

Water treatment using MIEX[®]DOC/ultrafiltration process

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Abstract

The objective of the study was to compare the treatment efficiency obtained with the MIEX[®]DOC process and ultrafiltration as well as to investigate the effect of MIEX[®]DOC water pretreatment on the performance of ultrafiltration membranes. The influence of MIEX[®] resin dose and membrane cut-off on natural organic matter removal (NOM) efficiency was analyzed.

Based on obtained results it might be stated that magnetic ion-exchange resin MIEX[®] is very effective in NOM separation from natural waters. For resin dose equal to 15 mL/L the reduction of abs 254 nm reached 90% for model solution and 80% for Odra river water. For UF membranes, their cut-off significantly influenced the NOM retention coefficient. The use of MIEX[®]DOC, process prior to ultrafiltration, increased permeate quality, especially for high MWCO membranes. Even very low MIEX[®] resin doses, significantly improved final water quality.

Keywords: MIEX[®]DOC; Ultrafiltration; Natural organic matter; Integrated process

1. Introduction

Incising demand for high quality drinking water results in seeking new effective processes of water treatment. Those requirements fulfil membrane processes that is why the use of membranes for treatment of water is nowadays growing rapidly. The two major topics in membrane water treatment processes are the quality

of the produced water, which is related to the rejection of targeted solutes, and the membrane fouling leading to permeate flux decline and consequent reduction in the efficiency of the filtration process. The economic use of membrane filtration systems is often limited by fouling, which increases applied pressure drops and cleaning frequencies, and the associated decrease in removal efficiency is observed.

Membrane fouling can be caused by the accumulation of rejected organic and inorganic

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substances. Natural organic matter (NOM) is considered a major cause of ultrafiltration membranes fouling during filtration of natural waters [1,2]. NOM is not of direct concern in drinking water, but it may affect its quality by increasing the disinfectant and coagulant demand, providing substrates for disinfection by-products (DBP) formation, form complexes with heavy metals and organic micropollutants, and enhancing regrowth in distribution system.

NOM is a mixture of organic compounds that are widespread in both surface and ground waters. Those substances range from macromolecules to low molecular weight compounds, such as simple organic acids and short-chained hydrocarbons. Aquatic humic substances generally comprise one-third to one-half of the dissolved carbon in water, thus are the dominant fraction of NOM in waters. 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 negative charge at pH values above 4.5 [3] and are generally soluble under these conditions.

Currently, the most common method to prevent fouling and to increase final water quality is by pretreating the influent to the membrane process with the application of conventional unit processes. A variety of pretreatment processes for UF has been investigated including coagulation, activated carbon adsorption, adsorption on iron oxides, or other preformed settleable solid phases, or ozonation.

Pretreatment process may cause an increase in the total cost of the water production and sometimes the expected results, i.e. reduction of membrane fouling and the increase of water quality, may not be achieved. Carroll et al. [4] stated that a small molecular weight and hydrophilic fraction of the NOM, which is responsible for membrane fouling and formation of disinfection

by-products, was not removed during the coagulation step. Bian et al. [5] reported that adsorption on PAC does not remove the NOM fractions which are highly responsible for fouling.

Currently many researches make studies on new and effective methods of the organic matter removal. 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 the natural matter removal appeared at the end of the 1970s [6].

The interest in the ion exchange process application in the water treatment increased when Orica, an Australian Company, developed the new Magnetic Ion EXchange resin, (MIEX[®]). The MIEX[®] resin was optimized for the removal of negatively charged organic particles from the water [7,8].

The process of the DOC removal based on the MIEX[®] resin includes resin contacting with water, resin separation and recycle, and resin regeneration with NaCl. The process differs from the 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 separate unit.

A review of the literature concerning MIEX[®] application in water treatment indicates its high potential in removing DOC and UV-absorbing substances from water [9–11]. The process is especially effective in separating the low molecular weight organic particles [12]. 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 post-treatment (coagulation and/or filtration) of water.

In order to take full advantage of ultrafiltration and MIEX[®]DOC processes the application of integrated process composed of both mentioned processes was examined. The aim of the work was to examine suitability of integrated process

to natural surface water treatment. The objective of the study was to evaluate the influence of membrane cut-off and MIEX[®] dose on the effectiveness of NOM removal from model solution and natural water.

