Trihalomethane Removal from Water Using Membrane Processes

A. Waniek[1], M. Bodzek[2], K. Konieczny[2]

[1] Department of Chemistry, Silesian Medical Academy,
Jordana 19, 41-808 Zabrze, Poland
[2] Silesian University of Technology, Institute of Water and Wastewater Engineering,
Konarskiego 18, 44-100 Gliwice, Poland,

Abstract

Trihalomethanes (THMs) are formed due to chlorination of water containing organic compounds. They have mutagenous and carcinogenic properties. The main representative of this effluent group is chloroform. The objectives of this paper are to determine the removal effectiveness of chloroform from natural water with the application of reverse osmosis, nanofiltration and ultrafiltration as well as modelling the flux of using a mathematical model based on resistance determination law and filtration model in constant pressure conditions (J. Hermia's model). The investigation carried out demonstrated the possibility of applying these processes for the removal of chloroform from water. The comparison of volumetric fluxes - the model flux and the experimental one, confirmed good congruence of the model calculations with the results of investigation studies.

Keywords: water treatment, trihalomethanes, chloroform, pressure driven membrane techniques, flux modelling

Introduction

In the degraded water environment we more and more frequently come across numerous micropollutants, principally in surface waters, but their presence is frequently detected in underground waters [1, 2]. The micropollutants penetrate surface waters, mainly with atmospheric rainfall, wastewaters (including leachates from dumpsites) as well as with downflow from the catchment basin, and their presence in surface waters disturbs and hampers the self-purification process of waters. The concentration of micropollutants in surface waters depends on the pollution level of atmospheric rainfall, the level of industrialization and population density of the catchment basin, and the pollution load washed away from the catchment basin and introduced to waters from sewage [1-3].

Correspondence to: Prof. M. Bodzek

Micropollutants present in natural waters can be divided into primary pollutants (present in raw watej) and secondary ones (formed during water treatment). The group of primary organic pollutants includes: polycyclic aromatic hydrocarbons (PAH), pesticides, surface active substances, chlorinated organic compounds (TOX), esters, alcohols, glycols, aliphatic and aromatic amines and phenols. The group of micropollutants also contains compounds which are not toxic, but their harmful properties are activated when they get into contact with other compounds present or introduced into water during its treatment. They include among others humic, fulvic compounds and other TOX precursors as well as nitrates [2]. The group of secondary micropollutants includes chloro- and bromoorganic compounds. With respect to this group, THMs (trihalomethanes) are distinguished as an indication of potential hazards; they constitute about 20% of the chlorinated organic compounds. The chlorination process may also result in the formation of chloroacetonitriles, chlorophenoles, chloroacids,

chlorinated ketones, organic chloramines, chlorines and chlorates [1]. What is more, trihalomethanes may penetrate surface waters due to the emission of these substances to the environment by production plants, and they may be formed, if effluents containing chlorine are discharged to surface waters, e.g. from plants producing chlorine or sodium.

Trihalomethanes (THMs) are formed due to chlorination of water containing organic compounds, principally humic and fulvic ones. The group of THM precursors also includes aliphatic compounds, metabolites of algae and bacteria, chlorophyll and substances originating from effluents, in particular from petrochemical industry [4-6]. The main representatives of this effluent group are as follows [7, 8]: chloroform ($CHCl_3$) - occurring in highest concentrations, bromodichloromethane ($CHCl_2Br$), dibrochloromethane ($CHClBr_2$) and bromoform ($CHBr_3$).

The formation process of THMs during water chlorination has not yet been fully explored. There are several opinions as to the reaction run of chlorine with humic substances. One of them has been presented in Fig. 1 [9]. The run of the reaction depends on many factors: pH, chlorine dose, and presence of bromine, temperature and the kind and concentration of organic compounds present in water [7J.

Fig. 1. Run of haloform reaction.
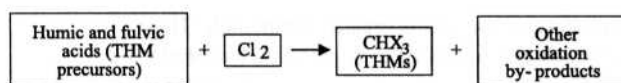
Trihalomethanes have mutagenous and carcinogenic properties. These compounds are aromatically insensible, yet their presence in water may be physiologically hazardous. Their harmful influence on the body is presented in Table 1 [10]. At present, these compounds are known to show carcinogenic properties in bioassays carried out in rodents [10]. Epidemiological research suggests that bladder, rectal and colon cancers are potentially associated with drinking chlorinated water [10]. Recent epidemiological studies have reported associations between the consumption of chlorinated drinking water and reproductive and developmental effects [10].

