Environment Protection Engineering

Vol. 35 2009 No. 1

KRYSTYNA KONIECZNY*, MARIOLA RAJCA*,
MICHAŁ BODZEK*, ANNA KWIECIŃSKA*

WATER TREATMENT USING HYBRID METHOD OF COAGULATION AND LOW-PRESSURE MEMBRANE FILTRATION

The paper presents the results of water treatment investigation, using UF/MF and a hybrid process coagulation–UF/MF. The experiments were conducted using capillary modules made of polyethersulfone (PES) for ultrafiltration and of polypropylene (PP) for microfiltration. Two coagulants, i.e. iron chloride ($FeCl_3 \cdot 6H_2O$) and aluminum sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$), were used during the coagulation. The hybrid water treatment process was carried out in coagulation–sedimentation–MF/UF and "in-line" coagulation (without sedimentation)–MF/UF systems. Unlike a direct UF/MF, the hybrid processes allow an improvement in water quality and reduction in fouling intensity. UF efficiency can be predicted employing relaxation and resistance models. The mechanism of fouling based on Hermia's equation was determined.

1. INTRODUCTION

Nowadays, low-pressure membrane techniques such as microfiltration and ultrafiltration are more frequently applied in water treatment processes. However, the disadvantages such as an insufficient separation of low-molecular weight particles of admixtures and impurities as well as the decrease of hydraulic efficiency during a process limit a common application of low-pressure membrane processes. The main cause of those phenomena is fouling, i.e. the accumulation of unwanted material on the surface and inside the pores of a membrane. In order to prevent or to decrease the impact of fouling on the process efficiency and to improve the final quality of water as well as to prolong the operation time of membrane modules, the integration of membrane processes with physicochemical or biological processes is proposed. Hybrid systems are a specific type of integrated sets, in which two or more processes are

* Institute of Water and Wastewater Engineering, Faculty of Energy and Environmental Engineering, Silesian University of Technology, Konarskiego 18, 44-100 Gliwice, Poland. Tel/fax: 0-32 237 23 68, e-mail: Krystyna.Konieczny@polsl.pl

run simultaneously, not sequentially [1]–[5]. To compare different systems of water treatment, using separate ultrafiltration/microfiltration, integrated and hybrid systems of coagulation–ultrafiltration/microfiltration, complex investigations were carried out.

The research included:

1. Experimental study of water treatment efficiency with the use of two-step system consisting of coagulation and ultrafiltration/microfiltration (integrated setup) as well as and the hybrid system of in-line (without sedimentation) coagulation–UF/MF.

2. Calculation connected with modelling the efficiency of both direct ultrafiltration/microfiltration and coagulation–ultrafiltration/microfiltration in integrated and hybrid systems with the use of [6], [7]:

- membrane filtration model in a non-stationary process,
- hydraulic model of filtration resistance

3. Study of microfiltration and ultrafiltration membranes fouling by the determination of fouling mechanism.

2. EXPERIMENTAL

Two types of water were used for investigating the efficiency of unit and integrated/hybrid operations:

- simulated water prepared by dissolving standard humic acid (manufactured by Sigma-Aldrich) in the amount of 7 and 10 mg of total organic carbon per 1 dm^3 of water,
- surface water from the Czarna Przemsza River (Silesia Region, Poland), which contained 5–10 mg/dm^3 of organic matter measured as TOC.

Membrane filtration studies were carried out using the membranes which differ in pore size and component material. Two configurations of capillary membrane systems were applied:

- capillary: supplied from inside capillaries made of polypropylene (PP-MF) and polyethersulphone (PES-UF) produced by Euro-Sep company in Warsaw (filtration area of 0.48 m^2 and 0.033 m^2 for PP and 0.556 m^2 for PES, the applied pressure of 0.1 MPa, cross-flow system; for PP membrane of the area of 0.033 m^2 and the pressure of 0.1 and 0.05 MPa, semi-dead-end flow),
- capillary: supplied from outside capillaries made of polyvinylidene fluoride (PVDF-UF) (ZeeWeed 10) produced by Zenon Systems company at Tychy (filtration area of 0.93 m^2, constant efficiency of $5.7\cdot10^{-6}$ $m^3/m^2\cdot s$).

In the coagulation process, the following coagulants were used: hydrated iron(III) chloride ($FeCl_3\cdot6H_2O$) and hydrated aluminum sulfate ($Al_2(SO_4)_3\cdot18H_2O$). The coagulation parameters, i.e., the reagent dose and pH, were determined by jar test (standard dose). In the in-line coagulation, a lower dose of coagulant was also added (75% and 50% of the standard dose).

Prior to the actual filtration, membrane-conditioning processes with deionized water were carried out in order to achieve a constant flux (J_0) through the membrane.

Membrane filtration of the simulated and surface waters was carried out in the direct ultra- and microfiltration as well as in integrated/hybrid systems with standard and in-line coagulation (figure 1).

