Prosimy cytować jako: Inż. Ap. Chem. 2012, 51, 6, 387-388

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Characterization of fouling in ultrafiltration ceramic membrane systems treating surface water

Introduction

Good quality water shortage has long been a problem in many countries across the world. The same problem is observed in Poland, where monitoring of surface water revealed a progressive increase of pollution content. In some rivers Polish standards on water quality for fish in natural condition are often exceeded [*Decree, 2002*]. Because of that the fish hatcheries must solve poor water quality problem by treatment both, water supplying the hatchery as well as process water from breeding apparatus. For this purpose pressure driven membrane processes such as ultrafiltration and nanofiltration based on ceramic membranes can be used [*Szmukala i Szaniawska, 2009*].

The major obstacle in the use of ultrafiltration/nanofiltration units in water treatment is the membrane fouling caused by inorganic and organic substances contained in water. Fouling is the process resulting in loss of performance of a membrane due to deposition of suspended or dissolved substances on its external surfaces at its pore openings or within its pores.

In the paper application of resistance-in-series model and ultrafiltration modified fouling index as a tool to measure fouling in UF membrane system is presented. The purpose of the work was to use several parameters, flux reduction, hydraulic resistance and fouling index for characterization fouling extent in ultrafiltration ceramic membrane process treating surface water taken from inlet and outlet of fish hatchery and breeding apparatuses.

Experimental

The experiments were carried out in the laboratory-scale membrane installation consisted of feed tank (45 dm^3), pressure pump, membrane module and heat exchanger. The ceramic membranes prepared of Al_2O_3/TiO_2/ZrO_2 with *cut-off* 1.0 and 3.0 kDa were used in the research. The ultrafiltration experiments were performed at constant temperature, 293 K for transmembrane pressure, *TMP* of 0.55 and 0.85 MPa. The membrane installation and characteristics of commercial membrane used in cross-flow filtration tests were described in details in previous work [*Szmukala i Szaniawska, 2009*].

Water quality analysis

The surface water samples for analysis and ultrafiltration tests were taken according to Polish and International standard *PN-ISO 5667-6:2003*. The samples were taken from four points (I-IV) of fish hatchery system, FHS, operating in opened-loop mode, consisted of weir – *1*, retention pond – *2*, mechanical filter – *3* and breeding apparatuses – *4* (Fig.1).

The surface water samples were taken once a month during the period of two years. Surface water quality was assessed using indicators such as *pH*; suspended solids, SS; absorbance at 254 nm, UVA; biochemical oxygen demand, BOD; chemical oxygen demand, COD_{Mn}; total phosphorus, P_{tot} and total nitrogen, N_{tot}. The water samples were analyzed according to *Polish and European Standards: PN:EN 872:2005, PN:EN 1899-2:2002, PN- 85/C-04578/02, PN-EN-ISO 6878:2004 and PN-EN-ISO 11905-1:2001* for SS, BOD, COD_{Mn}, P_{tot} and N_{tot}, respectively.

Ultrafiltration tests

Two kinds of cross-flow filtration tests were performed, short term (40 min) and long term (3 hours).

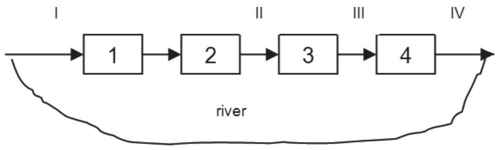

Fig. 1. Opened-loop fish hatchery system; *1* – weir; *2* – retention pond; *3* – mechanical filter; *4* – breeding apparatuses; I–IV – sampling points

During long term tests rejection, *r* as well as water and permeate fluxes, J_{0b}, J_{0a} and J_v, m^3/m^2s were determined. First, to determine clean water flux before membrane operation, J_{0b} which is the basis for comparison with the unfouled membrane the deionized water was filtered through both membranes, 1.0 and 3.0 kDa and transmembrane pressure, 0.55 and 0.85 MPa at constant temperature 20°C. Next, to determine permeate flux, J_v characteristic for fouled membrane, surface water was filtered at the same process conditions. Finally, to set clean water flux after membrane operation, J_{0a}, deionized water was filtered through fouled membrane.

The short term tests were performed by recording permeate volume produced per membrane area, *V/A*, m^3/m^2 at 300-s intervals over the filtration period 40 min.

In order to recover ceramic membranes filtrate capability after each test they were cleaned with acidic and basic solution according to protocols of membrane producer.

