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Retention of bisphenol A and caffeine on PES/PES-CNTs membranes—performance and effect of different conditions

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ABSTRACT

This study describes retention and fouling behavior of polyethersulfone/polyethersulfone-carbon nanotube (PES/PES-CNT) membranes in different filtration conditions. PES/PES-CNT membranes were prepared by inverse-phase method. Single-walled CNTs and single-walled CNTs functionalized with carboxyl group were employed for a modification. PES was selected as basic membrane material. Retention tests were carried out for two organic chemicals, that is, bisphenol A and caffeine. It was found that retention of micropollutants was mainly dependent on their physicochemical properties and membrane type. Removal of highly hydrophobic substance: bisphenol A was higher than for caffeine, which has hydrophilic character. Adsorption on membrane played a key role in their removal. Adsorption was more intensive on modified membrane as an effect of occurrence of nanotubes in its structure and surface. In other words, CNTs enhanced sorption potential of nanocomposite membranes. Moreover, modified membranes had better antifouling properties.

Keywords: Nanocomposite membrane; Micropollutants; Antifouling properties

1. Introduction

Ultrafiltration process which is employed to remove colloids, bacteria, and macromolecules can be also applied to eliminate micropollutants. Retention of these compounds reaches level of 80% and is an effect of adsorption on membrane material [1,2]. In that context of ultrafiltration special attention is focused on nanocomposite membrane. It is a new type of ultrafiltration membrane containing nanoparticles resulting in formation of structure and surface with better properties than conventional ultrafiltration membrane. Many authors suggest that nanocomposite membranes have better antifouling properties and combination of transport-retention characteristic [3,4].

Carbon nanotubes (CNTs) and nano-titanium dioxide (TiO_2), among other nanoparticles, seem to be the most promising to improve the transport and retention properties of polymer ultrafiltration membranes [5,6]. Larger specific surface area and other unique properties, which result from the nano size, make them better materials in comparison with their counterparts, that is, conventional activated carbons or non-nanosized metal oxides.

In case of CNTs or fullerene, membrane has very good adsorption potential and can be employed to micropollutant removal. Most likely, the first use of membranes modified with nanoparticles as an effective barrier to removal of xenoestrogens in the ultrafiltration was presented by Jin et al. [7]. A fullerene-modified polymer membrane (2–10 wt%) was used in their experiment. As a result, the obtained nanocomposite membrane was characterized by much greater porosity, which allowed for almost fivefold higher hydraulic efficiency and at the same

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time, for high retention coefficient for estrone, this is 98.8%. Another example is the use of a nanocomposite membrane (polyethersulfone [PES]-montmorillonite) for the removal of nitrophenol [8]. The study of Karkooti et al. [9] showed that graphene-based nanocomposite membrane demonstrates better water flux and removal of organic matter. You et al. [10] fabricated high-flux thin-film nanocomposite ultrafiltration membrane with high rejection rate (99.5%) in oil/water emulsion separation. Nanocomposite membranes are often used in nanofiltration and reverse osmosis for salt rejection and dye removal [11–14]. Besides water purification, many other applications have been tested by means of nanocomposite membranes, that is, proton exchange membrane fuel cells [15], sensor applications [16,17] and pervaporation [18,19].

With respect to the application of such nanocomposite film in pressure-driven membrane processes, the most important factors are the resulting changes of hydrophilicity and the coupled alterations of the fouling resistance of the membrane. Addition of CNTs functionalized with carboxylic groups to the polymer membranes is a strategy to control fouling by modifying their hydrophilicity and also giving the membrane an electric charge [20].

Our previous study showed that ultrafiltration with nanocomposite membranes has a potential to remove micropollutants. However, impact of pH and concentration of micropollutants in the feed is unknown. Therefore, in this study, we evaluate their retention potential vs. micropollutants with opposite properties. Additionally, filtration was carried out under different conditions.

