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Original Research

The Effect of Feed Water Pretreatment on Ultrafiltration Membrane Performance

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Abstract

The objectives of our study were to investigate the effects of water pretreatment by mean of coagulation, or MIEX® resin adsorption, on the removal of natural organic matter and on the fouling of membranes during the ultrafiltration process. In all cases water pretreatment resulted in an increase of permeate quality and a decrease of membrane fouling. However, the results indicated that treatment with MIEX® resin is much more effective than coagulation in organic substances removal. This was especially true for its low-molecular fractions, which are responsible for membrane fouling.

Keywords: coagulation, MIEX® resin, ultrafiltration, natural organic matter

Introduction

Increasing water scarcity and stringent water quality legislation have resulted in the expansion of membrane-based technologies in the water treatment sector. The low-pressure membrane processes (microfiltration and ultrafiltration) have received increased attention due to the quality of water and the cost reduction caused by improvements in membrane technology. Application of those techniques can simplify the treatment process by eliminating coagulation, flocculation and sedimentation processes. These processes have also been considered to be suitable for conventional drinking water treatment.

A more widespread application of membrane processes is limited by a decrease in membrane performance that occurs during potable water treatment as a result of fouling through the accumulation of particles and adsorption of the NOM [1-4]. Extensive research has been carried out to understand the factors influencing the intensification of membrane fouling, but these results are either not conclusive, or sometimes even contradictory. Generally, it might be said that the decrease in membrane permeability during water treatment depends on the type of the membrane used as well as on the amount and properties of the organic substances fractions in the feed water.

The water pretreatment process used to remove foulants (mainly particles and organic matter) prior to the membrane process has become an important aspect of any membrane operation. Moreover, water pretreatment prior to membrane filtration can improve the final quality of water. A variety of pretreatment processes for water ultrafiltration have been investigated recently. Among them, the most frequently applied were coagulation [5-10], or activated carbon adsorption [3, 11-14]. The pretreatment process may cause a significant increase in the total cost of water production and sometimes the expected results, i.e. reduction of membrane fouling, may not be achieved. For example Carroll et. al. [15] stated that a small molecular weight and hydrophilic fraction of the NOM, which is responsible for membrane fouling, was not removed during the coagulation step, and after the coagulation pretreatment no decrease of membrane flux was observed.

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Bian et. al. [16] reported that adsorption by PAC does not remove the NOM fractions, which are highly responsible for fouling.

Since neither coagulation nor carbon adsorption can remove all the organic foulants from the treated water prior to membrane filtration, much research has been carried out to a find new and effective method of organic matter removal. The ion exchange process seems to be a very effective solution to this problem.

The first studies demonstrating a strong potential of the anion exchange resin for natural matter removal appeared at the end of the 1970s [17] and were followed by numerous research works [18-20]. It has been proved that anion exchange resins can effectively eliminate the NOM from the treated water and are much more efficient at eliminating the low organic NOM fraction when compared to conventional processes [21, 22].

Interest in the ion exchange process application in water treatment increased when the new Magnetic Ion EXchange resin, MIEX® was developed. The MIEX® resin was developed by Orica, an Australian Company, and optimized for the removal of negatively charged organic particles from water [23, 24]. MIEX® resin is micro sized, macroporous, and strong base ion exchange resin made from a moderately cross-linked acrylic skeleton. The resin has a magnetic component incorporated into its polymeric structure. This makes individual resin beads behave like small magnets capable of agglomerating into large and heavy agglomerates. In this form they can be easily removed from water by sedimentation. The process for the DOC removal based on the MIEX® resin includes resin contacting with water, resin separation and recycling, and resin regeneration with NaCl. The process differs from conventional ion exchange technology in the way that the ion exchange part of the process is continuous, i.e. there is no need to stop the treatment unit for resin regeneration, because this phase is performed in a separate unit.

The MIEX® resin has a very small particle size – the diameter of a particle is only 150–180 µm. With a specific surface area comparable to other conventional macroporous resins, this resin has a lot more external bead surface. According to the theory proposed by Meyers [23], the initial NOM exchange occurs at the surface of the resin, and is followed by a slow diffusion of the organic molecule towards the inside of the resin bed by exchange from surface to inside active sites. In that way, surface active sites become available again for further NOM exchange. Maximizing surface size has a potential to dramatically increase NOM exchange kinetics.

