# Relationship between the addition of carbon nanotubes and cut-off of ultrafiltration membranes and their effect on retention of microcontaminants

# Michał Adamczak\*, Gabriela Kamińska\*, Jolanta Bohdziewicz

Department of Water and Wastewater Engineering, Silesian University of Technology, Konarskiego 18, 44-100, Gliwice, Poland, Tel./Fax: +48 32 237 29 81; emails: michal.adamczak@polsl.pl (M. Adamczak), gabriela.kaminska@polsl.pl (G. Kamińska), jolanta.bohdziewicz@polsl.pl (J. Bohdziewicz)

Received 30 April 2020; Accepted 2 June 2020

#### ABSTRACT

The addition of nanotubes changes the surface properties of the membrane – it affects the charge on the membrane surface, the contact angle, the porosity of the membrane, and thus its effectiveness on the retention of contaminants in water. Depending on the purpose for which the membrane is to be used, as well as the compounds to be retained, various modifications of nanotubes are used – their functionalization with strong acids cause functional groups such as carboxyls, hydroxyls, amines, or amides to appear on the surface of the membrane. In this paper, single-walled carbon nanotubes with carboxyl groups were used with high-purity, large surface area, single-walled nanotubes to test their properties in the removal of microcontaminants. In this work, the participation of nanotubes in the membrane matrix was combined with surface properties and cut-off measurements of the membrane. However, due to the addition of carbon nanotubes, the adsorption was improved; it also resulted in changes to the hydrophilicity of the membrane, porosity, and charge on its surface. Four substances were used in the study: caffeine, bisphenol A, carbamazepine, and endosulfan.

Keywords: Micropollutants; Carbon nanotubes; Ultrafiltration; Fouling; Cut-off

# 1. Introduction

Ultrafiltration (UF) is one of the low-pressure membrane techniques widely used for the elimination of macromolecular compounds. The main mechanism involved in the removal of contaminants is the selective filtration of the feed components through membrane pores. It is based on the sieve effect; thus, the particles bigger than membrane pores are effectively retained while smaller ones permeate the membrane [1]. According to Marshall [2], ultrafiltration membranes should have pore sizes between 2 and 100 nm and be able to retain 90% of contaminants with molar masses between 5,000 and 5,000,000 Da. Retention of 90% of molecules is the definition of molecular weight cut-off. This value can be calculated, tested by passive filtration of particles with a defined size (e.g., polyethylene glycol, polyethylene oxide, or dextrans), or confirmed by gel permeation chromatography. Emerging microcontaminants (pharmaceuticals, drugs, plasticizers, pesticides, or endocrine-disrupting compounds (EDCs) with low molecular mass are mostly removed by nanofiltration (NF), and reverse osmosis (RO)). UF rejects mostly organic matter, suspended solids, bacteria, and turbidity [2,3].

Improvement of ultrafiltration membranes has enabled organic micropollutants such as pharmaceuticals, personal care products, or pesticides to be separated by ultrafiltration. There is a new group of unconventional nanocomposite membranes that contain nanofillers in the structure, on the surface, or both. The most popular nanofillers are carbon materials such as carbon nanotubes, graphene, fullerenes,

<sup>\*</sup> Corresponding authors.

<sup>1944-3994/1944-3986 © 2021</sup> Desalination Publications. All rights reserved.

metals, or metal oxides [4]. However, due to the positive effect on pollutant removal and general UF performance, the most beneficial materials are carbon nanotubes for their strong adsorption effect.

Carbon nanotubes (CNTs) have a high total surface area, low mass and good adsorption properties. The functionalization of carbon nanotubes improves dispersion in a casting solution and enhances CNT adhesion to the polymer [5]. Furthermore, the presence of different functional groups on the membrane surface might improve membrane surface charge and hydrophilicity. Functionalization is mostly conducted by strong acids such as nitrate and sulfur acids. Raw CNTs and functionalized CNTs are used for membrane modification. They are applied for desalination and removal of microorganisms and organic and inorganic contaminants. and their presence in membranes positively affects membrane permeability because water can easily migrate through the carbon nanotubes [6]. Their occurrence also improves separation effect and antifouling properties. For example retention and adsorption of two microcontaminants, bisphenol A (BPA) and 17β-estradiol were improved by the addition of single-walled carbon nanotubes (SWCNTs) into the UF system [7]. Modification of polyethersulfone (PES) membranes with functionalized multi-walled carbon nanotubes increased natural organic matter retention for organic compounds [4,6]. The use of similar membranes in dead-end systems reduced BPA by 70%-80% for modified membranes in comparison to 25% of the unmodified PES membrane [9].