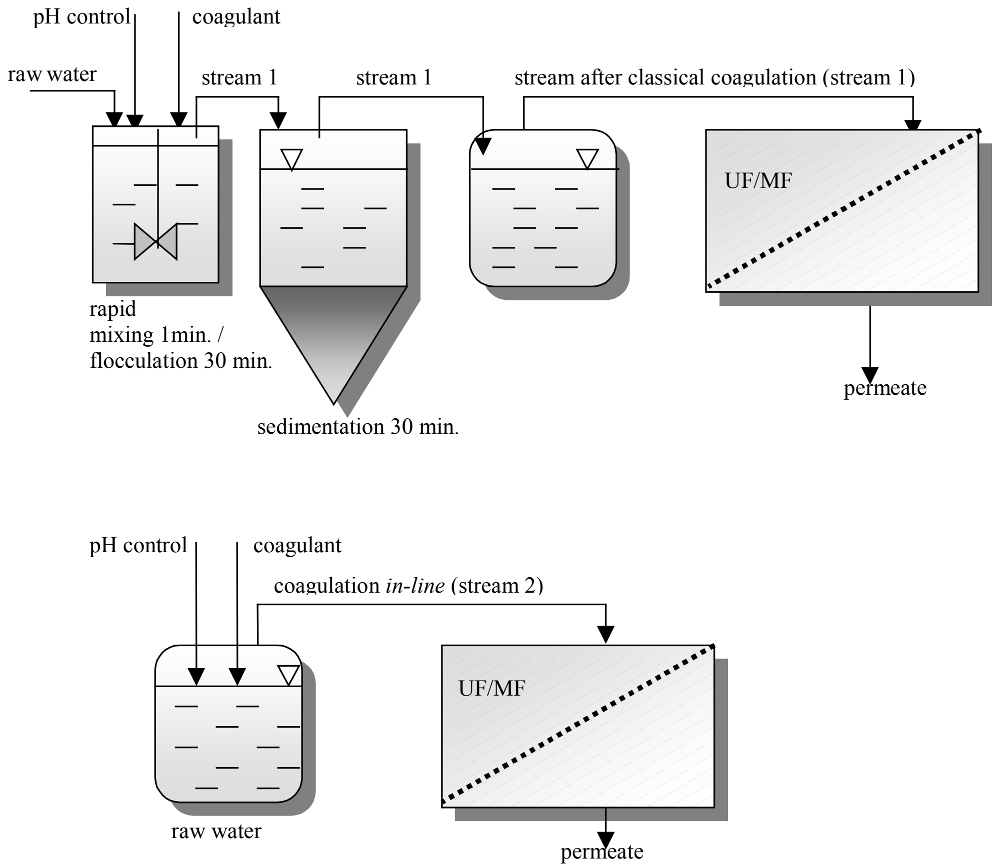


Fig. 1. Integrated/hybrid process diagram

In the integrated system, the coagulation took place in a separate tank, to which a proper amount of coagulant was added, and the supernatant from the coagulation tank (stream 1) was introduced to the membrane module. In the hybrid system, the coagulant was added directly to the recirculation loop (feed tank), where mixing occurred, and the water with flocs was subjected to membrane filtration (stream 2).

The membrane filtration was carried out in an open system, without returning the permeate to the raw water tank, constantly filling up the feed tank with supernatant in the integrated system, and with raw water and coagulant in the hybrid system. The membrane module with the immersed membrane (ZeeWeed 10) had a constant efficiency of $5.7\cdot10^{-6}$ $m^3/m^2\cdot s$. The efficiencies of other membranes were determined based on the following equation:

$$J(J_0) = \frac{V}{F \cdot t}, \tag{1}$$

where: V – the volume (dm^3), F – the membrane area (m^2), t – the filtration time (s).

The results obtained were used for the calculations of relative permeability (J/J_0) represented by the ratio of the volumetric flux of permeate (J) to the volumetric flux of deionized water (J_0). This allowed the fouling susceptibility of the membrane to be determined.

Based on the results of the calculations of volumetric permeate flux, it was possible to model membrane filtration, making use of the membrane filtration model in a non-stationary process and the hydraulic model of filtration resistance. The volumetric permeate flux was also used for fouling analysis during the filtration process under a constant pressure, which allowed us to determine the mechanism of fouling based on the Hermia's model. The separation properties of membranes were determined by the coefficient of impurities retention. Raw water and the permeate parameters such as: TOC, COD-Mn (with potassium permanganate), COD measured with a photometer (by Merc), UV_{254} absorbance, turbidity, conductivity, pH, iron and aluminum content were measured.

3. RESULTS OF INVESTIGATIONS

3.1. REMOVAL OF IMPURITIES

Simulated water. Tables 1 and 2 show the effectiveness of impurities removal due to direct coagulation in UF/MF and integrated/hybrid systems: coagulation–sedimentation–MF and in-line coagulation–UF/MF. Comparing the efficiencies of the water treatment processes it has been demonstrated that the membrane process with in-line coagulation yields the highest values of the coefficient of organic impurities retention. In this process, those impurities are effectively removed maintaining high volumetric permeate flux, and their retention coefficient, determined as the absorbance at 254-nm wavelength (UV_{254}), is in the range of 62–68% for MF, and determined as TOC varies from 59 to 67%. These results are confirmed by the analysis of COD-Mn, where the retention factors for the integrated/hybrid processes were by10–15% higher than those for the direct MF/UF.

Table 1 presents the results of water treatment with PP-MF capillary membrane used in direct MF and in hybrid in-line coagulation–MF processes, in which the coagulant dose was determined by jar test, and the amounts equal to 75% and 50% of that dose were added.

Table 1

Retention coefficients of water quality indicators determined for simulated water treated in unit MF and hybrid in-line coagulation–MF system (PP 11-channel capillary membrane, raw water with 10 mg TOC/dm^3, $FeCl_3$, $Al_2(SO_4)_3$ coagulants)

Parameter	Retention coefficient *R* (%)						
	Dose (mg Fe/dm^3)			Dose (mg Al/dm^3)			MF
	4.1	3.1	2.05	4.1	3.1	2.05	
Turbidity	92.1	91.4	91.6	95.6	91.4	93.2	92.5
COD-Mn	75.0	75.0	68.7	71.8	67.2	71.1	56.2
TOC	68.2	66.9	63.1	62.5	63.0	61.8	59.1

Table 2

Retention coefficients of water quality indicators for simulated water treated in direct UF and in integrated/hybrid system (ZeeWeed 10 immersed membrane module, raw water with 10 mg TOC/dm^3, $FeCl_3$, $Al_2(SO_4)_3$ coagulants – 4.1 mg Me/dm^3)

Parameter	Retention coefficient *R* (%)				
	UF	$FeCl_3$		$Al_2(SO_4)_3$	
		Coagulation –sedimentation–UF	In-line coagulation – UF	Coagulation –sedimentation – UF	In-line coagulation – UF
Turbidity	98.1	98.5	97.9	98.6	97.8
COD-Mn	41.6	47.1	54.5	47.5	53.5
UV_{254}	75.3	86.7	67.9	63.5	68.6

It was observed that with the increase in the coagulant dose, the retention coefficient in the in-line coagulation also increased; however, this increase was negligible. The dose of coagulant added to the in-line coagulation can be lower than the dose determined by jar test, because even the lowest dose of coagulant improved the permeate quality. The results obtained for organic matter and turbidity removal satisfied government regulations for drinking water. The addition of the lower amount of coagulant not only increased the efficiency of the process, but it also limited the amount of metal ions added with the coagulant.

