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Advantages of using the ion-exchange process in NOM removal prior to water ultrafiltration

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ABSTRACT

To enhance the efficiency of water treatment and reduce the extent of membrane fouling, the membrane separation process is frequently preceded by other physico-chemical processes. One of them might be ion exchange. The aim of this work was to compare the efficiency of natural organic matter removal achieved with various anion-exchange resins, and to verify their potential use in water treatment prior to the ultrafiltration process involving a ceramic membrane. The use of ion exchange prior to ceramic membrane ultrafiltration enhanced final water quality. The most effective was MIEX, which removed significant amounts of the VHA, SHA and CHA fractions. Separation of uncharged fractions was poor with all the resins examined. Water pretreatment involving an ion-exchange resin failed to reduce membrane fouling, which was higher than that observed in unpretreated water. This finding is to be attributed to the uncharged NOM fractions and small resin particles that persisted in the water.

1. INTRODUCTION

Ultrafiltration (UF) is an advanced treatment technology providing efficient removal of a broad spectrum of pollutants from the water being treated. That is why the application of this membrane process in water treatment plants has become increasingly frequent. Among the diversity of pollutants that ought to be removed, natural organic matter (NOM) deserves particular attention. Natural dissolved matter removal is an essential part of the treatment process, principally because this offers the possibility to reduce the risk that disinfection by-products may form during water chlorination. Another reason behind the necessity of NOM removal from the water being treated is the contribution of these organic species to the increase in the colour intensity of the water and the associated need to use much higher coagulant or disinfectant doses than those required for unpolluted water treatment.

Research reported in the literature has revealed that owing to their relatively large pores UF membranes are able to remove only large NOM fractions (Schäfer 2001). It has furthermore been demonstrated that natural organic matter is responsible for

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membrane fouling (Lee 2004, Raspati 2011). Thus, in order to enhance the efficiency of NOM separation and reduce the extent of membrane fouling, ultrafiltration is frequently combined with other physico-chemical processes. Among them preference is given to coagulation and active carbon adsorption, which are used for NOM removal prior to membrane filtration. However, in some instances such pretreatment fails to provide sufficient removal of organic matter fractions responsible for membrane blocking, and thus raises the treatment cost. These findings have spurred the search for more efficient methods. One of them might be the ion-exchange process.

Many NOM molecules contain carboxylic acid structures, which make them anionic in nature and removable by anion-exchange resins (AER). The removal of NOM via anion exchange is greatly influenced by the properties of the resin applied. Bolto *et al.* (2002) reported that weak-alkaline resins remove less NOM as compared with strongly alkaline ones, and that resins with a macroporous structure remove larger quantities of NOM than do gel-type resins. The latter result, however, contradicts the findings reported by Tan *et al.* (2005), who obtained higher NOM removal with gel-type resins. It is essential to note that the higher NOM removal observed in the case of gel-type resins should be attributed to their higher swelling capacity in water. Another contributory factor in NOM removal is the material from which the resins have been made. Gottlieb (1996) demonstrated that resins with a styrene structure display a greater affinity with aromatic components than do resins based on an acrylic skeleton.

New opportunities for the application of ion exchange to NOM removal have been created since Orica Watercare developed the MIEX®DOC process, which makes use of a magnetic ion-exchange resin (MIEX). Its grains, made of strong-base anion-exchange resin, are 2–5 times smaller than conventional AER beads, which provides a greater external surface area and thus allows rapid sorption kinetics. Moreover, the magnetic iron oxide incorporated in the resin structure causes the beads to agglomerate together over time allowing for easy removal once the treatment is complete.

The use of the combined process ion exchange/low pressure membrane filtration has been the subject of several laboratory and pilot-scale studies. Cornelissen (2009, 2010), who analyzed the influence of fluidized ion-exchange pretreatment on the performance of ultra- and nanofiltration membranes, noticed that the decrease in NOM concentration, even though significant, was not parallelled by a decline in membrane fouling. Li (2009) observed a decrease in the extent of UF membrane fouling, when the integrated process was carried out with a weak cation-exchange resin. This improvement in the transport properties of the membrane was attributable to the removal of calcium ions.

