Environment Protection Engineering

Vol. 34 2008 No. 2

MAŁGORZATA KABSCH-KORBUTOWICZ*,
AGNIESZKA KOZAK*, BARBARA KRUPIŃSKA**

ION EXCHANGE–ULTRAFILTRATION INTEGRATED PROCESS AS A USEFUL METHOD IN REMOVING NATURAL ORGANIC MATTER FROM WATER

The experiments conducted are focused on natural organic substances, removal from water in ion-exchange process, ultrafiltration process and ion exchange–ultrafiltration integrated process. The water from the Odra River and model solution were investigated. In treatment processes, various doses of 5 anion-exchange resins as well as polyethersulphone membranes with different cut-offs were used. The efficiency of process was determined by measuring a decrease both in the colour intensity and the UV 254 nm absorbance. The results show that separation efficiency in integrated process depends on resin dose added to water before ultrafiltration and on the membrane cut-off as well. Among the resins tested the most efficient was MIEX® resin. The ion-exchange process carried out prior to the ultrafiltration increased, especially for high cut-off membranes, NOM retention and resulted in the decrease of membrane fouling intensity.

1. INTRODUCTION

Drinking water treatment in terms of strict regulations imposed on drinking water quality and contamination of water sources arouses our considerable interest. Natural waters, used in technological train in a water treatment plant, contain numerous organic and inorganic contaminations of natural and anthropogenic origin. Natural organic matter (NOM) has a substantial share in the level of water pollution with organic compounds.

Natural organic matter is the mixture of molecular or dissolved components of an organic or inorganic origin [1]. Structurally complex organic compounds found in water are formed during biological and chemical decomposition of vegetalable or

---

* Institute of Environmental Protection Engineering, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland. E-mail: malgorzata.kabsch-korbutowicz@pwr.wroc.pl; agnieszka.kozak@pwr.wroc.pl

** Department of Chemistry, University of Antwerp, Universiteitsplein 1, B-2610 Wilrijk-Antwerpen, Belgium. E-mail: bkuniversity@interia.pl

animal matter. Moreover, a natural organic matter is heterogeneous mixture of the compounds of a wide range of molecular weight and with various functional groups (phenol, hydroxyl, carbonyl, and carboxyl).

Natural organic matter may be divided into the 3 groups:

- a hydrophobic fraction mainly containing substances of high molecular weight,
- a hydrophilic fraction composed of substances of low molecular weight (i.e., carbohydrates, proteins, amino acids),
- a transphilic fraction containing compounds of low molecular weight.

HENDRICKS [2] gives a classification of NOM into two major groups of hydrophobic and hydrophilic substances with a further subdivision into acids, bases and neutrals (table 1).

Table 1

NOM classification [2]

Category	Acid/base	Chemical group
Hydrophobic	Strong acids	Humic acid Fulvic acid High MW alkyl monocarboxylic and dicarboxylic acids Aromatic acids
	Weak acids	Phenols Tannins Intermediate MW alkyl monocarboxylic and dicarboxylic acids
	Bases	Proteins Aromatic amines High MW alkyl amines
	Neutrals	Hydrocarbons Aldehydes High MW methyl ketones
Hydrophylic	Acids	Hydroxyl acids, sugars, sulfonics Low MW alkyl monocarboxylic and dicarboxylic acids
	Bases	Amino acids, purines, pyrimidines Low MW amines
	Neutrals	Polysaccharides Low MW alkyl alcohols, aldehydes, ketones

Based on molecular weight of NOM fractions, they can be divided into (figure 1):

- biopolymers (polypeptides, proteins, aminosugars),
- humic substances (humic and fulvic acids),
- building blocks (hydrolysates of humics),
- low molecular-weight acids and neutrals (alcohols, aldehydes, ketones, amino acids).

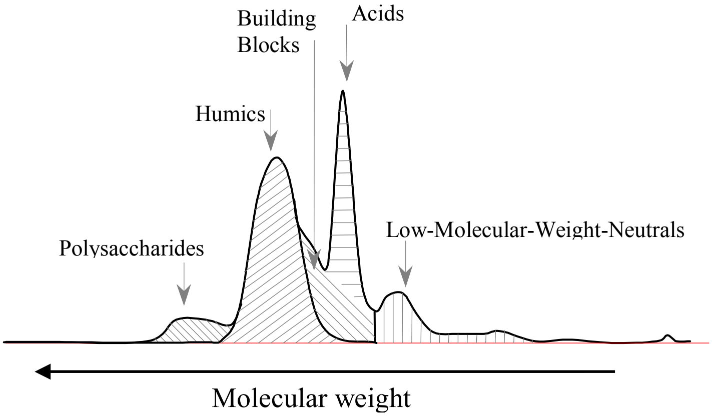


Fig. 1. Fractions of natural organic matter

The dissolved humic substances are the main fraction of natural organic substances in water. They may be divided into the 2 basic types, both of acidic character, i.e., the fulvic acids and the humic acids. Soil, peat, forest bed and vegetal remains can be the source of humic acids [1]. Aquatic humic substances constitute typically 40–60% of DOC in any natural water or even 80–90% in most brown coloured lakes [3].

