Membrane Filtration in the Sugar Industry*

A. HINKOVÁ**, Z. BUBNÍK, P. KADLEC, V. POUR, and H. ŠTARHOVÁ

Department of Carbohydrate Chemistry and Technology, Institute of Chemical Technology, CZ-166 28 Prague, Czech Republic
e-mail: hinkovaa@vscht.cz

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This research work deals with possibilities of raw sugar juice purification by micro-, ultra-, and nanofiltration. Conditions that enable to reach such a juice purity for proceeding of crystallization without the prerequisite of the whole complex of purification techniques, which involve liming, carbonation, and filtration, were sought. Samples were treated with cross-flow micro- and ultrafiltration on ceramic membranes having mean pore size 20 nm, 50 nm, and 100 nm. Increasing of juice purity and retention of almost 50 % of colour impurities by microfiltration is one of the most important results of this study. For nanofiltration tests, a special cross-flow testing cell with adjustable tangential speed of 0—3 m s^{-1} has been designed. Several flat polymeric membranes have been tested. The aim was to find a membrane capable to reject the main part of the melassigenic elements as potassium and sodium ions, *i.e.* elements that increase amount of waste product (molasses) during sugar crystallization.

Sugar processing is one of the most energy-intensive processes in the food industry, which is a challenge for membrane separation processes like microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) or reverse osmosis (RO). On the other hand, due to high volumes pumped, high viscosity, and high osmotic pressure of sugar juices some limitations exist, which inhibit extension of membrane separation methods to sugar production. For the above-mentioned reasons, application of membrane filtration has aimed namely at purification of juices from the extraction stage where viscosity, dissolved solid concentration, and temperature are lower. A number of papers deal with the application of UF or MF for purification of raw juice. *Mak* [1] described removal of colour impurities from raw juice by ultrafiltration. He applied an Alfa-Laval filtration unit with hollow fibre modules PM10. Proteins, starches, gums, colloids, and colour impurities were removed by filtration process. Filtration of juice prepared from raw sugar was either a single-stage process removing 75 % of colour impurities or it involved a recycled mode in which colour level fell by 60—90 %. During experiments with microfiltration of raw juice through Filmtec Selectflo synthetic membranes having mean pore size 0.2 μm *Vern et al.* [2] achieved such purity of raw juice that direct crystallization was possible without the complex process of traditional purification involving liming and carbonation processes, cake filtration, *etc.*

Some researches have focused on conditions of separation processes. Optimal cross-flow process conditions for microfiltration and ultrafiltration of sugar cane raw juice have been studied by *Dornier et al.* [3, 4]. They also reported that progressively increasing both transmembrane pressure and cross-flow velocity in the initial stage of microfiltration resulted in 13—26 % improvement of permeate flux compared to commonly used abrupt start-up procedure. Nevertheless, in numerous cases the permeate flux usually obtained is still too low to encourage any industrial application. *Hanssens et al.* [5] reported that no fouling problems occurred during ultrafiltration clarification of raw juice at a tangential velocity of 4 m s^{-1} and no prefiltration was needed to reach the same degree as it was achieved by the conventional process. *Mikulášek* [6] discussed various process conditions and factors influencing the effectiveness of microfiltration and filtration output decline caused by membrane fouling.

Attention was recently transferred to ceramic membranes which can operate in a wide range of pressures, temperatures, and pH. *Lancrenon et al.* [7] described the Applexion system with ceramic membranes Carbosep and Kerasep which were used for sugar cane and sugar beet refining. During ultrafiltration of sugar beet raw juice a permeate flux of 200 dm^3 h^{-1} m^{-2} was achieved. Authors believe that such flux

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**The author to whom the correspondence should be addressed.

brings the process to the point where it might be an alternative to the conventional carbonation. *Bubník et al.* [8, 9] studied effects of microfiltration on ceramic membranes and nanofiltration of sugar-beet raw juice on quality of juices in terms of purity, colour substance content, and melassigenic ion content.

Physicochemical interactions between particles of mineral membranes and sugar remelts during microfiltration [10] were studied with the aim to facilitate the choice of membrane in dependence on solution properties. *Vercellotti et al.* [11] reported results of their analysis of unknown compositional factors in processing of juices or sirups and markedly influencing flux through the membrane.

