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PRO-ENVIRONMENTAL TREATMENT TECHNOLOGY OF INDUSTRIAL BRINES USING CERAMIC MEMBRANES

PROŚRODOWISKOWA TECHNOLOGIA OCZYSZCZANIA SOLANEK PRZEMYSŁOWYCH Z ZASTOSOWANIEM MEMBRAN CERAMICZNYCH

Abstract: The paper presents the results of a multi-stage ultrafiltration process of industrial waste brines with the use of a pilot plant and commercial ceramic membranes. The purpose of the study was to analyse the applicability of ultrafiltration and membranes of various cut-off for the treatment of waste brines and fractionation of proteins contained therein. Research on the membrane process was performed under constant conditions: transmembrane pressure TMP = 0.2 MPa, velocity of a saline over the surface of the membrane CFV = 6 m/s, the temperature T = 25°C using ceramic membranes with a cut-off of 300, 150 and 50 kDa. In tests run in the semi-open ultrafiltration system (continuous discharge of a permeate and retentate recirculation) there were analysed the concentration of protein in permeate and retentate, as well as the recovery of the permeate Q_P. Results of microbiological tests on used brines and permeates after ultrafiltration process performed by an independent testing laboratory are also presented.

Keywords: ultrafiltration, ceramic membranes, industrial brine, fish processing, microbiological analysis

Implementation of the principle of sustainable development into practice in the protection of the aquatic environment requires the use in industrial plants, including food-processing plants, environmental solutions, whose primary task is to close the water loops in order to minimize water consumption and sewage discharge and additionally recovery of secondary raw materials. Fish processing plants are characterized by a very large consumption of water for technological purposes. In the production of salted and smoked fish average consumption of water per 1 Mg of the finished product is approx. 25 m^3, and the production of canned fish reaches up to 60 m^3. At the same time, due to the employment of process brines with a high content of NaCl, large volumes of polluting the environment high-salted wastewater are generated, in which the chloride content reaches up to 20/dm^3. This type of wastewaters is also characterized by the high values of pollutant concentrations such as BOD_5 and COD as well as total suspended solids, TSS, exceeding significantly limits of these indicators set out in the Regulation of the Minister of the Environment on the conditions to be met when discharging wastewater to waters or ground. In the process of treatment of wastewater from fish processing, the biggest problem creates the high content of NaCl, since up to now there is still lack of efficient and cost effective methods of removing chlorides from wastewater to levels required by law [1, 2].

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The proposed global and in-country solutions to this problem involve the use of appropriate technology of used brines reclamation for return to the process and the simultaneous recovery of valuable components. In recent years, more and more common to employ are hybrid technologies consisted of membrane processes as a main step. Within the hybrid technology, membrane techniques are employed as the separation processes - these use pressure membrane processes such as ultrafiltration and inorganic membranes. The main advantage of ultrafiltration in this case is not only a possibility of separation of fat and proteins but also of microbial contamination [3-5].

The purpose of the study was to analyse the applicability of ultrafiltration and the membranes of various cut-offs for treatment of waste brines and rejection of proteins contained in industrial brines. Studies performed under constant process conditions, determined influence of membrane cut-off protein rejection R and recovery coefficient Q_P.

Materials and methods

Research has been accomplished using pilot membrane installation, consisting of basic elements such as a feed tank, a pressure pump and a membrane module of industrial ceramic membranes. The parameters characterizing the membranes are summarized in Table 1. Waste brines from fish processing plant with an average fat content 22 g/kg, concentration of proteins 12 g/dm^3 and sodium chloride 13.5 wt.%, were treated with the use of ultrafiltration. Tests were run in semi-closed ultrafiltration cross-flow system, with continuous discharge of the permeate P, and the retentate R, recycle, in a controlled process maintained in the following conditions: transmembrane pressure, TMP = 0.2 MPa, feed velocity over the surface of the membrane, CFV = 6 m/s and temperature T = 25ºC.

