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COMPARISON OF POLYMERIC AND CERAMIC ULTRAFILTRATION MEMBRANES FOR SEPARATION OF NATURAL ORGANIC MATTER FROM WATER

The experiments were aimed at removing natural organic matter from water by ultrafiltration process. The water from the Odra River and model solution, being a mixture of dechlorinated tap water and humic water from peat-bog, were tested. 3 types of ceramic membranes with the cut-off values equal to 15, 50 and 300 kDa as well as 6 types of polymeric membranes made of polyethersulphone and regenerated cellulose with the cut-off of 5, 10 and 30 kDa were examined. The results obtained show the significant influence of membrane material on its transport and separation properties. For all the membranes examined, an increase in the cut-off value resulted in the rise in permeate flux. Among the membranes tested the highest permeate flux values were observed for polymeric membranes. The study has demonstrated that polymeric membranes are less prone to fouling. Polymeric membranes have separated natural organic matter particles more effectively compared with ceramic membranes of a similar cut-off. In the case of polymeric membranes, an increase in cut-off brought about a decrease in separation efficiency, while for ceramic membranes this relation was inverse.

1. INTRODUCTION

Membrane separation processes are widely used for water and wastewater treatment, and in food, chemical, nuclear, and pharmaceutical industries because this technology has high removal capacity and ability to meet multiple treatment objectives. In water and wastewater treatment, membrane processes provide an attractive alternative to conventional systems for desalination, ultra-pure water production, pathogen removal from water, and solid-liquid separation. With the membranes having high removal capacity, conventional coagulation/flocculation and sedimentation operations can be replaced with a single process. Nowadays membrane processes are considered to be the best available technologies (BAT).

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Currently, the development of membranes is encouraged by a scarcity of water resources, increasingly stringent regulations, and a consumer's demand for the water of higher quality. According to The Freedonia Group Report [1] membranes demand will be risen by 8.2% annually until 2012 and water/wastewater sector will remain the largest market (representing 51% of sales in 2007).

In drinking water treatment, ultrafiltration membranes are used for the removal or partial removal of microbiological contaminants, organic substances (e.g., natural organic matter (NOM)), and particles [2], [3]. In the treatment of natural waters, NOM is often found to be a major foulant [4]. Though NOM is not of a direct concern in drinking water, it may affect its quality by increasing the disinfectant and coagulant demand and providing substrates for disinfection by-products (DBP) formation. NOM can also form complexes with heavy metals and organic micropollutants and enhance bacterial regrowth in distribution system [5].

At present, in water treatment, polymeric membranes (e.g. made of cellulose materials or polysulphone) are of prime importance because of their low costs and great flexibility. However, it was found that such membranes were chemically and thermally susceptible and showed morphological changes when being in contact with solvents. Recently inorganic, mainly ceramic, membranes have been implemented in water treatment [6]. Ceramic membranes are prepared from metal oxides, e.g. alumina, zirconia or titania [7]. These membranes are of a great interest thanks to their mechanical, chemical, microbiological and thermal stability. Ceramic membranes are generally much more expensive with respect to membrane area compared with the membranes produced from organic materials, but in the last years their cost was sharply reduced [8]. The cost of using ceramic membranes is covered very quickly due to their high operating parameters and long service life (up to 10 years). According to The Freedonia Group Report [1], the demand for nonpolymeric materials, including ceramic, metal and composite types, is expected to record double-digit growth until 2012, mainly due to their better performance at extreme temperatures and greater pH ranges.

Ceramic membranes are not applied on a large scale in drinking water treatment; however, in the last years some big waterworks using inorganic membranes were built and run in Japan. In December 2006, the biggest in the world microfiltration ceramic membrane drinking water plant with the capacity of 38 000 m³/d started its operation in Hinogawa, Fukui, Japan. Treated water is provided to 170 000 people [9]. The cumulative capacity of Japanese waterworks using ceramic membranes amounted to 158 000 m³/d by August 2008 [10].

