Treatment of dairy effluent model solutions by nanofiltration and reverse osmosis

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Abstract

Introduction. Dairy industry generates a large amount of wastewaters that have high concentrations and contain milk components. Membrane processes have been shown to be convenient for wastewater treatment recovering milk components present in wastewaters and producing treated water.

Materials and methods. The experiments were carried out in an unstirred batch sell using nanofiltration membranes OPMN-P (ZAO STC "Vladipor", Russian Federation) and reverse osmosis membranes NanoRo, ZAO ("RM Nanotech", Russian Federation). The model solutions of dairy effluents – diluted skim and whole milk were used.

Results. The nanofiltration and reverse osmosis membranes showed the same permeate flux during the concentration of model solutions of dairy effluents. The reason of this was likely membrane fouling with feed components. The fouling indexes indicated the fouling factor that was higher for RO. The higher permeate quality was obtained with RO membranes. The NF permeate containing up to 0.4 g/L of lactose and 0.75 g/L of mineral salts can be discharged or after finishing treatment (e.g. RO or other) can be reused. The obtained NF and RO retentate corresponds to milk in composition and can be used for non-food applications or as feed supplement for animals.

Conclusions. The studied RO and NF membranes can be used for concentration of dairy effluents at low pressure. They showed better performance and separation characteristics comparing with data of other membranes available in the literature.

Introduction

Dairy industry generates a large amount of wastewaters, from 0.2 to 10 L of effluent per liter of processed milk [1] with an average value of about 2.5 liters of wastewaters per liter of the milk processed [2]. The effluents are produced in the starting, equilibrating, stopping and rinsing steps of the processing units [3] and during cleaning operations, especially between product changes. They are composed of milk components (lipid, protein and lactose) with cleaning chemicals (acids, alkalis and detergents). The dairy effluents are high loaded and have high concentrations. The first rinsing waters generated from the washing operations have the main contribution to the dairy effluents pollution load, since they content all components of milk. Because of its high chemical and biological oxygen demand and its high concentration the dairy wastewaters must be treated prior to discharge to the environment.

Dairy industry effluents are generally treated using biological and physico-chemical methods. Among these methods, membrane processes have been shown to be convenient for wastewater treatment [1, 4-8]. Membrane treatment of dairy wastewaters could simultaneously lower the total water consumption and the effluent production of the dairy plant by recovering milk components present in wastewaters (lactose, proteins) and producing treated water [3, 9, 10]. Several works dedicated to dairy wastewater treatment by membrane methods showed that one (UF, NF, RO) or two stage (NF+RO, RO+RO, UF+RO) operations allow recovering nutrients and producing reusable water [1, 3- 5, 11-13]. However, high transmembrane pressure (especially for RO) and membrane fouling weaken its application.

In this study, we investigated NF and RO concentration of dairy effluent model solutions (flushing waters, first rinse waters) by dead-end filtration at low pressure. The studied membranes were OPMN-P and NanoRo membranes (of Russian production) since they are cheaper and more available for Ukraine enterprises, and in addition their separation properties are poorly studied in this field.

Materials and methods

Dairy effluent model solutions. The dairy effluents are mainly generated in cleaning and washings steps of processing units. They are mixtures of water and milk without chemicals of various compositions (flushing waters, first rinse waters). Composition and concentration of these waters varies greatly and depend on the dairy plant main product and on the processing units used. That's why model solutions were used for the experiments to compare NF and RO. The solutions were prepared from skim and whole milk diluted with deionized water (dilution 1:4.5 and 1:5, respectively). The main characteristics of these model process waters are shown in Table 1.

Table 1

Main characteristics of dairy model effluent solutions

Characteristics	Skim milk	Whole milk
Fat, g/L	0.06-0.07	4.10-4.30
Proteins, g/L	4.40-4.60	4.45-4.70
Lactose, g/L	6.60-6.90	7.40-7.80
Mineral content, g/L	0.53-0.63	0.59-0.60
pH	6.45	6.7
Dry matter, g/L	17-18	18-20

Membranes. Two commercially available membranes were used in this study: one NF membrane OPMN-P (ZAO STC "Vladipor", Russian Federation) and one RO membrane NanoRo (ZAO "RM Nanotech", Russian Federation) with a NaCI rejection of 99.5%. Membranes are thin-film composite (NanoRo) with an active polyamide layer.

