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INFLUENCE OF WATER PROPERTIES ON FOULING INTENSITY AND FOULING MECHANISM DURING ULTRAFILTRATION

BADANIE WPŁYWU WŁAŚCIWOŚCI WODY NA INTENSYWNOŚĆ I MECHANIZM ZJAWISKA FOULINGU W PROCESIE ULTRAFILTRACJI

Abstract: Membrane techniques are an alternative water treatment method for classical processes. However, mostly their capacity and membrane lifetime are limited by the phenomenon called fouling, *ie* the accumulation of organic and/or inorganic substances on the surface and into the pores of the membrane. The results of the study presenting the dependence of water properties such as pH, kind of organic matters and ionic strength on membrane fouling are discussed in this article. *Unified Modified Fouling Index* (UMFI) was used to describe intensity of fouling. Also the influence of water properties on fouling mechanism are shown.

Keywords: ultrafiltration, NOM, fouling, pH, ionic strength

Both, inorganic and organic substances are present in surface waters. The Regulation of Minister of Environment in Poland on quality of surface waters used as drinking water supply [1] defines permissible pH, water hardness, concentrations of chlorides, sulphates and total organic carbon content. The classical water treatment methods *ie* coagulation, bed filtration, oxidation can be replaced by membrane processes. The main exploitation problem connected with low-pressure membrane techniques is the decrease of membranes capacity caused by fouling phenomenon. Different mechanisms of fouling can appear during the process. According to Hermia's model, the constant pressure filtration law can be described as:

$$\frac{d^2 t}{dV^2} = k\left(\frac{dt}{dV}\right)^n \tag{1}$$

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where: V – permeate volume;
t – filtration time;
n, k – constants typical for different fouling mechanisms.

Constant flux membrane processes are most often apply in the industry. Analogically to the Hermia's model, such processes can be described as follows:

$$\frac{dP'}{dV_s} = k_v P'n \tag{2}$$

where: P' – the ratio of the transmembrane pressure to the normal pressure [-];
V_s – cumulated permeate volume per unit membrane area [m^3/m^2];
k_v, n – constants typical for different fouling mechanisms.

Huang et al [2] derived the formula, which can be applied for both, constant pressure and constant flux filtrations:

$$-\frac{dJ'_s}{dV_s} = k_v {J'_s}^{2-n} \tag{3}$$

where: J_s' – specified normalized permeate flux [-],
k_v (UMFI) – fouling parameter [m^2/m^3].

General solutions of differential equation (3) depending on the fouling mechanism are shown in Table 1, where C – the integration constant. The slope of the straight line to the x axis determine the intensity of fouling and is called *Unified Modified Fouling Index* (UMFI). The introduction of normalized flux to the equation 3 allows to compare membranes with different separation properties (stream, porosity), while the introduction of V_s allows to compare the laboratory scale results with the industrial scale studies.

Table 1

Filtration laws – general solutions of differential equation

Mechanism	Solution equation
Standard bloking	$2\sqrt{J_s} = C - \text{UMFI} \cdot V_s$
Complete bloking	$J'_s = C - \text{UMFI} \cdot V_s$
Intermediate bloking	$\ln J'_s = C - \text{UMFI} \cdot V_s$
Cake formation	$\frac{1}{J'_s} = C + \text{UMFI} \cdot V_s$

According to Hermia's model following fouling mechanisms can be distinguished:
– standard blocking – the contraction of membrane pores caused by the adsorption which occur during the filtration; particles can block inside of pores depending on differences between pores shape and adsorbate particles shape;

– complete blocking – the blocking of pores on the membrane surface, however particles do not overlay on each other;

– intermediate blocking – the blocking of pores on the membrane surface, however particles cumulate one on another;

– cake or gel formation – the accumulation of substances on the membrane surface (particles do not penetrate the membrane interior), particles form precipitate or gel of different density degrees [3–6].

The fouling intensity depends on both, membrane and feed water properties. The ionic strength and pH influence on the solubility of organic substances present in water, and additionally, they can change interactions between particles and membrane surface. Properties of organic substances are also important. Chemical character and structure of organic particles are quite significant when transport through the membrane is considered. Linear particles of aliphatic structure are easier transported through the membrane pores than the cyclic ones. On the other hand, aliphatic particles are much easier adsorbed in pores what leads to the irreversible fouling, while cyclic compound can precipitate on the membrane surface and cause the reversible fouling appearance [7].

The aim of the study was to determine the influence of pH, ionic strength and type of chemical substances on UMFI value for different fouling mechanisms as well as on the degree of removal of organic substances.

