



Fouling behavior and micropollutants removal during treatment of surface water by ultrafiltration using nanocomposite membranes

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)*

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ABSTRACT

Fouling is an accumulation of pollutants from feed water on the membrane surface, a phenomenon in which feed impurities form a layer on the surface of the membrane. They are usually high molecular weight impurities forming so-called filter cake. The formation of such cake on one hand causes a deterioration of flow through the membranes, but on the other hand it can create an additional layer in which microcontaminants can be removed. This study presents fouling behavior of nanocomposite membrane during ultrafiltration treating water spiked with organic micropollutants with different properties (caffeine, bisphenol A, carbamazepine, and β -endosulfan). The river water was used as feed water to reflect ultrafiltration conditions in commercial scale. Ultrafiltration was conducted under constant transmembrane pressure and temperature in the cross-flow filtration system. Membranes were modified by single-walled carbon nanotubes functionalized with carboxyl groups. Obtained results showed, that the most antifouling membrane was that with the highest concentration of nanotubes, however, it was a membrane with the lowest retention level and highest flux. The most effective was the membrane with an intermediate amount of nanotubes in its structure.

Keywords: Micropollutants; Carbon nanotubes; Ultrafiltration; Fouling; Nanocomposite membranes

1. Introduction

Ultrafiltration (UF) is one of the low-pressure membrane techniques widely used for elimination of the macromolecular compounds. The main mechanism involved in the removal of contaminants is a selective filtration of the feed components through membrane pores. It bases on sieve effect, thus the particles bigger than membrane pores are effectively retained, while smaller one enters to permeate. Emerging microcontaminants (pharmaceuticals, drugs, plasticizers, pesticides, or endocrine disrupting compounds with low molecular mass are mostly removed by nanofiltration (NF) and reverse osmosis (RO). UF rejects mostly organic matter, suspended solids, bacteria, and turbidity [1].

Recently, owing to nanocomposite ultrafiltration membranes, even organic micropollutants (like pharmaceuticals or pesticides) can be separated by ultrafiltration. This is a new group of unconventional membranes that contain nanofillers in the structure or on the surface or both. The most popular nanofillers are metals and metal oxides and also carbon materials, like carbon nanotubes, graphene, or fullerenes [2]. However, due to the positive effect both on pollutants removal and general ultrafiltration performance the most beneficial are carbon nanotubes.

Carbon nanotubes (CNTs) have high total surface area, low mass, and good adsorption properties. Functionalization of carbon nanotubes improves their dispersion in a casting solution and enhances CNTs adhesion to the polymer [3].

* Corresponding authors.

Functionalization is mostly conducted by strong acids—nitrate and sulfur acids. As it was said, acid treatment does not only improve dispersion of CNTs in solvents but also removes amorphous carbon and improves concentration and stability of this material. Raw CNTs and functionalized CNTs are highly used for membrane modification. Their presence in membranes positively affects membrane permeability because water can easily migrate through the carbon nanotubes [4]. Their occurrence also improves separation effect and antifouling properties. For example retention and adsorption of bisphenol A (BPA) and 17 β -estradiol was improved by addition of single-walled CNTs into UF system [5]. In Celik et al. [6] work, modification of polyether-sulfone (PES) membranes with functionalized multi-walled carbon nanotubes highly increased natural organic matter retention and absorbance limitation (UV 254 nm) for organic compounds [6]. In another work of Adamczak et al. [7] with the use of the same membranes in dead-end system reduced BPA by 70%–80% for modified membranes in comparison to 25% of unmodified PES membrane.

Mentioned fouling occurs mostly in membrane processes as an effect of pollutant deposition on the membrane surface and pores blocking. It results in permeability loss and increase in operational cost as well as membrane deterioration. Flux decline for membranes with smaller pore size (10–50 kDa) is affected by accumulation of organic particles and formation of cake layer on the membrane surface [8]. Fouling in case of nanocomposite membranes is lower comparing with typical conventional ultrafiltration membranes. It is attributed to properties of nanofillers, which are able to make membrane surface more hydrophilic and thus more resistant to be fouled. The addition of nanofillers provides better fouling resistance and microcontaminants removal [3,9]. Most of these studies were carried out for artificial solutions containing typical synthetic foulants (BSA, humic substances). Moreover, they describe only fouling behavior rather than both fouling and treatment efficiency. Thus, these studies did not reflect conditions occurring in real water matrices, like surface waters, that contain many different organic and inorganic substances affecting the general performance. In that context, there is an increasing need to study the fouling behavior as well-separation ability of nanocomposite membranes treating surface water in ultrafiltration.

