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Desalination 241 (2009) 256–264
DESALINATION
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Concentration of blackcurrant juice by reverse osmosis

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Received 27 August 2007; revised 11 January 2008; accepted 18 January 2008

Abstract

The aim of this study was to examine the applicability of reverse osmosis (RO) for the concentration of blackcurrant juice by AFC-80 polyamide tubular membrane that has a salt rejection greater than 80%. The fresh juice had a total soluble solids content of about 16.5°Brix. The effect of centrifugation followed by depectinization with two commercially available pectinase enzyme preparations (Panzym Super E and Trenolin Rot DF) on the permeate flux has been evaluated. For the description of the concentration process, the resistance-in-series model has been used. It was concluded that the applied RO membrane is suitable for concentration of blackcurrant juice up to 28.6°Brix, which was achieved with the juice that had been treated with Panzym Super E. The total resistances were calculated and compared, taking into account membrane fouling and polarization layer resistance.

Keywords: Reverse osmosis; Concentration; Blackcurrant juice; Depectinization; Resistance-in-series model

1. Introduction

Blackcurrant juice is very popular among consumers due to its pleasant taste, as well as its numerous beneficial health effects. It contains great amounts of mineral salts and vitamins, which have beneficial effects to human health. Its C-vitamin concentration is 4–5 times higher than that of lemon. It is also rich in P-, B1- and B2-vitamins, provitamin A pigment, and anthocyanins [1].

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Presented at the Third Membrane Science and Technology Conference of Visegrad Countries (PERMEA), Siofok, Hungary, 2–6 September 2007.

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doi:10.1016/j.desal.2008.01.069

After harvesting the berries, blackcurrants are usually processed into juices. One of the basic unit operations of fruit juice technology is the concentration process to reduce liquid volume and, therefore, storage and transportation costs. Concentration is expected to increase the total solids content (TSS) of the juice from 10% up to 75% by weight [2,3].

To provide consumers with all the beneficial properties of the fresh berry, it is necessary to apply gentle processing method that promotes the preservation of the original characteristics of berries in the products. In recent years, membrane processes such as nanofiltration (NF), reverse osmosis (RO) and alternative membrane based separation: membrane distillation (MD) and pervaporation have been evaluated as fruit juice concentration processes [4]. RO has achieved some commercial success in fruit juice concentration: it presents the advantages of less thermal damage to the product, reduction in energy consumption and lower capital equipment costs. However, the final concentration of juices is limited to about 25–30°Brix due to the high osmotic pressure of the feed at those levels [5]. Leaving out prefiltration by microfiltration (MF) or ultrafiltration (UF), and the possibility to avoid enzyme treatment are significant from economical point of view [6]. There is also an indication that clarification by UF results in the loss of health promoting compound content of blackcurrant juices. Earlier research indicated that, during UF, about 36% of the anthocyains and 40% of flavonols have been released to the permeate, and most of them concentrated in the by-product stream [7].

The aim of this research was to concentrate blackcurrant juice at a pilot scale by RO. The effect of clarification by centrifugation and enzymatic depectinization was compared to the juice without any pretreatment, by means of achieved final TSS content and permeate flux during concentration. To evaluate the possibility of fouling during juice concentration, the resistance-in-series model was used, and the total resistance was calculated taking into account membrane fouling and polarization layer resistance.

2. Materials and methods

2.1. Extraction and pretreatment of juices

The blackcurrant berries were produced by Fitomark 94 Ltd Hungary farm. They were treated with enzymes (pre-press pectinases by Trenolin enzyme) to ease pressing and increase yield. They were pressed using a Pera PN BUCHER compressor. The juice was afterwards pasteurized and clarified conventionally by centrifugation. The blackcurrant juices were depectinized by pectolitic enzyme preparations (Panzym Super E and Trenolin Rot DF). The Panzym Super E liquid preparation (pectolytic activity of 2000 ferment depectinization unit, FDU 55°C mL^{-1}) is obtained from selected strains of *Aspergillus niger*. The Trenolin Rot DF was purchased at retail. The enzymes hydrolyze the methyl ester groups of pectin and reduce the viscosity of the blackcurrant juices. This in turn can ease the filtration of the juices. The time of depectinization depended on enzyme type and treatment temperature. A small amount of enzymes (8 mL/20 L) were used and the treatment time was 12 h in the case of Panzym Super E at 25°C and, in case of Trenolin, 24 h at 25°C and 96 h in refrigerator at 6°C.

