

## TiO<sub>2</sub> and halloysite-modified ultrafiltration membranes for treating wastewater treatment plants effluent

Ewa Puszczalo\*, Gabriela Kamińska, Jolanta Bohdziewicz

Faculty of Energy and Environmental Engineering, Silesian University of Technology, Gliwice, Poland,  
email: ewa.puszczalo@polsl.pl (E. Puszczalo)

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### ABSTRACT

The aim of this study was to determine the possibility of using polymeric ultrafiltration membranes modified with titanium dioxide and nanohalloysite nanoparticles to remove selected micropollutants from wastewater treatment plants (WWTP) effluent. Four types of membranes were used, which were prepared from polyacrylonitrile and polyethersulfone and then modified with halloysite and titanium(IV) oxide (TiO<sub>2</sub>). The feed water was obtained by adding organic micropollutants to the effluent obtained from Gliwice's wastewater treatment plant. Due to the different properties of the organic micropollutants, the following compounds were selected for this study: benzotriazole, bisphenol A, carbamazepine, and caffeine. The treatment efficiency of the effluent spiked with selected micropollutants varied depending on the membrane polymer and the type of nanoparticles used to modify the membranes. The results showed that titanium(IV) oxide nanoparticles improved the volumetric permeate flux, which improved the transport properties of the modified membranes. Polyacrylonitrile membranes, although highly hydrophilic, were the most susceptible to fouling, regardless of the type of nanoparticle they were modified with, which may be due to their high porosity. The PES16-HNT membrane showed the highest reduction in typical quality parameters, while the PES16-TiO<sub>2</sub> membrane showed the highest micropollutant retention. From these results, it can be concluded that the modified ultrafiltration membranes can be used to treat WWTP effluent, which is a source of micropollutants that enter the environment.

*Keywords:* Ultrafiltration; Nanoparticles; Micropollutants

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### 1. Introduction

Micropollutants occur in aquatic environments due to the discharge of inadequately treated wastewater into waterways [1–4]. They are removed from wastewater at different rates, and the costs associated with their removal are very high [5]. Micropollutants in water streams include pharmaceuticals, pesticides, polycyclic aromatic hydrocarbons (PAHs), corrosion inhibitors (heterocyclic aromatic compounds) such as benzotriazole (BTR) and benzothiazole, endocrine disruptors such as bisphenol A (BPA), dioxins, polychlorinated biphenyls (PCBs), and personal

care products [6–9]. These pollutants are introduced into water matrices by human activities, such as the intensification of agricultural activities and the use of pesticides [10,11]. The improper disposal of expired or unused pharmaceuticals and the fact that they are mostly excreted from humans or animals in their original forms contribute to their presence in water streams, including wastewater [12–14]. Most drugs exhibit chronic or acute toxicity to aquatic organisms [15]. Although micropollutants are found in low concentrations in aquatic environments, they still pose a threat due to their resistance to biodegradation and their toxic effects on living organisms [16–18].

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\* Corresponding author.

The main source of micropollutants entering aquatic environments in developed countries is municipal wastewater treatment plants (WWTP) [19,20]; therefore, the need to treat WWTP effluent is urgent. Ultrafiltration is an effective and economical method for removing pollutants due to the flexibility provided by a wide range of membrane materials (ceramics, polymers) with numerous different properties (molecular weight cut-off, porosity, hydrophilicity/hydrophobicity, surface charge, water permeability, thickness, mechanical stability, and thermal resistance) [21,22]. Recently, ultrafiltration with nanocomposite membranes has gained attention due to the high-efficiency removal of different water pollutants including dyes, nutrients, and micropollutants [23]. The addition of nanoparticles to a membrane improves its structural and surface properties, as well as its permeability and retention [24,25]. The most popular nanoparticles used to produce nanocomposite membranes are metal oxides ( $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{ZnO}$ ,  $\text{MgO}$ , and  $\text{Fe}_2\text{O}_3$ ), carbon-based nanomaterials (carbon nanotubes, graphene, graphene oxide, and carbon nanospheres), clay minerals in the form of nanoclays (halloysite and montmorillonite), cellulose nanocrystals, and nanosilver [26,27]. The higher specific surface area and other unique properties due to their “nano” size make them more effective materials than their macro-sized counterparts. For example, a mixed-matrix membrane containing fullerene was used to remove xenoestrogens via low-pressure membrane filtration. Compared with the pristine membrane, the fullerene-containing membrane was characterized by a much higher porosity, a nearly five-times higher permeability, and a high estrone retention degree of 98.8% [28]. Another example is polymer membranes modified with carbon nanotubes, which exhibit a high retention degree of triclosan, ibuprofen, and acetaminophen [29].

