# Water Treatment in Integrated Process Using Ceramic Membranes

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## Abstract

The objective of this study was to analyze the efficiency of water treatment in the ion exchange process (with the use of MIEX® resin), in ultrafiltration, and in a hybrid process composed of ion exchange and ultrafiltration. The influence of MIEX® resin dose on the efficiency of natural organic matter (NOM) removal was analyzed. CeramINSIDE ceramic membrane modules (TAMI Industries) were used in the experiments.

Based on obtained results, it might be stated that magnetic ion-exchange resin is effective in NOM separation from natural waters. The use of the MIEX®DOC process prior to ultrafiltration increased permeate quality and partly reduced the intensity of membrane fouling, especially for high MWCO membranes. Even very low MIEX® resin doses improved final water quality. Moreover, water treatment in the hybrid process eliminated secondary pollution of water by residual resin.

**Keywords:** ultrafiltration, ion-exchange, MIEX, hybrid process, natural organic matter

## Introduction

Production of drinking water from natural surface waters requires the use of processes that are likely to provide high removal rates of different pollutants. Natural organic matter (NOM) is one of the major groups of substances influencing water quality. Those substances range from macromolecules to low molecular weight compounds such as simple organic acids and short-chained hydrocarbons [1]. Aquatic humic substances, the dominant fraction of NOM, generally comprise one-third to one-half of the dissolved carbon in water [2]. Humic substances can be regarded as natural anionic polyelectrolytes of rather indeterminate structure. They have various functional groups, including carboxylic and phenolic, and a framework of randomly condensed aromatic rings. Because of ionization of carboxylic groups, humic substances will have a negative charge at pH values above 4.5, and are generally soluble

under these conditions [3, 4]. The presence of NOM not only results in yellow-brown colour of water but also affects odour and taste. Moreover, organic macromolecules form complexes with organic and inorganic pollutants and act as precursors of disinfection by-products [5, 6].

Low pressure membrane processes are nowadays widely applied in the production of potable water [7]. In this sector, more popular are membranes made of polymeric material. But recently ceramic membranes have frequently been applied. Ceramic membranes are increasingly being used due to their high resistance to mechanical, chemical, and thermal stresses, ensuring use for longer periods [8]. Moreover, a sharp decrease in ceramic membrane price [9] makes inorganic membranes competitive to commonly used organic membranes. Microfiltration (MF) and ultrafiltration (UF), due to relatively big pores, have been employed primarily for removal of microorganisms and particles from waters [10]. MF is effective in turbidity and particulate organic matter removal, as well as bacteria, protozoa and algae. UF can also remove viruses and some of

the organic matter particles. Efficiency of NOM separation by UF membranes is influenced by many factors, i.e. NOM character, molecular weight distribution, water pH and ionic strength, membrane cut-off, and material. Generally UF is effective in high-molecular weight fraction of NOM removal [11]. Moreover, low-pressure membrane processes suffer from fouling that result in a decrease of permeate flux. This has led to great interest in the integrated membrane processes application involving pretreatment of feed solution using chemical and/or physical techniques, to effectively remove NOM and reduce the incidence of any organic fouling. The application of integrated membrane processes allows us to achieve two main important goals: optimization of process hydrodynamics and the increase of final water quality. A variety of pretreatment processes for water ultrafiltration have recently been investigated. Among them, the most frequently applied were coagulation [12, 13] or activated carbon adsorption [14, 15].

Among the possible alternatives to coagulation for NOM removal, several studies [16, 17] highlighted the potential of the ion-exchange process in controlling the concentration of organic substances in drinking water. The interest in the ion exchange process application in the water treatment increased when a new MIEX®DOC process was developed by Orica. Magnetic Ion EXchange resin (MIEX®) was optimized for the removal of negatively charged organic particles from the water [18]. MIEX® is a strong base anion-exchange resin with ammonia functional groups of a macroporous, polyacrylic structure. The resin has a magnetic component incorporated into its polymeric structure. Its beads have a diameter of approximately 180 μm – 2~5 times smaller than traditional ion exchange resins [19]. This results in the increase of total surface area to volume ratio and a decrease in the resistance to solid-phase mass transfer. During the operation of the continuous process, NOM-rich water is contacted with the resin, allowing ion exchange of organics onto the resin. The high density and magnetic properties of the resin provide rapid clarification of water during sedimentation following the ion-exchange stage. The principle of the MIEX®DOC process is depicted in Fig. 1.

