0.9-1.9 m Pa s and was close to that of pure sucrose solutions of the same concentration.
6. The content of α-amino-acid nitrogen after membrane filtration decreased by 12% to 34%.
7. The higher the purity and the lower the viscosity of diffusion juice, the greater was the permeate flux.

Appendix no. 1. Process characteristics

The process was conducted in a 'Cell' device, made by Amicon. The diameter of the membrane was 5.8 cm. The pressure during filtration was 110 kPa. 'Cell' worked under the "DEAD-END" regime.

The cellulose nitrate membrane is a synthetic, flat, solid film, organic, porous and asymmetrical. According to studies done at the Institute of Chemical Engineering and Heat Machines of Wrocław Technical University, the membrane water flux is 1.86 $dm^3\ m^{-2}\ min^{-1}$ and retains:

- 100% of bovine albumin, whose limiting molecular mass is 69,000 D,
- 96% of egg albumin, whose limiting molecular mass is 42,000 D,
- 76% of trypsin, whose limiting molecular mass is 24,000 D.

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PRÓBA ZASTOSOWANIA MEMBRANY Z AZOTANU CELULOZY DO OCZYSZCZANIA SOKU DYFUZYJNEGO

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S t r e s z c z e n i e. Celem badań było określenie efektu oczyszczania soku dyfuzyjnego przy pomocy membrany z azotanu celulozy (CN) oraz porównanie zawartości niektórych składników i cech soku dyfuzyjnego i oczyszczonego. Stwierdzono, że proces filtracji membranowej może zastąpić tradycyjne metody defekacji i saturacji, przy czym efekt oczyszczania soków zależy od ich jakości.

Efekt oczyszczania soków dyfuzyjnych o dobrej jakości z zastosowaniem membrany z azotanu celulozy wynosił 34,8-41,4%, a więc był porównywalny z metodą tradycyjną. Zastosowanie filtracji membranowej umożliwiło oczyszczenie soków o złej jakości, których nie można oczyścić w warunkach przemysłowych, efekt oczyszczania wynosił około 13,1-15,6%. W sokach przefiltrowanych przy pomocy membrany z azotanu celulozy zawartość sacharozy i cukrów redukujących praktycznie nie zmieniła się. Lepkość przefiltrowanych soków zmniejszyła się o 0,9-1,8 mPas i była zbliżona do lepkości czystych roztworów sacharozy o tym samym stężeniu. Zawartość azotu α-aminokwasowego po filtracji membranowej zmniejszyła się o 12 do 34%. Im wyższa była czystość i mniejsza lepkość soku dyfuzyjnego, tym strumień permeatu był większy.

S ł o w a k l u c z o w e: sok dyfuzyjny, filtracja membranowa, efekt oczyszczania