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Polishing of ceramic ultrafiltration membrane permeates by ion exchange

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ABSTRACT

The growing demand for freshwater and the increasingly stringent regulations concerning drinking water quality are essentially driving the application of membrane processes in the water treatment sector. The removal of natural organic matter (NOM) from the water being treated has become imperative as these pollutants promote the formation of disinfection by-products. To remove NOM from water intended for human consumption, use is frequently made of a low-pressure membrane process, i.e. ultrafiltration (UF). An inherent limitation to the use of UF membranes for NOM removal is the poor retention of low-molecular-weight substances. It seemed therefore advisable to examine the potential of another polishing process, namely that of ion exchange, for enhancing the final quality of the water being treated. The aim of this work was to assess the efficiency of the ion exchange process as a method for upgrading the quality of the ceramic membrane permeate, with emphasis placed on NOM removal. The process was conducted using two UF ceramic membranes (molecular weight cut-off of 50 and 300 kDa) and four ion-exchange resins (A200, A400, SBW and MIEX®). The study has produced the following findings: the UF membranes provided a sufficiently high extent of NOM removal, and the ion exchange process performed after the process of ultrafiltration significantly improved the quality of the water being treated. Of the ion-exchange resins tested, MIEX® was found to be the most effective.

Keywords: Water treatment; Natural organic matter; Ion-exchange resin; Ceramic membrane; Ultrafiltration; Integrated process

1. Introduction

Potable water production from natural surface waters requires technologies providing high removal rates for both natural organic matter (NOM) and trace organic substances. NOM is a heterogeneous mixture of organic molecules formed from decomposing living matter and from substances released by water organisms [1,2]. The mixture is characterized by a wide range of molecular weights and by a variety of functional groups (phenol, hydroxyl, carbonyl and carboxyl). NOM found in natural waters is composed of both hydrophobic and hydrophilic fractions with the generally largest hydrophobic acids fraction (which accounts for approximately 50% of the total organic carbon in water) [3–5].

NOM acts as a precursor to disinfection by-products (DBPs), amongst which the products of chlorination, trihalomethanes (THMs) and haloacetic acids (HAAs), are considered to be dominant [6]. Since these DBPs pose a real risk to public health, their concentrations in drinking

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water are regulated in order to limit exposure. For example, in the United Kingdom the maximal concentration of DBPs admissible in drinking water is 100 µg/l for THMs; in the United States of America it includes 80 µg/l for THMs and 60 µg/l for HAAs [7]. Of the methods used for removing organic pollutants from water, membrane processes have found wide acceptance, with ultrafiltration and nanofiltration as the preferred ones.

Membranes made of polymeric materials such as polysulfone, polyethersulfone, polyamide or cellulose are regarded worldwide as suitable for many industrial applications. A major contributing factor in the popularity of polymeric membranes is their availability in a wide range of pore sizes, geometries and separation properties. The use of ceramic membranes dates back to the mid-20th century. Ceramic membranes have numerous advantages over the polymeric ones as they are thermally, biologically, chemically and mechanically stable, as well as ozone resistant [8,9]. A major benefit offered by ceramic membranes is their reproducible performance over a long service lifetime. Ceramic membranes can be cleaned with strong acids and bases, sterilized in flowing steam, and stored in a dry state. Spent membranes can be used as ceramic materials [10]. A tangible benefit of ceramic membranes is their price which makes them competitive with organic membranes [11].

Ultrafiltration fails to provide removal of all the organic substances that are present in the water being treated. Among those persisting in the permeate, the low-molecular-weight NOM fraction is especially prevalent. Some of the negatively charged NOM particles found in the permeate after UF can be removed by ion exchange.

The strong potential of the anion-exchange resins for NOM removal was first reported in the late 1970s [12]. NOM removal with anion-exchange resins strongly depends on the type of the resin used. Analysis of relevant literature data has revealed the following: with weak alkaline resins lower amounts of NOM are removed than with strong alkaline resins, and resins with a macroporous structure provide higher NOM removal than do gel-type resins [13,14]. Amongst the resins used, the MIEX® resin deserves special attention. MIEX®, a Magnetic Ion EXchange resin, has been developed (and is being marketed) by Orica Watercare (Melbourne, Australia). This magnetized anion-exchange resin was designed specifically for the removal of organic macromolecules from waters. The MIEX® resin is a strong-base macroporous resin with iron oxide integrated into a polyacrylic matrix. The diameter of the MIEX® resin particle averages 180 µm, being much smaller than that of traditional resin particles. The high surface area-to-volume ratio allows faster NOM diffusion paths within the resin [15,16].