The objective of the study was to compare the efficiency of water treatment by MIEX®DOC process and ultrafiltration with the use of ceramic membranes and to evaluate the effect of MIEX®DOC water pretreatment on UF performance.
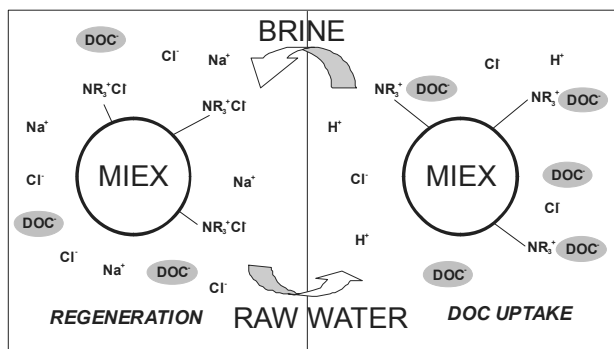
## Experimental

### Feed Water

The raw water was surface water from the Odra River (Poland). The concentration of natural organic matter expressed as colour was about 28.7 g Pt/m$^3$, while UV absorbance at 254 nm amounted to 0.158 cm$^{-1}$. The feed was characterized by a pH of 7.1 and a conductivity of 1,405 μS/cm.

### Ultrafiltration Experiments

In the ultrafiltration experiments we made use of CeramINSIDE 1-channel zirconium-titanium oxide membranes (TAMI Industries) of cut-off 15 and 50 kDa. The length of the membrane amounted to 0.25 m, and its effective filtration area equalled 0.0045 m$^2$.

A cross-flow system (J.A.M. INOX PRODUKT) was used in the ultrafiltration experiments. The experimental UF set-up is presented in Fig. 2. It consisted of a reservoir tank (10 dm$^3$), a pump, pressure gauges, membrane module and flow meter for retentate. Both retentate and permeate were recirculated to the stirred feed tank in order to achieve steady-state operation. The system was thermostated and the temperature of the water was kept at 20ºC. The process was run at a pressure range of 0.2~0.5 MPa.

### Ion-Exchange Process

Preliminary tests were conducted to determine the optimal MIEX® resin dose and mixing time. 1 dm$^3$ of the feed water was placed in a 2 l jar, dosed with an appropriate



Fig. 1. The idea of the MIEX®DOC process [19].



Fig. 2. Ultrafiltration cross-flow system: 1 – membrane module, 2 – feed tank, 3 –pump, 4 – flow meter, 5 – thermostat.

amount of the resin, and mixed at 150 rpm on a VELP Scientifica JLT4 jar test apparatus. Resin concentration amounted to 2.5, 5, 10 and 15 ml/l. While the samples were being mixed, aliquots were taken from the jar top at mixing times of 5, 10, 15, 20, 30, 40, 50, and 60 min. After 30 min., settling in each sample UV254 absorbance and colour intensity was measured.

In order to determine the secondary pollution of the water by resin, water was mixed with a particular amount of resin, afterwards undergoing sedimentation. The concentration of suspended solids was determined in the supernatant.

## Integrated Process

2.5 or 15 ml of MIEX resin per 1 l of feed water was added and mixed for 20 min., followed by 30 min. settling. Afterwards, 5 l of supernatant was placed in the pilot system and water underwent ultrafiltration. The MIEX®DOC/ultrafiltration process procedure is illustrated in Fig. 3.

## Methods of Process Investigation

Transport properties of membranes were investigated by measuring the rate of permeate flow through the membrane under steady conditions.

Permeate volume flux (J) was calculated as follows:

$$J = \frac{V}{t \cdot A}, \quad m^3/m^2d \qquad (1)$$

...where V is permeate volume ($m^3$), t stands for time (day), and A denotes the effective membrane surface area ($m^2$).
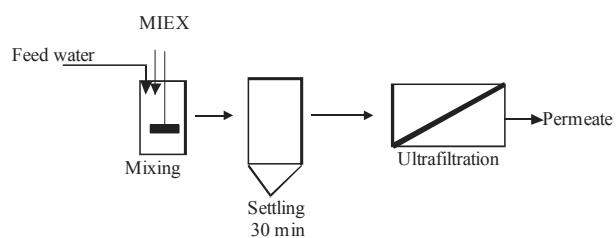


Fig. 3. Schematic diagram of the MIEX®DOC/ultrafiltration process.