A new membrane was used for each experiment. New membranes were soaked in deionized water for at least 12 h prior to use. Once installed, each membrane was compacted at a high pressure (2.0 MPa for NF, 4.0 MPa for RO) until reached steady-state conditions. The membrane pure water permeability was measured with deionized water at 20 °C before each experiment. After the filtration, membranes were flushed with deionized water and then pure water permeability was measured again to calculate irreversible fouling for each membrane. Then membrane was cleaned with a 0.1% NaCl solution (pH=8) for 20 minutes at 20 °C. After cleaning membrane permeability was checked again.

Experimental set-up and procedure. The dead-end filtration was performed in a laboratory-constructed magnetically stirred cell in concentration mode. A detailed description of the cell used can be found in a previous paper [16]. The working volume of the cell was 200 mL. The working pressure in the cell, applied by a nitrogen tank, was 1.0 MPa for NF and RO membranes. The membrane sheet area was $1.38 \cdot 10^{-3}$ m^2. Stirring of the solution was provided with a two blades stirrer.

The filtration unit can concentrate the solutions up to VRR 2 due to dead volume. Thus, to reach a higher concentration of retentate, the filtration was performed in several steps. The experiments were carried out until permeate flux decreased to 5-6 $L \cdot h^{-1} \cdot m^{-2}$.

Analysis. During experiments, feed, retentate and permeate were sampled and assessed for fat, proteins, lactose and mineral salts content.

Dry matter content was measured by a refractometer URL-1. The protein concentration in solution was measured using AM-2 unit. Lactose concentration was determined using iodometric titration GOST 8764. Fat concentration was determined by Gerber method GOST 5867-90. The mineral salts content was measured by a conductivity meter (HANNA Instruments DIST 1) and pH was measured with a pH-meter (Ionomer 120M).

For the different components, the observed rejection of the membrane was obtained by the following equation:

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

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

Calculated parameters. Permeate flux J was calculated according to following equation

$$J = \frac{3600 \cdot V}{S \cdot t} , \qquad (2)$$

V is permeate volume obtained at time t from the membrane area S.

Volume reduction ratio (VRR) vs. time

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

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

The pure water permeability L_p was calculated as follows:

$$L_p = \frac{J}{\Delta P}, \quad (4)$$

where J is the permeate flux of deionized water, ΔP is applied pressure.

The irreversible fouling index (*IF*) can be expressed as a percentage of pure water permeability decrease after the experiment.

$$IF = \frac{L_{pi} - L_{pf}}{L_{pi}} \cdot 100\% \quad (5)$$

L_{pi} and L_{pf} are the initial and final pure water permeability, respectively.

Results and discussion

Permeate flux. The dead-end filtration of effluent model solutions was performed in the continuous concentration mode to about VRR 6. During filtration experiments permeate flux decreased continuously with increase of retentate concentration (Fig. 1). As it can be seen (Fig. 1) permeate flux from the NF membranes was not higher than from RO ones during concentration of model solutions of skim and whole milk in spite of different membrane characteristics, although it was expected that NF flux would be higher. It was likely due to membrane fouling by the feed components and their adsorption on to the membrane surface, especially proteins [3]. One should note here that permeate fluxes were slightly lower for NF and RO membranes during concentration of model solutions of skim milk. Comparing the obtained fluxes with those in papers [1, 3, 12] it can be seen that the fluxes of studied membranes (OPMN-P and NanoRo) at 1.0 MPa are the same as of membranes in [1, 3, 12] at higher pressure of 2.0-2.5 MPa. Obviously, these membranes have better performance and can be used for concentration of dairy effluents at lower pressures reducing energy consumption.

