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Ultrafiltration as a method of separation of natural organic matter from water

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The objective of the study was to investigate the influence of membrane material, membrane cut-off and water composition on transport and separation properties of ultrafiltration membranes. Nadir membranes made of regenerated cellulose and polyethersulfone, with the cut-off of 5–100 kDa, were used. Experiments were performed for model solutions and for water from Odra river. It was found that compact ultrafiltration membranes (of low cut-off) allow one to remove efficiently natural organic matter from water. Transport and separation properties of ultrafiltration membranes are strongly influenced by membrane cut-off and membrane material. Retention of natural organic matter particles decreases with the increase of membrane cut-off while the opposite trend is observed in the case of permeability. The study shows that the degree of ultrafiltration membrane blocking by organic particles is related to membrane material (hydrophilic/hydrophobic properties of polymer) and its cut-off. Strongly hydrophilic membranes made of regenerated cellulose of low cut-off display a low proneness to fouling.

Key words: *membrane; water treatment; separation; fouling*

1. Introduction

Shortage of drinking water around the world, and increasing requirements concerning its quality result in seeking for new effective processes of water treatment. Raw water being a source of water supply contains suspended solids, colloids, and organics including bacteria and viruses. Suspended particles are generally larger than 1 μm and colloidal particles are in the range of 1–1000 nm. Those pollutants are of mineral and organic origin. Among organic substances the major fractions are natural organic matter substances.

Natural organic matter (NOM) is a mixture of organic compounds 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 hydro-

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carbons. Aquatic humic substances generally comprise from 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 ones, 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 [1] and are generally soluble under these conditions.

Due to unfavourable influence of NOM on water quality, this group of substances must be removed from potable waters. Among various physicochemical processes applied in water treatment, the most effective are coagulation, activated carbon adsorption and membrane separation. These water treatment processes can remove aquatic organic matter from water, with the efficiency depending on process operational conditions and the specific characteristics of the NOM such as molecular weight distribution, carboxylic acidity, and content of humic substances [2, 3].

Pressure driven membrane processes, i.e. reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF) are increasingly used in drinking water treatment. Depending on applied process they can remove a wide variety of substances from water. The basic parameters of pressure driven membrane processes are given in Table 1.

Table 1. Pressure driven membrane processes, their properties and applications [4, 5]

Process	Pore size [nm]	Pressure [MPa]	Separation capability
Microfiltration	50–5000	0–0.3	retention of bacteria, colloids, protozoa
Ultrafiltration	5–100	0.05–0.5	retention of viruses, bacteria and dissolved substances with MW 10–500 kDa
Nanofiltration	~ 1	0.5–2.5	separation of low MW substances (200–300 Da) and divalent salts
Reverse osmosis	< 1	1.5–10	retention of all dissolved ions

Microfiltration and ultrafiltration, due to relatively large membrane pores, have been employed primarily for removal of microorganisms and particles from waters. MF is effective in turbidity and particulate organic matter removal, as well as bacteria, protozoa and algae. UF can also remove viruses and some of the organic matter particles. Efficiency of NOM separation with use of the UF membranes is influenced by many factors, i.e. NOM character, molecular weight distribution, pH and ionic strength of water, and membrane cut-off. Generally, UF is effective in high-molecular weight fraction of the NOM removal.

A more widespread application of membrane processes is limited by the decrease in membrane performance occuring during potable water treatment as a result of fouling through the accumulation of particles and adsorption of the NOM [6, 7]. Extensive research has been carried out to understand factors influencing intensification of membrane fouling but these results are either inconclusive or sometimes even contradictory. Generally, it may 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 in the treated water.

The main objective of this investigation was to analyze the possibility of separation of natural organic matter from water by ultrafiltration. The influence of membrane properties such as their cut-off and membrane material on transport and separation properties was investigated. The molecular weight cut-off (MWCO) is the parameter used by manufacturers to characterize membrane separation properties. It indicates that at least 90% of dissolved macromolecules with molecular weight higher than the stated MWCO will be retained.

2. Experimental

Characterisation of the membranes. Nadir ultrafiltration membranes, made of regenerated cellulose and polyethersulfone, were used in the study. Their characterisation is given in Table 2. SEM picture of the investigated membranes is shown in Fig. 1.

