

## Article

# Application of Waste Polymers as Basic Material for Ultrafiltration Membranes Preparation

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**Abstract:** Polystyrene is a polymer commonly used in civil engineering as styrofoam for building isolation. It is also used in the packaging of glass and sensitive products such as electronics, household products, and other goods. Single-use products such as cups and plates made from synthetic materials are important for waste management. All of these products are responsible for the creation of 6200 kt of waste in 2015 alone. Quite a new idea of the application of styrofoam waste is to use it as basic material for preparation of membranes, which are widely used for water reclamation. Nowadays, membranes are prepared from different, non-waste polymers like polysulfone, poly(ether sulfone), polyacrylonitrile, and others. The aim of this study was to prepare polystyrene waste ultrafiltration membrane and assess its usage to treat river surface water. Conducted tests have been divided into two stages: the first part tested four membranes with different concentrations of waste polymer in order to determine the membrane with the most favorable properties. In the second part, selected membrane was modified with single-walled carbon nanotubes functionalized with hydroxyl groups in three different concentrations. The ultrafiltration process was conducted in a dead-end system under pressure of 0.1 MPa. The obtained results suggest that the ultrafiltration membranes with waste styrofoam guarantee similar treatment effects as with the usage of membranes made with other polymers or commercial membranes.

**Keywords:** membranes; ultrafiltration; polystyrene; waste; carbon nanotubes

## 1. Introduction

Polystyrene is a polymer commonly used for insulation in the form of foamed polystyrene, i.e., styrofoam [1]. Styrofoam is expanded polystyrene (EPS) and consists of 98% air and 2% of polymer. This product is used mostly as insulations but also as heat-insulating containers for food or filling of packaging during transport. It most often used as packaging for glass products and other delicate products, such as electronic equipment, household goods, and small accessories. In addition, a rather significant group of polystyrene waste are disposable items such as trays or cups [2]. The share of this type of waste is still growing. Polystyrene, due to its properties, belongs to environmental wastes. It can be decomposed only by photodegradation, because UV radiation causes the disintegration of foamed polystyrene forms, and the gas sealed in the pores evaporates. This process lasts from a dozen to several dozen years if there is no sunlight [3]. In 2015, 6200 kt of EPS was produced, and only 40% was reused. For this reason, it is necessary to effectively manage this waste and grow its reuse. One of the ways is to convert spent styrofoam into products related to construction. Among other things, it is processed into products for protection against moisture and water of mineral surfaces and it is also used in the form of styrofoam aggregate, lightweight concrete, an intermediate polystyrene concrete that is an insulating material [2].

A completely new idea is the use of styrofoam waste as a basic material for the production of polymer membranes for water purification. At present, other types of polymers are used, such as polysulfone, polyethersulfone (PES), polyacrylonitrile, polyvinylidene fluoride (PVDF), polyamide or polyimide, and many others [4]. The use of polystyrene is practically negligible. To our best knowledge study on waste polystyrene usage for membrane production is scant. The only available study on this subject comes from 2008 where membranes made of polystyrene were modified with a porogenic substance—polyvinylpyrrolidone and with nanoparticles of titanium oxide (TiO<sub>2</sub>) [5]. These membranes were made by phase inversion where the solvent was 1-methyl-2-pyrrolidone (NMP), while the non-solvent was deionized water. Additionally, in some studies, polystyrene was used for membranes and fibers production by electrospinning [6,7].

In this work, carbon nanotubes (CNTs) were modifiers. Presence of CNTs changes membrane surface for more hydrophilic and, by controlling their concentration, it is possible to control membrane fouling [8]. In this test, single-walled carbon nanotubes modified with hydroxyl groups were used. Micropollutants, such as bisphenol A (BPA), caffeine (CAF), carbamazepine (CBZ), and endosulfan (END) usually occur in surface water as an effect of anthropogenic activity. Each of the mentioned substances has different properties. BPA is a substance widely used in the plastics industry as a plasticizer. The compound is perceived as a substance that disrupts addicted secretion. Caffeine is a substance with relatively low environmental impact, although it is certainly the most commonly used in almost every household. CBZ is a drug used in mental illnesses, and END belongs to the group of pesticides. [9,10].

The aim of this work was to determine optimal content of polystyrene in the casting solution. Then, in order to improve their properties for micropollutants removal, the trial by adding nanotubes was undertaken membranes to achieve higher retention of micropollutants.

## 2. Materials and Methods

### 2.1. Materials and Feed Waters

Styrofoam waste was taken from the filling of packaging with electronic equipment, food products, and loose filling of postal parcels. The polymer obtained in this way was designated as rPS (recycled polystyrene). N, N-dimethylformamide (DMF) was purchased from Avantor Performance Materials (Gliwice, Poland). Micropollutants (BPA, CAF, CBZ, END) were purchased from Sigma Aldrich (Poznań, Poland). Single-walled carbon nanotubes functionalized with hydroxyl groups (SWCNT-OH) were purchased from Chengdu Organic Chemistry (Chengdu, China). Their properties are listed in Table 1. Deionized water was collected from the Direct-Pure adept Ultrapure Lab Water Systems by RephiLe Bioscience Ltd. (Shanghai, China).

