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Ultrafiltration od waste brine generated by fish meal industry

Introduction

Spent brine produced in food processing is troublesome by-product because of a very high content od sodium chloride amounting at least 13%. They also include valuable substances derived from the fish being processed, i.e., protein, fat, mineral substances and additives used in processing. The concept of the application of the ultrafiltration process and inorganic membranes for regeneration of used up brines includes cleansing worn brining and marinades for the return to the process and the separation of proteins and the hydrolysis products for further use as a secondary raw material.

This paper presents the results of research of the process of ultrafiltration of waste brine from two different fish processing plants. The aim of this research was to analyze the influence of selected parameters of the cross-flow ultrafiltration on the separation process performance and effectiveness of total protein rejection as well as the identification of the mass-transport resistance caused by fouling. Membrane fouling in the test systems was characterized by hydraulic resistances and modified fouling index.

Ultrafiltration of industrial brines

Advantage of using of membrane processes for treatment of food process water is that they can be used for both purifying water and recovering by-products. Moreover, removal of particles, preventing support of microbial regrowth. Pressure-driven membrane techniques has been offered as an environmental and economical alternative for regeneration of used brines with the aim of closing water loops in the fish processing [*Afonso and Borgues, 2002; Afonso et al, 2004*].

An application of ultrafiltration and ceramic membrane creates such possibilities in this field. Ceramic membranes have high practical application potential because they provide chemical and microbiological quality of treated effluents. Treating and reusing or recycling water within the food plant results in reduction of water use and wastewater production and discharge. If implemented water reuse should be integrated into existing HACCP system [*Casani et al., 2006*]. Fig. 1 presents scheme of salted herring production after implementation of spend brine ultrafiltration treatment and recycling [*Kuca and Szaniawska, 2009; Kuca, 2009*]

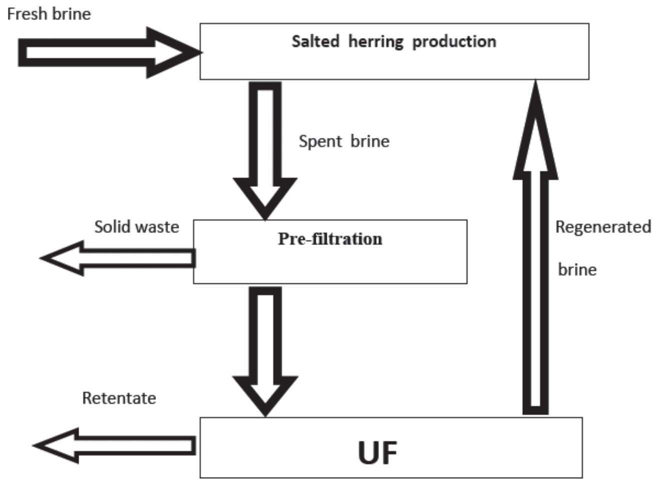

Fig. 1. Scheme of salted herring production after implementation of spend brine treatment and recycling

Experimental

The experiments were carried out in the laboratory-scale installation consisted of feed tank (2.0 dm^3), pressure pump, flat membrane module and heater exchanger. In this research ceramic membranes $Al_2O_3/TiO_2/ZrO_2$ with cut-off 300.0 and 150.0 kDa and filtering area of 0,0056 m^2 were used.

Actual industrial brine was initially cleaned before ultrafiltration using bag filters. Ultrafiltration runs were carried out in the process conditions presented in Tab. 1. During testing the ultrafiltration membrane system worked in the half-open mode, with the continuous permeate discharge (cleansed brine) and recycling of the retentate (concentrated brine). Fouled membranes were cleaned according to procedure recommended by membranes supplier. The waste brines from two fish processing plants (A and B) were used as a feed. The content of main components in tested brines are presented in Tab 2. Industrial supply brines for membrane module differ in protein (12÷16 g/dm^3) and fat (22÷42 g/kg) content.

The performance and selectivity of the tested membranes characterized by permeate flux, J_V and rejection coefficient, r respectively, were analyzed.