Material and methods

The study were carried out in Ultrafiltration Cell Millipore CDS10 System. CDS10 device cooperated with flat sheet membranes and the dead-end mode filtration was performed. The feed was introduced perpendicularly to the membrane surface. The applied pressure was kept constant and equal to 0.1 MPa. The scheme of the ultrafiltration system was presented in [8]. The new membrane was used in every experiment. The characteristic of applied membranes is presented in Table 2. The molecular weight cut off was defined by the membrane producer.

Fluxes of deionized water and contact angles were determined for all new membranes. Measurements of the contact angle were done using the goniometer and the sessile drop method was applied. The angle between drop of water, membrane surface and air was measured.

Table 2

The characteristics of membranes (J_m – water flux)

Producer	KOCH Membrane Systems
Membrane material	Poly(vinylidene fluoride) (PVDF)
MWCO [kDa]	30
Contact angle [^{o}]	57.5 ± 5.2
J_m [dm^3/hm^2] (t = 20 ^{o}C)	94

The absolute value of UMFI was applied to describe the intensity of fouling during ultrafiltration. Simulated waters containing humic substances (2–500) kDa and dextranes (3–110) kDa were used in the study. The intensity of fouling and the ultrafiltration effectiveness were determined for waters:

– of constant humic substances and dextranes mass ratio ($x_{H/D}$ = 0.5) and with low ionic strength and various pH (5–9),

– of constant humic substances and dextranes mass ratio ($x_{H/D}$ = 0.5) under constant pH equal to 7 and various calcium ions concentrations (0–200) mg/dm^3,

– of constant pH equal 7, low ionic strength and different composition of organic substances (different mass ratios of humic substances and dextranes, SUVA = (0.66–7.05) m^2/g C.

In order to determine the reversibility of fouling phenomenon the backflushing of membrane was performed and the percentage recovery of initial deionized water flux was defined.

Results and discussion

The fouling intensity was characterized by means of the modulus of Unified Modified Fouling Index. Least Squares Estimation was used to determine UMFI. Table 3 presents correlation coefficients (R) obtained for particular filtrations together with UMFI absolute values and uncertainty of measurements of UMFI.

Table 3

The statement of UMFI obtained during particular filtrations

pH [-]	Ca [mg/dm^3]	x_H [-]	Cake formation		Complete blocking		Interdirect blocking		Standard blocking	
			UMFI × 10^3 [m^2/dm^3]	R [-]	UMFI × 10^3 [m^2/dm^3]	R [-]	UMFI × 10^3 [m^2/dm^3]	R [-]	UMFI × 10^3 [m^2/dm^3]	R [-]
7	0	0.5	2.716 ± 0.058	0.9980	2.235 ± 0.080	0.9943	2.462 ± 0.070	0.9964	1.823 ± 0.065	0.9955
7	100	0.5	2.808 ± 0.065	0.9995	2.283 ± 0.057	0.9986	2.529 ± 0.056	0.9994	2.523 ± 0.080	0.9991
7	200	0.5	2.060 ± 0.052	0.9972	1.751 ± 0.068	0.9934	1.898 ± 0.061	0.9955	0.667 ± 0.016	0.9945
5	0	0.5	2.989 ± 0.052	0.9987	2.387 ± 0.087	0.9942	2.668 ± 0.072	0.9968	2.345 ± 0.075	0.9956
9	0	0.5	0.697 ± 0.014	0.9984	0.657 ± 0.016	0.9977	0.677 ± 0.015	0.9981	2.402 ± 0.056	0.9979
7	0	0.1	1.645 ± 0.015	0.9996	1.451 ± 0.023	0.9989	1.544 ± 0.018	0.9994	1.496 ± 0.021	0.9992
7	0	0.9	1.849 ± 0.039	0.9980	1.603 ± 0.054	0.9951	1.721 ± 0.047	0.9967	1.661 ± 0.050	0.9959

The exemplary diagram of dependences between permeate fluxes and V_s including confidence intervals determined for significance level (α) equal to 0.05 is shown in Fig. 1.