EXPERIMENTAL

Refractometric dry solid (RDS) content was measured on digital refractometer ABBEMAT (Dr. Kernchen, Germany). Polarization was determined by polarimeter SUCROMAT VIS/NIR (Dr. Kernchen, Germany). Purity was calculated as a ratio of polarization and RDS multiplied by 100. Anion and cation content was measured by isotachophoretic analyzer IONOSEP 900.1 (Recman, Czech Republic).

Equipment for Micro- and Ultrafiltration

The cross-flow filtration unit is a pilot plant type made by the French firm T.I.A. (Bollene) and is equipped with two ceramic membranes MEMBRALOX (France) having filtration area of 2×0.2 m^2, mean pore size 20—100 nm for ultrafiltration and 0.2—5 μm for microfiltration. The limits within which experiments may be done are: temperatures up to 85 °C, pressures up to 0.6 MPa with pH in a large range of 0.5—13.5. Tangential velocity is 5 m s^{-1} at the pressure 0.1 MPa.

Filtration used retentate recycling (centrifugal pump Hyginox SC, INOXPA, Italy) with a constant membrane pressure difference of 0.1 MPa or 0.2 MPa and constant temperature of 30 °C, 50 °C, and 60 °C. Test duration was 3—10 h. To observe the filtration kinetics, permeate flux was determined by measuring the volume of permeate collected for 10—60 s.

For fouling effect determination we measured the values of water flux before and after separation. Water flux (DE) was measured for temperature 20 °C, pressure difference 0.1 MPa, and membrane area 1 m^2.

Back flush with permeate was provided every 20 min for a period of 2 min with a pump Gamma/5 (ProMinent, Germany) at the pressure 1.3 MPa and discharge 9.5 dm^3 h^{-1}.

After filtration, the membranes were cleaned at 60 °C by recycling of NaClO solution (2 %) for a period of 40—60 min. Then water flux was measured and compared with the initial one. If cleaning was not sufficient, another steps were carried out (with HNO_3 solution (1 %) at 60 °C). The membrane cleaning time is thereby a total time needed to restore the initial water flux.

Equipment for Nanofiltration

A high-pressure nanofiltration dynamic cell with an adjustable tangential speed range of 0—3 m s^{-1} incorporated into the filtration unit ARNO 600 (MIKROPUR, Czech Republic) was used for experiments. The whole unit (Fig. 1) enables tests with different kinds of filtration modules such as ceramic membranes, spiral wound membranes, disc-tube module, or nanofiltration modules. NF tests were run on flat synthetic membranes with different properties (see Table 1). Conditions of nanofiltration were: tangential velocity: 1 m s^{-1}, temperature: 18—50 °C, pressure difference: 0.05 to 3.6 MPa, test duration: 2—3 h.

The filtration kinetics (*i.e.* the dependence of permeate flux velocity on time, temperature, and operating pressure) was particularly observed at given temperature and calculated for the temperature 20 °C. The calculation was based on the dependence of solution viscosity on temperature. The feed, permeate and retentate samples were measured in terms of colour, purity, content of refractometric dry solid, sucrose, anions, and cations.

Solutions for Micro- and Ultrafiltration

Fresh sugar-beet raw juice: raw juices were sampled during the campaign 1998 from different sugar refineries with various sugar-beet growing areas and representing different extractors. The value of dry solid varied between 14.2—16.8 % and sucrose content (purity) was 88.5—91.0 % of RDS. In the temperature range 30—60 °C, the dynamic viscosity of such solution is about 0.7—1.4 mPa s.

Sugar-beet raw juice concentrate: prepared by evaporating of fresh raw juice taken during the campaign 1998 on falling film evaporator (ARMFIELD, UK). After 8 months of storage, the concentrates were diluted to the RDS of 17 % and used for the filtration. Measurement was aimed to particularly verify the possibility of performing the newly designed technological process not only during a season but the whole year.

