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Ultrafiltration as a Method of Natural Organic Matter Separation From Water

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1. Introduction

Shortages of drinking water around the world and the increasing requirements concerning its quality result in seeking for new, effective processes of water treatment. Raw water used for a source of water supply contains suspended solids, colloids, and organics including bacteria and viruses. Suspended particles are generally larger than 1.0 μm and colloidal particles are in the range of 1.0-1000 nm. Those pollutants are of mineral and organic origin. Among organic substances the major fraction are natural organic matter substances.

Natural organic matter (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 [1] and are generally soluble under these conditions.

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

Pressure driven membrane processes, i.e. reverse osmosis, nanofiltration, ultrafiltration and microfiltration, 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 shown in Table 1.

Table 1. Pressure driven membrane processes with their properties and application [4, 5]
Tabela 1. Ciśnieniowe procesy separacji membranowej – parametry, zastosowania [4, 5]

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

Microfiltration (MF) and ultrafiltration (UF), 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, water pH and ionic strength, and membrane cut-off (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 stated MWCO will be retained). 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 that occurs 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 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 the 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 treated water.

The main objective of this investigation was to analyze the possibility of natural organic matter separation from water in ultrafiltration process. The influence of membrane properties, such as their cut-off and membrane material on transport and separation properties were investigated.

2. Experimental

2.1. Characterisation of the membranes

In the study, use was made of Nadir ultrafiltration membranes made of regenerated cellulose and polyethersulfone. Their characterisation is included in Table 1. SEM picture of investigated membranes is shown in Fig. 1.

Table 1. Major parameters of the experimental membranes [8, 9]
Tabela 1. Charakterystyka stosowanych membran [8, 9]

Membrane symbol	Membrane material	MWCO, kDa	mean pore radius, nm	Contact radius, °	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	polyethersul fone	5 10 30	0.62 2.04 8.38	50.01	44.27

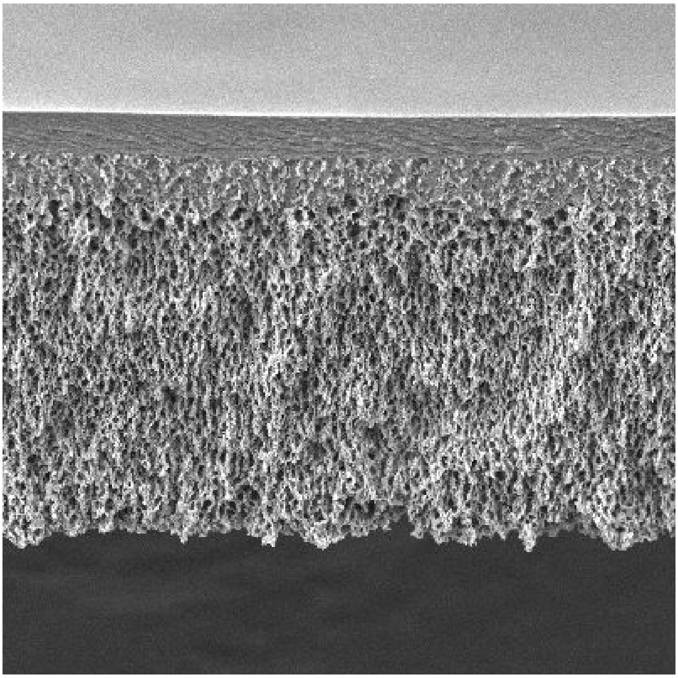

Fig. 1. SEM of C30 membrane cross-section
Rys. 1. Zdjęcie ze skaningowego mikroskopu elektronowego przełomu membrany C30

2.2. 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) dissolved in different proportions with dechlorinated tap water. Properties of feed waters are presented in table 2.

Table 2. Feed water properties
Tabela 2. Właściwości roztworów badawczych

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

2.3. Analytical methods

The efficiency of examined processes was determinate by measuring the amount of organic matter in samples before and after process. NOM concentration was monitored by measurement of UV_{254nm} absorbance and colour intensity (Shimadzu QP2000 spectrophotometer). Organic compounds that are aromatic or that have conjugated double bonds absorb light in the ultraviolet (UV) wavelength. UV absorbance at 254 nm is a good technique for measuring 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.