The content of THMs in drinking water in Poland, in congruence with the Regulation of the Ministry of Health, may total no more than 100 $\mu g/dm^3$, and of chloroform 30 $\mu g/dm^3$ [11]. Such concentration is also the permissible value for chloroform recommended by WHO [12].

The following can solve the problem involving the presence of THMs in drinking water and household water: minimizing the number of THM precursors in water prior to the chlorination process, replacing chlorine with a different oxidant and removing the formed THMs from the treated water. The removal of THMs present in water in low concentrations is difficult. Water aeration and adsorption on activated carbon [13-15] can traditionally effect it. Aeration is not very effective (up to

about 50%). Much better effects, although with higher costs involved, can be achieved using the adsorption on activated carbon [13, 15]. Another, more interesting proposition to remove THMs and their precursors from water involves the application of membrane techniques [14, 6].

Therefore, attempts have been undertaken to remove these groups of pollutants by the application of pressure-driven membrane processes such as reverse osmosis (RO), nanofiltration (NF) and ultrafiltration (UF).

The following objectives of the investigations were to be obtained:
- determining the removal effectiveness of chloro form from natural water with the application of reverse osmosis, nanofiltration and ultrafiltration,
- modeling the flux of the mentioned processes of natural water filtration using [17-20]:
- mathematical model based on Darcy's law, which describes time changes of mass transport resistance,
- filtration model in constant pressure conditions (J. Hermia's model) allowing determination of the most probable mechanism of membrane pores blocking.

The said modes have already been applied solely for modeling the yield of UF and MF of natural water [17].

Experimental

Apparatus for Membrane Filtration

Fig. 2 presents the diagram of the installation for research on membrane filtration process in laboratory conditions. The basic element of the installation is a membrane module produced by the American firm OSMONICS Inc. type SEPA SF-HP - high-pressure version, adapted to run the processes of reverse osmosis, nanofiltration as well as ultrafiltration. The design of the module enables to run the process in the cross-flow system. The module was designed in such a way that the replaceable distancing elements simulate the work of spiral or cellular module within a wide range of changeable pressure and flow rate under the membrane surface. The membranes used in the module have the form of a rectangular sheet of the dimensions 190 x 140 mm.
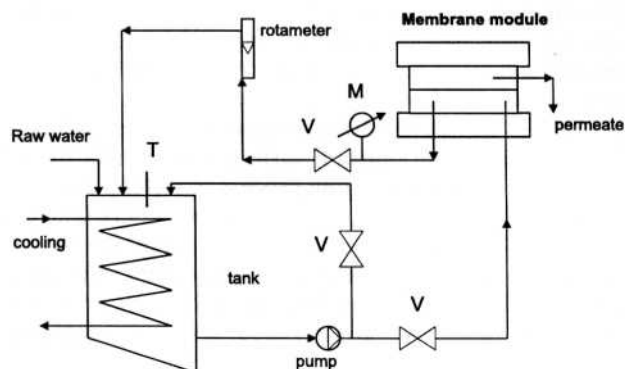

Fig. 2. Diagram of used apparatus.

Table 1, Harmfulness of the investigated compounds.

Compound	Formula	Influence
Chloroform	CHCl₃	carcinogenic, easily absorbable through, skin, lungs and food; accumulates in adipose tissue; may damage nervous system, liver, brain and kidneys
Bromodichloromethane	CHBrCl₂	causes liver and kidneys toxicity, possible carcinogenic influence on a man (according to IARC group 2B)
Dibromochloromethane	CHBr₂Cl	causes liver and kidneys toxicity, carcinogenic influence on a man not found (according to IARC group 3)
Bromoform	CHBr₃	genotoxix influence; causes liver and kidneys toxicity, carcinogenic influence on a man not found (according to IARC group 3)

Table 2. Characteristics of the applied membranes.

Parameter	RO Membrane SS10	NF Membrane MQ16	UF Membrane HP09
Pressure [MPa]	Recommended: 2.76 Max: 6.9	Recommended: 0.69 Max: 6.9	Recommended: 0.3 Max: 0.7
pH	2-8	2-12	0.5-13
Temperature [°C] (max)	50	80	100
Retention coefficient of NaCl [%]	≥ 98	30-50	–
Cut-off [Da]	100-200	400-800	1000-8000
Material	Cellulose	Polyamide	Polysulphone

Membranes

For the treatment of natural water polymeric flat membranes of the firm Osmonics were applied, for: reverse osmosis, nanofiltration and ultrafiltration. The characteristics of membranes provided by the manufacturer are presented in Table 2.