UF process with polymer membranes can be conducted as cross-flow or dead-end mode. Unlike the dead-end filtration, in cross-flow fluid flow is axial along the membrane surface. It results in better mass transfer and lower fouling. In order to maintain a constant flux, fouling control is one of the most important aspects of membrane separation [10]. Another approach is to prepare membrane with maximum flux and maximum solute rejection, minimizing capital, and operating costs. Lifetime of membrane is defined by its fouling tendency [3].

The aim of this study was to investigate fouling behavior nanocomposite membrane (modified with SWCNT-COOH) during ultrafiltration treating surface water spiked with organic micropollutants with different properties (CAF, caffeine; BPA, bisphenol A; CBZ, carbamazepine; END, β -endosulfan). Effect of SCWNT-CCOH concentration in membrane on treatment efficiency, micropollutants removal, and fouling behavior was investigated.

2. Materials and methods

2.1. Materials

Single-walled carbon nanotubes functionalized with carboxyl groups (SWCNT-COOH) were obtained from Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences and used for membrane modification (Chengdu, China). PES as the basic material for membrane preparation was supplied by BASF Company (Ludwigshafen, Germany). N,N-dimethylformamide (DMF), hexane, acetonitrile, and methanol (all analytically pure) were purchased from Avantor Performance Materials (Gliwice, Poland). Chemicals (BPA, END, CAF, CBZ) with purity of 99% were provided by Sigma Aldrich (Poznań, Poland). Deionized water was taken from RephiLe Ltd. system (Shanghai, China).

2.2. Feed water and micropollutants

The feed water for this study was taken from the Kłodnica River in Katowice, Silesian Voivodeship, Poland. Kłodnica water was spiked with a sufficient volume of stock solution of micropollutants (1 g/L in methanol) to obtain a final concentration of 1 mg/L for each compound. Prepared water was the feed water in all experiments. Given micropollutants commonly occur in the aquatic environment and belong to the main groups of environmental and hazardous micropollutants. For example, CBZ is a pharmaceutical, BPA is an endocrine disruptor, END belongs to a group of pesticides, and CAF is a psychoactive drug [11,12]. They show different physicochemical properties, which are presented in Table 1. The physicochemical properties of Kłodnica feed water are shown in Table 2.

2.3. Chromatographic analysis of micropollutants

Concentration of micropollutants in feed and permeate were determined by gas chromatography with flame ionization detector 6500GC System GC-FID by YI Instrument Co. Ltd. (Hogye-dong, Anyang, Korea). Chromatograph was equipped with 30 m \times 0.25 mm i.d. SLB@5 ms fused silica capillary column of 0.25 μ m film thickness supplied by Sigma-Aldrich (Poznań, Poland). Helium 5.0 was used as the carrier gas. The quantitative calculations was carried out on the basis of measurements of peak area that was compared with data for analysis of standard solutions. Chromatographic separation of micropollutants was performed by 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 sample was passed through the columns. Then, when column was completely dried, analytes were eluted with 3 mL of methanol and 3 mL of hexane. Eluted portion was dried in nitrogen stream and then analyzed using GC-FID. The analytical procedure allowed the recovery of compounds at the level of 100%. Retention of micropollutants were calculated according to the following Eq. (1):

Table 1
Physicochemical properties of micropollutants [13–16]

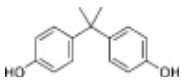
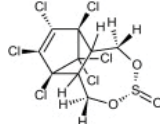
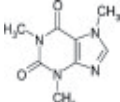

Properties	Bisphenol A	β -Endosulfan	Caffeine	Carbamazepine
Structure				
Formula	C ₁₅ H ₁₆ O ₂	C ₉ H ₆ Cl ₆ O ₃ S	C ₈ H ₁₀ N ₄ O ₂	C ₁₅ H ₁₂ N ₂ O
Molar mass (g/mol)	228.291	406.93	194.194	236.3
pKa	10.10	–	10.4	14.00
LogK _{ow}	3.32	3.83	–0.55	2.45
Water solubility (mg/L) 20°C	<1	0.45	21,600	17.7

Table 2
Physicochemical parameters of water collected for testing (Kłodnica, Katowice, Poland)

Parameter	Values of parameters
pH	7.21
Conductivity (μ S/cm)	6,400.00
Color (mg Pt/dm ³)	56
Absorbance (–)	0.18
Nitrate (mg N–NO ₃ [–] /dm ³)	4.23
Phenol index (mg/dm ³)	0.872

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

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

2.4. 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 and 84.98–84.90 wt.% of DMF as presented in Table 3. Proper amounts of SWCNT-COOH and PES were added to the DMF. Casting solution was shaken 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 $\pm 40^\circ\text{C}$. Precipitated membranes were stored in deionized water for 24 h for their stabilization.