2.4. Apparatus

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

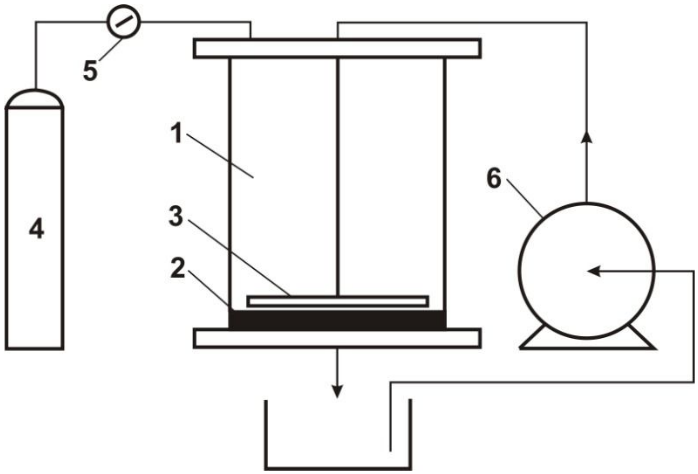

Fig. 2. Experimental set-up: 1 – ultrafiltration cell (Amicon 8400); 2 – membrane; 3 – stirrer; 4 – gas cylinder; 5 – reducer; 6 – recirculation pump

Rys. 2. Stanowisko badawcze: 1 – komora ultrafiltracyjna (Amicon 8400), 2 – membrana, 3 – mieszadło, 4 – butla z gazem, 5 – reduktor, 6 – pompa recyrkulacyjna

2.5. Assessment of separation and transport properties

To estimate the separation and transport properties of the membranes under study the following two parameters were used:
(1) volume flux of the permeate J, which describes the volume of liquid passing across a membrane surface unit per unit time and it takes the form

$$J = \frac{V}{A t}, \frac{m^3}{m^2 d}$$

where V is permeate volume, m^3; A denotes effective surface area of the membrane, m^2, and t stands for duration of measurement, d;
(2) retention factor R, which defines the efficiency of separation of a natural organic matter macromolecules from the feeding solution and it can be written as

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

where c_f denotes value of measured parameter in the feed, and c_p is its value in the permeate.

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 cut-off on membrane permeability is shown in Fig. 3. The volume flux of distilled water varied from 0.412 m^3/m^2d for C5 membrane to 8.258 m^3/m^2d for C100 membrane, and from 0.397 m^3/m^2d to 2.992 m^3/m^2d for PES5 and PES30 membranes, respectively. The increase of membrane cut-off is connected with the increase of pore radius, and this results in higher convective flux of the water. For membranes of cut-off 5 kDa the hydrophilicity of membrane material didn't affected transport properties of membranes, but for membranes of cut-off 30 kDa higher water flux was observed for more hydrophilic C membrane.

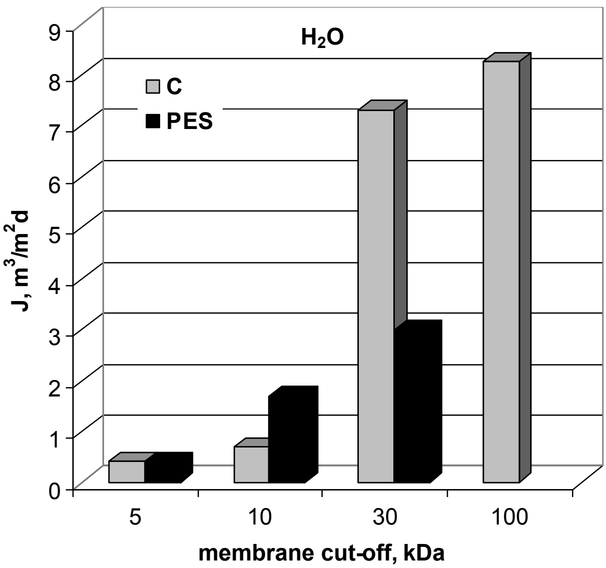

Fig. 3. Transport properties of ultrafiltration membranes (for distilled water) at transmembrane pressure 0.1 MPa
Rys. 3. Właściwości transportowe membran w odniesieniu do wody destylowanej przy ciśnieniu transmembranowym 0,1 MPa

The efficiency of natural organic matter separation 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. As can be inferred from the results presented, the increase of membrane cut-off resulted in decrease of NOM removal efficiency. Slightly higher values of retention factors obtained for PES membranes, as compared to observed for C membranes of the same value, result from higher hydrophobic sorption of macromolecules on strongly hydrophobic PES membranes (see 3.2.). For all membranes preferential decrease of colour over the UV 254 nm absorption was observed. This is evident, as the colour of water is related to the presence of the large fractions of NOM. 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 have no UV absorbance.