Methodology

Surface water from the intake at Kozlowa Gora in the Province of Silesia (Poland) was applied in the experiment. The water taken for the experiment had been subjected to pre-ozonation. When selecting the water of the required parameters, the emphasis was placed to ensure that the membranes did not get damaged during their work. The parameters of raw water before the process of pre-ozonation, in particular turbidity, color and dry residue were considerably higher than the permissible values for drinking water. The water was to a high degree polluted with suspended matter and colloids.

As the first stage, the deionized water was filtrated through a new membrane for six hours. Then the investigated water was passed through, after adding chloroform of the rated concentration of 124 $\mu g/dm^3$. After the 6h-filtration process of the investigated water, again the deionized water was passed through the membrane. During membrane filtration, permeate was being drained from the system. The above filtration cycle was treated as one series. Each of the membranes was subjected to fil-

tration process in three series. The process of membrane filtration was carried out at the pressure 2.0 MPa for the membranes for reverse osmosis and nanofiltration, whereas 0.3 MPa for the ultrafiltration membrane. The flow rate under the membrane surface was 0.75 m/s and temperature 20 ± 2°C for all processes.

Checking the effectiveness of the process was based on measuring the volume of permeate flux in time and the removal level of chloroform from the investigated water.

In order to effect the determination of chloroform in water, a sample was taken before the process of membrane filtration and after 6 hours. The permeate from the first 30 minutes of the filtration was discarded.

To determine the content of THMs both in raw water and in permeate, the chromatographic method was applied [10]. Gas chromatograph type A-14 (Shimadzu) was applied. It was furnished with an ECD detector (63Ni) and capillary column HP-1 (Hewlett Packard) 25 m x 0.2mm x 0.33 μm.

The following parameters of GC-ECD analysis were applied:
- injector temperature: 150°C
- detector temperature: 250°C
- flow of carrier gas He: 20 cm/s
- flow of supportive gas N₂: 40 cm/s
- flux separator split/splitless: 20 s
- temperature program: 32C (5 min), 32-120C (107min), 120C(10 min).

In order to isolate chloroform from raw water and from permeate, we applied the method of direct extrac-

tion with a solvent which does not mix with water. Isooctane was applied as the solvent. For each sample of determined water, 2-3 extractions were carried out. The results were read out from the analytical curve. Due to high instability of the samples, adding 0,1g of sodium thiosulphate to 100 cm^3 of determined water protected them.

Results and Discussion

Effectiveness of Membrane Filtration of Waters Containing Chloroform

In order to define the yield of the membrane the following was determined (Fig. 3):
- dependence of the volumetric deionized water flux (J_w) on time for a new membrane - not used before,
- dependence of natural water volumetric flux (J_v) on time,
- dependence of deionized water volumetric flux (J_w*) on time, after 18 hours of membrane's work.

It was observed, that with respect to each membrane the value of volumetric permeate flux obtained for the investigated water was lower than for the deionized water. This might have been caused by the lower temperature of surface waters, and/or the presence of numerous micropollutants and bacteria, which might effect blocking of the membrane pores (fouling). For the membranes RO-SS10 and NF-MQ16 the permeate flux was stable and the decrease of yield was inconsiderable. We can conclude from the above that the fouling was small. With respect to the membrane UF-HP09 the permeate flux was not that stable and the drop of yield was much higher, which might have been effected by higher fouling. After 18 hours of work the flux of deionized water increased again, but the membrane did not reach the previous yield level. Since the values of deionized water flux increased as compared to the flux value of the investigated water, a partial regeneration of the membrane took place, caused by washing out the pollutants by a turbulent flow of deionized water under the membrane's surface.

In each case, at the beginning of the filtration process, the drop of volumetric permeate flux is rapid, and then it gets stabilized at a certain level. The deposition of particles on the membrane's surface and the formation of polarization layer (gel layer) cause it.

For the membranes RO-SS 10 and NF-MQ 16 the fluxes of natural water have similar values: for RO the value of volumetric permeate flux is 3.16 • 10^{-6} [m^3/m^{2}s], and for NF - 3.27 • 10^{-6} [m^3/m^{2}s]. In the case of ultrafiltration the value of permeate flux is much lower: it equals ca. 0.43 • 10^{-6} [m^3/m^{2}s] (the value after 6 hours of filtration). Lower yield of the membrane UF-HP09 is connected with lower value of transmembrane pressure (0.3 MPa) and high compactness of the UF membrane.

