

## NOM FOULING MECHANISM DURING ULTRAFILTRATION

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### Abstract

The paper presents the results of the study focused on membrane fouling during ultrafiltration water treatment. Natural organic matter (NOM) plays a significant role in the fouling of ultrafiltration membranes. Surface water from Paprocany Lake (Tychy) and Czarna Przemsza River (Bedzin) were used in the experiments. The aim of the study was to get a better understanding of the interactions between the fractional components of NOM (fraction  $<0.22 \mu\text{m}$ , HFO and HFI) and hydrophilic cellulose membranes by Nadir (cut-off 30 kDa) under different pH conditions (pH equal to ca.7 and ca.2). The NOM fractionation showed that surface water contained small amount of colloids and suspended substances  $>0.22 \mu\text{m}$  and in the fraction  $<0.22 \mu\text{m}$  the hydrophilic fraction was predominated. The results of the filtration of NOM fractions (fraction  $<0.22 \mu\text{m}$ , HFO, HFI) suggested that the decrease of pH of filtered streams (to pH ca.2) as well as the hydrophobic fraction exerted an essential influence on the ultrafiltration membranes fouling. The analysis of the fouling mechanism based on Hermia's model allowed to declare that the membrane blocking (complete, standard and transient blocking) observed during the one-hour filtration could be described by the mixed mechanism.

### Streszczenie

W pracy przedstawiono wyniki badań foulingu membran podczas oczyszczania wody za pomocą ultrafiltracji. Naturalne substancje organiczne (NOM) zawarte w wodzie odgrywają znaczną rolę w foulingu membran ultrafiltracyjnych. W badaniach zastosowano wodę powierzchniową z jeziora Paprocany (Tychy) oraz z rzeki Czarna Przemsza (Będzin). Przedmiotem badań było rozpoznanie i zrozumienie wzajemnego oddziaływania pomiędzy frakcjami NOM (frakcja  $<0.22 \mu\text{m}$ , HFO i HFI) dla dwóch odczynów (pH ok. 7 i 2) i hydrofilowymi membranami z celulozy firmy Nadir (cut-off 30 kDa). Wyniki frakcjonowania NOM wykazały, że charakterystyczną cechą wody powierzchniowej jest niewielka zawartość substancji koloidalnych i zawieszonych  $>0.22 \mu\text{m}$  oraz przeważa w niej frakcja hydrofilowa. Wyniki filtracji frakcji NOM (frakcja  $<0.22 \mu\text{m}$ , HFO, HFI) sugerują, iż obniżenie odczynu filtrowanych strumieni (do pH ok. 2) oraz frakcja hydrofobowa (HFO) mają istotny wpływ na fouling membran ultrafiltracyjnych. Analiza mechanizmu foulingu oparta o model „Hermii” pozwoliła stwierdzić, że blokowanie membran z celulozy podczas godzinnej filtracji (kompletne, standardowe i przejściowe) zachodzi według mechanizmu mieszanego.

Keywords: Natural organic matter (NOM), ultrafiltration, mechanism of fouling, fractionation, water treatment.

## 1. INTRODUCTION

Natural Organic Matter (NOM) is a very important factor when the fouling of ultrafiltration membranes applied for surface water treatment is concerned. This type of fouling is often called an organic fouling [1]. NOM appears almost in every surface water and its amount and properties depend on climate, ground shape and transformations that occur during its trans-

port in lakes and rivers [2]. NOM is a mixture of high-molecular weight (proteins, carbohydrates, humus) and low-molecular weight (simple organic acids) organic compounds [3,4] and it is responsible for the membrane fouling of a type that depends on a membrane specificity.

The mechanism of fouling which occurs during ultrafiltration is based on the adsorption of substances inside

pores of a membrane what results in the decrease of an internal pores diameter. It can lead to the increase of the efficiency of substances removal including medium- and low-molecular weight compounds [2]. On the other hand, the decrease of membrane capacity caused by coating and/or blocking of membrane pores is observed. The decrease of a permeate stream during ultrafiltration mainly depends on: hydrophilicity/hydrophobicity of a membrane material and a size of NOM molecules and their chemical potential (which is dependent on pH and water temperature). Physico-chemical interactions between NOM and a membrane as well as the use of integrated/hybrid systems (coagulation, activated carbon adsorption, oxidation, ion exchange – UF) are crucial for the ultrafiltration process. The listed systems allow to limit fouling phenomenon while the effects of membranes exploitation improvement depend on a kind of compounds present in water [5, 6].