Although permeate fluxes were almost similar for NF and RO during concentration of model solutions the fouling indexes were different. The fouling indexes indicated the fouling factor of membranes with feed components. As it was expected the higher fouling index was observed for RO membranes (Fig. 2). It may be explained by the higher membrane fouling during RO experiments due to properties of RO membranes to retain all the components present in the wastewater in contrast to NF membranes. However, the fouling index of RO membrane was not much higher than of NF after concentration of effluent model solutions of skim milk (Fig. 2, a). Furthermore, it should be outlined that the fouling index was lower for OPMN-P membranes in 2-3 times at VRR 6 compared to the index that was obtained for NF-270 at VRR 3 [5]. The fouling was removed with an appropriate chemical cleaning, described in section 2, after which the initial membrane permeability was restored.

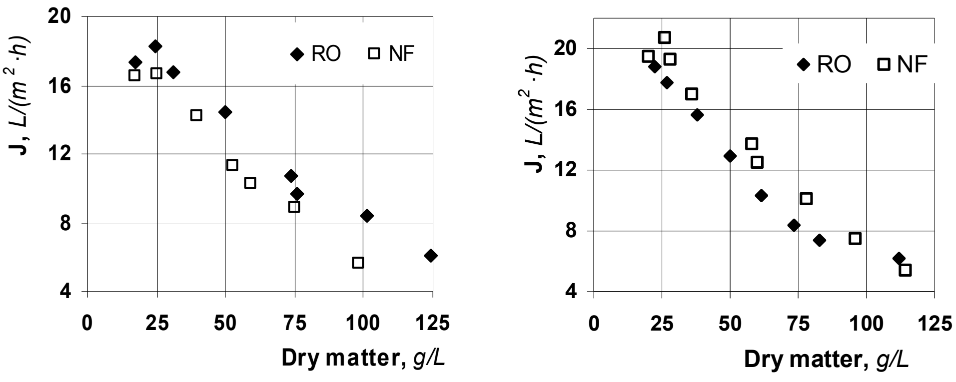

Fig. 1. Permeate flux vs. retentate dry matter during concentration of dairy model wastewaters of skim milk (a) and whole milk (b) by NF and RO

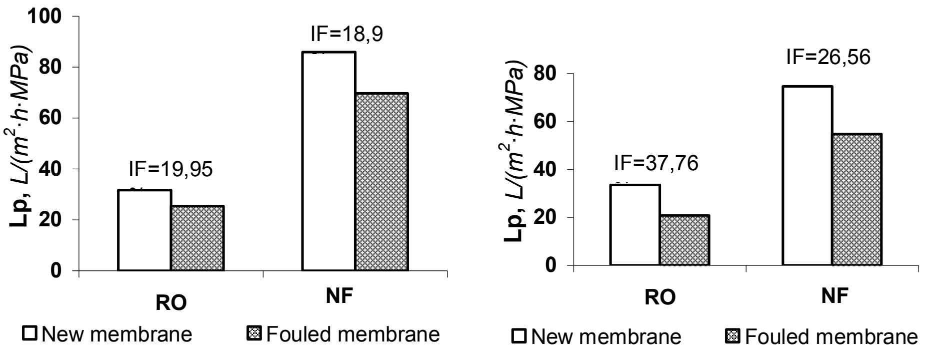

Fig. 2. Pure water permeability decline for RO and NF membranes after filtration of dairy effluent model solutions of skim milk (*a*) and whole milk (*b*)

Permeate and retentate characteristics. The main permeate characteristics are summarized in Table 2. As expected, concentrations in permeate were higher with NF membranes than with RO. NF and RO membranes totally retained fat and lipids. Lactose rejection was 97 and 95% for NF membrane for model effluent solutions of skim and whole milk respectively and 99.9% for RO membrane. Rejection of mineral salts was 62-63% for NF and 98-99% for RO. High mineral content of NF permeates (Table 2) and its low rejection is caused by permeability of NF membranes to monovalent ions Na^{+}, K^{+}, Cl^{-}. Multivalent ion concentrations were low (1 mg/L for Mg^{2+} and 3 mg/L for Ca^{2+}). Since lactose, which has an important contribution to COD, and mineral salt content are high in NF permeate, one single NF step is insufficient for producing water suitable for reuse, but these water can be discharged. Therefore a finishing step (e.g. RO or other) is needed for the production of reusable water. RO permeate of both model effluent solutions was low mineralized (50 mg/L). Thus it can be reused in dairy plants, e.g. for washing floors and the outside of plant vehicles [3]. Comparing the obtained results of permeate characteristics with those in [12] it should be noted that the studied membranes in this study had better separation characteristics and showed better rejection of mineral salts and lactose at higher VRR.