It should also be noted that modified nanocomposite membranes have better transport and separation properties, and they are also less susceptible to fouling and have a longer life [30,31]. Greater resistance to fouling is the result of the increased hydrophilicity of the membrane due to the introduction of hydrophilic nanoparticles, for example, halloysite, graphene oxide (GO), or carbon nanotubes functionalized with carboxyl groups [32]. Mozia et al. [33] reported that modification with halloysite promoted the hydrophilicity, water permeability, and antifouling properties of polyethersulfone (PES) membranes due to the  $-\text{OH}$  groups of halloysite.  $\text{TiO}_2$  nanoparticles improve the antifouling properties of polymer membranes [34]. Kumar et al. [35] showed that doping a polysulfone membrane with  $\text{GO-TiO}_2$  reduced fouling during the ultrafiltration of a 10 mg/L humic acid solution. The relative deionized water flux increased from 75% for the unmodified membrane to 97% for the membrane containing 5 wt.%  $\text{GO-TiO}_2$ . Additionally, the irreversible fouling resistance decreased from 25% to 3.2% upon increasing the  $\text{GO-TiO}_2$  loading from 0 to 5 wt.%. Many nanoparticles have been used to produce numerous types of nanocomposite membranes with a low fouling tendency and better treatment efficiency. Nevertheless, currently-available literature data do not clarify which nanoparticles are the most beneficial for pollutant removal and fouling mitigation; therefore, the aim of this study was to compare the separation properties and fouling tendency

of four different nanocomposite membranes during the treatment of WWTP effluent spiked with emerging organic micropollutants.  $\text{TiO}_2$  and halloysite nanoparticles were used to modify polyethersulfone (PES) and polyacrylonitrile (PAN) membranes.

## 2. Materials and methods

### 2.1. Preparation of nanoparticle-modified membranes

Four types of ultrafiltration membranes were fabricated by a phase inversion method using polyethersulfone granules or polyacrylonitrile powder. The casting solutions were enriched with nanoparticles at a fixed concentration of 0.1 wt.%. The membranes used in this study were:

- PES16-HNT – polyethersulfone membrane, modified with halloysite nanoparticles (HNT) at a concentration of 16 wt.% (15.9 wt.% polymer and 0.1 wt.% nanoparticles).
- PES16- $\text{TiO}_2$  – polyethersulfone membrane, modified with titanium(IV) oxide ( $\text{TiO}_2$ ) nanoparticles at a concentration of 16 wt.% (15.9 wt.% polymer and 0.1 wt.% nanoparticles).
- PAN9-HNT – polyacrylonitrile membrane modified with halloysite nanoparticles at a concentration of 9 wt.% (8.9 wt.% polymer and 0.1 wt.% nanoparticles).
- PAN9- $\text{TiO}_2$  – polyacrylonitrile membrane modified with titanium(IV) oxide nanoparticles at a concentration of 9 wt.% (8.9 wt.% polymer and 0.1 wt.% nanoparticles).