This study investigated the fouling behavior of nanocomposite membranes modified with single-walled carbon nanotubes functionalized with carboxyl groups (SWCNT-COOH) or high purity large surface area single-walled carbon nanotubes (HPLSA-SWCNT) during ultrafiltration treatment of surface water spiked with four organic micropollutants: caffeine – CAF, carbamazepine – CBZ, bisphenol A – BPA, and  $\beta$ -endosulfan – END). The physicochemical properties of the micropollutants are presented in Table 1. The effect of carbon nanotubes concentration in membranes on treatment efficiency and micropollutant removal was investigated. Furthermore, membrane molecular cut-off, water contact angle, porosity, and zeta potential were tested.

# 2. Materials and methods

Table 1

Physicochemical properties of micropollutants [10-13]

#### 2.1. Materials and feed water

SWCNT-COOH and HPLSA-SWCNT were obtained from Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences, and used for membrane modification (Chengdu, China). Their properties are presented in Table 2. PES as the basic material for membrane preparation was supplied by BASF Company (Ludwigshafen, Germany). N.Ndimethylformamide (DMF), hexane, acetonitrile, and methanol (all analytically pure) were purchased from Avantor Performance Materials (Gliwice, Poland). Chemicals (BPA, END, CAF, and CBZ) with the purity of 99%, polyethylene glycol (20,000 and 35,000 Da) and polyethylene oxide (100,000 and 200,000 Da) were provided by Sigma Aldrich (Poznań, Poland). Deionized water was taken from RephiLe Ltd., system (Shanghai, China). The stock solutions of micropollutants were prepared with methanol (1 g/L). The feed solution for retention tests was prepared by diluting the stock solution with deionized water to achieve a concentration of 1 mg/L.

# 2.2. Chromatographic analysis of micropollutants

Concentration of micropollutants in feed and permeate were determined by gas chromatography with flame ionization detector (GC-FID) 6500GC System GC-FID by Yl Instrument Co., Ltd., (Hogye-dong, Anyang, Korea). Chromatograph was equipped with 30 m × 0.25 mm i.d. SLB<sup>®</sup> 5 ms fused silica capillary column of 0.25  $\mu$ m film thickness supplied by Sigma-Aldrich (Poznań, Poland).

## Table 2

Properties of used carbon nanotubes

Properties	HPLSA-SWCNT	SWCNT-COOH
Purity (wt.%)	>95	>90
Specific surface area SSA	>1,075	>320
(m²/g)		
Ash (wt.%)	<2.5	<5
Density (g/cm <sup>3</sup> )	0.018	0.14
-COOH functionalized	-	2.73
(wt.%)		

Properties	Bisphenol A	β-Endosulfan	Caffeine	Carbamazepine
Structure	но СССон		H <sub>3</sub> C <sub>N</sub> O CH <sub>3</sub> CH <sub>3</sub>	
Formula	$C_{15}H_{16}O_{2}$	C <sub>9</sub> H <sub>6</sub> Cl <sub>6</sub> O <sub>3</sub> S	$C_8 H_{10} N_4 O_2$	$C_{15}H_{12}N_{2}O$
Molar mass (g/mol)	228.291	406.93	194.194	236.3
рКа	10.10	-	10.4	14.00
logK	3.32	3.83	-0.55	2.45
Water solubility (mg/L) 20°C	<1	0.45	21,600	17.7

Helium 5.0 was used as the carrier gas. The quantitative calculations were carried out on the basis of measurements of peak area, which was compared with data for analysis of standard solutions. Chromatographic separation of micropollutants was performed by a temperature program of column oven for all substances 80°C-320°C. The injector temperature was set at 240°C. Before GC-FID analysis micropollutants were extracted from the samples using solid-phase extraction (SPE). 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 methanol, and 5 mL of deionized water. After this, 25 mL of the sample was passed through the columns. Then, when the column was completely dried, analytics were eluted with 3 mL of acetonitrile/methanol 60/40 solution and 3 mL of hexane. Eluted portion was dried in a nitrogen stream and then analyzed using GC-FID. The analytical procedure allowed for the recovery of compounds at the level of 100%. Retention of micropollutants were calculated according to the following equation:

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

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

#### 2.3. Membrane preparation

Three types of nanocomposite membranes were prepared by phase inversion method. Casting solutions consisted of 15 wt.% of PES, 0.02–0.1 wt.% of SWCNT-COOH or HPLSA-SWCNT and 84.98–84.90 wt.% of DMF as presented in Table 3. Proper amounts of nanotubes and PES were added to the DMF. Casting solution was stirred for 20 h to obtain homogeneous solution. After that, membranes were casted using automatic film applicator Elcometer 4340 (Elcometer Ltd., Manchester, UK) with a doctor blade gap of 0.22 mm on glass plate and immediately immersed in deionized water at ±22°C. Precipitated membranes were stored in deionized water for 24 h for their stabilization.