The efficiency of the examined processes was determined by measuring the amount of the organic matter in the samples before and after each process. The NOM concentration was monitored by measuring the UV absorbance at 254 nm, and colour intensity (Shimadzu UV1240 spectrophotometer). The retention coefficient of the measured water parameters was determined using the following expression:

$$R = \frac{c_0 - c_p}{c_0} \cdot 100, \quad \% \qquad (2)$$

...where R is the retention coefficient, and $c_0$ and $c_p$ are the parameter values of the feed and permeate, respectively.

In order to determine organic substance molecular weight distribution, high-performance size execution chromatography was used. A detailed description of HPSEC procedure has been given elsewhere [20].

## Results and Discussion

### Ultrafiltration

Transport properties of ceramic membranes were determined in the transmembrane pressure range 0.2~0.5 MPa. Distilled water and surface water were passed though the modules. The effect of applied pressure on membrane permeability is shown in Fig. 4. The volume flux of distilled water varied from 0.69 $m^3/m^2d$ to 3.15 $m^3/m^2d$ for the 15 kDa membrane, and from 1.59 $m^3/m^2d$ to 7.95 $m^3/m^2d$ for the 50 kDa membrane. For both membranes the permeate volume flux versus transmembrane pressure was represented by a linear relationship as TMP was increased from 0.2 to 0.5 MPa. An essential drop in membrane permeability was noticed when surface water was filtered. Due to membrane fouling caused by organic and inorganic substances occurring in water, the permeate flux decreased to the range of 0.173~1.21 $m^3/m^2d$ and 0.38~2.94 $m^3/m^2d$, respectively, for 15 and 50 kDa membranes. The higher intensity of membrane blocking resulting in a decrease of permeate flux observed for the 50 kDa membrane was probably caused by penetration of NOM macromolecules into membrane pores and their accumulation in the membrane structure.
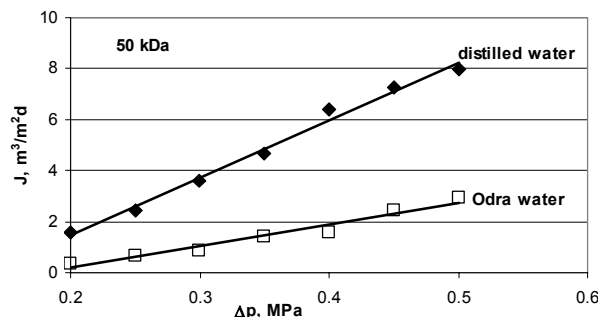
a)
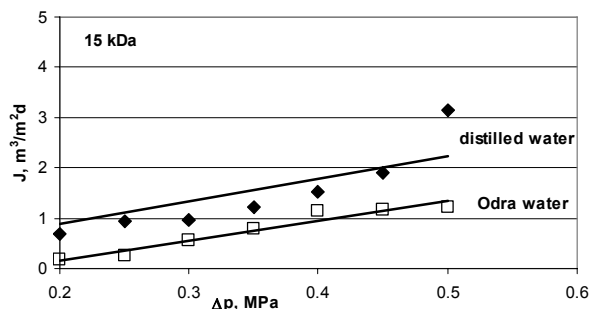


b)