Table 2. Principal parameters of the experimental membranes [8, 9]

Membrane	Membrane material	MWCO [kDa]	Mean pore radius [nm]	Contact angle [deg]	Polarity [%]
C5 C10 C30 C100	regenerated cellulose	5 10 30 100	0.82 5.01 12.55 no data	54.76	49.92
PES5 PES10 PES30	polyethersulfone	5 10 30	0.62 2.04 8.38	50.01	44.27

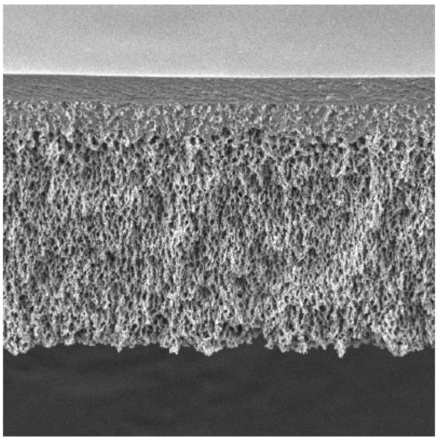

Fig. 1. SEM of the membrane cross-section [10]

Solutions. Water model solution and surface water from Odra river (Wrocław, Poland) were used in this study. The model solution was prepared from natural water flowing out from The Great Batorow Peatbag (southwest Poland) dissolved in various proportions with dechlorinated tap water. Properties of feed waters are presented in Table 3.

Table 3. Properties of feed water

Parameter	Mean value				
	Model solutions				Odra river
	1	2	3	4	
Colour, g Pt/m^3	33.0	64.3	93.3	120.6	25.3
Absorbance at 254 nm, cm^{-1}	0.210	0.411	0.598	0.777	0.170

Analytical methods. The efficiency of examined processes was determined by measuring the amount of organic matter in samples before and after the process. NOM concentration was monitored by measurement of UV absorbance at 254 nm and colour intensity (Shimadzu QP2000 spectrophotometer). UV absorbance at 254 nm is a good measure of the presence of naturally occurring organic matter, such as humic substances, because they contain aromatic moieties and they are the dominant form of organic matter in natural waters. UV absorbance at 254 nm has been used in Europe for several years as a surrogate measure of TOC and THM precursors' concentration [11].

Apparatus. The experiments were carried out in a laboratory ultrafiltration cell (Fig. 2) at a pressure difference of 0.1 MPa. The main part of the system was an Amicon 8400 ultrafiltration cell with the total volume of 350 cm^3 and the diameter of 76 mm. The effective surface of the membrane amounted to $4.52 \times 10^{-3} m^2$.

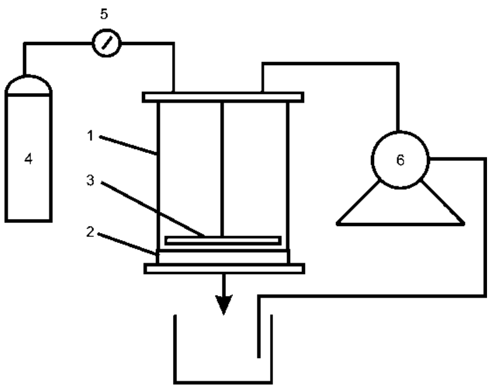

Fig. 2. Experimental set-up: 1– ultrafiltration cell (Amicon 8400), 2 – membrane, 3 – stirrer, 4 – gas cylinder, 5 – reducer, 6 – recirculation pump

Assessment of separation and transport properties. To estimate the separation and transport properties of the membranes under study, the volume flux of the permeate *J* and the retention factor *R* have been determined.

Volume flux of the permeate J describes the volume of liquid passing across a membrane surface unit per unit time:

$$J = \frac{V}{A\,t}, \quad \left[\frac{\mathrm{m}^3}{\mathrm{m}^2 \cdot \mathrm{d}}\right]$$

where V is the permeate volume, m^3, A denotes an effective surface area of the membrane, m^2, and t stands for duration of measurement, d.