Removing natural dissolved matter is very important in water treatment processes, especially in order to reduce the risk of disinfection by-products formation during natural water chlorination. The disinfection by-products are formed as a result of organic compounds oxidation with chlorine or ozone [4]. The necessity of NOM removal from water results also from their responsibility for deeper colour of water as well as from the need to use much higher coagulant or disinfectant doses compared to those for unpolluted water. NOM may also block membrane surfaces or ion exchange resin and is responsible for microorganism development in water supply system. According to the Polish Ministry of Health the regulation of March 29th, 2007, the amount of organic compounds in drinking water expressed as colour intensity, COD-Mn and DOC cannot exceed 15 g Pt/m^3, 5 g O_2/m^3 and 5 g C/m^3, respectively.

Of several physicochemical processes used in water technology to remove NOM, membrane ultrafiltration is considered to be one of the most effective. This process enables the removal of microorganisms, viruses, colloidal metal oxides and hydroxides and other substances causing – among other things – water colour and turbidity. This method allows a wide range of contaminants to be removed and is competitive with other popular processes if we take account of water treatment costs. One of the obstacles in the wide application of this process in water technology is a decrease in hydraulic efficiency observed during membrane system using. A permeability decline may be caused by several factors, but all of them result from accumulation of substances present in water on a membrane surface and/or in its pores. Another limitation of ultrafiltration application is connected with the inefficiency of this process in the removal of low-molecular weight fraction of NOM.

The processes most frequently used to remove natural organic substances from water before membrane filtration are coagulation and active carbon adsorption. However, sometimes water pretreatment is not effective enough in removing organic matter fractions responsible for membrane blocking and also increases the treatment costs [5], [6]. For this reason there is a constant need to use other, more efficient methods.

As most of NOM in water has ionic character, ion-exchange processes gain popularity. At pH 7, humic compounds behave like negatively charged colloids or anionic polyelectrolytes due to the abundance of ionized carboxylic (–COOH) and hydroxyl (–OH) functional groups. The efficiency of NOM removal in ion-exchange processes ranges from 10% to 100% [7], [8] and depends – among others – on the properties of organic matter fractions (charge, molecular weight).

The removal of NOM with anion-exchange resins strongly depends on the type of resin. Weak-alkaline resins remove less NOM compared to strongly alkaline resins [9]. It is reported that resins with a macroporous structure remove more NOM than gel-type resins [9]. This is explained by the fact that organic anions, such as humic acids, can diffuse easier within a macroporous structure. This result, however, is in contradiction to the results of TAN's et al. [4], who found more NOM removal with gel-type resins. This is ascribed to a higher swelling capacity of the gel-type resins in water. The water content of a resin is another important property influencing NOM removal. The resins with high water content remove more NOM due to a more open structure allowing a better entry of larger compounds [10]. Finally, the material of the resins influences NOM removal. The resins with a styrene structure display a greater affinity with aromatic components than the resins based on an acrylic structure [10], [11].

In very recent years, ion-exchange processes based on a new magnetic ion-exchange resin, i.e., the MIEX® resin [12] developed by Australian company Orica, have received considerable attention. Such a resin enables adsorption of dissolved organic matter from water. Two main features make this strong anion-exchange resin (AER) different from traditional ones. First, the MIEX beads (around 150 μm in diameter) are 2–5 times smaller than conventional AER beads, which provides a greater external surface area and thus allows rapid sorption kinetics. Second, the MIEX backbone contains a high proportion of a magnetic iron oxide compound, transforming the agglomerate of fine resin beads into larger, fast-settling particles. The MIEX process corresponds to an innovative water treatment process based on this strong AER that incorporates contactors, a settler (the resin is separated from the treated water) and a continuous resin regeneration/recirculation side process.

The MIEX® process makes it possible to remove 40–90% of NOM [13], [14]. MIEX® resin preferentially removes substances of low molecular weight (below 10 kDa) responsible for membrane blocking. During regeneration process, the effectiveness of resin separation amounts to 99.9% [15]. Micro-magnets built into a resin structure facilitate a faster accumulation of resin and consequently its quick separation from water. After separation only smaller fractions are left in water that can be removed in further processing.