2.5. Membrane characterization

Zeta potential is a measure of the electrical charge of the membrane surface and was measured using an electrokinetic analyzer SurPASS™ 3 (Anton Paar, Graz, Austria). Measurements of contact angle were performed using the goniometer PG-1 (Fibro System AB, Sweden) and the sessile drop method was applied, where 10 strips of dried tested

Table 3
Composition of casting solutions

Symbol	PES (wt.%)	SWCNT-COOH (wt.%)	DMF (wt.%)
PES 15 0.02	15	0.02	84.98
PES 15 0.05	15	0.05	84.95
PES 15 0.1	15	0.1	84.90

membrane was inserted into a device. By syringe on top drop of distilled water were applied on membrane surface. Trough enlarged projection of water drop on gauge, value of contact angle was measured. For every type of membrane, 10 samples were measured and the average value was calculated.

2.6. Setup and filtration run

UF was carried out in a plate-and-frame membrane module SEPA CF-NP (GE Osmonics, USA). The experimental installation was operated in the cross-flow filtration mode. The permeate was continuously collected from the setup. The filtration surface area of the membrane was 155 cm². UF was carried out for all membranes at constant pressure of 5.00 bar and temperature of 20°C and velocity of 0.7 m/s. Experiments were carried out in two types of modes (with forward flushing—in short UF-FF and without FF—in short UF). UF run included 240 min of feed filtration with flux measurement for each 30 min. Membrane was not cleaned and the thickness of the cake layer increased over time. Each filtration run of UF-FF consisted of four cycles including 60 min of feed filtration followed by forward flushing with deionized water. Before each experiment, the membranes were conditioned with deionized water. For each stage flux was measured and calculated from the following Eq. (2):

$$J_v = \frac{V}{A \cdot t} \quad (2)$$

where J_v is the flux (L m^{–2} h^{–1}), V is the permeation volume (L), A is the membrane effective surface area (m²), and t is the permeation time (h).

Subsequently, relative flux was calculated according to the following Eq. (3):

$$\alpha = \frac{J_V}{J_{V0}} \quad (3)$$

where J_{V0} is the flux of deionized water through the membrane (h).

Reversible (rev) and irreversible (irr) resistances of ultrafiltration were also calculated. Reversible resistance is formed by cake layer formation on membrane surface, which can be easily removed by physical (hydraulic flushing or backwash) and chemical cleaning. Meanwhile, irreversible resistance was caused by internal blocking of membranes pores and cannot be removed by hydraulic cleaning. Additionally, back-flushing for flat membranes is often not allowed due to its structural vulnerability [17]. Irreversible resistance also means a loss of permeability due to the irreversible sorption of materials that resists physical or chemical cleaning [18]. The fouling behavior of membrane filtration can be described by Darcy's law. For constant pressure filtration, the resistance-in-series model is expressed as:

$$R_m + R_f = \frac{\Delta P}{\mu \cdot J} \quad (4)$$

where J is the permeate flux ($\text{L m}^{-2} \text{h}^{-1}$), ΔP is the transmembrane pressure (bar), μ is the water viscosity (bar·h), R_m is the membrane resistance, and R_f is the total fouling resistance. R_f is the sum of hydraulically reversible (R_{rev}) and hydraulically irreversible (R_{irr}) fouling resistances [m^{-1}]:

$$R_f = R_{\text{rev}} + R_{\text{irr}} \quad (5)$$

The resistance of a clean membrane was determined by filtering deionized water until a constant flux was achieved. Then, Kłodnica feed water was filtered and flux was monitored in order to determine R_f [19].

Volume reduction ratio was also calculated for the end of experiments, according to this Eq. (6):

$$\text{VRR} = \frac{V}{V_r} \quad (6)$$

where VRR is volume reduction ratio and V_r is concentrate volume [L].

3. Results and discussion

3.1. Membrane surface properties

As seen in Fig. 1, clean nanocomposite PES membranes had similar contact angle values, in a range of 47.4–49.2°. These values corresponded to moderate hydrophobic-hydrophilic properties. Slightly lower contact angle for PES 15 0.1 and PES 15 0.05 confirmed slightly better hydrophilic properties that results in higher membrane permeability. It seems to be clear that higher concentration of SWCNT-COOH affected on hydrophilicity of these membranes. Pristine PES membranes, according to many authors, had contact angle between 62.1° and 73.5° and all of them confirmed that addition of nanocomposites lowered this parameter with slight increase in water permeability [7,20–22]. Membranes after the ultrafiltration process had different properties. They were definitely more hydrophobic after the process than before the ultrafiltration. It was caused by deposition/adsorption of hydrophobic pollutants of the feed on the membrane surface. This phenomenon was confirmed by Świerczyńska et.al. [22] and Kertész et.al. [23]. Contact angle of fouled membrane prepared from pristine PES was 3° higher than clean membrane [22].