In recent years focus has also been placed on the MIEX®DOC process when used as a pretreatment step to MF or UF (Fabris 2007, Zhang 2007, Kabsch-Korbutowicz 2006, Humbert 2007, Dixon 2010, Drikas 2011). All of the investigators arrived at the conclusion that although those integrated processes produced high quality water, their effect on the extent of membrane fouling was discouraging, as it largely depended on the properties of the membrane used (e.g. pore size) and the composition of the water being treated (e.g. NOM properties or Ca^{2+} concentration).

Despite the importance attached to the integration of different treatment technologies in order to improve the quality of finished water, no references have been found in the literature to the application of the anion-exchange process as a prior step to ultrafiltration carried out with ceramic membranes. At present, in the sector of water treatment preference is given to the use of polymeric membranes. Nevertheless, owing to the excellent separation properties of inorganic membranes, as well as to the sharp decrease in the cost of their manufacture, the use of ceramic membranes in water treatment plants shows a tendency to increase.

The aim of this work was to compare the efficiency of natural organic matter removal achieved with various anion-exchange resins, and to verify their potential use in water treatment prior to the ultrafiltration process involving a ceramic membrane.

2. MATERIALS AND METHODS

2.1 Feed solution

The experiments were carried out using a model solution prepared from dechlorinated tap water and humic-rich water flowing out from a peat-bog in the Table Mountains (Poland) (sampling point 50º27'29.97''N; 16º23'16.87''E). NOM concentration was monitored by measuring DOC, UV absorbance at 254 nm, and colour intensity (Shimadzu UV1240 spectrophotometer). The properties of the feed solutions are shown in Table 1.

Table 1 Properties of feed solution

Parameter	Range	Average
Colour, g Pt/m^3	51.7 – 53.1	52.3
UV absorbance at 254 nm, cm^{-1}	0.339 – 0.346	0.339
Dissolved organic carbon, g C/m^3	7.9 – 8.3	8.1
pH	7.3 – 7.4	-
Conductivity, µS/cm	720 – 770	735

The efficiency of NOM separation was analyzed in terms of change in retention coefficient (R).

2.2 Ion exchange

For the purpose of this study use was made of five anion-exchange resins. Their characteristics are specified in Table 2. The resins differed in skeleton matrix, ion-exchange capacity and particle diameter. The experimental resin doses amounted to 2.5 cm^3/dm^3. An appropriate amount of the resin was dosed to 1 dm^3 of treated water, and then the resin-enriched solution was stirred at 135 rpm for 20 min. After that the samples were left for sedimentation for 30 min.

Table 2 Anion-exchange resin characteristics

Resin name	Resin type	Polymer structure	Ion-exchange capacity, mmol/cm^3	Water content, %	Particle diameter, mm
Purolite A100	weak base	macroporous polystyrene	0.885	53–60	0.60 – 0.85
Purolite A200	strong base type II	gel polystyrene crosslinked with divinylbenzene	1.040	45–54	0.60 – 0.85
Purolite A400	strong base type I	gel polystyrene crosslinked with divinylbenzene	1.040	48–54	0.60 – 0.85
Wofatit SBW	strong base type I	sulphonated gel polystyrene crosslinked with divinylbenzene	0.731	45–48	0.30 – 1.20
MIEX®	strong base type I	macroporous polyacrylate	0.400	65	0.15 – 0.18

2.3 Ultrafiltration

Ultrafiltration experiments were performed with a 1-channel 15 kDa ceramic ZrO_2/TiO_2 membrane made by Tami Industries. Channel diameter and effective filtration surface amounted to 6 mm and 40 cm^2, respectively. The cross-flow pilot set-up used in the experiments was delivered by J.A.M. INOX PRODUKT (Fig.1) and consisted of a reservoir tank (10 dm^3), a pump, pressure gauges, a membrane module and a flowmeter for retentate. Both retentate and permeate were recirculated to the stirred feed tank in order to enable steady-state operation. The system was thermostated and water temperature was kept at 20 °C. The process was run at a pressure of 0.3 MPa.

2.4 Integrated process

The integrated ion exchange/ultrafiltration process was carried out using a decanted water sample, which after treatment in the ion-exchange process, followed by 30-min sedimentation, was ultrafiltered at a pressure of 0.3 MPa.

