Application of Cross-Flow Ultrafiltration on Inorganic Membranes in Purification of Food Materials

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Abstract

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This paper brings data on ultrafiltration on inorganic membranes (MEMBRALOX, France, mean pore size 20 and 100 nm, 0.8 m long, filtration area 0.2 m^2), which were used for the purification of different liquid materials from the food industry; in particular egg blend, amaranth starch suspension, and caramel (i.e. natural colorant). The ultrafiltration was carried out on a pilot plant filtration unit TIA (Bollene, France), cross-flow permeate fluxes being measured at first. Using the experimental data, mathematical models describing membrane fouling were suggested. The obtained permeate steady-state fluxes (40 l/h/m^2 for amaranth starch solution, 20 l/h/m^2 for egg blend and 5–30 l/h/m^2 for caramel) depended partially on the filtration temperature (15–17°C for egg blend, 40°C for amaranth, and 50–70°C for caramel) but mostly on the character of the medium filtered.

Keywords: membrane separation; ultrafiltration; starch suspension; egg blend; caramel

Membrane separation processes find their application in almost all branches of food and biotechnological industry. Apart from the biotechnology, the most wide-spread applications are in dairy and beverage industries, e.g. for whey protein concentration and purification (Schkoda & Kessler 1997), whey desalination and demineralisation, milk standardisation by ultrafiltration, etc. In the beverage industry, membranes are applied for beer and wine stabilisation to prevent the microbial decomposition, for the yeast and colloid removal, or for non-alcoholic beer production by pervaporation (Karlsson & Tragardh 1996). Membranes are also very useful in fruit and vegetable juices production for juice purification by ultrafiltration or concentration by reverse osmosis or nanofiltration (Koseoglu *et al*. 1991). Tests were carried out aimed at the concentration of egg-white using reverse osmosis (Conrad *et al*. 1993). The process was compared with vacuum evaporation. The products obtained by evaporation revealed better foaming properties, however, globulin content was significantly decreased in comparison to the RO product.

Another large area of the membrane process application involves the wastewater treatment, starch industry, edible oil production (Cuperus & Derksen 1995), etc. In starch industry, a great attention is paid to the refinement of raw starch syrups and the eventual replacement of diatomite

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filters with such membrane types that would reduce the amount of waste filtration aids (Singh & Cheryan 1998a, b). Mineral membranes are more utilisable and more efficient in the purification of starch hydrolysate than the conventional techniques (Lancrenon *et al*. 1994; Hinkova *et al*. 2004). However, the permeate fluxes achieved are negatively influenced by membrane fouling (Singh & Cheryan 1997). Therefore, many studies focused on the working conditions during filtration (Ousman & Bennasar 1996) or the properties of the substrate (Szlominska & Grzeskowiak-Przywecka 2004), such as turbidity, viscosity, composition, etc., which all influence the effectiveness of filtration.

Besides the low operation costs, the main advantage of the membrane techniques in food industry resides in that they do not affect the sensory properties and the activity of the biological compounds. For these and many other reasons, new possible applications of the membrane processes are sought.

The aim of this paper is to investigate the possibilities of ultrafiltration on inorganic membranes for the purification and concentration of different real liquid materials from food industry; in particular egg blend, amaranth starch suspension, and caramel (i.e. natural colorant).

MATERIAL AND METHODS

On the whole, five different types of cross-flow ultrafiltration experiments (Filtration I–V) under different conditions were carried out (Table 1) on the pilot-plant filtration unit TIA (Bollene, France – Figure 1) using inorganic membranes (MEMBRALOX, France, 0.8 m long, filtration area of 0.2 m^2 – Figure 2). The filtration was run in the mode of retentate recycling and permeate was removed. Tangential velocity was 5 m/s at the pressure of 0.1 MPa. The filtration module was described in detail in a previous work (Hinková *et al*. 2000).