The carried out investigation studies on the elimination of chloroform during the filtration through the membranes RO-SS 10, NF-MQ 16 and UF-HP 09 have showed that the highest efficiency involving the removal of that compound was obtained in the ultrafiltration pro-
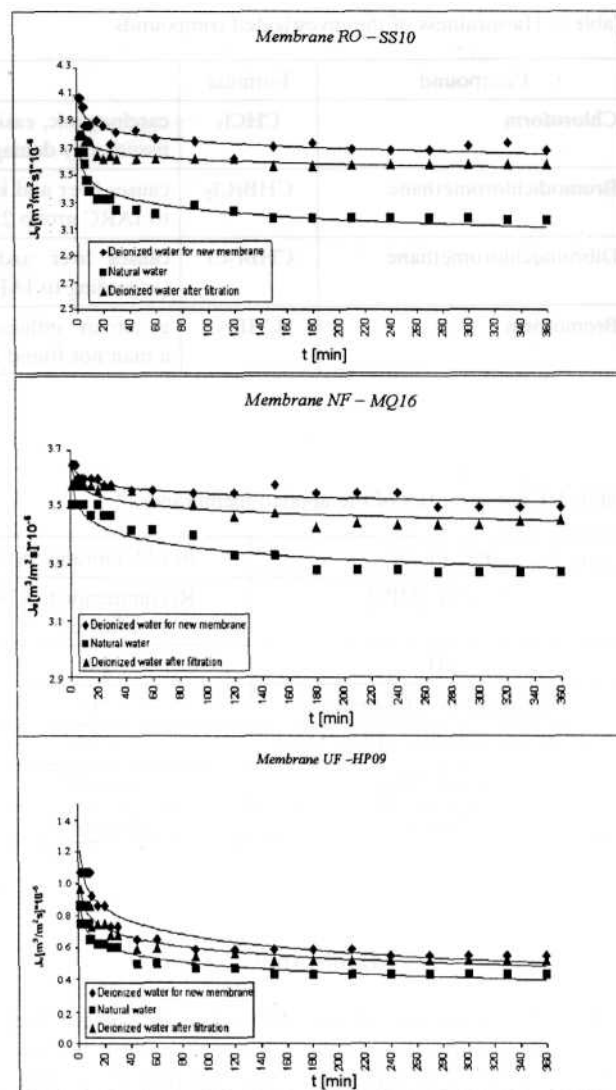

Fig.3. Dependence of volumetric flux of deionized water and natural water on time for the membranes

cess (retention coefficient 93.0%). The values of the other retention coefficients for particular membranes are as follows:
- for the membrane RO-SS 10 retention coefficient was R=81.1%,
- for the membrane NF-Q 16 retention coefficient was R=75.0%.

In theory, the membrane for reverse osmosis, whose structure was more compact and which had higher separation potentials as compared to the other membranes, should have removed chloroform better. But at that stage of investigation studies it is difficult to define unequivocally why the ultrafiltration process is more effective. It might be connected with mutual reaction between the membrane UF-HP 09 and the compound being removed. Such a high elimination level of the pollutant by the filtration process through the membrane UF-HP 09 can also be connected with process parameters, i.e. with transmembrane pressure, filtration yield, which, as compared to reverse osmosis and nanofiltration, are much different.

The difference in chloroform removal results also from different properties of the investigated membranes, i.e. pore size, and material the membranes are made of. For the ultrafiltration process, the membrane made of hydrophobic polymer (polysulfone) was applied, whereas the membranes RO-SS 10 and NF-MQ 16 were made of hydrophilic materials (cellulose, polyamide). Hydrophobic membranes are more sensitive to fouling, which is manifested by instability of volumetric permeate flux and a considerable drop of the yield of filtration process. With respect to reverse osmosis and nanofiltration the effect of fouling is of minor importance. But the filtration cake formed on the membrane surface during the ultrafiltration process additionally supports the removal process of chloroform. We should also allow for the fact that in the analyses involving the content of chloroform in waters, differences were observed between the nominal concentration and the results obtained with chromatographic analysis. This is connected with incomplete extraction of chloroform from water with isooctane.

Modeling of Membrane Processes

Based on the obtained results involving the dependence of permeate flux on time (Fig. 3) an attempt to model RO, NF and UF processes was undertaken, based on two models applied so far solely in UF and MF processes of natural waters [17-20]:
- hydraulic resistance model of membrane filtration process,
- model elaborated by J. Hermia which enables approximate estimation of pore blocking mechanism of a membrane [21].

Hydraulic Resistance Model of Membrane Filtration Process

This model is based on the equation describing the dependence of permeate flux on pressure, which allows for hydraulic resistance which is encountered by the liquid flowing through the membrane:

$$J_v = \frac{\Delta P}{\eta \cdot (R_m + R_{fo} + R_{fn})} \quad (1)$$

where: R_m - membrane resistance, R_{fo} - resistance connected with reversible fouling, R_{fn} - resistance connected with irreversible fouling, ΔP - transmembrane pressure, η - viscosity of the liquid.