The concentration of PAN in the casting solution was determined experimentally. In preliminary studies, the PAN membranes that were prepared from a casting solution containing less than 9 wt.% PAN showed insufficient mechanical strengths, while an insufficient hydraulic permeability under a typical ultrafiltration pressure range (0.1–0.5 MPa) was observed for membranes prepared from solutions containing >12 wt.% PAN. *N,N*-Dimethylformamide (DMF) was used to prepare all casting solutions, with a concentration of 84 wt.% for PES membranes and 91 wt.% for PAN membranes. The casting solutions were poured onto a glass plate and spread using an automated film applicator (Elcometer 4340). The thickness of the polymeric film was adjusted to 220  $\mu\text{m}$  for PES and 500  $\mu\text{m}$  for PAN membranes. Gelation (polymer precipitation) of the membranes was carried out in a bath of deionized water at ambient temperature for PES membranes, and at 40°C for PAN membranes. Additionally, for PAN membranes, 10 min solvent evaporation was performed before gelation. The PES membranes were subjected to gelation immediately after film distribution. After gelation, the membranes were left in deionized water for 24 h to remove residual solvent.

### 2.2. Feed water preparation

The feed water was obtained by adding organic micropollutant analytical standards (in methanol) to the effluent from Gliwice’s wastewater treatment plant. The characteristics of the raw effluent are presented in Table 1. Due to their different properties, the following compounds were

Table 1  
Physical–chemical properties of WWTP effluent

Parameter	Value
Colour (mg Pt/L)	55
pH	6.9
Absorbance UV 254 nm	0.312
Phosphate (mg P-PO <sub>4</sub> /L)	2.8
Nitrate (mg N-NO <sub>3</sub> /L)	5.5
Phenolic index (mg/L)	2.3

used in this study: benzotriazole (BTR), bisphenol A (BPA), carbamazepine (CBZ), and caffeine (CAF) with a dosage of 1 mg of micropollutants per 1 L of effluent. The characteristics of the micropollutants are given in Table 2.

### 2.3. Apparatus

The ultrafiltration process was carried out in a 400 mL steel cell equipped with a magnetic stirrer, into which membranes with a filtration area of 0.00385 m<sup>2</sup> were placed (Fig. 1). The system was operated in a dead-end system, and the feed solution was introduced perpendicular to the membrane surface.

The driving force of the ultrafiltration process was transmembrane pressure (TMP) generated by nitrogen (an inert gas), which was 0.5 MPa for PES membranes and 0.1 MPa for PAN membranes. The different TMPs used for PAN and PES membranes were because both processes were run at a similar permeate flux (the permeability of PAN was much higher than that of PES). The membranes were conditioned with deionized water. The measuring chamber was then filled with WWTP effluent spiked with micropollutants. When the transmembrane pressure was established, the

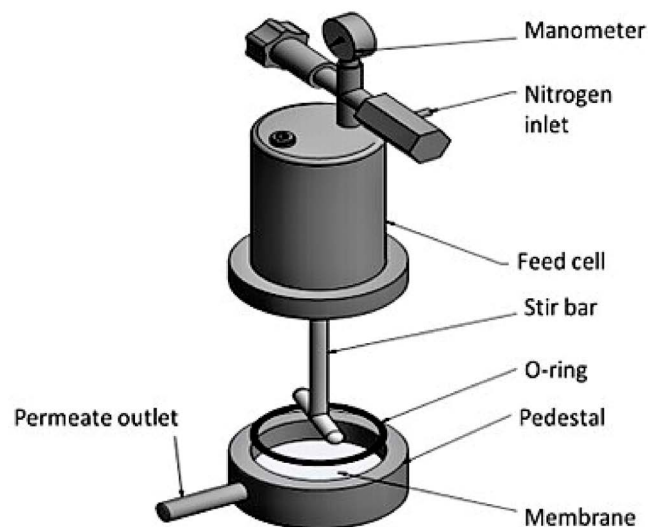


Fig. 1. Ultrafiltration setup (dead-end system).