#### 2.4. Membrane characterization

Zeta potential is a measure of the electrical charge of the membrane surface and was measured using an

Table 3		
Composition of	casting	solutions

electrokinetic analyzer SurPASS™ 3 (Anton Paar, Graz, Austria). Measurements of the contact angle were performed using the goniometer PG-1 (Fibro System AB, Sweden) and the sessile drop method was applied, where 10 strips of the dried tested membrane were inserted into the device. By syringe on the top drop of distilled water were applied on the membrane surface. Trough enlarged projection of water drop on gauge, the value of contact angle was measured. For every type of membrane, 10 samples were measured and the average value was calculated. Sheet of the membrane with the calculated surface was dried by paper towel, then weighted in the wet state. After this, the same membrane was dried in an oven in 60°C for 24 h and then weighted in a dry state. Five sheets of each membrane were used for this measurement. Eq. (1) for a calculation of the membrane porosity is as following:

$$\varepsilon = \frac{m_w - m_d}{AL\rho} \times 100\%$$
<sup>(2)</sup>

where  $\varepsilon$  is porosity (%),  $m_w$  is weight of wet membrane (g),  $m_d$  is weight of dry membrane (g), A is the area of membrane (cm<sup>2</sup>), L is membrane thickness (cm), and  $\rho$  is pure water density (about 0.998 g/mL).

Membrane pore size was calculated according to Hamachi et al. [14]:

$$MWCO = 3d^{5/3} \tag{3}$$

where MWCO is the molecular weight cut-off (Da) and *d* is the membrane pore diameter in (nm).

Membranes cut-off were determined by separated filtration of polyethylene glycol (PEG) and polyethylene oxide (PEO) solutions (1 g/L) with different molar weight in DI water. Achieved permeates were tested by total organic carbon (TOC) analyzer (Shimadzu, Japan) and compared to feed water results. Separation level was calculated by following equation:

$$R[\%] = \frac{T_F - T_P}{T_F} \cdot 100 \tag{4}$$

where *R* [%] is PEO/PEG retention level,  $T_F$  (mg/L) is TOC concentration in feed, and  $T_P$  (mg/L) is TOC concentration in permeate.

Symbol	PES (wt.%)	SWCNT-COOH (wt.%)	HPLSA-SWCNT (wt.%)	DMF (wt.%)
PES 15	15.00	-	_	85.00
PES 15 0.02	15.00	0.02	-	84.98
PES 15 0.05	15.00	0.05	-	84.95
PES 15 0.1	15.00	0.1	-	84.90
PES 15 HP02	15.00	-	0.02	84.98
PES 15 HP05	15.00	-	0.05	84.95

# 2.5. Setup and filtration run

Retention tests were carried out in the ultrafiltration setup consisted of a bottle of nitrogen gas, pressure reducer, filtration cell, and volume measuring system. membranes had an area 38.5 cm<sup>2</sup>. Ultrafiltration was carried out for all membranes at 0.1 MPa. The experiment included three stages: (1) membrane conditioning with deionized water, (2) retention tests with feed water, and (3) membrane fouling testing after the main filtration. 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:

$$J_V = \frac{V}{A \cdot t} \tag{5}$$

where  $J_V$  is the flux (L/m<sup>2</sup>/h), *V* is the permeation volume (L), *A* is the membrane effective surface area (m<sup>2</sup>), and *t* is the permeation time (h).

Retention level of selected microcontaminants was calculated by the following equation:

$$R\left[\%\right] = \frac{C_F - C_P}{C_F} \cdot 100\tag{6}$$

where R(%) is microcontaminants retention level,  $C_F$  (mg/L) is concentration in feed, and  $C_p$  (mg/L) is concentration in permeate.

# 3. Results and discussion

#### 3.1. Membrane contact angle

All membranes prepared by PES had intermediate hydrophobic-hydrophilic properties (Fig. 1). Modified membranes had slightly lower contact angles. The addition of SWCNT-COOH affected the hydrophilicity of these membranes. Similar results have also been observed by Majeed et al. [15] and Zhang et al. [16]. Slightly lower contact angle for all modified membranes confirmed better hydrophilic properties that resulted in higher membrane permeability and higher repulsion of hydrophobic contaminants. Membranes were also more hydrophilic after filtration, which was caused by deposition and adsorption of microcontaminants on the membrane surface. Contact angle of the fouled membrane was 3°–5° lower than for clean membranes. Higher hydrophilicity directly affected permeate flux, as is explained in section 3.5 (Permeate flux).