Solutions for Nanofiltration

Fresh sugar-beet raw juice: taken during the campaign 1999 and pretreated by ultrafiltration before nanofiltration tests. Conditions of pretreatment: membrane mean pore size 100 nm, TMP of 0.1 MPa, temperature of 30 °C.

Mathematical Fouling Model

Most mathematical models describing fouling are

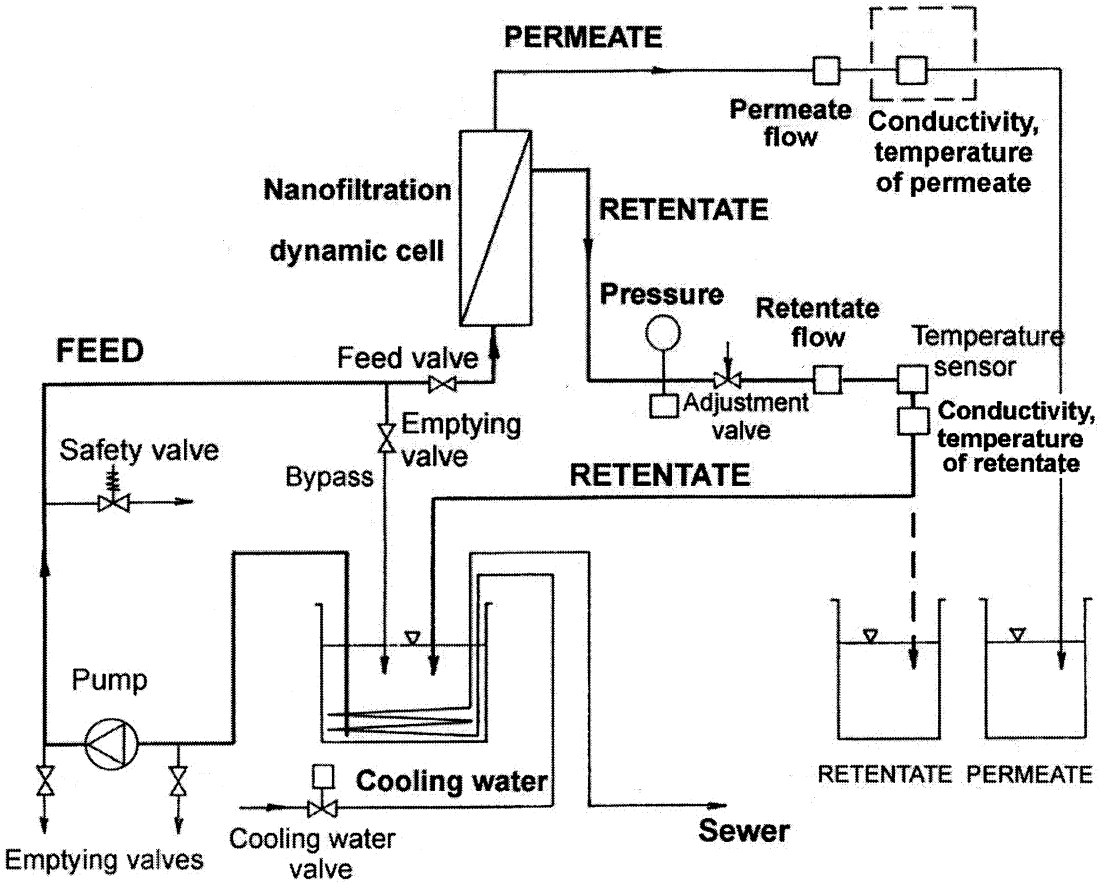

Fig. 1. Scheme of the filtration unit ARNO 600 with nanofiltration cell.