It seems that water pretreatment with the use of ion-exchange process might be effective way of increasing the separation and transport properties of ultrafiltration membranes. The aim of the work was to compare the efficiency of removing natural compounds from water using various anion-exchange resins and to define their usability for water treatment before ultrafiltration process.

2. EXPERIMENTAL

2.1. FEED SOLUTIONS

The experiments were carried out on water from the Odra River and on a model solution prepared from dechlorinated tap water and humic substance-rich water flowing out from peat-bog in the Table Mountains (Poland). The properties of feed solutions are given in table 2.

Table 2

The feed water properties

Parameter	The Odra River water	Model solution
Colour, g Pt/m^3	22.14	52.96
UV-absorbance 254 nm, cm^{-1}	0.15	0.34

2.2. ION-EXCHANGE RESINS

Five anion-exchange resins were used in experiments. Their characteristics are presented in table 3.

Table 3

Anion-exchange resin characteristics

Resin	Resin type	Polymer structure	Ion-exchange capacity[*] (mol/dm^3)
Purolite A100	weak base	polystyrene microporous	0.885
Purolite A200	strong base	polystyrene gel	1.040
Purolite A400	strong base	polystyrene gel	1.040
Wofatit SBW	strong base	polystyrene gel	0.731
MIEX®	strong base	polystyrene macroporous	0.400

[*] Determined by authors.

2.3. MEMBRANES

In the study, ultrafiltration Microdyne-Nadir flat-sheet membranes made of polyethersulfone were used. The cut-off of the membranes amounted to 5, 10 and 30 kDa.

2.4. ION EXCHANGE

The kinetic tests of ion-exchange process were run using 1 dm^3 samples of each solution and the following doses of each resin: D_1 = 2.5 cm^3/dm^3, D_2 = 5 cm^3/dm^3, D_3 = 10 cm^3/dm^3, D_4 = 15 cm^3/dm^3. Solutions with resins were placed on a mechanical stirrer and mixed for 5–60 min at 135 rpm. Then the samples were left for sedimentation for 30 min.

2.5. ULTRAFILTRATION

Experiments were carried out in a laboratory system at a transmembrane pressure of 0.1 MPa. The main part of the system was an Amicon 8400 ultrafiltration cell under the pressure of gas escaping from a cylinder. The effective surface of the membrane amounted to $4.52\cdot10^{-3}$ m^2.

2.6. INTEGRATED ION-EXCHANGE–ULTRAFILTRATION PROCESS

In an integrated ion-exchange–ultrafiltration process, a decanted water sample, after being treated in ion-exchange process and left for 30-min sedimentation, was ultrafiltered at a pressure of 0.1 MPa.

2.7. ANALYTICAL METHODS

The efficiency of the processes examined was determined by measuring the proportion of the organic matter in the samples before and after the process. The NOM concentration was monitored by the measurement of the absorbance of UV at 254 nm and the colour intensity (Shimadzu QP2000 spectrophotometer).

3. RESULTS

3.1. ION-EXCHANGE PROCESS EFFECTIVENESS

The kinetic tests of water treatment in ion-exchange process showed a significant influence of resin dose and the contact time of resin with microcontaminants on the efficiency of natural organic matter removal. It can be noticed that the higher the resin dose and the longer the contact time, the higher the efficiency of both colour and absorbance removal. This relationship is valid for all the samples examined. The results of colour intensity removal are presented in figure 2.