This paper reports the results of natural organic matter removal from water, using organic and inorganic ultrafiltration membranes. Its main aim was to compare the transport and separation properties of polymeric and ceramic membranes of various cut-off with respect to organic mater separation from model solution and riverine water.

2. EXPERIMENTAL

2.1. FEED SOLUTIONS

The experiments were carried out on the Odra River water and on model solution prepared from dechlorinated tap water and humic acid-rich water flowing out from peat-bog in the Table Mountains (Poland) (sampling point 50°27'29.97''N; 16°23'16.87''E). The NOM concentration was monitored by the measurements of the UV absorbance at 254 nm and the colour intensity (Shimadzu UV1240 spectrophotometer). The properties of feed solutions are given in table 1.

Table 1

The feed water properties (mean values)

Parameter	The Odra River	Model solution
Colour, g Pt/m ³	25.4	32.0
UV 254 nm absorbance, cm ⁻¹	0.154	0.225

2.2. MEMBRANES AND EXPERIMENTAL PROCEDURE

3 ceramic and 6 polymeric membranes were tested and compared with respect to NOM removal. Tubular ceramic membranes of 15, 50 and 300 kDa MWCO supplied by Tami Ind. were made of zirconium-titanium oxides. The length of the membranes amounted to 0.25 m, their internal diameters were equal to 6 mm and 2 mm, respectively, for 1-channel (15 and 50 kDa) and 7-channel (300 kDa) membranes. The filtration area of 1-channel 15- and 50-kDa membranes amounted to $4 \cdot 10^{-3} \text{ m}^2$, while the surface of 7-channel 300-kDa membrane was equal to $13 \cdot 10^{-3} \text{ m}^2$. Membrane experiments were performed in a pilot plant delivered by J.A.M. INOX PRODUKT. The experimental UF set-up is presented in figure 1. It consisted of reservoir tank (10 dm³), a pump, pressure gauges, membrane module and flowmeter for retentate. Both retentate and permeate were recirculated to the stirred feed tank in order to achieve steady-state operation. The system was thermostated and the temperature of the water was kept at 20 °C. The process was run at a pressure of 0.2 MPa. All experiments were carried out in two replications to validate the results obtained.

Polymeric membranes of 5, 10 and 30-kDa cut-off were made of polyethersulphone (PES) and regenerated cellulose (C). Flat membranes were delivered by Microdyn Nadir and used for the experiments carried out in a laboratory system at a trans-membrane pressure of 0.2 MPa. The main part of the system was an Amicon stirred ultrafiltration cell (model 8400) with gas coming out from a cylinder. The effective surface of the membrane amounted to $4.52 \cdot 10^{-3} \text{ m}^2$.



Fig. 1. Ultrafiltration cross-flow system

Volumetric fluxes (J , $\text{m}^3/\text{m}^2\text{d}$) and solute rejections (R , %; calculated as $(1 - C_P/C_F) \cdot 100$, where C_P and C_F are the solute concentrations in the permeate and feed streams, respectively) were measured in order to characterize the transport and separation properties of membranes.

3. RESULTS AND DISCUSSION

3.1. TRANSPORT PROPERTIES OF MEMBRANE

The transport properties of membranes were determined based on their permeate flux (J), and the results obtained are given in figure 2. It shows that membrane hydraulic efficiency depends significantly on membrane cut-off and material. For all the membranes examined, the distilled water flux increases with an increase in the cut-off value.

Of all the polymeric membranes tested the membrane with 30-kDa cut-off made of regenerated cellulose ($12.79 \text{ m}^3/\text{m}^2\text{d}$) has the highest permeability. For 30-kDa polyethersulfone membrane permeate flux amounted to $4.11 \text{ m}^3/\text{m}^2\text{d}$. In the group of ceramic membranes tested, the highest permeate flux, i.e. $3.43 \text{ m}^3/\text{m}^2\text{d}$, was observed for 300-kDa membrane. Based on the present results it may be inferred that hydraulic permeability of polymeric membranes was higher than that of ceramic membranes.