2. Materials and methods

2.1. Solutions

Water model solution and surface water from Odra river (Wroclaw, Poland) were used in this study. Model solution was prepared from natural water flowing out from The Great Batorow Peatbag (southwest Poland) and dechlorinated tap water. Detail characteristic of NOM in model solution was given in [13]. Properties of feed waters are presented in Table 1.

2.2. Membranes

In the study, use was made of ultrafiltration membranes made of regenerated cellulose. Their characterisation is included in Table 2. Cut-off of the investigated membranes amounted to 5, 10 and 30 kDa.

2.3. Ultrafiltration

Ultrafiltration experiments were carried out in a laboratory ultrafiltration cell at a pressure difference of 0.1 MPa. The main part of the

Table 1
Feed water properties

Parameter	Mean value	
	Model solution	Odra river
Colour, g/m ³	54.3	22.2
Abs 254 nm, cm ⁻¹	0.345	0.149
conductivity, μS/cm	380	1405
pH	7.6	7.1

Table 2
Major parameters of the experimental membranes

Membrane symbol	Cut-off, kDa	Producer	Volume flux, m ³ /m ² d (distilled water, ΔP = 0.1 MPa)
C5	5	Nadir	0.455
C10	10	Nadir	0.635
C30	30	Nadir	7.368

system was an Amicon 8400 ultrafiltration cell with total volume of 350 mL and a diameter of 76 mm. The effective surface of the membrane amounted to 4.52×10^{-3} m².

2.4. MIEX[®]DOC

Preliminary test were conducted for each water to determine the optimal MIEX[®] resin dose and mixing time. UV₂₅₄ absorbance and colour were monitored to determine these optimal conditions.

One litre of the feed water was placed in 2 L jars, dosed with appropriate amount of the resin, and mixed at 150 rpm on a VELS 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 top of each jar at mixing time 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 (Shimadzu QP2000 spectrophotometer).

2.5. Integrated MIEX[®]/ultrafiltration process

Appropriate dose of MIEX[®] resin was added to feed water and mixed for 10 min followed by 30 min settling. Afterwards supernatant was placed in Amicon 8400 cell for ultrafiltration at transmembrane pressure of 0.1 MPa. The MIEX[®]/ultrafiltration set-up is illustrated in Fig. 1.

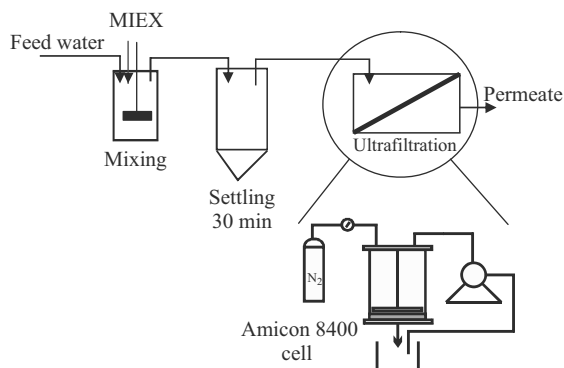


Fig. 1. Schematic diagram of the MIEX[®]/ultrafiltration process.

3. Results and discussion

3.1. Kinetics of MIEX[®] DOC process

Preliminary jar test experiments were conducted in order to determine the influence of

MIEX[®] dose and mixing time on NOM removal efficiency. As it can be inferred from the Fig. 2, the removal of organic substances from the both analysed types of water increased with an increase of MIEX[®] resin dose. The increase of resin dose from 2.5 to 15 mL/L (after 5 min mixing) resulted in the increase of colour removal from 30.5 to 77.0% and from 14.6 to 75.2% for Odra river and model solution respectively. For resin doses equal to 10 and 15 mL/L the removal efficiency reached a plateau within the 10 min of contact time, while for smaller doses this effect was achieved after 20–30 min. Although the NOM removal efficiency increased (for low resin doses) with the contact time, 10 min of mixing was chosen as optimal for integrated process experiments.