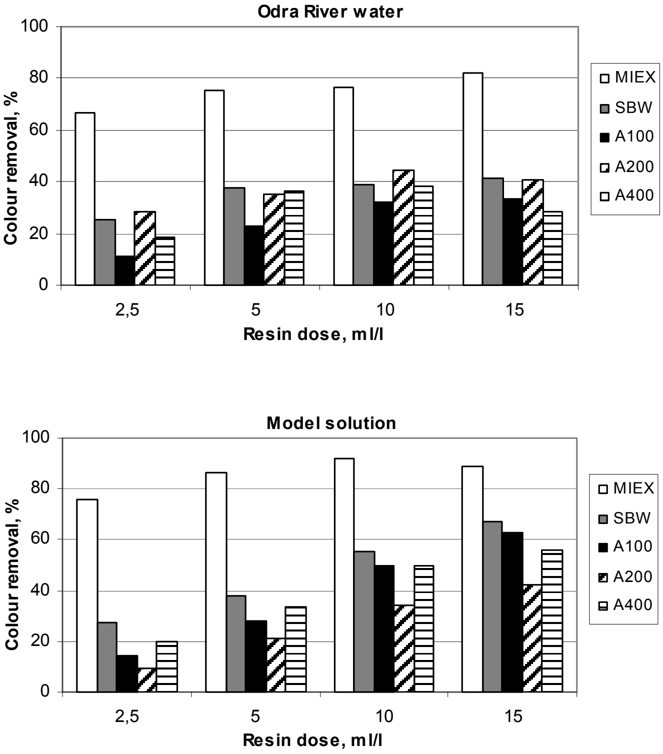


Fig. 2. The influence of the resin type and its dose on colour removal from the Odra River water and model solution (contact time t = 60 min)

It can easily be noticed that the most effective was MIEX® resin, as from the Odra River water and from the model solution it removed up to 82% and 91% of colour, respectively. SBW proved to be less effective resin (the colour retention coefficient amounted to 41% for the Odra River water and 67% for model solution), while the efficiency of A100, A200 and A400 resins was still lower.

Similar effects were observed analyzing the efficiency of absorbance removal (figure 3). Of the resins investigated MIEX® proved to be most efficient: it reduced the absorbance of the Odra River by 66–79% and by 77–91% in the model solution. Other resins were less effective, which was observed in the case of colour removal.

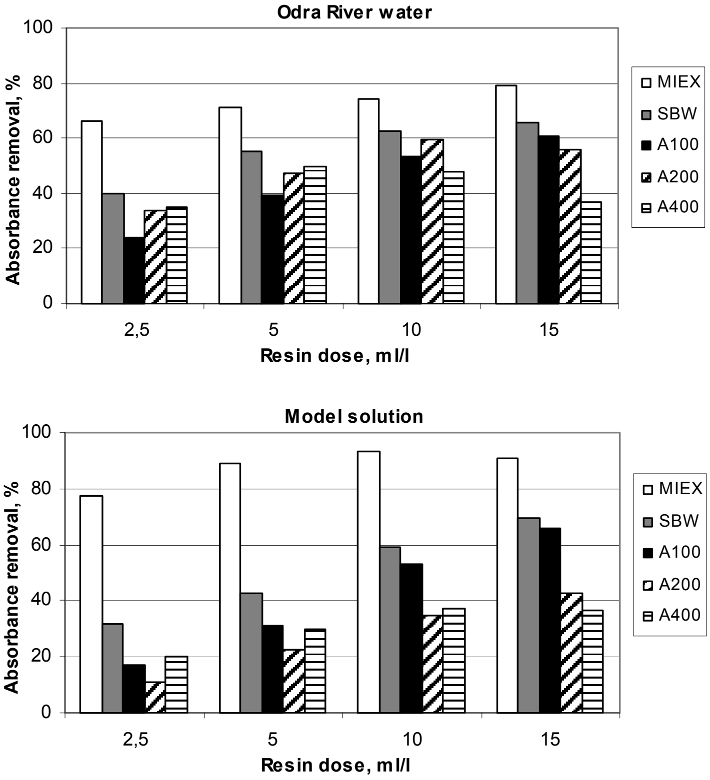


Fig. 3. The influence of resin type and its dose on the removal of absorbance (254 nm) from the Odra River water and model solution (contact time *t* = 60 min)

As can be inferred from figure 4, the removal of organic substances from water as a result of ion-exchange process was strongly affected by the contact time. Experimental results revealed that the best results were obtained at the resin dose of 15 cm^3/dm^3, while the worst at the dose of 2.5 cm^3/dm^3. For the Odra River water, at the MIEX® dose equal to 2.5 cm^3/dm^3 and 5 min contact time, the efficiency of macromolecules separation measured by the absorbance removal (at 254 nm) amounted to 33% and after 60 min it reached 67%. This tendency was observed for both colour and absorbance removal (at 254 nm). Separation efficiency for the resin dose of 5 cm^3/dm^3 was higher and ranged from 45 to 75%. The highest dose (15 cm^3/dm^3) brought about the best separation efficiency reaching 82% for colour and 80% for absorbance (after 60 min). For all of the resins applied and their doses, the increase of NOM removal was observed up to 20 min of resin contact with organic macromolecules. Further lengthening of the mixing time did not increase the removal efficiency.