The filtration of simulated water using an immersed membrane module (table 2) revealed that the integrated system with iron chloride coagulant removed organic impurities (measured as UV_{254} absorbance) most effectively, whereas the in-line coagulation with aluminum sulfate indicated higher efficiency in COD-Mn decrease. The application of integrated/hybrid systems did not improve the removal of turbidity in comparison with the direct ultrafiltration process.

Comparing both coagulation types, it has been demonstrated that both of them yield satisfying results; however, the in-line configuration allows us to decrease the doses of coagulant and seems to be technologically more attractive. In all process arrangements, the traces of iron and aluminum can be found (all below legal regulations for drinking water – 0.2 mg/dm^3).

Surface water. In table 3, the results of the efficiency of impurities removal from the surface water subjected to treatment are collected. The water was introduced to the direct filtration and integrated coagulation/sedimentation/UF systems with immersed ZeeWeed 10 membrane module.

Table 3

Retention coefficients of water quality indicators determined for surface water treated in direct UF process and in integrated system (immersed ZeeWeed 10 membrane module, $FeCl_3$ coagulant – 6.0 mg Fe/dm^3)

Parameter	Retention coefficient *R* (%)	
	UF	$FeCl_3$ + UF
Turbidity	72.1	91.4
COD-Mn	34.2	42.5
UV_{254}	34.3	74.8

The water treatment with ZeeWeed 10 module turned out to be very effective in turbidity elimination, which is quite significant in terms of drinking water. The ultrafiltration process supported by coagulation resulted in an increase in the coefficient of organic matter retention determined as UV_{254} absorbance.

Table 4 presents the results for the hybrid process with in-line coagulation – UF and PES-UF capillary membrane and for the direct UF process.

Table 4

Retention coefficients of impurities' removal from surface water treated in UF (PES), hybrid in-line coagulation–UF system ($FeCl_3$ coagulant – 2.4 mg Fe/dm^3)

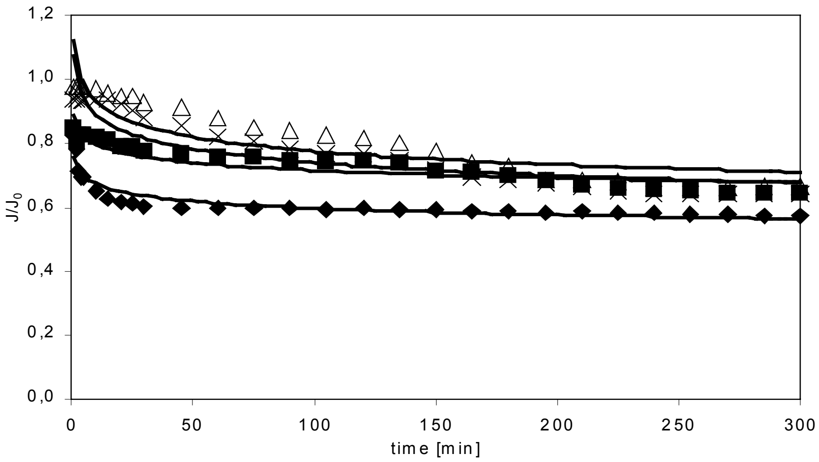
Parameter	Retention coefficient *R* (%)	
	UF	$FeCl_3$ + UF
Turbidity	80.0	88.3
COD-Mn	32.4	35.8
UV_{254}	33.7	48.1

The outcome of the studies suggests that the hybrid in-line coagulation–UF process results in a significant increase in the removal of organic matter (determined as UV_{254} absorbance) and turbidity in comparison with the direct UF process.

3.2. PROCESS YIELD

Figure 2 presents the comparison of the relative permeability for the hybrid in-line coagulation and direct membrane filtration process of simulated water with the use of a capillary PP-MF membrane (11-channel membrane, ΔP = 0.1 MPa) with the optimum coagulant dose (4.1 mg Al/dm^3) as well as 75% and 50% of that dose.

In the direct microfiltration, relative permeability coefficient reaches lower values (0.57) than those obtained in the hybrid process (0.64–0.66). This proves that fouling decreases in the hybrid in-line coagulation.



♦ direct MF, ■ coagulation + MF(4.1 mg Al/dm^3), Δ coagulation + MF (3.1 mg Al/dm^3), x coagulation + MF (2.05 mg Al/dm^3)

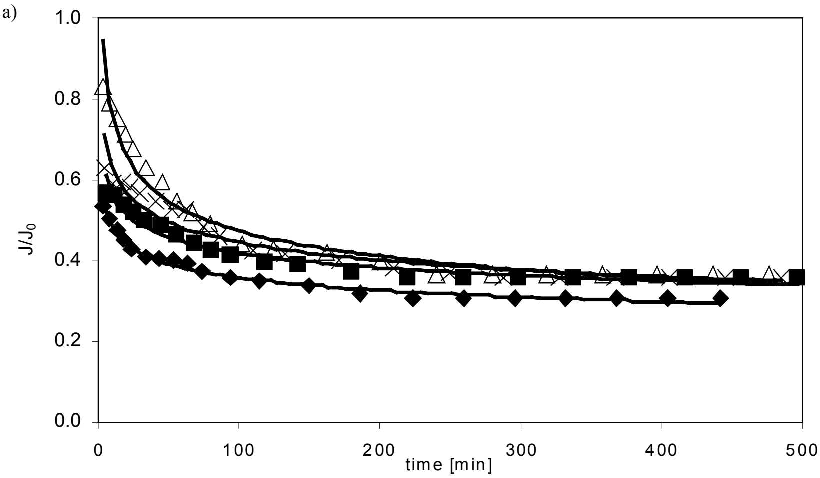
Fig. 2. Comparison of relative permeability change for capillary PP-MF membrane in direct MF and hybrid in-line coagulation–MF system, with various coagulant doses