2. Materials and methods

2.1. Materials

Single-walled carbon nanotubes (SWCNT) and SWCNTs functionalized with carboxyl groups (SWCNT-COOH) were obtained from Chengdu Organic Chemicals Co. Ltd. (Chengdu, China), Chinese Academy of Sciences, and used for membrane modification. PES as the basic material for membrane preparation was supplied by BASF company (Ludwigshafen, Germany). *N,N*-dimethylformamide (DMF), acetonitrile and methanol for high-performance liquid chromatography (HPLC), (all analytically pure) were purchased from Avantor Performance Materials, Inc. (Central Valley, Pennsylvania, USA). Deionized water was taken from Milli-Q water purification system (Millipore LLC, Poland).

2.2. Micropollutants and feed water

Bisphenol A (BPA) and caffeine (CAF) were purchased from Sigma-Aldrich (Poland) in analytical purity grade. Their physicochemical properties are presented in Table 1. The stock solutions of BPA and CAF were prepared with methanol (1 g/L). The feed solution for retention tests was prepared by diluting the stock solution with deionized water. pH of feed solution was adjusted to 5.6, 7.25, or 9 using 0.1 M NaOH and 1 M HCl.

Concentrations of BPA and CAF in feed and permeate were determined by solid-phase extraction and HPLC. For SPE, plastic columns filled with C18 phase (Supelco) were used. At first, C18 cartridges were washed with 5 ml of acetonitrile, 5 ml of methanole and 5 ml of deionized water. After this, 20 mL of sample was passed through columns. Then, when column was completely dried, cartridges were flushed with ACN/methanole (60/40) solution. Eluted portion was analyzed using HPLC at a wavelength 272 nm (for CAF) and 220 nm (for BPA). Chromatograph was equipped with chromatographic column and UV-vis detector. Mobile phase contained 95% of ACN and 5% of deionized water. Recovery of compounds had level 85%–100% and 75%–86% for CAF and BPA, respectively. Retention of BPA and CAF was calculated according to the following equation:

$$R = \frac{C_f - C_p}{C_f} \cdot 100\% \tag{1}$$

where R is removal degree (%), C_f and C_p are concentrations of micropollutants in feed and permeate water, respectively (mg/L).

2.3. Membrane preparation

Membranes were prepared by phase-inversion method. Casting solution consisted of 16 wt% of PES and less than 84 wt% of DMF. Content of SWCNT and SWCNT-COOH in solution was kept at 0.02 and 0.05 wt%. Exact contribution of CNTs and PES in casting solutions was presented in Table 2. Proper amount of CNTs and PES was added to the DMF. Casting solution was shaken for 20 h to obtain homogeneous solution. After that, membranes were cast using doctor blade with 0.2 mm thickness on glass plate and immediately immersed in deionized water at ± 20°C. Precipitated membranes were stored in deionized water at temperature 7°C for 24h for their stabilization.

2.4. Measurement of contact angle (CA)

Measurements of CA were performed using the goniometer (Pocket Goniometer PG-1) and the sessile drop

Table 1
Selected properties of micropollutants

Symbol	Bisphenol A	Caffeine
Molar mass, g/mol	228.29	194.19
Solubility in water at 25°C, mg/L	120	21,600
Log K_{ow}	3.32	–0.07
pKa	9.6	14.0

Table 2
Contribution of ingredients in casting solution

Symbol	PES (wt%)	CNTs contribution (wt%)	DMF (wt%)
PES-pristine	16	–	84.00
PES-SWCNT-COOH-0.02	16	0.02	83.98
PES-SWCNT-COOH-0.05	16	0.05	83.95
PES-SWCNT-0.05	16	0.05	83.95

method was applied, where 10 strips of dried tested membrane were inserted into device. By syringe on top drop of distilled water was applied on membrane surface. Trough enlarged projection of water drop on gauge, value of CA was measured. For every type of membrane, 10 samples were measured and average value was calculated.