Table 1. The list of ultrafiltration experiments with various media

Experiment	Filtration I	Filtration II	Filtration III	Filtration IV	Filtration V
Material	amaranth suspension	egg blend	caramel	caramel	caramel
Membrane pore size (nm)	100	20	20	20	20
Temperature (°C)	40	40	49–51	40–65	50–71
Feed-side pressure (kPa)	150	100	200	200	200
Filtration duration (min)	120	50	170	68	123

Table 2. Compositions and amounts of materials used for ultrafiltration

Experiment	Material	Composition	Amount (kg; l)	Dry solids[1] (%)	Dry solids[2] (%)	Colour[3] (1)
Filtration I	amaranth suspension	feed	40 l	–	–	–
Filtration II	egg blend	feed	10 l	–	20.31	–
Filtration III	caramel	concentrate	10.00 kg	81.30	69.06	0.152
		diluted feed	36.72 kg	20.76	–	0.078
Filtration IV	caramel	concentrate	10.00 kg	81.30	69.06	0.152
		diluted feed	34.20 kg	23.94	23.90	0.165
Filtration V	caramel	concentrate	10.00 kg	81.08	68.33	0.162
		diluted feed	27.6 kg	29.98	33.36	0.105

[1]dry solids determined by refractometer; [2]dry solids determined by drying for 3 h at 104°C; [3]colour determined as an absorbance at 560 nm

Figure 1. Filtration unit TIA

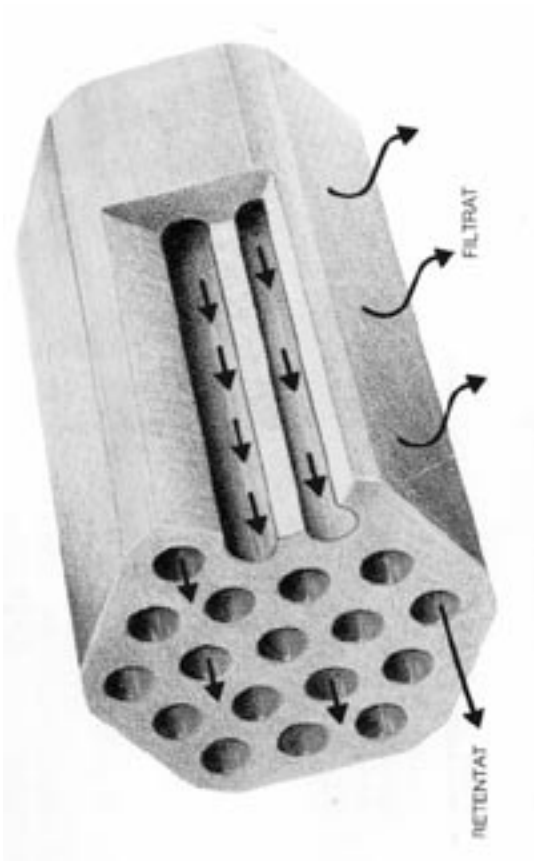

Figure 2. Membranes MEMBRALOX

The samples of caramel were diluted before filtration by the addition of tap water to the concentrate (Table 2). Amaranth suspension (containing 3% of starch and maximum 3% of proteins) and egg blend were used without any pre-treatment.

Different kinds of the settings of the filtration process were tested as well. Amaranth starch solution and egg blend were filtered in one-step purification. Here, we measured the permeate fluxes (expressed as the permeate flow rate achieved under the given conditions from 1 m^2 of the membrane; $l/h/m^2$), calculated the total mass balance and determined the volume concentration ratios (*VCR*) according to formula:

$$VCR = V_F/V_R \quad (1)$$

where: V_F – volume of feed
V_R – retentate volume

Diluted caramel solutions were filtered with gradual additions of water into the feed, thus the individual solutions were diluted several times during filtration. Besides the *VCR*, mass balance and filtration kinetics, the rejection (*R*) of different components on the membrane was evaluated and calculated using equation:

$$R = (c_F - c_P)/c_F \quad (2)$$

where: c_F – concentration of the component in the feed
c_P – concentration of the component in the permeate

