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STUDIES ON SEPARATION OF OIL AND PEPTIDES FROM SALINE WASTEWATERS WITH THE USE OF CERAMIC MEMBRANES

BADANIE SEPARACJI OLEJU ORAZ BIAŁEK Z WÓD ZASOLONYCH Z ZASTOSOWANIEM MEMBRAN CERAMICZNYCH

Abstract: The work evaluates the effect of main process parameters, i.e. transmembrane pressure, TMP and cross-flow velocity, CFV on oil and protein rejection r_i and permeate flux J_{Vi} using 2^2 experimental design. The ultrafiltration experiments were carried out using pilot installation with tubular ceramic 300 kDa membrane and model oil-in-water and BSA - water solutions. Ultrafiltration data obtained using experimental design technique was used to determine the regression coefficients of polynomial equations. These equations give information on non-conjugated as well as conjugated effects of two operating parameters on ultrafiltration process of model oil and BSA water solutions. Moreover, these equations helped to determine optimal conditions for ultrafiltration process from the point of view of membrane permeability and selectivity. Furthermore they can be useful while assessing the experimental conditions of ultrafiltration in real complex systems such as oily wastewaters produced by petroleum industry or marine transport and waste brines produced by fish industry.

Keywords: experimental design, ceramic membrane, model oil wastewaters, model protein wastewaters

Introduction

Recently, membrane technologies have been studied and applied in various industries. Pressure-driven membrane techniques, such as microfiltration, ultrafiltration and nanofiltration can be used to improve the quality of treated wastewaters before getting into the environment or turn to industrial processes [1]. The use of these membrane processes for wastewater applications is becoming increasingly popular and has being considered as alternative options for traditional treatment methods [2-6].

The application of membrane techniques in treatment of oily wastewaters generated by industry or transport [7] and used brine produced by fish industry [8] can lead to technologies that would be cleaner in terms of environmental impact. Usually, in the first step of the research on ability of applying of ultrafiltration process and ceramic membrane for development of integrated technology for oily and salted wastewater treatment is analysis using model systems.

The paper presents the results of the process of ultrafiltration of two different model systems: oil-in water emulsion obtained as a result of ultra-sonication and water-protein solution gained by BSA (bovine serum albumin) dissolution in water. Research was performed with a use of pilot installation equipped with commercial ceramic membrane possessing the filtration area of 0.35 m^2. Tests were carried out under constant process conditions such as temperature 20 ºC, oil 500 ppm and BSA 5 g/dm^3 concentration in the

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feed. During ultrafiltration tests the membrane installation was working in a semi-open mode, with continuous discharge of permeate and retentate being recycled constantly. Performance of the membrane was characterized by the volume flow of permeate J_V [m^3/m^2s] and selectivity by rejection coefficient, r_i. The influence of two main operating parameters TMP and CFV on membrane permeability and selectivity was investigated. The experiments were performed using 2^2 experimental design [9, 10]. The first aim of this research was to obtain mathematical relationships between dependent variables (membrane permeability and selectivity) and independent ones (CFV and TMP). Next purpose was to use these equations for analysis of effect of investigated process parameters on membrane permeability and selectivity. Finally, polynomial equations were used for identification of optimal ultrafiltration conditions resulting in high rejection of protein and oil as well as high membrane permeability.

Materials and methods

Ultrafiltration installation and ceramic membrane

Ultrafiltration tests were performed with a use of pilot installation (Fig. 1) equipped with commercial 23-channel ceramic membrane with a cut-off 300 kDa (Fig. 2) under defined process conditions: temperature 20 °C, oil concentration in the feed 500 ppm, BSA concentration in the feed 0.05 g/dm^3.

Fig. 1. Membrane installation used in experiments (author: Konrad Cwirko)

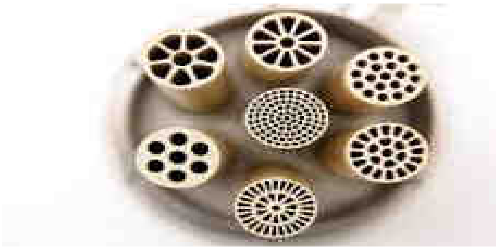

Fig. 2. Ceramic tubular membranes with different number of channels [11]

Technical parameters of ceramic tubular membrane used in experiments are given in the Table 1.