2.5. Measurement of membrane porosity

Sheet of membrane with calculated surface was dried by paper towel and then weighted in wet state. After this, the same membrane was dried in an oven in 60°C for 24 h and then weighted in dry state. Five sheets of each membrane were used for this measurement. Equation for a calculation of the membrane porosity is as following:

$$\varepsilon = \frac{m_w - m_d}{AL\rho} \cdot 100\% \tag{2}$$

where ε is porosity (%), m_w is weight of wet membrane (g), m_d is weight of dry membrane (g), A is area of membrane (cm$^{2)}$, L is membrane thickness (cm), and ρ is pure water density (about 0.998 g/mL).

2.6. Setup and filtration run

Retention tests were carried out in ultrafiltration setup consisted of (a) bottle of nitrogen gas, (b) pressure reducer, (c) filtration cell, and (d) volume measuring system, as shown in Fig. 1. Mounted membranes had an area 38.5 cm^2.

Ultrafiltration was carried out for all membranes at 0.75 bar. Experiment included two stages: (1) membrane conditioning with deionized water and (2) retention tests with feed water. All stages were conducted in the same conditions, that is, transmembrane pressure, temperature, and velocity. For each stage flux was measured and calculated from the following equation:

$$J_V = \frac{V}{A \cdot t} \tag{3}$$

where J_v is flux (L·m^{-2}·h$^{-1)}$, V is permeation volume (L), A is membrane effective area (m^2), and t is permeation time (h).

Additionally, fouling index was calculated, following to the equation:

$$\text{FI} = \frac{J_p}{J_{\text{pw}}} \tag{4}$$

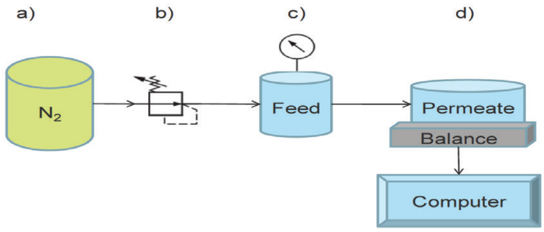

Fig. 1. Ultrafiltration setup.

where FI is fouling index (–), J_p is permeate flux, and J_{pw} is pure water flux.

3. Results

3.1. Membrane characterization

As seen in Fig. 2, the CA of membranes varied from 54.8° to 77.6°, which corresponds to moderate hydrophobic–hydrophilic properties. The pristine PES membrane had an initial CA 65.8°, similarly to membrane PES-SWCNT-COOH-0.05 with CA 68.1°. Interestingly, significantly better hydrophilic properties had membrane PES-SWCNT-0.05, while the highest hydrophobicity was observed for PES-SWCNT-COOH-0.02. This effect is difficult to explain. On one hand, oxygen functional groups located on the surface of SWCNT-COOH should have increased the hydrophilicity of the membrane. On the other hand, membrane PES-SWCNT-0.05 should have exhibited the highest hydrophobicity as was to be expected, due to hydrophobic character of unfunctionalized CNTs. This divergence could be caused by haphazard distribution of nanotubes in the membrane structure. It can lead to the lack of nanotubes in some parts of the membrane and their very high concentration in another part.

Apart from PES-SWCNT-COOH-0.02, modification of membranes with CNTs did not affect significantly porosity of membranes (Table 3). More specifically, porosity varied from 32.6% for PES-SWCNT-0.05 to 37% for PES-SWCNT-COOH-0.05.