Results and discussion

Membrane selectivity

Membrane selectivity was accessed on the basis of rejection coefficients calculated using formula, $r = 1 - C_P/C_F$, where C_p and C_F are values of water quality indicators in permeate (after UF) and feedwater (before UF), respectively. The obtained results are summarized in Tab. 1.

Tab.1. Characteristic data for ceramic membranes selectivity in surface water ultrafiltration (mean annual values) [*Szmukala, 2010*]

Indicator/coefficient	Membrane 1 kDa		Membrane 3 kDa	
	0.55 MPa	0.85 MPa	0.55 MPa	0.85 MPa
feed indicator, C_F				
SS, mg/dm^3	178.0	84.0	160.0	227.0
UVA	0.455	0.496	0.518	0.490
BOD, mg O_2/dm^3	3.1	2.8	4.8	3.7
COD, mg O_2/dm^3	9.5	12.0	10.5	9.5
P_{tot}, mg P/dm^3	0.285	0.353	0.306	0.321
N_{tot}, mg N/dm^3	0.563	0.607	0.705	0.487
permeate indicator, C_P				
SS, mg/dm^3	9.0	8.0	16.0	22.0
UVA	0.143	0.227	0.18	0.192
BOD, mg O_2/dm^3	0.4	0.7	1.4	1.1
COD, mg O_2/dm^3	4.4	7.7	5.2	5.7
P_{tot}, mg P/dm^3	0.143	0.185	0.167	0.161
N_{tot}, mg N/dm^3	0.487	0.489	0.608	0.407
rejection coefficient, *r*				
SS, mg/dm^3	0.95	0.90	0.90	0.90
UVA	0.69	0.54	0.65	0.61
BOD, mg O_2/dm^3	0.87	0.74	0.71	0.71
COD, mg O_2/dm^3	0.63	0.36	0.50	0.40
P_{tot}, mg P/dm^3	0.50	0.48	0.45	0.50
N_{tot}, mg N/dm^3	0.14	0.19	0.14	0.16

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The performed analysis showed that mean annual values of *pH* were in the range of 7.7÷8.3. Water quality indicators measured at the sampling point I (Fig. 1) exceeded limit values of water quality parameters for fish in natural conditions apart total nitrogen [*Decree, 2002*]. The differences in water quality above and below fish hatchery (sampling points III-IV) were negligible in the light of *Decree of Polish Ministry of Environment* on growth of maximum allowable levels of substances in water used for fish aquaculture [*Decree, 2006*]. Application of both ceramic membranes with cut-off 1.0 and 3.0 kDa enables achievement of water quality in conformity with environmental regulations. Moreover, microbiological analysis indicated that both membranes 1.0 and 3.0 kDa retained *Coli* bacteria in 99 and 93%, respectively [*Szmukala, 2010*].

Fouling characterization

Characterization of fouling in investigated ceramic membrane systems was performed using several tools, flux reduction, hydraulic resistances and fouling index.

Flux reduction can be described as the difference between permeate flux , J_v and clean water flux, J_{0b} as follows:

$$FR_P = 1 - \frac{J_v}{J_{0b}} \tag{1}$$

The value of fluxes J_{0a}, J_{0b} and J_v were measured during long term tests, when ultrafiltration process has reached pseudo steady state.

Hydraulic resistances involved in ultrafiltration process were evaluated using resistance-in-series model. This model is based on *Darcy's* law, which relates the permeate flux with transmembrane pressure, *TMP* [Pa], water viscosity, η [Pa·s] and total resistance, R_T [1/m]:

$$J_v = \frac{TMP}{\eta R_T} \tag{2}$$

where R_T is the sum of clean membrane resistance, R_M and fouled membrane resistance, R_F consisted of reversible and irreversible fouling resistances, R_R and R_{IR}, respectively:

$$R_T = R_M + R_R + R_{IR} \tag{3}$$

Thus, various hydraulic resistances can be calculated as follows:

$$R_M = \frac{TMP}{\eta J_{0b}} \tag{4}$$

$$R_T = \frac{TMP}{\eta J_v} \tag{5}$$

$$R_{IR} = \frac{TMP}{\eta J_{0a}} - R_M \tag{6}$$

Ultrafiltration modified fouling index, UF-MFI was developed based on the same *Darcy's* law making the hypothesis that the total resistance to flow in the membrane system is the sum of membrane resistance, R_M and cake resistance, R_C. Thus, after integration the conventional equation of filtration at constant pressure and some simplification the following relationship is obtained:

$$\frac{tA}{V} = a + MFI\frac{V}{A} \tag{7}$$

where *t* is time in seconds and *A* is membrane area, m^2. The Eq. (8) predicts the linear relationship between *t/V/A* and *V/A* during cake filtration and the slope and ordinate of the linear region is *MFI* and *a*, respectively:

$$MFI = \frac{\eta I_C}{2TMP} \tag{8}$$

$$a = \frac{\eta R_M}{TMP} \tag{9}$$

In Eqs. (7-9) *V/A*, m^3/m^2 is the permeate volume produced per membrane area and I_C, 1/m^2 is resistivity of the cake [*Khirani, et al., 2005*].