Retention factor R defines the efficiency of separation of a natural organic matter macromolecules from the feeding solution:

$$R = \frac{c_f - c_p}{c_f} \times 100\%$$

where c_f, c_p denote the values of the measured parameter in the feed, and in the permeate, respectively.

3. Results and discussion

3.1. Transport and separation properties of the membranes

The study aimed at the evaluation of the ultrafiltration membranes for separation of natural organic matter particles from aqueous solutions. The effect of membrane

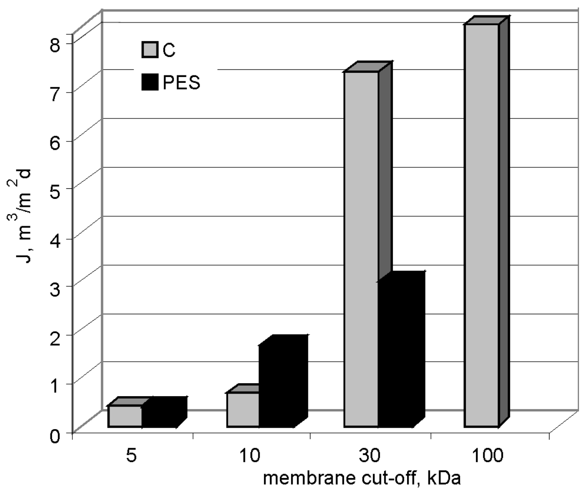

Fig. 3. Transport properties of ultrafiltration membranes (for distilled water)

cut-off on membrane permeability is shown in Fig. 3. The volume flux of distilled water varied from 0.412 m^3/(m^2·d) for C5 membrane to 8.258 m^3/(m^2·d) for C100 membrane, and from 0.397 $m^3/(m^2 \cdot d)$ to 2.992 $m^3/(m^2 \cdot d)$ for PES5 and PES30 membranes, respectively. The increase of membrane cut-off is connected with the increase of pore radius, resulting in a higher convective flux of the water. For membranes of cut-off 5 kDa, the hydrophilicity of membrane material did not affect transport properties of membranes but for membranes of cut-off 30 kDa a higher water flux was observed for a more hydrophilic C membrane.

