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FOULING OF MEMBRANES DURING ULTRAFILTRATION OF SURFACE WATER (NOM)

FOULING MEMBRAN PODCZAS ULTRAFILTRACJI WODY POWIERZCHNIOWEJ

Abstract: The results of studies focused on membrane fouling during surface water treatment by use of ultrafiltration, coagulation/sedimentation/ultrafiltration and in-line coagulation/ultrafiltration processes were presented. Medium- and low-molecular organic compounds (NOM) that are not rejecting in UF/MF process can be removed by use of pre-coagulation. The surface water used in the tests coming from Smieszek Lake located in Zory (Silesia province, Poland) contained organic matter of about 14 mg/dm³ TOC. Aluminum sulfate was used in both coagulations (4.9 mg Al/dm³, pH = 7.0). Molecular mass distribution in feed water and permeates was determined by use of high performance size exclusion (HPSEC). Applications of coagulation/sedimentation/ultrafiltration and in-line coagulation/ultrafiltration processes in water treatment allowed to get better quality of permeate than in ultrafiltration process alone. The smallest flux decline and the highest membrane capacity were observed in in-line coagulation/ultrafiltration process. Molecular weight distribution showed that integrated/hybrid processes allow rejecting molecules > 10 kDa in the highest degree. These molecules were responsible for membrane blocking as they deposit on surface and/or in membrane pores. The paper also presents impact hydrophobicity/hydrophilicity of NOM on UF membrane fouling. From isolated fractions the hydrophobic fraction of NOM caused the largest flux decline, while hydrophilic fraction – the smallest. Transphilic fraction pollutants were removed in highest grade. They might have a significant influence on membrane fouling.

Keywords: ultrafiltration, coagulation, natural organic matter (NOM), hydrophobicity/hydrophilicity, chromatography – HPSEC

Low-pressure membrane techniques are applied in drinking water production as an alternative for standard filtration. The conventional water treatment does not always guarantee total removal of low-molecular weight colloids and microorganisms. Ultrafiltration (UF) and microfiltration (MF) membranes separate colloids as well as ionic and nonionic organic substances depending on UF membrane limiting permeability (cut-off) and MF membrane pore sizes, however they pass through ionic inorganic

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substances. Especially they are able to retain protozoan, bacteria and viruses (membranes with cut-off < 100 kDa), natural high-molecular weight colored substances and other organic compounds (to a certain degree) as well as turbidity. Practically direct UF/MF processes are not able to retain medium and low-molecular weight compounds; however in hybrid configuration system (with coagulation or activated carbon) the removal of natural and synthetic organic matter is possible [1]. Difficulties in common application of UF/MF processes are connected with membrane lifetime. During the process, the accumulation of organic and/or inorganic matter on membrane surface or inside membrane pores takes place, what significantly decreases membrane yield. This phenomenon is generally known as fouling. Organic fouling connected with natural organic matter (NOM) is the most popular in water treatment processes [2]. NOM present in water comes mainly from soil and its amount and properties depend on climate, geology and topography of the source area and real changes, which take place during transport through lakes and rivers to the ocean [3]. NOM is a mixture of various organic compounds, both high-molecular weight (proteins, sugars, humus) and low-molecular weight like simple organic acids [4, 5]. It is possible to control fouling with use of special techniques, what allows elongating membrane lifetime and decreasing operational costs. These control techniques are physical methods, like periodic backwashing of membrane or membrane filtration process parameters optimization, and chemical methods (eg application of chemical cleaning agents). Proper membrane selection and membrane module construction are also significant regarding fouling [1]. Raw water pretreatment processes taking place before water introduction on membrane are very popular. Those pretreatment processes are: coagulation, adsorption on activated carbon, biological filtration and oxidation, and they are applied before proper UF/MF processes [6, 7]. Associated membrane systems are very useful especially in surface water treatment, as in comparison with groundwater surface water has high load of impurities.

Systems with coagulation allow improving the quality of treated water and decreasing membrane fouling caused by impurities present in raw water. Coagulation process can be run together with sedimentation or without it (in-line coagulation). Final effects of increase membrane yield when coagulation is applied mainly depend on character of impurities responsible for fouling and their interactions with membrane [1].