**Table 1.** Properties of -OH functionalized single-walled carbon nanotubes.

Properties:	Values:
-OH content	3.96%
Special Surface Area	>300 m <sup>2</sup> /g
Bulk density	0.14 g/cm <sup>3</sup>
True density	2.1 g/cm <sup>3</sup>

### 2.2. Membrane Preparation

Membranes in the form of flat polymer sheets using rPS polymer, DMF, and SWCNT-OH were prepared by phase inversion using automatic film applicator (Elcometer 4340) (Figure 1). The polymer content in the casting solution varied in the range from 14 to 20 wt.%. Due to the presence of gas bubbles in the solutions, they were subjected to an ultrasonication for about 120 s. Membranes in the form of a polymer film with a casting thickness of 0.15 mm were stored in deionized water for 24 h.

The membranes are designated with the symbol rPS X, where X is wt.% share of the polymer contained in the membrane casting solution. Additionally, three membranes with nanotubes were prepared and described as rPS 0.02, rPS 0.05, and rPS 0.1. Numbers represent SWCNT-OH contribution in membrane casting solution. The details about the content of membrane casting solutions are described in Table 2.



Figure 1. Elcometer 4340 Automatic Film Applicator.

Table 2. Content of casting solution.

Membrane:	rPS [wt.%]	Solvent (DMF) [wt.%]	SWCNT-OH [wt.%]
rPS 14	14	86	-
rPS 16	16	84	-
rPS 18	18	82	-
rPS 20	20	80	-
rPS 0.02	16	83.98	0.02
rPS 0.05	16	83.95	0.05
rPS 0.1	16	83.90	0.10

### 2.3. Membrane Characterization

As part of the research, some structural and surface membrane properties were determined. The thickness of the membrane was measured using a Hogetex electronic micrometer with 0.001 mm precision. Porosity measurements were carried out using 5 pieces of a 4 cm<sup>2</sup> moist membrane. They were dried using tissue paper and then weighed. Subsequently, the same membrane fragments were placed in an oven for 24 h at 60 °C and then weighed. The result was the arithmetic mean of five measurements. The results obtained in this way were calculated using the Formula (1):

$$\varepsilon = \frac{m_w - m_d}{A \cdot L \cdot p} \cdot 100 \quad (1)$$

where:

$\varepsilon$ —porosity [%],

$m_w$ —weight of the moist diaphragm section [g],

$m_d$ —weight of the membrane dried in the dryer [g];

$A$ —membrane area [cm<sup>2</sup>],

$L$ —thickness of the membrane [cm],

$p$ —water density (assumed value 0.998 g/cm<sup>3</sup>).

In addition, the hydrophobicity/hydrophilicity of the membrane surfaces was determined using a goniometer (Pocket Goniometer PG-1), allowing the measurement of the water contact angle between a drop of water and the surface of the membrane. The result was arithmetic mean obtained from ten measurements.

#### 2.4. Feed Waters

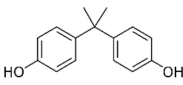
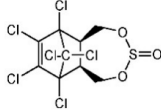
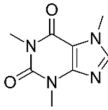
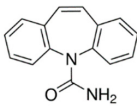
The surface water for this study was taken from the Kłodnica river in Katowice, Silesian Voivodeship, Poland. The physicochemical properties of Kłodnica water were shown in Table 3. This water was used in first part of the study to determine the optimal content of polystyrene in the casting solution.

**Table 3.** Physicochemical parameters of water collected for testing (Kłodnica, Katowice, Poland).

Parameter	Values of Water for First Part of Study	Values of Water for Second Part of Study
pH	7.61	7.21
Conductivity [ $\mu\text{S}/\text{cm}$ ]	671	640
Color [ $\text{mg Pt}/\text{dm}^3$ ]	46	56
Absorbance 254 nm [-]	0.12	0.18
Nitrate [ $\text{mg N-NO}_3^-/\text{dm}^3$ ]	2.63	4.23
Phenol index [ $\text{mg}/\text{dm}^3$ ]	0.29	0.872

For second part of the study, 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. These 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 endocrine disruptors, END belongs to pesticides group, and CAF is a psychoactive drug. They show different physicochemical properties, which are presented in Table 4.

**Table 4.** Physicochemical properties of tested compounds [11–14].

Properties	Bisphenol A	$\beta$ -Endosulfan	Caffeine	Carbamazepine
Structure				
Formula	$\text{C}_{15}\text{H}_{16}\text{O}_2$	$\text{C}_9\text{H}_6\text{Cl}_6\text{O}_3\text{S}$	$\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$	$\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}$
Acronym	BPA	END	CAF	CBZ
Molar mass [ $\text{g}/\text{mol}$ ]	228.291	406.93	194.194	236.3
pKa	10.10	-	10.4	14.00
Log Kow	3.32	3.83	-0.55	2.45
Water solubility [ $\text{mg}/\text{L}$ ] 20 °C	<1	0.45	21600	17.7

#### 2.5. Ultrafiltration Tests

Pressure filtration was conducted in the ultrafiltration setup with a capacity of 400 cm<sup>3</sup> and a membrane filtration surface area of 0.003848 m<sup>2</sup> in the “dead-end” system at a transmembrane pressure of 0.1 MPa. The construction of ultrafiltration setup cell was presented in Figure 2. Before the actual filtration, the membranes were conditioned with deionized water under the same pressure. The volume of permeate was measured at the same time intervals and then volumetric permeate flux was calculated from the Equation (2):

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

where:

$J_v$ —Permeate flux [ $\text{m}^3 \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ ],  
 $V$ —Permeate volume [ $\text{m}^3$ ],  
 $A$ —Effective membrane surface [ $\text{m}^2$ ],  
 $t$ —Filtration time [h].