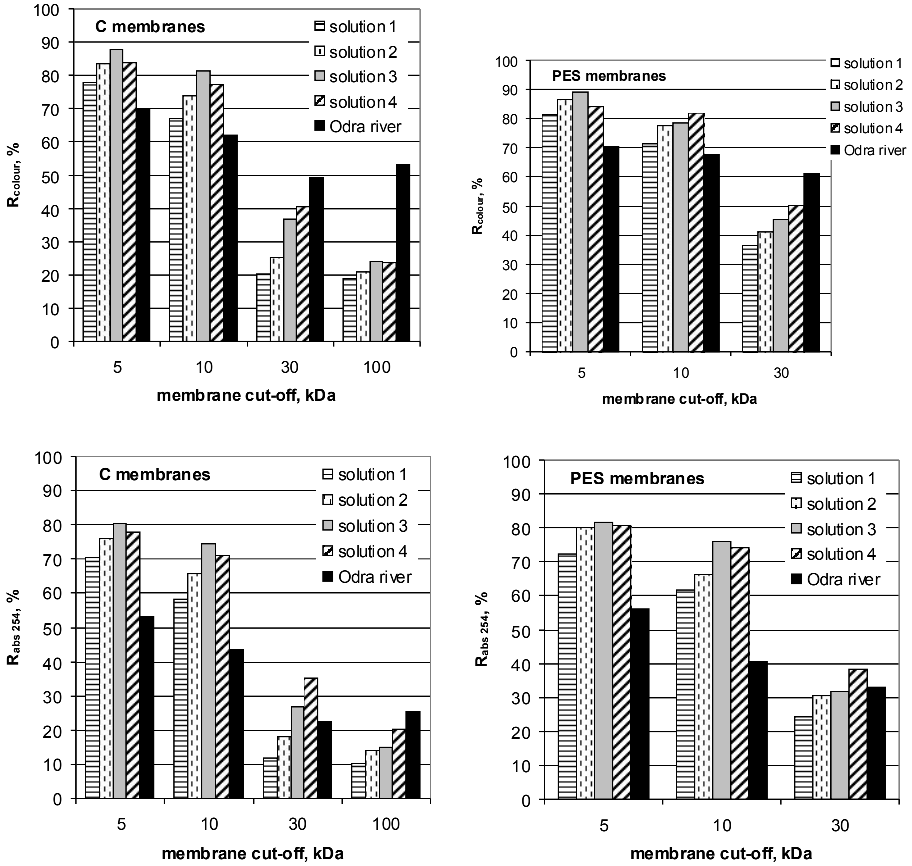

Fig. 4. Separation efficiency of natural organic matter by ultrafiltration membranes
Rys. 4. Skuteczność usuwania naturalnych substancji organicznych przy użyciu membran ultrafiltracyjnych

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 of experiments with different water compositions are presented in Fig. 5.

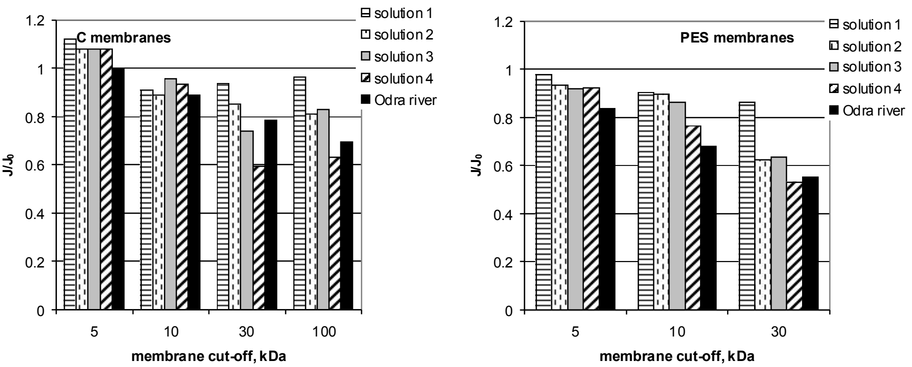

Fig. 5. The effect of membrane type and water properties on normalized flux
Rys. 5. Wpływ rodzaju membrany oraz właściwości roztworu na względną przepuszczalność membran