RESULTS AND DISCUSSION

Filtration I

During the ultrafiltration of the amaranth suspension, we achieved a *VCR* of 5 after 120 min of the filtration (Figures 3 and 4). The membrane fouling was expressed by equation (3) obtained from the experimental data:

$$J_i = 0.0001\tau^2 - 0.027\tau + 44.45 \quad (3)$$

where: J_i – the permeate flux ($l/h/m^2$)
τ – time (min)

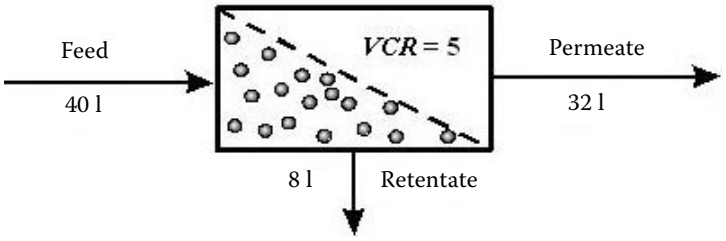

Figure 3. The mass balance of amaranth suspension filtration (filtration I)

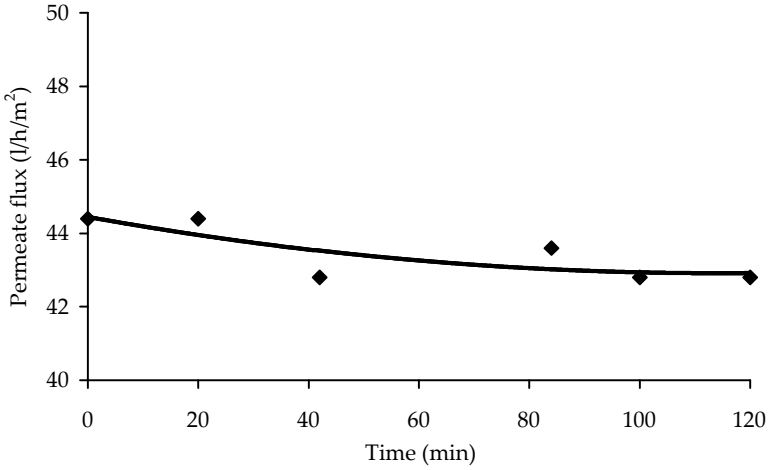

Figure 4. The permeate flux during amaranth suspension filtration (filtration I)

Although the membrane fouling was not so rapid, the permeate flux was very low to comply with the possible industrial application. The experiment had to be discontinued after 120 min due to an intensive foam formation (caused by the presence of proteins and other surface-active compounds) and the high risk of the foam intake into the centrifugal pump. However, the concentration of the retentate obtained (containing about 15% of starch) was sufficient. Further tests with membranes of a lower mean pore size, higher pressures or temperatures need to be carried out to verify the possible application.

Filtration II

We tested the possibility to concentrate egg blend to improve the microbiological stability in this experiment. The *VCR* achieved was 1.9, and the retentate dry solids content obtained was 35.5% after 50 min of the filtration (see mass balance in Figure 5). The permeate flow was even lower compared to the amaranth filtration (about 20 l/h/m^2 at the temperature of 40°C).

The restoration of the water flux after the filtration was very complicated; we had to use a three-step purification process consisting of: (a) 1% sodium hypochlorite (i.e. bleach) at 60°C for 60 min, (b) 1% nitric acid at 60°C for 60 min, (c) distilled water back-flushing for 40 min. Ultrafiltration can improve the microbial stability due to the removal of bacteria, however, the permeate fluxes and thus the effectiveness of the process are low.