# 3.2. Membrane zeta potential

Zeta potential of the membranes had a similar tendency for each kind, as seen in Fig. 2. For clean pristine membranes, a PES 15 value of zeta potential at pH 7 was around 25 mV. Similar values were achieved for commercial PES pristine membranes, NF-3, and NF-4 (Ande Membrane Separation Technology and Engineering Co., Ltd., Beijing, China) provided by Yu et al. [17]. The properties of PES membranes might originate from the sulfonic group occurring in the polymer structure [18]. The addition of SWCNT-COOH nanotubes changed membranes properties. A small number of nanotubes caused potential increase (less negative) at neutral pH (6-7). However, zeta potential lines crossed below pH 5, and the isoelectric point shifted drastically; PES 15 and PES 15 0.02 had the highest zeta potential, respectively, at pH 3.6 and 2.35. Other membranes showed intermediate zeta values, which increased with the addition of nanotubes. These results can be explained by the specific properties of carboxylated carbon nanotubes. In comparison to other types of nanotubes, carboxylated nanotubes have the much lower (more negative) potential [19]. Additionally, they cause the isoelectric point to shift to lower values [20]. In similar studies, a membrane filled with identical nanotubes (SWCNT-COOH) was more negatively charged due to dissociation of carboxylic groups of functionalized nanotubes, which strongly increased the negative charge [21]. The negative charge of the modified membrane should provide better antifouling and separation properties at acidic pH. For membranes modified with high-purity carbon nanotubes, the opposite phenomenon occurred. The addition of pristine nanotubes caused an increase in zeta potential value (less negative) and a shift of isoelectric point



Fig. 1. Water contact angle of tested membranes.



Fig. 2. Zeta potential (mV) of tested membranes: clean (a and c) and fouled (b and d).

to higher pH value in comparison to pristine membranes; PES 15 values were identical for Figs. 2a and c). Addition of this nanocomposite caused a change on the membrane surface to a more positive charge.

The increase in the zeta potential of fouled membranes proved that the deposition of microcontaminants on membrane surface occurred. Both BPA and END were highly absorbed on the surface and their presence mostly affected membrane properties. These results were caused by a high  $\log K_{ow}$  coefficient for these two substances.  $\log K_{ow}$ informs about the hydrophilicity and hydrophobicity of a given substance. Substances with high coefficients are more susceptible to adsorb on the membrane surface. Also, all fouled membranes had an isoelectric point between pH 4 and 4.5, regardless of the isoelectric point of clean membranes. In many research articles, the zeta potential of membranes was higher (less negative) for the fouled membrane than for the clean membrane in neutral pH [22–24]. This was mostly caused by the accumulation of substances from water on the membrane surface. In these studies, the model is valid for membranes with COOH nanotubes, while membranes with pristine nanotubes had opposite trends than data from the literature. This can be explained by the difference in nanotubes properties; pristine nanotubes caused changes into higher (less negative) zeta potential of membranes. Isoelectric points of fouled membranes centred around one value, regardless of membrane modification.

# 3.3. Membrane porosity

Porosities were between 25% and 36.5% for membranes with carboxylated nanotubes and between 32.6% and 38.0% for HPLSA nanotubes (Table 4). For all membranes except the pristine one with relatively high porosity, a constant increase of porosity was observed. These results were similar to the results achieved by Vatanpour et al. [5] and Celik et al. [8]. According to these studies, this effect might also be affected by a change in the viscosity of the membrane-forming solution as the proportion of nanotubes increases. For example, increasing the membrane viscosity slows down the exchange process between solvent and non-solvent during phase inversion, and thus reduces

Table 4 Porosity of tested membranes

Symbol	Porosity (%)
PES 15	$35.8 \pm 1.2$
PES 15 0.02	$25.0 \pm 2.1$
PES 15 0.05	$36.5 \pm 1.3$
PES 15 0.1	$36.0 \pm 1.1$
PES 15 HP02	$32.6 \pm 1.5$
PES 15 HP05	$38.0 \pm 1.6$

the size and number of pores. A slight decrease in porosity at 0.1% nanotube concentration was because, during the phase inversion, nanotubes blocked larger pores and caused increased retention of contaminants [25,26].

#### 3.4. Membranes molecular cut-off

Membrane cut-off of SWCNT-COOH membranes was almost identical – around 170,000 Da (Fig. 4a). This value is typical for ultrafiltration membranes; similar and higher values for ultrafiltration PES membrane were found by Mantel et al. [27] and Fang et al. [28]. Moreover, the addition of carbon nanotubes did not affect the change of membrane molecular weight cut-off (MWCO). Similar conclusions were achieved by Majeed et al. [15] where MWCO of modified and unmodified polyacrylonitryle membranes had values around 50,000 g/mol. However, the addition of nanotubes caused changes in the distribution of values in Fig. 3. For PES 15 and 15 0.02, a retention range of 20,000–100,000 Da PEG/PEO is lower than for PES 15 0.05 and 0.1. The higher addition of nanotubes decreases the size of pores; for pristine membranes, there also can be



Fig. 3. Molecular weight cut-off of tested membranes. Modified with (a) SWCNT-COOH and (b) HPLSA-SWCNT.