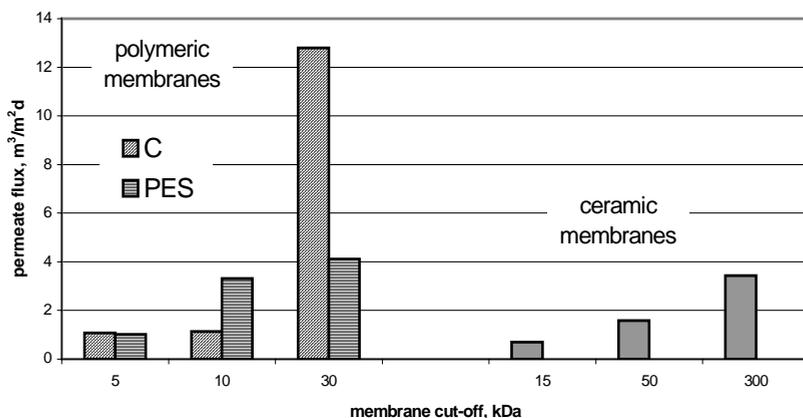


Fig. 2. Distilled water flux for polymeric and ceramic membranes

A similar dependence as that for distilled water was observed for all the membranes used for filtering the Odra River water and model solution (figure 3) – the membranes with higher cut-off values allowed higher permeate flux to be achieved. It was also observed that permeate flux values for the Odra River water and model solution were lower than those for distilled water.

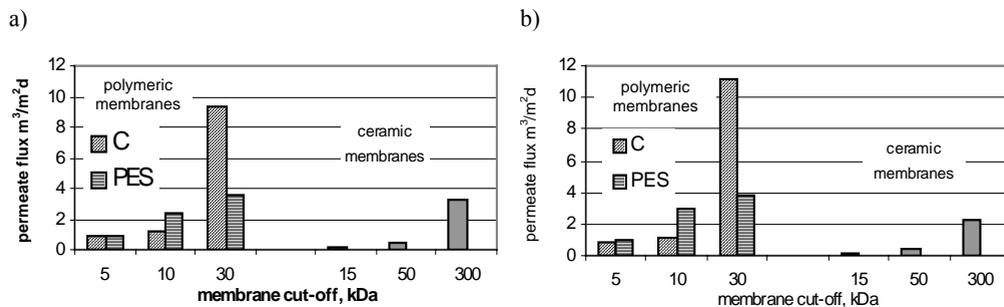


Fig. 3. Influence of membrane type and cut-off value on permeate flux for: the Odra River water (a) and model solution (b)

Membrane material significantly influenced the transport properties of membranes when solutions containing different additives (the Odra River or model solution) were filtered. As in the case of distilled water, the highest permeate flux was observed for polymeric membranes. For example, the value of model solution permeate flux for regenerated cellulose 30-kDa membrane amounted to $11.22 \text{ m}^3/\text{m}^2 \cdot \text{d}$ and for polyethersulphone membrane – $3.79 \text{ m}^3/\text{m}^2 \cdot \text{d}$. When ceramic membranes were used in filtration of model solution the permeate flux was significantly lower, i.e. $0.14 \text{ m}^3/\text{m}^2 \cdot \text{d}$ and $2.33 \text{ m}^3/\text{m}^2 \cdot \text{d}$, respectively, for 15-kDa and for 300-kDa membranes (figure 3b).