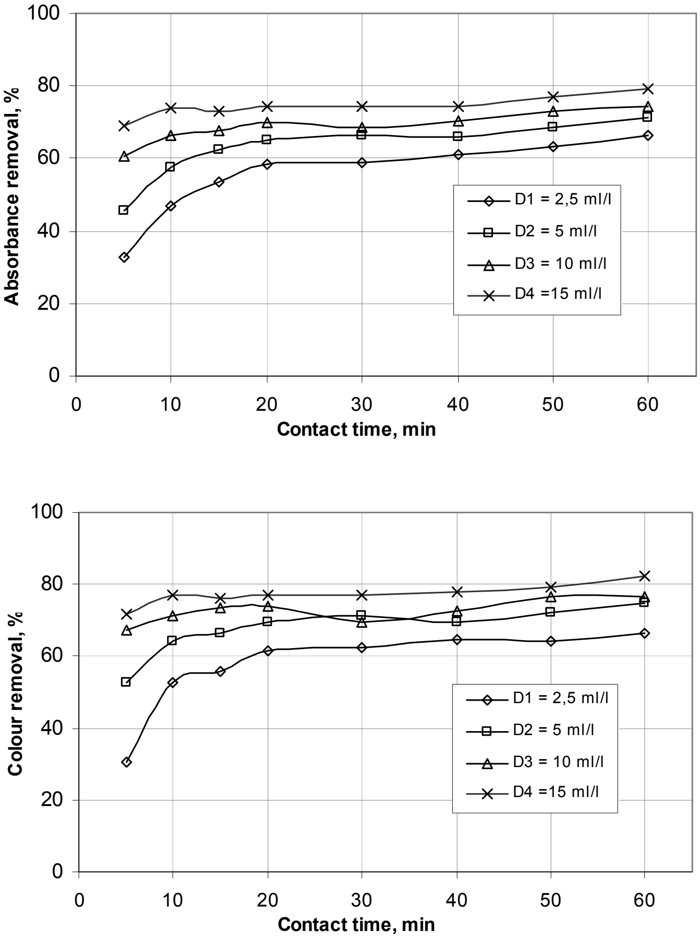


Fig. 4. The influence of MIEX® resin dose and contact time on the removal of organic substances from the Odra River water

3.2. ULTRAFILTRATION EFFECTIVENESS

The efficiency of natural organic matter separation in ultrafiltration process was found to be strongly influenced by membrane properties. Figure 5 shows the effect of membrane cut-off on the removal of colour and UV absorbance at 254 nm. As can be inferred from the results obtained, the increase of membrane cut-off resulted in the decrease of NOM removal efficiency. For all the membranes we observed the preference for the decrease of colour over the decrease of UV absorption as 254 nm. This is evident, as the colour of water is related to the presence of the large fractions of NOM.

The UV absorption at 254 nm monitors the amount of the NOM fraction containing aromatic structures in their molecules.

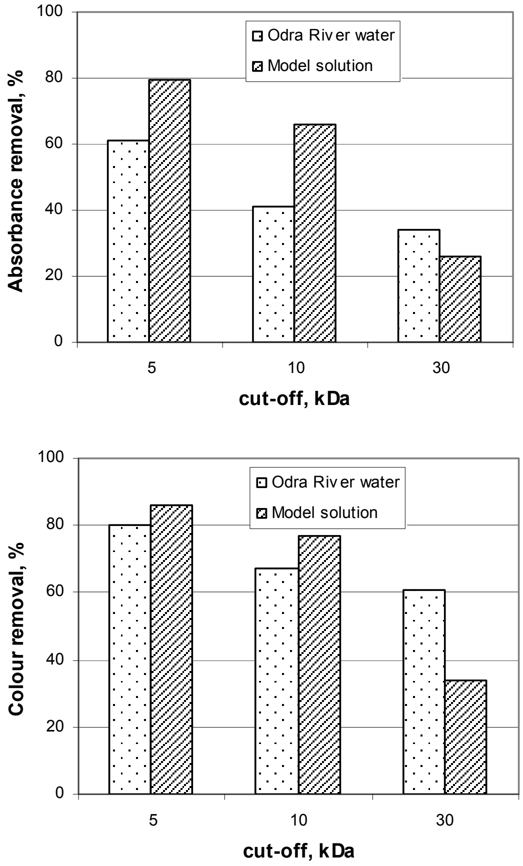


Fig. 5. The influence of membrane cut-off on natural organic matter removal

The increase of membrane cut-off is connected with the increase of pore radius [16], and this results in higher convective flux of the solution (figure 6). For the Odra River water and 5 kDa membrane, the permeate flux amounted to 0.33 $m^3/m^2 \cdot d$, while for 30 kDa membrane it reached 2.2 $m^3/m^2 \cdot d$. For the model solution these values amounted respectively to 0.37 and 1.86 $m^3/m^2 \cdot d$.