The aim of studies was to determine intensity of membrane fouling during treatment of water containing natural organic matter (NOM) in different configurations of the process: direct UF, integrated coagulation/sedimentation/ultrafiltration and hybrid in-line coagulation/ultrafiltration systems. The influence of coagulation on membrane filtration and membrane life-time as well as on fouling was analyzed. The molecular weight of NOM in dissolved fraction, supernatant after coagulation and in treated water (permeate obtained in integrated and hybrid process) was determined in order to find, which molecular sizes of compounds are responsible for fouling. The influence of hydrophilicity/hydrophobicity of organic matter (NOM) on UF membrane blocking also was investigated.

Experimental

The range of studies covered:

- surface water membrane filtration under constant pressure in direct ultrafiltration (membrane cut-off 30 kDa) and systems with standard and in-line coagulation;
- determination of molecular weight distribution in dissolved fraction, supernatant after coagulation and in permeate obtained in coagulation/sedimentation/ultrafiltration and in-line coagulation/ultrafiltration processes using size exclusion liquid chromatography (SEC);
- separation of dissolved fraction ($< 0.22 \mu\text{m}$) from surface water;
- fractionation of dissolved substances into hydrophobic (HPO), hydrophilic (HPI) and transphilic (TPI) fractions;
- membrane filtration of particular streams (dissolved substances, HPO, HPI and TPI) through cellulose ultrafiltration membranes.

Surface water from Smieszek lake (Silesia Region, Zory, Poland) contained organic substances in the amount of around 14 mgTOC/dm^3 , was used in the studies.

Investigations were made with use of Stirred Ultrafiltration Cell Milipore CDS-10 System, model 8400. Figure 1 represents the scheme of the installation.

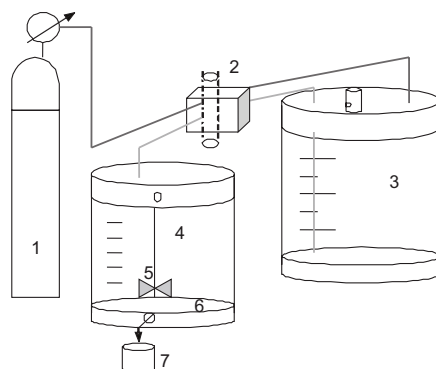


Fig. 1. Diagram of Milipore CDS-10 System installation: 1 – pressure source; 2 – selective valve; 3 – feeding tank; 4 – ultrafiltration cell; 5 – mixer; 6 – membrane; 7 – permeate

Continuous membrane filtration of feed of volume three times greater than the ultrafiltration membrane cell capacity was allowed by the system as it was equipped with selective valve CDS-10, which connected three main elements of installation: gas tank, ultrafiltration cell (capacity 400 cm^3) and feed tank (volume 800 cm^3). CDS-10 device cooperated with flat-sheet membranes in dead-end mode, in which feed was introduced perpendicularly to membrane surface.

Three types of membranes were used during studies: microfiltration membrane of pore diameter $0.22 \mu\text{m}$ in order to remove colloids ($0.22 \mu\text{m}$) from surface water, and two ultrafiltration membranes with cut-off 10 and 30 kDa. Both types of ultrafiltration membranes were used to determine the influence of hydrophilicity/hydrophobicity of NOM on membrane fouling. In proper investigations of water ultrafiltration in direct

UF, hybrid (in-line coagulation/ultrafiltration) and integrated (coagulation/sedimentation/ultrafiltration) processes membrane with cut-off 30 kDa was used. Table 1 represents characteristics of particular membrane given by producer.

Table 1

Characteristics of membrane used

Membrane type	MF membrane	UF membrane	UF membrane
Name of the product	Membrane filter Milipore Express Plus	UF membrane from Nadir	UF membrane from Millipore
Configuration	Flat-sheet		
Material	polyethersulphone	cellulose	regenerated cellulose
Pore diameter	0.22 μm	30 kDa	10 kDa
Area	38.5 cm^2		
Wettability	hydrophilic		
Pressure	0.1 MPa		