Zeta potential of clean membranes was similar to each other as seen in Fig. 2. Value of zeta potential at pH 7 varied from –21.4 to –22.6 (mV) for PES 15 0.1 and PES 15 0.02, respectively. Identical values for commercial PES pristine membranes NF-3 and NF-4 [Ande Membrane Separation Technology & Engineering (Beijing) Co. Ltd., China] were provided by Yu et.al. [24]. The properties of PES membranes might originate from the sulfonic group occurred in the polymer structure [22]. Decrease in zeta potential of fouled membranes was caused by deposition of hydrophobic components of matter contained in river water. This kind of contaminant, like humic acids, are negatively charged at pH values of natural waters (pH 6–9) [25]. Large amount of the negatively charged organic matter accumulated on the membranes, resulting in a decrease (more negative) of membrane

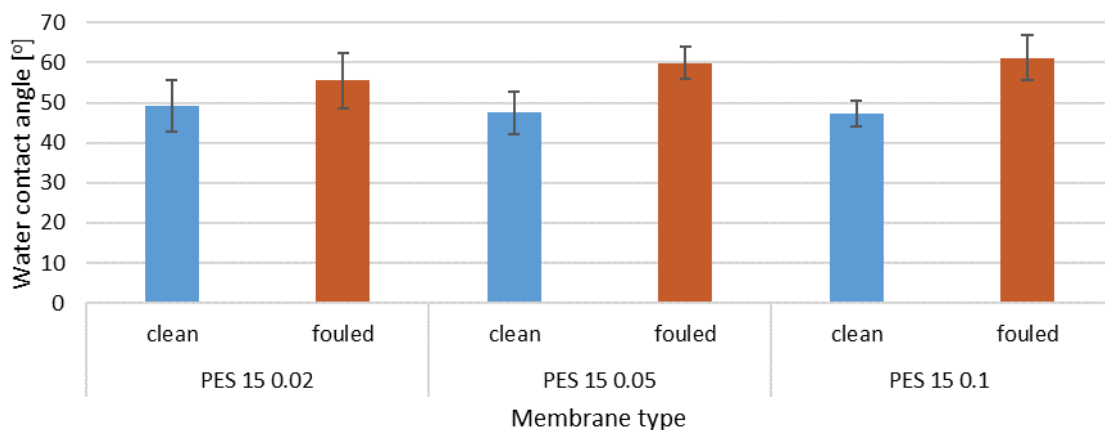


Fig. 1. Water contact angle of tested membranes (clean and fouled).