One of the most important problems arising during membrane water treatment is the decline of permeate flux due to membrane fouling. In order to determine the membrane blocking intensity, the relative membrane permeability (J/J_0) (J – the permeate flux and J_0 – the flux of distilled water for a brand-new membrane) was determined. The plots of figure 7 demonstrate how the membrane cut-off affected the intensity of its fouling. Membranes of higher cut-off were less prone to fouling (figure 7). A relative permeability reached 55–62% for 5 kDa membranes and 84–95% for 30 kDa membranes.

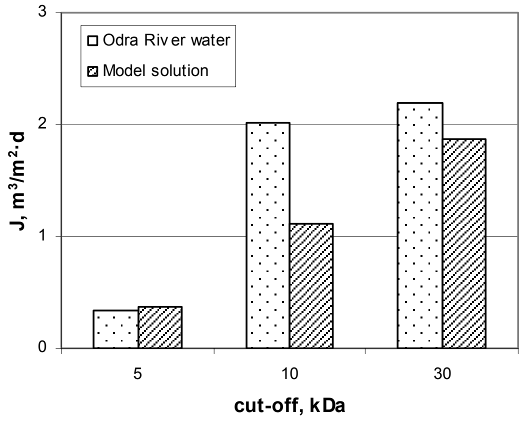


Fig. 6. Transport properties of ultrafiltration membranes

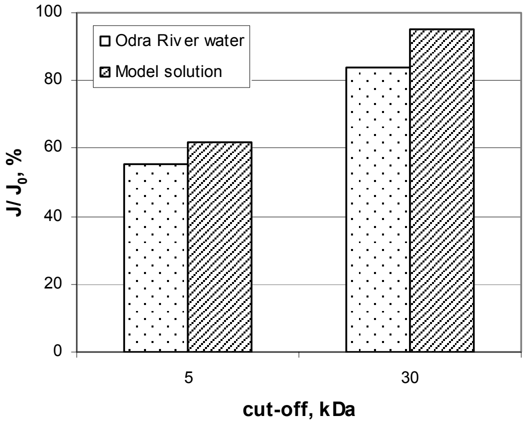
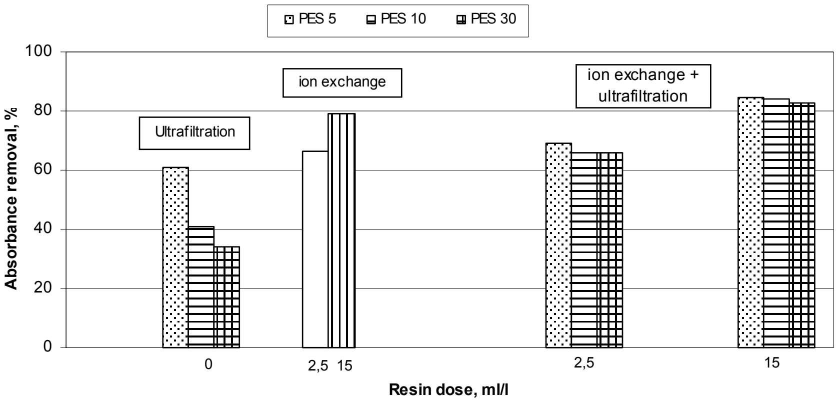


Fig. 7. The influence of membrane cut-off on the permeate flux decline

3.3. WATER TREATMENT IN THE INTEGRATED ION EXCHANGE–ULTRAFILTRATION

The integration of ultrafiltration with ion-exchange process significantly increased the efficiency of NOM removal. As presented in figure 8, the efficiency of the NOM separation in the integrated process was found to be strongly influenced by membrane type and resin dose. This tendency was observed for all the resins tested. However, especially significant improvement took place for the membranes of high cut-off. For example, at the MIEX® resin dose of 15 cm^3/dm^3 and 5 kDa membrane, colour removal amounted to 94% and was slightly higher than that observed for both independently used processes. In the case of 30 kDa membrane, the differences in NOM retention were much significant. Colour removal in UF reached 61%, while in integrated process it exceeded 85%. Another advantage of the integration of ion-exchange process with membrane filtration is the elimination of fine particles of resins, which remain in the solution after sedimentation.