The experimental results obtained during ultrafiltration of water containing natural organic matter through C and PES membranes show that membrane fouling was strongly influenced by membrane type and amount of organic particles in treated water. The observed decrease in permeate flux for more hydrophilic C membrane was lower than that for more hydrophobic PES membrane. It is worth nothing that J/J_0 values decrease with increasing membrane cut-off. The obtained results suggest that decrease of membrane permeability results from NOM particles adsorption 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 with good agreement with findings of Dal-Cin et all. [10], who stated that when the pore size is considerably smaller than the foulant, the pore size of the membrane remains unchanged and the decrease of flux might be caused only due to surface adsorption of macromolecules. At the opposite, when the pore size is much larger than the foulant, macromolecule enters the pore, adsorbing on the pore walls and reducing the effective pore size. In such a situation 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. Moreover, high intensity of membrane fouling observed for all tested membranes in the case of Odra water ultrafiltration indicate, that inorganic substances present in water stimulate NOM particles deposition on membranes. They may act as bridges between NOM particles and membrane matrix or change spherical properties of organic macromolecules.

4. Conclusions

The objective of the reported research was to investigate the suitability of membrane ultrafiltration process to the treatment of waters containing natural organic matter. The results led to the following conclusions:

- compact ultrafiltration membranes (of low cut-off) allow to remove efficiently natural organic matter from water,
- the transport and separation properties of ultrafiltration membranes are strongly influenced by membrane cut-off and membrane material; retention of NOM particles decrease with the increase of membrane cut-off; while the opposite tendency 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. Membrane fouling increase when solutions of higher concentration of inorganic substances are treated.

Acknowledgments

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Ultrafiltracja jako metoda usuwania naturalnych substancji organicznych z wody

Streszczenie

Pogarszająca się jakość wód oraz rosnące wymagania stawiane wodzie przeznaczonej do spożycia przez ludzi powodują konieczność stosowania nowoczesnych procesów technologicznych ich uzdatniania. Taką techniką jest ultrafiltracja, proces membranowy pozwalający na usunięcie bardzo szerokiego spektrum zanieczyszczeń: zarówno mikroorganizmów jak i makrocząsteczek o wielkości 1 -100 nm. Do tej grupy zanieczyszczeń należą naturalne substancje organiczne, które zarówno niekorzystnie wpływają na jakość wody jak i na wydajność hydrauliczną membran poprzez ich blokowanie (*fouling*). O skuteczności usuwania naturalnych substancji organicznych z wody w procesie ultrafiltracji oraz podatności membran na blokowanie decyduje bardzo wiele czynników związanych zarówno z właściwościami membran jak i składem oczyszczanej wody.

Celem przeprowadzonych badań było określenie wpływu właściwości membran ultrafiltracyjnych; tj. ich granicznej masy molowej (*cut-off*) oraz polimeru z którego wykonane zostały membrany, jak również właściwości roztworu poddawanego oczyszczeniu na zmianę skuteczności oczyszczania wody, wydajność hydrauliczną membran oraz ich podatność na blokowanie. W badaniach zastosowano membrany ultrafiltracyjne firmy Nadir wykonane z regenerowanej celulozy oraz polieterosulfonu o cut-off 5 – 100 kDa. Testy przeprowadzone zostały dla roztworów modelowych oraz dla wody z rzeki Odry.

Przeprowadzone badania wykazały, iż dla wszystkich testowanych membran wzrost wartości ich granicznej masy molowej skutkował wzrostem wydajności hydraulicznej membran. Wykazano też, że zastosowanie membran o większych wymiarach porów skutkuje spadkiem skuteczności usuwania makrocząsteczek organicznych. Zaobserwowano, że charakter hydrofilowo/hydrofobowy polimeru membranotwórczego istotnie wpływał na intensywność blokowania membran. Większy spadek przepuszczalności hydraulicznej membran stwierdzono w przypadku użycia silniej hydrofobowych membran z polieterosulfonu. Analiza uzyskanych wyników badań pozwoliła także wykazać, że wzrost wartości *cut-off* membran skutkował silniejszym ich blokowaniem, będącym rezultatem zatykania porów membrany.