The well fit of regression lines to measuring points was observed what additionally was confirmed by high value of correlation coefficients. Small measurement uncertain-

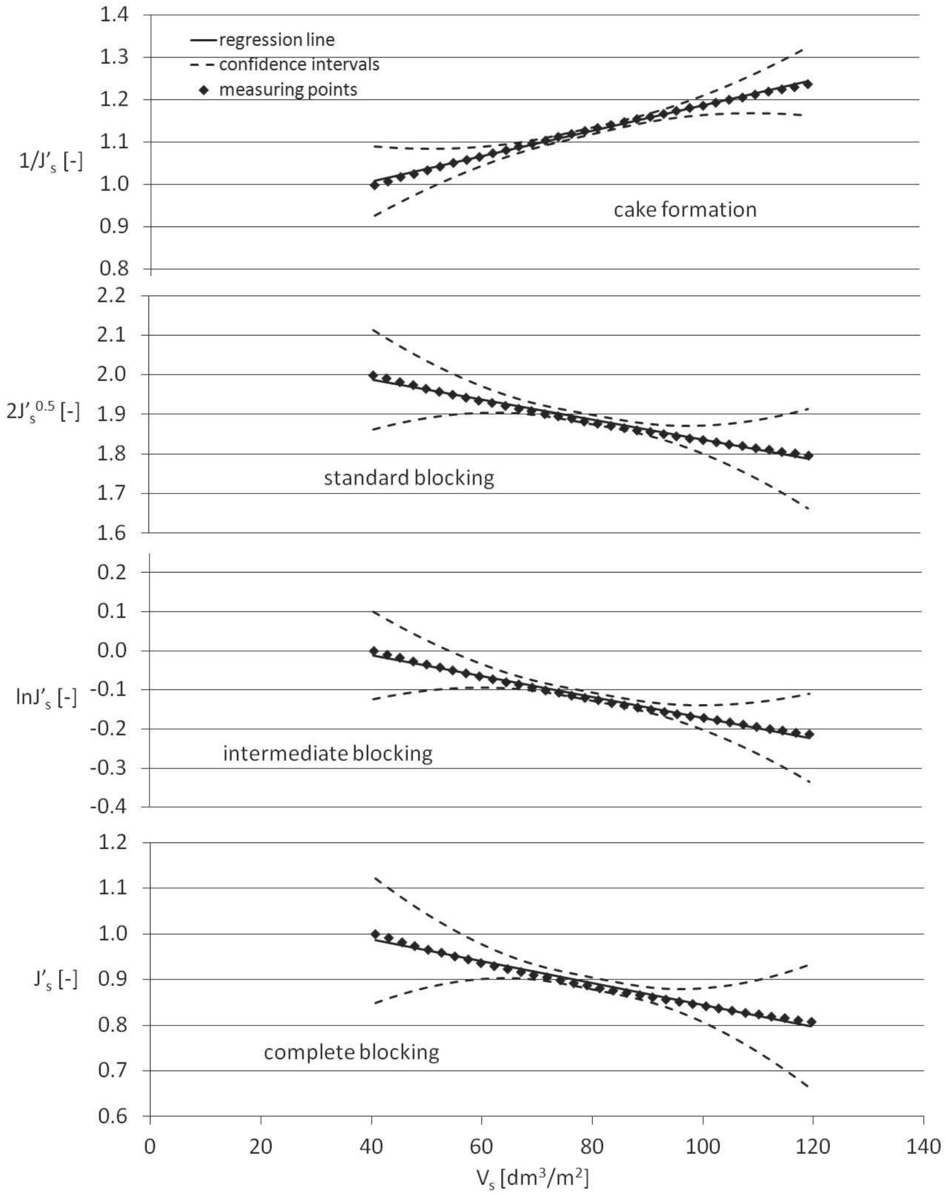

Fig. 1. The diagram of dependences between permeate fluxes and V_s (for water containing 100 mgCa/dm^3, pH = 7, $x_{H/D}$ = 0.5)

ties of UMFI were obtained in almost all of cases and did not exceed 4 %. All measuring points and regression lines were covered by the determined confidence interval *ie* interval to which estimated parameter value belongs with 95 % probability.

One of the main factors which influences on the fouling intensity is pH of the feed. The impact of pH on the intensity of fouling and its mechanisms occurred during filtrations is shown in Fig. 2.