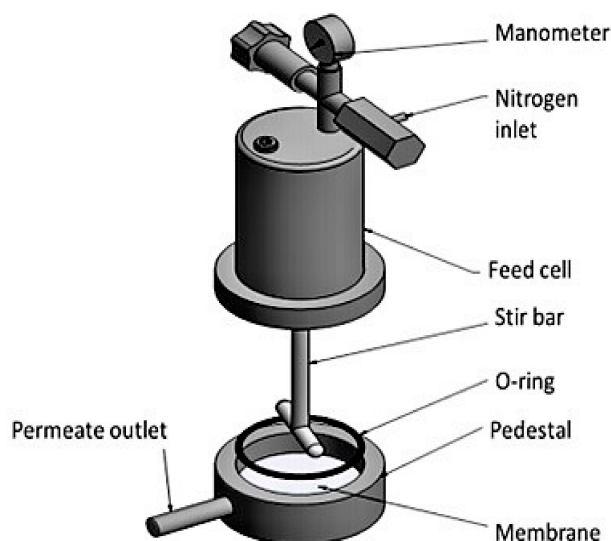


Figure 2. Ultrafiltration setup cell construction [15].

## 2.6. Water Quality Analysis

The treatment efficiency of Kłodnica river in ultrafiltration was evaluated by monitoring of typical quality parameters (color, pH, conductivity, phenolic index, absorbance, nitrate) and measurements of removal of micropollutants. pH and conductivity were measured with the Elemetron CPC-505 pH meter/conductometer. The color, total nitrogen, and phenol index were measured using a Spectroquant® Pharo 100 spectrophotometer connected to the TR 620 thermoreactor using ready-made tests (MERC Test kits) for these parameters. In addition, the absorbance of the feed and permeate sample at a wavelength of 254 nm in a Cecil spectrophotometer with a UV-Vis detector was also measured. Concentration of micropollutants in feed and permeate were determined by gas chromatography with flame ionization detector (GC-FID) 6500GC System by YI Instrument Co. Ltd. (Hogye-dong, Anyang, Korea). Chromatograph was equipped with 30 m × 0.25 mm i.d. SLB® 5-ms fused silica capillary column of 0.25 µm film thickness by Sigma-Aldrich. 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 temperature program of column oven for all substances at 80–320 °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. 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 columns. Then, when column was completely dried, analytes were eluted flushed with 3 mL of methanol and 3 mL of hexane. Eluted portion was dried in nitrogen stream and then analyzed using GC-FID. The degree of reduction of selected water quality indicators and retention of micropollutants were determined based on the retention factor (3):

$$R = \frac{C_i - C_f}{C_i} \cdot 100\% \quad (3)$$

where:

$R$ —Retention level [%],

$C_f$ —Concentration of pollutant/micropollutant in feed [mg/L].

$C_i$ —Concentration of pollutant/micropollutant in permeate [mg/L].

The phenomenon of blocking membranes was determined by calculating membrane relative permeability (4):

$$\alpha = \frac{J_v}{J_w} \quad (4)$$

where:

$J_v$ —Permeate flux after process [ $\text{m}^3 \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ ]

$J_w$ —Permeate flux during conditioning [ $\text{m}^3 \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ ]

## 2.7. Investigation of Polystyrene Content in Permeate Water

Presence of polystyrene in permeate water was investigated by rPS 16 membrane in two ways. First, permeate water was investigated in comparison with pure water by photospectrometer at a wavelength of 254 nm in a Cecil spectrophotometer with a UV-Vis detector. Permeate water was also tested by TOC-L (Shimadzu) by assessment of the quantity of organic and inorganic carbon in permeate water. Achieved results were presented in Table 5.

**Table 5.** Carbon and absorbance after filtration of pure water with rPS 16 membrane.

rPS 16	TOC (Total Organic Carbon), mg/L	IC (Inorganic Carbon), mg/L	Absorbance, A
DI water (feed)	3.490	6.185	0.00
Permeate DI water	66.95	15.64	0.058

## 3. Results and Discussion

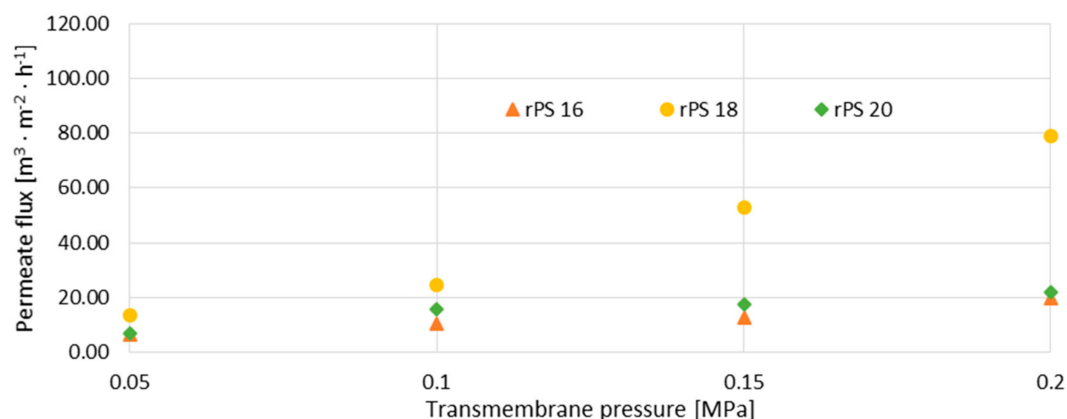
### 3.1. Pristine Membranes Characteristic