The description of the mechanism of fouling of UF membranes caused by different NOM components is the topic of many studies [7-10]. The characterization of NOM is made by different techniques among which fractionation with the use of polymeric adsorbent i.e. XAD-8 and XAD-4 is one of the most popular. This technique is based on the separation of dissolved organic compounds (DOC) into a highly hydrophobic fraction (isolated on the resin XAD-4), a slightly hydrophobic fraction (isolated on the resin XAD-4) and a hydrophilic fraction (which is not adsorbed on any of the resins). However, the results of the study presented in the literature do not allow to precise which fraction is mainly responsible for fouling and membrane capacity decrease e.g. the study of [7] suggests that hydrophilic fraction has a greater influence on fouling than hydrophobic and transient fractions while the study of [2] insists that the hydrophobic fraction is the most important membrane foulant.

The inconsistency of membrane fouling causes can be explained by the application of various NOM fractionation procedures and different filtration conditions. Most of the authors suggest the NOM fractionation in highly acidic conditions (pH ca.2) in order to increase the adsorption of NOM on resins [11-13], while others [14] propose to apply neutral conditions without pH modification and the separation of hydrophobic and hydrophilic fraction by means of XAD-8 resins adsorption.

The fractioning in present work was applied was the NOM in strongly acidic conditions, and the realization of investigations of influence was the aim the

NOM in surface water on intensity and the mechanism of the fouling phenomenon in the ultrafiltration process. The identification of NOM fraction and ultrafiltration of separated streams with the use of cellulose membranes and different pH values to confirm the influence of hydrophilicity/hydrophobicity of NOM and water pH on UF membrane coating/blocking were the aim of the presented study.

## 2. MATERIAL AND METHODS

### 2.1. Water, membranes and apparatus

Two surface water from Silesia region were used in the study. The characteristics of water samples is presented in Table 1.

Two types of flat membranes were used: microfiltration polyethersulphone membrane of pore diameter 0.22  $\mu\text{m}$  by Millipore to remove colloids ( $>0.22 \mu\text{m}$ ) from water and hydrophilic cellulose membrane of cut off 30 kDa by Nadir to determine the influence of hydrophilicity/hydrophobicity of NOM on the membrane fouling. The effective filtration area of both membranes was equal to 38.5  $\text{cm}^2$ .

The membrane filtration was performed in the Stirred Ultrafiltration Cell Millipore CDS – 10 System, model 8400. The system was equipped with selective valve which connected gas tank and feed tank of 800  $\text{cm}^3$  volume with the ultrafiltration chamber of 400  $\text{cm}^3$  volume. The system worked in the dead end mode in which the feed is directed perpendicularly to the membrane surface.

### 2.2. Fractionation NOM

Organic substances present in surface water samples were fractionated. Firstly, surface waters were filtered through PES MF filter of pore diameter 0.22  $\mu\text{m}$  to remove colloids. Next, the fraction containing substance  $<0.22 \mu\text{m}$  was introduced on polymeric Amberlite adsorbents i.e. XAD7HP and XAD4 by Rohm&Haas to separate hydrophobic (HPO), hydrophilic (HPI) and transient – transphilic (TPI) fractions. The detail description of the fractionation procedure based on [12, 13] and the resins specification provided by the producer were discussed at [8].

### 2.3. Ultrafiltration tests

The fractions obtained during the NOM fractionation of two surface waters were introduced to the ultrafiltration process and the hydrophilic cellulose membrane (cut-off 30 kDa) was used to determine

the influence of particular NOM fractions on membrane fouling. Before the UF process fractions needed to be standardized according to DOC, pH and temperature. The modification of pH was made with the use of 0.1 M HCl and 0.1 M NaOH solutions. Two pH ranges were used in the study i.e. pH=7 and pH=2. A new membrane was used for every filtration and the process was preceded by a membrane conditioning in order to obtain constant deionized water stream ( $J_0$ ). The ultrafiltration of NOM fractions was performed under constant transmembrane pressure equal to 0.1 MPa and during the one-hour process the dependence of permeate stream on time ( $J$ ) was determined. Next, the relative permeability of the membrane –  $J/J_0$  was assigned in order to describe the tendency to fouling caused by a given NOM fraction.