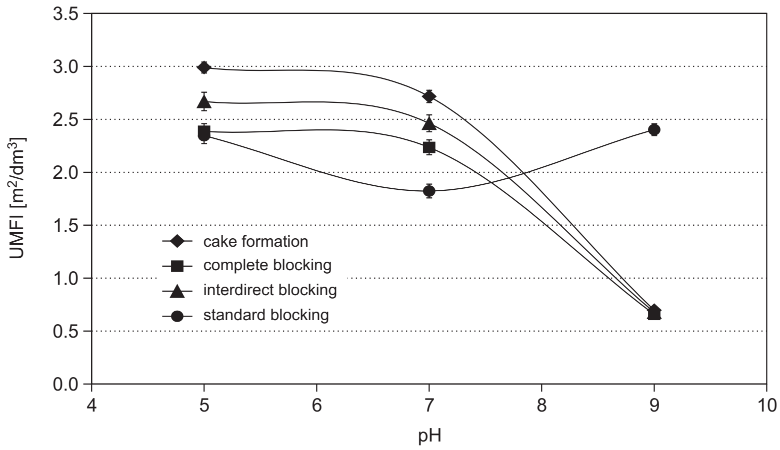

Fig. 2. Influence of pH on fouling (UMFI)

In case of membrane fouling the cake formation mechanism was the most significant, except from the filtration carried out under pH = 9. The mechanism in which pores contraction caused by the adsorption of organic substances takes place (*ie* standard blocking) had the negligible influence on fouling for pH range 5 to 7, while it was of the greatest importance in case of water pH equal to 9. The increase of alkalinity caused the increase of solubility of humic substances. It resulted in the increased number of molecules which were able to penetrate membranes pores and adsorb on their surface. For other fouling mechanisms *ie* cake formation, complete blocking and intermediate blocking the increase of pH caused the decrease of fouling intensity, which also could be explained by the change of solubility of organic substance in water. In feeds of alkaline character the similar influence of fouling mechanisms dominant in acidic waters (*ie* complete blocking, intermediate blocking and cake formation) was observed.

Simultaneously, with the decrease of fouling intensity the decrease of values of TOC (*Total Organic Carbon*) (Fig. 3), DOC (*Dissolved Organic Carbon*) and UV_{254} absorbance coefficients was observed. Additionally, values of retention coefficients indicated the better removal of humic substances than polysaccharides (dextranes) from the feed. PVDF (*Polyvinichidene fluoride*) membrane fouling was almost completely reversible (71–82 %). The higher pH of the feed the better recovery of the initial membrane capacity could be obtained, and the highest difference was noticed especially between pH = 5 or 7 and pH = 9 (11 % increase).

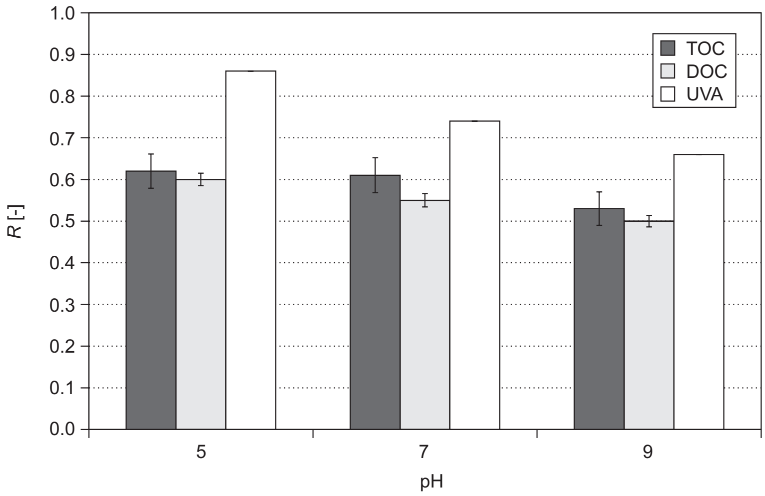

Fig. 3. Influence of pH on retention coefficients of organic matters

Calcium ions (high ionic strength) had also changed interactions in the membrane--feed system. The influence of calcium ions on the intensity of fouling is shown in Fig. 4 and on retention coefficients of organic impurities in Fig. 5. The increase of concentration of calcium ions resulted in the decrease of the fouling intensity. The appearance of 3 fouling mechanisms: cake formation, intermediate blocking and complete blocking was similar in case of various ionic strength waters as for various pH waters. However, the decrease of the fouling intensity was not as significant as when the feed pH was varied except from the index determined for the standard blocking mechanism. In case of the contraction of membrane pores the significant decrease of the UMFI index value with the increase of calcium ions concentration was observed (almost 3 times smaller UMFI for waters containing 200 mg/dm^3 of calcium in