The contact angle of membranes was in the range from 50 to 60° (Table 6). Results should be identical due to the lack of a modifier. These values are comparable for those obtained by other authors and suggest the hydrophilic–hydrophobic properties of the membranes. For comparison, Guruvenket et al. [16] set the contact angle of pure polystyrene of 66°. In addition, membranes made of PES had similar values (60.3–63.3°) [17]. The results obtained in the porosity tests for rPS 18 and rPS 20 membranes assumed a value ranging from about 57 to 62% (Table 6), for this reason, they exhibit a similar permeation characteristic (Figure 3). The rPS 16 membrane had a different porosity, below 40%, which directly affected its low permeability at low pressures from 0.05 to 0.1 MPa. A slight difference in porosity between rPS 18 and 20 rPS membranes did not have a significant impact on the difference in the value of the streams. A slight increase in flux was noted for the rPS 18 membrane due to its lower angle of wettability and hence greater hydrophilicity. For rPS 16, the permeate stream, contrary to common assumptions, was definitely lower than expected. This phenomenon can be explained by the presence of a large number of closed pores, which were opened only when applying a higher pressure above 0.1 MPa. This is visible in Figure 3, where the flow rate for the rPS 18 membrane increases rapidly at pressures of 0.15 and 0.2 MPa. The rPS 14 membrane was not tested due to its excessive permeability, over 100 [ $\text{m}^3 \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ ]. For this membrane, only surface tests were performed, according to which it has a similar water contact angle and the highest porosity. There is a relationship between porosity and permeability confirmed by Abdel Aal et al. [18], in which the most permeable membrane had the highest porosity.



**Table 6.** Surface properties of pristine membranes.

Membrane Type:	Porosity [%]	Contact Angle [°]
rPS 14	46.49 ± 3.90	51.30 ± 3.35
rPS 16	38.52 ± 2.27	53.30 ± 3.98
rPS 18	62.47 ± 3.11	49.60 ± 4.86
rPS 20	57.10 ± 5.31	58.50 ± 5.50

**Figure 3.** Permeate flux versus transmembrane pressure for tested membranes.

### 3.2. Reduction Degree of Pollutants in Ultrafiltration with Unmodified Membranes

The treatment efficiency of Kłodnica water is shown in Figure 4. Higher reduction degrees of all water quality parameters were observed for membranes with lower permeability. This trend has been repeatedly observed by Tiron et al. [19]. Apart from the reduction of conductivity, rPS 16 membrane had the highest performance for treatment of Kłodnica water. Comparable results were obtained using the rPS 20 membrane, while the rPS 18 membrane had the lowest degree of reduction of all selected parameters. The highest reduction degree was noted for the color, which ranged from 63% to 86%. In the second place, it was a decrease in the absorbance and the phenol index, where the level of reduction ranged from 21% to 44%. The intermediate retention of phenolic compounds (expressed by phenolic index) requires explanation because these substances belong to low molecular weight organic micropollutants and their retention in the ultrafiltration process is usually low. However, sometimes these substances may adsorb or form complexes with other pollutants (e.g., colloids, polymers, natural organic matter) present in surface water. It results in the formation of larger agglomerates, which are retained due to the molecular sieve effect in the UF process [20]. The least effective removal was observed for nitrates, which ranged from 0% for rPS 16% to 3.5% for rPS 20%. The conductivity was reduced by 1.7%, 3.5%, and 5.2% by membranes rPS 18, rPS 20, and rPS 16, respectively. The reduction of nitrates and conductivity was not possible with the use of ultrafiltration membranes because the conductivity is primarily responsible for dissolved salts in the form of ions, which are not retained in the UF process [21]. Similarly for nitrates that are mainly removed in the reverse osmosis process [13].

Comparing the obtained results with literature data, it can be noticed that the reduction of color and absorbance was at the level obtained for commercially available PES and cellulose ultrafiltration membranes. Kabsch-Korbutowicz and Urbanowska [22] reported that color and absorbance of Odra river water were reduced by 40–100% and 40–90%, respectively. Importantly, the reduction of color depended on cut-off of membranes [19]. However, in the Xia and Ni [23] studies on membranes made of PVDF and graphene oxide, the absorbance was reduced by 23–28%. Similarly in Dudziak et al. studies [24], turbidity was reduced by commercial ultrafiltration membranes by about 90%, the color by 80%, and the absorbance by less than 60%. The concentration of bisphenol A was reduced by only a few percent, which was a much lower value, however, not having a full ratio in relation to the phenol index. Said et al. [25] indicated that using PES membranes and neutral pH, phenols removal was

around 70%. Conductivity cannot be removed by ultrafiltration membranes; however, some trials had been undertaken. Wandera et al. [26] reported a very low reduction degree of conductivity from 1108  $\mu\text{S}/\text{cm}$  to 1038  $\mu\text{S}/\text{cm}$  by means of a commercial unmodified membrane made of polypropylene and cellulose.