Fig. 1 Ultrafiltration cross-flow system

2.5 NOM fractionation

The NOM fractionation procedure was performed according to the method described by Chow (2004). Prior to fractionation, the water samples were pre-filtered using a 0.45 μm membrane. A 500 cm^3 volume of water adjusted to pH 2 was passed through a column packed with 15 cm^3 DAX-8 resin to adsorb very hydrophobic acids (VHA). The effluent from the first column was passed through the column packed with 15 cm^3 XED-4 resin to adsorb slightly hydrophobic acids (SHA). The effluent from the second column was alkalized to pH 8 and passed through the column containing 15 cm^3 IRA-958 resin to adsorb charged hydrophilic substances (CHA). The effluent from the third column contained neutral hydrophilic substances (NEU).

The concentrations of particular NOM fractions were calculated according to the following equations

$$VHA = DOC_{raw} - DOC_{DAX\text{-}8\ effluent}$$
$$SHA = DOC_{DAX\text{-}8\ effluent} - DOC_{XAD\text{-}4\ effluent}$$
$$CHA = DOC_{XAD\text{-}4\ effluent} - DOC_{IRA\text{-}985\ effluent}$$
$$NEU = DOC_{IRA\text{-}985\ effluent}$$

3. RESULTS AND DISCUSSION

The efficiency of NOM removal obtained with the resins tested is depicted in Fig. 2. The best water purification effect, *i.e*. the highest NOM removal, was achieved with the MIEX resin. Colour intensity was reduced by 54.2 %, and DOC retention reached 36.7 %, although for the other resins examined, regardless of their properties, it did not exceed 10 %. The positive treatment effects achieved with MIEX can be attributed to the macroporous structure and the high water content of this resin. Moreover, smaller

MIEX particles provide greater external surface areas. Under such conditions, organic anions can easily diffuse into the pores of the resin.

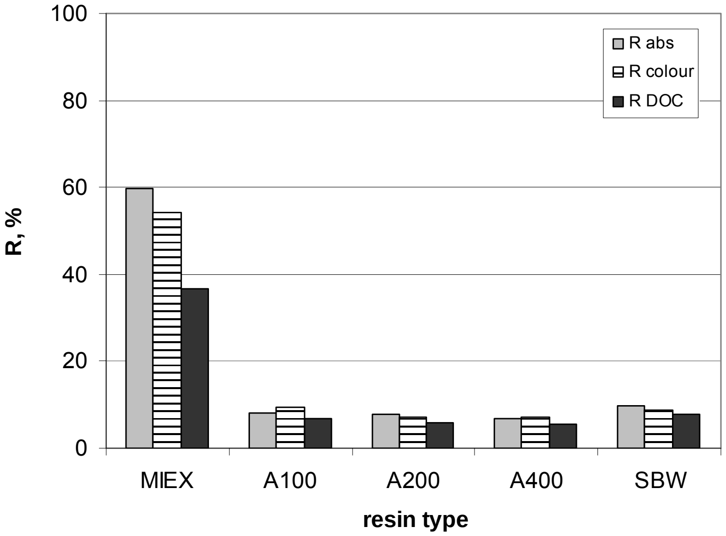

Fig. 2 Influence of resin type on NOM removal

Analysis of the amount of the residual resin that persisted in the water after 30-minute sedimentation (Fig. 3) suggests that some fine particles remaining in the water may affect the quality of the stream that feeds the UF membrane. Surprisingly, the highest residual resin concentration was measured when the process was carried out with MIEX. This resin contains magnetic elements which should accelerate the formation of easily settleable aggregates. Probably, due to multiple use and regeneration of the resin, some of its beads pulverized, and thus deteriorated the efficiency of their removal during sedimentation.