Surface water containing NOM was treated in direct UF, in hybrid system: in-line coagulation/UF and in integrated system: coagulation/sedimentation/UF. Ultrafiltration membrane with cut-off 30 kDa was used for that purpose. In coagulation process aluminum sulfate was applied. Coagulation process conditions: $\text{pH} = 7.0$ and coagulant dose $D = 4.9 \text{ mgAl/dm}^3$ were determined by means of jar test. In coagulation/sedimentation process after coagulant addition rapid 1-minute-long and slow 30-minute-long mixing were applied. Then created flocs settled down for 30 minutes. Obtained supernatant served as feed in ultrafiltration process. In in-line coagulation (without sedimentation) coagulant was added directly to ultrafiltration cell and feed tank, and prepared feed was rapidly mixed for 1 minute and introduced to ultrafiltration process. Proper filtration tests were carried out under constant transmembrane pressure 0.1 MPa. During one-hour tests dependence of permeate flux (J_t) on time was determined, firstly after every minute, and after five minutes of run in five-minute periods. Obtained results were used in estimation of relative membrane permeability – $\alpha = J_t/J_0$, and allowed to determine tendency of fouling caused by particular NOM fractions. Simultaneously investigations focused on membrane effectiveness were carried out, during which retention coefficient (R) regarding TOC/DOC (total/dissolved organic carbon), absorbance UV_{254} , turbidity, pH, conductivity and aluminum content were determined.

Molecular weight distribution in streams created during treatment process was determined using high performance size exclusion chromatography (HPSEC). PL-GPC 50 Integrated GPC system chromatograph (Varian company), equipped with PL aquagel-OH 80 $8 \mu\text{m}$ and PL aquagel 30 $8 \mu\text{m}$ ($300 \times 7.5 \text{ mm}$) columns and UV detector, was used during studies. Phosphoric buffer of $\text{pH} = 6.8$ with 0.1 M HCl was applied as eluent. The column was calibrated using sodium polystyrenesulfonate. Detection was carried out at $\lambda = 254 \text{ nm}$ wavelength.

Fractionation of NOM using Amberlite XAD-7HP and XAD-4 resins (Rohm&Haas Company) was made in order to determine influence of hydrophilicity/hydrophobicity on membrane fouling. Fractionation procedure, described in detail in [8], allowed to obtain hydrophobic (HPO), intermediate (transphilic – TPI) and hydrophilic (HPI) fractions. Fractionation was made with water from which 0.22 μm diameter particles were already removed and which was acidified to $\text{pH} = 2$ using 0.1 M HCl. Particular fractions were introduced to ultrafiltration process carried out under constant transmembrane pressure 0.1 MPa and dependence of permeate flux (J_t) on time and membrane relative permeability ($\alpha = J_t/J_0$) were estimated regarding DOC and UV_{254} absorbance.

Every proper UF required application of new membrane, which firstly was conditioned by five-hour filtration with deionized water. The operation was run under pressure 0.1 MPa, and was necessary to remove protection layer from the membrane and condition it. During deionized water filtration volumetric water stream (J_0) was determined.

Results and discussion

Fouling during water treatment in direct UF and coagulation/UF systems

Relative permeability changes (for transmembrane pressure 0.1 MPa) during direct UF, integrated (coagulation/sedimentation/UF) and hybrid (in-line coagulation/UF) process run are shown in Fig. 2.

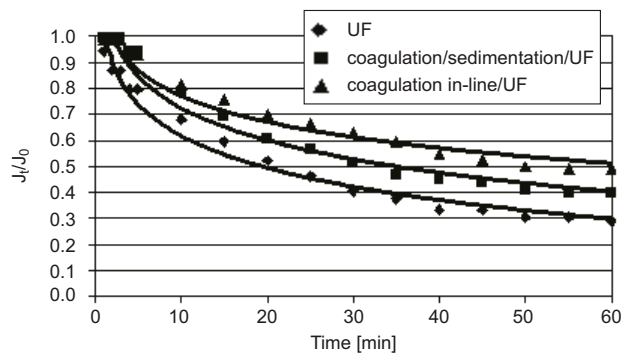


Fig. 2. Membrane relative permeability change during filtration for all water purification processes

Application of coagulation/sedimentation/UF and in-line coagulation/UF systems allows obtaining higher organic compounds retention coefficients in comparison with direct UF process (Table 2).