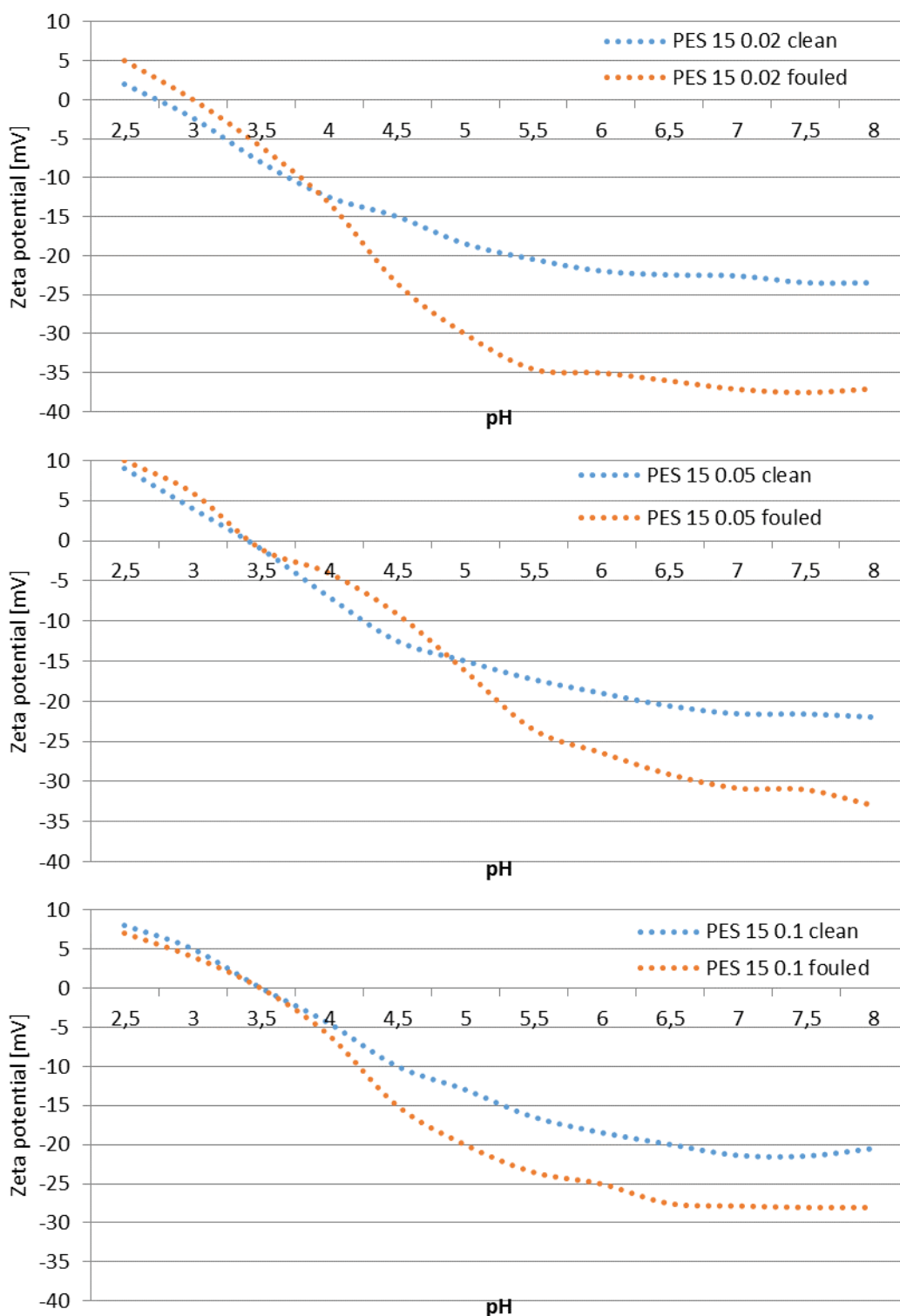


Fig. 2. Zeta potential (mV) of tested membranes (clean and fouled).

surface charge [26]. Similar results were achieved by Xu et al. [26]. In mentioned research, authors also discovered, that all tested commercial membranes after filtration had even more negative values below -20 mV. As can be seen in Fig. 2, fouled membrane had isoelectric point at higher pH value than clean

membranes. It could be caused by biopolymers. Biopolymers were recognized as part of river water natural organic matter. Due to small fractal dimension they block membrane pores through interaction between hydrophobic membrane surface and hydrophilic biopolymers [24]. They were negatively

charged and caused a decrease in zeta potential of membranes. Also, isoelectric point shifted to higher pH values for all membranes, what is typical during filtration of water containing organic matter [22]. In many research articles zeta potential of membranes was higher (less negative) for fouled membrane than for clean membrane (in neutral pH) [27–29]. This phenomenon was mostly caused by accumulation of natural substances from water on membrane surface. In our study course of zeta potential curve for fouled nanocomposite membranes had opposite trend than data from the literature due to conditions of the experiments. Filtration of river water was conducted like in industrial scale which typically includes flushing and backwashing. Zeta potential was measured directly after fourth flushing and deposited substances was washed out from the membrane surface during forward flushing.

3.2. Membrane flux in UF

During filtration of Klodnica feed water flux decrease was observed (Fig. 3). For membranes PES 15 0.02 and PES

15 0.05, final flux was reduced by 33% and 44%, respectively. Highly better performance showed membrane PES 15 0.1 with flux reduction by 28%. PES 15 0.05 was the most blocked membrane due the lowest flux. However, this layer could have positive effect on retention of microcontaminants. The most antifouling membrane was PES 15 0.1, with gradual flux decrease. Similar results were achieved by Guo et al. [30] where increase of CNTs concentration on PES membrane smoothed the line of permeate flux during filtration of wastewater effluent.