Table 1

Characteristic parameters of ceramic membrane used in ultrafiltration tests

Parameter	Cut-off [kDa]	Number of channels	Channel hydraulic diameter [mm]	Length [m]	Filtration area [m^2]	Membrane permeability for water [dm^3/(h m^2) ·10^5 Pa]
Value	300	23	3.5	1.178	0.35	450-500

Samples collection and analysis

The model solutions of oil-in-water (10 dm^3) were prepared for each ultrafiltration process. Solutions were made using ultrasounds with Sonics VCX-500 processor in certain parameter conditions. The homogenization process was used hydraulic oil in a concentration of 500 ppm. After preparing the oil-in-water solution in each case immediately they proceeded to carry out the ultrafiltration process to preserve the structure of these liquids. At the beginning of each UF process, sample of feed *F* and during ultrafiltration process, samples of permeate *P* were measured by turbidimeter TN-100 Eutech Instruments in order to determine oil rejection.

The model solutions (10 dm^3) of water-protein BSA with molecular weight 69 kDa were prepared directly dissolving protein in water in a concentration of 0.05 % m/m. During the ultrafiltration process of water-BSA solution samples of feed and permeate were collected in order to measure protein rejection r_i. Measurements were carried out using spectrometer HITACHI UV/VIS U-5100.

The flow rate of the feed, at a surface of the membrane i.e. CFV was determined from the graph of pressure drop in the membrane module (Fig. 3).

Volume flow of permeate (the membrane performance) J_V [m^3/(m^{2}s)] was calculated using the equation:

$$J_v = \frac{V_p}{t \cdot S} \tag{1}$$

where: V_p - volume of permeate [m^3], t - ultrafiltration time [s], S - membrane filtration surface [m^2].

The degree of rejection (oil retention coefficient/protein rejection coefficient), r_i that characterizes the selectivity of the membrane was calculated with a use of relation:

$$r = \left(1 - \frac{C_P}{C_F}\right) \tag{2}$$

where: C_F - oil concentration in the feed [ppm]/ BSA concentration the feed [g/dm^3], C_P - oil concentration in permeate [ppm] / BSA concentration in permeate [g/dm^3].

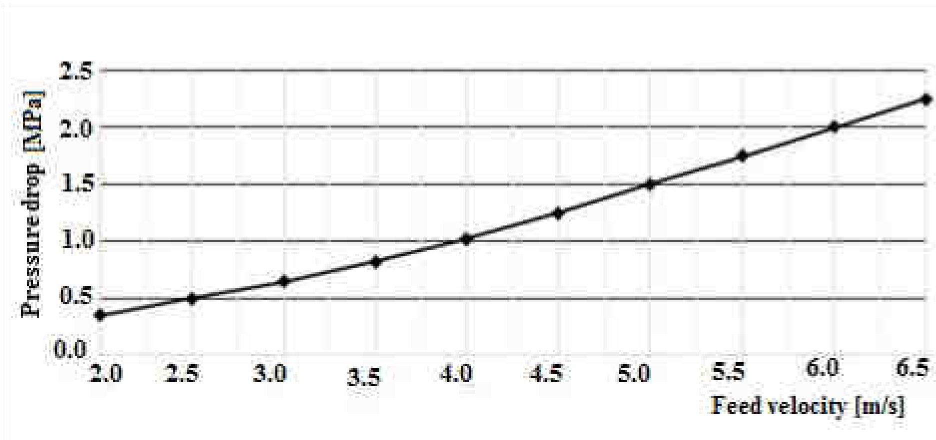

Fig. 3. Pressure drop in a module vs. feed velocity for 23-channel membrane

The experimental design

According to the two-level experimental design the investigated object can be approximated by function of Eqs. (3) and (4). The ultrafiltration tests were performed according design matrix presented in Table 2. For the ultrafiltration systems 1 - ceramic 300 kDa membrane-BSA-water and 2 - ceramic 300 kDa membrane-oil-water being investigated, two independent variables (x_1, x_2) and two levels (+1,–1) were set to determine oil/BSA rejection r_i and permeate flux J_{vi}. The total number of experiments according to 2^2 factorial design plan was 4 (n = 4). The cross-flow velocity CFV [m/s] and transmembrane pressure TMP [MPa] were chosen as independent variables, x_1 and x_2. The standardized values of independent variables x_1 and x_2 correspond to real values of operating parameters, i.e.: CFV 4 and 5 m/s and TMP 0.1 and 0.2 MPa, respectively.