Filtration III

A diluted caramel solution (initial dry solids content 29.3%) was further diluted two-times during ultrafiltration; the first addition of water (5.6 kg) was made in the 85th min of the filtration when

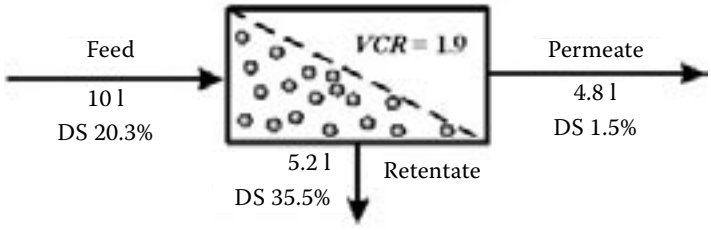

Figure 5. The mass balance of egg blend filtration (filtration II); DS – dry solid

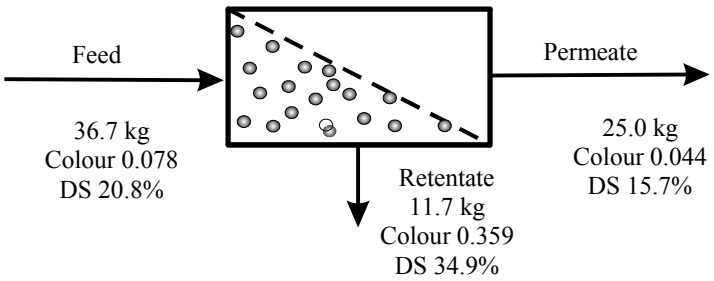

Figure 6. The mass balance of caramel solution (filtration III); DS – dry solid

the dry solids content in the feed reached 33% and the permeate flux decreased rapidly, the second water addition (5 kg) followed in the 100th min. The filtration was further carried out without any dilution with water until we achieved dry solids content of 40.3% and colour content 0.450. At this moment (154th min), the risk of the irreversible membrane fouling was so high that we decided to dilute the feed with permeate (6 kg), however, the fouling was so severe that we were not able during further filtration to concentrate the retentate up to 40% again and the experiment was discontinued (170th min). Thus, the DS of retentate obtained was 34.9% and colour 0.36 only.

The mass balance of the process (Figure 6) and the rejection are shown in Table 3. It is evident that colour substances are retained 1.8-times faster than the dry solids. That is why we can obtain a retentate with a higher content of colour substances compared to the concentrate (Table 2) and a lower dry solids content.

The process kinetics is shown in Figure 7. The permeate flux declined rapidly from the initial 110 l/h/m^2 during the first 60 min. The fouling was retarded by water addition (85th and 100th min). During further concentration, the flux dropped slowly to 10–20 l/h/m^2. It is evident that the fastest fouling occurs at the beginning stage of filtration when the dilution of feed has the most significant effect on the permeate flux increase. The slight flux increase in the 166th min was due to the feed dilution with the permeate, which negatively affected the colour content in the retentate.

Filtration IV

The permeate and the retentate from filtration III were mixed and used again for ultrafiltration IV. The caramel was continuously concentrated with

Table 3. The total mass balance and concentration of components during filtration III

Total mass balance	Weight (kg)	Dry solids[1] (%)	Colour[2] (1)
Retentate	11.76	34.87	0.359
Permeate	24.96	15.68	0.044
Feed	36.72	20.76	0.078
Rejection	–	24.5	43.0

[1]dry solids determined by refractometer; [2]colour determined as an absorbance at 560 nm

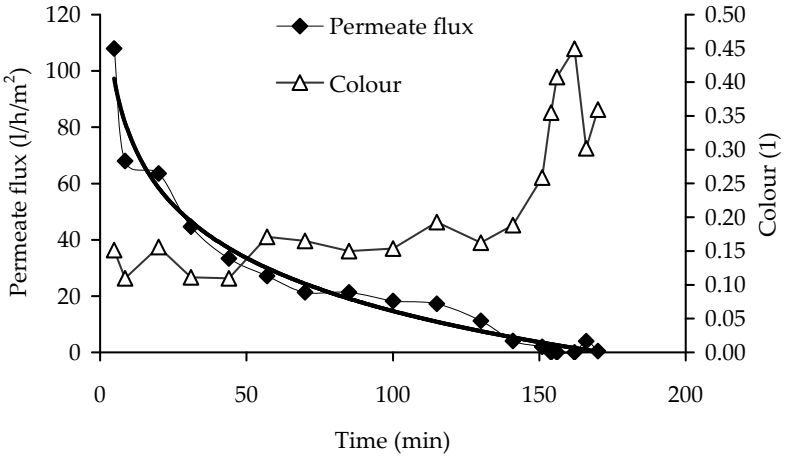

Figure 7. The permeate flux and colour substance content in retentate during filtration III