Fig. 4. Transport properties of ceramic membranes: 15 kDa (a) and 50 kDa (b).
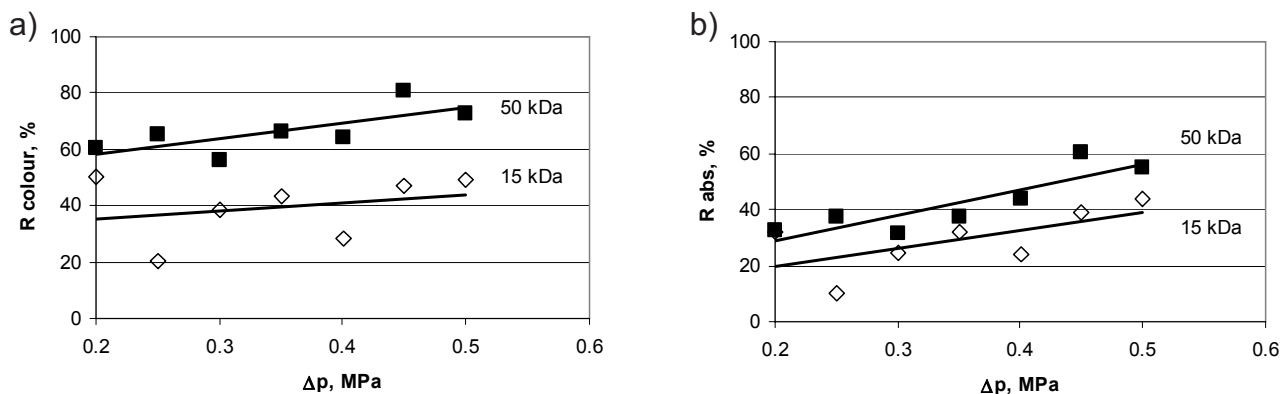
a)



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Fig. 5. Separation properties of ceramic membranes: colour retention (a) and absorbance 254 nm retention (b).

The relationship between transmembrane pressure and membranes separation properties is plotted in Fig. 5. Generally for both membranes, the driving force increase resulted in slight increase of NOM retention, but surprisingly higher retention coefficients were observed for 50 kDa membrane as compared to the values noticed for the 15 kDa one. This phenomenon may result from stronger 50 kDa membrane fouling and accumulation of NOM particles in the membrane structure. Moreover, internal membrane fouling results in a decrease of membrane pore diameter, and thus the improvement of separation properties may be achieved.
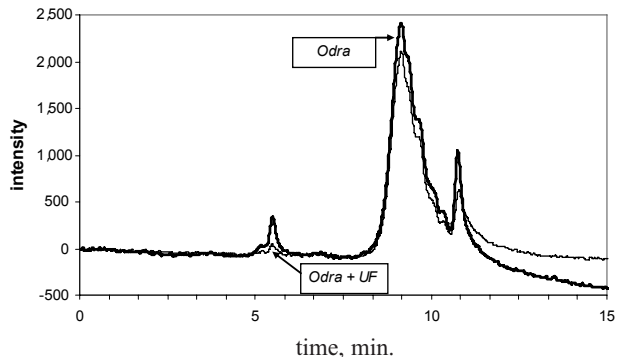


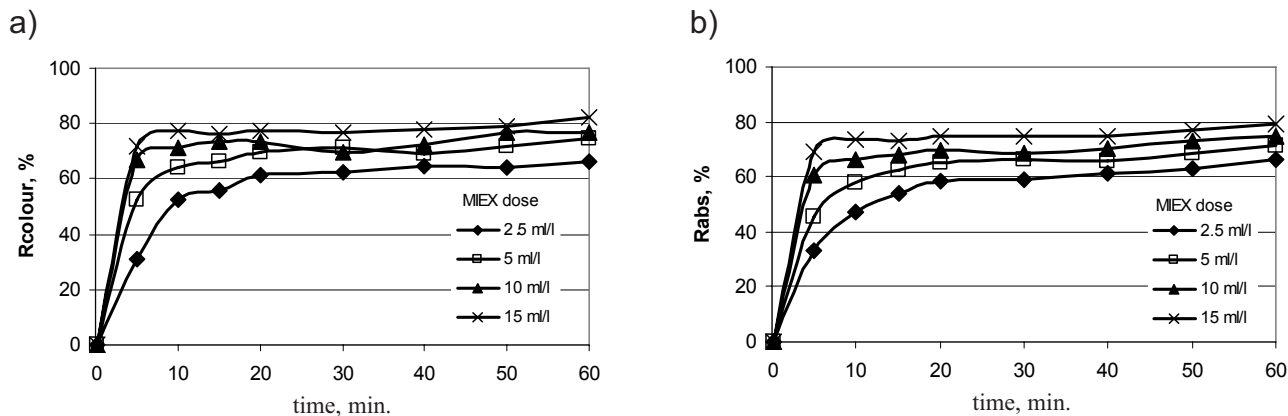Fig. 6. The HPSEC chromatogram of feed and ultrafiltered water (50 kDa membrane).

