Two-stage whey treatment by nanofiltration and reverse osmosis

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Abstract

Introduction. Treatment of whey, which is a by-product of cheese manufacturing process, is of great interest for dairy industry due to its high content of valuable and nutritional compounds. Although the development of complex whey treatment by membrane processes and use of its derivative products is still current.

Materials and methods. The raw whey and permeate after nanofiltration of whey were used for the study. The experiments were carried out in the pressure-driven laboratory setup of dead-end type using nanofiltration OPMN-P and reverse osmosis NanoRo membranes.

Results and Discussion. Considering high lactose content in whey and results obtained during lactose solutions filtration using OPMN-P membrane, it was proved that whey should be concentrated by nanofiltration to total solids of 20-22%. During whey concentration it was observed two stages of permeate flux decrease: rapid decrease of flux at the beginning of the process and further gradual flux decrease. The first is caused by membrane fouling and the latter is attributed to concentration polarization, formation and growth of the cake layer.

From the analysis of the obtained permeate flux-pressure and retention-pressure curves for reverse osmosis membrane NanoRO it was found that the rational value of pressure for the concentration of nanofiltration whey permeate is 3.0 MPa. At this pressure, permeate flux decreased twice with increase of solution concentration from 6 to 40 g/L, while average salt and lactose retention was 96.0% and 97.5% respectively. Based on the obtained results, the scheme of two-stage whey treatment was developed.

Conclusions. The obtained results of the study on two-stage whey treatment by nanofiltration and reverse osmosis can be used in the technology of complex whey processing in the dairy plant. It allows using all the whey components, obtaining the purified water for reuse and partially eliminating problem of environmental pollution by dairy plants.

Introduction

Whey is a by-product of cheese production which is rich in valuable components. Up to 1960's it was considered to be a waste of cheese manufacture, until the beginning of application of membrane processes in the dairy industry. Whey contains lactose (4.0-5.0%), proteins (0.6-1.0%), minerals (0.5-0.9 %), e.g., calcium, magnesium, phosphorus, vitamins, and milkfat in small concentrations [1-3]. It cannot be discharged to the environment or released into wastewaters because of its high content of organic compounds, high volume (often 90% of the mass of milk used) and its extremely high biological and chemical oxygen demand.

Nowadays, whey treatment by membrane processes is of great interest for researchers as via their using it is possible to recover useful products and to alleviate the pollution problem. The advance of whey treatment is caused by three main factors: an increase in costs of its release, the emergence of new technologies in extraction of whey protein and scientific researches, due to which valuable nutritional and biological properties of this product was found.

Among the membrane processes nanofiltration is the most suitable process for pre-concentration and partial demineralization of whey at the same time [4-6]. Due to high permeability of nanofiltration membranes for monovalent salts (such as NaCl, KCl) it is possible to remove them from whey. Monovalent ions (sodium, potassium and chloride) are undesirable components of food products due to their salty taste and negative health impacts [7, 8]. Moreover, such pre-concentration by nanofiltration is desirable before further whey treatment by electrodialysis for deep demineralization [9]. It can be explained by increasing whey conductivity and reducing its volume that results in lowering of load on electrodialysis equipment and increasing its efficiency [10]. However, nanofiltration membranes have low permeability for organic compounds with molecular weight less than 300 Da. That's why nanofiltration permeate may contain some lactose (up to 0.3%) that mainly depends on the nanofiltration membranes properties [11-14].

Whey permeate, which volume is approximately 65% of treated whey, is not usually used and is discharged to the waste. Considering the current demands to the composition and concentration of wastewaters its chemical oxygen demand must not exceed 500 mg O_2/dm^3. Although, according to the literature data, chemical oxygen demand of nanofiltration whey permeate can reach up to 3000 mg O_2/dm^3 [5, 15], mainly because of the lactose. Therefore, it must be pretreated before be released. The most appropriate method for its purification is reverse osmosis since reverse osmosis membranes allow concentrating and removing all the solutes presented in the feed and obtaining water for reuse.

The aim of this work was to study two-stage whey treatment by nanofiltration and reverse osmosis for the development of the whey processing technology. The choice of NF in the first stage was based on higher water flux at lower pressure. Reverse osmosis was chosen for the second stage due to high lactose and minerals rejection.

Materials and methods

The raw whey was used for the experiments. Its composition is presented in the Table 1. "Edible" lactose was used for preparation of model solutions of lactose.