Table 2

2^2 factorial experimental design matrix with independent and dependent variables (responses); 1 - water-BSA model solution, 2 - water-oil model solution

Exp.	x_1	CFV [m/s]	TMP [MPa]	x_2	x_1x_2	J_{v1} [m^3/(m^{2}s)]	r_1	J_{v2} [m^3/(m^{2}s)]	r_2
1.	–1	4	0.1	–1	+1	y_{11}	r_{11}	y_{21}	r_{21}
2.	+1	5	0.1	–1	–1	y_{12}	r_{12}	y_{22}	r_{22}
3.	–1	4	0.2	+1	–1	y_{13}	r_{13}	y_{23}	r_{23}
4.	+1	5	0.2	+1	+1	y_{14}	r_{14}	y_{24}	r_{24}

The effect of independent variables (x_1, x_2) on object response (y) is presented by function (Eq. 3) and polynomial equation (Eq. 4):

$$y = f(x_1, x_2) \tag{3}$$

$$y_i = b_0 + b_1 x_1 + b_2 x_2 + b_{12} x_1 x_2 \tag{4}$$

Results and discussion

The data summarized in Table 3 show the results of ultrafiltration tests performed according to experimental plan of 2^2 type for two investigated model UF systems, 1. ceramic 300 kDa membrane-BSA-water (J_{v1}, r_1) and 2. ceramic 300 kDa membrane - oil-in-water (J_{v2}, r_2).

Table 3

Experimental data obtained as a result of UF processes of model solutions: 1 - water-BSA and 2 - water-oil; temperature 20 °C, oil concentration in the feed 500 ppm, BSA concentration in the feed 0.05 g/dm^3

Exp.	**CFV [m/s]**	**TMP [MPa]**	Jv_1 **[10^{-5}(m^3/(m^{2}s)]**	r_1	Jv_2 **[10^{-5} (m^3/(m^{2}s)]**	r_2
1	4	0.1	4.63	0.736	7.55	0.986
2	5	0.1	4.94	0.771	7.09	0.987
3	4	0.2	5.10	0.719	14.0	0.988
4	5	0.2	6.48	0.854	13.5	0.989

Using experimental data presented in Table 3, the regression coefficients (b_0, b_1, b_2, b_{12}) of the polynomial equation, Eq. (4) are determined and summarized in Table 4. For ultrafiltration oil-in-water model emulsions, the oil rejection coefficients on the level of 0.99 are independent on CFV and TMP in investigated range of these operating parameters.

Table 4

Evaluated coefficients, b_{ij} according to Eq. (4)

Model system	**Flux/rejection**	b_0	b_1	b_2	b_{12}
1. Ceramic 300 kDa membrane-oil-in-water	Jv_1	$10.5\cdot10^{-5}$	$0.24\cdot10^{-5}$	$3.22\cdot10^{-5}$	$-0.01\cdot10^{-5}$
	r_1	-	-	-	-
2. Ceramic 300 kDa - BSA-water	Jv_2	$5.29\cdot10^{-5}$	$0.42\cdot10^{-5}$	$0.50\cdot10^{-5}$	$0.27\cdot10^{-5}$
	r_2	0.770	0.043	0.017	0.025

The developed polynomial equation (Eq. (4)) with regression coefficients (Table 4) gives following information on non-conjugated and conjugated effect of two inlet variables on investigated system 1 and 2 responses:

- influence of CFV on permeate flux in system 1 (oil-in-water emulsions) is presented by coefficient b_1 and b_{12}; comparison of values of these coefficients indicates that non-conjugated coefficient b_1 is of crucial importance; J_{v1} decreases with CFV increasing,
- effect of TMP on permeate flux in system 1 should be considered taking into account coefficients b_2 and b_{12}; coefficient b_2 has essential meaning; transmembrane pressure has clear positive impact on permeate flux,

- analysis values of all coefficients for system 1 indicates that conjugated influence of both operating parameters representing by coefficient, b_{12} can be omitted,
- in the case of system 2 (BSA-water solution) dependence of permeate flux on CFV and TMP is presented by coefficients, b_1, b_{12} and b_2, b_{12}, respectively with decisive meaning of all ones (the value of coefficients are similar),
- CFV and TMP has an effect on BSA rejection due to the non-conjugated coefficients b_1 and b_2, respectively as well as conjugated coefficient b_{12}; a larger influence can be seen of coefficient b_1 than b_2 and b_{12},
- analysis values of all coefficients for system 2 indicates that both non-conjugated and conjugated coefficients have essential meaning for permeate flux and protein rejection.

The conclusions concerning effect of CFV and TMP on permeate flux and solute rejection drawn using analysis of coefficients of Eq. (4) is consistent with experimental data presented graphically in Figure 4. As it is seen from Figure 4 and Table 3, greater impact of analyzed process parameters on permeate flux is observed for ultrafiltration of model system 2 (UF2).

a)
b)