As solution pH may influence the membrane properties and the character of natural organic matter, in the next step of experiments the influence of this parameter on membrane transport properties was analysed. Generally, an increase in pH from 5 to 10 brought about the decline of permeate flux (figure 4). For example, for 10-kDa PES membrane at pH of feed solution equal to 5, the permeate flux reached $1.99 \text{ m}^3/\text{m}^2\cdot\text{d}$, while at pH 10 it was $1.30 \text{ m}^3/\text{m}^2\cdot\text{d}$. For the polymeric membranes made of regenerated cellulose the influence of feed pH on membrane permeability was not unequivocal. For those membranes, in the analysed feed solution range of pH, the permeate flux approached $1.1 \text{ m}^3/\text{m}^2\cdot\text{d}$. The operation of ceramic membranes with a cut-off value comparable to that of polymeric membranes (15 kDa) is similar to the operation of polyethersulphone membranes: a permeate flux declined together with pH increase – for the model solution with pH 5 the permeate flux equalled $0.62 \text{ m}^3/\text{m}^2\cdot\text{d}$, for pH 10 it was significantly lower and equalled $0.21 \text{ m}^3/\text{m}^2\cdot\text{d}$.

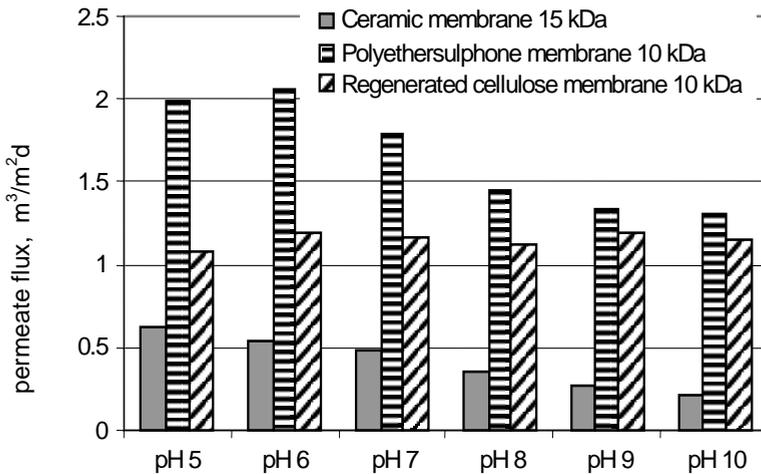


Fig. 4. pH of feed solution versus permeate flux for organic and inorganic membranes (model solution)

Membrane susceptibility to fouling proved to be a very important factor if the membrane usability in water treatment was taken into account. Membrane proneness to fouling was studied in terms of the normalized permeate flux J/J_0 (J – the permeate flux, J_0 – the distilled water flux). Analysing the data given in figure 5 it might be noticed that ceramic membranes, especially those with lower cut-off values, were much more prone to fouling than polymeric ones. J/J_0 values for organic membranes cover the range from 0.7 to 1.0, while for inorganic membranes the value was below 0.3 except 300-kDa ceramic membrane (J/J_0 was close to 1.0).

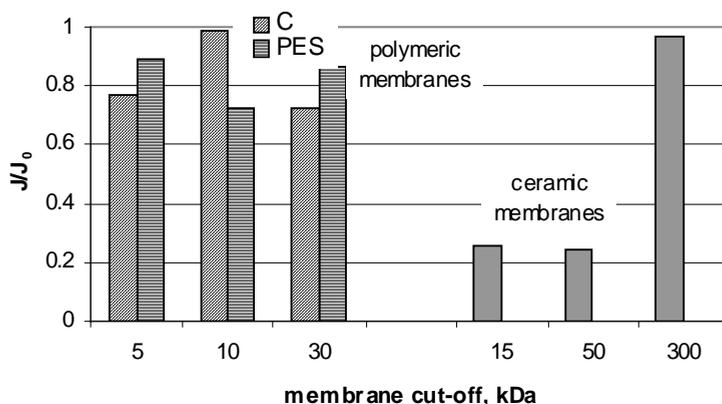


Fig. 5. The influence of membrane type on relative permeate flux (the Odra River water)

A decrease in the membrane permeability was due to the changes in its total resistance. The resistance depends on the membrane cut-off, membrane material and feed solution composition. It can be calculated using the Hagen–Poiseuille equation:

$$J = \frac{\Delta p}{\mu \cdot R},$$

where:

Δp – the transmembrane pressure (MPa),

μ – the dynamic viscosity factor (Pa·s),

R – the total membrane resistance (m^{-1}).