In integrated/hybrid processes TOC retention was more than 40 %, DOC was around 30 % and UV_{254} achieved more than 50 %, while for the direct process those values were less than 30 % for TOC, DOC around 10 % and UV_{254} around 40 %. In all cases turbidity was removed in more than 98 %. In integrated/hybrid processes organic

compounds removal degree (which did not achieved even 50 %) is connected with SUVA (specific ultraviolet absorption $SUVA = UV_{254}/DOC$) value of raw water ($2.62 \text{ dm}^3/\text{mg} \cdot \text{m} \leq 3 \text{ dm}^3/\text{mg} \cdot \text{m}$), which does not indicate the susceptibility of water to DOC removal in coagulation process. According to that 8.8 % of TOC was removed.

Table 2

Physicochemical parameters of raw and purified water and retention coefficients of pollutants obtained during water purification processes

Process		TOC [mgC/dm ³]	DOC [mgC/dm ³]	UV ₂₅₄ [1/cm]	Turbidity [NTU]	pH	Conductivity [mS/cm]
Ultrafiltration alone UF	Raw water	11.92	9.34	0.222	10.03	8.00	0.446
	Permeate	8.43	8.43	0.134	0.12	7.98	0.432
	Retention R [%]	29.3	9.70	39.6	98.80	—	—
Coagulation /sedimentation	Raw water	11.27	—	0.217	16.63	7.00	0.428
	Supernatant	10.28	—	0.155	5.93	6.68	0.457
	Retention R [%]	8.8	—	28.6	64.3	—	—
Coagulation /sedimentation/UF	Raw water	11.27	9.34	0.217	16.63	7.00	0.428
	Permeate	6.60	6.60	0.092	0.20	6.92	0.481
	Retention R [%]	41.4	29.30	57.6	98.8	—	—
Coagulation in-line/UF	Raw water	11.15	9.34	0.208	16.28	7.00	0.457
	Permeate	6.28	6.28	0.090	0.34	6.93	0.471
	Retention R [%]	43.7	32.80	56.7	98.10	—	—

Volumetric permeate flux in integrated/hybrid systems was higher than one obtained in direct UF. Application of in-line coagulation before membrane filtration improves membrane yield in 18 % comparing with standard coagulation. The effect of membrane fouling was determined using relative permeability α . After one-hour filtration α coefficient decreased in direct UF to 0.29, in integrated process to 0.40 (coagulation/sedimentation/UF), and in hybrid process to 0.49 (in-line coagulation/UF). This proves that application of in-line coagulation before UF process mostly decreases membrane fouling.

Pre-coagulation applied before membrane filtration results in creation of particles with greater diameters, which accumulate on membrane surface blocking membrane pores in lower degree. It is confirmed by chromatographic analysis (Fig. 3, Tables 3 and 4). Dissolved fraction contained 38.7 % of particles in range $> 10 \text{ kDa}$, while in supernatant 39.5 % of particles varied from 1–5 kDa. Dissolved fraction was more diversified regarding particles sizes than supernatant, what was confirmed by polydispersion of samples ($d = 5.71$ and $d = 4.15$). Investigations showed that standard coagulation caused greater fouling compared with in-line coagulation. Filtration cake created during in-line coagulation, as distinguished from standard coagulation and direct UF, probably possessed greater porosity and lower ability to bond with membrane surface, what limited membrane contamination, especially inside its pores [9].

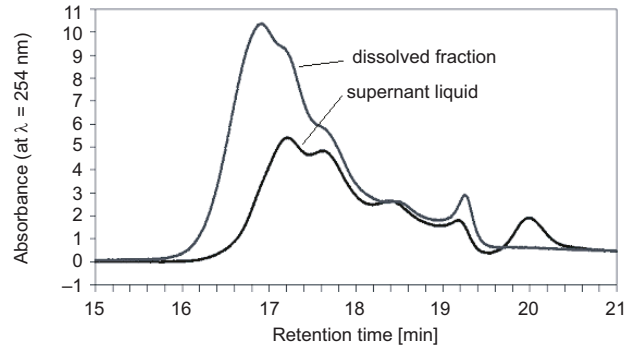


Fig. 3. Chromatograms of NOM in dissolved fraction and water after coagulation/sedimentation