The amount of the coagulant affects the values of permeability coefficient. The results obtained confirm the usefulness of lower coagulant dose in contrast to what had been done in the conventional coagulation (with sedimentation). The filtration cake formed has a greater porosity and lower ability to affect membrane surface, which decreases its contamination, especially inside membrane pores.

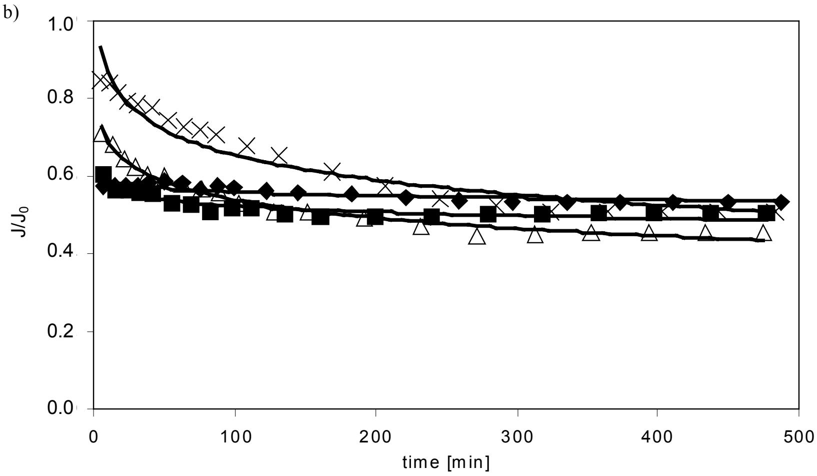
Figure 3 presents the results of the studies focused on the relative changes of permeability coefficient determined for capillary membranes: PP-MF (figure 3a) and PES-UF (figure 3b) during surface water treatment in the direct and integrated coagulation–sedimentation–MF/UF processes.

In contrast to the direct MF/UF, the application of coagulation increased a permeate flux. This is confirmed by the relative values of permeability coefficient, which for the integrated system were in the range of 0.3–0.35 (figure 3a), while for the direct ultrafiltration they varied from 0.45 to 0.53 (figure 3b). However, the improvement of membrane efficiency was lower for surface water than for simulated water which contained only the impurity of one type (humic acids). In the case of surface water, other impurities, e.g. calcium ions, and water ionic strength have a significant influence on fouling. Calcium ions decrease the solubility of humic substances, and high ionic strength of the feed has a strong influence on the velocity of molecular transport through the membrane.

a)



b)



♦ direct MF/UF, ■coagulation $FeCl_3$ (2.4 mg Fe/dm^3)–MF/UF,
x coagulation $Fe_2(SO_4)_3$ (2.2 mg Fe/dm^3)–MF/UF, Δ coagulation $Al_2(SO_4)_3$ (2.9 mg Al/dm^3)–MF/UF

Fig. 3. Comparison of relative permeability change during surface water treatment in direct MF/UF process and in integrated coagulation–sedimentation–MF/UF system: a) capillary PP+MF membrane, b) capillary PES-UF membrane

To conclude, in this stage of studies, the pretreatment of water by coagulation and sedimentation resulted in the removal of significant amounts of organic compounds, which formed complexes, aggregates or were sorbed on flocs (metals hydroxides) precipitated by metals, the components of coagulants. When coagulation was applied, the membrane filtration process was run with high flux kept on constant level. The filtration cake formed during the hybrid in-line coagulation–MF/UF process was more porous and less prone to be adsorbed on the membrane surface, which decreased membrane contamination, especially inside its pores. This resulted in a lower frequency of hydraulic and chemical cleaning of the membrane and prolonged its operation time.

3.3. FLUX MODELLING

The studies were focused on the prediction of the yield of UF/MF water treatment in the case of water contaminated with natural organic matter (NOM). The calculations were done based on experimental data, which determined permeate fluxes in the integrated conventional coagulation–membrane filtration system and in the hybrid in-line coagulation–membrane filtration system. Simulated and surface waters were treated using capillary membrane modules supplied from the inside and outside.

Membrane filtration model in a non-stationary process. In the model of filtration in the non-stationary process (relaxation model), the mass transfer balance equation is used, in which the decrease in permeate flux is proportional to its value [6], [7]:

$$\frac{d}{dt}(J - J_{\infty}) + \frac{1}{t_0}(J - J_{\infty}) = 0\,. \tag{2}$$

The solution of equation (2) allows us to predict the changes in permeate flux during the exploitation of membrane modules, provided that we know the initial flux (J_0), the equilibrium flux (J_{∞}) and the time constant (t_0), which characterize the velocity of permeate flux decrease (table 5) and lead to the dependence:

$$J_t(t) = (J_0 - J_{\infty})\mathrm{e}^{t/t_0} + J_{\infty}\,, \tag{3}$$

where J_t is a theoretical volumetric permeate flux after the time t.

The calculated values of the time constant t_0 (table 5) were generally higher for integrated/hybrid processes than for direct ultra- and microfiltration, which prolonged the time of permeate flux decline and reduced the frequency of membrane washing after the processes with coagulation in comparison with direct membrane filtration processes.