2.2. RO unit and experimental procedures

A RO tubular B1 module of Paterson Candy International (PCI) was used, which comprises of 18 perforated stainless steel tubes. Each tube is lined with a 1.2-m long membrane element 12.5 mm in diameter (total area of 0.9 m^2). The tubes are connected in series. The module contained AFC 80 polyamide tubular membrane.

This compact tubular method was developed to ease the concentration of highly viscous fluids. The temperature of the feed was controlled by a heat exchanger and set to 25°C. After the juice was fed through the membrane module, the concentrate was recirculated back to the store tank (Fig. 1). The trans-membrane pressure was fixed at 60 bar, and 60 L of the juices were concentrated in each batches. The duration of the concentration experiments were the same (120 min). The permeate was collected and measured continuously by using an electronic balance connected with a computer during each experimental run. The overall accuracy of the measurements was below ± 5%, which is usual in this type of experiments [1,3].

Cleaning of the membranes was carried out after every test run as follows. The membrane was first rinsed with tap water at a recirculation flow rate of 900 L h^{-1} and trans-membrane pressure of 60 bar for 30 min. This was followed by circulating 0.1 w/w% EDTA + SDS + NaOH solution at same conditions for 30 min and rinsed with tap water [8]. Finally, a 0.5% citric acid solution was used and circulated for 30 min, followed by rinsing with tap water. Pure water flux was measured before and after each cleaning procedure, and used later on for the calculation of the total resistance from the resistance model.

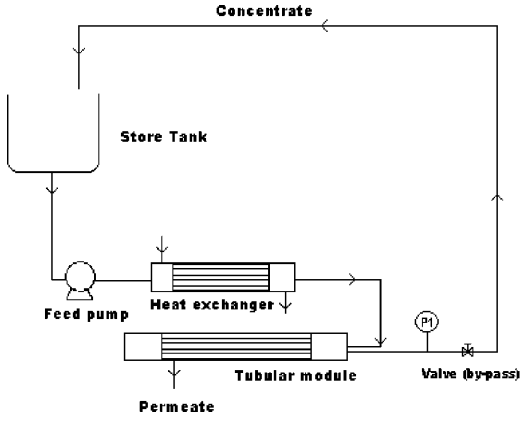

Fig. 1. Flow sheet of the experimental set-up using tubular modules (PCI).

2.3. Analytical and calculation methods

The TSS content was measured using an Atago PR-101 α digital refractometer. Measurements were made at ambient temperature. TSS was expressed as °Brix. Prior to each set of measurements, the instrument was calibrated at 0°Brix using deionized water.

3. Results and discussion

3.1. Permeate flux during RO

The measured physical properties and the calculated Reynolds numbers of the feed and the final concentration as well as the volume reduction ratios (VRR) of different pretreated juice types are presented in Table 1. The initial total soluble solid (TSS) content of the feed varied between 16.1 and 18.9°Brix and by the end of the concentration reached 28.2°Brix for Panzym Super E.; 25.7°Brix for Trenolin Rot at 6°C; 25.4°Brix for Trenolin Rot at 25°C and 22.4°Brix for Control frozen juice. As it can be seen in Table 1, with an increase of the concentration of the blackcurrant juice the viscosity and the density also increased. While the viscosity increased 2–3 times, the changes of the density were smaller, 2–10%. The calculated Reynolds numbers in all cases were in transitional flow regime, and the values followed the viscosity changes. The VRR were already the same in Trenolin enzyme treated and the control samples, while in case of the PSE enzyme treated experiment the value was much higher due to concentration changes from feed to final.