3.2. Micropollutants removal

Fig. 3 illustrates removal of BPA and CAF on nanocomposite membranes in comparison with pristine membrane. It seems clear that filling of PES membranes with CNTs is favorable to improve their retention performance. Retention of CAF on pristine membrane was negligible (7%), while average (41%) on PES-SWCNT-COOH-0.05 and very high (86%) on PES-SWCNT-0.05 membrane. BPA, as a compound with

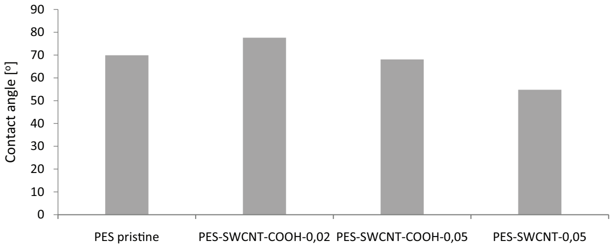

Fig. 2. Water contact angle of the PES/PES-CNTs membranes modified with carbon nanotubes.

Table 3
Porosity of PES/PES-CNTs membranes

Symbol	Porosity (%)
PES-pristine	35.8
PES-SWCNT-COOH-0.02	23.3
PES-SWCNT-COOH-0.05	37.0
PES-SWCNT-0.05	32.6

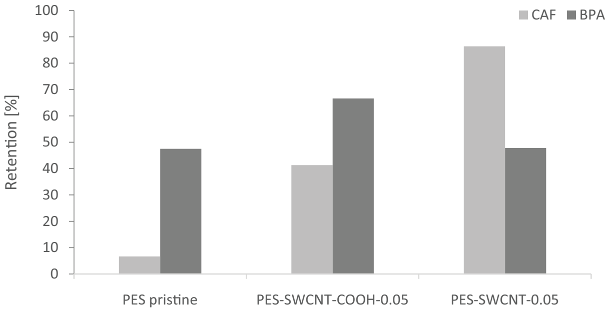

Fig. 3. Effect of membrane type on BPA and CAF retention.

high value of log Kow, has higher affinity to adsorption than CAF, therefore retention behavior of both chemicals was different. Retention of BPA on pristine PES membrane was at the same level (47%) like on PES-SWCNT-0.05 and the highest for PES-SWCNT-COOH-0.05. This effect is difficult to explain. On one hand, CNTs in the membrane should intense sorption. On the other hand, the CA of PES-SWCNT-0.05 is evidently lower than pristine PES. In this case, the higher hydrophilicity of PES-SWCNT-0.05 lead to higher fluxes and faster mass transport through membrane that could disturb and hold back micropollutant adsorption and retention. The highest adsorption of BPA on PES-SWCNT-COOH-0.05 can be effect of high hydrophobicity of membrane (similar to pristine PES) and additional adsorption sites from SWCNT-COOH.

Fig. 4 shows the removal degree of BPA and CAF for different loadings of SWCNT-COOH in membranes. Obviously, loading of nanotubes affect the retention efficiency of membranes. The increase of SWCNT-COOH loading caused a considerable increase in the retention of micropollutants. Addition of nanotubes changed hydrophilicity and structure of membrane. Through this change, membrane with higher content of SWCNT-COOH retained more contaminants. Some authors suggest that introduction of CNTs into membrane enhance retention of micropollutants as an effect of their adsorption by CNTs [3,6,8].

Fig. 5 shows that retention of BPA increased with an increase in initial concentration. On the contrary, retention of CAF decreased with the increase of initial concentration. Differences in physicochemical properties of BPA and CAF affected their opposite behavior during filtration. BPA is hydrophobic compound, while CAF is highly hydrophilic. In case of BPA, as highly hydrophobic compound, the initial concentration supplies the indispensable driving force to overcome the mass transfer resistance of compounds between the aqueous phase and the solid phase. Higher initial concentration can enhance the interaction between adsorbate molecules and the available sorption sites on the PES-SWCNT-COOH-0.05 membrane. Therefore, an increase of BPA initial concentration boosted the retention. This effect was not observed for CAF due to its high solubility in water and hydrophilic character.