### 3. RESULTS AND DISCUSSION

#### 3.1. Characteristics of surface water

The characteristic of surface water samples collected from a lake and a river on Silesia region is presented in Table 1.

**Table 1.**  
Characteristics of used water

Parameter	Water from Paprocany Lake(Tychy)	Water from Czarna Przemsza River (Bedzin)
pH	7.21	7.89
Conductivity, $\mu\text{S cm}^{-1}$	335	720
Turbidity, NTU	1.35	3.15
Absorbance at $\text{UV}_{254\text{nm}}^{1\text{m}}$	34.8	16.7
TOC*, mgC/l	14.09	4.40
SUVA**, $\text{m}^3/\text{gC}\cdot\text{m}$	2.46	3.80

\* – total organic carbon, \*\*– specific UV absorbance

The physico-chemical parameters of waters indicated their similarity in case of pH, however, the organic compounds content was much higher in the lake water than in the river water.

The fractionation of organic substances present in investigated waters by means of filtration with of MF 0.22  $\mu\text{m}$  membrane and adsorbance on Amberlite resins XAD 7HP/4 allowed to determine composition and percentage share of isolated NOM fractions. The characteristics of obtained fractions are shown in Table 2.

It was observed that the lake water contained 64% of total organic compounds content in the form of the fraction  $<0.22\ \mu\text{m}$ , while in the river water this fraction share was equal to 95%. It was also indicated that in the fraction  $<0.22\ \mu\text{m}$  hydrophilic fraction was dominant.

The organic compounds content in the investigated waters was determined by means of DOC analysis and absorbance at  $\text{UV}_{254}$ . The high value of  $\text{UV}_{254}$  absorbance obtained for hydrophobic fraction indicated the presence of organic molecules containing aromatic groups [15]. The highest content of these compounds was observed in the hydrophobic fraction separated from Paprocany Lake water.

Specific UV absorbance SUVA ( $\text{SUVA}=\text{UV}_{254}/\text{DOC}$ ) is a parameter that describes organic compounds present in water and allows to determine correlation between the aromaticity of a compound and its hydrophilicity. SUVA equal to ca.  $4\ \text{m}^3/\text{g}\cdot\text{m}$  and greater indicates high content of hydrophobic, aromatic and high-molecular weight DOC fractions, while SUVA below  $2\ \text{m}^3/\text{g}\cdot\text{m}$  suggests the presence of non-humic, hydrophilic low-molecular weight compounds [7, 15]. The results of analyses of dissolved NOM fraction and further obtained separated

**Table 2.**  
Characteristics of NOM fractions isolated from surface water

Fraction	V sample	DOC*	Absorbance	SUVA	Part prop.
	$\text{dm}^3$	$\text{mgC/l}$	$\text{UV}_{254\text{nm}}^{1\text{m}}$	$\text{m}^3/\text{gC}\cdot\text{m}$	%
Water from Paprocany Lake (Tychy)					
$<0.22\ \mu\text{m}$	2.50	8.69	23.9	2.75	64
HPO	0.11	66.4	220.5	3.32	33
TPI	0.11	37.5	92.7	2.47	19
HPI	2.54	3.47	5.90	1.70	41
Water from Czarna Przemsza River (Bedzin)					
$<0.22\ \mu\text{m}$	3.00	4.17	10.5	2.51	95
HPO	0.12	32.2	84.6	2.62	32
TPI	0.12	17.5	26.8	1.53	18
HPI	3.00	2.00	2.10	1.05	48

\*– dissolved organic carbon

fractions strictly determined the dependence between aromaticity and hydrophilicity of compounds. The greatest SUVA value was obtained for the hydrophobic fraction while the lowest values for hydrophilic one. In both cases SUVA of dissolved fraction ( $<0.22 \mu\text{m}$ ) represented the intermediate value between SUVA hydrophobic fraction and transphilic and hydrophilic ones as it was a mixture of all isolated fractions.