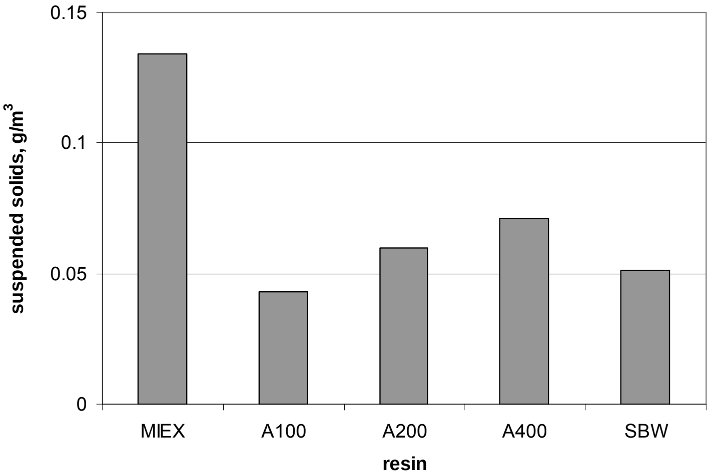

Fig. 3 Concentration of residual resin particles after 30-minute sedimentation

Our previous research (Kabsch-Korbutowicz 2009) has established the following: ultrafiltration with ceramic membranes as a sole process fails to provide sufficiently high NOM removal, and the extent of membrane fouling still remains high. In the study reported on in this paper, integration of the ultrafiltration process with ion exchange as a prior step enhanced NOM separation for all the membranes tested, the best treatment effects being achieved with the MIEX resin (Fig. 4). Combination of the MIEX®DOC process with UF accounted for an approximately 84 % reduction in DOC and a 94 % reduction in colour intensity. The use of the other resins also improved NOM separation, but the improvement was not as spectacular as in the case of MIEX. With all the resins tested, the retention coefficient values achieved for UV absorbance and colour intensity were noticeably higher than those obtained for DOC. Water colour and UV absorbance indicate the quantity of large NOM fractions containing, among others, aromatic structures, whereas DOC concentration describes the amount of all organic substances in the water being treated.

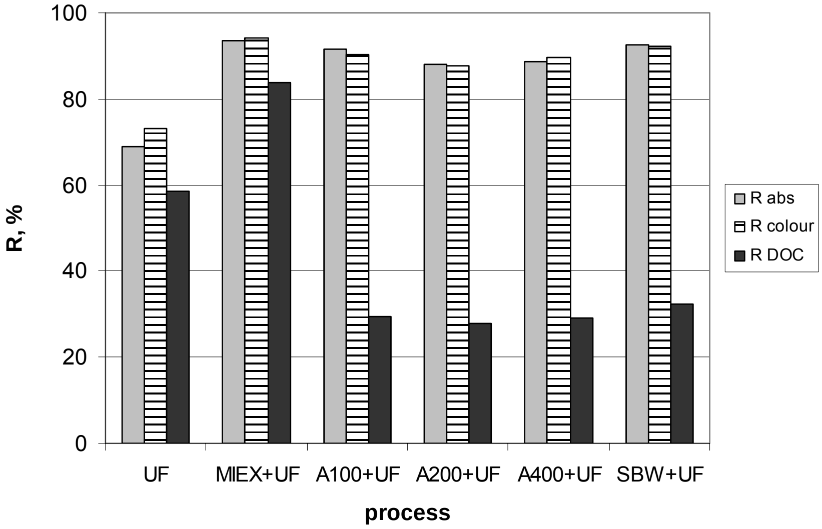

Fig. 4 Efficiency of NOM removal in the integrated ion exchange/UF process

Apart from enhancing the efficiency of NOM separation, the integration of ion exchange with the UF process is intended for reducing the extent of membrane fouling. In our study, however, such integration failed to sufficiently reduce the fouling effect, when the solution was pretreated by ion exchange before being passed to the process of ultrafiltration on the ceramic 15 kDa membrane. Fig. 5 shows the contribution of ion-exchange pretreatment to the decline in permeate flux. The normalized permeate flux represents the flux of the model solution (J), with or without pretreatment, compared to the clean water flux (J_0) of the membrane using redistilled water. Without pretreatment, J/J_0 declined to approximately 0.67. When the solution was subject to anion-exchange pretreatment before ultrafiltration, the normalized permeate flux ranged between 0.46 and 0.53. The most significant decline in permeate flux was observed when the MIEX resin was used.