268



Fig. 4. Permeate flux tested during conditioning (blue), permeation (orange), and fouling tests (gray). Modified with (a) SWCNT-COOH and (b) HPLSA-SWCNT.

macropores and smaller pores simultaneously, but none larger than 170,000 Da. By improving membrane pores size, greater selectivity of particle size is possible, as well as better interactions in narrow pores between the solution, the polymer, and the nanotube matrix.

The retention of PES/PEG for the pristine membrane at 20,000–100,000 Da PEG/PEO is lower than for PES 15 0.02 and 15 0.1 (Fig. 4b). Different properties of these membranes were caused by nanotubes with different characteristics. In HPLSA membranes, MWCO was slightly lower than for COOH membranes and the pristine membrane. This dissimilarity can be explained by the reaction between the dissolved polymer and added nanotubes, resulting in membranes with slightly smaller pores, but higher porosity (Table 2).

Membrane MWCO values were used to calculate membrane medium pore size. The results showed that medium pore size was 16.6–18.5 nm for prepared membranes. These values were representative of ultrafiltration membranes, which should be between 2 and 100 nm [2]. Calculations performed by this mathematic method do not have high accuracy, but they confirm that the membranes belong to a group of ultrafiltration membranes.

#### 3.5. Permeate flux

Flux for all membranes increased with greater nanotubes addition, except for PES 15 0.1. In this membrane, the flux decreased and is even lower than for the pristine membrane. This result was caused by an excess of nanotubes, which blocked membrane pores and reduced its flux values. Similar results were achieved in previous research [9,29]. The permeation flux was also higher than the conditioning flux, and the fouling flux was higher than the permeation flux (Fig. 4). These results can be explained by micropollutants adsorbed on membrane surfaces, which can change membranes surface properties, such as greater hydrophilicity and zeta potential. For this reason, the permeate stream after the process is higher than the permeate stream. Also, the permeate stream was higher than the stream during conditioning. Membranes modified with HPLSA-SWCNT had significantly higher flux values than SWCNT-COOH membranes; the flux was doubled for 0.02 concentration and around 10% higher for 0.05 concentration.

#### 3.6. Micropollutants removal in UF

Micropollutants removed in this test were divided into two groups. Chemicals with  $\log K_{ow}$  coefficient below value 2.5 were mostly hydrophilic; substances with  $\log K_{ow}$  higher than 2.5 can interact with membranes by hydrophobic interactions [30].

Retention of caffeine was very low. This result is similar to results from Khanzada et al. [31]. Caffeine had a low  $\log K_{ow}$  coefficient, which means that it is more hydrophilic than hydrophobic. It did not absorb as highly on the membrane surface as other compounds and it passed through the membrane into the permeate. The addition of nanotubes caused a further decrease in caffeine retention



Fig. 5. Retention of tested microcontaminants. Modified with (a) SWCNT-COOH and (b) HPLSA-SWCNT.

(Figs. 5a and b). This result was caused by a lower contact angle and changes in zeta potential at the filtration pH. A higher retention of caffeine for membrane PES 15 0.1 was caused by a simultaneous decrease in permeate flux influenced by the addition of nanotubes. For UF membranes modified with carbon nanotubes and combined with other methods, the retention of CAF reached 34% [32]. Removal of CAF from wastewaters with pristine UF membrane was also conducted by Sheng et al. [33] with retention up to 5%. CBZ had properties nearest to CAF properties in this survey. This compound was similar to CAF and had lower retention with membranes modified by carboxylated nanotubes than for the pristine membrane. Use of HPLSA nanotubes with high SSA was successful in removing CBZ from water at a range of 77%-87%. For the pristine membrane, CBZ removal was 57%. Lower results were obtained by Vergili [34] and Chtourou et al. [35] using a nanofiltration membrane and a membrane bioreactor, respectively; they achieved a removal between 30% and 40%.