The literature of MIEX® indicates high efficiency of the process in DOC removal. UV254 and DOC removal ranged from 50 to 85%, respectively, depending on raw water quality [18, 25, 26]. The process is especially effective in separating the low molecular weight organic particles [27]. MIEX® does not remove turbidity and even may generate secondary pollution, since a small part of a resin might be carried away from the system. In order to eliminate water turbidity and remove larger organic particles from water it is required to use coagulation with low doses of coagulants as a post-treatment of water.

The aim of this work was to evaluate the suitability of the process composed of the MIEX® treatment and membrane ultrafiltration on final water quality and to assess the influence of this pretreatment method on membrane fouling.

Experimental

Water Samples

Raw water (RW), water from Mokry Dwor waterworks (MD) (after coagulation and sand filtration) and raw water treated with the MIEX® resin followed by sand filtration were collected between March and April 2005.

The Mokry Dwor waterworks takes its raw water from the Olawa River and produces about 40% of the distributed drinking water for the city of Wrocław, Poland. The plant has an average water flow of about 80,000 m^3/h. The treatment process at Mokry Dwor includes coagulation with PAX XL3 – polyaluminium chloride (Kemipol) (coagulant dose equal to 2.9 g Al/m^3; pH=7.7), and sand filtration. The characteristics of raw (RW) and treated water (MD) are given in Table 1.

MIEX® Process Description

The experiments with MIEX® resin were performed at a semi-automatic pilot plant module delivered by ORICA WATERCARE, which was installed on the raw water intake of Mokry Dwor waterworks. The main parts of the installation set-up of the system included the following major parts: contactor (250 dm^3), settler (260 dm^3), regeneration vessel (45 dm^3), fresh resin tank (120 dm^3), brine tank (30 dm^3), overflow tank (55 dm^3), compressor, pumps, mixers and a distribution/control box. Parameters of MIEX® process performance were determined in jar tests [28] and are presented in Table 2.

Table 1. Results of raw and treated water quality at Mokry Dwor waterworks plant.

	Raw water	MD treated water
Colour, g Pt/m^3 *(σ)*	15.0 *(2.2)*	9.2 *(1.43)*
DOC, g C) m^3 *(σ)*	4.8 *(0.41)*	3.9 *(0.48)*
UV abs 254 nm, m^{-1} *(σ)*	13.0 *(0.83)*	10.0 *(0.71)*
SUVA	2.71	1.09

σ – standard deviation

The Ultrafiltration Module and Testing Set-Up

In the ultrafiltration experiments we made use of hollow-fibre UF modules (prepared in the Institute of Biocybernetics and Biomedical Engineering PAS, Warsaw, Poland) with polysulfone (PS 1700 NT-LCD) membranes of cut-off 30 kD (the membrane cut-off was determined using dextrans). The module consisted of 127 hollow fibres with an internal diameter of 0.96 mm. The effective surface area of the membranes in the module amounted to 0.0567 m^2.

In the ultrafiltration experiments Millipore ProFlux M12 cross-flow system was used. During membrane filtration tests the feed solution volume amounted to 2 dm^3 and, in order to maintain constant feed parameters, permeate was recirculated to the feeding tank.

Methods of Process Investigation

Prior to each ultrafiltration cycle, the membrane module was treated with distilled water at 0.03 MPa until a constant volume flux was established. Transport properties of membranes were investigated at 0.03 MPa by measuring the rate of permeate flow through the capillaries under steady conditions. The membrane system was operating at constant pressure.

Permeate volume flux (J) was calculated as follows:

$$J = \frac{V}{t \cdot A},\ \mathrm{m^3/m^2day}$$

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

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 DOC (TOC 5050 Analyser, Shimadzu), the absorbance of UV at 254 nm, and colour intensity (Shimadzu UV1240 spectrophotometer). The retention coefficient of the measured water parameters was determined using the following expression:

$$R = \frac{c_o - c_p}{c_o} \cdot 100,\ \%$$

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

High-performance size exclusion chromatography (HPSEC) has been used to determine the molecular weight distribution of the organic substances in the water samples. In HPSEC analysis, organic substances are separated primarily on the basis of differences in the molecular sizes, i.e. the largest molecules are eluted first in the column, while the smallest molecules are eluted last.