Table 3

Distribution of NOM molecular weight in water after sedimentation and in permeates after coagulation/sedimentation/UF and coagulation in-line/UF processes

Apparent molecular weight [Da]	Percent of fraction [%]			
	Dissolved fraction	Supernatant	Permeate in-line	Permeate on-line
> 10000	38.70	13.69	8.87	8.92
10000–5000	22.99	24.15	24.31	23.96
5000–1000	25.20	39.46	42.68	42.14
< 1000	13.12	22.70	24.14	24.98

Table 4

Comparison of molecular weight data for dissolved fraction, water after sedimentation and permeates after coagulation/sedimentation/UF and coagulation in-line/UF processes

Characteristic data	Dissolved fraction	Supernatant	Permeate in-line	Permeate on-line
M _p [Da]	12654	7334	6936	7154
M _n [Da]	1679	1172	1141	1093
M _w [Da]	9589	4863	4140	4117
M _z [Da]	17486	9338	7454	7513
d [-]	5.71	4.15	3.63	3.77

More detailed analysis of molecular weight distribution of fractions obtained during water treatment can be made basing on chromatographic data collected in Tables 4 and 5 and in Figures 4 and 5. Data described below is shown in Table 4:

- M_n – average molar number, $M_n = (\sum N_i M_i) / (\sum N_i)$,
- M_w – average molecular weight, $M_w = (\sum N_i M_i^2) / (\sum N_i M_i)$,
- M_z – the value calculated from the equation, $M_z = (\sum N_i M_i^3) / (\sum N_i M_i^2)$,
- M_p – molecular weight estimated for maximum peak,
- d – polydispersion, $d = M_w / M_n$ ($d = 1$ for polymer of defined molecular weight).

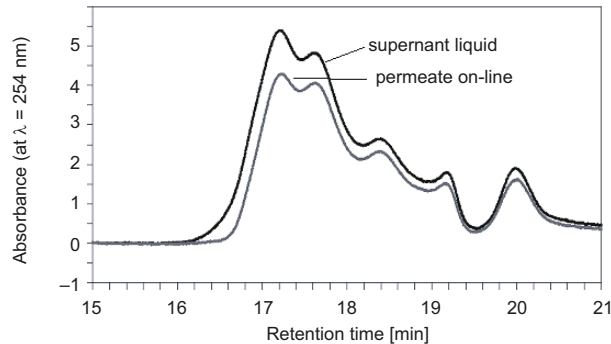


Fig. 4. Chromatograms of NOM in water after coagulation/sedimentation and permeate after coagulation/sedimentation/UF process

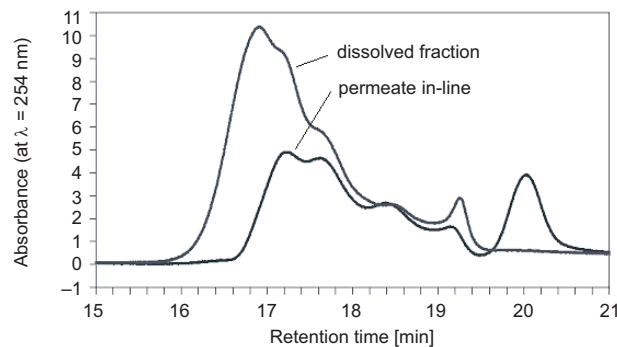


Fig. 5. Chromatograms of NOM in dissolved fraction and permeate after coagulation in-line/UF

Comparing molecular weight distribution of on-line (coagulation/sedimentation/UF) and in-line (in-line coagulation/UF) permeates with dissolved fraction in can be noticed that both permeates are characterized with the same curve progress. Both permeates have similar polydispersion ($d = 3.63$ and $d = 3.77$, respectively), lower than polydispersion of supernatant. It can be concluded that hybrid and integrated process separate particles with the same molecular weight. Analysis of particle size distribution showed, that in dissolved fraction particles > 10 kDa predominated, while in other cases more particles were in range 1–5 kDa.