Analyzing the HPSEC chromatograms of riverine water and water treated with the use of the 50 kDa ceramic membrane (Fig. 6), it is evident that the membrane was effective in high molecular weight substances separation. The concentration of organic fractions of MW>70 kDa decreased by almost 77%. At some time the changes of organic substances of MW<10 kDa content were negligible.

## MIEX®DOC Process

Preliminary kinetic tests were conducted in order to determine the influence of MIEX® doses and mixing times on NOM removal efficiency. As can be inferred from Fig. 7, the increase of resin dose resulted in the increase of NOM removal from treated water. For resin doses equal to 10 and 15 ml/l, removal efficiency reached maximum values within 10 minutes of contact time, while for smaller doses this effect was achieved after approximately 20 minutes. Based on obtained results, mixing time equal to 20 min. was chosen as optimal for integrated process experiments.

Comparable values of $R_{colour}$ and $R_{abs}$, obtained in kinetic tests of the ion-exchange process suggest that removed NOM fractions responsible for water colour contained aromatic rings well detected by UV measurements.

As seen in Fig. 8, the ion-exchange process is effective in the separation of low molecular weight organic substances.
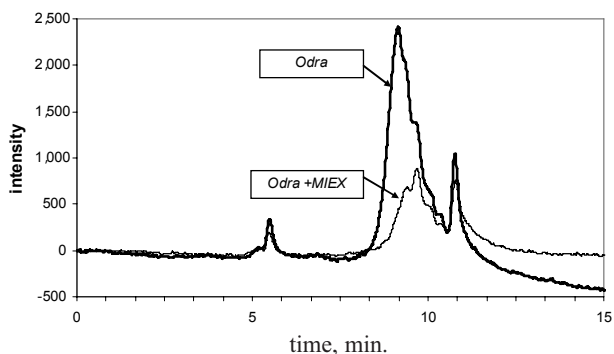
a)



b)



Fig. 7. Natural organic matter removal efficiency in the MIEX®DOC process: colour removal (a) and absorbance 254 nm removal (b).

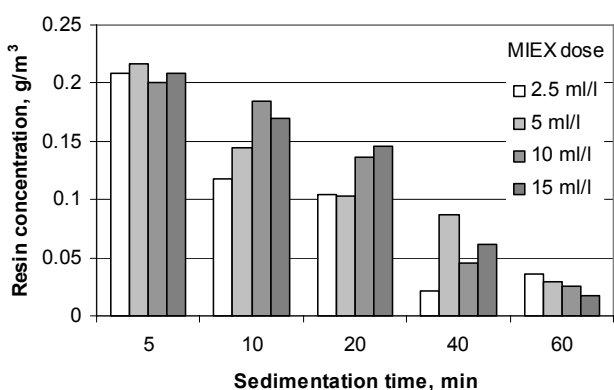Fig. 8. The HPSEC chromatogram of feed and MIEX®DOC-treated water (resin dose 2.5 ml/l).



Fig. 9. The influence of sedimentation time on the concentration of residual resin.

When Odra water was treated in the MIEX®DOC process (resin dose 2.5 ml/l) the amount of organic fraction of MW<10 kDa decreased by circa 62%. It should be noted that water treatment with the use of MIEX® resin does not influence the content to high MW fraction of organic substances. These conclusions are compatible with findings of other researchers [21].

One of the limitations of the MIEX®DOC process application in water treatment without any further treatment is the secondary pollution of water caused by the residual resin particles. As can be seen from Fig. 9, sedimentation of some fine particles of resin are still suspended in solution even after 60 min. Those particles generate turbidity of water and, moreover, may cause a hazard for consumer health. In water treatment plants applying the MIEX®DOC process, typically sand filtration follows the ion-exchange step. This guarantees obtainment of water free of any suspended solids. Replacement of the sand filtration step by UF may eliminate the problem of secondary water pollution and decrease resin losses.