### 3.2. Investigations the mechanism of the fouling membranes UF

Membrane filtration tests were performed using three types of fractions i.e. the fraction containing substances  $<0.22 \mu\text{m}$ , hydrophobic and hydrophilic fractions which were filtered through the ultrafiltration cellulose membrane of cut off 30 kDa. The streams were standardized according to:

- DOC (ca.  $2 \text{ mg/dm}^3$ )
- pH (pH equal to ca. 7 and ca. 2 were applied)
- temperature (ca.  $20^\circ\text{C}$ ).

The change of membrane capacity during NOM fractions filtration are shown in graphs in figure 1 while in Table 3 the results of percentage comparison of membrane capacity decreases observed during one hour filtration of particular fraction are presented.

The constant decrease of membranes capacity was observed during one-hour filtration and it depended on type and pH of filtered streams.

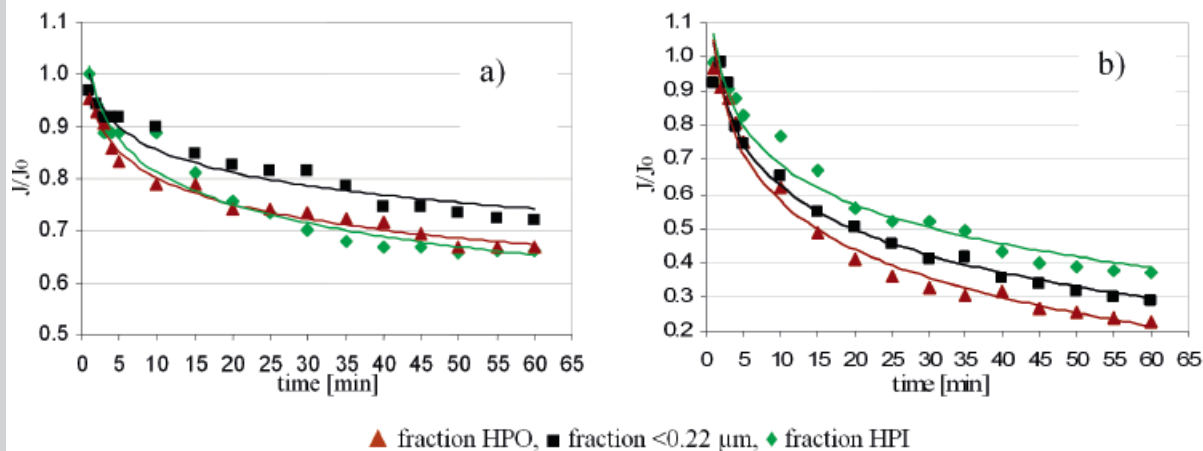
It was observed that during the filtration of fractions under pH equal to 7 the fouling occurred similarly in

all investigated cases, which corresponds to the results in [16-18] in which it was indicated that the filtered hydrophobic, hydrophilic and colloidal fractions caused the same decrease of membrane capacity under the same pH conditions. The decrease of pH to ca. 2 resulted in the significant decrease of the membrane capacity. It could be explained by the increase of charges of carboxylic and phenol groups under higher pH which resulted in the limitation of adsorption of NOM on the membrane surface and avoided the decrease of the capacity [16].