According to Schäfer et al. [36], bisphenol A, in contrast to CAF and CBZ, was removed at a higher level. The use of membrane module ZW-1 (Zenon Environmental) indicated removal of 30%–45% BPA from greywater. In this research, BPA removal was in the ranges of 60%–78% for membranes with carboxylated nanotubes and 74%–85% for membranes with HPLSA nanotubes. The addition of nanotubes improved the retention of hydrophobic compounds BPA and END (Fig. 4). END was removed by all modified membranes to 100%. A retention test of END by low-pressure filtration was also conducted by Utami et al. [37], who found that END was removed by hydrophilic ultrafiltration membrane. In almost all tests, END was removed in the range of 80%-100%, regardless of pH and feed concentration. END is the compound with the highest  $\log K_{ow}$  coefficient and highest hydrophobicity among the micropollutants tested. BPA and END were the substances that were adsorbed to the greatest extent on the membrane surface. Substances with  $\log K_{out}$  higher than 2.5 can interact with membranes by hydrophobic interactions [38]; this result was confirmed by tests of the contact angle and zeta potential presented in this work. Wanda et al. [39] reported that the removal of micropollutants in the filtration with PES membranes modified with nitrogen-doped single-walled nanotubes decreased following the order of their  $logK_{ow}$  values: BPA > CBZ > CAF. A similar result was found in the present study for given micropollutants as follows: END > BPA > CBZ > CAF.

#### 4. Conclusions

The results confirmed that the tested membranes belong to ultrafiltration membranes, both in terms of PES and PEG retention, as well as the calculated pore size. The results also confirmed that it is possible to remove microcontaminants through ultrafiltration membranes, relying mostly on hydrophilicity/hydrophobicity and adsorption. The retention results show that an unmodified membrane was partially able to retain microcontaminants, but not at a sufficient level. The presence of a modifier – carbon nanotubes – facilitated a higher level of retention. This particularly applied to membranes modified with HPLSA-SWCNT nanotubes, where the increase in the retention of all substances except CAF followed the nanotube concentration increase. For each modified membrane, an increase in BPA and END retention was observed, while among the SWCNT-COOH membranes, PES 15 0.1 turned out to be the best, and among the PES 15 HP05 modified membranes for microcontaminants retention.

Membrane modification affects the contact angle, made the membrane more hydrophilic, and influenced its porosity. At the same time, the presence of used nanocomposites influenced the shape of the PEG and PEO retention curves, and thus the retention of other substances. In addition, the presence of microcontaminants on the surface of the membrane caused a change in its properties, increased its hydrophilicity, and changed the surface charge. Consequently, membrane transport and separation properties also changed.

# Acknowledgments

This work was performed with financial support from the National Science Centre, Poland under grant no. UMO-2016/21/B/ST8/03128.

# Symbols

Α	—	Membrane area, cm <sup>2</sup>
$A_{e}$	_	Membrane effective surface area, m <sup>2</sup>
BPA	_	Bisphenol A
CAF	_	Caffeine
CBZ	_	Carbamazepine
$C_{f}$	—	Concentration of micropollutants in
,		feed, mg/L
$C_{p}$	_	Concentrations of micropollutants in
r		permeate water, mg/L
d	_	Membrane pore diameter in, nm
3	_	Porosity, %
END	—	Endosulfan
HPLSA-SWCNT	—	High purity large surface area
		single-walled carbon nanotubes
$J_{V}$	—	Membrane flux, L/m²/h
Ĺ	_	Membrane thickness, cm
$\log K_{ow}$	—	Log octanol/water partition
		coefficient
$m_{w}$	—	Weight of wet membrane, g
m <sub>d</sub>	—	Weight of dry membrane, g
MWCO	—	Molecular weight cut-off, Da
ρ	—	Pure water density, about 0.998 g/mL
PES	—	Polyethersulfone
R	—	Removal degree, %
SWCNT-COOH	—	Carboxylated single-walled carbon
		nanotubes
t	—	Permeation time, h
$T_{F}$	_	TOC concentration in feed, mg/L