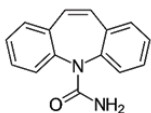
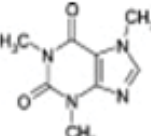
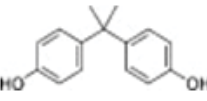
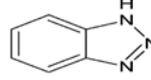
volume of permeate was measured. For both PES and PAN membranes, measurements were taken every 5 min.

The surface contact angle of the membranes before and after filtration measured by the droplet deposition method using a goniometer was also tested to determine their hydrophilicity or hydrophobicity.

### 2.4. Sample analysis

For the obtained permeates and inflows (WWTP spiked with micropollutant), the basic quality parameters (phenolic index, phosphate phosphorus (P-PO<sub>4</sub><sup>3-</sup>), nitrate nitrogen (N-NO<sub>3</sub><sup>-</sup>), ammonium nitrogen (N-NH<sub>4</sub><sup>+</sup>), UV absorbance 254 nm, color, and pH) were determined using Supelco test

Table 2  
Properties of micropollutants

Compound	Chemical structure	Molecular mass <sup>a</sup> (g/mol)	logK <sub>ow</sub> <sup>a</sup> (-)	Solubility in water 20°C <sup>a</sup> (mg/L)	pKa <sup>a</sup> (-)
Carbamazepine		236.3	2.45	17.7	13.9
Caffeine		194.20	-0.55	21,600	10.4
Bisphenol A		228.3	3.32	<1	10.10
Benzotriazole		119.12	1.44	20,000	8.2

<sup>a</sup>Data taken from <https://pubchem.ncbi.nlm.nih.gov/>

kits (except absorbance and pH) and a Merck spectrophotometer (Pharo 100). pH indicator papers were used to measure the pH. The procedure for monitoring the micro-pollutant concentration included solid-phase extraction (SPE) and gas chromatography using a flame-ionization detector (YL 6500).

The SPE method consisted of passing an analyzed sample (50 mL) through a bed located in an extraction column, after pre-conditioning the bed with 5 mL of acetonitrile (ACN), 5 mL of methanol (MeOH), and 5 mL of deionized water. The adsorbed analytes were then eluted with 3 mL of a mixture of acetonitrile and methanol (ACN/MeOH) in a volume ratio of 6:4. The resulting solution was dried with nitrogen at 36°C. The resulting precipitate (solid-phase) was dissolved in 100 µL of MeOH and subjected to chromatographic analysis.

The equations used to determine the permeate flux, fouling intensity, and the treatment effectiveness of WWTP effluent by ultrafiltration with nanoparticle-modified polymeric membranes are presented below:

$$J_v = \frac{V}{A \cdot t} \quad (1)$$

where  $J_v$  is the permeate volumetric flux ( $\text{m}^3/\text{m}^2 \text{ s}$ ),  $V$  is the permeation volume (L),  $A$  is the membrane's effective surface area ( $\text{m}^2$ ), and  $t$  is the permeation time (h).

$$\text{IF} = \frac{J_v}{J_w} \quad (2)$$

where IF is the fouling index, and  $J_w$  is the average deionized water flux.

$$R_i = \left( \frac{C_n - C_p}{C_n} \right) \times 100\% \quad (3)$$

where  $R_i$  is the removal/ reduction degree of contaminants/ quality parameters,  $C_n$  is the concentration of impurities in the feed, mg/L, and  $C_p$  is the concentration of impurities in the permeate, mg/L.

### 3. Results and discussion

The average contact angles of the membranes tested before and after filtration are summarized in Table 3. Due to the almost instantaneous adsorption of water droplets by polyacrylonitrile membranes, it was not possible to measure their contact angle, probably due to the high hydrophilicity of the PAN membranes. These membranes also became very brittle and unstable after drying.