Dissolved fraction comprised of particles > 10 kDa in 38.7 %, 23 % were particles in the range of 5–10 kDa, 25.2 % in the range of 1–15 kDa, and 13.1 % of particles smaller than 1 kDa. Application of coagulation and sedimentation changed particles size distribution. The greatest particles (> 10 kDa) were retained in 65 %. On the other hand, coagulation turned out to be ineffective process, as it allowed removing only around 9 % of TOC. It can be explained by the fact that analyzed water has hydrophilic properties with greater amount of non-humic substances, which are still present in water after coagulation [10]. In supernatant increase of the amount of particles with size varying from 5–10 kDa was negligible comparing with dissolved fraction, the amount

of particles of size 1–5 kDa increased 1.5 times and the amount of particles < 1 kDa was almost 2 times greater.

Molecular mass distributions in permeate after coagulation/sedimentation and in-line coagulation/sedimentation are very similar. It confirms the fact, that it is difficult to estimate which method should be applied in investigated process treatment. In both cases similar retention coefficients of particular impurities indicators were obtained. Particles > 10 kDa were separated ($R = 35\%$). The amount of particles of range 1–5 kDa increased around 17 %, comparing with dissolved fraction, while regarding supernatant this increase was negligible.

To sum up, particles greater than 10 kDa were separated in the highest degree in integrated/hybrid processes, what had an influence on UF membrane fouling. Particles from range 5–10 kDa were not separated. The amount of particles < 5 kDa actually increased. The most probable explanation of this phenomenon is connected with coagulation process, during which created flocs were not big enough to be effectively separated, and particles of sizes smaller than membrane pores passed through membrane.

Influence of hydrophilicity/hydrophobicity of NOM on UF membrane fouling

Organic substances fractionation

Fractionation with microfiltration membrane filtration (0.22 μm) and adsorption on Amberlite XAD7HP/4 resins allowed isolating 4 fractions from surface water:

- dissolved (< 0.22 μm),
- hydrophobic HPO,
- transphilic (TPI),
- hydrophilic (HPI).

Dissolved fraction was 65 % of total organic substances content in analyzed natural water. Table 5 presents mass balance of organic substances in water containing dissolved substances after acidification to $\text{pH} = 2$, and also in particular fractions. Mass balance analysis was carried out basing on DOC measurements.

Table 5

Mass balance of organic substances in surface water

Sample	DOC	Sample volume V	DOC mass [m]	Percent
	[mgC/dm ³]	[dm ³]	[mg]	[%]
Dissolved fraction – after acidification	8.38	5.0	41.90	100.00
Hydrophobic fraction	31.76	0.310	9.85	23.51
Transphilic fraction	17.65	0.322	5.68	13.56
Hydrophilic fraction	5.18	5.0	25.90	61.81
Σ (HPO + TPI + HPI)			41.43	98.88

In investigated water the greatest part of natural organic substances comprised hydrophilic fraction – around 62 % DOC. Hydrophobic fraction was around 24 % of DOC, while the smallest part was transphilic fraction containing around 14 % of DOC. However, mass balance of organic substances, measured as DOC of particular NOM fractions, is not equal to 100 %. In feed introduced to resins the amount of organic substances was 1.12 % higher than sum of isolated fractions. It is connected with presence of wall effect (0.1 M NaOH used in elution of absorbed particles probably did not have a good contact with bed, simply streamed down column walls and did not elute all absorbed particles) or with way of elution of absorbed particles, what is equivalent with resins regeneration. Elution was carried out in the direction of proper feed flow, what caused migration of washed particles from upper bed layer to lower parts and resulted in contamination of unused layers. Characteristic of particular fractions is shown in Table 6.

Table 6

Characteristics of NOM fractions isolated from surface water

Probe	DOC	UV ₂₅₄	SUVA	Turbidity	pH	Conductivity
	[mgC/dm ³]	[1/cm]	[dm ³ /mg · m]	[NTU]	[-]	[mS/cm]
Dissolved fraction	8.38	0.220	2.62	0.45	2.0	4.49
Hydrophobic fraction	31.76	0.917	2.89	1.79	2.0	8.90
Transphilic fraction	17.65	0.345	1.95	2.04	2.0	8.77
Hydrophilic fraction	5.18	0.058	1.12	0.35	2.0	5.57

Dissolved fraction contained all isolated NOM fractions like aromatic and aliphatic compounds and possessed lower SUVA value comparing with HPO, however regarding HPI and TPI this value was higher, what agrees with previously observed dependences [8]. Analysis of obtained results allows to conclude that organic substances present in natural water have combined character what is confirmed by $SUVA = 2.62 \text{ dm}^3/\text{mg} \cdot \text{m}$. Literature [11] suggests that in this range of ultraviolet absorbance ($SUVA \leq 3 \text{ dm}^3/\text{mg} \cdot \text{m}$) the degree of DOC removal during coagulation does not exceed 30 %. In such a case sorption methods are recommended.