Table 1. Nanofiltration Membrane Designation and Properties

Producer	Type	Membrane properties
Osmonics Desal	DL	rejection $MgSO_4$ = 96 %, at 25 °C, 690 kPa max. temperature = 50 °C pH = 2—11
Osmonics Desal	DK	rejection $MgSO_4$ = 98 %, at 25 °C, 690 kPa max. temperature = 50 °C pH = 2—11
Hydranautics	ESNA 99	rejection NaCl = 85 %, at 25 °C, p = 0.52 MPa max. temperature = 45 °C, pH = 3—10 polyamide
Hydranautics	ESNA 97	rejection NaCl = 85 %, at 25 °C, p = 0.52 MPa max. temperature = 45 °C, pH = 3—10 polyamide
Nitto Denko	7450	rejection at 25 °C, p = 1 MPa Sucrose = 36 %, NaCl = 51 % $MgSO_4$ = 32 %, at 25 °C, p = 1 MPa glycerine
Filmtec	NF 45	rejection NaCl = 96—98 %, at 25 °C max. temperature = 45 °C pH = 3—10

Table 2. Values of Coefficient from Membrane Fouling Model for MF and UF

Solution	Filtration conditions	J_{SS} / dm^3 m^{-2} h^{-1}	b / dm^3 m^{-2}	Correlation coefficient
Fresh raw juice	temperature 30 °C	126	849	0.94
Fresh raw juice	temperature 50 °C	221	696	0.89
Fresh raw juice	temperature 60 °C	303	1723	0.89
Raw juice concentrate	30 °C, $\Delta p = 0.1$ MPa	122	507	0.86
Raw juice concentrate	30 °C, $\Delta p = 0.2$ MPa	109	176	0.78

Table 3. The Influence of Different Filtration Conditions on Water Output before and after Filtration of Concentrates and Membrane Cleaning Time

Filtration condition	Membrane cleaning time/min	Water output fall of initial value / %
Membrane: ceramic Mean pore size: 20 nm, TMP: 0.1 MPa Temperature: 30 °C	60	78.3
Membrane: ceramic Mean pore size: 20 nm, TMP: 0.2 MPa Temperature: 30 °C	90	74.1
Membrane: ceramic Mean pore size: 20 nm, TMP: 0.1 MPa Temperature: 60 °C	180	85.1
Membrane: ceramic Mean pore size: 50 nm, TMP: 0.1 MPa Temperature: 30 °C	120	77.4
Membrane: ceramic Mean pore size: 20 nm, TMP: 0.1 MPa Temperature: 30 °C – back flush	40	75.9

relating the flux to the time and generally take an exponential form. *Cheryan* [12] suggested a model (*1*), where J_i (dm^3 h^{-1} m^{-2}) is the permeate flux at any time t (min), J_{SS} (dm^3 h^{-1} m^{-2}) is the steady-state permeate flux, and a and k are the constants characterizing the fouling process.

$$J_i = J_{SS} + k \cdot e^{-at} \qquad (1)$$

Our fouling model issues from the one suggested by Cheryan and is expressed by eqn (*2*). Values of coefficients J_{SS} and b were obtained from experimental data using a method of least-squares regression. Since the model is empirical, it may not explain the phenomenon itself.

$$J_i = J_{SS} + b/t \qquad (2)$$

RESULTS AND DISCUSSION

Micro- and Ultrafiltration of Fresh Sugar-Beet Raw Juice

During UF tests with different juices under different conditions (*i.e.* temperatures, pressures, and mean pore sizes of membranes) we obtained similar results concerning improvement of permeate properties. An interesting result was achieved in increasing the juice purity of fresh juice (on the average by 2 %). A decrease of the colour impurity content in the original raw juice by 60—70 % and 50—60 % in the concentrate shows a good purification effect.

Colour matter rejection (R), expressed as (*3*) (where Cb_P and Cb_R are contents of colour components in permeate and retentate), reached an average value 0.61 at temperature 30 °C and 0.55 at 50 °C.

$$R = \left(1 - \frac{Cb_P}{Cb_R}\right) \cdot 100 \qquad (3)$$

During other micro- and ultrafiltrations of different raw juices and diluted concentrates this rejection varied from 0.49 to 0.62. The turbidity (colloid content) fell to less than 1 % of its initial value. These effects are necessary for further treatment of permeate to white sugar.