3.3. Micropollutant removal in UF

Retention values are presented in Fig. 4. Micropollutant removal in this test could be divided into two groups. Chemicals with $\text{Log}K_{ow}$ coefficient below value 2.5 were mostly soluble in water. Substances with $\text{Log}K_{ow}$ higher than 2.5 can interact with membranes by hydrophobic interactions [31]. This coefficient highly affects the separation effect. END was removed in range from 83% to 95%, for PES 15 0.1 and PES 0.05, respectively. BPA removal was in range from

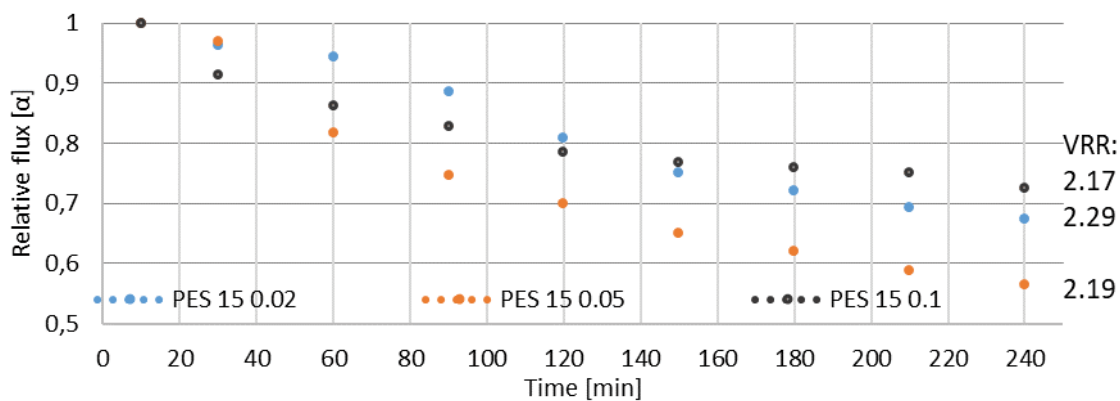


Fig. 3. Permeate flux vs. time for UF with different nanocomposite membranes.

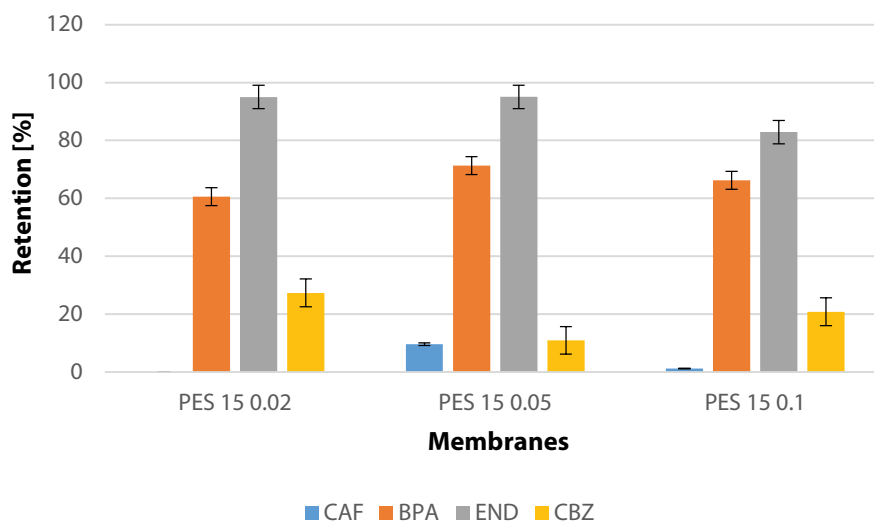


Fig. 4. Retention of micropollutants in UF.

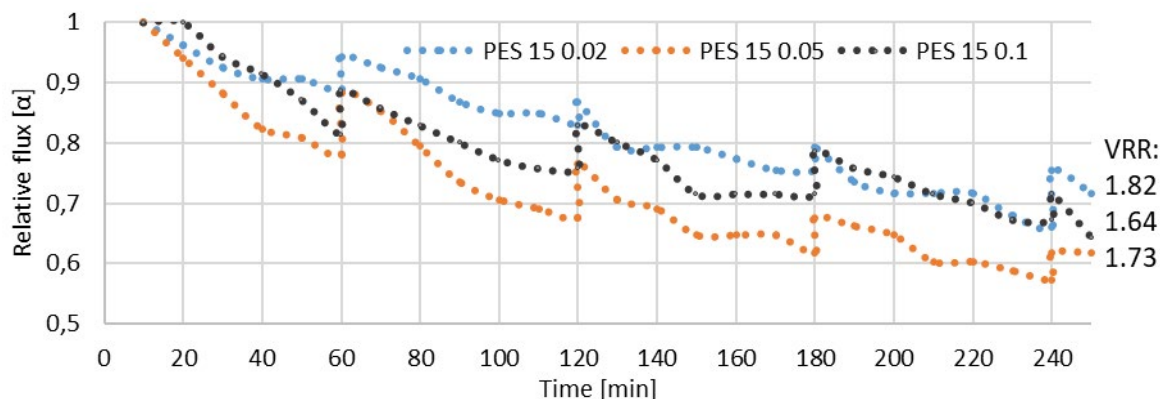


Fig. 5. Relative permeate flux vs. time within four cycles of filtration in UF-FF experiments.