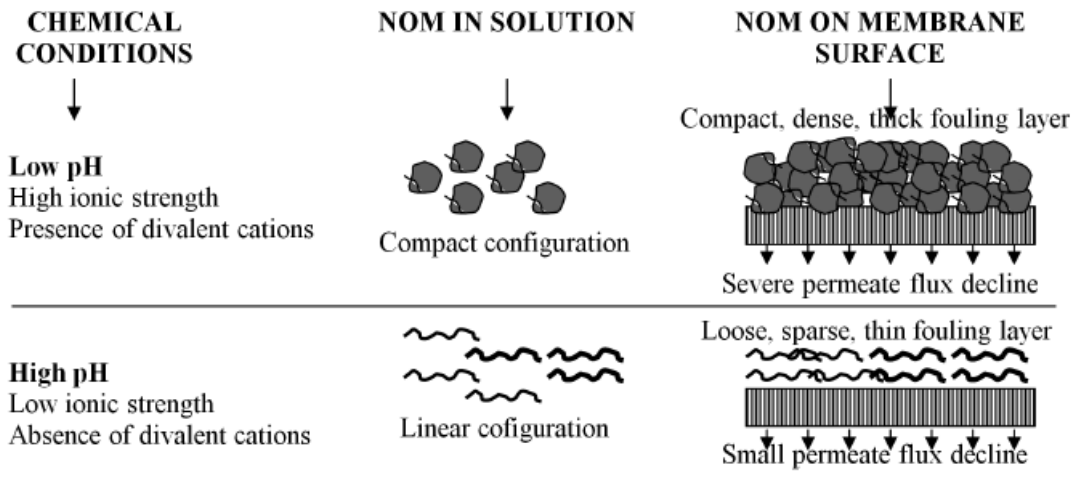
**Table 3.**  
The comparison of the relative permeability decline for ultrafiltration

Fraction	Membrane relative permeability decline, %	
	Paprocany Lake water (Tychy)	Czarna Przemsza River water (Bedzin)
	pH~7	pH~2
$<0.22 \mu\text{m}$	28.6	71.4
HPO	33.3	77.2
HPI	37.8	63.1

The strength of fouling according to the decrease of permeate stream was in the following order: under pH ca. 2 – hydrophobic fraction  $>(0.22 \mu\text{m})$  fraction  $>$  hydrophilic fraction while under pH = 7 hydrophobic and hydrophilic fractions influenced capacity in the similar manner while the least significant effect on the capacity was observed for the mixture of HPO and HPI. It can be said that the decrease of the membrane capacity was mainly caused by the character of impurities. The fraction  $<0.22 \mu\text{m}$  contained the mix-



**Figure 1.**  
Relative permeability change during filtration of  $<0.22 \mu\text{m}$ , HPO and HPI fractions a) pH 7 (the lake water), b) pH 2 (the river water)



**Figure 2.**  
The influence of the chemical composition of the solution of NOM deposition on the membrane

ture of particles of various sizes and in such a case bigger particles were able to form a filtration cake which avoided the penetration of smaller particles inside pores and, consequently, their blocking.

In figure 2 the mechanism of fouling caused by different chemical conditions (different pH) applied for investigated streams (fractions isolated from NOM) is shown.

As it can be seen in figure 2 the lower pH of water leads to the aggregation of NOM particles and their adsorption on the membrane surface which results in the formation of a filtration cake while with the higher pH the layer of NOM deposited on the membrane is thin and loose and does not cause such a significant capacity decrease than in the case of lower pH conditions.

The mechanism of UF was determined based on the model suggested by Hermia, which associates the “rate of blocking” of the membrane ( $d^2t/dV^2$ ) with the instantaneous resistance (reciprocal of the flow rate –  $dt/dV$ ) expressed by the equation [19]:

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

where: V – cumulative volume of the permeate (l), t – time of filtration (s), k – constant value ( $s^{1-\beta}l^{\beta-2}$ ),  $\beta$  – exponent. Four values of  $\beta$  parameter are proposed and they suggest that:  $\beta=2$  (complete blocking),  $\beta=1.5$  (standard blocking),  $\beta=1$  (intermediate blocking) and  $\beta=0$  (mechanism of cake filtration).

Coefficient  $\beta$ , which may be applied in monitoring the assessment of the transition from blocking mech-

anism to cake filtration mechanism, was determined by taking the logarithm of equation (1) and by calculating the slope of equation (2) [20]:

$$\log \left( \frac{d^2t}{dV^2} \right) = \log k + \beta \cdot \log \left( \frac{dt}{dV} \right) \quad (2)$$

Figure 3 presents changes of the parameter  $\beta$  in the course of filtration HPI and HPO fraction.