The retentate purity decreased to 87—88 % at 30 °C and to 86—87 % at 50 °C. A similar effect was found by microfiltration of all used juices and diluted

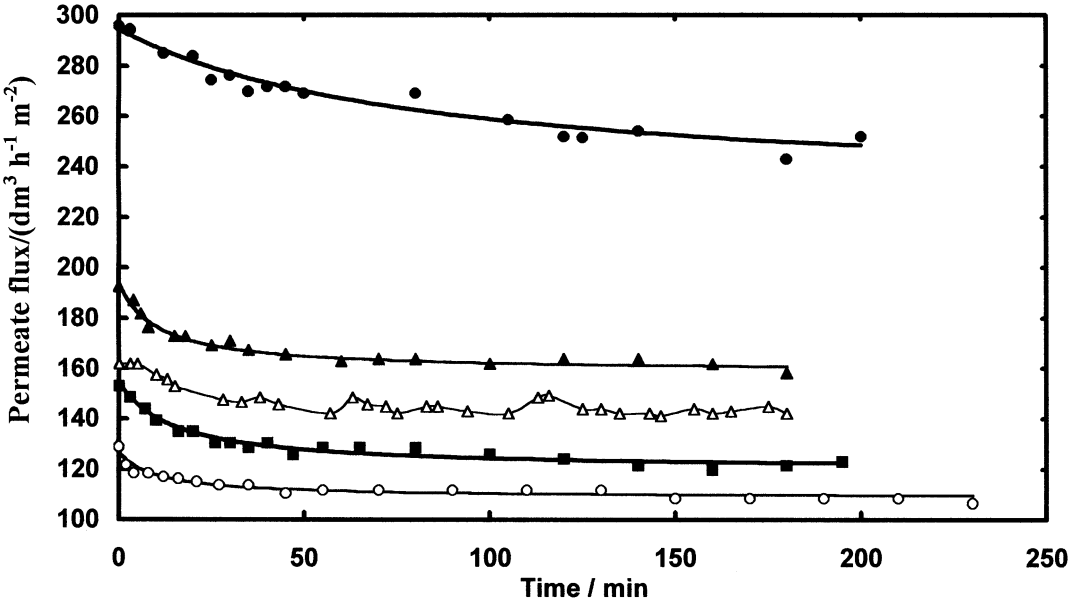

Fig. 2. Permeate flux during UF and MF of raw juice concentrates: ■ 30 °C, 0.1 MPa, 20 nm; ○ 30 °C, 0.2 MPa, 20 nm; ● 60 °C, 0.1 MPa, 20 nm; ▲ 30 °C, 0.1 MPa, 50 nm; △ 30 °C, 0.1 MPa, 20 nm, back flush.

concentrates. A number of substances (particularly proteins, polysaccharides) concentrated in the retentate making this product a high-quality feed, which would improve the economic balance of costs and production when membrane filtration is applied.

Permeate Flux during Micro- and Ultrafiltration

During the most of experiments, the flux of permeate declined rapidly in the first 30—40 min, then a very slow decrease followed (see Fig. 2). This two-stage gradual flux decline is characteristic of membrane fouling. The exception are the curve shapes obtained during back washing and at the temperature 60 °C. The explanation is that the first back flushing was carried out after 20 min of filtration process and due to the fouling component removing, the flux decline in the first stage was not so fast. During filtration at 60 °C it is possible to suppose that if the filtration process would last longer, the curve shape would be similar with the others. Total permeate output fell during the process to 40 % (fresh juice) and 55 % (concentrated juice) of their initial values.

As it was mentioned, membrane fouling model was suggested and values of coefficient at different conditions were obtained from experimental data (Table 2). Comparing values of J_{SS} for fresh juice it is obvious that there is the effect of lower viscosity at higher temperature and thereby higher steady-state fluxes. The influence of pressure difference during concentrate filtration is shown, too. At higher Δp the value of steady-state flux is lower. It is possible to explain this phenomenon by the start up procedure. Due to higher pressure, the permeation velocity was also higher and that is why the big pores were plugged rapidly and the flux declined. To minimize this effect, it would be necessary to start up the system at lower pressure. Nevertheless, the pressure influence on membrane fouling will be a subject of further investigation.