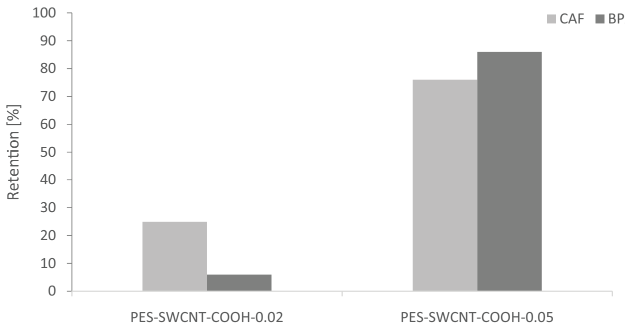

Fig. 4. Effect of SWCNT-COOH loading on micropollutants removal.

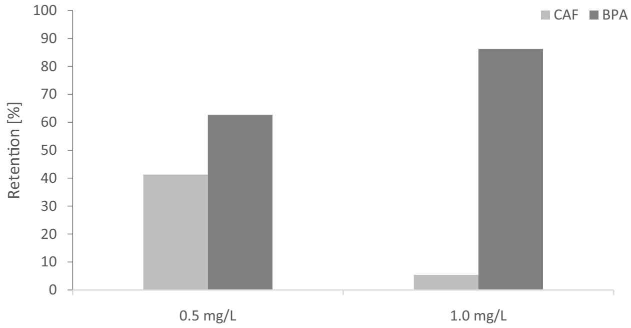

Fig. 5. Effect of concentration of micropollutants on their retention (for PES-SWCNT-COOH-0.05).

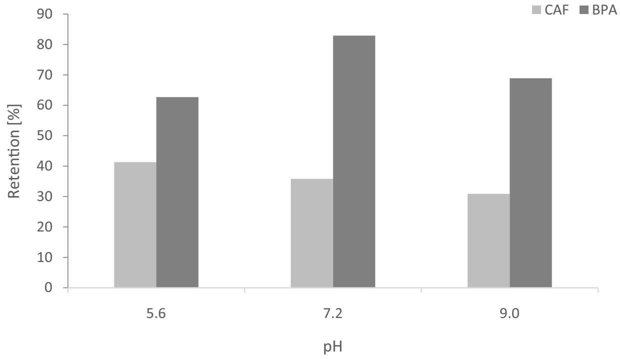

Fig. 6. Effect of pH on BPA and CAF retention for membrane PES-SWNCT-COOH-0.05.

The pH of feedwater affects the retention performance because of its impact on the surface properties of membrane and stability and chemical structure of BPA. This test was conducted for membrane PES-SWCNT-COOH-0.05, because pH has an impact on the chemical form of carboxyl group (Fig. 6). The retention of CAF was at relatively similar level between pH 5 and 9, due to unchangeable form of CAF at these conditions. On the contrary, retention of BPA varied greatly depending on pH. The lightly lower retention at pH 5.6 arose from the incomplete solubility of BPA in an acid medium. The highest retention of BPA was obtained at pH 7 as an effect of the most intensive adsorption. Interestingly at pH 9 retention of BPA was reduced to 69%. On the one hand, in alkaline condition, retention of weak acid micropollutants such as BPA is higher as an effect of repulsion between dissociated form of chemical and negatively charged membrane surface. On the other hand, this repulsion weakens the adsorption process considered as main retention mechanism for nanocomposite ultrafiltration membrane.

3.3. Flux and fouling behavior

Fig. 7 shows volumetric permeate flux for studied membranes. Differences in flux came from divergences in their structural and surface properties. Important factors are in this case: membrane structure, porosity, and hydrophobicity/hydrophilicity. For example, porosity as well as CA of membranes PES pristine and PES-SWCNT-COOH-0.05 were similar and permeation of these membranes was practically at the same level. The combination of the lowest porosity and hydrophilicity (CA = 77°) of membrane PES-SWCNT-COOH-0.02 results in the lowest flux. Membrane PES-SWCNT-0.05 had very good hydrophilic properties and on the other hand average porosity and therefore intermediate flux of this membrane is related to these properties.