To further enhance the efficiency of ultrafiltration and ion exchange, the two processes were integrated in the study reported on here. A major objective of this research was to ascertain whether the ion exchange process conducted after ceramic membrane ultrafiltration could be efficiently used as a method of water polishing.

2. Experimental

2.1. Feed solutions

Samples of model solutions and surface water from the Odra river (Wroclaw, Poland) were used in this study. Model solution samples were prepared from natural water (effluent from the Great Batorow Peatbog in the south-west of Poland) and dechlorinated tap water (at the volume ratio of 1:5). Dechlorination of water was performes by bubbling air inside water for 10 min followed by keeping it stand for 24 h. The properties of both feed solutions are compiled in Table 1.

2.2. Membranes

The experiments were carried out using two ceramic ZrO_2/TiO_2 membranes (INSIDE CéRAM™, manufactured by Tami Industries Nyons, France) with molecular weight cut-off (MWCO) values of 50 and 300 kDa (Tables 2 and 3).

Table 1
Properties of feed solutions

Parameter	Model solution		Odra river water	
	Range	Average	Range	Average
UV absorbance 254 nm, cm^{-1}	0.186–0.245	0.211	0.120–0.144	0.131
Colour, g Pt/m^3	29.4–34.8	32.7	18.0–23.8	21.2
Total organic carbon, g/m^3	6.4–6.8	6.6	4.7–5.1	4.9
Temperature, °C	20–22 (room temperature)			
pH	7.3–7.4		7.8–8.2	
Conductivity, µS/cm	720–770	735	1280–1860	1720

Table 2
Membrane characteristics

MWCO	Membrane type	Effective filtration surface, mm^2	Module length, mm	External diameter, mm	Channel diameter, mm
50 kDa	1-channel	4000	250	10	6
300 kDa	7-channel	12500	250	10	2

Table 3
Hydraulic properties of the membranes

TMP*, MPa	Distilled water flux, m^3/m^2 d	
	MWCO 50 kDa	MWCO 300 kDa
0.03	0.17	1.13
0.06	0.59	1.66
0.09	1.18	3.21
0.12	1.35	3.43

*transmembrane pressure

2.3. Anion-exchange resins

For the purposes of this study use was made of four strong-base anion-exchange resins: three of type I and one of type II. Their characteristics are presented in Table 4. The resins differed in skeleton matrix (polystyrene or polyacrylic) and morphology (gel or macroporous). At the stage of production, type I resins were aminated with trimethylamine and type II resins with dimethyl-ethanolamine. From the analysis of the data in Table 4 it follows that the resins examined also differed in ion-exchange capacity and particle diameter.

2.4. Ultrafiltration

The experiments were performed using a cross-flow Millipore ProFlux M12 (Billerica, MA, USA) laboratory set-up (Fig. 1). The set-up provides liquid circulation between the feed tank (3 dm^3) and the membrane module at a constant concentration of the circulating solution. A control panel with pressure and pump efficiency indicators is entailed in the ProFlux M12 system. Additional sensors protect the set-up against unexpected variations in pressure or in the liquid level in the feeding tank. The system operates at constant transmembrane pressure (TMP).

During the experiments the TMP value ranged from 0.03 to 0.12 MPa. Process efficiency was determined by measuring, in the samples before and after the process, the colour intensity and UV light absorbance of at 254 nm wavelength (Shimadzu UV mini 1240 spectrophotometer). Taking into account their widespread acceptance by water treatment operators as parameters for the assessment of treatment plant performance, we decided that in our present study measured UV absorbance and colour intensity should be used as surrogate parameters to monitor the concentration of NOM.