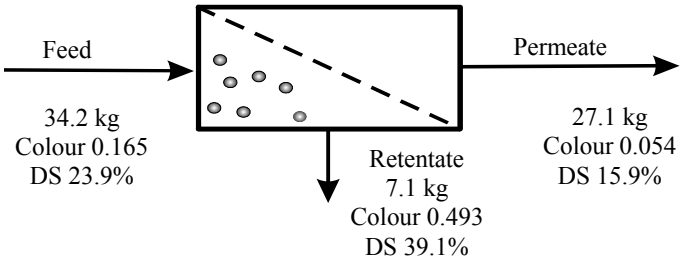

Figure 8. The mass balance of caramel solution (filtration IV); DS – dry solid

no water addition; for a higher permeate output, the temperature was increased up to 65°C. The total mass balance (Figure 8) was calculated from the experimental data. The duration of filtration was 68 min.

Filtration was carried out on a membrane fouled in the previous experiment (Filtration III), thus the permeate fluxes were very low (5 l/h/m^2) although the temperature was increased. Therefore, we focused mainly on the quality of the retentate obtained, which is important from the technological point of view.

Table 4 shows that the retention of dry solids was higher by 10% as compared to filtration III. Also, the colour substance retention was higher but this increase was apparent only due to the turbid retentate which affected negatively the absorbance measurement. The retentate contained 39% of dry solids and the colour was 0.493.

Filtration V

In this experiment we tested the possibility to improve the permeate flux by gradual feed dilution from the early beginning of the filtration when the fouling is the most rapid. Simultaneously, we wanted to prevent high feed dilution, which causes an unsatisfactory retentate concentration and a longer time is needed for filtration. Therefore, the caramel concentrate was at first diluted up to 40% of dry solids and then, after the first 10 min, about 3.8 kg of water was added to the feed. This was repeated in the 20th min. That is why the dry solids content in the feed did not drop under 30% during the whole filtration process.

From Table 4 it is evident that the colour substance retention is 2-times higher than the retention of dry solids, which is comparable with the rejection of filtration III and IV. Thus, we can

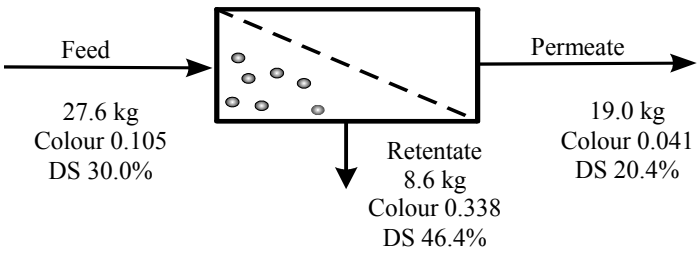

Figure 9. The mass balance of caramel solution (filtration V); DS – dry solid

Table 4. The total mass balance and concentration of components during filtrations IV and V

Total mass balance	Filtration IV				Filtration V			
	weight (kg)	dry solids[1] (%)	dry solids[2] (%)	colour[2] (1)	weight (kg)	dry solids[1] (%)	dry solids[2] (%)	colour[2] (1)
Retentate	7.07	39.14	30.7	0.493	8.6	46.38	32.82	0.338
Permeate	27.13	15.93	13.84	0.054	19.0	20.39	18.36	0.041
Feed	34.20	23.94	23.9	0.165	27.6	29.98	33.36	0.105
Rejection	–	33.5	–	67.3	–	32.0	–	61.0

[1]dry solids determined by refractometer; [2]dry solids (DS) determined by drying for 3 hours at 104°C; [3]colour determined as an absorbance at 560 nm