The total membrane resistance (R) equals the membrane structure resistance (R_{mem}) while filtering distilled water, but when filtering the Odra River water or model solution, R is the sum of R_{mem} , R_f and R_{pol} , where R_f stands for the resistance coming from membrane surface and pore blocking by substances present in solution (m^{-1}); R_{pol} is the resistance of polarizing layer near membrane surface (m^{-1}).

The total membrane resistances to distilled water, the Odra River water and model solution ultrafiltration at the transmembrane pressure $\Delta p = 0.2$ MPa were given in table 2.

Based on the data in table 2 one can conclude that for both types of the membranes tested (organic and inorganic) the membrane total resistance decreased along with the cut-off increase. This effect was observed when both distilled water and water contaminated with organics were ultrafiltered. The comparison of the total resistance values of organic and inorganic membranes (of similar cut-offs) revealed that R for inorganic membranes was significantly higher than that for organic ones. For example, R for the model solution subjected to ultrafiltration through 10-kDa PES membrane amounted to $0.55 \cdot 10^{13} \text{ m}^{-1}$, while for 10-kDa C membrane – $1.53 \cdot 10^{13} \text{ m}^{-1}$. For 15-kDa ceramic membrane the resistance was $11.93 \cdot 10^{13} \text{ m}^{-1}$.

Table 2

Total membrane resistances to various feed solutions

Membrane	Polymeric membranes						Ceramic membranes		
	C			PES					
Cut-off (kDa)	5	10	30	5	10	30	15	50	300
Feed solution type	Membrane total resistance (m^{-1})								
Distilled water	$1.53 \cdot 10^{13}$	$1.45 \cdot 10^{13}$	$0.13 \cdot 10^{13}$	$1.63 \cdot 10^{13}$	$0.50 \cdot 10^{13}$	$0.40 \cdot 10^{13}$	$2.38 \cdot 10^{13}$	$1.04 \cdot 10^{13}$	$0.48 \cdot 10^{13}$
Odra River water	$2.00 \cdot 10^{13}$	$1.47 \cdot 10^{13}$	$0.18 \cdot 10^{13}$	$1.83 \cdot 10^{13}$	$0.68 \cdot 10^{13}$	$0.46 \cdot 10^{13}$	$9.51 \cdot 10^{13}$	$4.33 \cdot 10^{13}$	$0.50 \cdot 10^{13}$
Model solution	$2.00 \cdot 10^{13}$	$1.53 \cdot 10^{13}$	$0.15 \cdot 10^{13}$	$1.77 \cdot 10^{13}$	$0.55 \cdot 10^{13}$	$0.43 \cdot 10^{13}$	$11.93 \cdot 10^{13}$	$3.97 \cdot 10^{13}$	$0.71 \cdot 10^{13}$

As can be inferred from table 2 and figure 6, the type of feed solution significantly affected membranes' resistance and their vulnerability to fouling, especially in the case of inorganic membranes. A total membrane resistance to the Odra River water was much higher than that to model solution. The riverine water contained, apart from natural organic matter, various inorganic additives, which stimulated interactions between pollutants and membrane and were responsible for a stronger membrane blocking.