Ultrafiltration membrane fouling investigations

Filtration of dissolved, hydrophobic, transphilic and hydrophilic fractions was carried out using two types of cellulose membranes of cut-off 10 kDa (regenerated cellulose) and 30 kDa (cellulose). Particular streams were standardized regarding pH, conductivity, DOC and temperature before they were introduced to membrane filtration. Obtained results are presented graphically in Fig. 6 and 7.

During one-hour filtration continuous decrease of membrane yield was observed. This decrease was higher for 30 kDa cut-off membrane in comparison with 10 kDa cut-off membrane (Table 7).

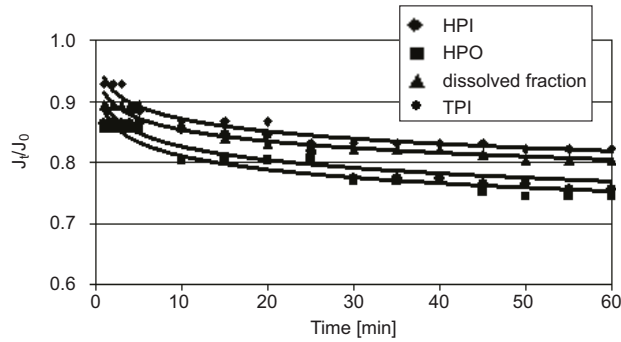


Fig. 6. Relative permeability change during filtration of dissolved, HPO, TPI and HPI fractions through membrane with cut-off 10 kDa

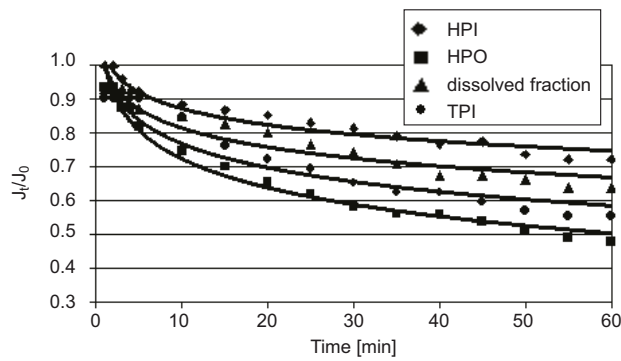


Fig. 7. Relative permeability change during filtration of dissolved, HPO, TPI and HPI fractions through membrane with cut-off 30 kDa

Table 7

Comparison of relative permeability decline for ultrafiltration membranes with cut-off 10 and 30 kDa

Probe	Membrane relative permeability decline [%]	
	10 kDa	30 kDa
Dissolved fraction	19.6	36.0
Hydrophobic fraction	25.6	52.1
Transphilic fraction	24.5	44.4
Hydrophilic fraction	17.8	27.8

In both cases fouling potential regarding permeate flux decrease appeared in the same order: hydrophobic fraction > transphilic fraction > dissolved fraction > hydrophilic fraction. The highest decrease of permeate flux was caused by hydrophobic fraction, which contained mainly high molecular weight DOC fraction. The greatest effectiveness of membranes separation was obtained during filtration of hydrophilic fraction, which was composed mainly from non-humic low-molecular weight substances [12]. Both membranes effectively separated transphilic fraction pollutants

($R = 79\%$, $R = 22.78\%$). It can be said that DOC fractions successfully removed by membranes are not the same fraction, which causes higher decrease of flux. Similar results obtained by Zularisam et al [10], however in their studies on the one hand the highest flux decrease was obtained for HPI fraction, but on the other hand from this fraction the lowest amount of DOC was removed. The significant influence of hydrophobic fraction on fouling was already described in literature [13–16].