$$T_p$$
 — TOC concentration in permeate, mg/L  
V — Permeation volume, L

# References

- D.M. Warsinger, S. Chakraborty, E.W. Tow, M.H. Plumlee, C. Bellona, S. Loutatidou, L. Karimi, A.M. Mikelonis, A. Achilli, A. Ghassemi, L.P. Padhye, S.A. Snyder, S. Curcio, C.D. Vecitis, H.A. Arafat, J.H. Lienhard V, A review of polymeric membranes and processes for potable water reuse, Prog. Polym. Sci., 81 (2018) 209–237.
- [2] H. Marshall, Environmental Nanotechnology, ED-Tech Press, Waltham Abbey Essex, 2018.
- [3] E. te Brinke, D.M. Reurink, I. Achterhuis, J. de Grooth, W.M. de Vos, Asymmetric polyelectrolyte multilayer membranes with ultrathin separation layers for highly efficient micropollutant removal, Appl. Mater. Today, 18 (2020) 1–5, doi: 10.1016/j.apmt. 2019.100471.
- [4] M. Adamczak, G. Kamińska, J. Bohdziewicz, Preparation of polymer membranes by *in situ* interfacial polymerization, Int. J. Polym. Sci., 2019 (2019) 1–13.
- [5] V. Vatanpour, S.S. Madaeni, R. Moradian, S. Zinadini, B. Astinchap, Fabrication and characterization of novel antifouling nanofiltration membrane prepared from oxidized multiwalled carbon nanotube/polyethersulfone nanocomposite, J. Membr. Sci., 375 (2011) 284–294.
- [6] S. Ali, S.A.U. Rehman, H.-Y. Luan, M.U. Farid, H. Huang, Challenges and opportunities in functional carbon nanotubes for membrane-based water treatment and desalination, Sci. Total Environ., 646 (2019) 1126–1139.
- [7] J. Heo, J.R. Flora, N. Her, Y.-G. Park, J. Cho, A. Son, Y. Yoon, Removal of bisphenol A and 17Bestradiol in single-walled carbon nanotubes-ultrafiltration (SWNTs-UF) membrane systems, Sep. Purif. Technol., 90 (2012) 39–52.
- [8] É. Celik, H. Park, H. Choi, H. Choi, Carbon nanotube blended polyethersulfone membranes for fouling control in water treatment, Water Res., 45 (2011) 274–282.
- [9] M. Adamczak, G. Kamińska, J. Boohdziewicz, The effect of various conditions on the ultrafiltration process of bisphenol A using nanocomposite membranes modified with carbon nanotubes, E3S Web Conf., 44 (2018) 1–7.
- [10] H. Yang, J. Guo, P. Yan, H. Gong, F. Fang, Sorption-desorption behavior of sulfamethoxazole, carbamazepine, bisphenol A and 17α-ethinylestradiol in sewage sludge, J. Hazard. Mater., 368 (2019) 739–745.
- [11] N. García-Vaqueroa, E. Lee, R. Jiménez Castañeda, J. Cho, J.A. López-Ramírez, Comparison of drinking water pollutant removal using a nanofiltration pilot plant powered by renewable energy and a conventional treatment facility, Desalination, 347 (2014) 94–102.
- [12] Y. Deng, Y. Sik Ok, D. Mohan, C.U. Pittman Jr., X. Dou, Carbamazepine removal from water by carbon dotmodified magnetic carbon nanotubes, Environ. Res., 169 (2019) 434–444.
- [13] L.J. Banasiak, B. Van Der Bruggen, A.I. Schäfer, Sorption of pesticide endosulfan by electrodialysis membranes, Chem. Eng. J., 166 (2011) 233–239.
- [14] M. Hamachi, B.B. Gupta, R. Ben Aim, Ultrafiltration: a means for decolorization of cane sugar solution, Sep. Purif. Technol., 30 (2003) 229–239.
- [15] S. Majeed, D. Fierro, K. Buhr, J. Wind, B. Du, A. Boschetti-de-Fierro, V. Abetz, Multi-walled carbon nanotubes (MWCNTs) mixed polyacrylonitrile (PAN) ultrafiltration membranes, J. Membr. Sci., 403–404 (2012) 101–109.
- [16] J. Zhang, Z. Xu, M. Shan, B. Zhou, Y. Li, B. Li, J. Niu, X. Qian, Synergetic effects of oxidized carbon nanotubes and graphene oxide on fouling control and anti-fouling mechanism of polyvinylidene fluoride ultrafiltration membranes, J. Membr. Sci., 448 (2013) 81–92.
- [17] W. Yu, T. Liu, J. Crawshaw, T. Liu, N. Graham, Ultrafiltration and nanofiltration membrane fouling by natural organic matter: mechanisms and mitigation by pre-ozonation and pH, Water Res., 139 (2018) 353–362.