Table 1

Composition of whey

Parameter	Fat	Protein	Lactose	Mineral salts	Dry matter
Concentration, %	0.35	1.0	3.5	0.7	6.0

A pressure-driven laboratory setup of dead-end type (Fig. 1) with membrane effective area of $1.38 \cdot 10^{-3}$ m^2 was used for the study of membrane separation of whey and its nanofiltration permeate. It consists of gas cylinder (not shown), membrane cell and magnetic stirrer 4. The membrane cell include two covers 1, 2 and metal cylinder 10. The porous support 6 and membrane 5 were placed in its bottom part and pressed by metal cylinder 10. Stir bar 3 impelled by magnetic stirrer 4 was put over the membrane 5. The special hole was made in the bottom cover 2 of the membrane cell for collecting permeate through the tube 11. With open fittings 7 and 8, a feed solution was introduced through one of them into the working chamber. Pressure gauge 9 was attached to fitting 8 for monitoring pressure in the middle of the unit and fitting 7 was connected to a pressure regulator mounted on the inert gas cylinder (not shown). The working pressure in the cell was created by opening the valves on the gas cylinder and the pressure regulator 12. The temperature of solutions during the experiments was in the limits 20±2°C. The temperature inside the membrane cell was measured controlled by thermal couple 13.

Nanofiltration membrane OPMN-P (ZAO STC "Vladipor", Russian Federation) was used for whey concentration. Reverse osmosis membrane NanoRO (ZAO "RM Nanotech", Russian Federation) was used for separation of nanofiltration whey permeate. Before separation, each membrane was soaked in deionized water for at least 12 h. Then they were compacted at pressure of 2.0 MPa for nanofiltration membrane and 4.0 MPa for reverse osmosis membrane by filtering distilled water through them until a steady flux was established.

The chemical composition of feed, retentate and permeate was determined by standard methods. Dry matter content was measured by a refractometer URL-1. Lactose concentration was determined by iodometric method. The mineral salts content was measured by a conductivity meter (HANNA Instruments DIST 1). Ion content of Ca^{2+}, Mg^{2+} was determined by atomic absorption (Pye Unicam 8800 UV/VIS, Philips). K^+, Na^+ ion content was measured by flame photometer (PFM-U4.2, Analitpribor).

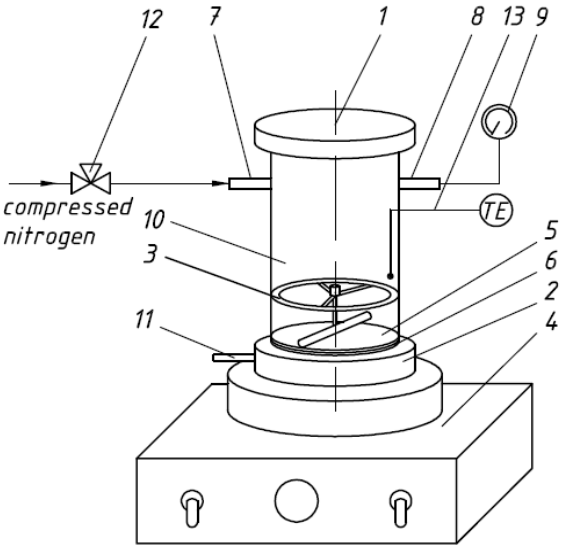


Fig. 1. Schematic diagram of the dead-end laboratory setup:
1, 2 – covers; 3 – stir bar; 4 – magnetic stirrer; 5 – membrane; 6 – porous support; 7, 8 – fittings; 9 – pressure gauge; 10 – metal cylinder; 11 – tube for permeate outlet; 12 – pressure regulator; 13 – thermal couple.

Permeate flux J (L/(m^{-2}·h^{-1}) is the volume of permeate V (L) collected per unit membrane area S (m^2) per unit time t (s):

$$J = \frac{3600 \cdot V}{S \cdot t}. \tag{1}$$

The membrane retention R of any feed component was calculated as:

$$R = \left(1 - \frac{C_P}{C_R}\right) \cdot 100\%, \tag{2}$$

where C_P and C_R are the permeate and the retentate concentrations respectively.

Volume reduction ratio (VRR) vs. time was calculated as:

$$VRR = \frac{V_f(t)}{V_R(t)} = \frac{V_f(t)}{V_f(t) - V_P(t)}, \tag{3}$$

where $V_f(t)$, $V_R(t)$, $V_P(t)$ is the feed, retentate and permeate volume at time t, respectively.