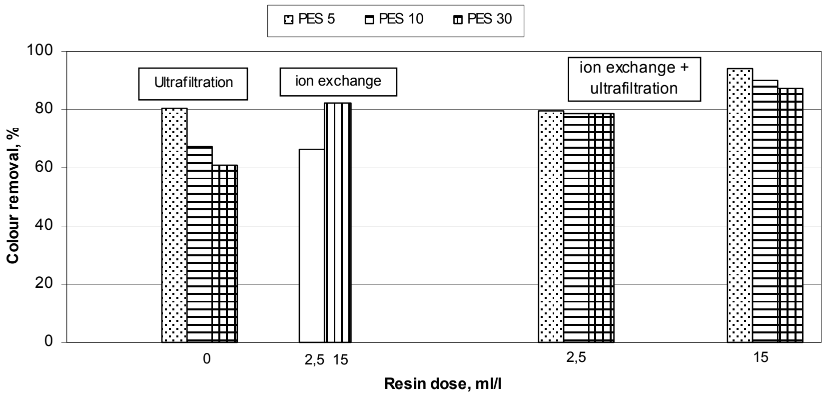


Fig. 8. The influence of MIEX® resin dose and membrane cut-off on absorbance and colour removal from the Odra River water using ion exchange, ultrafiltration, and integrated process

In the case of 30 kDa membranes, the process of ion exchange applied before ultrafiltration also decreased membrane fouling (figure 9). Even if the smallest resin dose was used, a relative permeability increased. For 5 and 10 kDa membranes no significant difference in relative membrane permeability was observed between separate ultrafiltration process and ion exchange–ultrafiltration integrated process.

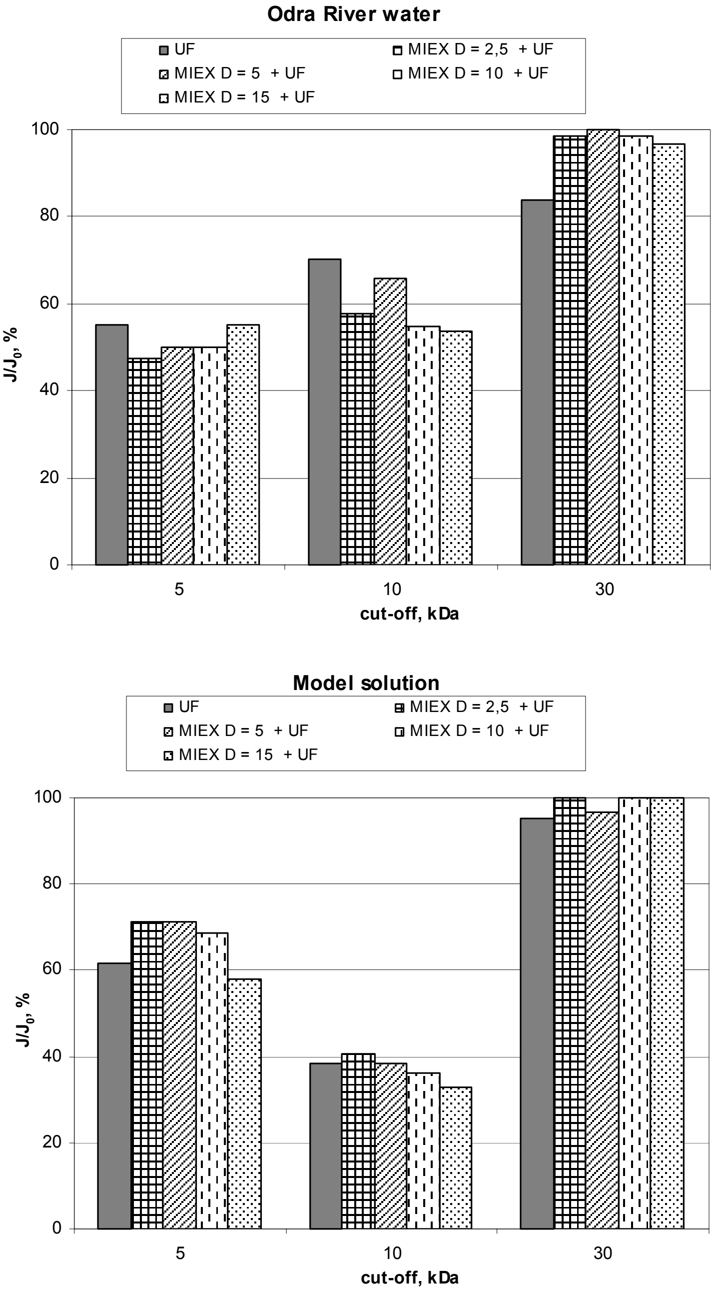


Fig. 9. The dependence of relative membrane permeability
on polyethersulphone membrane cut-off
for the Odra River water and model solution

4. SUMMARY

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 to reduce the intensity of membrane blocking. This tendency is especially strong for high cut-off membranes. Of the anion-exchange resins tested the most efficient was the MIEX® one. The differences in the integrated process efficiency observed in the case of natural water and model solution indicate that solution properties (NOM character and amount of co-pollutants) should be taken into account when the parameters of integrated process performance (resin type and its dose as well as membrane type) are determined.