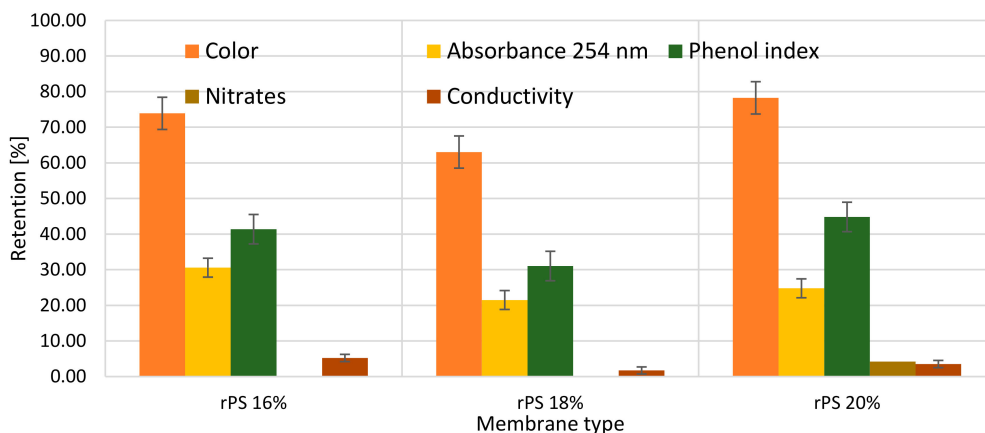


Figure 4. Reduction degree of water quality parameters in ultrafiltration.

During ultrafiltration of Kłodnica river, flux decline was observed suggesting occurrence of membrane fouling. This unfavorable phenomenon was caused by the macromolecular compounds present in the surface water. To better understand, the intensity of fouling was expressed by relative permeability (Figure 5). The permeate flux decreased over time for each of the virgin membranes. The highest decrease was observed for the rPS 18 membrane with the highest permeate flow. The decrease was about 35% (for 240 min  $\alpha = 0.65$ ). This membrane should have the highest degree of contaminant retention according to its relative permeability but has the lowest. However, this phenomenon can be explained as follows: this membrane has the lowest water wettability and the highest porosity. The combination of these two features caused that large hydrophobic compounds more readily bind with the surface of the membrane, while high porosity promoted the simultaneous passing of small compounds through the membrane. A similar explanation can be used for the rPS 20 membrane where relative permeability was smaller and decreased only by 24% (for 240 min  $\alpha = 0.76$ ). This membrane had one of the highest treatment performances. The high porosity of this membrane caused a slower growth of the fouling layer. For the best membrane in contaminant removal, the decrease was about 31% (for 240 min  $\alpha = 0.69$ ), which corresponds to expectations. A similar tendency was received by Dudziak [27], where the membrane with the lowest relative permeability had the highest removal performance.

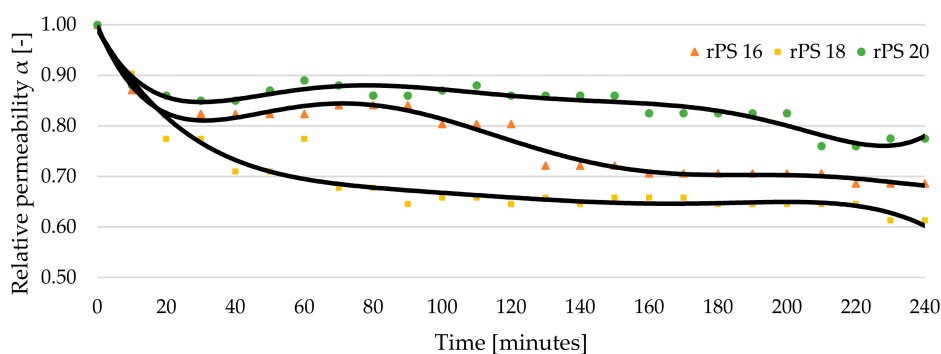


Figure 5. Relative permeability  $\alpha$  in time.



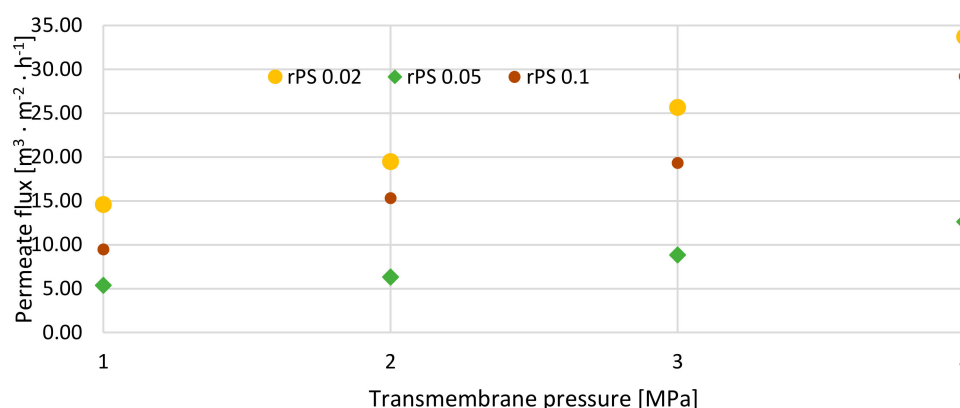
### 3.3. Modified Membranes Characteristic

In the first part of the work, the membrane rPS 16 turned out to be the best and have the most interesting properties. Because of this reason, rPS16 membrane was chosen for second part of study aiming at modification by nanotubes and high removal of micropollutants from water. In these studies, Kłodnica water spiked with micropollutants was used.