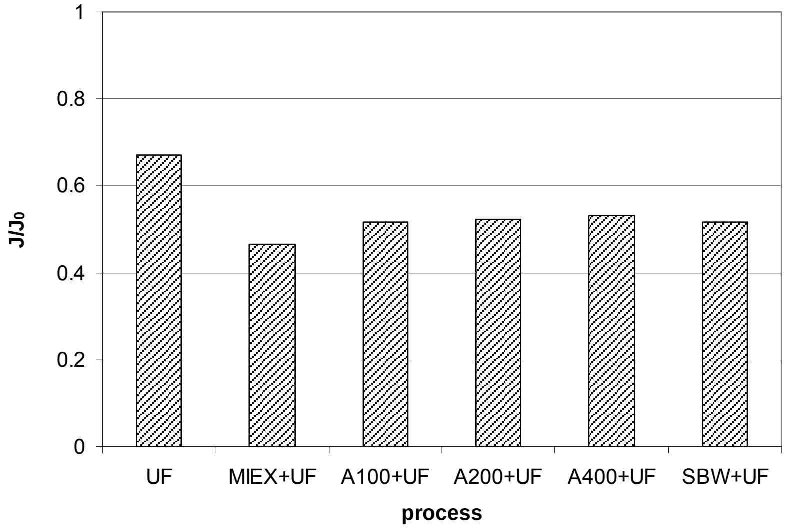

Fig. 5 Influence of water pretreatment on relative permeate flux

The explanation lies in the composition of the fractions removed *via* ion exchange. As shown in Fig. 6, the raw solution was composed of very hydrophobic acids (34.2 % of total DOC), slightly hydrophobic acids (15.9 %), charged hydrophilic substances (7.9 %), and hydrophilic neutrals (42 %). We observed that all of the charged compounds (very hydrophobic, slightly hydrophobic, and charged hydrophilics) were removed with high efficiency in the MIEX process, whereas the neutral fractions remained unaffected. With the other resins examined, the efficiency of charged species separation was very low. We may assume that it is the uncharged hydrophilic fraction of NOM that should be blamed for membrane fouling. Such assumption is consistent with the findings reported by other researchers (Cho 2000, Kimura 2004) who suggested that larger-sized hydrophilic neutrals (e.g. polysaccharide-like organics) are the strongest foulants. Cornelissen *et al.* (2010) observed that although pretreatment with AER provided removal of humic substances and hydrophobic organic carbon, it failed to produce the removal of biopolymers, building blocs or neutrals. Seemingly, it is also the presence of residual resin in the water after pretreatment that may intensify membrane blocking. Fine resin particles that occur in the water may plug the pores of, or form a compact cake on, the membrane and thus increase the fouling effect. We are not ruling out the possibility that the interactions between fine resin particles and NOM may also be regarded as contributory factors in the intensification of membrane blocking.

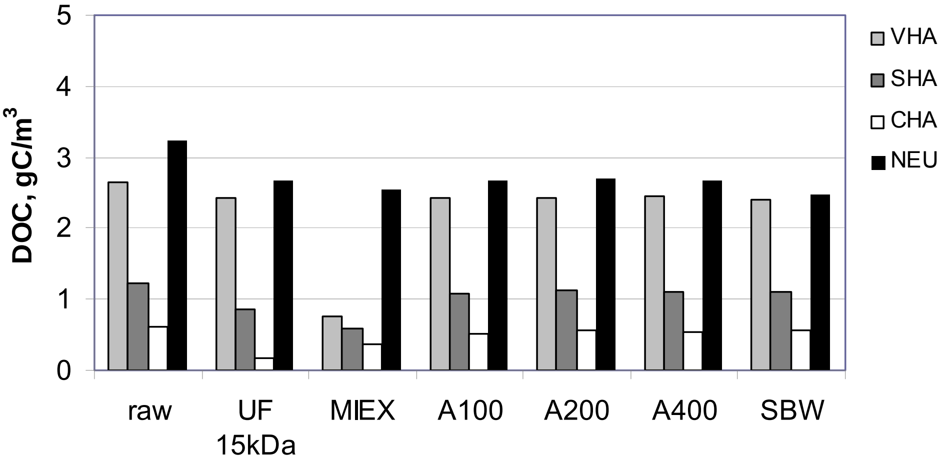

Fig. 6 Proportion of NOM fraction in raw solution, permeate of 15 kDa membrane and samples after ion exchange

4. CONCLUSIONS

The use of ion exchange prior to ceramic membrane filtration of water containing natural organic matter enhances the efficiency of the treatment process. Among the resins tested, definitely best results were achieved with the MIEX resin. Despite the removal of natural organic matter by the anion-exchange resin, the hydraulic performance of the ceramic 15 kDa ultrafiltration membrane did not improve. Seemingly, the increase in the extent of membrane fouling is to be attributed to the presence of the neutral NOM fraction and fine resin particles, which persisted in the water after pretreatment.

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