The HPSEC was carried out using the HPLC system with a UV detector (Shimadzu) equipped with a BIOSEP-SEC-S2000 column (7.5 x 300 mm, Phenomenex). The column packing consisted of a hydrophilic bonded silica with particle size of 5μm and pore size of 145 Å. The eluent that has been used was a 0.1 M NaCl solution buffered at pH 6.8 with 2 mM phosphate solution. A water sample of 20 μl was injected into the column. The flow rate was 1 ml/min and analysis time was 15 min. All solutions were prepared using analytical grade chemicals and the MiliQ water. The absorbance at 254 nm was used for detection. As the pretreatment for the HPSEC fractionation of the NOM, water samples were filtered through a 0.45 μm membrane. The HPSEC column was calibrated with protein standards such as insuline (5.7 kD), ovalbumin (45 kD), bovine serum albumine (69 kD), and γ-globuline (150 kD).

The area of the peak in the chromatogram refers to the amount of UV absorbing fraction of the DOM in a specific molecular size fraction.

Table 2. The operating parameters of the MIEX® pilot plant trial.

Parameter	Unit	Value	
		for trial range	for UF samples
Raw water flow	L/h	500	500
Resin concentration	$mL_{resin}/L_{suspension}$	10 – 29	20
Resin/water contact time	min	30	30
Resin bed volumes	L_{water}/L_{resin}	1000 – 3000	1230
Regeneration rate	%	4 – 8	5
Fresh resin concentration	$mL_{resin}/L_{suspension}$	180 – 240	210
Recycle resin concentration	$mL_{resin}/L_{suspension}$	60 – 150	120
Regeneration frequency	day^{-1}	1	1
Brine Dosage	L_{brine}/L_{resin}	2.5 – 3.0	2.5

Results and Discussion

MIEX® Process Effectiveness

A one-month pilot trial of the MIEX®DOC process gave average results as shown in Fig.1 [29]. The average effectiveness of UV_{254}, colour and the DOC removal were very close to these obtained in the jar tests a year before [28], although ranges of the results were rather wide. This was not only due to the raw water quality and the NOM fractions changes, but also to the programmed changes of the main process parameters like resin concentration and resin bed volumes (see Table 2).

The Influence of Pretreatment Method on Permeate Quality

The plots of Fig.2 demonstrate how the quality of water has changed after application of the investigated methods of pretreatment. As shown by these data a commonly applied method of surface water treatment, i.e. coagulation and sand filtration, may decrease the colour intensity by 38.7%, absorbance at 254 nm by 23.1% and the DOC concentration by 18.7%. A much higher degree of organic matter removal, i.e. 74.0%, 61.5% and 41.7%, respectively for colour, abs 245 nm and the DOC concentration, was achieved when the MIEX® process was applied.

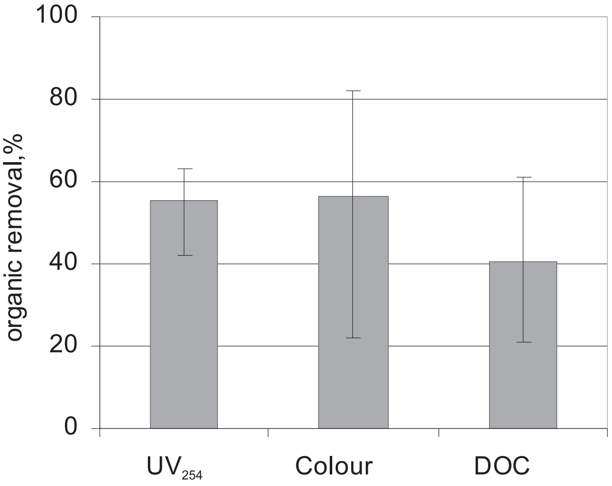

Fig. 1.The average efficiency of organics removal in pilot MIEX®.

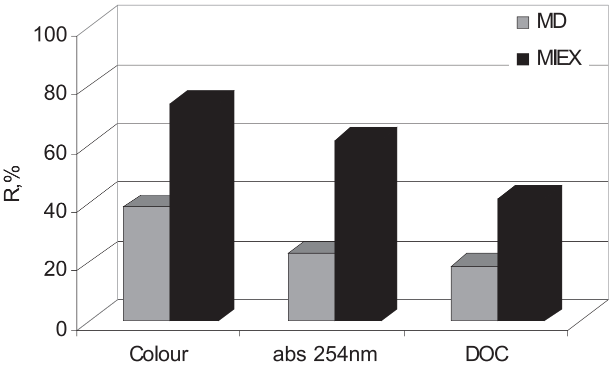

Fig.2. The effect of raw water treatment method on NOM efficiency removal (MD – water after coagulation and sand filtration – Mokry Dwor waterworks, MIEX – water after the MIEX® process).