## Integrated Process

The main goal of membrane separation process integration with other physico-chemical processes is to increase system performance by improvement of separation properties and decrease of fouling intensity. As shown by data presented in Figs. 10 and 11, both targets may be achieved when ultrafiltration on ceramic membranes is integrated with the MIEX®DOC process.
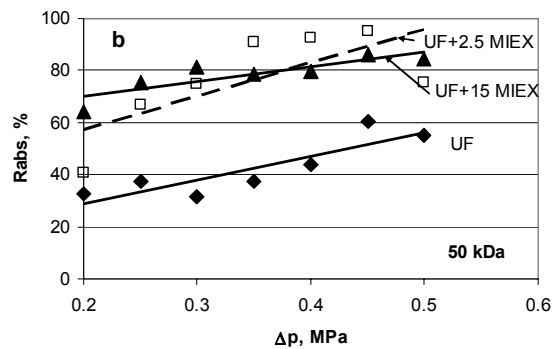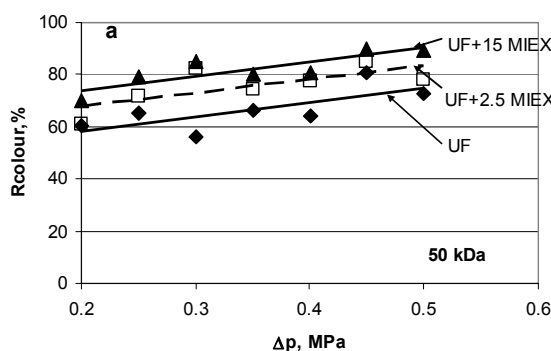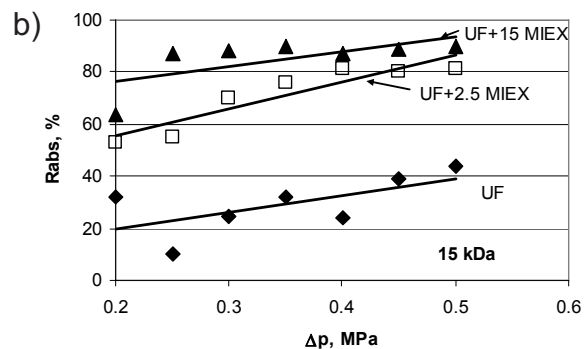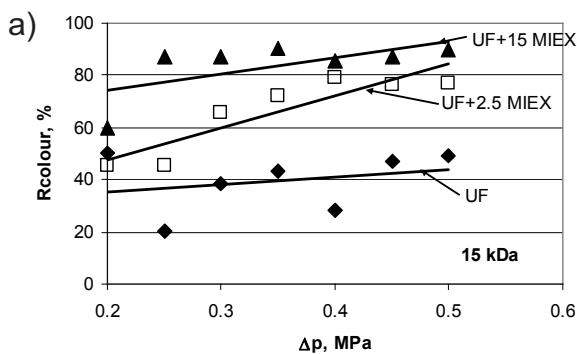


Fig. 10. The efficiency of NOM separation in the integrated MIEX®DOC/ultrafiltration process: colour retention (a) and absorbance 254 nm retention (b).

Even for a small resin dose (2.5 ml/l), the increase of NOM separation efficiency was significant. For example, at $\Delta p = 0.5$, MPa $R_{colour}$ increased from 49.4% to 77.2% for the 15 kDa membrane, and from 72.9% to 77.9% for the 50 kDa membrane. Analogically, $R_{abs}$ increased from 43.7% to 81.1%, and from 55.3% to 75.6%, respectively, for 15 and 50 kDa membranes. The increase of resin dose (up to 15 ml/l) brought about farther improvement of NOM retention. It might be assumed that improvement of NOM retention is due to the elimination of small organic particles in the ion-exchange step; as presented in Fig. 6 the efficiency of those fraction removals using ultrafiltration membranes is limited. Moreover, application of ultrafiltration after the MIEX®DOC process guarantees 100% retention of resin particles remaining in water after the sedimentation step. In this way, losses of resin, observed in the typical MIEX®DOC process, may be excluded and water of turbidity close to 0 NTU may be produced. In an investigated integrated process it may be also possible to decrease the time of sedimentation, as the ultrafiltration process may retain suspended resin.