Comparing the values of water flux before and after filtration at different conditions (pressure difference, temperature, membrane mean pore size, see Table 3) it is obvious that all named parameters did not influence membrane fouling too much. Permeate flux at higher temperature (60 °C) apparently increased (see Fig. 2) but on the other hand, the time necessary for membrane cleaning was threefold higher. This is probably caused by thermal decomposition of raw juice and forming of worse removable layer.

Nanofiltration of Sugar-Beet Raw Juice

The nanofiltration experiments were focused on testing of separation properties of different polymeric membranes under slight conditions (low temperature: 20 °C and small pressure: up to 3.6 MPa) and showed differences in a separation effect of various membranes. The aim was to find a membrane which would have a high rejection for sugars and low for melassigenic cations Na^+ and K^+. Such membrane would enable concentration of raw juice (with minimum sugar lost in permeate) accompanied by elimination of components responsible for sugar losses in molasses. Rejection (R_S) of sugars retained by membrane was calculated according to the formula (*4*), where C_P and C_R are contents of component in permeate and/or in retentate.

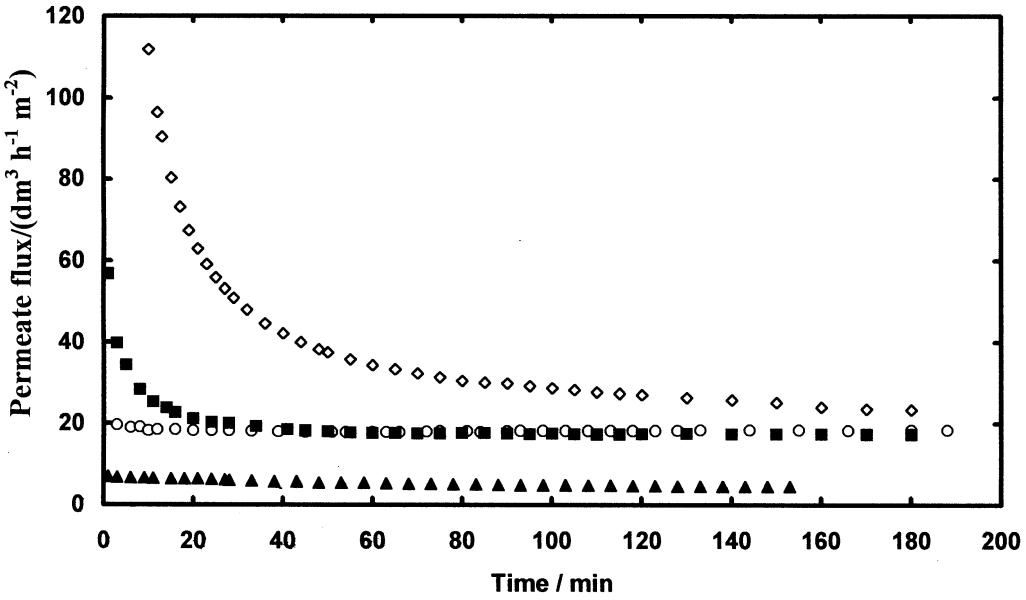

Fig. 3. Permeate flux during nanofiltration of sugar-beet raw juice: ○ Osmonics Desal DL, 2 MPa; ▲ Osmonics Desal DK, 2 MPa; ■ Osmonics Desal DK, 3.6 MPa; ◊ Filmtec NF 45, 3.2 Mpa.