The resistance of the membrane (R_m) is calculated from the dependence of the deionized water volumetric flux on time for a new membrane. From the same dependence, but obtained for the investigated natural water, we can determine total resistance ($R_m + R_{fo} + R_{fn}$). Making use of the relation $J_v = f(t)$ for deionized water after the testing on natural water we determine the sum of membrane resistance (R_m) and of irreversible fouling (R_{fn}). From the difference of total resistance, membrane resistance and the sum of membrane resis-

tance and irreversible fouling we obtain the values of reversible resistance (R_{fo}) and of irreversible resistance (R_{fn}). Fig. 4 presents relations calculated in this way involving the changes of resistance during the filtration of the investigated water as time function, for all investigated membranes.

The values of resistance for membranes RO-SS 10 **and** NF-MQ 16 are similar, but there is a considerable difference with respect to the values of hydraulic resistance for the membrane UF-HP 09. This results from different characteristics of the membranes and from the processes themselves.
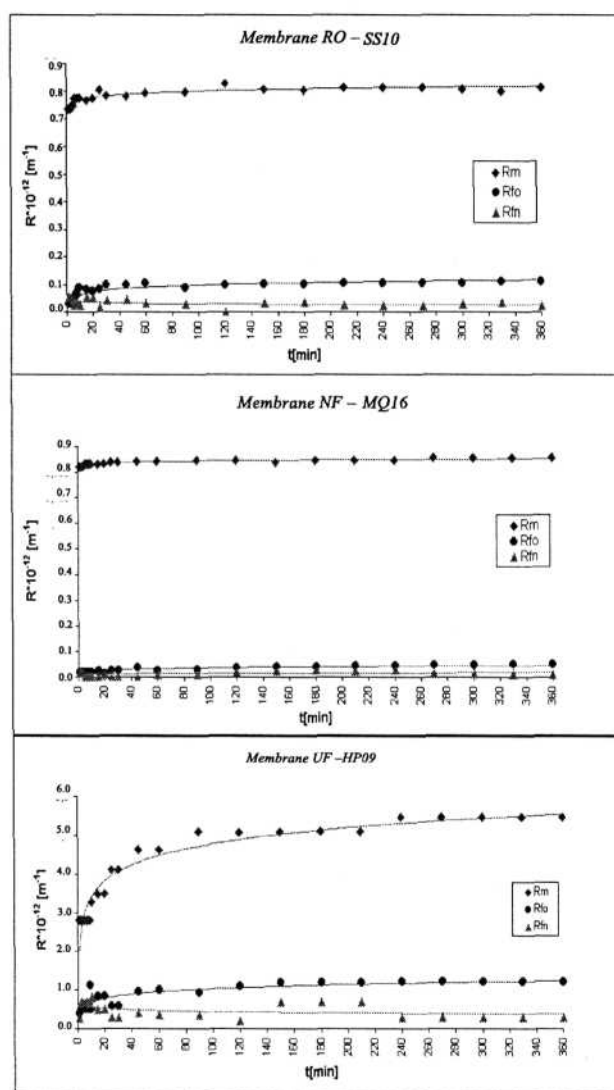

Fig. 4. Dependence of resistance change R_m, R_{fo}, R_{fo} on time during filtration of natural water for the membranes.

The results obtained from the analysis of resistance confirmed the thesis forwarded earlier, stating that the irreversible resistance is formed at the initial, short time of the process and the yield depends on the changing in time reversible resistance [17]. In order to determine the dependence involving the changes of reversible resis-

tance, it was assumed that it was proportional to the amount of substance deposited on the membrane [17]:

$$\frac{d}{dt}(R_\infty - R) + \frac{1}{t_{Ro}}(R_\infty - R) = 0 \qquad (2)$$

Integrating the equation (2) we obtain:

$$R_{fo} = R_\infty \left[1 - \exp\left(-\frac{t}{t_{Ro}}\right) \right] \qquad (3)$$

where: R_{fo} - resistance of reversible "fouling" after time t; we can assume that $R_{fo} = 0$ in $t = 0$, R_∞ - resistance of reversible fouling after infinitely long time, t_{Ro} - equation coefficient.

