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Polyacrylonitrile membranes modified with carbon nanotubes: characterization and micropollutants removal analysis

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ABSTRACT

The phase inversion method was used to prepare polyacrylonitrile membranes modified with single-walled carbon nanotubes. The influence of the amount and the kind of carbon nanotubes (CNTs) (pristine and functionalized with carboxyl groups) were determined analysing the structure of membranes, hydrophobic–hydrophilic characteristics, zeta potential, and transport-separation properties. Based on the microscopic analysis, it was established that their structure changed depending on the amount of nanotubes added. The membranes with the highest content of CNTs were characterized by the highest membrane capacity. Those membranes were used in low pressure filtration in order to remove micropollutants from synthetic wastewater. The effectiveness of micropollutants removal was dependant on the kind of membrane—in the range 15–65% for bisphenol A, and 25–87% for nonylphenol. The key mechanism in separation of low molecular organic compounds was the sorption phenomenon intensified by the presence of CNTs.

Keywords: Membrane modified with carbon nanotubes; Micropollutants; Adsorption; Membrane filtration

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1. Introduction

Pressure membrane techniques have been commonly used worldwide for industrial and environmental goals. As far as membrane techniques are concerned, they can be regarded as well-known. However, in connection with the growing needs of industry and cleaning technology—the current research is looking for new materials and techniques which could improve the properties of existing membranes [1]. The main purpose is to increase the hydraulic capacity and at the same time to maintain the effect of high retention. The combination of these two factors is extremely difficult since a permeable membrane with a loose structure is not an effective barrier for retaining the micropollutants [2]. Due to their low molecular weight and particle size, they are not retained by a permeable membrane [3].

The solution to this problem can be the application of nanomaterials. Carbon nanotubes (CNTs), among

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other nanomaterials, seem to be the most appropriate to improve the transport and retention properties of polymer membranes [4]. A larger specific surface area and other unique properties, which are caused by the nano size, make them better materials in comparison with their counterparts, i.e. conventional activated carbons [5]. Modification of polymer membranes with nanomaterials allows for changing their structure and properties, and most of all, it enables changing their transport and retention characteristics [6–9]. It might be the result of the phase inversion process occurring in a different manner. It was found that nanotubes, due to their shape and mutual interaction, undergo appreciable aggregation, which leads to the formation of larger molecules. On the one hand, they can be the reason of the formation of macrovoids in the membrane structure. On the other hand, they block the pores, especially when their concentration in the casting solution exceeds the optimal amount [10–12]. Diversified properties of modified membranes are the results of a large variety of nanomaterials, their size, composition, attached functional groups, which are responsible for the variability in the interaction polymer—nanomaterial. Moreover, even small modification of the membrane preparation conditions may result in completely different structure and properties of the membrane [1,13]. A notable example is the situation in which the amount of nanotubes affected the membrane structure by increasing its porosity [14–16]. Therefore, the introduction of hydrophilic nanoparticles (for instance, functionalized CNTs or nano-TiO_2) increases the hydrophilicity of the casting solution which ensures quicker exchange of the solvent to nonsolvent and consequently leads to formation of more porous membrane structure. On the other hand, creating a more porous structure may be the result of electrostatic interactions between the nanotubes and the polymer chains. This effect may also be related to the tendency of nanotubes to create stable agglomerates, which are larger than typical nanoparticles [17]. Larger nanoparticles embedded in the polymer structure may form macrovoids in the structure of the membrane, rendering it very permeable [18]. However, a very high content of the modifiers can give the opposite effect, namely, it may cause reduction in the pore size of the membrane due to the aforementioned increase in viscosity of the casting solution and slower penetration of nonsolvent into the membrane structure during its precipitation [19].

Separation properties of membranes modified with nanomaterials can be similar to both nanofiltration and ultrafiltration. Their selectivity should be determined at the stage of manufacturing the membrane by selecting the optimum concentration and the type of the polymer and the nanotubes, as well as the conditions under which the membrane is prepared. The study of Saranya et al. showed that the cut-off of a polyethersulfone nanocomposite membrane containing 0.5 wt.% of nanoparticles was two times lower compared to the unmodified membrane [18]. In a different study, no significant effect of CNTs on the cut-off of the polyacrylonitrile (PAN) membranes was observed [14]. In both cases the cut-off value was approx. 50 kDa. Similar results were obtained by Celik et al. for the polyethersulfone membranes modified with CNTs in the range of 0.4–4 wt.%. The cut-off value for these membranes was approximately 25–33 kDa [13]. A number of authors indicate that obtaining favourable transport-separation properties of modified membranes is only possible in a certain concentration range of the modifying agent, which should be individually selected for prepared membrane from certain polymer [10,13].