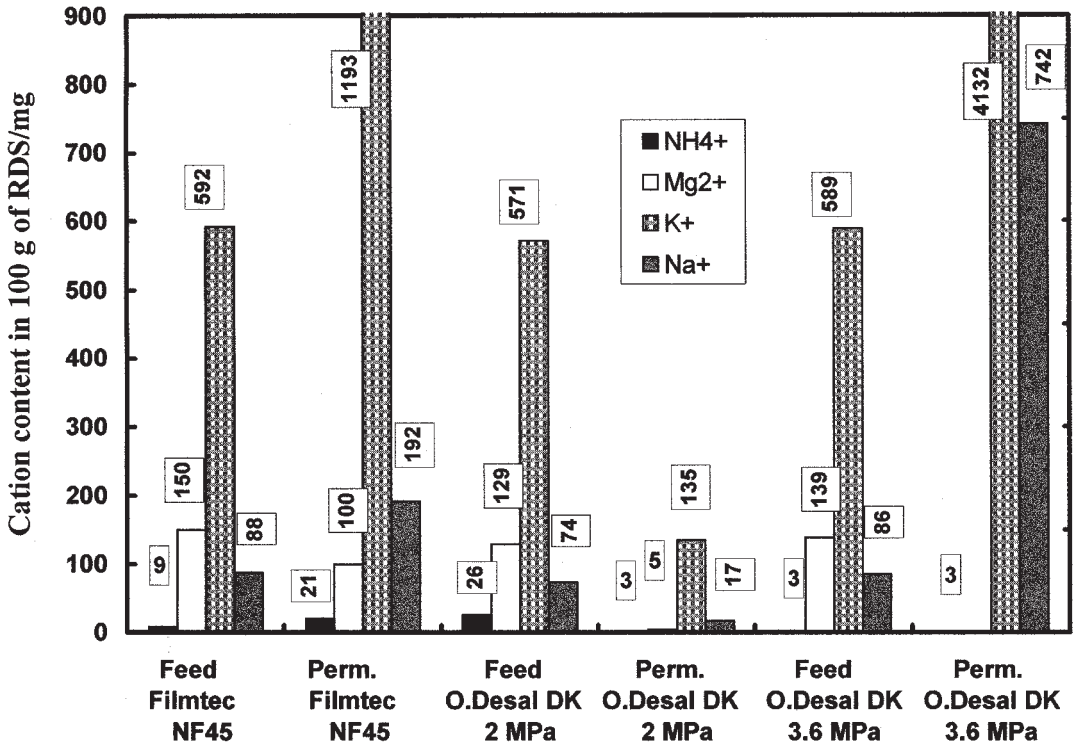

Fig. 4. Cation composition during nanofiltration of sugar-beet raw juice.

$$R_{\mathrm{S}} = \left(1 - \frac{C_{\mathrm{P}}}{C_{\mathrm{R}}}\right) \cdot 100 \qquad (4)$$

Similarly, rejection of impurities (R_{NS}) is expressed as a ratio (5) where Q_{P}, Q_{R} are purities of permeate and retentate.

$$R_{\mathrm{NS}} = \left(1 - \frac{100 - Q_{\mathrm{R}}}{100 - Q_{\mathrm{P}}}\right) \qquad (5)$$

The retention of sugars varied in the range of 73—95 % and of impurities in the range of 29—83 %. Process kinetics is shown in Fig. 3 and composition of feeds and permeates is given in Figs. 4 and 5 and Table 4. On the membrane Desal DK at the pressure 3.6 MPa, high transport of impurities ($R_{\mathrm{NS}} = 83$ %) and small loss of sugars ($R_{\mathrm{S}} = 95$ %) can be seen. This resulted in increasing of retentate purity from initial