Integration of ultrafiltration with the ion-exchange process also resulted in the decrease of membrane fouling intensity. As presented in Fig. 11, the values of normalized permeate flux $J/J_0$ ($J$ is the permeate flux and $J_0$ is distilled water flux) increased when water prior to ultrafiltration was treated in the ion-exchange process. For example, for 50 kDa membrane the $J/J_0$ value increased from 0.24 to 0.37 when feed water was pretreated with the MIEX® dose equal to 2.5 ml/l (in the process carried out at $\Delta p=0.3$). However, the increase of membrane permeability was not as strong as might be expected, taking into account the efficiency of NOM separation in the MIEX®DOC process. First of all, as reported elsewhere [22, 23], MIEX® treatment removes UV-absorbing organics to a greater extent than overall DOC. Moreover, it seems likely that MIEX®DOC pretreatments do not remove all NOM particles responsible for membrane fouling. This finding is consistent with Son et al. [24] observations, who found that MIEX® pre-treatment leads only to a minor decrease in membrane fouling.

Based on the literature review, the question of which fraction of NOM is responsible for membrane fouling remains unresolved. Some researchers [25, 26] suggest that high MW NOM fraction is mainly responsible for membrane blocking while others [27, 28] have proven that low MW fraction of organic substances plays a dominant role in the intensity of the fouling phenomenon. Analyzing results obtained in our experiments, it seems that for tested ceramic membranes the NOM fraction of high molecular weight was mainly responsible for filter fouling.

## Conclusions

The experiments performed show that integration of the membrane processes with ion exchange makes it possible to improve the efficiency of natural organic matter removal and partly reduce the intensity of ceramic membrane blocking. This tendency is especially strong for high cut-off
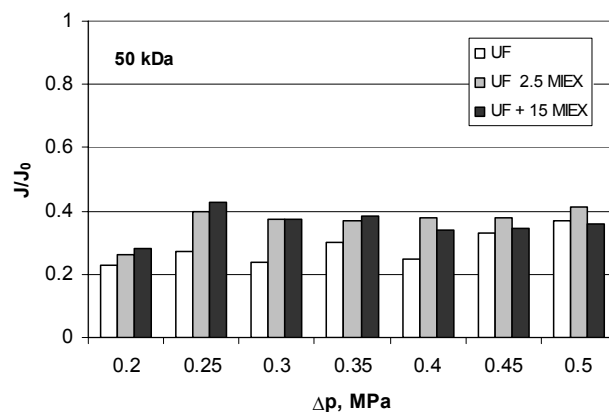


Fig. 11. The influence of feed water pretreatment in MIEX®DOC process on permeate flux decline ($J/J_0$) for 50 kDa ceramic membrane.

membranes. MIEX® resin can be used to adsorb low-molecular weight fractions of NOM, and ultrafiltration can be used to purify waters from colloidal matter and residual resin remaining in water after the sedimentation step. The results obtained in this study reveal that such a combined process could beneficially be used for the treatment of natural waters.

## References

1. STEVENSON F.J. Humus Chemistry, Wiley, N.York, **1982**.
2. McDONALDS S., BISHOP A.G., PRENZLER P.D., ROBARDS K. Analytical chemistry of freshwater humic substances. Analytica Chimica Acta, **537**, 105, **2004**.
3. BOOGS S., LIVERMORE G., SEITZ M.G. Humic macromolecules in natural waters. Journal Macromol. Sci. – Rev. Macromol. Chem.Phys., **C25**, 599, **1985**.
4. HAGG M., GHABBOUR E.A. Humic Substances: Structures, Properties and Uses. The Royal Society of Chemistry, **1999**.
5. EIKEBROKK B., GJESSING E., ØDEGAARD H. Why NOM is important. Proc. AWWARF/ AWQC/Vivendi/ Berlin Wasser Workshop: Utilizatrion of NOM Characteristics to improve Process Selection and Performance. Berlin, October 9-12, 2001.
6. KOWAL A.L., ŚWIDERSKA-BRÓŻ M. Water Tretment. 5 Ed. Wydawnictwo Naukowe PWN, **2007** [In Polish].
7. DURANCEAU S. Membrane Practices for Water Treatment. American Water Works Association, **2001**.
8. Inorganic Membranes: Synthesis, Characterization and Applications. Ed. Malleda R., Menéndez M.; Elsevier, **2008**.
9. KABSCH-KORBUTOWICZ M., URBANOWSKA A. Application of ceramic membranes to the removal of natural organic mater from water. Ochrona Środowiska, **31**, (1), 15, **2009** [In Polish].