Results and discussion

Analyzing the composition of whey (Table 1) [1, 2] it can be seen that lactose is up to 70% of its total solids. It is very important to concentrate all the lactose while whey processing because of its high chemical oxygen demand. That's why lactose rejection of nanofiltration membrane OPMN-P must be high. Therefore the separation characteristics of OPMN-P membrane were previously studied during filtration of lactose solutions.

Lactose filtration was carried out at pressure of 2.0 MPa. The obtained results are presented in Fig. 2. It can be seen that increase of lactose concentration from 5 to 18% leads to permeate flux decrease approximately by 10 times while lactose retention is very high and remains almost constant within 98%. The decrease in permeate flux is caused by concentration polarization and increase in osmotic pressure of the solution near the membrane surface. The osmotic pressure of lactose solution at concentration of 5% and 18% is 0.4 and 1.28 MPa respectively. Besides, the initial lactose crystallization may occur at high lactose concentration. Saturation of aqueous solution with lactose happens at concentration of 19.2 g /100 g H_2O at temperature of 20 °C [16]. Thus whey should be concentrated to dry matter content of 20-22%. High retention of OPMN-P membrane is probably caused by formation of dynamic membrane on membrane surface that additionally prevents lactose penetration through nanofiltration membrane into permeate. This phenomenon was discussed in the previous paper during reverse osmosis of lactose solutions [17].

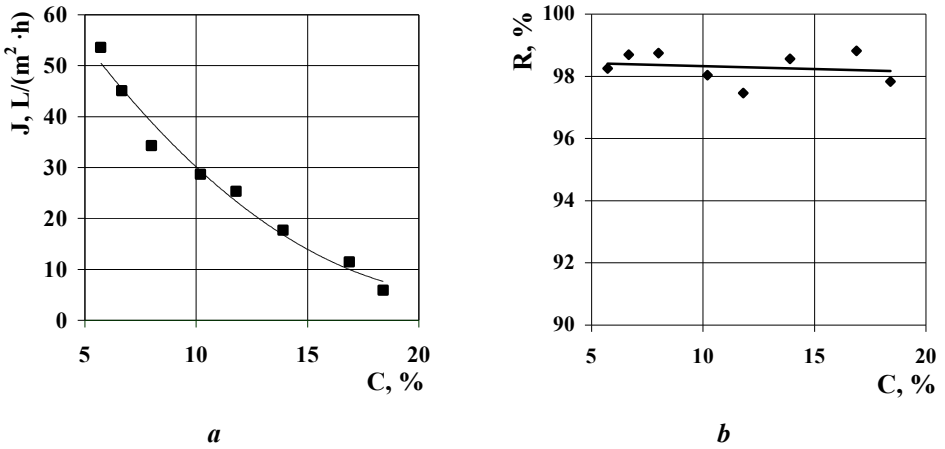


Fig. 2. Dependence of permeate flux *J* (a) and retention *R* (b) of OPMN-P membrane on concentration *C* of lactose solution (*ΔP*=2.0 MPa, t=20 °C)

Whey concentration by nanofiltration was performed at 2.0 MPa that corresponds to high permeate flux and retention as was established in paper [12]. Appliance of higher pressure can cause severe membrane fouling and pore blocking [18]. Lower pressure is insufficient because of the low permeate flux and large membrane area needed for separation.

In Fig. 3 permeate flux is plotted vs. dry matter content during the concentration of whey. It can be observed that flux decreases with concentration mainly due to the increase in the osmotic pressure. The curve at the Fig. 3 can be divided into two parts: the rapid

permeate flux decrease at the beginning of the filtration and further gradual flux decrease. At the first stage, flux reduced almost twice, when the concentration of 8% was reached. The reason of this can be fouling of the membrane by whey components caused by adsorption of proteins on membrane surface [19]. Due to large molecular size of proteins, i.e. α-lactalbumin (3.0 nm), β-lactalbumin (4.0 nm), caseins (25-130 nm), its low mobility and small pore size of nanofiltration membrane (in the range of 0.1-1.0 nm) they deposit on membrane surface and form a dynamic membrane. At the second stage, the further decrease of permeate flux is attributed to concentration polarization, formation and growth of the cake layer [11, 19]. A cake layer is formed mainly of salts (calcium and phosphate ions) and partially of lactose. This layer creates an additional resistance to permeate flow.