The calculation of the theoretical values of volumetric permeate flux (equation (3)) allowed their comparison with the values of volumetric permeate flux determined during experimental water treatment. In figure 4, the results obtained in the surface water filtration process with PES-UF membrane and the values calculated from the model are shown [6].

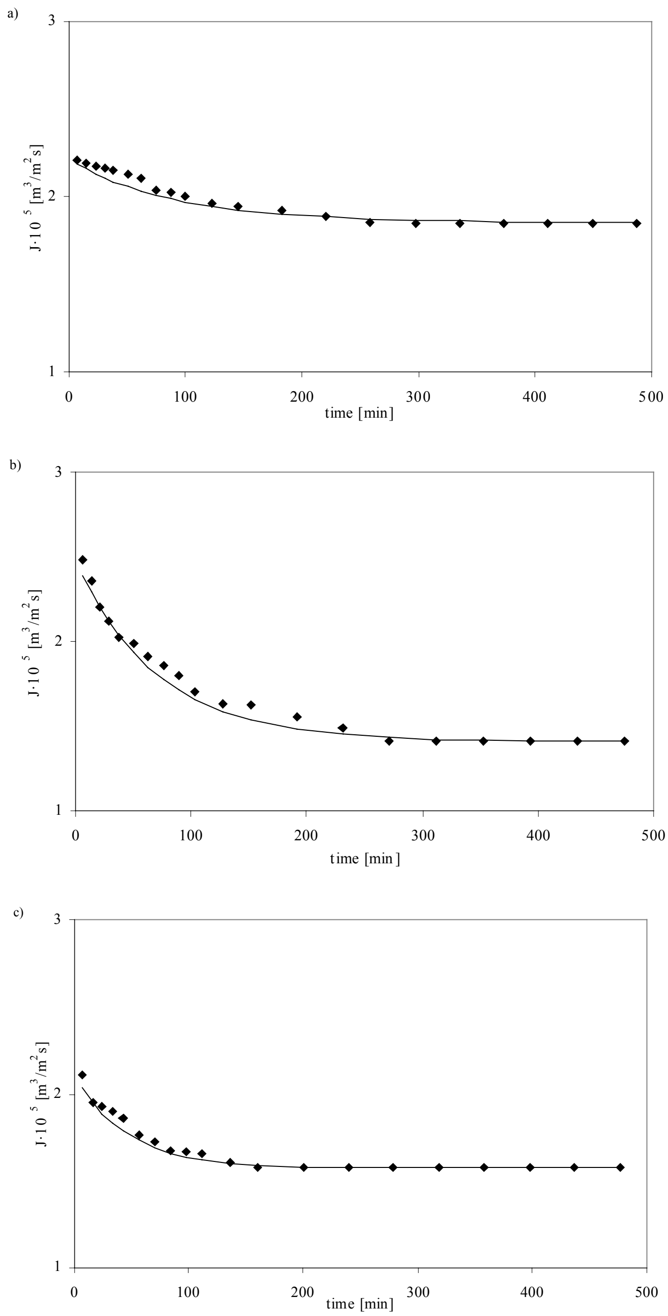


Fig. 4. Experimental and theoretical permeate fluxes
for UF–PES capillary membrane in surface water filtration process: a) direct UF,
b) coagulation $Al_2(SO_4)_3$–sedimentation–UF, c) coagulation ($FeCl_3$)–sedimentation–UF

The data analysis shows that the correlation of an experimental curve with a model curve is less close in the initial stage of filtration process, where equilibrium is not reached, than in its further run. At the beginning of the process more complex phenomena take place than it is assumed by model equation (3), especially in the case of direct UF/MF processes. When coagulation is applied, the system reaches equilibrium in shorter time than in the direct filtration, and this can be observed for each coagulant used (figure 4). This is confirmed by high correlation coefficients (table 5) obtained for all the membrane types and all the water treatment processes of simulated and surface waters.

It is shown that most of the correlation coefficients calculated reach the values in the range of 0.92–0.99, which confirms that the model matches closely the experimental results. The model of filtration in a non-stationary process also well describes the efficiency of direct ultra- and microfiltration as well as coagulation–sedimentation–UF/MF and in-line coagulation–UF systems, and the calculated data does not differ much from the experimental results.

Table 5

Time constant t_0 values and correlation coefficients for experimental and model data of direct UF/MF and integrated coagulation–sedimentation system–filtration of simulated and surface waters: simulated water – 7 mg TOC/dm^3, b) simulated water – 10 mg TOC/dm^3

Process		Time constant (t_o)/Correlation coefficient			
		Simulated water		Surface water	
		MF-PP	UF-PES	MF-PP	UF-PES
MF/UF	a	24/0.9870	49/0.9724	63/0.9866	71/0.9911
	b	23/0.9939	47/0.9972		
		coagulation–sedimentation–MF/UF		coagulation–sedimentation–MF/UF	
$Al_2(SO_4)_3$–MF/UF	a	28 /0.9685	–	64/0.9952	90/0.9941
	b	23 /0.8130	43 /0.9274		

Hydraulic model of filtration resistance. The model is based on the dependence of permeate flux on pressure and hydraulic resistance of a membrane [6]–[9]:

$$J_v = \frac{\Delta P}{\eta \cdot (R_m + R_{fr} + R_{fir})}, \tag{4}$$

where: R_m – the membrane resistance, R_{fr} – the resistance caused by reversible fouling, R_{fir} – the resistance caused by irreversible fouling, ΔP – the transmembrane pressure, η – the viscosity of liquid.

The particular resistance elements were determined as follows:

• the membrane resistance (R_m) from the dependence of deionized water flux on time; the use of a new (clean) membrane,

• total resistance ($R_{tot} = R_{m.} + R_{fr} + R_{fir}$) from the dependence of the water flux on time:

$$R_{tot} = \frac{\Delta P}{J_v \cdot \eta}, \tag{5}$$

• the sum of the resistances: $R_{m.} + Rf_{ir}$ from the dependence of deionized water flux on the time for the membrane after water filtration,

• reversible (R_{fr}) and irreversible (R_{fn}) resistances from the difference in the resistances obtained in three measuring series.