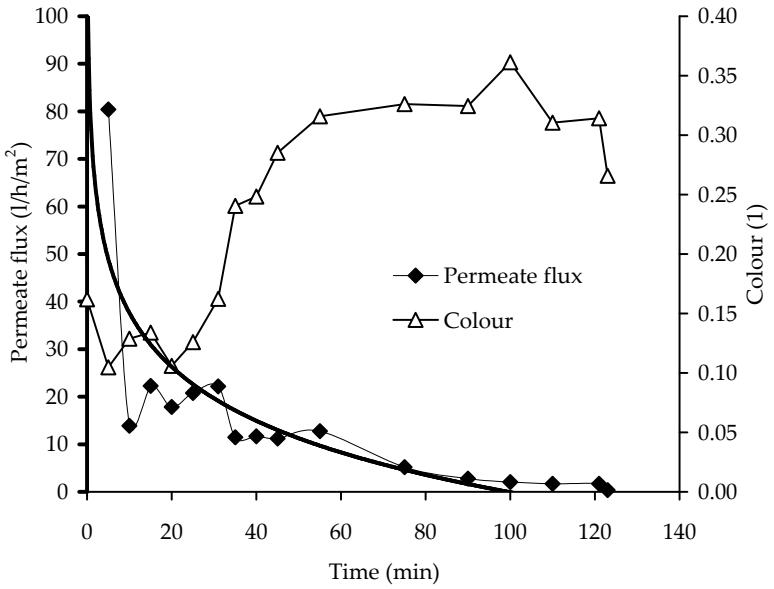

Figure 10. The permeate flux and colour substance content in retentate during the filtration

obtain retentates with 46% of dry solids and colour of 0.34 (mass balance in Figure 9).

Process kinetics is shown in Figure 10 together with the amount of the colour substances present in the retentate. The permeate flux declined rapidly from the initial 80 l/h/m^2 to 15 l/h/m^2 during the first ten minutes. It partly increased by dilution with water. During the following 20 min, the permeate flux remained between 10 and 20 l/h/m^2 and then it dropped again to the value of 0.5 l/h/m^2. The colour substance content did not improve in the final stage of the filtration (beginning in the 55th min), thus the filtration was stopped at this moment.

CONCLUSIONS

The experiments were aimed at the verification of the possible ultrafiltration applications for the concentration and purification of food materials, i.e. amaranth starch suspension, egg blend, and caramel. The required concentration of the respective product was achieved in most experiments; amaranth starch solution was concentrated 5-times, egg blend approximately 2-times in one-step ultrafiltration process.

The caramel solution was filtered under gradual dilution with water added into the feed. The retention of the colour substances was 2-times higher than the retention of dry solids, thus the resulting retentate contained a higher amount of colour substances and a lower amount of dry solids as compared to the initial caramel concentrate. The composition of permeates and retentates with all caramel filtrations is shown in Table 5. Filtrations III and V show similar distributions of colour substances and dry solids between the permeate and the retentate. The results obtained with filtration IV were affected by the turbidity of the retentate.

The addition of water into the caramel solution enables to increase the colour content in the prod-

Table 5. Composition permeates and retentates for all caramel filtrations

Mass balance		Dry solids (%)	Colour substances (%)
Filtration III	content in retentate (i.e. in product)	51	79
	content in permeate (i.e. in waste)	49	21
Filtration IV	content in retentate (i.e. in product)	39	70
	content in permeate (i.e. in waste)	61	30
Filtration V	content in retentate (i.e. in product)	51	79
	content in permeate (i.e. in waste)	49	21

uct (i.e. in the retentate), but large volumes cannot be added because of the possible colloid instability and turbidity formation in the product.

The permeate steady-state fluxes achieved (40 l per h/m^2 for amaranth starch solution, 20 l/h/m^2 for egg blend and 5–30 l/h/m^2 for caramel) are, however, very low to comply with the industrial application and further tests to limit the membrane fouling would be necessary.

List of symbols and abbreviations

c_F	component concentration in feed (%)
c_P	component concentration in permeate (%)
DS	dry solids
J_i	permeate flux (l/h/m^2)
R	rejection (1)
RO	reverse osmosis
VCR	volume concentration ratio (1)
V_F	feed volume (l)
V_R	retentate volume (l)
τ	time (min)

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