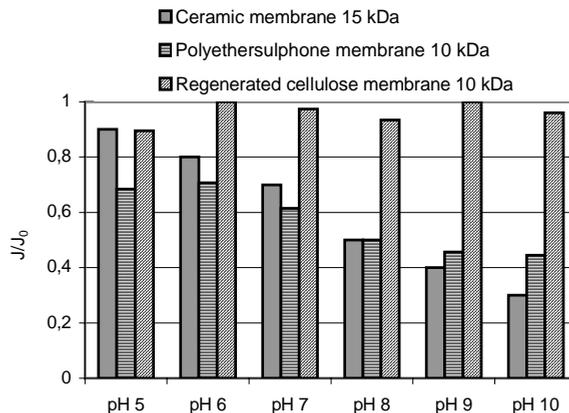


Fig. 6. Solution pH versus relative permeate flux (model solution)

The results obtained during ultrafiltration of water model solution of various pH (figure 6) show that membrane fouling was greatly affected by the changes of water acidity/alkalinity, which can be exemplified by an increase in pH that caused the decrease of J/J_0 values of PES and ceramic membranes. As ELIMELECH et al. [11] observed with an increase in the solution pH, preferential anion adsorption on mem-

branes may be observed. As anions are less hydrated than cations, they can approach more closely the membrane and reduce their pore sizes. In pH range from 5 to 10, the relative membrane permeability (J/J_0) for 10-kDa PES membrane decreased from 0.68 to 0.45, while for 15-kDa ceramic membrane – from 0.90 to 0.30.

3.2. SEPARATION PROPERTIES OF MEMBRANES

The effectiveness of water purification was evaluated on the basis of colour and absorbance removal. As can be seen in figure 7, with an increase in the polymeric membrane cut-off the NOM retention decreases. The results obtained for ceramic membranes display different tendency: NOM removal increases together with the membrane cut-off increase. This completely unexpected tendency was observed for the Odra River water and for model solution. For example, 30-kDa PES membrane retained colour in 59% (the Odra River water) and 68% (model solution), while 50-kDa ceramic membranes – in 60% (the Odra River water) and in 61% (model solution).

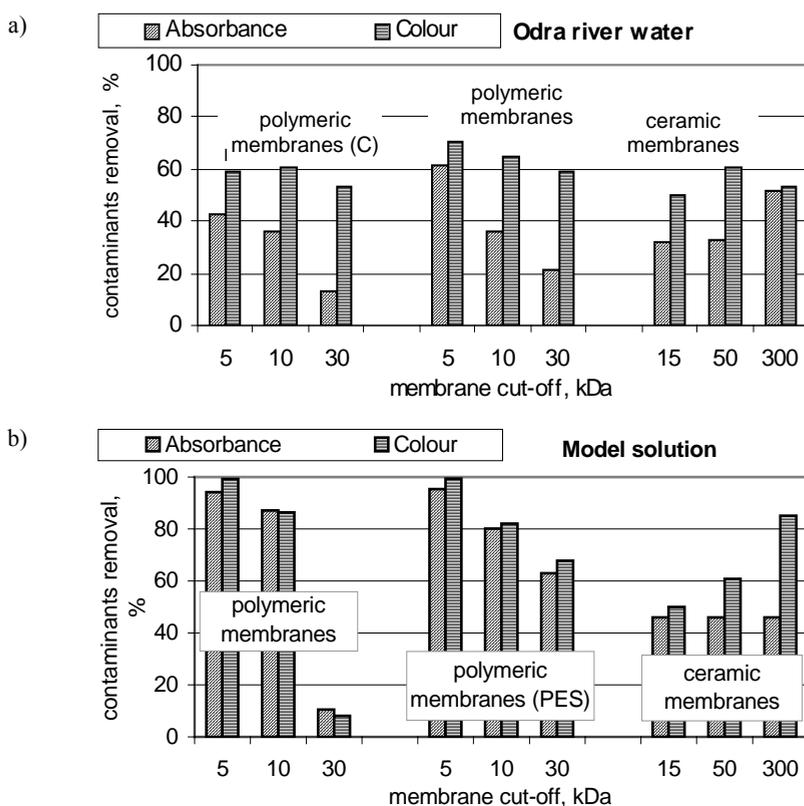


Fig. 7. The efficiency of organic substance removal on organic and inorganic membranes for: the Odra River water (a) and model solution (b)