REFERENCES

[1] GOMÓŁKA E., SZAYNOCH A., *Chemia wody i powietrza*, Oficyna Wydawnicza Politechniki Wrocławskiej, Wrocław, 1997.

[2] HENDRICKS D., *Water Treatment Unit Processes Physical and Chemical*, CRC Press, Taylor & Francis Group, 2006.

[3] THURMAN E.M., *Organic Geochemistry of Natural Waters*, Martinus Nijhoff/Dr W. Junk Publishers, Dordrecht, The Netherlands, 1985.

[4] TAN Y., KILDUFF J.E., KITIS M., KARANFIL T., *Dissolved organic matter removal and disinfection byproduct formation control using ion exchange*, Desalination, 2005, 176, 189–200.

[5] BIAN R., WATANABE Y., OZAWA G., TAMBO N., *Membrane fouling of ultrafiltration: evolution of influence of pretreatment with batch test*, Journal Jpn. Water Works Assoc., 1998, 67, 11–19.

[6] CARROL T., KING S., GRAY S.R., BOLTO B.A., BOOKER N.A., *The fouling of microfiltration membranes by NOM after coagulation treatment*, Water Res., 2000, 34, 2861–2868.

[7] BOLTO B., DIXON F., ELDRIDGE R., *Ion exchange for the removal of natural organic matter*, Reactive and Functional Polymers, 2004, 60, 171–182.

[8] FETTIG J., *Removal of humic substances by adsorption exchange*, Water Science and Technology, 1999, 40(9), 173–182.

[9] BOLTO B., DIXON D., ELDRIDGE R., KING S., LINGE K., *Removal of natural organic matter by ion exchange*, Water Res., 2002, 36, 5057–5065.

[10] GOTTLIEB M., *The reversible removal of naturally occurring organics using resins regenerated with sodium chloride*, Ultrapure Water, 1996, Nov., 53–58.

[11] HUMBERT H., GALLARD H., SUTY H., CROUÉ J.P., *Performance of selected anion exchange resins for the treatment of a high DOC content surface water*, Water Res., 2005, 39, 1699–1708.

[12] www.miexresin.com

[13] 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* (in Polish), Ochrona Środowiska, 2005, 27(2), 3–7.

[14] MOŁCZAN M., BIŁYK A., SLUNJSKI M., SICIŃSKI T., STRÓŻ J., *Pilot investigations into the MIEX®DOC process* (in Polish), Ochrona Środowiska, 2005, 27(4), 19–26.

[15] SEMMENS M.J., BURCKHARDT M., SCHULER D., DAVICH M., SLUNJSKI M., BOURKE M., NGUYEN H., *An evaluation of magnetic ion exchange (MIEX®) for NOM removal*, Proc. AWWA Conf., Denver, USA, 2000, www.miexresin.com

[16] KABSCH-KORBUTOWICZ M., *Ultrafiltration as a method of natural organic matter separation from water*, Materials Science, Poland, 2008 (in press).

ZINTEGROWANA WYMIANA JONOWA–ULTRAFILTRACJA JAKO PROCES PRZYDATNY W USUWANIU NATURALNYCH SUBSTANCJI ORGANICZNYCH Z WODY

Usuwano naturalne substancje organiczne z wody w procesach: wymiany jonowej, ultrafiltracji i zintegrowanego procesu wymiany jonowej–ultrafiltracji. Do badań użyto wodę z Odry i roztwór modelowy będący mieszaniną wody wodociągowej i wody z torfowiska. Badania przeprowadzono dla 5. typów żywic jonowymiennych. Testy ultrafiltracji wykonano, używając membran z polietersulfonu o *cut-off* 5, 10 i 30 kDa. Skuteczność procesu określano, mierząc zmniejszanie się intensywności barwy i absorbancji UV 254 nm. Otrzymane wyniki pokazały, że dla membran o *cut-off* 30 kDa ultrafiltracja poprzedzona wymianą jonową zwiększa skuteczność usuwania naturalnych substancji organicznych oraz ogranicza intensywność blokowania membran. Spośród testowanych żywic najskuteczniejsza zarówno w procesie samodzielnym, jak i w układzie zintegrowanym była makroporowata żywica MIEX®.