The polyethersulfone membranes showed a very low hydrophilicity (bordering on hydrophobic) before filtration and a moderate hydrophilicity after filtration. In the case of the PES16-HNT membrane, there was a 19% decrease in its contact angle value after ultrafiltration, while for the PES16-TiO<sub>2</sub> membrane its contact angle decreased by about 20%. Such a large increase in the hydrophilicity of the membranes was associated with a decrease in the

Table 3

Average contact angle values of the membranes tested before and after filtration

Membrane type	Contact angle, °	
	Before filtration	After filtration
PES16-HNT	90	73
PAN9-HNT	–	–
PAN9-TiO <sub>2</sub>	–	–
PES16-TiO <sub>2</sub>	91.3	73.3

membrane roughness due to cake layer deposition due to fouling. The relationship between the membrane contact angle and roughness was developed by Wenzel et al. [36]. Many authors have indicated that a lower membrane roughness produces lower contact angles [37,38].

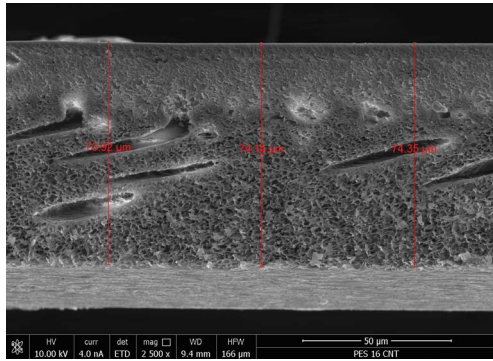
Fig. 2 presents a cross-section of PES16-HNT and PES16-TiO<sub>2</sub>. Both membranes exhibited sponge-like structures with a denser active layer and more porous sublayer and support. As can be seen, the PES16-HNT membrane was almost twice as thick, with a denser structure than that of PES16-TiO<sub>2</sub>. This was attributed to the different viscosities of the casting solutions of TiO<sub>2</sub> and halloysite, which affect the rate of phase inversion during membrane precipitation. Many authors have shown that even a slight modification of the composition of casting solution changes the structural properties of membranes such as their thickness and pore size [39,40].

Table 4 presents the deionized water permeability of membranes. Clearly, the PAN membranes exhibited a much higher permeability than PES, which was related to the much higher surface hydrophilicity of the PAN membranes. Another reason may be the higher porosity of the PAN membranes compared with the PES membranes.

Fig. 3 shows the reduction in selected quality parameters when WWTP effluent was treated via ultrafiltration by PES and PAN membranes modified with nanoparticles. The ultrafiltration performance using the modified membranes to treat WWTP effluent was very high. In most cases, the reduction in selected quality parameters was higher than 70%. More specifically, the highest reduction in the phenolic index (95%) occurred for the PES16-TiO<sub>2</sub> membrane, while the lowest (82%) occurred for the PES16-HNT membrane. P-PO<sub>4</sub><sup>3-</sup> reduction (91%) was the same for all membranes. The highest reduction degree of N-NO<sub>3</sub><sup>-</sup> (93%) occurred for the PAN9-HNT membrane, while the lowest (87%) occurred for the PES16-TiO<sub>2</sub> membrane. The highest reduction of N-NH<sub>4</sub><sup>+</sup> (83%) occurred for the PES16-HNT membrane, and the lowest (more than five-times lower than that of the PES16-HNT membrane) occurred for the PAN9-HNT membrane. The maximum color decrease was observed for ultrafiltration using the PES16-HNT membrane and the minimum was observed for the PAN9-HNT membrane. The highest reduction in the absorbance was noted for the PES16-HNT membrane and the lowest for the PAN9-HNT membrane.