Table 2

Main characteristics of permeate produced by NF and RO from dairy model process waters

Characteristics	NF		RO	
	Skim milk	Whole milk	Skim milk	Whole milk
Fat, g/L	-	-	-	-
Proteins, g/L	-	-	-	-
Lactose, g/L	0.230	0.370	0.02	0.02
Mineral content, g/L	0.670	0.75	0.05	0.03
Ca^{2+}, g/L	0.003	0.003	0.001	0.001
Mg^{2+}, g/L	0.001	0.001	0.001	0.001
Na^{+}, g/L	0.07	0.12	0.006	0.004
K^{+}, g/L	0.21	0.28	0.017	0.009
Cl^{-}, g/L	0.38	0.34	0.026	0.015

The retentate composition of model effluent solutions is shown in Table 3. There are also characteristics of skim and whole milk to make a comparison. As it can be seen NF retentate had lower content of the main components in the skim and whole milk, obviously due to penetration of some components (lactose, minerals) through the membrane into the permeate. For RO the concentration of components in the retenates of model solutions was higher and was almost the same as in the milk. The obtained NF and RO retentates can be used for non-food applications [17] or after the appropriate treatment (e.g. pasteurization) as feed supplement for animals [18].

Considering the obtained permeate and retentate characteristics it is recommended to use RO for concentration of dairy effluents. Such a treatment of dairy wastewaters allows achieving the set of targets:

-to recover valuable products (lactose, protein);
-to receive purified water suitable for reuse;
-to reduce the amount of wastewaters and its pollution load;
-to reduce the load of treatment plant.

Table 3

Comparison of main characteristics of retentate produced by NF and RO from dairy model effluents with skim and whole milk

Characteristics	NF		RO		Skim milk	Milk with fat content of 2.7%
	Solution of skim milk	Solution of whole milk	Solution of skim milk	Solution of whole milk		
Fat, g/L	0.4	23.5	0.5	25.8	0.5	26.0
Proteins, g/L	26.5	25.4	31.7	28.2	30.0	28.2
Lactose, g/L	40.8	41.6	47.5	46.8	45.0	47.2
Mineral content, g/L	5.8	7.0	6.9	8.8	7.0	9.0
Dry matter, g/L	98.0	114.0	124.0	112.0	96.0	112.0

Conclusions

1. The permeate flux of NF and RO membranes was the same during concentration of model effluent solutions in spite of different membrane characteristics. This was likely caused by severe membrane fouling with solution components (proteins).

2. The calculated fouling indexes showed that fouling with RO membranes was higher than with NF. The fouling layer formed on the membrane surface was removed with chemical cleaning, after which the initial membrane permeability was restored.

3. The higher permeate quality was obtained with RO membranes that showed better rejection of milk components. The low mineral content of RO permeate makes it possible to be reused in the dairy industry for washing floors and the outside of plant vehicles.

4. One single NF step is insufficient for producing water suitable for reuse, but allows the milk constituents to be concentrated in the retentate. These permeate can be discharged or reused in the dairy plant after finishing step (e.g. RO or other).

5. The NF and RO retentates corresponded in composition to skim and whole milk and could be used for non-food applications or after the appropriate treatment (e.g. pasteurization) as feed supplement for animals.

6. The studied NF and RO membranes showed better performance and separation characteristics at lower pressure comparing with data of membranes of foreign manufactures available in the literature. Considering the economic benefit it is better to use these membranes for concentration of dairy effluents.

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