Prepared membranes, despite the addition of carbon nanotubes, had quite similar surface properties in comparison to the unmodified membrane. The nanotubes did not have such a strong influence both on porosity and contact angle (Table 7). Modification with hydroxyl groups was only aimed at an increase in the removal of micropollutants, while not changing the properties. The porosity of the membranes has been preserved as compared with pristine membrane rPS16. Contact angle was slightly lower, suggesting a more hydrophilic surface. This property could slightly influence the increase in flux through the membrane compared to an unmodified membrane (Figure 6). The nanotubes positively influenced the mechanical stability of the membrane. A similar influence of nanotubes was confirmed by other authors [28,29]. Membranes made of PES with the addition of SWCNT-OH have similar surface properties as in the work of Kamińska et al. [8].

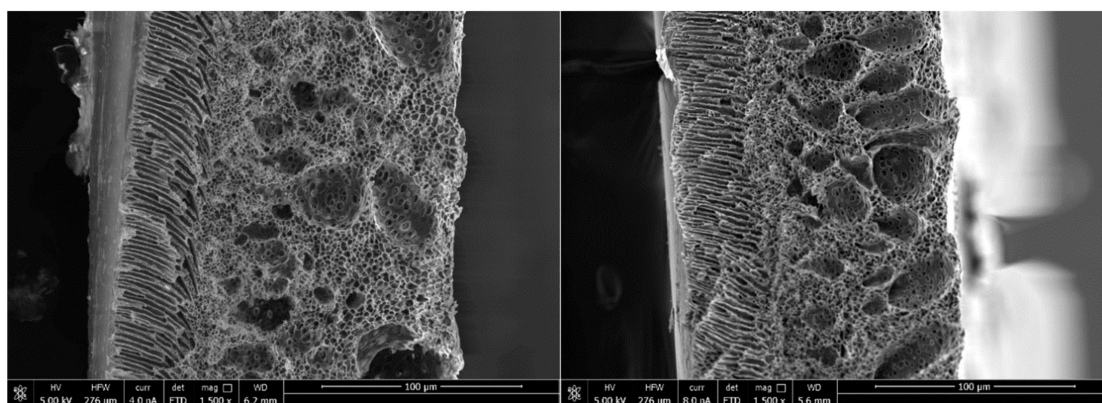
**Table 7.** Surface properties of unmodified and modified rPS 16 membranes.

Membrane Type:	Porosity [%]	Contact Angle [°]
rPS 0.02	52.40 ± 6.75	48.20 ± 6.26
rPS 0.05	40.48 ± 9.22	47.20 ± 3.25
rPS 0.1	44.63 ± 8.54	43.50 ± 6.34



**Figure 6.** Permeate flux versus transmembrane pressure for tested membranes.

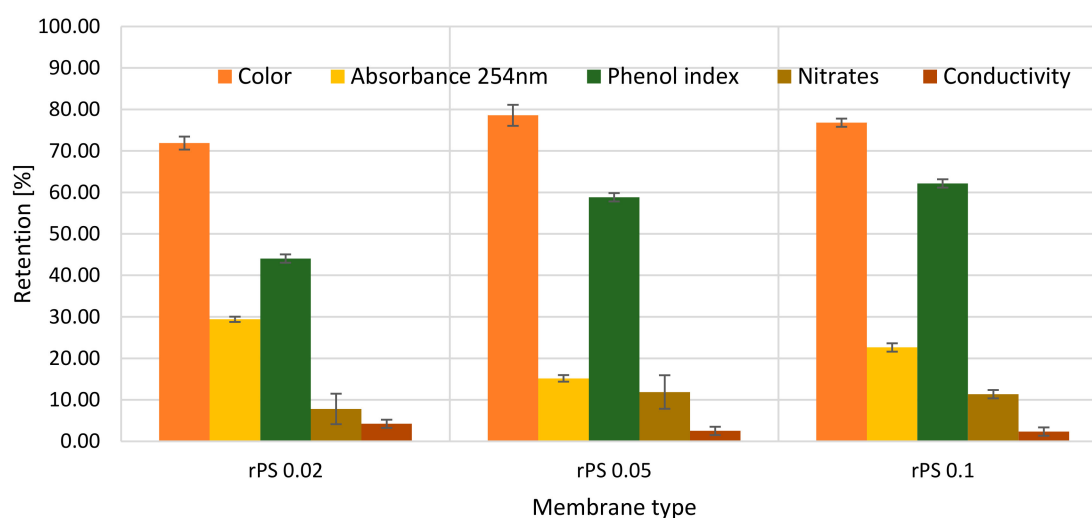
The cross-sections of unmodified and modified membranes were shown in Figure 7. It was found that all membranes had a typical asymmetrical structure, which was composed of a dense skin layer, a fingerlike structure below, and a macrovoid structure at the bottom. Macrovoids in rPS 16 were less visible than in rPS 16 0.1 membrane [30]. Addition of nanotubes to the unmodified rPS membrane decreased the thickness of the membrane. A possible explanation is that the addition of nanocomposites slows down the solvent/anti-solvent exchange rate in the coagulation bath and this caused the formation of thinner membranes with a thicker skin layer due to the entrapment of more CNTs at the top surface during phase separation. These macrovoids and the developed finger-like structures enhance the permeation of water, thereby allowing for increased membrane flux [31].