In the light of world literature, presented in the article an attempt to determine the degree of retention of low molecular weight micropollutants in the low-pressure separation with PAN membranes modified with CNTs can be regarded as a new standpoint.

2. Materials and methods

2.1. Substances for membrane preparation and their characterization

Single-walled carbon nanotubes (SWCNT) and single-walled carbon nanotubes functionalized with carboxyl groups (SWCNT-COOH) were used in the present experiment. CNTs were purchased from Chengdu Organic Chemistry Ltd, Chinese Academy of Science. Characteristics of the nanotubes are shown in Table 1. In order to calculate specific surface area of CNTs, nitrogen adsorption–desorption isotherms of CNTs were estimated at 77 K, by means of a volumetric adsorption analyzer ASAP 2010 (Micrometrics, USA). A detailed description of the structure parameters of CNTs can be seen elsewhere [20]. PAN was supplied by Anilina Łódź. N,N-dimethylformamide (DMF), isopropanol, potassium chloride, sodium hydroxide and hydrochloric acid (all analytically pure) were purchased from POCH, Inc. (Poland). Deionized water was taken directly from Milli-Q water purification system (Millipore LLC, Poland).

2.2. Synthetic and municipal wastewater

For experiments, a solution of synthetic wastewater (simulated solution) was prepared as the last step of developing the treatment (effluent). This was done by

Table 1
Characteristics of CNTs

Symbol	Outer diameter (nm)[a]	Length (μm)[a]	Purity (%)[a]	Specific surface area (m^2/g)[b]
SWCNT	1–2	5–30	95	467
SWCNT-COOH	1–2	10–30	90	425

[a] Data from manufacturer.
[b] Own measurement [20].

adding to pure water the following substances (mg/dm^3): broth 2.5; peptone 2.0; NH_4Cl 3.5; NaCl 1.5; $CaCl_2$ 5.0; $MgSO_4{\cdot}7H_2O$ 1.0; K_2HPO_4: 1.5; KH_2PO_4 2.5. All chemicals were of analytical grade, purchased from POCH, Inc. (Poland). Appropriate volumes of bisphenol A (BPA) and 4-NP stock solutions were added to achieve the concentration of 100 $\mu g/dm^3$. Analytical standards of these substances were supplied by Sigma–Aldrich. The properties of selected micropollutants are shown in Table 2 [21,22].

The concentration of BPA and NP was determined using a modified method described elsewhere [23], which was based on solid phase extraction (SPE) and HPLC analysis. For SPE, glass columns filled with C18 phase (Supelco) were used. Before extraction, C18 beads were washed with methanol (1 cm^3), acetonitrile (1 cm^3), deionized water (1 cm^3). 200 cm^3 of sample was drawn through the columns. After the samples had completely passed, SPE bed was dried under vacuum. The extract was eluted with two portions of 1 cm^3 acetonitrile/methanol (60/40, v:v); then, the eluate was dried under high-purity nitrogen flux. Dried residue was redissolved in 1 cm^3 of acetonitrile. The concentration of micropollutants was analysed using high performance liquid chromatography at a wavelength of $\lambda = 220$ nm. The chromatograph was equipped with a chromatographic column (Hypersil Gold C18, 5 μm particle size, 205 mm × 4.6 mm) and a UV–vis detector. The flow rate of the mobile phase (acetonitrile/deionized water, 85/15, v:v) through the column was 1 cm^3/min. The limit of detection of this method was 0.5 ng/cm^3 for BPA; and 2 ng/cm^3 for NP; limit of quantification was 1 $\mu g/dm^3$ for both analytes. The analytical procedure allowed the recovery of compounds from 200 cm^3 of synthetic wastewater at the level of 100 and 40% for BPA and NP, respectively.

2.3. Membrane preparation

Flat PAN membranes modified with CNTs were synthesized via the phase inversion method. The casting solution consisted of 20 wt.% PAN or PAN-SWCNT/SWCNT-COOH (modified membranes) and 80 wt.% DMF. The content of SWCNT/SCWNT-COOH in modified casting solution was kept at 0.2; 0.5; 1 wt.%. The membranes were denoted as: PAN (membrane without nanotubes); PAN 0.2% SWCNT; PAN 0.5% SWCNT; PAN 1% SWCNT; PAN 1% SWCNT-COOH. In the case of modified membranes, firstly, a proper amount of the CNTs was added to the DMF. This mixture was subjected to ultrasonication (30 min) in order to minimize the aggregation effects of nanotubes. Next, that proper amount of PAN was put in the mixture nanotubes in DMF. A casting solution was intensively shaken for 12 h to obtain a homogeneous casting solution. Before casting the membrane, solution was degassed in order to remove the air bubbles.