Table 1

Characteristics of ceramic membranes used in ultrafiltration tests

Parameter	Cut-off	No of channels	Channel hydraulic diameter [mm]	Length [m]	Filtration area [m^2]
Value	300 150 50	23	3.5	1.178	0.35

Results and discussion

Multi-stage ultrafiltration tests

Table 2 lists the test results obtained in two series of measurements. In the first series S_1, industrial brine was pre-filtered (bag filters 100, and 1 mm), then the obtained filtrate with a volume of 18 dm^3 was subjected to ultrafiltration with the use of a membrane of 300 kDa. In the last stage of the series S_1, the resulting permeate with a volume of 11.5 dm^3 was subjected to ultrafiltration with the use of a membrane of 150 kDa. In the second series S_2, the filtrate from prefiltration of the initial volume of 22 dm^3 was subjected to ultrafiltration using a 150 kDa membrane and the resulting permeate volume of 11.3 dm^3 was again ultrafiltered using a membrane of 50 kDa. Graphical representation of the industrial treatment of brines in the hybrid filtration-ultrafiltration process is shown in a paper [6]. The protein content in permeates and retentates has been determined based on measurements of *TKN* (Kjeldahl total nitrogen).

Table 2

Results of experimental two-stage ultrafiltration of industrial brines after prefiltration

Series of measurements	Membrane cut-off [kDa]	UF time t [min]	Feed volume V_F [dm^3]	Permeate volume V_P [dm^3]	Permeate recovery $Q_P = V_P/V_F$	Average protein content in P after time t [g/dm^3]	Average protein content in R after time t [g/dm^3]
S_1	300 150	40 20	18.0 11.5	11.5 6.0	0.64 0.52	1.97 -	5.0 -
S_2	150 50	75 45	22.0 11.3	11.3 5.0	0.51 0.44	1.65 1.31	3.2 2.1

Results presented in Table 2 show that a two-step ultrafiltration process preceded by a prefiltration leads to the concentration of proteins in the retentates. At the same time, the permeate protein contents have decreased in comparison to the raw brine to a level in the range of 1.97-1.31 g/dm^3, depending on the cut-off of the membrane. Permeates obtained using ultrafiltration process were transparent with good smell. Figure 1 shows photos of brine (feed), permeate after ultrafiltration with a use of 150 kDa membrane, and a retentate after long-term test.

Microbiological analysis

Food industry is very much focused on ensuring the microbiological cleanliness of the processes used. Therefore, in assessing the applicability of the tested membranes for brine treatment, one of the most important criteria, in addition to the technological effectiveness are the results of microbiological tests.

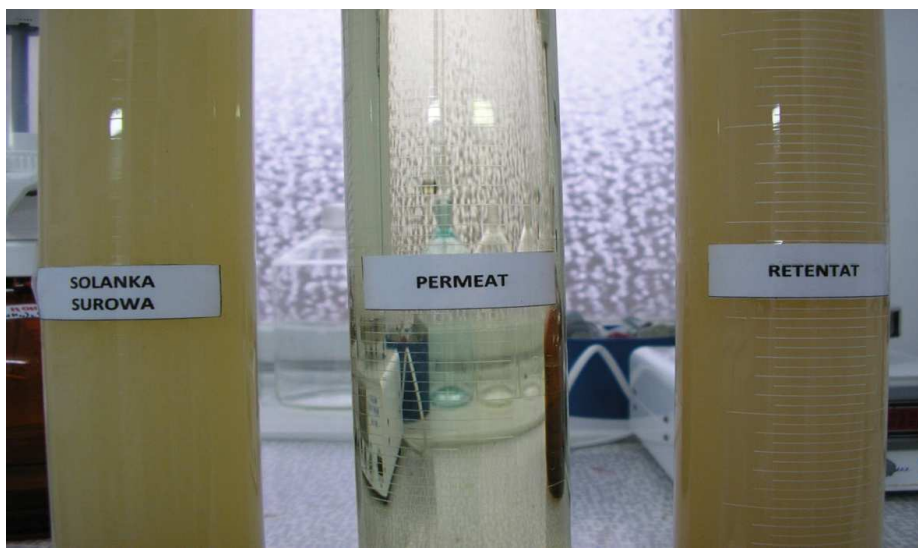

Fig. 1. The samples of raw brine as well as permeate and retentate after ultrafiltration process with a use of 150 kDa membrane [7]

Microbiological tests were performed in two independent laboratories. Testing involved samples obtained from the ultrafiltration process (feed, F_i) and after ultrafiltration (permeate, P_i), for ultrafiltration process with the use of membranes 300 and 150 kDa. Ultrafiltration with the use of membranes 150 and 300 kDa concerned the brines from two different fish processing plants, respectively, F_1 and F_2. Performed microbiological analyses determined the total number of psychrophilic microorganisms at 7 and 20ºC as well as number of halophilic microorganisms. Determination of the total number of psychrophilic microorganisms were performed in accordance with a Polish standard PN-90 A-75052/05, while in a case of halophilic microorganisms substrate after Burbianka and Pliszka was used [8].