The equation contains two constants: Roo and t_{Ro}, which can be determined based on experimental data. The constant R_∞ is determined directly from experimental data, and the constant t_{Ro} is defined using equation (3) which, after finding its logarithm, assumes the form of a straight-line equation running through the beginning of the co-ordinate system. From the inclination of this straight line we can determine the coefficient t_{Ro}:

$$\ln\left(\frac{R_\infty - R_{fo}}{R_\infty}\right) = -\frac{t}{t_{Ro}} \qquad (4)$$

Table 3 presents the calculated values of constants in equation (4).

Table 3. Values of R_∞ and t_{Ro} for the investigated membranes.

Membrane type	Resistance $R_\infty \cdot 10^{-12}$ [m^{-1}]	Values of t_{Ro} [min^{-1}]
RO-SS 10	0.112	90.1
NF-MQ 16	0.051	114.9
UF-HP 09	1.210	43.4

To verify the proposed model, the volumetric permeate flux described by equation (1) was calculated, substituting the values of membrane resistance and irreversible fouling resistance determined from the experiment as well as the value of reversible resistance calculated from the model equation (3). The relations obtained from model calculations and experimental measurement points are presented in Fig. 5. The presented examples for natural water and for the investigated membranes confirmed good congruence of the proposed model with the obtained experimental results, which is reflected by high correlation coefficients: membrane RO-SS10 - 0.912055, membrane NF-MQ16 - 0.9919 and membrane UF-HP09 - 0.9799.
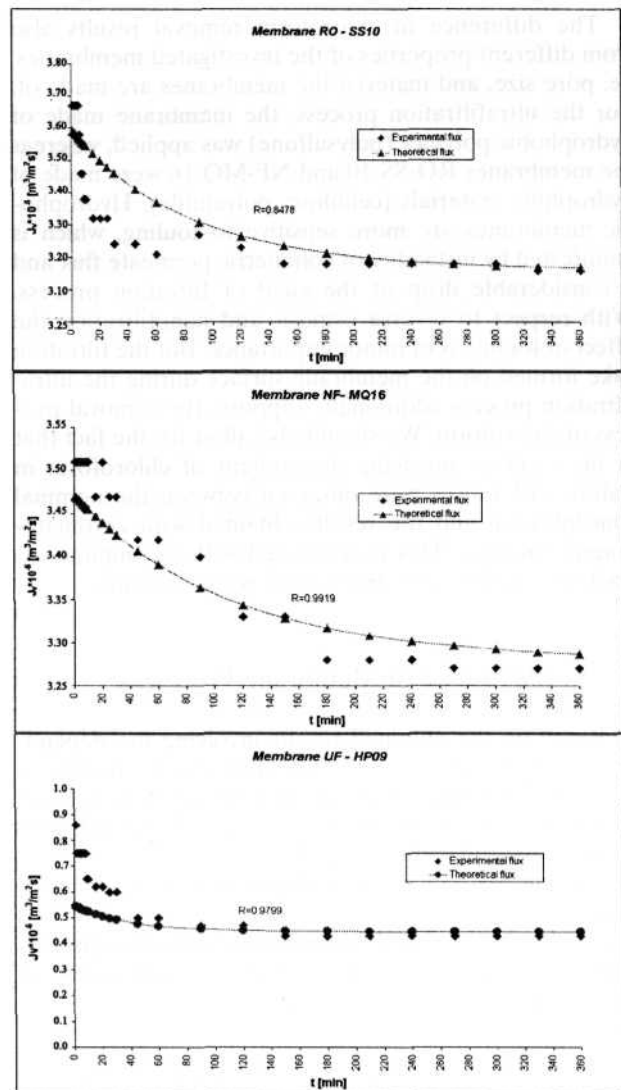

Fig. 5. Dependence of experimental and theoretical volumetric flux (calculated with reversible resistance model) on time for membranes.

Hermia Model

This model describes the change of process yield using a two-parameter equation [21]:

$$\frac{d^2 t}{dV^2} = k\left(\frac{dt}{dV}\right)^n \qquad (5)$$

where: V - permeate volume, t - time of filtration process, n,k - constants characteristic for different mechanisms of flux reduction (Fig. 6) during the filtration in constant pressure conditions.