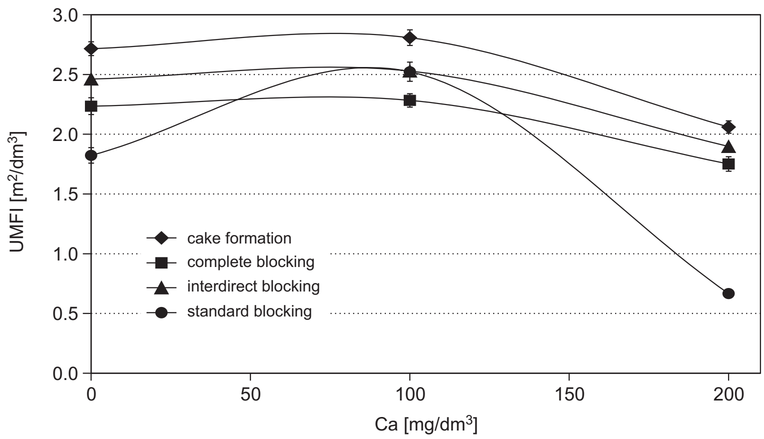

Fig. 4. Influence of calcium concentration on fouling

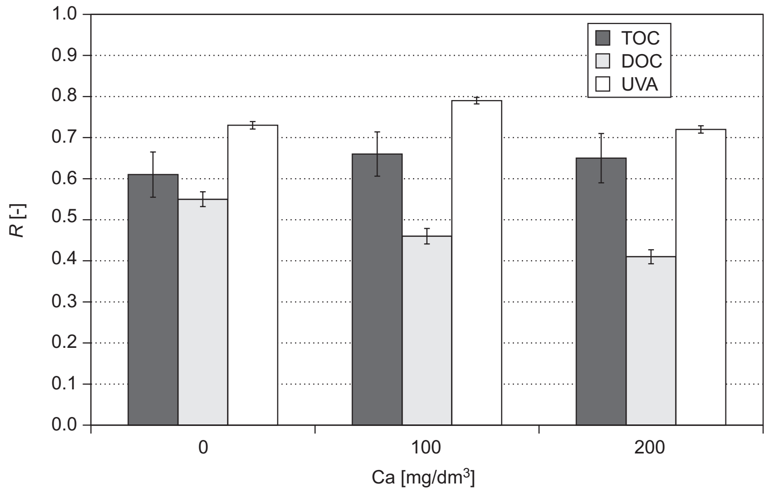

Fig. 5. Influence of calcium concentration on retention coefficients of organic metters

comparison with waters without calcium ions). In case of the feed of high ionic strength on the one hand organic substances form aggregates, while on the other hand the decrease of the apparent molecular weight is observed. According to that phenomenon, particles which firstly were adsorbed on membrane pores in case of high ionic strength were easily transported through the membrane or precipitated on the filtration cake formed by aggregates.

Calcium ions had a greatest influence on the removal of organic impurities indicated as DOC. The higher ionic strength in the feed the lower retention coefficients of DOC was observed. In the presence of calcium ions the retention of TOC increased negligibly. It can be explained by the aggregation of organic particles caused by the high ionic strength what resulted in the filtration cake formation. The increased calcium ions concentration caused also the more reversible form of fouling. The recovery of water flux increased more than 30 % in case of the feed containing 200 mgCa/dm^3 (the recovery degree exceeded 100 % what can be explained by the change of properties of membrane material caused by adsorption of organic and inorganic impurities) in comparison with the feed in which calcium ions were absent.

$SUVA_{254}$ index was used to determine the qualitative composition of natural water. The value of $SUVA_{254} \geq 4$ m^2/gC is characteristic for water which contains significant amount of hydrophobic, aromatic and high-molecular weight organic substances. The value of $SUVA_{254} \leq 2$ m^2/gC indicates that water contains mainly non-humic, hydrophilic, low-molecular weight substances. The mixture of hydrophilic and hydrophobic, low- and high-molecular weight substances is present in water with $SUVA_{254}$ value in the range 2–4 m^2/gC [9]. The influence of organic substances composition on fouling is shown in Fig. 6.

The parabolic dependence of UMFI indexes on SUVA was observed. The intensity of fouling during the filtration of feed waters containing mainly polysaccharides or