From Fig. 2, it is obvious that the fluctuation of TSS concentration is rather diverse for samples with different pretreatment. After 100 min., the concentration was 26.6, 24.7,

Table 1
The concentration, viscosity, density, Reynolds number and VRR of the different pretreated juice types at 25°C

Pretreatment type		c_R (°Brix)	η (m Pas)	ρ (kg m^{-3})	*Re*	VRR
PSE enzyme	Feed	16.1	3.73	1079.4	7365	1.752
	Final	28.2	11.89	1118.8	2398	
Trenolin enzyme, (1 day, 25°C)	Feed	18.9	4.88	1080.8	5641	1.344
	Final	25.4	9.09	1199.4	3361	
Trenolin enzyme (4 day, 6°C)	Feed	18.6	4.74	1079.6	5799	1.382
	Final	25.7	9.36	1111.6	3027	
Control	Feed	16.7	3.95	1071.8	6905	1.341
	Final	22.4	6.82	1095.1	4089	

24.2 and 21.7°Brix for PSE, Trenolin at 6°C, Trenolin at 25°C and the Control sample, respectively. As shown in Fig. 2, there is no significant difference between the Trenolin samples at different temperatures. However, the TSS of Trenolin treated juices was higher than the PSE treated until the first 50 min, after which this tendency changed. It seems to be that the juice treated with PSE enzyme does not attach in the pores of the RO membrane as much; therefore, fouling will occur later.

The permeate fluxes varied during the concentration procedure depending on the feed and applied pretreatment. As indicated by Fig. 3, permeate flux decreased with rise of TSS. The data in Fig. 3 illustrate depectinized juices (PSE and Trenolin Rot) and the Control juice. The greatest permeate flux was achieved during the concentration of juice that has been previously depectinized by PSE enzyme. As the experiment progressed, the °Brix increased and the largest drop in flux was in the case of PSE. In addition, the decreasing rates of all the concentration experiments were already the same, because the slope of the trend lines was similar. There were no significant differences between the two Trenolin treatments in terms of permeate flux at the end of the run when the concentrate achieved

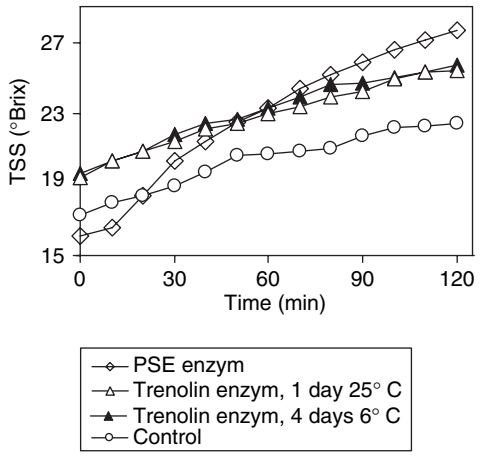

Fig. 2. Comparison of TSS values at different pretreatments.

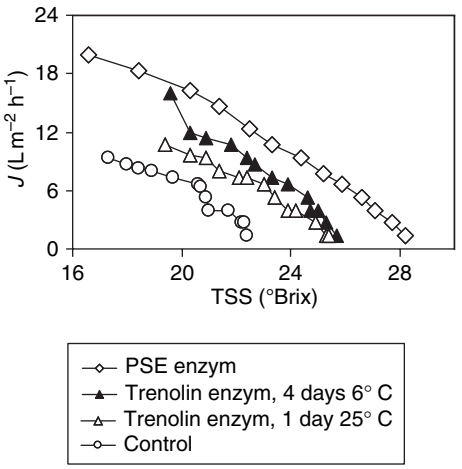

Fig. 3. The effect of TSS on the fluxes.

24°Brix; however, at the starting point, a moderate gap can be observed between the two lines. It can be noted that, from all juice samples, the lowest permeate flux was achieved when no enzymatic treatment had been applied. The achievable maximum TSS was the lowest in the Control case, only 22.4°Brix. It is advisable to carry out the depectinization process with the PSE enzyme since it is the one that gives the higher increase on the permeate fluxes. Another advantage is that this treatment is performed at ambient temperature without extra energy requirements for refrigeration.

The dynamic of the flux decline is measured by the ratio J/J_0, where J_0 is the measured initial permeate flux value ($L\,m^{-2}\,h^{-1}$). In Fig. 4 the normalized fluxes (J/J_0) are plotted as the function of TSS. The normalized fluxes of the different pretreated juices decreased as the TSS rose, which was in agreement with the literature [9]. Since the decreasing rate of the Control and Trenolin treated samples were much higher than the PSE treated sample, it is concluded that the application of PSE for pretreatment is the most economical.