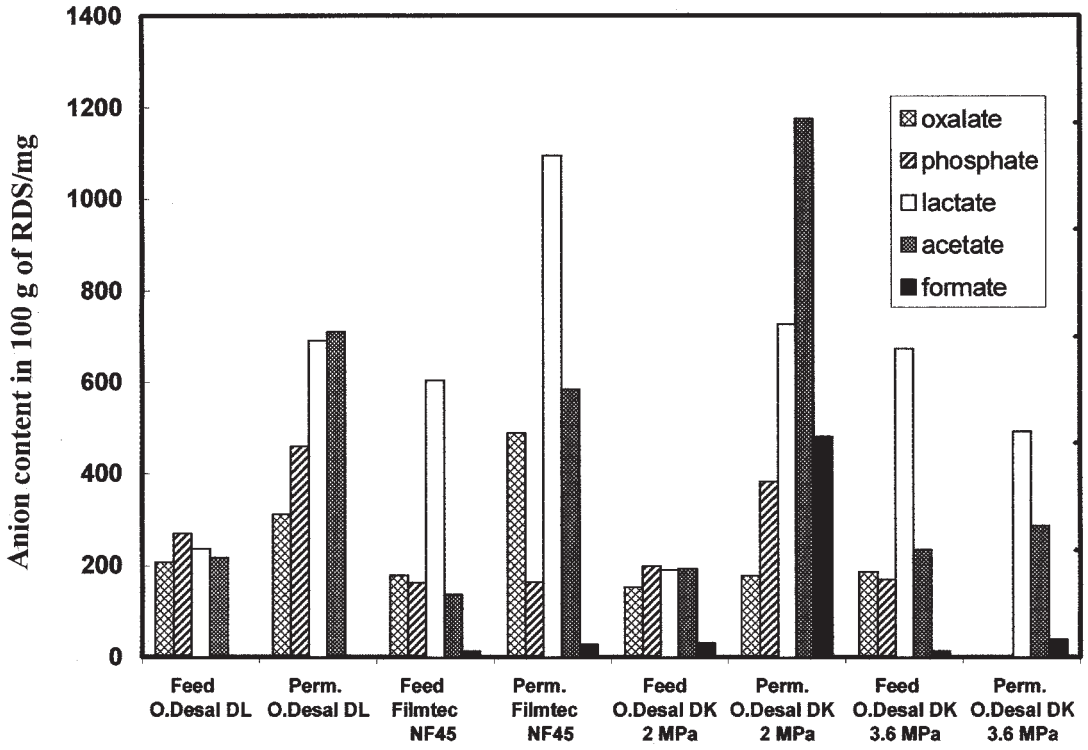

Fig. 5. Anion composition during nanofiltration of sugar-beet raw juice.

Table 4. Analytical Composition of Feed, Permeate, and Retentate during Nanofiltration

Membrane	Osmonics Desal DL TMP: 2 MPa			Filmtec NF 45 TMP: 3.2 MPa		
Analysis	Feed	Permeate	Retentate	Feed	Permeate	Retentate
Dry solid content/%	16.01	5.15	16.26	16.46	4.46	16.7
Polarization/%	14.47	3.78	14.39	14.46	3.69	14.65
Purity/%	90.38	73.40	88.50	87.85	82.74	87.72
pH	6.06	6.06	6.01	5.5	5.5	5.5
Colour/IU	506	471	862	267	415	405
Rejection sugars/%		73.4			74.8	
Rejection impurities/%		56.8			28.9	
Membrane	Osmonics Desal DL TMP: 2 MPa			Osmonics Desal DK TMP: 3.6 MPa		
Analysis	Feed	Permeate	Retentate	Feed	Permeate	Retentate
Dry solid content/%	16.03	2.20	16.39	16.54	1.28	16.34
Polarization/%	14.36	1.60	14.42	14.44	0.77	15.24
Purity/%	89.58	72.73	87.98	87.30	60.16	93.27
pH	5.87	5.65	5.89	5.51	5.4	5.48
Colour/IU	459	118	457	427	218	319
Rejection sugars/%		88.9			95.0	
Rejection impurities/%		55.9			83.1	

87 % to 93 %. Permeate purity decreased to 60 %. With the tighter DK membrane, a higher percentage of K^+ in RDS of permeate (4.13 %) was found in comparison to the feed value of 0.59 %. The looser NF45 membrane gave 1.19 % K^+ in RDS of permeate. The rejection of impurities on NF45 membrane was very low (30 %) what allows concentration of impurities in permeate. On the other hand, the rejection of sug-

ars (75 %) was not sufficient to prevent sugar losses in permeate. Membrane Desal DL did not show very good separation effect.

The results, however, require verification in industrial scale since the quality of juices varied a lot during the campaign.

CONCLUSION

Obtained results showed that UF/MF allows such a purification of raw juice that these treated juices can be processed by direct crystallization. On the other hand, ceramic membrane price with insufficient permeate flux and low total performance of the filtration process due to membrane fouling is not satisfactory enough to encourage an industrial application.

Nanofiltration tests showed that proper membrane for NF of raw juice might be sought on the dense side of the NF membrane spectrum where some tested membranes exhibited higher retention for sucrose than for nonsugars. Higher pressure and tangential velocities membranes from more open side of the spectrum which have desirable small NaCl rejection exhibited no separation for sugar and inorganic nonsugars under given conditions.

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