60% for PES 15 0.02% to 71% for PES 15 0.05. Hydrophilic compounds as CBZ were removed in 27% by membrane PES 15 0.02 and in 11% by PES 15 0.05. CAF was removed only by PES 15 0.05 membrane in 10%. According to Celik et al. [6] PES membranes modified with carbon nanotubes with carboxyl groups below 0.5 wt.% were able to repulse negatively charged contaminants. Wanda et al. [32] reported that removal of micropollutants in filtration with PES membranes modified with nitrogen-doped single-walled nanotubes decreased following the order of their $\text{Log}K_{ow}$ values: BPA > CBZ > CAF. Similar tendency was found for given micropollutants as follows END > BPA > CBZ > CAF.

The most effective membrane was PES 15 0.05 membrane because of the highest retention of BPA, END, and CAF. For membrane PES 15 0.1 its hydrophilicity could affect the lower removal of END and BPA and slightly higher for CBZ. BPA was able to create a hydrogen bonding between compound and membrane surface that enhanced removal [33]. In addition, the highest degree of adsorption onto membrane was observed for pH 7 according to Siyal et al. [34], for Adamczak et al. was pH 6.5 [7]. Retention test of endosulfan by low-pressure filtration was also conducted by Utami et al. [35]. In this work, END was removed by hydrophilic ultrafiltration membrane. In almost all tests, END was removed in the range 80%–100% regardless of pH and feed concentration. Similarly as in our study, high hydrophobicity was the most important reason of its high removal.

3.4. Fouling and membrane resistances in UF-FF experiment

During ultrafiltration of Kłodnica river water flux decline was observed, suggested occurrence of membrane fouling. This unfavorable phenomenon was caused by the macromolecular compounds present in the surface water. The less fouled membrane was membrane with the highest addition of nanotubes (PES 15 0.1) which suggests the best antifouling properties. For PES 15 0.02 and PES 15 0.05 flux decline was very intensive, while PES 15 0.1 revealed slower decrease in flux. Relative flux was presented in Fig. 5. It is attributed with different antifouling properties of membranes. When flux decline is very fast, fast deposition of pollutants also occurs. It might be related with the lowest contact angle of this membrane. Membranes with lower contact angle were less susceptible for fouling phenomenon.

To investigate fouling behavior further, reversible and irreversible resistances were calculated. As seen in Fig. 6, the major part of fouling was irreversible in nature. The irreversible resistance increased over time due to incremental foulants accumulation, while reversible resistances did not change greatly in cycles 1–4. Based on the obtained results, it can be observed that membrane PES 15 0.05 had the greatest fouling. It can be also seen, that the lowest fouling was for PES 15 0.1 membrane. PES 15 0.02 had intermediate properties.

Achieved results can be related with values of contact angle for membranes. For example the least blocked membrane (PES 15 0.1) had the lowest contact angle and thus the higher hydrophilicity. This corresponded well with changes in the zeta potential curve. Difference of this factor between clean and fouled membrane PES 15 0.1 was lower than in other membranes. This could happen due to the smaller amount of contaminants deposited on its surface. Achieved results of the flow rate and the degree of removal of microcontaminants can be directly compared with fouling. This phenomenon can be also observed visually on the surface of the membranes: the most blocked PES 15 0.02 membrane after the filtration process was much more contaminated than the others, while PES 15 0.1 with the highest permeability and the lowest retention exhibited the lowest visual contamination. Photographs of the membranes can be found in Fig. 7.

The most fouled membrane had the highest retention level (for BPA and END). This could be caused by cake layer formation that improves separation effect. However, membrane modification was conducted to obtain antifouling properties with the lowest irreversible resistance. According to Zinadini et al. [36] fouling resistance of PES membrane mixed with graphene plates was definitely lower for unmodified membrane. A greater concentration of modifier also decreased fouling resistance factor of membrane.