It was assumed that the irreversible resistance was developed in a short time at the beginning of the process, and the yield mainly depended on the reversible resistance, which varied with time, being directly proportional to the amount of the substance deposited on the membrane, which was expressed by the formula:

$$\frac{d}{dt}(R_\infty - R) + \frac{1}{t_{RO}}(R_\infty - R) = 0\,. \tag{6}$$

By integrating equation (6) we arrive at:

$$R_{fr} = R_\infty\left[1 - \exp\left(-\frac{t}{t_{RO}}\right)\right], \tag{7}$$

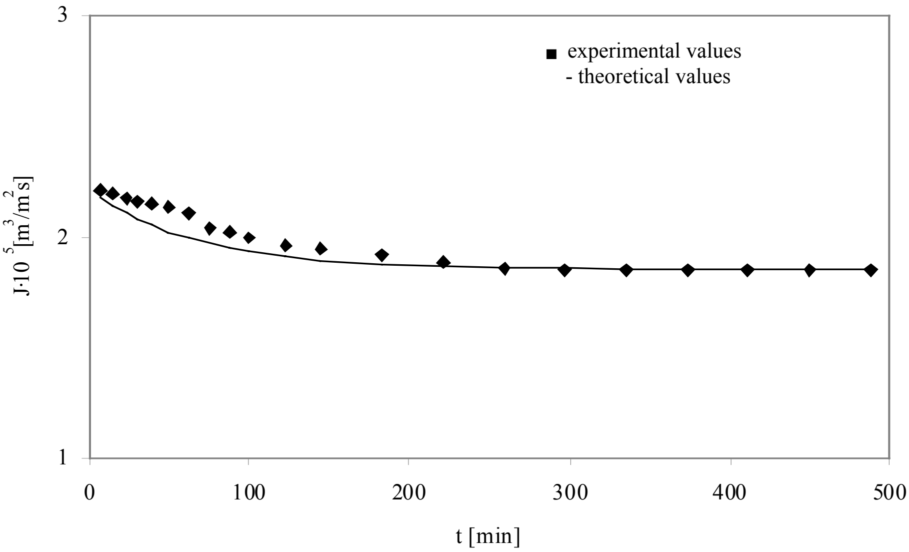
where: R_{fr} – a reversible fouling resistance after the time t (assuming that $R_{fr} = 0$ at $t = 0$), R_∞ – a reversible fouling resistance after an infinite time, t_{RO} – the equation coefficient.

In order to verify the model proposed based on experimental results, volumetric permeate flux was calculated from equation (4) being transformed in such a way that it comprises membrane resistance and irreversible fouling resistance obtained experimentally, whereas the reversible fouling resistance was calculated from model equation (7). The calculations performed were used to compare volumetric fluxes: experimental and theoretical.

Figure 5 shows a graphical comparison of both fluxes (experimental and theoretical) for surface water passing through the capillary PES-UF membrane.

The calculated values of the constant t_{RO} and the correlation coefficients of theoretical and experimental data sets are collected in table 6. The results obtained show that the model developed is in conformity with experimental data for the direct ultra- and microfiltration and integrated coagulation–UF/MF system. Lower values of correlation coefficients and t_{RO} coefficients for the direct process (table 6) were confirmed by correlation coefficients and the time constant t_0 obtained for the non-stationary model (table 5). The application of the coagulation–membrane filtration system allows us to maintain high fluxes for longer time and to decrease hydraulic resistance of liquid flow through the membrane.

a)



b)

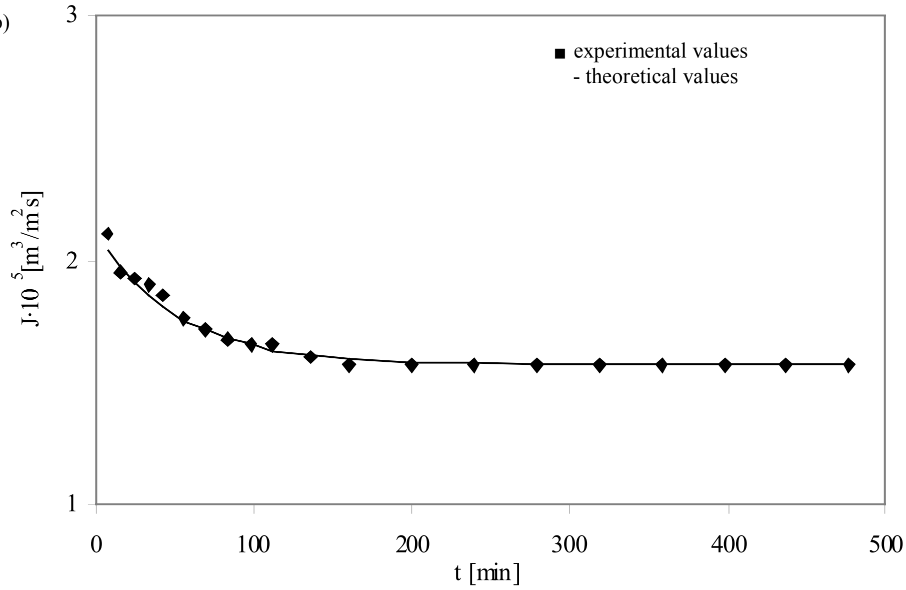


Fig. 5. Experimental and theoretical volumetric permeate fluxes vs. Time: a) direct UF, b) coagulation with $FeCl_3$–sedimentation–UF (capillary UF-PES membrane)

In the process of water treatment, an irreversible fouling had a smaller impact on the total resistance than a reversible fouling. This is a significant advantage of this process arrangement, as contaminations accumulated on the membrane surface can easily be removed by back-flushing. In view of that, the integrated/hybrid process application is recommended. Lower impact of irreversible resistance prolongs a working life of membranes, which decreases significantly the costs in terms of membrane replacement and their chemical cleaning.