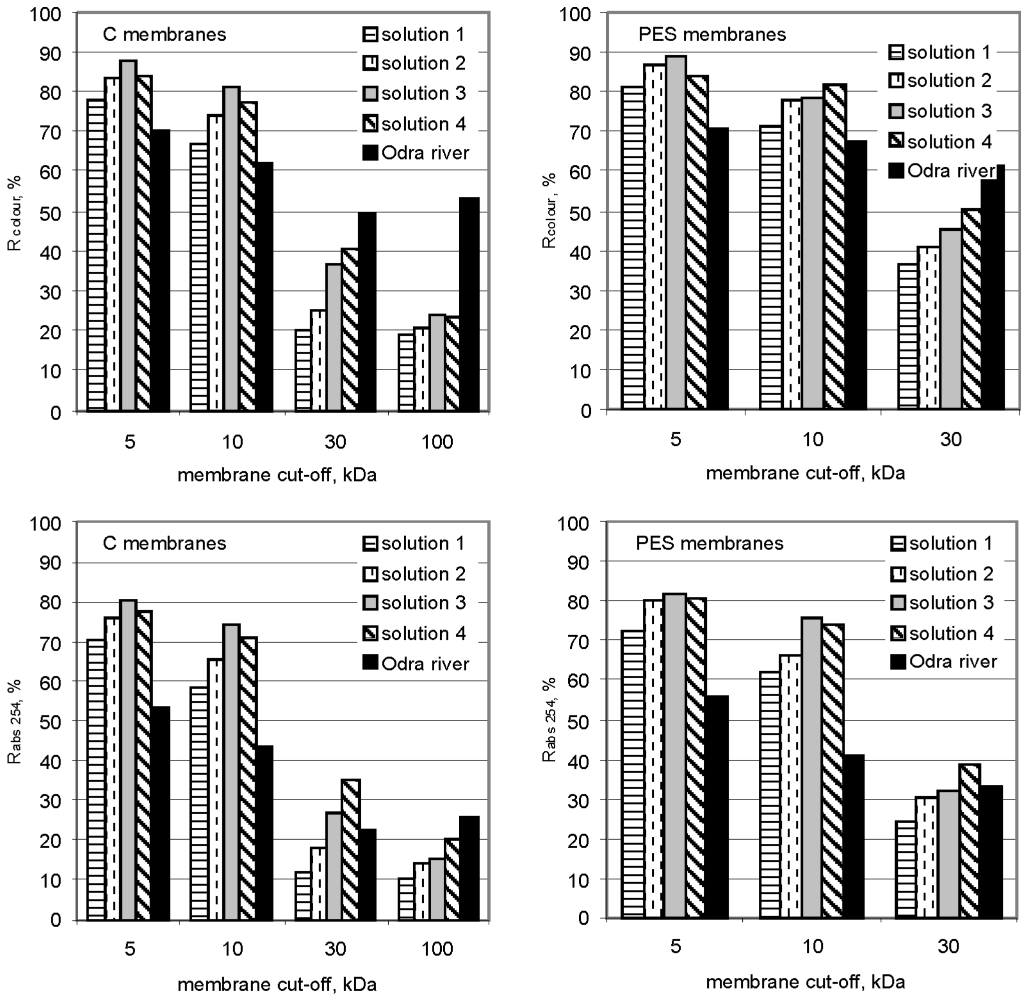

Fig. 4. Separation of natural organic matter by ultrafiltration membranes

The efficiency of separation of natural organic matter was found to be strongly influenced by membrane properties. Figure 4 shows the effect of membrane cut-off on the removal of colour and UV absorbance at 254 nm. The increase of membrane cut-off resulted in decrease of NOM removal efficiency. Slightly higher values of the retention factors obtained for PES membranes as compared to those for C membranes result from higher hydrophobic sorption of macromolecules on strongly hydrophobic PES membranes (see Sect. 3.2.).

A preferential decrease of colour over the UV 254 nm absorption was observed. This is understandable, as the colour of water is related to the presence of NOM fractions. The UV absorption at 254 nm monitors the amount of the NOM fraction containing aromatic structures in their molecules. The smallest fractions may even contain compounds which exhibit no UV absorbance.

3.2. Membrane proneness to fouling

The flux decline of ultrafiltration membranes was studied in terms of the normalized flux J/J_0 (J is the permeate flux and J_0 is distilled water flux) – the highest the value J/J_0, the less capable of membrane fouling is a given membrane. Normalized flux values for various water compositions are presented in Fig. 5.

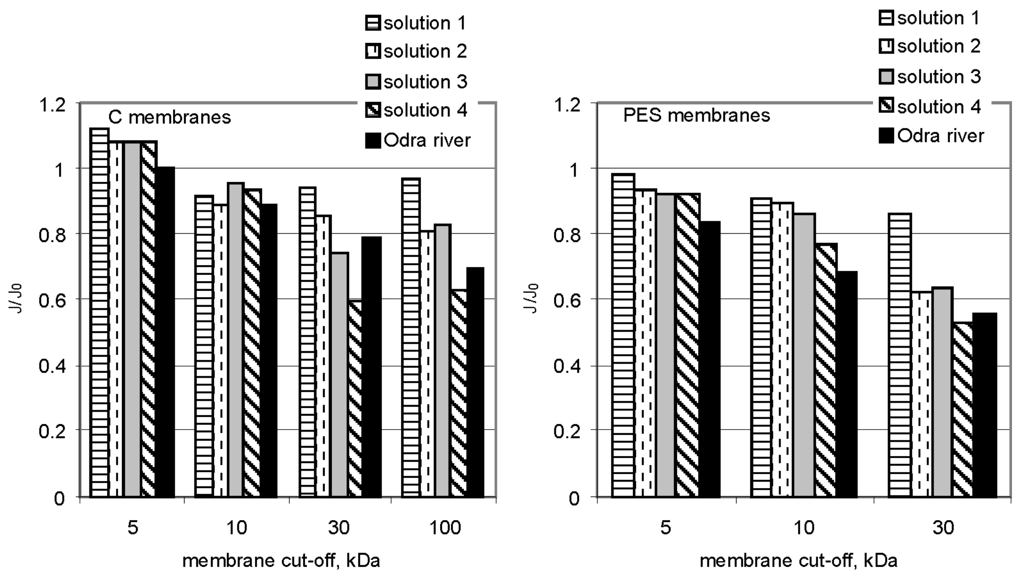

Fig. 5. The effect of the membrane type and properties of water on the normalized flux