10. Advanced Membrane Technology and Applications. Ed. Li N.N., Fane A.G., Ho W.S.W., Matsuura T.. A John Wiley Sons, Inc., Pub., **2008**.

11. SCHÄFER A.I. Natural Organics Removal Using Membranes. Technomic Pub., **2001**.

12. HOWE K. J., CLARK M. M. Coagulation pretreatment for membrane filtration. AWWA Research Foundation Report, ISBN 1583212655, **2002**.

13. KONIECZNY K., SAKOL D., BODZEK M. Efficiency of the hybrid coagulation–ultrafiltration water treatment process with the use of immersed hollow-fiber membranes. Desalination, **198**, 102, **2006**.

14. SHON H. K., VIGNESWARAN S., NGO H. H. Effect of partial flocculation and adsorption as pretreatment to ultra-filtration AIChE Journal, **52**, (1), 207, **2006**.

15. BARBOT E., MOULIN P. Swimming pool water treatment by ultrafiltration–adsorption process. Journal of Membrane Science, **314**, 50, **2008**.

16. CORNELISSEN E. R., MOREAU N., SIEGERS W. G., ABRAHAMSE A. J., RIETVELD L. C., GREFTE A., DIGNUM M., AMY G., WESSELS L. P. Selection of anionic exchange resins for removal of natural organic matter (NOM) fractions. Water Research, **42**, (1-2), 413, **2008**.

17. BOLTO B., DIXON D., ELDRIDGE R. Ion exchange for the removal of natural organic matter. Reactive and Functional Polymers, **60**, 171, **2004**.

18. SEMMENS M. J., BURCKHARDT M. M., SCHULER D., DAVICH P., SLUNJSKI M., BOURKE M., NGUYEN H. An evaluation of magnetic ion exchange (MIEX®) for NOM removal. In Proceedings of AWWA Conference, 11-15 June, Denver, USA, **2000**.
http://www.miexresin.com/files/publishedPapers/SPRWS_AWWA_Paper_2000.pdf

19. www.miexresin.com/index.asp?page=6

20. KABSCH-KORBUTOWICZ M., BIŁYK A., MOŁCZAN M. The effect feed water pretreatment of ultrafiltration on membrane performance. Polish J. of Environ. Stud., **15**, (5), 719, **2006**.

21. SLUNJSKI M., BOURKE M., O'LEARY B. MIEX®DOC process for removal of humics in water treatment. http://www.miexresin.com

22. MOŁCZAN M., BIŁYK A., SLUNJSKI M., CELER K. Application of jar tests to estimating the efficiency of organic substances removal in the MIEX®DOC water treatment process. Ochrona Środowiska, **27**, (2), 3, **2005** [In Polish].

23. SINGER P.C., BILYK K. Enhanced coagulation using a magnetic ion exchange resin. Water Research, **36**, (16), 4009, **2002**.

24. SON H.J., HWANG Y.D., ROH J.S., JI K.W., SIN P.S., JUNG C.W., KANG L.S. Application of MIEX pre-treatment for ultrafiltration membrane process for NOM removal and fouling reduction. Water Sci. Technol.: Water Supply, **5**, 15, **2005**.

25. LIN C-F., HUANG T-J., HAO O.J. UF process for removing humic substances: effect of molecular weight fractions and PAC treatment. Water Research, **33**, 1252, **1999**.

26. YUAN W., ZYDNEY A.L. Humic acid fouling during microfiltration. J. Membrane Sci., **157**, 1, **1999**.

27. CARROL T., KING S., GRAY S.R., BOLTO B.A., BOOKER N.A. The fouling of microfiltration membranes by NOM after coagulation pretreatment. Water Research, **34**, (11), 2861, **2000**.

28. LI C-W., CHEN Y-S. Fouling of UF membrane by humic substance: effect of molecular weight and powder-activated carbon (PAC) pretreatment. Desalination, **170**, 59, **2004**.