2.5. Polishing of membrane permeate by ion exchange

After passage through the UF membrane, the solutions were further treated in the ion exchange process. The flow diagram for the process is shown in Fig. 2. The resin doses used in the experiments amounted to 2.5 and

Table 4
Characteristics of the anion-exchange resins [17–20]

Resin name	Manufacturer	Resin type	Matrix	Structure	Ion- exchange capacity, mmol/cm^3	Particle diameter, mm
A200	Purolite (Bala Cynwyd, PA, USA)	Strong base type II	Polystyrene	Gel	1.040	0.60 – 0.85
A400		Strongbase type I	Polystyrene	Gel	1.040	0.60 – 0.85
SBW	Wofatit (VEBFarbenfabriken Wolfen, Bitterfeld, Germany)	Strong base type I	Polystyrene	Gel	0.731	0.30 – 1.20
MIEX®	Orica (Melbourne, Australia)	Strong base type I	Polyacrylic	Macroporous	0.400	0.15 – 0.18

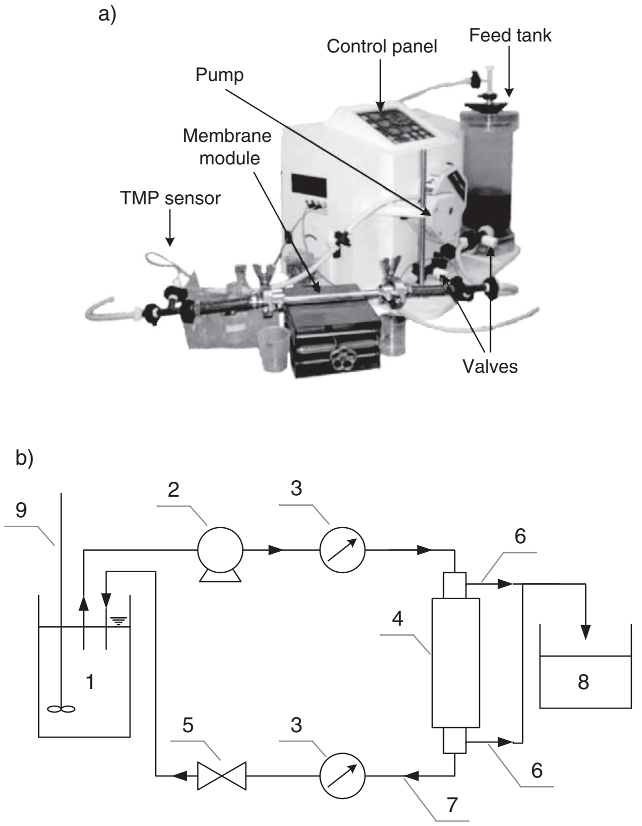


Fig. 1. Millipore Proflux M12 UF installation: (a) experimental set-up; (b) flow diagram: 1 – feed tank, 2 – pump, 3 – pressure sensor, 4 – membrane module, 5 – valve, 6 – permeate, 7 – concentrate, 8 – permeate tank, 9 – stirrer.

15 cm^3/dm^3. Upon addition of an appropriate dose of the ion-exchange resin, the permeate was subjected to 20 min stirring followed by 30 min settling. Afterwards each sample was analyzed for UV 254 nm absorbance and colour intensity.

3. Results

3.1. *Efficiency of ultrafiltration*

The efficiency of UV absorbance at 254 nm and colour intensity decrease in the UF process was found to be significantly influenced by the properties of the membranes. Relevant retention data are presented in Figs. 3 and 4.

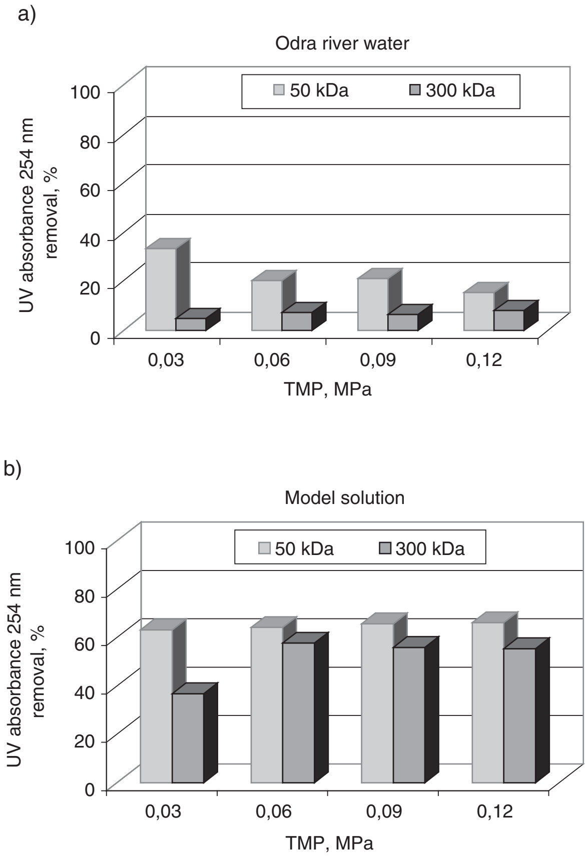


Fig. 3. Influence of TMP on the removal of UV absorbance 254 nm from natural riverine water (a) and model solution (b), using 50 kDa and 300 kDa membranes.