It was observed that values of  $\beta$  coefficient changed rapidly in the first 10 minutes of the filtration while as the process proceeded the decrease of  $\beta$  values was not as fast but progressive. Blocking of membrane was due to the mixed mechanism i.e. a part of particles caused blocking of membrane pores while the rest of impurities were deposited on the membrane surface. It is assumed that the phase of the membrane blocking is finished when  $\beta=1$ . The results suggest that during one-hour membrane filtration the mixed blocking mechanism (complete, standard and transient) was not ended as  $\beta$  value did not reach 1. However, it can be concluded that pH of water significantly affects the time of the blocking phase which shortens as pH is decreasing. It is supposed that the elongation of the filtration process under pH=2 would cause faster transition from the membrane blocking phase to the cake filtration mechanism than in the case of pH=7.



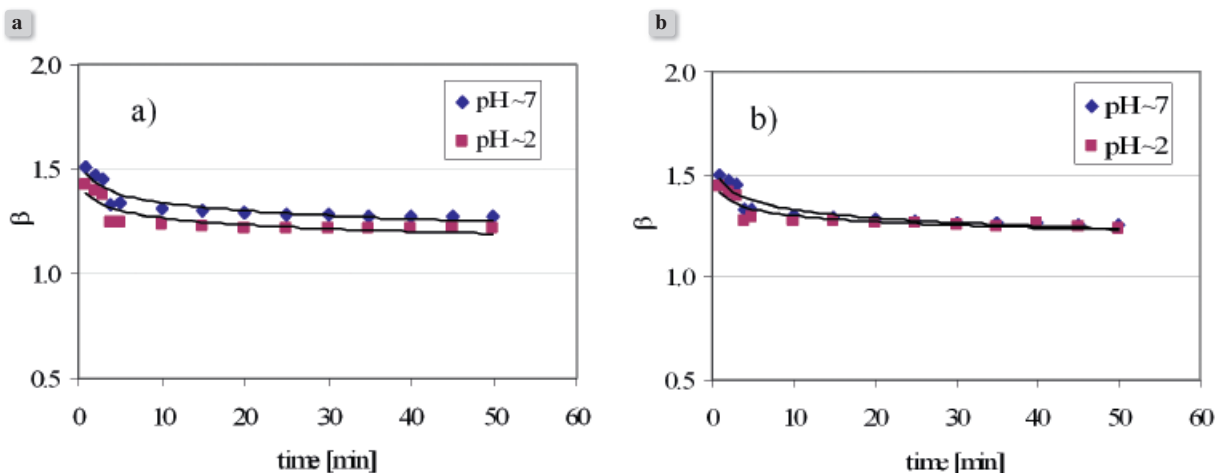


Figure 3. Values of coefficient  $\beta$  as a function of time concerning a) HPI fraction, b) HPO fraction

#### 4. CONCLUSIONS

- The characteristics of investigated waters showed that surface water was a mixture of hydrophilic and hydrophobic substances of various sizes.
- The study of the membrane filtration confirmed complex character of fouling phenomena whose intensity depended on NOM properties and water pH.
- The hydrophobic fraction of NOM has a significant influence on the cellulose membrane fouling. The filtration of the hydrophobic fraction and the decrease of its pH caused the greatest decline of the permeate stream and the determined value of the relative permeability coefficient was low and equal to 0.21
- The fouling mechanism based on Hermia's model is of a mixed character during one hour filtration and it was observed that under low pH obtained values of  $\beta$  coefficient used to monitor the progress of the membrane blocking phase were lower what indicated the shorter blocking step and the transition into the cake filtration cake.