Then, the membranes were cast using doctor blade with 150 μm thickness on glass plate and after 60 s evaporation, they were immersed in a coagulation bath (deionized water/isopropanol 90/10, v:v) at 15 ± 1˚C. After membrane precipitation, the membranes were stored in deionized water at 4˚C for 24 h to ensure complete phase separation.

2.4. Characteristic of PAN and PAN-SWCNT membranes

2.4.1. Microscopic study

Scanning electron microscopy (Environmental Scanning Electron Microscope FEI—Quanta 200FEG-SEM) was employed to analyse the structure of the prepared membranes. The test samples were frozen in

Table 2
Characteristic of micropollutants

Compound	Molecular mass (g/mol)	Solubility in water (mg/dm^3)	log K_{ow}	pKa	Stokes radius (nm)
Bisphenol A	228.29	120–200 (20–25˚C)	3.64	9.6–10.2	0.329
4-Nonylphenol	220.35	5.43 (20˚C)	5.92	10.7–11.7	0.324

liquid nitrogen and fractured. The roughness of membranes was observed by atomic force microscopy (AFM) with a Nanoscope IIIa microscope from Digital Instruments. Tapping mode was used in air, with silicon monocantilever probes.

2.4.2. Zeta potential

Electrokinetic properties of the membrane were determined by measuring tangential streaming potential on the membrane described in previous works [24]. In the membrane holder, two membranes are placed in such a way that their active layers face each other and no permeation is allowed through them. They leave a single channel of length 75 mm, width 20 mm and height 160 mm with a transversal area of 3.2×10^{-6} m^2. Two Ag/AgCl$_2$ selective electrodes placed at both the channel entrance and exit. The electrical potentials have been measured using a high impedance voltmeter from Transmille (8081) with 8 ½ to 4 ½ digit resolution. The experiments were conducted in 0.001 M KCl solution at 20°C. Different streaming potentials were measured in the pH range 3–9 using 1 M of HCl and NaOH for pH adjustment. The transmembrane pressure varied from 0.1 to 0.9 bar. The Smoluchowski equation was used to correlate streaming potential data with zeta potential:

$$\zeta = \frac{K_m \eta}{\varepsilon} v_p \tag{1}$$

where is the zeta potential, solution conductivity, the solution viscosity, the dielectric constant and is the slope of the streaming potential vs. transmembrane pressure.

2.4.3. Contact angle

The surface hydrophobicity of the membranes has been studied by contact angle measurements by the sessile drop method with water. The measurements have been made using commercial FTA200 equipment, manufactured by First 10 Å. As the final result, the average of five values of contact angle in different spots of the membranes was used.

2.5. Potential of the membranes modified with CNTs for the removal of organic micropollutants

2.5.1. Sorption capacity of the membranes

Sorption capacity of the membranes was determined for BPA contained in the synthetic wastewater. Adsorption experiments were conducted under ambient conditions, using a batch system for 24 h until achieving equilibrium. Fragments of membranes, each of 0.15 g, were immersed in 0.2 dm^3 of synthetic wastewater solution. In order to determine the impact of the solution pH on the adsorption of BPA, the pH of the wastewater was adjusted in the range pH 3–9 using 0.1 M HCl and 0.1 M NaOH solutions. After 24 h, the concentration of BPA was determined and the amount of BPA adsorbed on the sorbents was calculated according to Eq. (2):

$$q_e = \frac{(C_0 - C_e) * v}{m} \tag{2}$$

where q_e (μg/g) is the equilibrium adsorption amount, C_0 and C_e (μg/dm^3) are the initial and equilibrium concentration of BPA, m (g) is the mass of membrane, V (dm^3) is the volume of the synthetic wastewater.

2.5.2. Removal of micropollutants from synthetic wastewater—performance and effectiveness of the process

The filtration process was carried out in a membrane cell equipped with a magnetic stirrer (volume 0.4 dm^3, membrane filtration area 0.00385 m^2), operating in a dead-end mode at the transmembrane pressure 0.5 bar. Prior to the first application, the membranes were conditioned by means of filtration of demineralized water. During filtration of synthetic wastewater, the volume of permeate was measured and then permeate flux (J_v) was calculated according to Eq. (3).

$$J_v = \frac{V}{S * t} \tag{3}$$

where J_v—permeate flux (dm^3/m^2*h), V—volume of permeate (dm^3); S—active surface area of membrane (m^2); t—time (h)

Retention characteristics were determined based on removal degree of micropollutants from synthetic wastewater. The process was operated until the volume of permeate reached 200 cm^3. In this study, the impact of the content and type of CNTs used for the preparation of the membranes was studied. The effectiveness (E) of BPA and NP removal was calculated in Eq. (4):

$$E = \frac{C_f - C_p}{C_f} * 100\% \tag{4}$$

where C_f and C_p (μg/dm^3) are the initial concentrations of micropollutants in the feed and permeate, respectively.