Table 3

Results of microbiological analysis

Membrane cut-off	Determined microorganisms	Analysed samples	Cell number [cfi/cm^3]
150 kDa	Halophilic	Feed, F_1	$8.6 \cdot 10^2$
		Permeate, P_1	ng
	Psychrophilic, 20ºC	Feed, F_1	$2.3 \cdot 10^3$
		Permeate, P_1	ng
	Psychrophilic, 7ºC	Feed, F_1	ng
		Permeate, P_1	ng
300 kDa	Psychrophilic, 20ºC	Feed, F_2	$9.8 \cdot 10^3$
		Permeate, P_2	ng
	Psychrophilic, 7ºC	Feed, F_2	$1.7 \cdot 10^2$
		Permeate, P_2	ng

ng = no growth; cfi = colony-forming individuals

As it is apparent from Table 3, there was no presence of test microorganisms in the ultrafiltration permeates for both membrane 150 and 300 kDa. Decreasing the temperature from 20 to 7ºC had a beneficial effect on the microbiological test samples before ultrafiltration (F_1 and F_2), substantially reducing the amount of cells present. While implementing the technology into practice it is strongly recommended that storage of spent brine takes place in the refrigerator.

Conclusions

The aim of the research is to develop pro-environmental regeneration technology of used brines generated at fish processing plants with the use of pressure-driven membrane processes and ceramic membranes, allowing the treatment of brine to a level enabling the recycling to a technological process and recovery of proteins and their hydrolysis products. Pro-environmental and economic aspects of the implementation of such technology in fish processing plants and other salt-using processes make them fully deserving underline. Regeneration of waste brines and their re-use in the process will lead to significant reduction of their consumption. This will reduce the quantity and pollution load discharged to the wastewater treatment plant and translate into lower fees for wastewater management. Simultaneously the production costs associated with the purchase, transportation and storage of fresh brines as well as with waste brine disposal will be substantially reduced.

Literature data analysis and the results of this study indicate that the abovementioned is possible if a hybrid system consisting of prefiltration and ultrafiltration in several steps using membranes with a suitable cut-off is designed and developed. It will be also undoubtedly necessary to identify the optimal process parameters and develop a technological database characterizing performance and selectivity of applied membranes.

Analysis of the research results clearly indicates that a hybrid process composed of the filtration on a pre-filter and a bag filter of 100 and 1 mm followed by several steps of ultrafiltration on ceramic membranes with cut-off of 300, 150 and 50 kDa, allows for protein removal from waste brine to less than 2 g/dm^3 and 100% elimination of psychrophilic microorganisms. Ultrafiltration tests completed in time up to 75 min under constant process conditions: TMP = 0.2 MPa, CFV = 6 m/s at 25ºC have allowed for achievement of the recovery factor of the treated brine, Q_P up to 64%.

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Abstrakt: Przedstawiono wyniki badań wieloetapowego procesu ultrafiltracji zużytych solanek przemysłowych z zastosowaniem instalacji pilotowej oraz komercyjnych membran ceramicznych. Celem badań była analiza możliwości zastosowania ultrafiltracji i membran o różnym *cut-off* do oczyszczania zużytych solanek i frakcjonowania protein w nich zawartych. Badania procesu membranowego wykonano w stałych warunkach:

ciśnienie transmembranowe TMP = 0,2 MPa, prędkość solanki nad powierzchnią membrany CFV = 6 m/s, temperatura T = 25ºC z zastosowaniem membran ceramicznych o cut-off 300, 150 i 50 kDa. W testach ultrafiltracyjnych realizowanych w systemie półotwartym (ciągłe odprowadzanie permeatu i zawracanie retentatu) analizowano zawartość protein w permeatach i retentatach oraz stopień odzysku permeatu Q_p. Przedstawiono również wyniki badań mikrobiologicznych zużytych i oczyszczonych solanek wykonane przez dwa niezależne laboratoria.

Słowa kluczowe: technologie prośrodowiskowe, ultrafiltracja, membrany ceramiczne, solanki przemysłowe, przetwórstwo ryb, analiza mikrobiologiczna