Table 6

Correlation coefficients of permeate flux obtained from experiments and calculated based on resistance model and t_{RO} values for capillary UF-PES and MF-PP membranes

Process	t_{RO} value (min^{-1})		Correlation coefficient	
	PES	PP	PES	PP
Surface water				
UF/MF	69	85	0.9742	0.9663
Integrated process				
Coagulation ($FeCl_3$)–sedimentation–UF/MF	56	105	0.9939	0.9759
Coagulation ($Al_2(SO_4)_3$)–sedimentation–UF/MF	126	128	0.9837	0.9879

Applying a mathematical model that is based on the membrane hydraulic resistance analysis, the change of the yields of the unit UF/MF and integrated/hybrid coagulation–UF/MF systems can be predicted independently of the coagulation process arrangement (coagulation–sedimentation or in-line coagulation) and of the properties of the treated water (simulated water or surface water). High correlation between the experimental and calculated results for all process arrangements and membrane types has been found.

Fouling mechanism investigation. Fouling mechanism was investigated based on Hermia's model [6], [8], [9]. Simulated water (10 mg TOC/dm^3) and a capillary PP-MF 11-channel membrane in a semi-dead-end system were used for those studies. Membrane filtration was carried out under 0.05 and 0.1 MPa transmembrane pressure.

Hermia's equation combines UF/MF membrane blocking velocity (d^2t/dV^2) with an instantaneous resistance (dt/dV) in the following way:

$$\frac{d^2t}{dV^2} = k\left(\frac{dt}{dV}\right)^{\beta}, \qquad (8)$$

where: V – a total volume of permeate (dm^3), t – the filtration time (s), k – the constant ($s^{1-\beta}(dm^3)^{\beta-2}$), β – the power index.

The model represented by equation (8), depending on β value, can be used for identifying membrane blocking mechanisms during filtration processes carried out under constant pressure. When $\beta = 2$ we deal with a complete blocking, when $\beta = 1.5$, it is a standard blocking, $\beta = 1$ represents a transient blocking and $\beta = 0$ shows the mechanisms of filtration with cake formation and can be used to monitor the process consisting in the change from blocking mechanism to filtration with cake formation.

To calculate β the logarithm of equation (8) should be taken (in a new form of equation (9) β becomes a directional index):

$$\log\left(\frac{d^2t}{dV^2}\right) = \log k + \log\left[\frac{dt}{dV}\right]. \tag{9}$$

Figure 6 presents the dependence of β on filtration time under the pressure of 0.05 and 0.1 MPa in the direct and hybrid processes

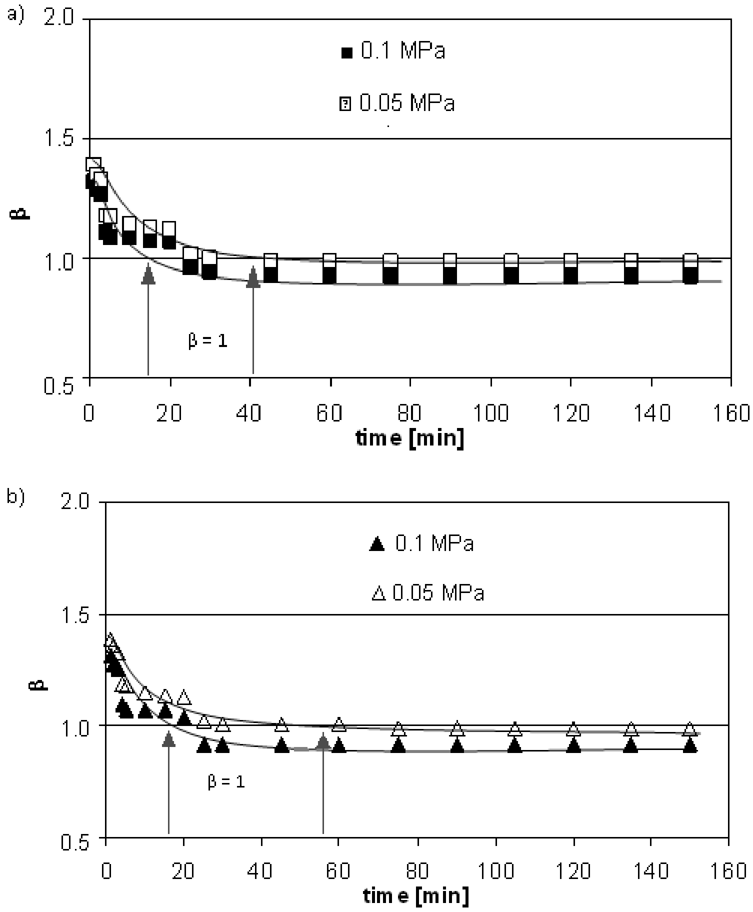


Fig. 6. β coefficient versus time of filtration under 0.05 and 0.1 MPa pressures: a) direct MF, b) $Al_2(SO_4)_3$–MF (4.1 mg Al/dm^3)

At the beginning of the process the values of β coefficient decrease below unity, and during the process they stabilize and become constant for both raw water and water treated by coagulation. It is impossible to distinguish between complete, standard and transient blocking as the values of β change quite fast at the beginning of the process. It can be supposed that we deal with various blocking mechanisms: one, which causes the blocking of membrane pores, and the second, which is connected with the accumulation of particles on membrane surface. Assuming that the blocking process is completed when β reaches a constant value equal to 1, the blocking time can be measured. It can be seen that for the hybrid process carried out under the pressure of 0.05 MPa this time is longer than for direct MF. This is due to a smaller amount of small particles present in water treated by in-line coagulation. It is the cake formation that is the main blocking mechanism.