The results suggest that the permeate quality was influenced mostly by the MWCO value of the membrane while the influence of the TMP value was insignificant. With the increase in the membrane's MWCO, which also meant larger sizes of membrane pores, the separation of organic macromolecules deteriorated. This effect was observed with both riverine water and model solution samples. For example, the removal values obtained with the 50 kDa membrane for the Odra river water samples ranged from 42% to 58% for colour and from 15% to 34% for UV absorbance; those achieved with the 300 kDa membrane varied from 22% to 27% and from 5% to 8%, respectively. It is evident that with the increase in the MWCO value a higher amount of NOM particles was allowed to pass through the membrane.

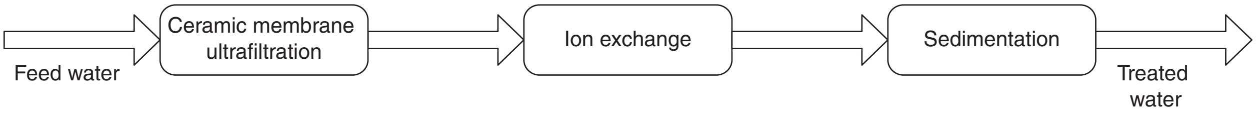
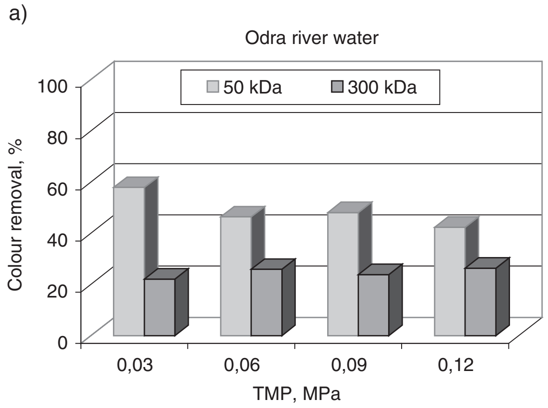


Fig. 2. Flow diagram for the integrated process ultrafiltration/ion exchange.



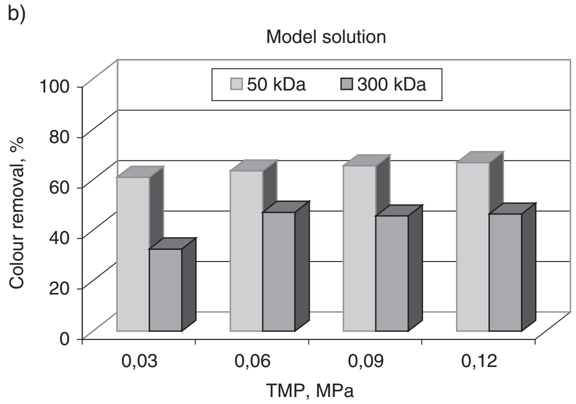


Fig. 4. Influence of TMP on colour removal from natural riverine water (a) and model solution (b), using 50 kDa and 300 kDa membranes.

The source of the water being treated was also a contributing factor in the efficiency of separation. In this study, the permeate produced from natural riverine water was of significantly lower quality as compared with the permeate from the model solution. Assuming that the samples of the model solution and those of the Odra river water show comparable levels of pollution (in terms of colour intensity and UV absorbance), it might be expected that the properties of the permeates will also be comparable for the same membrane. Actual results contrasted with the expected ones but this contrast can be attributed to the presence of inorganic substances in the Odra river water (conductivity of the riverine water was twice that of the model solution). Inorganic substances might induce changes in the spatial configuration of organic macromolecules – causing them to "shrink"– and thus facilitate membrane penetration by organic substances [21]. This phenomenon might be also attributed to the difference in the MW properties of the NOM in both examined solutions. For example, colour removal obtained with the 300 kDa membrane ranged from 32 to 47% for the model solution, whereas that for the riverine water sample only from 22 to 27% (Fig. 4).