Membrane of cut-off 10 kDa separated in the lowest grade hydrophobic fraction impurities ($R = 26.7\%$), while membrane of cut-off 30 kDa was inefficient separating dissolved fraction ($R = 4.83\%$). It is undoubtedly connected with size of separated particles. Probably particles of size similar or smaller than membrane pore sizes pass through and are not separated by membrane.

Conclusions

Application of hybrid/integrated system in water containing organic matter treatment allowed to obtain permeate of better quality in comparison with direct UF, what is confirmed by higher organic compounds retention coefficients. In-line coagulation/UF process decreased UF membrane fouling most effectively and improved membrane yield. Coagulation/sedimentation/UF process turned out to be less effective, as it removed only around 9 % of TOC. It is connected with raw water value of $SUVA = 2.62 \text{ dm}^3/\text{mg}\cdot\text{m}$. In that case sorption methods are recommended.

Molecular weight distribution in analyzed water showed that particles of size > 10 kDa were effectively separated in integrated/hybrid systems. Probably those particles are responsible for membrane blocking as they deposit on membrane surface and/or inside its pores.

Dissolved fraction accounts for 65 % of total organic matter content in analyzed natural water. From all isolated fractions, hydrophilic fraction had the greatest part and contained around 62 % of DOC. Hydrophobic NOM fraction caused greatest decrease of permeate flux, while hydrophilic fraction the lowest. It shows that HPO has the highest influence on membrane fouling caused by natural organic matter. Membrane of cut-off 10 kDa had higher efficiency in organic compounds removal in comparison with 30 kDa cut-off membrane. Both membranes separated mainly transphilic fraction impurities, which can significantly increase fouling. According to that it is claimed that DOC fractions removed most effectively by membrane are not the same fraction, which causes higher decrease of permeate flux.

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FOULING MEMBRAN PODCZAS ULTRAFILTRACJI WODY POWIERZCHNIOWEJ

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Abstrakt: Przedstawiono wyniki badania intensywności foulingu membran podczas oczyszczania wody naturalnej w procesie jednostkowym ultrafiltracji, zintegrowanym koagulacji klasycznej/ultrafiltracji oraz hybrydowym koagulacji in-line/ultrafiltracji zawierającej naturalne substancje organiczne (NOM). Wstępna koagulacja umożliwia usunięcie średnio- i małowymiarowych związków organicznych, które w samodzielnym procesie UF/MF nie są usuwane. W badaniach stosowano wodę powierzchniową z jeziora Śmieszek, zlokalizowanego na terenie miasta Żory, charakteryzującą się zawartością związków organicznych na poziomie ok. 14 mg TOC/dm³. W procesie koagulacji zastosowano siarczan glinu (4,9 mg Al/dm³, pH = 7,0). W strumieniach powstających podczas procesu oczyszczania wyznaczono rozkład mas molekularnych za pomocą HPSEC. Zastosowanie układu hybrydowego/zintegrowanego do oczyszczania wody zawierającej substancje organiczne pozwoliło na uzyskanie permeatu lepszej jakości niż w bezpośredniej UF. Ponadto proces koagulacji in-line/UF w największym stopniu zmniejszył fouling membrany UF i w konsekwencji polepszył jej wydajność. Rozkład mas molekularnych wykazał, iż w procesach zintegrowanych/hybrydowych w największym stopniu zostały zatrzymane molekuly o rozmiarach > 10 kDa. Molekuly te są odpowiedzialne za zjawisko blokowania membran, osadzając się na powierzchni i/lub w porach. Określano również wpływ hydrofilowości/hydrofobowości substancji organicznej na zjawisko blokowania membran ultrafiltracyjnych. Spośród wyizolowanych frakcji NOM frakcja hydrofobowa NOM spowodowała największy spadek strumienia permeatu, podczas gdy hydrofilowa najmniejszy. W największym stopniu zatrzymane zostały zanieczyszczenia frakcji transfilowej, które mogą znacząco przyczynić się do zjawiska foulingu.

Słowa kluczowe: ultrafiltracja, koagulacja, naturalne substancje organiczne (NOM), hydrofilowość/hydrofobowość, wysokosprawną chromatografię wykluczenia objętościowego (HPSEC)