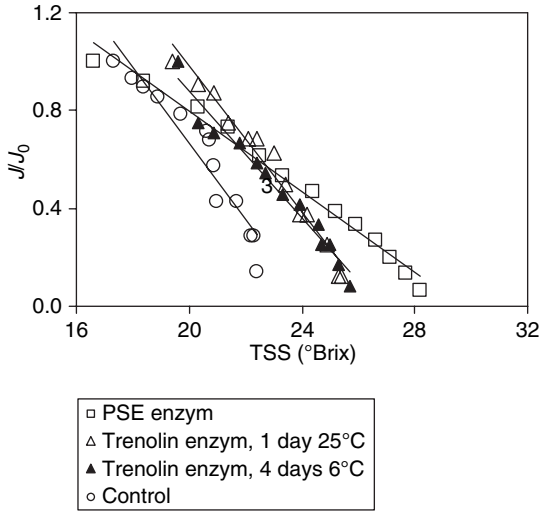

Fig. 4. The normalized flux values.

3.2. Mathematical modeling

The resistance-in-series model of the membrane separation defines pure water flux as the quotient of the trans-membrane pressure — driving force (Δp_{TM}, Pa) – and the resistance (R_M, m^{-1}, calculated by water dynamic viscosity η_W, Pas) arising from the pore size of the membrane – material feature [10,11].

$$J_W = \frac{\Delta p_{TM}}{\eta_W R_M} \quad (L\,m^{-2}\,h^{-1}) \tag{1}$$

The fouling resistance of the applied membranes can be determined from the water flux (J_F, $m\,s^{-1}$) – measured on a fixed temperature – after flushing the membrane with tap water after concentration test using the following formula:

$$R_F = \frac{\Delta p_{TM}}{J_F \eta_W} - R_M \quad (m^{-1}) \tag{2}$$

The total resistance is composed of three resistances:

$$R_T = R_M + R_F + R_P \quad (m^{-1}) \tag{3}$$

where R_P (m^{-1}) is the polarization layer resistance.

At membrane filtration of liquid mixtures the osmotic pressure model is valid, which determines the flux (J, $m\,s^{-1}$) as the quotient of difference of the trans-membrane pressure (Δp_{TM}, Pa), the osmotic pressure difference ($\Delta\pi$, Pa), and the total membrane resistance (R_T, m^{-1}). The effect of temperature is integrated into the equation knowing the permeate (practically water) viscosity (η_w, Pas).

$$J = \frac{\Delta p_{TM} - \Delta\pi}{\eta_W R_T} \quad (L\,m^{-2}\,h^{-1}) \tag{4}$$

It is possible that the glucose molecules in the boundary layer near the membrane play a role in the creation of the osmotic pressure. The van't Hoff model can be applied for this phenomenon which determines the osmotic pressure dependence on the difference of concentrate (c_R, $kmol\,m^{-3}$) and permeate (c_P, $kmol\,m^{-3}$)

concentration ($R = 8314.472\,\mathrm{J\,kmol^{-1}\,K^{-1}}$ universal gas constant, $T = 298.15\,\mathrm{K}$ temperature of experiment).

$$\Delta\pi = (c_R - c_P)RT \quad (\mathrm{Pa}) \tag{5}$$

The concentration of the permeate side (c_P) in all experimental runs was very low $\sim 0.1^{\circ}$Brix, two order of magnitude lower than the retentate concentration. Neglecting the permeate side concentration and introducing the concentration polarization $\beta = c_M/c_R$ in the previous equation, the following formula is obtained:

$$\Delta\pi = \beta c_R RT \quad (\mathrm{Pa}) \tag{6}$$

By the combination of the above equations, the following one is obtained:

$$J = \frac{\Delta p_{TM}}{\eta_w R_T} - \frac{\beta RT}{\eta_w R_T} c_R \quad (\mathrm{L\,m^{-2}\,h^{-1}}) \tag{7}$$

Plotting the permeate flux (J, $\mathrm{L\,m^{-2}\,h^{-1}}$) versus c_R (kmol $\mathrm{m^{-3}}$; Fig. 5), from the intercept of the fitted straight line the average values of the total resistances during the concentration of the blackcurrant juice can be estimated/calculated. From the estimated total resistances it is evident that the highest total resistance has been determined for the Control sample, and the enzyme treated juices had lower total resistances.