4. Conclusions

Fouling behavior of three membranes with different content of carbon nanotubes with carboxyl groups were examined in the conducted tests. Membranes had similar surface properties in relation to each other, as well as in relation to membranes with similar properties, tested by other

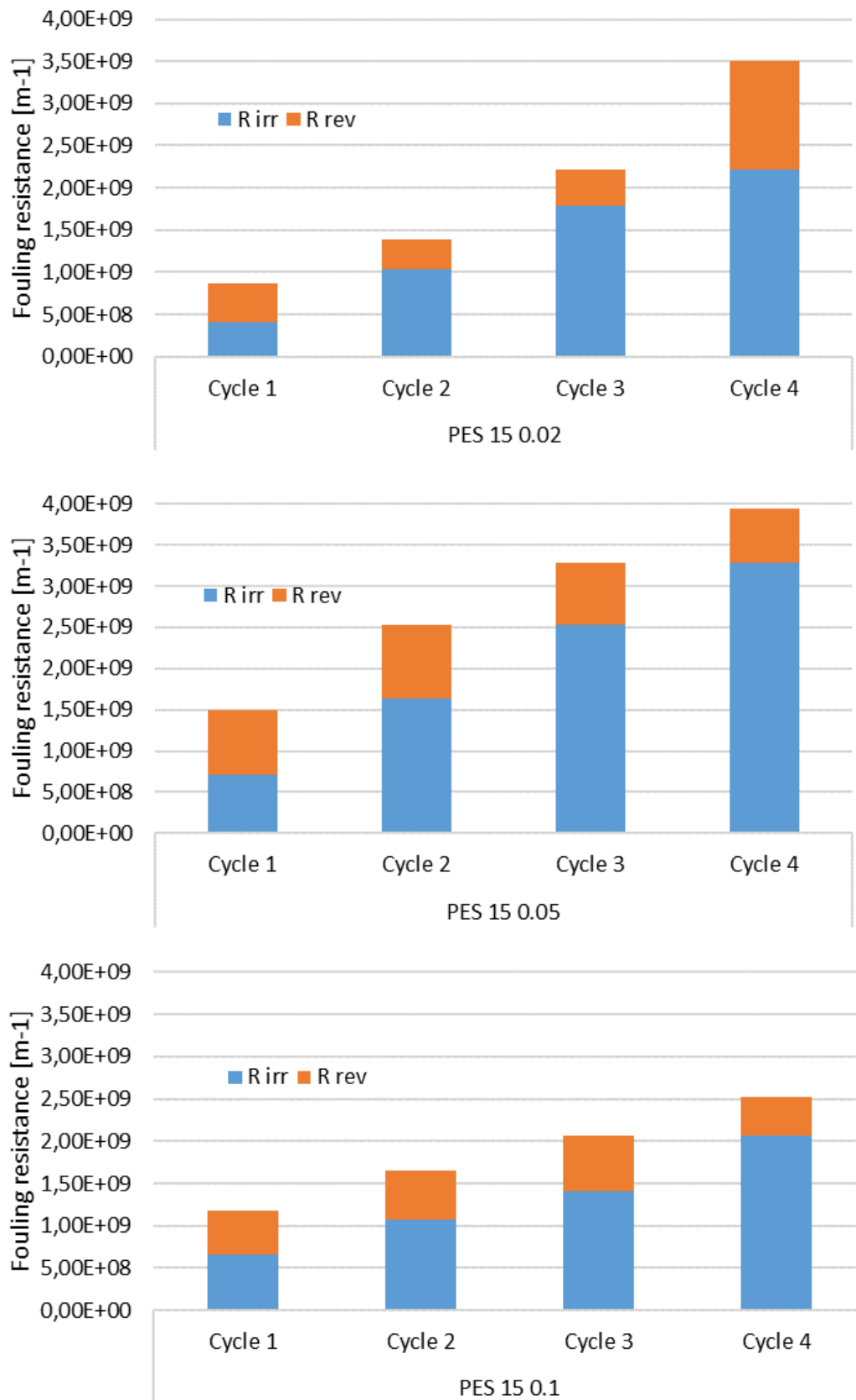


Fig. 6. Reversible and irreversible fouling of membranes in four cycles in UF-FF.



Fig. 7. Photographs of membrane surfaces after filtration: PES 15 0.02, PES 15 0.05, and PES 15 0.1.

authors. The most antifouling membrane was PES 15 0.1 because of the lowest total fouling resistance and irreversible fouling resistance values. However, at the same time it was a membrane with the lowest retention level and highest flux. The major part of fouling was irreversible in nature. The most fouled membrane had the highest retention level (for BPA and END). This could be caused by cake layer formation that improves separation effect. However, membrane modification was conducted to obtain antifouling properties with the lowest irreversible resistance. Combining the results of retention, flow, and antifouling properties of membranes, it can be said that the most effective membrane was membrane PES 15 0.05 with the highest retention level, highest fouling resistance, and lowest flux. Anyway, these membranes need to be more improved for further cross-flow filtration of water contaminated with micropollutants.

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