Tab. 1. The operand and dependent variables of UF process of industrial brines

UF process and feed operands	Ultrafiltration dependent variables
1. Membrane cut-off: 300.0 and 150.0 kDa 2. Transmembrane pressure, TMP: 0.1 and 0.2 MPa 3. Cross-flow velocity, CFV: 60 dm^3/h 4. Brine pH 5.0÷6.7 5. Protein content in brine, g/dm^3 6. Fat content in brine, g/kg 7. NaCl concentration, % 8. Temperature, 20±5^{o}C 9. Ultrafiltration time, t, s	1. Membrane permeability – permeate flux, J_v, m^3/m^{2}s 2. Membrane selectivity – retention coefficient, $r = 1 - C_P/C_F$; where: C_P – component content in permeate P, g/dm^3 C_F – component content in feed, F, g/dm^3 3. Transport resistance in membrane module, R_M – membrane resistance, MPa·s/m, R_F – fouling resistance, MPa·s/m, calculated from equation: J_{VSS} = TMP/ $(R_M + R_F)$

Tab. 2. Average content of main components in tested brines

Brine	pH	Fat, F, g/kg	Total protein, TP, g/dm^3	NaCl, g/dm^3	Total solids, TS, g/dm^3
A	5,1	21,9	12,2		
B	6,1	41,7	16,1	129,0	173,0

Ultrafiltration results

The experimental results characterizing membrane selectivity are presented in Tab. 3. According to expectation dense membrane (150 kDa) showed better rejection characteristics than looser one (300 kDa). For both tested brines, A and B rejection coefficients of total protein, r_{TB} and fat, r_F were in the range of 42÷57% and 91÷96% respectively.

The experimental results characterizing membrane permeability versus ultrafiltration time, transmembrane pressure and cut-off are presented in Fig. 2. There was observed decline in permeate flux with time during UF test of brines A and B. After about 1 h pseudo-steady state values of permeate flux were observed.

After 1 h ultrafiltration tests permeate flux declines to 70% of initial flux for both investigated membranes at transmembrane pressure of 0.1 MPa exhibiting pseudo-steady state values, J_{VSS} summarized in Tab.4. For higher TMP 0.2 MPa flux decline is a little bit higher to about 60% of initial flux.

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Tab. 3. Membrane selectivity during ultrafiltration processes of brine A and B

Tested sample	TKN	Content of total protein, TB, g/dm^3	Content of fat, F g/kg	r_{TP}	r_F
Brine A	1.95 1.93	12.2; 12.1 Average 12.1	21,88	–	–
Permeate A 150 kDa	0.82 0.84	5.1; 5.3 Average 5.2	8,36	0,57	0.62
Permeate A 300 kDa	1.02 1.06	6.4; 6.6 Average 6.5	2,0	0,46	0,91
Brine B	2.58 2.60	16.1; 16.3 Average 16.2	41,74	–	–
Permeate B 150 kDa	1.49 1.52	9.3 9.5 Average 9.4	2,84	0,42	0,93
permeate B 300 kDa	1.42 1.40	8.9; 8.8 Average 8.8	1,68	0,46	0,96

TKN – total *Kjeldahl* nitrogen; TB = 6,29 x TKN

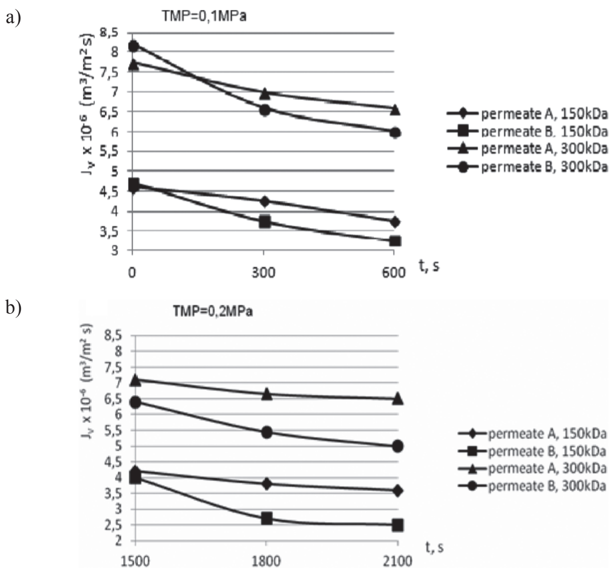

Fig. 2. Effect of time, membrane cut-off and transmembrane pressure: 0,1 MPa (a); 0,2 MPa, (b) on permeate flux during ultrafiltration of brines A and B