These results do not show clear impact of CNTs addition on permeability of nanocomposite membranes. Probably it was caused by a complex impact of CNTs on some properties of membranes such as structure, porosity, and hydrophilic/hydrophobic character. On the contrary, many authors observed an increase of permeate flux in nanocomposite membranes [21–23]. Zhao et al. [24] suggested that the higher water flux of polyamide/MWCNTs composite membranes compared with pristine polyamide membrane was attributed to (1) the formation of water channel by aligned MWCNT and (2) stronger hydrophilicity and charge of membrane. An increase in water flux with an increase in amount of nanoparticles in the membrane was observed in many studies [25]. Interestingly some authors point out concentration threshold (or range) of nanoparticles, which enhances membrane water flux. Other concentrations of nanotubes affect unfavorably on membrane water permeation [26,27].

To evaluate fouling tendency of studied membranes fouling index was calculated (Fig. 8). It was found that there is much difference between fouling tendency of PES/PES-CNTs membranes. The highest fouling was observed for PES-SWCNT-COOH-0.02. The high hydrophobicity and low porosity of this membrane can be considered as the two main factors responsible for its low fouling resistance. For PES-SWCNT-COOH-0.05 and PES-SWCNT-0.05, fouling index was higher than 1 meaning that feed permeation was higher than initial water permeation. In other words, the tendency of modified membranes with higher CNTs loading (0.05% wt) to fouling is low compared with pristine PES membrane.

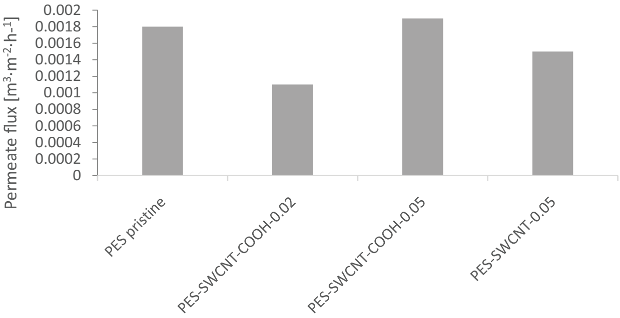

Fig. 7. Permeate flux of PES/PES-CNTs membranes.

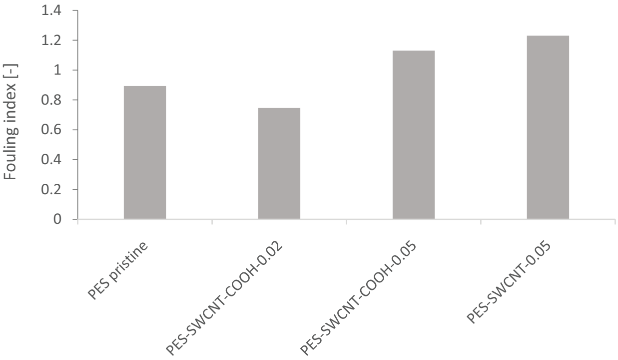

Fig. 8. Fouling index for PES/PES-CNTs membranes.

4. Conclusions

Nanocomposite PES membranes were prepared by introduction of CNTs to the casting solution at different concentration. No clear influence of the CNTs loading on porosity and hydrophilic/hydrophobic properties has been detected. This was related to uneven distribution in the membrane structure.

It was found that removal of BPA and CAF was higher for nanocomposite membranes than for pristine PES. Increasing the SWCNT-COOH content increased the removal of micropollutants. The retention effect was related to adsorption of micropollutants in membrane material, therefore nanocomposite membrane with higher adsorption potential was more effective in the removal of micropollutants. Differences between removal of BPA and CAF were related to different physicochemical properties of these compounds. Retention of BPA was higher for higher initial concentration while the higher concentration of CAF resulted in lower retention. Feed pH affected more retention of BPA than CAF due to impact of pH on chemical form of BPA. Membrane modified with higher CNTs amount had better antifouling properties due to higher hydrophilicity.

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