The composition of feed solution considerably influenced the effectiveness of organic substance removal (figure 7). Except for the cellulose membranes with the 30-kDa cut-off, the colour and absorbance removal increased along with NOM concentration increase. For example, the absorbance removal by 5-kDa regenerated cellulose membrane reached only 43% for the Odra River water, while for the model solution it amounted to 94%. Similar phenomenon was observed for ceramic membranes, i.e. for 15-kDa membrane the absorbance removal reached only 32% for the Odra River water, but 46% for model solution. The effect of NOM separation was also affected by the presence of different inorganic substances in the riverine water. Inorganic ions may change the structure of NOM macromolecules and their surface charge, and as a result the facilitated transport of organic substances may occur.

The analysis of the results obtained reveals a significant influence of solution pH on the separation efficiency of the membranes tested (figure 8). For all the membranes tested an increase in solution pH from 5 to 10 resulted in an increase in retention of NOM particles (expressed as removal of absorbance at 254 nm or colour). At pH 5, NOM molecules are slightly dissociated – their hydrodynamic radii are small and they can easily penetrate through the membranes. With an increase in solution pH, dissociation of phenolic and carboxylic groups appears and expansion of macromolecule structure is observed. As a result, a high concentration of NOM particles is observed. Moreover, as we mentioned in paragraph 3.1, a possible sorption of anions onto pore walls may decrease the pore diameter and cause higher retention of organic substances. When pH of feed solution exceeded 6, over 90% retention of organic substances was observed on both organic and inorganic membranes of comparable cut-off values.

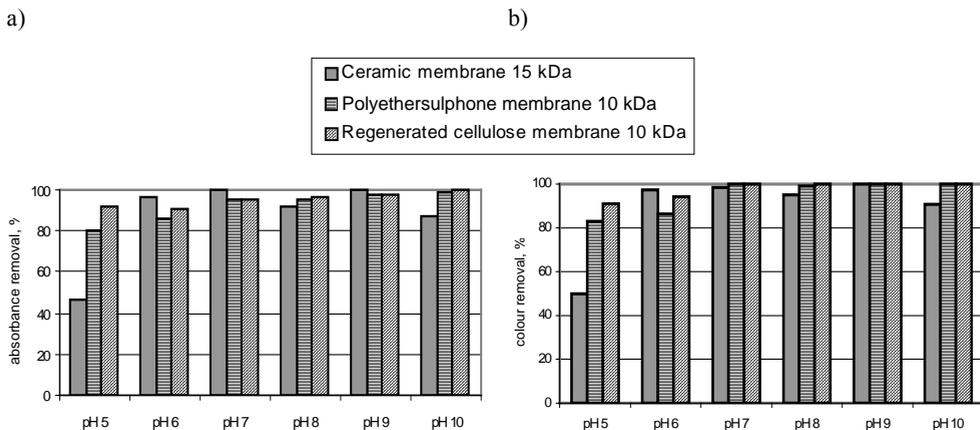


Fig. 8. pH of feed solution versus absorbance (at 254 nm) removal (a) and colour removal (b) by organic and ceramic membranes (model solution)

4. SUMMARY

The objective of the research was to compare the transport and separation properties of organic and inorganic ultrafiltration membranes when applied in natural organic matter removal from water. The results obtained led to the following conclusions:

- polymeric membranes are characterized by higher values of hydraulic permeability compared to ceramic membranes;
- organic membranes are less prone to fouling;
- separation properties of ceramic and organic membranes are comparable; an increase in the ceramic membrane cut-off resulted in an increase in NOM retention, while in the case of polymeric membranes this relationship was inverse;
- for both types of the membranes tested the changes of solution pH resulted in an increase in membrane fouling intensity as well as in organic substance retention.

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