The experimental results show that membrane fouling was strongly influenced by the membrane type and amount of organic particles in treated water. The decrease in permeate flux for a more hydrophilic C membrane was lower than that for a more hydrophobic PES membrane. J/J_0 values decrease with increasing membrane cut-off. The obtained results suggest that decrease of membrane permeability results from adsorption of NOM particles on the membrane surface and in the pore interior. Hydrophobic organic particles adsorb strongly on more hydrophobic membranes. They can also penetrate into membrane pores (especially of higher radius) and block them.

This is in a good agreement with findings of Dal-Cin et al. [12] who stated that when the pore size is considerably smaller than the foulant size, the pore size of the membrane remains unchanged and the decrease of flux might be only due to surface adsorption of macromolecules. On the other hand, when the pore size is much larger than the foulant size, macromolecules enter the pores, adsorbing on the pore walls and reducing the effective pore sizes. In such a situation the flux decrease is due to the reduced flow area.

The results of the experiment also indicate that the increase of organic matter concentration in treated water strongly affected the decrease of permeate flux.

4. Conclusions

The suitability of membrane ultrafiltration process to the treatment of waters containing natural organic matter has been investigated. The results led to the following conclusions:

• Compact ultrafiltration membranes (of low cut-off) allow one to remove efficiently natural organic matter from water.

• Transport and separation properties of ultrafiltration membranes depend strongly on the membrane cut-off and membrane material; retention of NOM particles decreases with the increase of membrane cut-off; while an opposite trend is observed in the case of permeability.

• The degree of ultrafiltration membrane blocking by NOM particles is related to membrane material (hydrophilic/hydrophobic properties of polymer) and its cut-off. Strongly hydrophilic membranes made of regenerated cellulose of low cut-off display a low proneness to fouling.

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References

[1] STEVENSON F.J., *Humus Chemistry,* Wiley, New York, 1982.
[2] COLLINS M.R., AMY G.L., STEELINK C., Environ. Sci. Techn., 20 (1986), 1028.
[3] MATILAINEN A., LINDQVIST N., KORHONEN S., TUHKANEN T., Environ. Int. , 28 (2002), 457.
[4] VAN RIJN C.J.M., *Nano and Micro Engineered Membrane Technology*, Elsevier, Amsterdam, 2004.
[5] SINGH R., *Hybrid Membrane Systems for Water Purification*, Elsevier, Amsterdam, 2006.
[6] KIMURA K., HANE Y., WATANABE Y., AMY G., OHKUMA N., Water Res., 38 (2004), 3431.
[7] LI C.-W., CHEN Y.-S., Desalination 170 (2004), 59.
[8] MAJEWSKA-NOWAK K., KABSCH-KORBUTOWICZ M., BRYJAK M., WINNICKI T., *Separation of dyes by hydrophilic ultrafiltration membranes*, [in:] Proc. of 7th World Filtration Congress, Budapest, Hungary, 20–22.05.1996, Vol. 2, p. 885.

[9] KOCHKODAN V., HILAL N., NIGMATULLIN R., GONCHARUK V., *Lipase-immobilized biocatalytic membranes in enzymatic esterification*, [in.] M. Bryjak, K. Majewska-Nowak, M. Kabsch -Korbutowicz (Eds.), *The Impact of Membrane Technology to Human Life*, e-book, Oficyna Wyd. PWr., Wrocław, 2006, p. 85.
[10] http://www.millipore.com
[11] EDZWALD J.K., BECKER W.C., WATTIER K.L., J. AWWA 77 (1985), 122.
[12] DAL-CIN M.M., STRIEZ C.N., TWEDDLE T.A., CAPES C.E., MCLELLAN F., BUISSON H., Desalination, 101 (1995), 155.

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