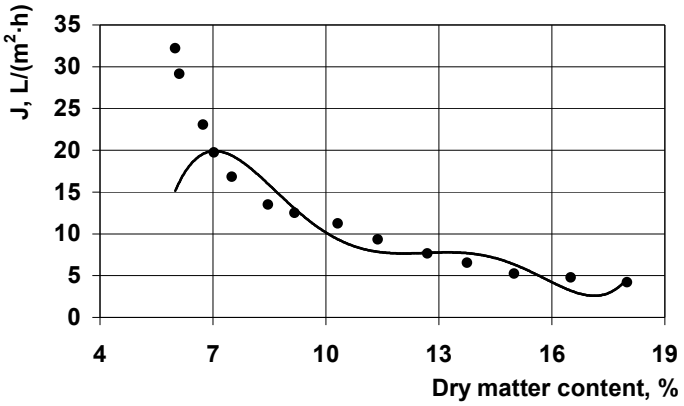


Fig. 3. Relationship of the permeate flux as a function of the dry matter content for OPMN-P membrane during whey concentration (*ΔP*=2.0 MPa, t=20 °C)

The whey concentration was carried out until dry matter content reached 18-19%. At this point the permeate flux was less than 5 L/(m^2·h) (Fig. 3). Retention of OPMN-P membrane was high for macromolecular substances (fat and protein). Lactose retention was in the range of 93-96% during whey concentration, and minerals retention was 56-62%. The composition of obtained permeate is shown in Table 2. As it can be seen, nanofiltration whey permeate consists of lactose (50% of total solids) and minerals (50%) presented by multivalent ions Ca^{2+}, Mg^{2+} and monovalent ions Na^{+}, K^{+}, Cl^{-}. In the complex processing technology for whey this permeate should be concentrated by reverse osmosis.

Table 2

Composition of nanofiltration whey permeate

Parameter	Total solids	Lactose	Minerals	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Cl^{-}
Value, g/L	6,0±0,1	3,0±0,1	2,9±0,1	0,015	0,009	0,264	1,248	1,364

The dependence of the permeate flux and retention for NanoRO membrane on pressure is shown in the Fig. 4 during filtration of whey permeate. It can be observed almost proportional rise of permeate flux J to the increase of the pressure ΔP to 4 MPa (Fig. 4 curve 1). Retention R for dry substances (Fig. 4 curve 2) increases with pressure up to a transmembrane pressure of 3.0 MPa. It increases slowly from 3.0 to 4.0 MPa, and obviously it will remain constant with further pressure rise. Based on this, pressure of 3.0 MPa was chosen to minimize energy consumption and to perform concentration of nanofiltration whey permeate by reverse osmosis.

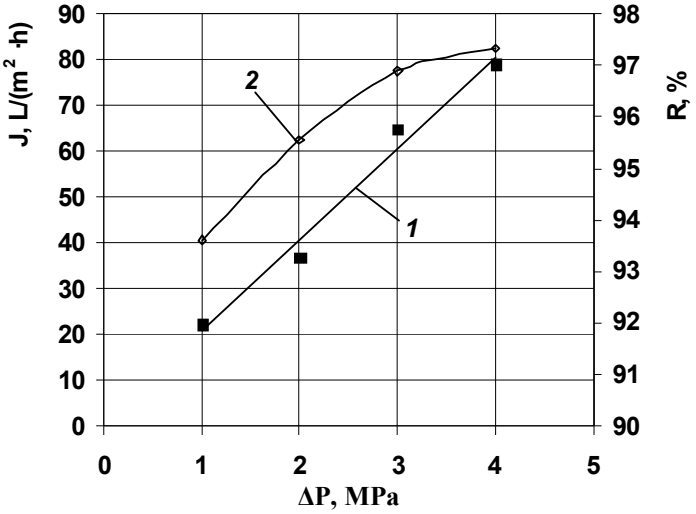
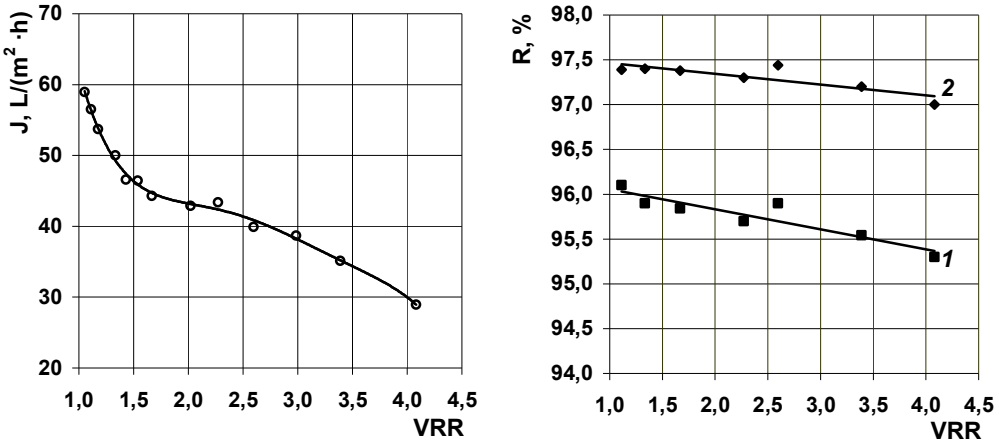