#### 5. REFERENCES

- [1] Hörsch P., Gorenflo A., Fuder C., Deleage A., Frimmel F.H.; Biofouling of ultra- and nanofiltration membranes for drinking water treatment characterized by fluorescence in situ hybridization (FISH), *Desalination*, 172, 2005, p.41-52
- [2] Zularisam A.W., Ismail A.F., Salim R.; Behaviours of natural organic matter in membrane filtration for surface water treatment – a review, *Desalination*, 194, 2006, p.211-231
- [3] Kabsch-Korbutowicz M.; Application of ultrafiltration together with coagulation for improved NOM removal, *Desalination*, 174, 2005, p.13-22
- [4] Raczek-Stanisławiak U., Świetlik J., Nawrocki J.; Badania wpływu chloru, dwutlenku chloru i ozonu na stabilność biologiczną wody (Effect of Chlorine, Chlorine Dioxide and Ozone on the Biological Stability of Water) *Ochrona Środowiska*, 3, 2005, p.33-37 (in Polish)
- [5] Bodzek M., Konieczny K.; Wykorzystanie technik membranowych w uzdatnianiu wody do picia – stan wiedzy (Application of membrane processes in water treatment – state of art.) *Instal*, 4, 2007, p.58-61 (in Polish)
- [6] Jung C.W., Son H.J.; Evaluation of membrane fouling mechanism in various membrane pretreatment processes, *Desalination and Water Treatment*, 2, 2009, p.195-202
- [7] Kennedy M., Hyoungh H., Yangali V., Heijman B., Schippers J.; Natural organic matter (NOM) fouling of ultrafiltration membranes: Fractionation of NOM in surface water and characterization by LC-OCD, *Desalination*, 178, 2005, p.73-83
- [8] Bodzek M., Zawadzka D., Rajca M., Konieczny K.; Badanie foulingu membran podczas oczyszczania wody metodą ultrafiltracji (Investigation of the fouling of membranes during water treatment by means of ultrafiltration) *Inżynieria i Ochrona Środowiska*, 10, 2007, p.249-267 (in Polish)
- [9] Rajca M., Bodzek M., Gembolys B., Konieczny K.; Wpływ własności hydrofilowo/ hydrofobowych NOM na fouling membran w procesie oczyszczania wody metodą ultrafiltracji (Influence of hydrophilic-hydrophobic properties of NOM onto membrane fouling in water treatment using UF) *Monografie Komitetu Inżynierii Środowiska PAN, Lublin* 49, 2008, p.215-222 (in Polish)

- [10] *Jung Ch-W., Son H-J., Kang L-S.*; Effects of membrane material and pretreatment coagulation on membrane fouling: fouling mechanism and NOM removal, *Desalination*, 197, 2006, p.154-164
- [11] *Fan L.H., Harris J.L., Roddick F.A.; Booker N.A.*; Influence of the characteristics of natural organic matter on the fouling of microfiltration membranes, *Water Research*, 35, 2001, p.4455-4463
- [12] *Aiken G. R., McKnight D. M., Thorn K. A.; Thurman E. M.*; Isolation of hydrophilic organic acids from water using nonionic macroporous resins, *Organic Geochemistry*, 4, 1992, p.567-573
- [13] *Thurman E. M., Malcolm R. L.*; Preparative isolation of aquatic humic substances, *Environmental Science&Technology*, 4, 1981, p.463-466
- [14] *Kim H-Ch., Dempsey B.A.*; Effects of wastewater effluent organic materials on fouling in ultrafiltration, *Water Research*, 42, 2008, p.3379-3384
- [15] *Mołczan M., Szlachta M., Karpińska A., Bilyk A.*; Zastosowanie absorpcji właściwej w nadfiolecie (SUVA) w ocenie jakości wody (Water Quality Assessment in Terms of Specific UV Absorbance) *Ochrona Środowiska*, nr 4, 2006, p.11-16 (in Polish)
- [16] *Braghetta A., DiGiano F.A., Ball W.P.*; Nanofiltration of natural organic matter: pH and ionic strength effects, *J. Environ. Eng. ASCE* 123, 7, 1997, p.628-641
- [17] *Nilson J.A., DiGiano F.A.*; Influence of NOM composition on nanofiltration, *J. Am. Water Works Assoc.*, 88, 5, 1996, p.53-66
- [18] *Park CH., Lee YH., Lee S., Hong S.*; Effect of cake layer structure on colloidal fouling in reverse osmosis membranes, *Desalination*, 220, 2008, p.335-344
- [19] *Hermia J.*; Constant pressure blocking filtration laws – application to power-law non-newtonian fluids, *Trans IChemE.*, 60, 1982, p.183-187
- [20] *Kennedy M., Zhizhong L., Febrina E., Van Hoof S., Schippers J.*; Affects of coagulation on filtration mechanism in dead-end ultrafiltration, *Proceedings of “Membranes in Drinking and Industrial Water Production MDIW 2002”*, Mulheim an der Ruhr, Germany, 37a, 2002, p.185-192