**Figure 7.** The cross-sectional SEM images of membranes: **left**—bare rPS 16 membrane, **right**—modified with nanotubes rPS 16 0.1 membrane.

### 3.4. Reduction Degree of Pollutants and Micropollutants in Ultrafiltration Modified Membranes

Figure 8 presents the reduction degree of water quality parameters in ultrafiltration process with waste polystyrene membranes modified with carbon nanotubes. The biggest change in relation to Figure 4 is the highest removal of phenols. The reduction of other coefficients is maintained at a similar level to unmodified membranes. The only perceived dependence is the increasing removability of phenols, along with the increase in the concentration of nanotubes in the membrane. There is also a slight increase in the retention of nitrates and substances responsible for the conductivity of the sample.



**Figure 8.** Reduction degree of water quality parameters in the ultrafiltration process with modified membranes.

Much more interesting relationships were obtained in micropollutants removal studies presented in Figure 9. A slight or complete lack of caffeine retention was caused by the specific properties of this substance. At the same time, it was the smallest substance with the lowest octanol–water partition ( $\log K_{ow}$ ) coefficient, indicating low hydrophobic property, thus low affinity to adsorption. The same property was also responsible for low CBZ removal rates. Substances with  $\log K_{ow}$  below value 2.5 are mostly soluble in water. Substances with  $\log K_{ow}$  higher than 2.5 can interact with membranes by hydrophobic interactions [32]. This is the reason BPA and END were always removed by all three membranes. In particular, the rPS 0.1 membrane had high removal rates of these two micropollutants (CAF and CBZ) compared to the others. Modified membranes were not able to remove compounds with low  $\log K_{ow}$ . In many works, polystyrene acts as a phenol adsorbent in technological processes. For example, Siyal et al. [33] achieved removal of 75% to almost 90% of phenols from industrial

wastes by the use of modified polystyrene. This demonstrates the high capacity of this polymer to remove these types of compounds as well as the adsorption potential of phenols themselves. BPA is able to create a hydrogen bonding between compound and membrane surface [34]. In addition, the highest degree of adsorption was observed at neutral pH; for Siyal et al. [33], it was pH 7, and for Adamczak et al., it was pH 6.5 [17].

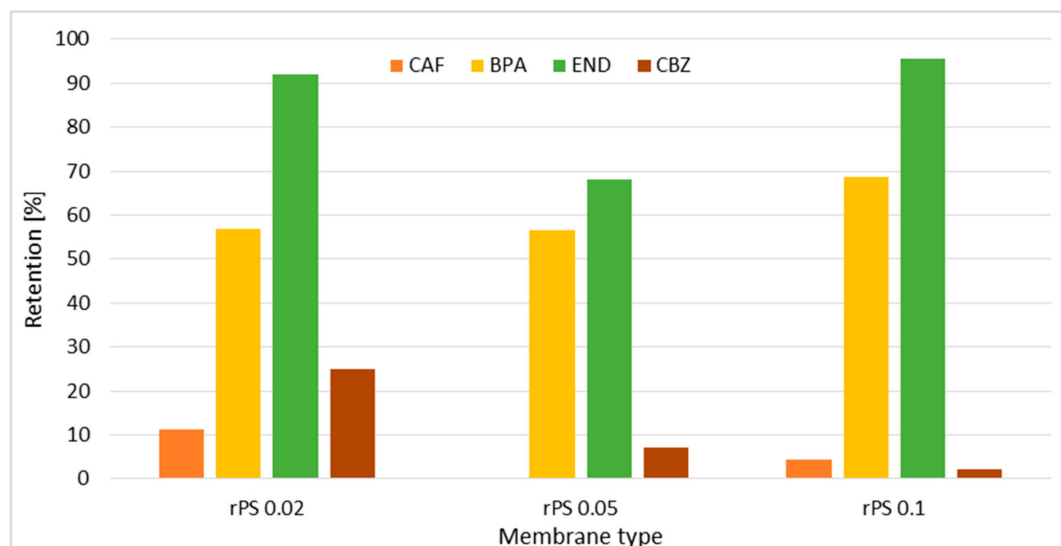


Figure 9. Effectiveness of micropollutants removal in ultrafiltration process.