For both types of water comparable values of R_{colour} as compared to $R_{\text{abs } 254}$ were obtained. This

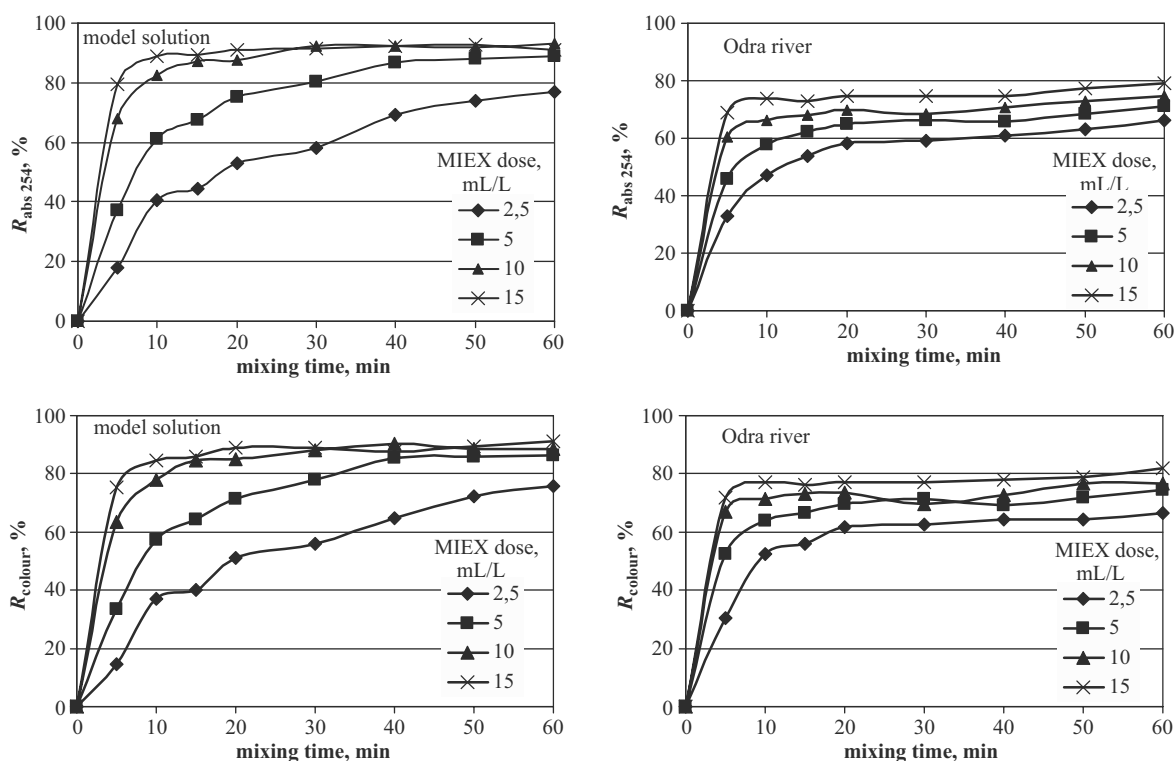


Fig. 2. Natural organic matter removal efficiency under different MIEX[®] doses and mixing time.

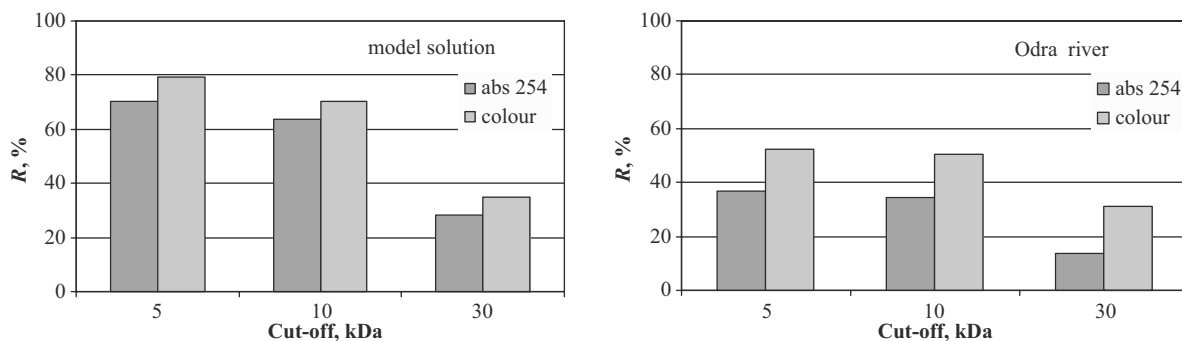


Fig. 3. The influence of membrane cut-off on NOM removal efficiency.

is evident, as colour of water is related to the presence of chromophore groups containing aromatic structures well detected by UV absorbance measurements. Slightly lower retention

coefficient factors obtained for water from Odra river may suggest that NOM particles present in natural water have lower negative charge and are poorly removed in ion exchange process.