The parameters characterizing fouling in the ceramic membrane-water system obtained using Eqs. (1-9) are presented in tab. 2. The values of fouling parameters summarized in table 2 were calculated using mean experimental data of 10-20 ultrafiltration tests.

Flux reduction FR_P with regards to permeate flux is slightly dependent on membrane cut-off and *TMP*. In the light of flux reduction both investigated membranes are susceptible on fouling to a similar extent.

Hydraulic resistances, R_R and R_{IR} determine fouling mechanism in the system. R_R is mainly caused by reversible cake formation due to particle deposition on membrane surface. R_{IR} is related to irreversible deposition of particles on the membrane surface and irreversible adsorption/adhesion of small molecules inside membrane pores. The internal fouling inside membrane pores can be negligible because the membranes used in UF tests are negatively charged at *pH* above 6.9 (the point of zero charge membrane). Comparison of R_T, R_R and R_{IR} leads to the conclusion, that membrane 3.0 kDa is less prone to fouling.

Tab. 2. Fouling parameters for ultrafiltration process of surface water

Fouling parameter	Membrane 1.0 kDa $A = 0.35$ m^2 cross-flow velocity 4 m/s		Membrane 3.0 kDa $A = 0.20$ m^2 cross-flow velocity 5.7m/s	
	0.55 MPa	0.85 MPa	0.55 MPa	0.85 MPa
flux reduction, (Eq.1) FR_P	0.64	0.48	0.57	0.58
hydraulic resistance, $R_i \cdot 10^{12}$, 1/m (Eqs. 2-6)				
R_M	11.9	12.0	6.5	6.5
R_T	36.6	24.3	15.7	15.5
R_R	12.8	7.3	5.7	4.1
R_{IR}	11.9	4.9	3.5	4.9
ultrafiltration modified fouling index, (Eqs. 7-9)				
UF-MFI · 10^5, s / m^2	5.4	1.5	0.9	1.0
resistivity, $I_C \cdot 10^{14}$, 1/m^2	6.5	2.6	1.0	1.7
$R_M \cdot 10^{12}$, 1/m	11.0	11.0	6.9	6.4

It is difficult to directly correlate R_R and R_{IR} with UF-MFI but is clear from tab. 2 that values of UF-MFI are small for small fouling resistances. In the case of membrane 3.0 kDa, UF-MFI is almost the same for different *TMP* due to the compressibility of the formed cake. The resistivity I_C can be used also as representative parameter of fouling ability. In the case of compressible cake, I_C is pressure dependent and allows to choose operating transmembrane pressure.

Conclusions

This study showed that:

– both ceramic membranes with cut-off 1.0 and 3.0 kDa yielded the water quality in conformity with environmental regulations
– with regarding all fouling parameters membrane 3.0 kDa has better fouling characteristics for both investigated transmembrane pressure than membrane 1.0 kDa
– the values of R_M obtained from pure water flux (Eq. 1) and from the ordinate at the origin (Eq. 7) are similar
– characterization of fouling in membrane systems using different tools gives comprehensive evaluation of this critical parameter which should be considered in ultrafiltration process design.

LITERATURE

Decree of Polish Ministry of Environment dated 4 October 2002. Dz.U. 2002 nr 176 poz. 1455. Rozp. Min. Środ. z 4.10.2002 r. w sprawie wymagań, jakim powinny odpowiadać wody śródlądowe będące środowiskiem życia ryb w warunkach naturalnych

Decree of Polish Ministry of Environment dated 24 July 2006, Annex 9. Dz.U. 2006 nr 137 poz. 984. Rozp. Min. Środ. z 24.07.2006 r. w sprawie warunków, jakie należy spełnić przy wprowadzaniu ścieków do wód lub ziemi, oraz w sprawie substancji szczególnie szkodliwych dla środowiska wodnego

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