Based on the experiments it can be inferred that the higher the transmembrane pressure, the shorter the time necessary for membrane blocking. In the direct microfiltration process carried out under the pressure of 0.1 MPa, the blocking time was shorter than 20 minutes, whereas in the same process carried out under the pressure of 0.05 MPa it was as long as ca. 40 minutes. A similar dependence was observed in the hybrid system, where pores were blocked after 20 minutes and after ca. 60 minutes under the pressure of 0.1 MPa and 0.05 MPa, respectively. When a higher transmembrane pressure was applied for both direct and hybrid operations, the cake formation lasted ca. 20 minutes (figure 6). This shortening of time can be explained by the higher velocity of particles being transported to the membrane surface. It is crucial to carry out the process, especially in the case of microfiltration, with the velocity maintained below the critical flux. The hypothesis of "critical flux" is based on the assumption that there exists a flux below which the fouling is negligible and above which the blocking of membrane pores is observed. The value of critical flux depends on the size of particles dissolved in the treated water and the interactions between them, which has an influence on the mass transport during membrane filtration. It is supposed that when the membrane filtration was carried out under the pressure of 0.1 MPa, the critical flux value was overcome, which resulted in a stronger membrane fouling confirmed by the shorter blocking time (figure 6).

4. CONCLUSIONS

1. To improve the yield of membrane filtration and prolong the membrane operation time (fouling prevention), the process should be carried out in an integrated or hybrid system. Coagulation combined with ultra- or microfiltration improves the treatment process of water with higher organic matter load. The content of organic matter as well as turbidity can be significantly decreased during an integrated/hybrid process to the amount suitable for drinking water.

2. The effectiveness of membrane filtration depends on the type of membrane module and coagulation arrangement as well as on the type and amount of coagulant

applied. The comparison of the coagulation applied in the integrated and hybrid processes leads to conclusion that the in-line coagulation arrangements seem to be more effective. The results obtained for this type of arrangement are not much different from those obtained in coagulation–sedimentation system, whereas the in-line coagulation allows us not only to reduce the amount of coagulant used, but also to decrease the necessary space for water treatment installation.

3. Mathematical models based on hydraulic resistance and membrane efficiency in unsteady state analysis allow the permeate flux values in both direct UF/MF and coagulation–membrane filtration systems to be predicted. They also show that the integrated or hybrid process arrangements prolong the maintenance of permeate flux on high level and decrease hydraulic resistance of liquid flow through the membrane in comparison with direct MF/UF.

4. The investigation of fouling shows various mechanisms of this phenomenon during the process run: at the beginning of the process a membrane blocking (complete, standard and transient) takes place, and the dominant mechanism is the filtration cake formation. Carrying out the process under lower transmembrane pressure results in the longer time of membrane blocking in unit membrane processes and those combined with coagulation.

LITERATURE

[1] BODZEK M., KONIECZNY K., *Membrane processes in water treatment*, Projprzem-EKO, Bydgoszcz, 2005.

[2] KABSCH-KORBUTOWICZ M., *Pressurized processes in membrane separation*, Wodociągi Kanalizacja, 2007, 5 (39), 40–44.

[3] BODZEK M., KONIECZNY K., RAJCA M., *Hybrid membrane processes used in impurities removal from natural water*, [in:] Monografie Komitetu Inżynierii Środowiska PAN, 2005, 32, 143–153.

[4] ZULARISAM A.M., ISMAIL A.F., SALIM R., *Behaviors of natural organic matter in membrane filtration for surface water treatment – a review*, Desalination, 2006, Vol. 194, 211 – 231.

[5] CHEN Y., DONG B.Z., GAO N.Y., FAN J.C., *Effect of coagulation pretreatment on fouling of an ultrafiltration membrane*, Desalination, 2007, Vol. 204, 181–188.

[6] KONIECZNY K., *Treatment of waters polluted with organic substances*, [in:] *Environmental Engineering*, Pawłowski L., Dudzińska M. & Pawłowski A. (eds), Taylor & Francis, London, 2007, 245–252.

[7] KONIECZNY K., SĄKOL D., BODZEK M., KORYCKI M, RAJCA M., *Porównanie skuteczności wybranych koagulantów do usuwania substancji organicznych w procesie hybrydowym koagulacja/mikrofiltracja*, Instal., 2007, nr 4, 53–57.

[8] BODZEK M., RAJCA M., BARGIEŁ J., KONIECZNY K., *Investigations concerning the mechanism of the "fouling" of membranes in the course of the direct microfiltration and in the hybrid system of coagulation and microfiltration*, Polish J. Envirn. Studies, 2007, 16, (2A), 172–176.

[9] KONIECZNY K., *Modelling of membrane filtration of natural water for potable purpose*, Desalination, 2002, Vol. 143, 123–139.

UZDATNIANIE WODY HYBRYDOWĄ METODĄ KOAGULACJI I NISKOCIŚNIENIOWEJ FILTRACJI MEMBRANOWEJ

Przedstawiono wyniki uzdatniania wody metodami bezpośredniej UF/MF oraz metodą hybrydową koagulacja–UF/MF. Badania prowadzono z wykorzystaniem kapilarnych modułów ultrafiltracyjnych z polieterosulfonu (PES) oraz modułów mikrofiltracyjnych z polipropylenu (PP). Zastosowano dwa rodzaje koagulantów: chlorek żelaza ($FeCl_3 \cdot 6H_2O$) oraz siarczan glinu ($Al_2(SO_4)_3 \cdot 18H_2O$). Proces hybrydowy prowadzono w układach koagulacja klasyczna–UF/MF oraz w układzie koagulacja *in-line* (bez sedymentacji)–UF/MF. Stwierdzono poprawę jakości wody oraz mniejszą intensywność *foulingu* w procesach hybrydowych w porównaniu z bezpośrednią UF i MF. Wydajność UF modelowano, opierając się na modelu relaksacyjnym oraz na modelu oporów filtracji. Wykorzystując model Hermii, określono mechanizm *foulingu*.