Among all membranes, the highest treatment efficiency of the WWTP effluent was observed for PES16-HNT and PES16-TiO<sub>2</sub> membranes, while a slightly lower efficiency

PES-16HNT



PES-16 TiO<sub>2</sub>

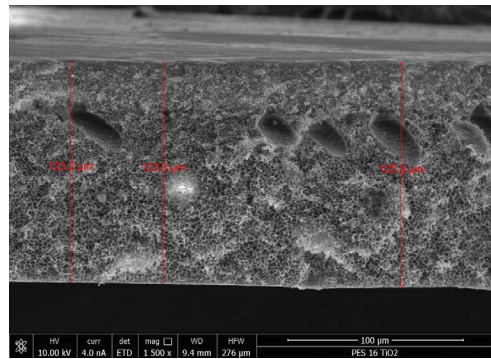


Fig. 2. Scanning electron microscopy images of cross-sections of the PES membranes.

Table 4  
Permeability of membranes for deionized water

Membrane type	Permeability, m <sup>3</sup> /m <sup>2</sup> s MPa
PES16-HNT	1.11 × 10 <sup>-5</sup>
PAN9-HNT	4.77 × 10 <sup>-3</sup>
PAN9-TiO <sub>2</sub>	3.52 × 10 <sup>-3</sup>
PES16-TiO <sub>2</sub>	7.37 × 10 <sup>-5</sup>

was noted for PAN9-HNT and PAN9-TiO<sub>2</sub> membranes. This may be related to the lower permeability of the PES membranes than that of PAN.

Since conventional ultrafiltration membranes do not retain nutrients or dissociated substances, the high reduction degree of P-PO<sub>4</sub><sup>3-</sup>, N-NO<sub>3</sub><sup>-</sup>, and N-NH<sub>4</sub><sup>+</sup> indicates improved retention characteristics of modified membranes. The improved rejection of P-PO<sub>4</sub><sup>3-</sup>, N-NO<sub>3</sub><sup>-</sup>, and N-NH<sub>4</sub><sup>+</sup> was related to their adsorption on the surface of nanoparticles within membranes. Many authors have suggested that mixed-matrix nanocomposite membranes can retain phosphate or nitrate because they are adsorptive membranes [41,42].

Fig. 4 shows the pH values of the feed water (wastewater before filtration) and permeates (wastewater after filtration). The pH of the studied streams changed from slightly acidic (pH = 6.5) for the feed water to neutral (pH = 7) for the permeates.

Fig. 5 shows the removal efficiency of selected micropollutants through PES and PAN membranes modified

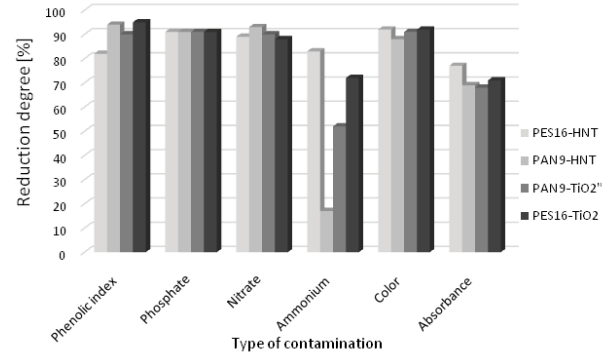


Fig. 3. Influence of the type of ultrafiltration membrane modified with nanoparticles on the effectiveness of reducing the values of selected pollutant indices.

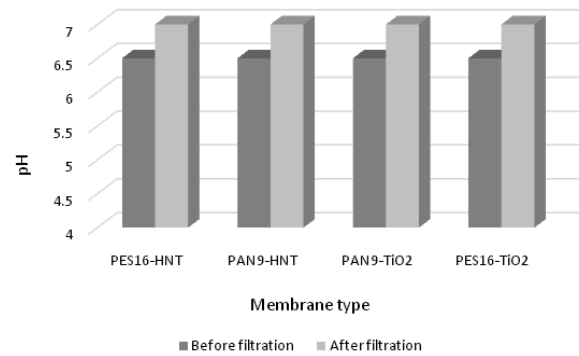


Fig. 4. Effect of membrane type on the change of pH of filtered wastewater.