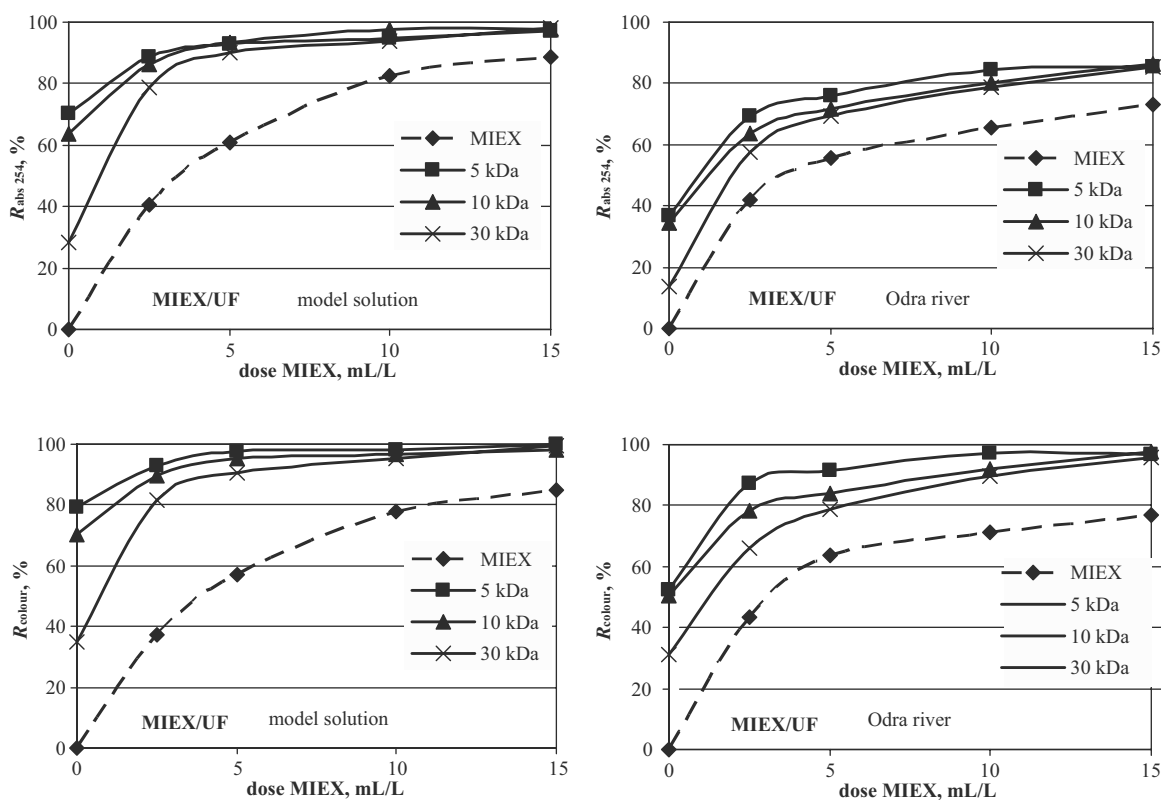


Fig. 4. The influence of membrane cut-off and MIEX[®] dose on NOM removal efficiency in integrated MIEX[®]/DOC/ultrafiltration process.

3.2. Ultrafiltration

The organic matter removal efficiency (reduction of colour and UV_{254}) with the use of ultrafiltration membranes of different cut-off is shown in Fig. 3. For the UF membrane of cut-off equal to 5 kDa R_{colour} amounted to 79.3 and 52.5% for model solution and Odra river water respectively. With the increase of membrane cut-off, the retention of NOM decreased and for 30 kDa membrane R_{colour} reached values of 35.0% for model solution and 31.3% for Odra river water. Higher values of R_{colour} over $R_{\text{abs } 254}$ result from size exclusion mechanism of ultrafiltration membrane separation. NOM fractions responsible for colour intensity has generally large molecular weight, and are better retained by membrane that smaller fractions with aromatic rings in their structure (indicated by abs 254 nm).