Using Eqs. (1)–(3) the individual resistances could be calculated. The results are illustrated in Table 2. The membrane resistance was the same in all cases after effective cleaning, as it was mentioned in experimental procedures. It should be noted that the fouling resistance (R_F) was found to be one order of magnitude lower than the membrane resistance. The highest fouling resistance was measured with Control and with Trenolin enzyme after 1 day treatment.

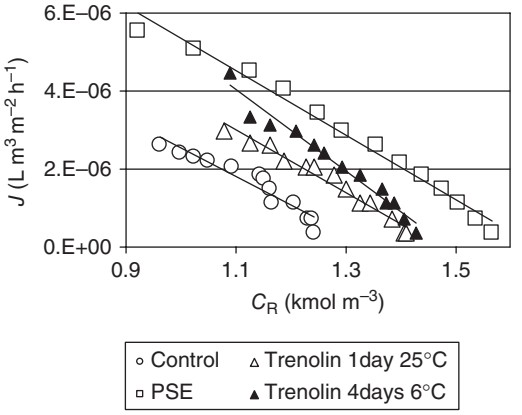

Fig. 5. Influence of retentate glucose concentration during the measurements.

On the other hand, the fouling resistance seemed not to be a determining influence in the matter of permeate flux, because it is an order of magnitude lower than the membrane resistance or the polarization layer resistance, and it has practically no influence on the permeate flux of the juice. The polarization layer resistances are similar to membrane resistance and influenced the permeate flux, the highest was for the Control, which is two times higher than the

Table 2
Calculated resistances of different pretreated juice types

Pretreatment	R_M ($\mathrm{m^{-1}}$) $\times 10^{-14}$ (contribution, %)	R_F ($\mathrm{m^{-1}}$) $\times 10^{-14}$ (contribution, %)	R_P ($\mathrm{m^{-1}}$) $\times 10^{-14}$ (contribution, %)	R_T ($\mathrm{m^{-1}}$) $\times 10^{-14}$ (contribution, %)
Control	2.920 (41.9)	0.199 (2.9)	3.850 (55.3)	6.970 (100)
PSE enzyme	2.920 (58.3)	0.114 (2.5)	1.964 (39.2)	5.025 (100)
Trenolin enzyme (4 days, 6°C)	2.920 (66.1)	0.158 (3.6)	1.338 (30.3)	4.416 (100)
Trenolin enzyme (1 day, 25°C)	2.920 (50.4)	0.196 (3.4)	2.678 (46.2)	5.794 (100)

polarization layer resistance of the PSE enzyme treated juice and also much higher than the Trenolin enzyme treated ones.

It is possible that the glucose molecules in the boundary layer near the membrane play a role in the creation of the osmotic pressure. Due to concentration polarization phenomena, assuming that the TSS in the blackcurrant juice is mostly glucose, calculating the glucose based molar concentrations of the retentate and plotting the flux with this concentration (Fig. 5), from the slopes of the fitted straight lines, the average concentration polarization values for each experiment can be estimated.

The calculated values of the concentration polarization (β) are presented in Table 3. From the data presented in the table it is apparent that the highest concentration polarization effect was observed in the Control and the lowest in the juice treated with PSE enzyme. Taking into account the total resistances (Table 2), the concentration polarization and the normalized flux decreasing rate (Fig. 4), the treatment of the blackcurrant juice to improve filterability of the juice and to reach high end concentration of the retentate, application of the PSE enzyme pretreatment should be recommended in industrial size application. To improve the economy of the concentration of blackcurrant juice by using RO, the optimal enzyme treatment parameters (concentration, temperature and treatment time) should be optimized in the future.