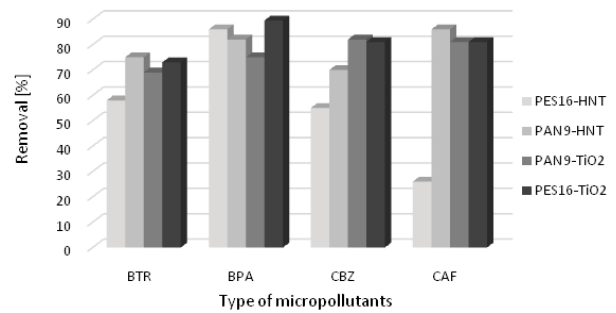


Fig. 5. Removal of micropollutants in ultrafiltration with PES and PAN membranes modified with nanoparticles.

with nanoparticles. The retention of micropollutants via ultrafiltration was generally high. Excluding membrane PES16-HNT, the removal efficiency exceeded 70% for all organic micropollutants. Each compound was also removed via ultrafiltration with different efficiencies. More specifically, BTR retention was the highest for the PAN9-HNT membrane and the lowest for the PES16-HNT membrane. BPA retention was the highest for the PES16-TiO<sub>2</sub> membrane and the lowest for the PAN9-TiO<sub>2</sub> membrane. For CBZ, the PAN9-TiO<sub>2</sub> membrane showed the highest retention, while the PES16-HNT membrane showed the lowest.