3.3. Integrated MIEX[®]DOC/ultrafiltration process

As presented in the Fig. 4 the efficiency of the NOM separation significantly increased when integrated process composed of ion exchange with MIEX[®] resin and ultrafiltration was applied. Even for very small resin doses the increase of NOM separation efficiency was significant. For example for model solution and MIEX[®] dose of 2.5 mL/L R_{colour} amounted to 37.2% in MIEX[®]DOC process, 35.0% in ultrafiltration with 30 kDa membrane, and increased up to 81.4% when integrated process was applied. For water from Odra river the tendency was similar.

It is worth noting that the efficiency of the integrated MIEX[®]DOC/ultrafiltration process was found to be only slightly influenced by resin dose and membrane cut-off. In the integrated process for all applied membranes the value of NOM retention coefficients was comparable apart from membrane cut-off. For example for model solution and MIEX dose of 10 mL/L R_{colour} amounted to 98.3, 96.9 and 95.5%, respectively for 5, 10 and 30 kDa membranes.

4. Conclusions

Integrated process composed of MIEX[®]DOC process and ultrafiltration was found to be very effective in removing NOM from the examined waters. The efficiency of the integrated MIEX[®]DOC/ultrafiltration process was found to be only slightly influenced by resin dose and membrane cut-off. Even for very small resin doses and UF membranes of high MWCO, the retention of NOM particles was high. The obtained results indicate that combination two mechanisms of NOM removal: ion exchange with size exclusion, allow to separate wide spectrum of organic substances. Moreover, application of ultrafiltration after MIEX[®]DOC process keep to a minimum the secondary pollution caused by resin carried away from the system. It also eliminates the losses of resin.

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References

- [1] Committee Report: Recent advances and research needs in membrane fouling, J. AWWA, 97 (8) (2005) 79–89.
- [2] A.W. Zularisam, A.F. Ismail and R. Salim, Behaviours of natural organic matter in membrane filtration for surface water treatment — a review, Desalination, 194 (2006) 211–231.
- [3] Committee Report: Organics removal by coagulation: a review and research needs, J. AWWA, 71 (1979) 588–603.
- [4] T. Carroll, S. King, S.R. Gray, B.A. Bolto and N.A. Booker, The fouling of microfiltration membranes by NOM after coagulation treatment, Water Res., 34 (2000) 2861–2868.
- [5] R. Bian, Y. Watanabe, G. Ozawa and N. Tambo, Membrane fouling of ultrafiltration: evaluation of influence of pretreatment with batch test, J. Jpn. Water Works Assoc., 67 (1998) 11–19.

- [6] C.T. Anderson and W.J. Maier, Trace organics removal by anion exchange resins, *J. AWWA*, 71 (1979) 278–283.
- [7] M.J. Semmens, M. Burckhardt, D. Schuler, P. Davich, M. Slunjski, M. Bourke and H. Nguyen, An evaluation of magnetic ion exchange (MIEX[®]) for NOM removal, Proc. AWWA Conference, 11–15 June 2000, Denver, USA.
- [8] P.C. Singer and K. Bilyk, Enhanced coagulation using a magnetic ion exchange resin, *Water Res.*, 36 (2002) 4009–4022.
- [9] T.H. Boyer and P.C. Singer, Bench-scale testing of a magnetic ion exchange resin for removal of disinfection by-product precursors, *Water Res.*, 39 (2005) 1265–1276.
- [10] M. Molczan, A. Bilyk, M. Slunjski and K. Celer, Application of jar tests to estimating the efficiency of organic substances removal in the MIEX[®]DOC water treatment process, *Ochrona Srod.*, 27 (2) (2005) 3–7 (in polish).
- [11] H. Humbert, H. Gallard, H. Suty and J.-P. Croué, Performance of selected anion exchange resin for the treatment of high DOC content water, *Water Res.*, 39 (2005) 1699–1708.
- [12] M. Slunjski, M. Bourke and B. O’Leary, MIEX[®]DOC process for humics in water treatment. www.miexresin.com.
- [13] M. Kabsch-Korbutowicz, Application of ultrafiltration integrated with coagulation for improved NOM removal, *Desalination*, 174 (2005) 13–22.