In all cases a preferential decrease of colour over the UV absorption at 254 nm and the DOC was observed. This is evident, as the colour of water is related to the presence of large fractions of the NOM and coagulation is much better at removing the larger hydrophobic molecules, or acidic molecules than the smaller ones. The UV adsorption at 254 nm monitors the amount of the NOM fraction containing aromatic structures in their molecules. The smaller the molecular size of the humic fractions is, the less reliable is the quantitative estimation of the NOM concentration due to the scarcity of aromatic structures. The smallest fractions may contain compounds which have no UV absorbance. The DOC concentration, as the most reliable method to determine the total amount of the NOM, has lower values and is the best parameter to characterise process efficiency.

When analyzing the quality of water after membrane filtration (Table 3) it should be noted that the application of any treatment method prior to ultrafiltration results in an increase of permeate quality. Adsorption of the organic matter on the MIEX® resin followed by ultrafiltration brought about 80% reduction of water colour (retention of organic matter was determined with reference to raw water). Also, the retention factor for other measured parameters (i.e. abs 254 nm and DOC concentration) was higher than that observed for the un-membrane filtered samples (Fig.3).

The Influence of the Water Pretreatment Method on the UF Membrane Flux Decline

Fig. 4 shows the flux decline of ultrafiltration membranes when raw water, or pretreated solutions were filtered. The ratio of the initial flux (J_0) to that at *i*th time (J_i) was employed to evaluate flux decline.

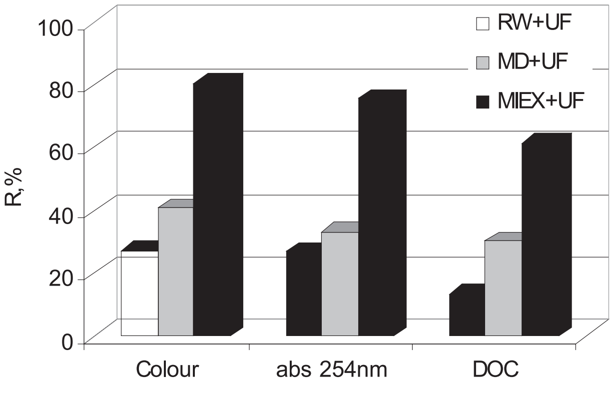

Fig.3. The effect of water pretreatment method on NOM retention in ultrafiltration.

The flux of the membrane with pre-coagulation or the MIEX® adsorption decreased slowly compared to that of the membrane without any pretreatment. As a general observation, ultrafiltration of raw water caused flux to decrease by 35%, while for the pretreated feed streams it amounted to 21% and 11%, respectively, for the pre-coagulated, or MIEX®-adsorbed samples. A rapid flux decline followed by stabilization of permeability during the initial stages of filtration was observed for all membrane-treated samples.

The Effects of the Water Treatment Process on the HPSEC Chromatograms

Typical chromatograms of the NOM fractions of raw water, pure water from Mokry Dwor waterworks and raw water treated with the MIEX® resin are presented in Fig.5. In all analyzed samples three distinct fractions of the NOM were detected. The dominant fraction was the one of MW below 30 kD. Conventional water treatments (i.e. coagulation and sand filtration) as well as the MIEX® process are quite effective in separating these organic particles. Coagulation and sand filtration eliminated about 51% of the organic fraction of MW ~25 kD and 37% of 1 kD fraction, while MIEX® was able to remove about 85% and 38%, respectively. Comparing information obtained from the HPSEC chromatograms with data presented in Fig.4, it can be stated that elimination of organics of MW<30kD results in a decrease of membrane fouling and improves membrane permeability.

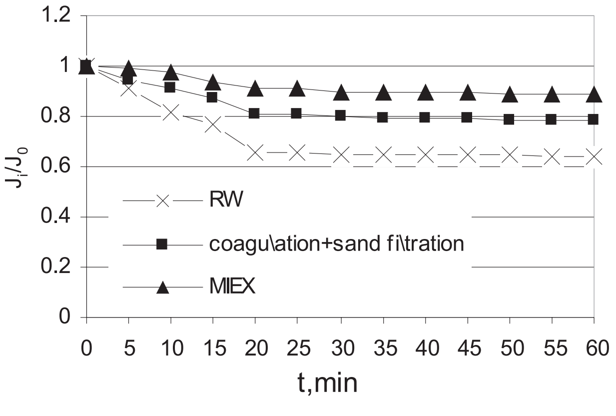

Fig.4. The influence of feed water pretreatment method on permeate flux decline (J_i/J_0).