As already mentioned, the high BPA and END retention were due to the properties of the substances themselves. The highest degree of BPA and END removal was observed for rPS 0.02 and rPS 0.1 membranes. In studies of Adamczak et al. [35], identical relationship was observed: much better separation properties had membranes with 0.02 wt.% and 0.1 wt.% than the membrane with the concentration of 0.05 wt.% of carbon nanotubes functionalized with carboxyl groups. The introduction of nanotubes to the structure of membranes is only beneficial in a well-defined range of concentration. According to many authors, finding the optimum nanotubes concentration is a crucial factor [36]. It is a small number of nanoparticles that make the membrane then have the most favorable separation properties [37,38]. A very large number of nanotubes can block the pores and promote a strong separation effect [39]. On the other hand, this type of pore-blocking mechanism leads to a reduction in the permeate flow and a reduction in membrane performance, as can be seen in Figure 4. All modified membranes had similar porosity, while the contact angle indicates indirect hydrophobic–hydrophilic properties, which may limit the adsorption of compounds with a hydrophilic character. The porosity of the membrane was sufficient to remove macromolecular compounds responsible for turbidity or color but promoted the penetration of hydrophilic micropollutants through the membrane.

Figure 10 presents relative permeability in time for modified membranes. Comparing this result to unmodified membranes (Figure 5), modified membranes had higher values of relative permeability, indicating better antifouling properties. Among rPS 0.02, rPS 0.1, and rPS 0.05 membranes, the rPS 0.05 membrane had the best resistance to fouling. This membrane had the lowest flow as well as the weakest retention properties. However, it showed the highest stability with a stream decrease of only 10% (for 240 min  $\alpha = 0.90$ ). The other modified membranes had a decrease of 20% ( $\alpha = 0.80$ ) and 25% ( $\alpha = 0.75$ ) for rPS 0.02 and rPS 0.1, respectively. These results also indicate slightly better properties than for unmodified membranes. We can also observe a similar phenomenon as in the first part of the study, where the best retention membrane had the lowest  $\alpha$  coefficient [27].

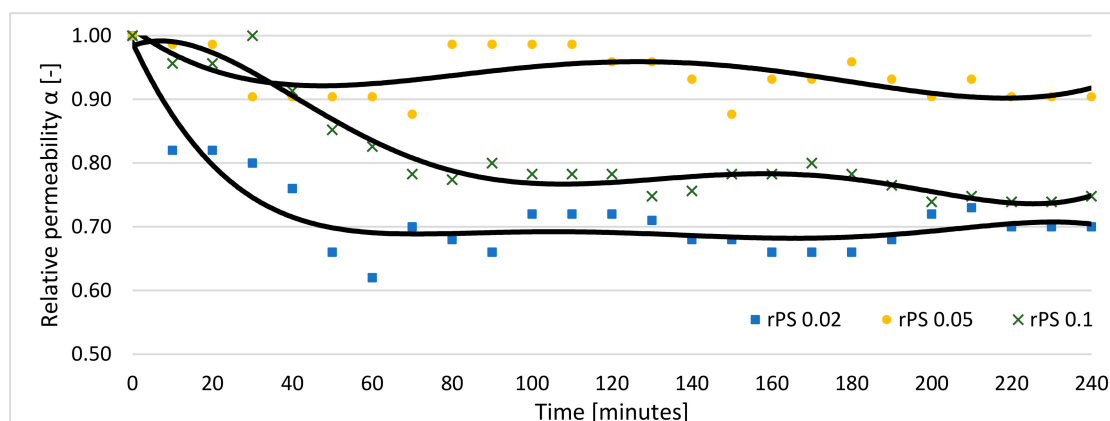


Figure 10. Relative permeability  $\alpha$  in time.

However, ultrafiltration is not the absolute method for wastewater treatment. The addition of nanotubes highly improved contaminants retention, but nitrates and salts removal were still low. This inconvenience could be improved by using posttreatment processes. Usually, complementary treatment is achieved by the addition of nanofiltration (NF) or reverse osmosis (RO). UF-NF and UF-RO systems are a combination of low- and high-pressure processes and removal of salts and nitrates is much higher in comparison to only UF process. For example, Zhou et al. [40] reduction of conductivity in UF-only process was unnoticeable, after the use of UF-NF it was higher for 90–95%. Mielczarek et al. [41] were using UF-RO system for coke plant wastewater treatment. Reduction of conductivity after UF and after RO process was around 7% and 90%, respectively. Removal of ammonia values was 25.5% and 84.0%, respectively. Ultrafiltration process can be also combined with other processes like electrocatalysis or electrooxidation for removal of the smallest substances: ammonia and salts [42,43].

#### 4. Conclusions

The tests have been divided into two stages: the first part tested four membranes with different concentrations of waste polymer in order to determine the best. In the second course, the selected membrane was modified by means of carbon nanotubes in three different concentrations. The obtained results suggest that the pristine styrofoam (polystyrene) membranes can be used interchangeably with the membranes made of other polymers and have similar surface properties. The effects of surface water purification are also comparable to those obtained with commercial membranes in other works. Obtaining a relatively high degree of removal of phenolic compounds in relation to other studies indicates a high potential of these membranes to remove these contaminants. Modification of these membranes was also possible. Due to the similar surface properties of the membrane, their main mechanism for the retention of microcontaminants was the adsorption process on the membrane surface. In addition, the modification of membranes also allowed to obtain better values of relative permeability, which indirectly reduces fouling. Furthermore, the use of waste as a raw material for the preparation of membranes will reduce the costs of manufacturing the membrane itself and will contribute to a smaller number of generated wastes.

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