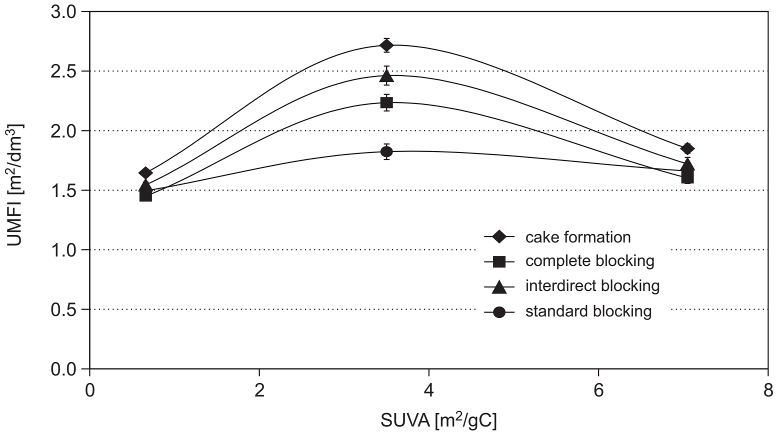

Fig. 6. Influence of SUVA on fouling (UMFI)

mainly humic compounds was insignificant and similar in both cases, while during the filtration of waters containing equal amounts of humic substances and dextranes the intensity of fouling was the greatest. In the second case the least reversible fouling was observed (*ca* 70 % recovery of the initial water flux). Similarly as in the study of the influence of pH and Ca on fouling the cake formation was the most significant mechanism.

The influence of SUVA on the degree of retention of organic substances defined by TOC, DOC and UVA is shown in Fig. 7. The decrease of UVA retention coefficient with the increase of SUVA was observed. However, the degree of UVA removal was the higher the smaller amount of substances able to absorb UV was present in the feed (the value of UVA for the water of the greatest SUVA indicator value was the order of magnitude higher than for the water of the smallest SUVA value). Both, retentions of

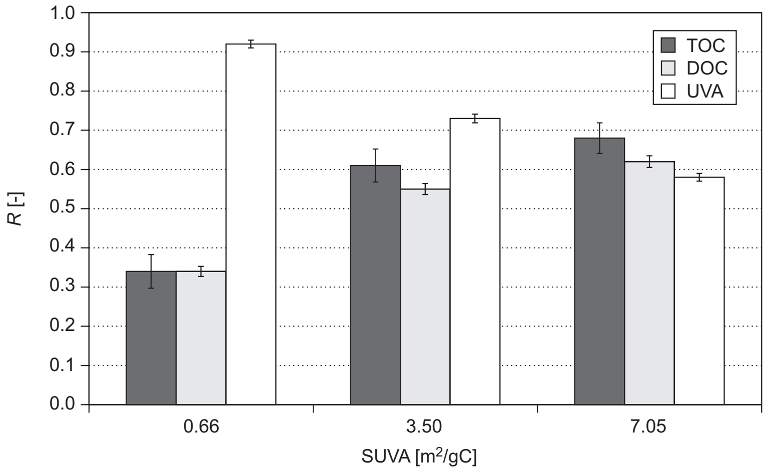

Fig. 7. Influence of SUVA on retention coefficients

TOC and DOC were greater for the greater value of SUVA index. It showed that PVDF membrane removed humic substances more effectively than polysaccharides.

Conclusions

The performed study showed that:

1. for the pH range 5–7 the cake formation mechanism is the most significant in case of membrane fouling, next the intermediate and complete blocking, while for pH = 9 standard blocking is of the greatest importance,
2. the increase of ionic strength and pH cause the decrease of fouling intensity and increase of its reversibility,
3. the substances of properties between hydrophilic and hydrophobic cause greater PVDF membrane blocking in comparison with strictly hydrophilic or hydrophobic substances,
4. PVDF membrane removes humic substances more effectively than polysaccharides,
5. the best removal of organic substances with the use of PVDF membrane occurs in waters which characterize with high ionic strength, low pH and hydrophobic substances content,
6. among parameters like pH, ionic strength and SUVA the feed water pH has the greatest influence on pH.

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BADANIE WPŁYWU WŁAŚCIWOŚCI WODY NA INTENSYWNOŚĆ I MECHANIZM ZJAWISKA FOULINGU W PROCESIE ULTRAFILTRACJI

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Abstract: Alternatywną metodą oczyszczania i uzdatniania wody w stosunku do metod klasycznych są procesy membranowe, którym towarzyszy nieodłącznie zjawisko foulingu, związane z obniżeniem wydajności i z akumulacją substancji organicznej bądź nieorganicznej na powierzchni membrany. W artykule omówiono wyniki badań wpływu właściwości wód (pH, rodzaj substancji organicznej, siła jonowa) na intensywność foulingu, wyrażoną za pomocą jednostkowego indeksu foulingu UMFI (U*nified Membrane Fouling Index*) i na mechanizm zjawiska.

Słowa kluczowe: ultrafiltracja, NOM, fouling, pH, siła jonowa