- [18] A. Świerczyńska, J. Bohdziewicz, G. Kamińska, K. Wojciechowski, Influence of the type of membrane-forming polymer on the membrane fouling, Environ. Prot. Eng., 42 (2016) 197–210.
- [19] T. Sun, H. Fan, Q. Zhuo, X. Liu, Z. Wu, Covalent incorporation of aminated carbon nanotubes into epoxy resin network, High Perform. Polym., 26 (2014) 892–899.
- [20] S. Ali, S.A.U. Rehman, I.A. Shah, M.U. Farid, A.K. An, H. Huang, Efficient removal of zinc from water and wastewater effluents by hydroxylated and carboxylated carbon nanotube membranes: behaviors and mechanisms of dynamic filtration, J. Hazard. Mater., 365 (2018) 64–73.
- [21] G. Kamińska, J. Bohdziewicz, L. Palacio, A. Hernandez, P. Pradanos, Polyacrylonitrile membranes modified with carbon nanotubes: characterization and micropollutants removal analysis, Desal. Water Treat., 57 (2015) 1344–1353.
- [22] Y. Chun, D. Mulcahy, L. Zou, I.S. Kim, P. Le-Clech, Influence of hydrophobic and electrostatic membrane surface properties on biofouling in a submerged membrane bioreactor under different filtration modes, Desal. Water Treat., 57 (2017) 26641–26647.
- [23] M. Simonič, Compost leachate treatment using polyaluminium chloride and nanofiltration, Open Chem., 15 (2017) 123–128.
- [24] J. Wang, S. Yang, W. Guo, H.-H. Ngo, H. Jia, J. Yang, H. Zhang, X. Zhang, Characterization of fouling layers for in-line coagulation membrane fouling by apparent zeta potential, RSC Adv., 5 (2015) 106087–106093.
- [25] A. Rahimpour, S.S. Madaeni, A.H. Taheri, Y. Mansourpanah, Coupling TiO, nanoparticles with UV irradiation for modification of polyethersulfone ultrafiltration membranes, J. Membr. Sci., 313 (2008) 158–169.
- [26] A. Sotto, A. Boromand, S. Balta, J. Kim, B. Van der Bruggen, Doping of polyethersulfone nanofiltration membranes: antifouling effect observed at ultralow concentrations of TiO<sub>2</sub> nanoparticles, J. Mater. Chem., 21 (2011) 10311–10320.
- [27] T. Mantel, P. Benne, S. Parsin, M. Ernst, Electro-conductive composite gold-polyethersulfone-ultrafiltration-membrane: characterization of membrane and natural organic matter (NOM) filtration performance at different *in-situ* applied surface potentials, Membranes, 8 (2018) 1–18.
- [28] X. Fang, J. Li, X. Li, X. Sun, J. Shen, W. Han, L. Wang, Polyethyleneimine, an effective additive for polyethersulfone ultrafiltration membrane with enhanced permeability and selectivity, J. Membr. Sci., 476 (2015) 216–223.

- [29] M. Adamczak, G. Kamińska, J. Bohdziewicz, Influence of polymer and carbon nanotubes concentration for caffeine retention in UF process, PECO, 12 (2018) 371–381.
- [30] A.I. Schäfer, I. Åkanyeti, A.J. Semião, Micropollutant sorption to membrane polymers: a review of mechanisms for estrogens, Adv. Colloid Interface Sci., 164 (2010) 100–117.
- [31] N.K. Khanzada, M.U. Farid, J.A. Kharraz, J. Choi, C.Y. Tang, L.D. Nghiem, A. Jang, A.K. An, Removal of organic micropollutants using advanced membrane-based water and wastewater treatment: a review, J. Membr. Sci., 598 (2020) 117–672.
- [32] Y. Wang, H. Huang, X. Wei, Influence of wastewater precoagulation on adsorptive filtration of pharmaceutical and personal care products by carbon nanotube membranes, Chem. Eng. J., 33 (2018) 66–75.
- [33] C. Sheng, A.G. Agwu Nnanna, Y. Liu, J.D. Vargo, Removal of trace pharmaceuticals from water using coagulation and powdered activated carbon as pretreatment to ultrafiltration membrane system, Sci. Total Environ., 550 (2016) 1075–1083.
- [34] I. Vergili, Application of nanofiltration for the removal of carbamazepine, diclofenac and ibuprofen from drinking water sources, J. Environ. Manage., 127 (2013) 177–187.
- [35] M. Chtourou, M. Mallek, M. Dalmau, J. Mamo, E. Santos-Clotas, A.B. Salah, K. Walha, V. Salvadó, H. Monclús, Triclosan, carbamazepine and caffeine removal by activated sludge system focusing on membrane bioreactor, Process Saf. Environ., 118 (2018) 1–9.
- [36] A.I. Schäfer, L.D. Nghiem, N. Oschmann, Bisphenol A retention in the direct ultrafiltration of greywater, J. Membr. Sci., 283 (2006) 233–243.
- [37] W.N. Utami, R. Iqbal, G. Wenten, Rejection characteristics of organochlorine pesticides by low pressure reverse osmosis membrane, J. Air Indonesia, 6 (2018) 103–108.
- [38] Y. Wang, X. Wang, M. Li, J. Dong, C. Sun, G. Chen, Removal of pharmaceutical and personal care products (PPCPs) from municipal waste water with integrated membrane systems, MBR-RO/NF, Int. J. Environ. Res. Public Health, 15 (2018) 1–12.
- [39] E.M. Wanda, B.B. Mamba, T.A. Msagati, Nitrogen-doped carbon nanotubes/polyethersulfone blend membranes for removing emerging micropollutants, Clean Soil Air Water, 45 (2017) 1–12.