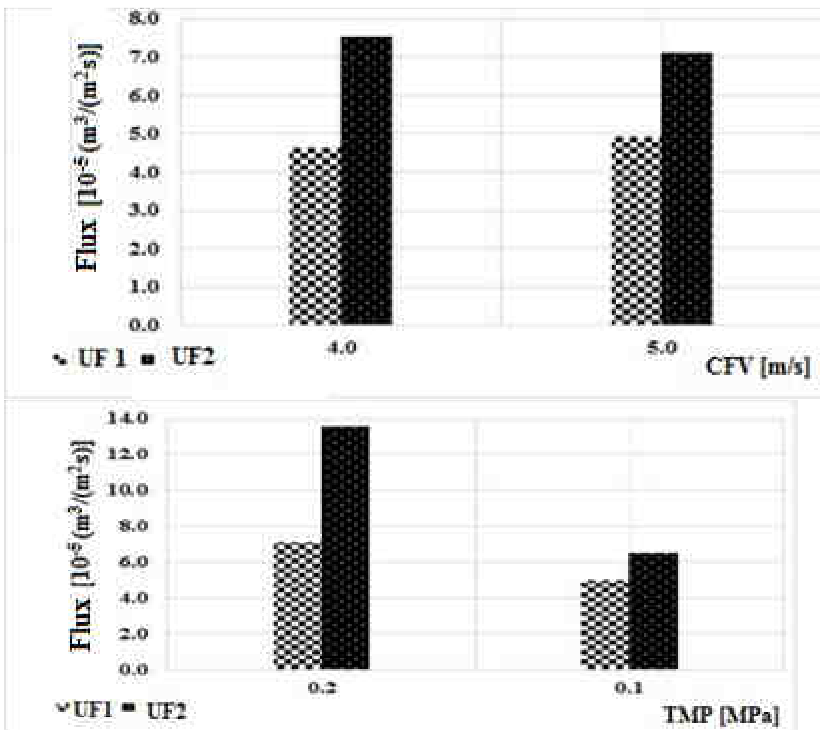

Fig. 4. Effect of CFV (a) and TMP (b) on permeate flux J_v in ultrafiltration of model oil-in-water solution (UF2) and model BSA-water (UF1)

The biggest value of permeate flux was observed for TMP 0.2 MPa and CFV 5 m/s (Fig. 4a-b). For this system the greatest impact on permeate flux and protein rejection has CFV and TMP, respectively. The biggest value of permeate flux and protein rejection was obtained for TMP 0.2 MPa and CFV 5 m/s, $6.48 \cdot 10^{-5}$ $m^3/(m^2s)$ and 0.854, respectively.

Conclusions

In this study ultrafiltration tests using pilot installation and commercial ceramic 300 kDa membrane are performed with the aim of identifying and analyzing the effect of main operating parameters CFV and TMP on permeate flux and solute rejection for oil-in-water solutions and BSA-water solutions. The experiments were realized using experimental design method. By employing statistical design with small number of experiments and the resulting polynomial equation a helpful tool for describing of ultrafiltration systems has been obtained. The polynomial equation as interpolation formula provides both analysis of effect and significance of inlet variables on permeate flux and solute rejection. It also allowed the evaluation of level of CFV and TMP resulting in maximum rejection and flux, 5 m/s and 0.2 MPa, respectively. For complete picture of investigated ultrafiltration system future studies taking into account more operating parameters are necessary.

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BADANIE PROCESU SEPARACJI OLEJU ORAZ BIAŁEK Z WÓD ZASOLONYCH Z ZASTOSOWANIEM MEMBRAN CERAMICZNYCH

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Abstrakt: W pracy dokonano oceny wpływu parametrów procesowych, takich jak ciśnienie transmembranowe TMP oraz prędkość przepływu nadawy nad powierzchnią membrany CFV, na stopień odzysku oleju i białka r_i oraz strumień permeatu J_{vi} z zastosowaniem planu czynnikowego dwupoziomowego. Doświadczenia prowadzono za pomocą pilotowej instalacji membranowej z ceramiczną membraną rurową o granicy rozdziału 300 kDa oraz modelowych roztworów oleju w wodzie oraz białka BSA w wodzie. Dane doświadczalne z przeprowadzonych procesów ultrafiltracji z zastosowaniem techniki planowanego eksperymentu zostały wykorzystane do określenia współczynników regresji równań wielomianowych. Równania te dostarczają informacji zarówno o niezwiązanym, jak i sprzężonym wpływie dwóch parametrów operacyjnych na proces ultrafiltracji modelowych roztworów wód zaolejonych oraz roztworów białka BSA w wodzie. Umożliwiają także określenie optymalnych warunków procesu ultrafiltracji z punktu widzenia przepuszczalności i selektywności membrany. Ponadto mogą być przydatne przy ocenie eksperymentalnych warunków tego procesu w układach rzeczywistych, takich jak ścieki zaolejone produkowane przez przemysł naftowy lub transport morski i solanki odpadowe produkowane przez przemysł rybny.

Słowa kluczowe: planowanie eksperymentu dwupoziomowego, membrany ceramiczne, modelowe roztwory wód zaolejonych, modelowe rozwory białek w wodzie