Fig.6 compares the HPSEC chromatograms of raw water and ultrafiltered samples of the raw and pretreated water. As seen in the figure, applied membrane completely eliminates the organic fraction of MW>70 kD, but its effectiveness in separation of small NOM particles is limited. The intensity of the profiles substantially depends on the applied pretreatment method. Integration of the MIEX® process with ultrafiltration resulted in the highest elimination of the organic particles. It plays a meaningful role in respect to the low MW organic fraction. In water samples pretreated with the use of conventional coagulation, the amount of low MW organic structures was higher.

However, the reliability of the HPSEC method is affected by the size calibration of the column and also by the

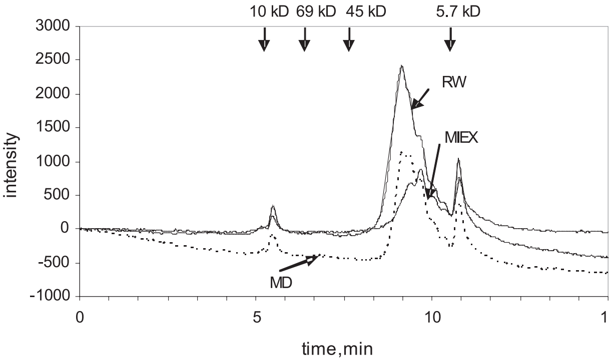

Fig.5. The HPSEC chromatogram of raw and pretreated water (RW –raw water, MD – water from Mokry Dwor waterworks, MIEX – raw water after MIEX® process).

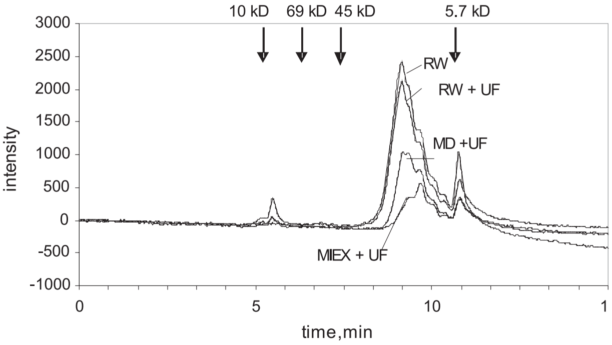

Fig.6. The HPSEC chromatogram of permeates after water pretreatment.

Table 3. Influence of the water pretreatment method on UF permeate quality.

Sample (pretreatment method)	UF permeate quality			
	colour, g Pt/m^3	abs 254 nm, m^{-1}	DOC, g C/m^3	SUVA
Raw water (no pretreatment)	10.9	9.5	4.15	2.29
Mokry Dwor waterworks (coagulation + sand filtration)	8.9	8.7	3.35	2.59
MIEX® process	2.9	3.2	1.85	1.73

adsorption interactions and the charge exclusion (electrostatic repulsion effects) between the humic compounds and the HPSEC gel [30]. In this study column calibration was performed using proteins. Since the molecular structure of proteins is different from that of the NOM, protein standards tend to overestimate the molecular size of the humic substances [31]. Therefore, the largest fraction might be lower than 150 kD and the smallest fraction might be lower than 1 kD. Thurman [32] reported that molecular size of the aquatic fulvic acids and the humic acids are in the range 500-2000 and 2000-5000 D, respectively.

Conclusions

The objective of the reported research was to investigate the effect of water pretreatment by mean of coagulation or the MIEX® resin adsorption on natural organic matter removal and on membrane fouling during the ultrafiltration process. The conclusions of this research are as follows:

- water treatment with the MIEX® resin results in much higher elimination of the organic matter as compared to the coagulation and sand filtration realized at Mokry Dwor waterworks,
- coagulation, or treatment with the MIEX® resin prior to membrane ultrafiltration results in the increase of permeate quality and decrease of the UF membrane fouling,
- generally, water pretreatment with MIEX® seems to be a good method to increase the effectiveness of the ultrafiltration process, i.e. elimination of the organic substances and the hydraulic efficiency.

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