Values of pseudo-steady state permeate fluxes, J_{VSS} and water fluxes by clean membranes, J_W summarized in Tab. 4 were used for calculating fouling resistances, R_F, according the Eqs (1) and (2) with the aim of short analysis of the fouling phenomenon in investigated ceramic membrane – brine systems:

$$R_F = \frac{TMP}{J_{VSS}} - R_M \qquad (1)$$

$$R_M = \frac{TMP}{J_W} \qquad (2)$$

where:

TMP – transmembrane pressure [MPa]

J_{VSS} – pseudo-steady state permeate flux in the process of UF of brine [m^3/m^{2}s]

J_{WFM} – water flux through fouled membrane [m^3/m^{2}s]

J_W – water permeate flux through clean membrane [m^3/m^{2}s]

R_F – fouling resistance [MPa·s/m]

R_M – membrane resistance [MPa·s/m]

The calculated values of fouling resistances, R_F indicate that fouling phenomenon has major influence on permeate flux in comparison with active layer membrane resistance, R_M. Moreover, fouling resistance increases when transmembrane pressure increases from 0.1 to 0.2 MPa in larger extent for brine B with higher content of fouling substances, fat and protein.

Tab. 4. Experimental data of pseudo-steady state permeate fluxes, J_{VSS} and water fluxes, J_W for fouling characterization

Brine	Cut-off, kDa	TMP, MPa	$J_{VSS} \cdot 10^{-6}$ m^3/m^{2}s	$J_W \cdot 10^{-5}$, m^3/m^{2}s	$R_M \cdot 10^5$, MPa s/m	$R_F \cdot 10^5$, MPa s/m
A	150	0.1	3.8	3.9	0.026	0.24
		0.2	3.5	7.7		0.54
	300	0.1	6.5	6.0	0.020	0.14
		0.2	6.5	9.1		0.29
B	150	0.1	3.3	3.9	0.026	0.28
		0.2	2.5	7.7		0.77
	300	0.1	6.0	6.0	0.020	0.15
		0.2	5.0	9.1		0.38

Conclusions

During the salting of herring, approximately 200 dm^3 of brine is formed per ton of fish, which should be treated to fulfill environmental requirements. Seeking environmental and economic solutions for spent brines utilization the concept of comprehensive membrane technology with the aim of closing water loops as well as reusing of recovered by-products is the most perspective.

Due to the high concentration of suspended matter in fish brines several steps in developed treatment technology are required, pretreatment by microfiltration, protein fractionation by ultrafiltration with different cut-offs and nanofiltration to clean thoroughly water with salts.

The results from this work show that ultrafiltration using ceramic membranes can be efficient and ecologically suited environmental separation method for decontamination and recycling of salted aqueous effluents, as it allows both the recycling of permeate (water with salt) and reducing of organic load (fat and proteins in retentate stream) for next reclaiming, besides environmental pollution abatement.

The ultrafiltration database obtained for two kind of industrial brines A and B with different fat and protein content indicate that the investigated ceramic membranes can be used as a main step of waste brine regeneration hybrid technology. Both ceramic membranes exhibit high rejection of fat with rejection coefficients, $r_F > 90\%$ and lower rejection of total protein, in the range of 0.42÷0.57. Permeability of ceramic membranes in ultrafiltration process of fish brines is controlled by fouling phenomenon. For both tested membranes the lower fouling resistances R_F were obtained for lower transmembrane pressure 0.1 MPa. Although ceramic membranes undergoes sever fouling they can be easily cleaned according to procedure consisting of complete basic-acid washing, recommended by membrane producers.

The experimental results on protein rejection, r_{TB} pointed out that further investigation should be dedicated to use ultrafiltration membranes of lower cut-off than 300 and 150 kDa or even nanofiltration membranes in order to achieve higher effectiveness in proteins recovery and regeneration of water-salt stream.

Further investigation should be focused on the continuous experiments during long operation periods, thereby optimize water-salt recovery rate as well as frequency and duration of washing procedure between filtration runs.

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