Fig. 4. Experimental data on separation of nanofiltration whey permeate for reverse osmosis membrane NanoRO:
1 – relationship of the permeate flux J as a function of the pressure ΔP;
2 – relationship of retention R as a function of the pressure ΔP.

During concentration of nanofiltration whey permeate, flux decreased continuously with increasing VRR, i.e. feed concentration factor (Fig. 4 a). It reduced in 15 L/(m^2·h) when VRR 1.5 was reached. At concentration factor higher than 1.5, the flux decreased gradually. This fact can be explained as a consequence of the concentration polarization layer formation on the membrane surface and membrane pore blocking by solution components. The pore blocking increases the membrane resistance while the retained particles on membrane creates an additional layer of resistance to the permeate flow. It also leads to the raise of osmotic pressure of the solution. At the end of the filtration, the concentration of nanofiltration whey permeate was 40 g/L including 26.2 g/L of lactose and 13.8 g/L of minerals.

Retention for lactose and minerals decreased gradually with VRR increase (Fig. 4 b). It can be explained as follows: due to formation of concentration polarization layer on membrane surface the filtration through the membrane occurs from the layers with the enhanced concentration. Thus the permeate concentration increases and retention decreases. The average salt retention was 96.0% and lactose retention was 97.5%. As the result, permeate contained 0.21 g/L of lactose and 0.12 g/L of mineral salts.



a *b*

Fig. 4. Permeate flux *J* (a) and retention *R* (b) of NanoRO membrane during the concentration of nanofiltration whey permeate (Δ*P*=3.0 MPa):
1 – minerals; 2 – lactose.

The scheme of two-stage whey treatment was developed based on the results of the study (Fig. 5). It includes nanofiltration at the first stage and reverse osmosis at the second. The obtained whey retentate after nanofiltration can be further concentrated up to 50% total solids by evaporation or demineralized by electrodialysis. The retentate after reverse osmosis can be used in non-lactose milk production to recover the mineral salt content [RU Patent No. 2305196, 2007]. Reverse osmosis permeate with low lactose and salt content can be discharged or used for cleaning, pre-rinsing, for washing floors and the outside of plant and vehicles. Such a two-stage membrane treatment allows all the whey components to be completely used and up to 90% of purified water on the amount of treated permeate after nanofiltration of whey to be received that can be reused in the dairy plant.

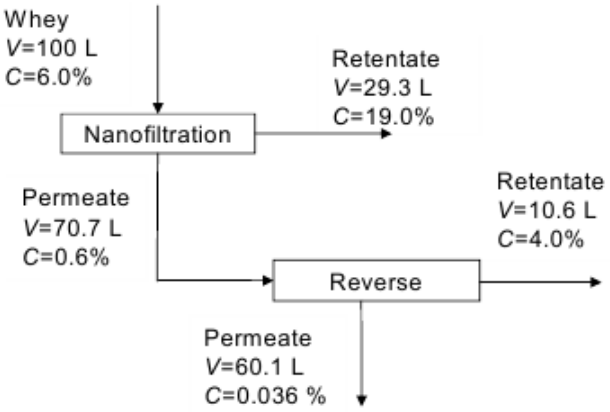


Fig. 5. Material flows on the process flow diagram of two-stage whey treatment by nanofiltration and reverse osmosis:
V – volume of the solution; C – concentration of total solids.

Conclusions

Based on the results of the study it can be concluded that whey should be concentrated to total solids of 20-22% by nanofiltration according to the results of lactose solutions separation by nanofiltration. It was found that nanofiltration whey permeate contains 50% of organic compounds (lactose) and 50% of inorganic components. Due to its high chemical oxygen demand it should be previously treated before be discharged. The rational pressure for its concentration by reverse osmosis is 3.0 MPa. The benefit of using NF+RO cascade treatment of whey is full use of its components and the recovery of water suitable for reuse in the dairy plant.

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