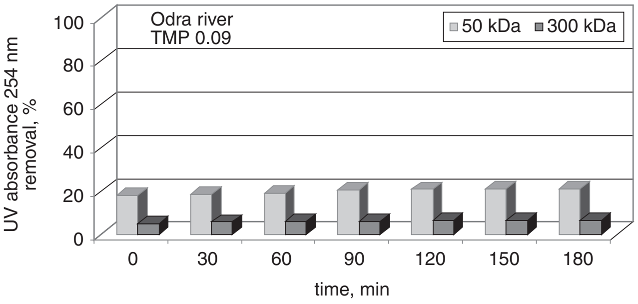


Fig. 5. Influence of time on the change in UV absorbance (natural riverine water, TMP 0.09 MPa).

The mechanism of NOM removal during ultrafiltration was determined by analyzing the change in UV absorbance retention in the course of the process. The data in Fig. 5 clearly show that the removal of organic substances was governed by the sieving mechanism. The slight changes in the UV absorbance retention factors over time suggest that the sorption mechanism was not involved in the separation of organic substances.

3.2. *Polishing of the ceramic ultrafiltration membrane permeate by ion exchange*

As already mentioned, the UF membranes examined failed to remove all of the organic substances that were present in the water being treated. It seemed therefore advisable to choose a polishing process which would upgrade the final quality of the water. Figs. 6 and 7 show the final quality of the water treated using an integrated process, where ultrafiltration was followed by ion exchange.

The results compiled in Figs. 6 and 7 demonstrate that the application of ion exchange after UF significantly improves the efficiency of colour and UV 254 nm absorbance removal as compared to ultrafiltration as a single process. Final water quality was found to depend on the membrane's MWCO value. The high NOM surrogate parameters removal achieved in the UF process with the more dense 50 kDa membrane accounted for a considerably higher final water quality after the polishing stage. High-molecular-weight fractions of NOM were removed during membrane filtration, whereas the substances of a lower molecular weight were separated in the course of the ion exchange process. For example, at TMP of 0.12 MPa, the 50 kDa membrane reduced colour intensity and UV absorbance of the model solution by about 66%, while the 300Da membrane brought about a reduction of 42% and 48% in the two parameters, respectively. The polishing step upgraded the removal efficiency to 100% with the 50 kDa membrane, and to about 90% with the 300 kDa membrane).