It can be applied as a criterion identifying different mechanisms of pore blocking in a membrane, after the investigation studies on the volume of permeate flux in time, in constant pressure conditions. Assuming that parameter n can have four discrete values: n=2 (complete blocking of pores), n=3/2 (standard blocking of pores; inside part of pores), n=1 (transitory blocking of pores)
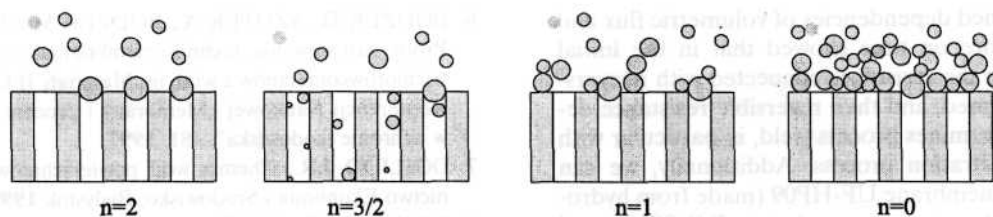
Fig. 6. Mechanism of complete membrane blocking (n=2), standard pore blocking (n=3/2), intermediate (n=1) and cake pore blocking (n=0) (according to To J. Hermia).

and n=0 - (cake blocking of pores), the second constant k has in each case a different value, to insure that the physical interpretation of the phenomena presented in the model is preserved.

By means of the computer program Micromath Scient, equation (5) was solved and the constant n, describing the process mechanism is presented in Table 4, in sequence for respective values: n=0; 1; 3/2; 2. Also, correlation coefficients (r) were determined for particular values of constant n. Its highest value reflects the best congruence of the model with experimental results as well as the blocking mechanism for a given membrane.

Analyzing the values of correlation coefficients as dependent on the value of constant n, it has been stated that the highest values of this coefficient occur for the following membranes:
  - membrane RO-SS10 and NF-MQ16 for n=2
  - membrane UF-HP09 for n=0.

Based on the values of correlation coefficients, we can observe that the mechanism of pore blocking in the membrane for reverse osmosis consists of complete blocking of pores (n=2). This means that all particles of suspended matter present in the filtrated water take part in blocking the membrane's pores. With respect to the membrane UF-HP09, the highest values of correlation coefficient correspond with the constant n=0. This means that in this membrane the cake blocking mechanism is taking place, which is connected with the formation of a layer of substances retained on the membrane's surface. This phenomenon lowers the yield of the membrane filtration process. The above findings confirm results obtained in previous investigation studies on the ultrafiltration and microfiltration of natural waters [17, 20]. The values of correlation coefficients indicate that the way in which the pores of the investigated membranes are blocked cannot be uniquvocally defined, since the values of correlation coefficients for particular values of

n are not much different from each other. Therefore, it is safer to say that during the membrane filtration process a mixed blocking mechanism of membrane's pores is taking place. For reverse osmosis and nanofiltration it will be a mixed blocking mechanism of pores with the predominance of complete blocking, which means that the majority of particles present in the filtrated water and which penetrate the pores effect their partial blocking. In the case of ultrafiltration process also a mixed blocking mechanism of pores in taking place, but with the predominance of cake blocking mechanism, which means that the majority of particles present in water effect the formation of a thin layer on the membrane's surface through the accumulation of the substances retained during the filtration process. The above observations are confirmed by the results involving the dependence of permeate flux on time presented in Fig. 3.

Conclusions

1. This study investigates the elimination of chloro form from natural water and demonstrates the possibility to apply membranes RO-SS10, NF-MQ16 and UF-HP09 for the removal of these pollutants from waters. The re sults of chromatographic analyses showed that the most efficient removal of chloroform was effected in the UF process.

2. The yield of the process depended on the type of applied membrane filtration process.

3. The results of the investigation were applied to model the processes of RO, NF and UF. The calculations were based on the verified model of hydraulic resistance of filtration and on the model elaborated by J. Hermia.

4. The resistance model consisted of the determina tion of resistance connected with reversible and irrevers ible fouling as well as with the resistance of the mem-

Table 4. Correlation coefficients r of matching the experimental curve and model curves depending on the value n for the filtration process of waters using different membranes.

Membrane type	Correlation coefficients r				
	n=0	n=1	n=3/2	n=2	Maximum value of correlation coefficients r
RO-SS10	0.95925	0.95977	0.96011	0.96859	0.96859
NF-MQ16	0.99134	0.99161	0.99174	0.99186	0.99186
UF-HP09	0.98497	0.98304	0.98144	0.97944	0.98497

brane. The obtained dependencies of volumetric flux and hydraulic resistance on time showed that in the initial phase of filtration the resistance connected with irreversible fouling is formed, and then reversible resistance develops, which determines process yield, in particular with respect to ultrafiltration process. Additionally, we can observe that the membrane UF-HP09 (made from hydrophobic polymer), as compared to RO-SS10 and NF-MQ16, is more sensitive to fouling, which is confirmed by the diagrams presenting the dependence of hydraulic resistance on time. The comparison of volumetric fluxes - the model flux and the experimental one, confirmed good congruence of the model calculations with the results of investigation studies.