Table 3
Calculated concentration polarization values of different pretreated juice types

Pretreatment	Fitted equation	R^2	β
Control	-7.25×10^{-6} x $+9.78\times10^{-6}$	0.910	2.035
PSE enzyme	-8.21×10^{-6} x $+1.36\times10^{-5}$	0.984	1.467
Trenolin enzyme (4 days, 6°C)	-1.04×10^{-5} x $+1.54\times10^{-5}$	0.969	1.627
Trenolin enzyme (1 day, 25°C)	-7.97×10^{-6} x $+1.188\times10^{-5}$	0.972	1.640

4. Conclusions

The scope of this study was to examine the applicability of a RO process for the concentration of blackcurrant juice by AFC-80 polyamide tubular membrane. Blackcurrant juice is very popular among consumers due to its high content of mineral salts, C-vitamin, P-, B1- and B2-vitamins and also provitamin A.

The different enzyme pretreatment, with two commercially available pectinase enzyme preparation (Panzym Super E and Trenolin Rot DF) of the fresh juice for enzymatic depectinization was investigated. The highest concentration ratio was observed in case of PSE pretreatment. The TSS content of the concentration rose to 28.2 for Panzym Super E., 25.7 for Trenolin Rot at 6°C, 25.4 for Trenolin Rot at 25°C and 22.4 for Control frozen juice. The highest permeate flux of $20\,L\,m^{-2}\,h^{-1}$ and TSS of 28.2°Brix was achieved in the concentration of juice that has been previously depectinized by Panzym Super E. There were no significant differences between the two Trenolin treatments in the terms of permeate flux; therefore, it is advisable that the depectinization process is carried out at room temperature as it does not require the extra energy needed for refrigeration.

The greatest permeate flux was achieved in the concentration of juice that has been previously depectinized by PSE enzyme. The highest drop of flux was observed in case of PSE as a result of the highest concentration and viscosity growth.

During the concentration of blackcurrant juices by RO, the dominant resistances were the membrane resistance and the polarization layer resistance. The depectinization effects of PSE and Trenolin enzymes were obvious, which decreased the different resistances and increased

the flux. PSE strongly decreased fouling, while the effect of Trenolins was lower. The highest concentration polarization effect was observed in the Control and the lowest in the juice treated with PSE enzyme.

Finally, it can be concluded that RO is a viable method for concentration of blackcurrant juice with the applied membrane at 60 bar transmembrane pressure and 25°C operating temperature. To improve the filterability of blackcurrant juice and to reach high end concentration of the retentate, application of the PSE enzyme is recommended in industrial size application.

Acknowledgements

The authors are grateful for the support of this work provided by KPI – GAK2-MEMBRAN5 (OMFB-009972/2005) and RET07/2005 projects. Additonally, Nora Pap acknowledges the financial support of The Graduate School in Chemical Engineering and University of Oulu Foundation.

Nomenclature

A	active membrane filtration area (m^2)
β	concentration polarization
c_P	permeate concentration (kmol m^{-3})
c_R	concentrate concentration (kmol m^{-3})
FDU	ferment depectinization unit
J	permeate flux (L m^{-2} h^{-1} or m s^{-1})
J_0	measured initial permeate flux (L m^{-2} h^{-1} or m s^{-1})
J_F	fouled membrane water flux (L m^{-2} h^{-1} or m s^{-1})
J_w	clean water flux (L m^{-2} h^{-1} or m s^{-1})
η	viscosity of the blackcurrant juice (Pas)
η_W	viscosity of water at 25°C [Pas]
$\Delta\pi$	osmotic pressure difference (Pa)
Δp_{TM}	pressure difference between the two sides of the membrane (Pa)
ρ	density of the blackcurrant juice [kg/m^3]
PCI	Paterson Candy International
R	universal gas constant (J $kmol^{-1}$ K^{-1})
R_F	fouling resistance (m^{-1})
R_M	membrane resistance (m^{-1})
R_P	polarization layer resistance (m^{-1})
R_T	total resistance (m^{-1})
Re	Reynolds number
RO	reverse osmosis
VRR	volume reduction ratio
τ	time (h)
T	temperature (K)
TSS	total soluble solids (°Brix)
V	volume of the permeate (dm^3)

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