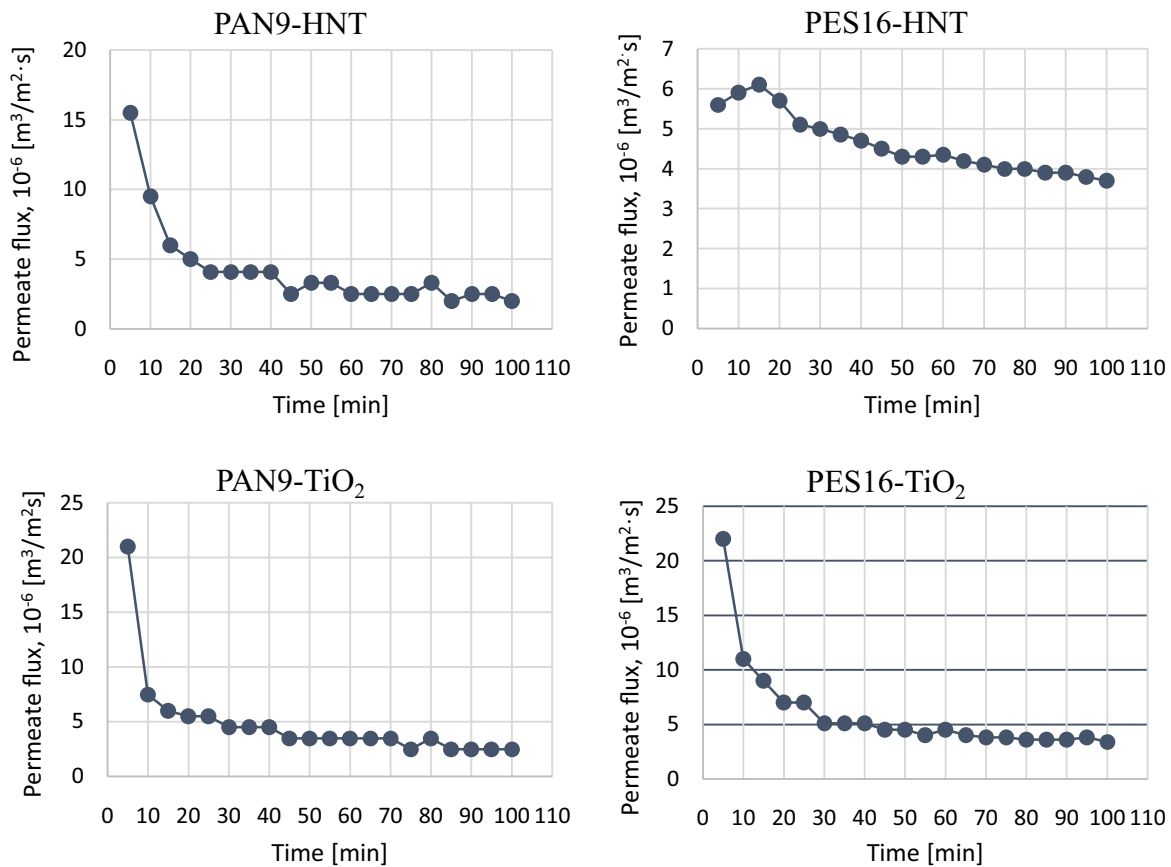


Fig. 6. Permeate volume flux vs. filtration time (TMP was 0.5 and 0.1 MPa for PES and PAN membranes respectively).

CAF retention was the highest using the PAN9-HNT membrane and the lowest (more than three-times lower than that of the PAN9-HNT membrane) for the PES16-HNT membrane. These different removal efficiencies were related to the different properties of the membranes and micropollutants. These properties determine the interactions between micropollutants and membranes such as adsorption, sieve effects, and electrostatic interaction [43,44]. In each micropollutant-membrane combination, a different process was likely dominant, which consequently resulted in different removal degrees [45].

Fig. 6 shows changes in the permeate volume flux during membranes filtration. The decrease in permeate fluxes over time indicates an increase in the intensity of the membrane fouling, which was observed for all membranes. The lowest fouling was observed for PES16-HNT, while the other membranes showed a comparable decrease in permeate flux, which was confirmed by the fouling index (Table 5). A smaller value indicates more intense membrane surface fouling by substances contained in the WWTP effluent. The fouling index values for PAN9-HNT and PAN9-TiO<sub>2</sub> membranes were 0.009 and 0.016, respectively, while those of PES16-HNT and PES16-TiO<sub>2</sub> membranes were 0.829 and 0.2, respectively. Despite having the highest hydrophilicity, PAN9-HNT and PAN9-TiO<sub>2</sub> membranes were the most susceptible to blocking. This was probably due to the more open structure of PAN

Table 5  
Fouling index determined for applied nanoparticle modified membranes

Membrane type	Fouling index
PES16-HNT	0.829
PAN9-HNT	0.009
PAN9-TiO <sub>2</sub>	0.016
PES16-TiO <sub>2</sub>	0.2

membranes compared with PES. This was evidenced by the much higher permeability of PAN membranes than PES membranes. In open membrane structures with large pores, internal pore blockage easily occurs, as even large contaminant particles can penetrate the membrane.

#### 4. Conclusion

The results showed that titanium(IV) oxide nanoparticles improved the permeate flux, and thus the transport properties of the modified membranes. The PAN membranes exhibited a higher permeability than PES membranes.

The treatment performance of WWTP effluent via ultrafiltration using modified membranes efficiently removed micropollutants, nutrients, and other pollutants,

as determined by basic quality parameters. The reduction in the phenolic index, phosphate, nitrate, ammonium, color, and UV absorbance at 254 nm for most membranes was higher than 70%. Importantly, nutrient retention was at a level typical for nanofiltration, which is a much more energy-intensive process. The highest retention of micropollutants (73.8%–89.6%) was obtained for the PES16-TiO<sub>2</sub> membrane.

It was also shown that polyacrylonitrile membranes, although highly hydrophilic, were the most susceptible to fouling, regardless of the type of nanoparticle they were modified with. This may have been influenced by the high porosity of PAN membranes, which resulted in more pore blocking.

Taking into account the results of this study, it can be concluded that modified ultrafiltration membranes can be used to treat the effluent from wastewater treatment plants, which is still a source of micropollutants entering the environment.

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