5. The model elaborated by J. Hermia provided the means to define the mechanism of pore blocking for each of the investigated membranes. Based on the investigation and using a computer program, coefficients of the model were calculated which confirmed good congruence of the experimental results with the theoretical ones. In reverse osmosis and nanofiltration, complete blocking of pores is taking place whereas in the case of ultrafiltration, a cake blocking mechanism of pores in this membrane is effected.

Acknowledgements

References

1. KOWAL A.L., SWIDERSKA-BROZ M, Oczyszczanie wody, PWN, Warszawa-Wrodaw **2000.**
2. SWIDERSKA-BROZ M., Mikrozanieczyszczenia w srodowisku wodnym, Wydawnictwo Politechniki Wrodawskiej, Wroclaw **1993.**
3. SWIDERSKA-BROZ M, Mikrozanieczyszczenia wod i mozliwosc ich usuwania, Ochrona Srodowiska, 50 (3), 23, **1993.**
4. GIERAK A., CHARMS B., LEBODO R., Oznaczanie trihalometanow w wodzie, Ochrona Srodowiska **51** (4), 23, **1993.**
5. SZOTEK A., BODZEK D., BODZEK M, Eliminacja chlorowcopochodnych w^glowodorow z wod naturalnych przy wykorzystaniu procesow membranowych, in: Materialy I Ogolnopolskiej Konferencji Naukowej „Membrany i procesy membranowe w ochronie srodowiska", 63, 1995.
6. BODZEK D, SZOTEK A., BODZEK M., ZMARZLY J., Proby zastosowania technik membranowych do usuwania trichlorowcometanow z wod, in: Materiaty II Ogolnopolskiej Konferencji Naukowej „Membrany i procesy membranowe w ochronie srodowiska", 181, 1997.
7. DOJLIDO J.R., Chemia wod powierzchniowych, Wydaw nictwo Ekonomia i Srodowisko, Biatystok **1999.**
8. DOJLIDO J.R., ZBIEC E., Uboczne produkty dezynfekcji wody, Ochrona Srodowiska, **74** (3), 37, **1999.**
9. DOJLIDO J.R., Chemia wody, Wydawnictwo Arkady, Warszawa **1987.**
10. LUKS-BETLEJ K., BODZEK D, Occurrence of trihalomethanes, particularly those containing bromide, in Polish drinking waters, Polish J. Environ. Studies, **2002,** in press.
11. ROMAN M., Jakosc wody do picia w przepisach Unii Europejskiej i w przepisach polskich, Monografie PZITS, Seria: Wodociagi i Kanalizacja Nr 9, Wyd.: Polskie Zrzeszenie Inzynierow i Technikow Sanitarnych, Warszawa **2001.**
12. Wytyczne WHO dotyczace jakosci wody do picia, Wyd.: Polskie Zrzeszenie Inzynierow i Technikow Sanitarnych, Warszawa **1998.**
13. WOLBORSKA A., Trojhalometany w wodzie - rozwiazanie problemu ?, Zeszyty Naukowe Politechniki todzkiej 7(32), 397, **1996.**
14. WATSON B.M., HORNBURG CD., Low-energy membrane nanofiltration for removal of color, organics and hardness from drinking water supplies, Desalination, **72,** 11, **1989.**
15. UMPHRES M.D, TATE C.H., KAVANAUGH M.C., TRUSSELL R.R., Trihalomethane removal by packet-tower separation, Journal AWWA **75,** 414, **1983.**
16. TAYLOR J.S., THOMPSON D.M., CARSWELL J.K., Applying membrane processes to groundwater sources for trihalomethane precursor control, Journal AWWA **79,** 72, **1987.**
17. KONIECZNY K., Ultrafiltracja i mikrofiltracja w uzdatnianiu wod do celow komunalnych, Zeszyty Naukowe Politechniki Slaskiej, Seria: Inzynieria srodowiska, Z.42, Wydawnictwo Politechniki Slaskiej, Gliwice **2000.**
18. KONIECZNY K., Modelling of ultrafiltration and microfiltration of natural water for potable purpose, Desalination, **2002,** in press.
19. KONIECZNY K., BODZEK M., Modelling of UF/MF process of natural water, in: Conference Proceedings .Engineering with Membranes", **1,** 320, **2001,** Granada, Spain,
20. KONIECZNY K., RAFA J., Modelling of the membrane filtration process of natural waters, Polish J. Environ. Stud., **9,** 57, **2000.**
21. HERMIA J., Constant presure blocking filtration laws- application to power-law non-newtonian fluids, Trans IChemE, **60,** 183, **1982.**