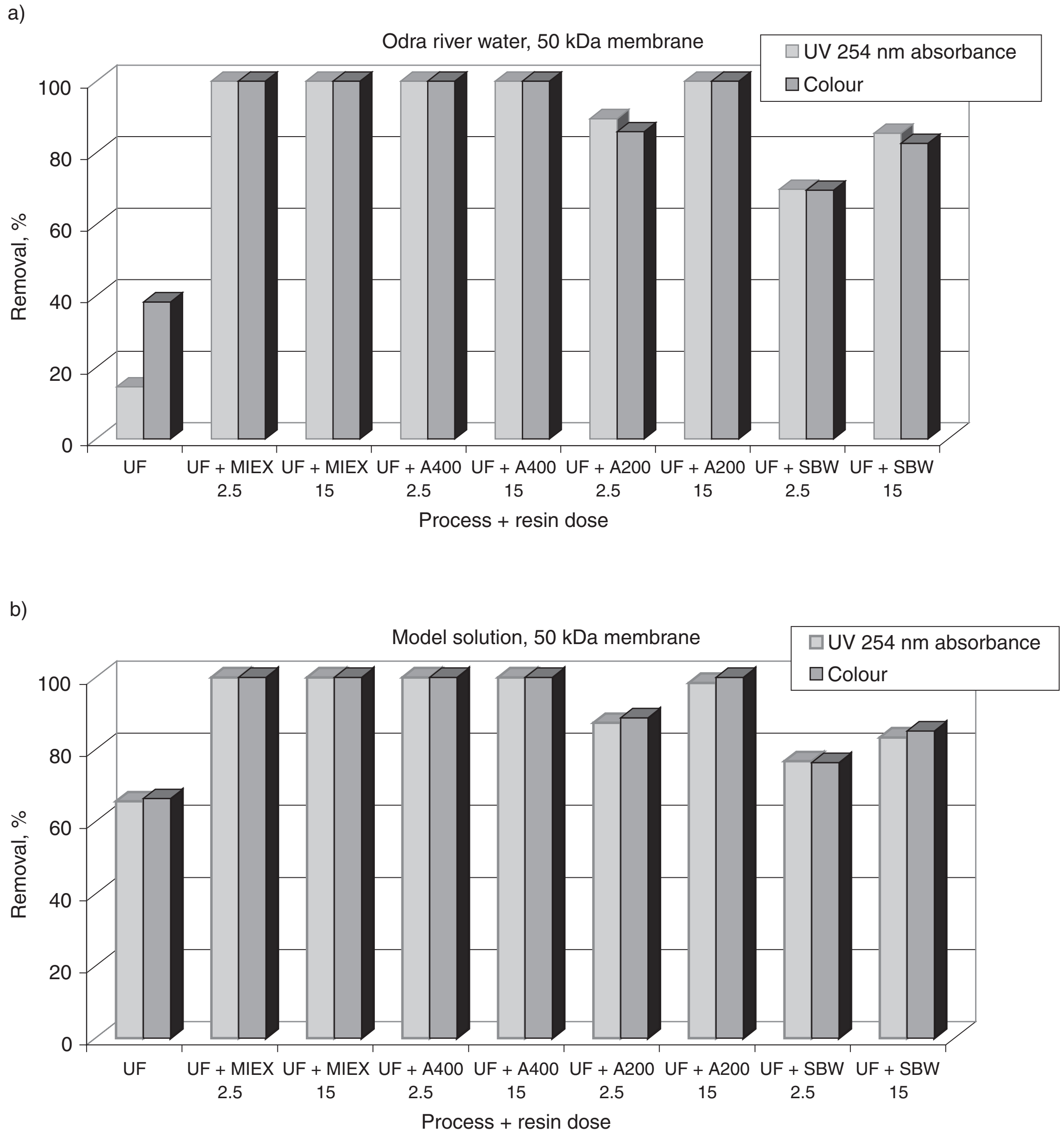


Fig. 6. Efficiency of colour and UV 254 nm absorbance removal from natural riverine water (a) and model solution (b) by the integrated process ultrafiltration/ion exchange, using the 50 kDa membrane (TMP 0.12 MPa).

It was also observed that the increase in resin dose enhanced the efficiency of the treatment process. The highest resin dose tested (15 cm^3/dm^3) produced the best results in terms of colour and UV 254 nm absorbance decrease.

Analysing the influence of resin type on the final water quality one can see that among the evaluated resins MIEX® and A400 were the most effective. With these resins, the removal of colour and UV absorbance from the 50 kDa membrane permeate approached 100% for both the feed solutions examined. However, when use was made of the 300 kDa membrane, this was concomitant with the deterioration of both permeate quality and final product quality. Thus, with the MIEX® dose of 15 cm^3/dm^3, colour removal and UV absorbance removal for the model solution amounted to 91% and 90%, respectively. For natural riverine water, the same MIEX® dose provided colour and UV absorbance removal of 89%.

The highest extent of measured parameters removal from the permeate after ultrafiltration was obtained with strong-base resins of type I, and the efficiency of separation was found to increase with the decrease in the resin's particle size. It was, furthermore, observed that the macroporous structure of the resin was also a contributing

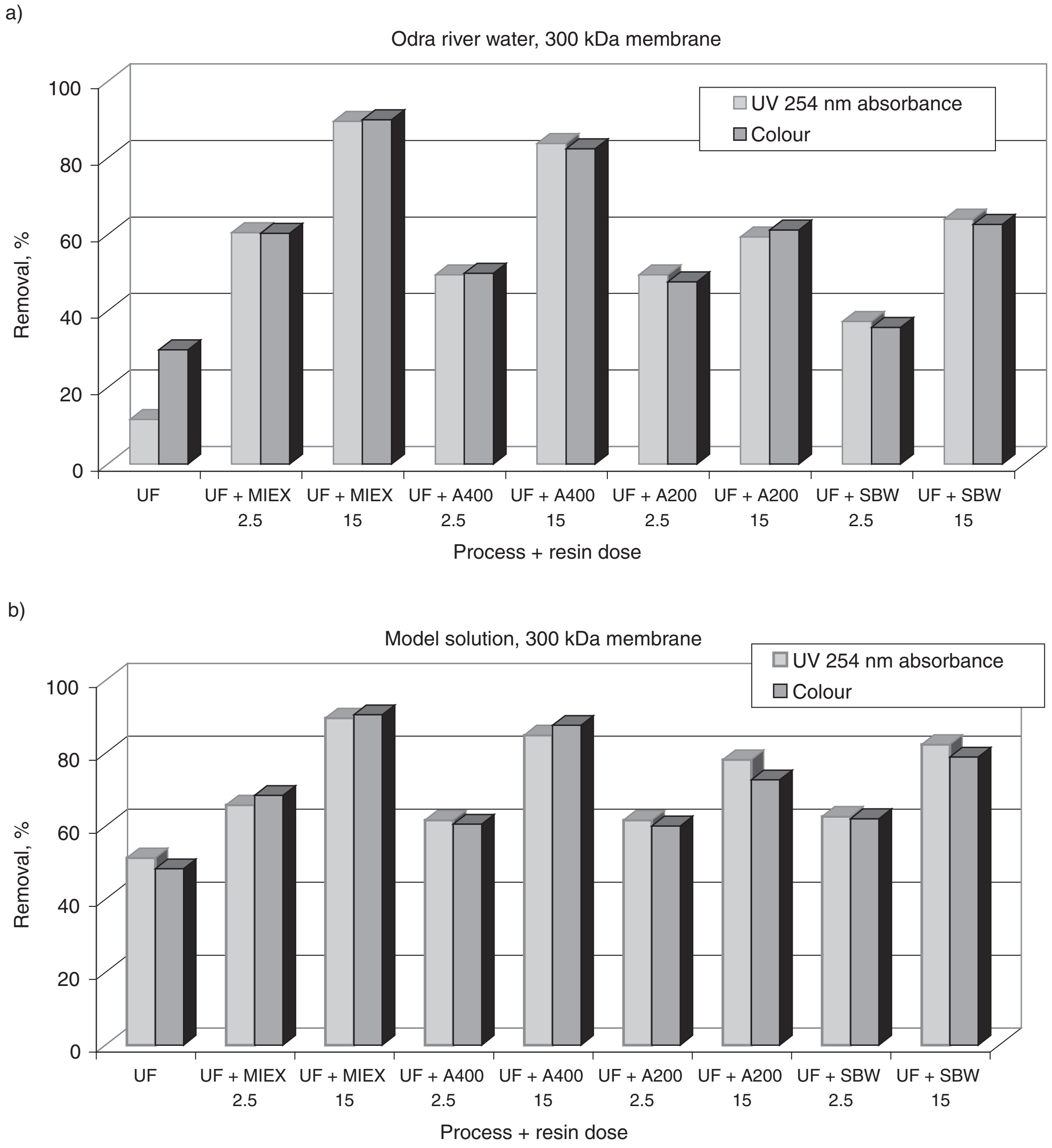


Fig. 7. Efficiency of colour and UV 254 nm absorbance removal from natural riverine water (a) and model solution (b) by the integrated process ultrafiltration/ion exchange, using the 300 kDa membrane (TMP 0.12 MPa).

factor in the enhancement of separation efficiency. Macroporous resins have permanent pores with diameters ranging between 20 and 200 nm. These diameters are much larger in comparison with the distance between adjacent hydrocarbon chains of gel-type materials (0.5 to 20 nm) [22]. Large pores in the resin structure, as well as the smaller particles of the ion exchanger, enhance the diffusion of macroanions toward the active sites of the resin. The superiority of MIEX® over A400 may also be attributed to its polyacrylic skeleton. Symons et al. have reported that the acrylic skeleton facilitates the removal of hydrophilic organic substances [23].

Analysis of the influence of the feed properties on the final amount of organic substances shows that the efficiency of organic substances removal in the integrated process was lower when natural riverine water was treated. It can be assumed that inorganic substances (specifically those of an anionic nature), whose concentrations are higher in riverine water than in the model solution, compete with organic macroanions for the active sites in the resin structure. As the size of inorganic ions is smaller than that of organic ions, the resin may preferentially adsorb the inorganic ones.

4. Conclusions

The use of an integrated process where ultrafiltration was followed by ion exchange upgraded the extent of organic matter removal in comparison with ultrafiltration as a single process.

The final quality of the water being treated was influenced by the membrane's MWCO, as well as the type and dose of the resin:

- the increase in the membrane's MWCO value from 50 to 300kDa deteriorated the final quality of the water;
- strong-base type I resins were the most efficient in UV absorbance at 254 nm and colour intensity removal. Among tested resins MIEX® was the most effective one;
- the increase in resin dose from 2.5 to 15 cm^3/dm^3 enhanced final water quality.

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