3. Results and discussion

3.1. Microscopic characterization of membranes

In order to reveal the impact of the SWCNT content in the PAN membranes on their final morphology and structure, SEM and AFM analyses of the membranes without nanotubes—PAN and with the highest amount of nanotubes—PAN 1% SWCNT were performed (Figs. 1 and 2). A great difference between the surfaces of these membranes was observed. The surface analysis using AFM indicates that the membranes without nanotubes have more hollows (dark regions) in comparison with PAN 1% SWCNT with numerous hills (bright regions). It indicates worse antifouling properties of the PAN membrane due to higher tendency to coating and sorption of pollutants in valleys than on hills. Moreover, the surface roughness of the modified membranes ($R_q = 4.67$ nm) was obviously higher than that of the unmodified PAN ($R_q = 3.00$ nm) membranes. It is well established that incorporation of nanoparticles into the structure of the polymer membranes makes the surface more heterogeneous [16]. This is caused by aggregation of the nanotubes in high concentration of nanoparticles. It leads to the formation of larger bundles of the nanotubes and their irregular dispersion in the polymer matrix and to an increase in their concentration in some regions of the membrane surface.

The cross-sectional analysis showed that the structure of the membranes, regardless of the nanoparticles content, was asymmetric. Typically, for PAN membranes, their cross-section exhibited finger-like structure consisting of porous support and thicker top layer (Fig. 2). The size of pores in support was higher in the PAN 1% SWCNT than in the unmodified PAN.

3.2. Zeta potential

Due to impact of carboxyl group on the electric charge of membrane, the apparent zeta potential was determined for PAN and PAN 1% SWCNT-COOH (Fig. 3). It was found that the PAN membrane modified with SWCNT-COOH exhibited more negative charge than the unmodified PAN. However, the unmodified PAN membrane was positively charged at low pH. It could be a consequence of adsorption of positive ions from solute during streaming potential measurements. This membrane had the isoelectric point at pH 3.96. The membrane filled with nanotubes was more negatively charged at alkaline conditions due to dissociation of carboxylic groups of functionalized nanotubes, which strongly increased negative charge. The enhancement in zeta potential due to addition of functionalized nanotubes to polymer matrix was also observed by Shen et al. [19]. The negative charge of modified membrane gives better antifouling and separation properties in wide range of pH.

3.3. Hydrophobic/hydrophilic properties of PAN/nanocomposite membranes

As it can be seen in Fig. 4, the contact angle of membranes varied from 65.8° to 70°, which indicates intermediate hydrophobic–hydrophilic character of the

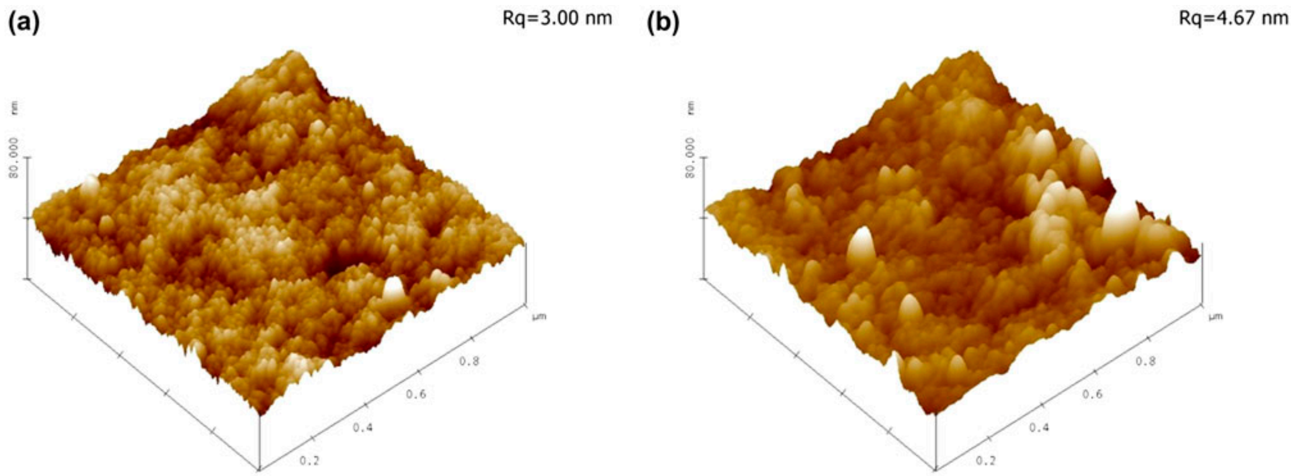

Fig. 1. Surface roughness of the membranes: PAN (a), PAN 1% SWCNT (b).

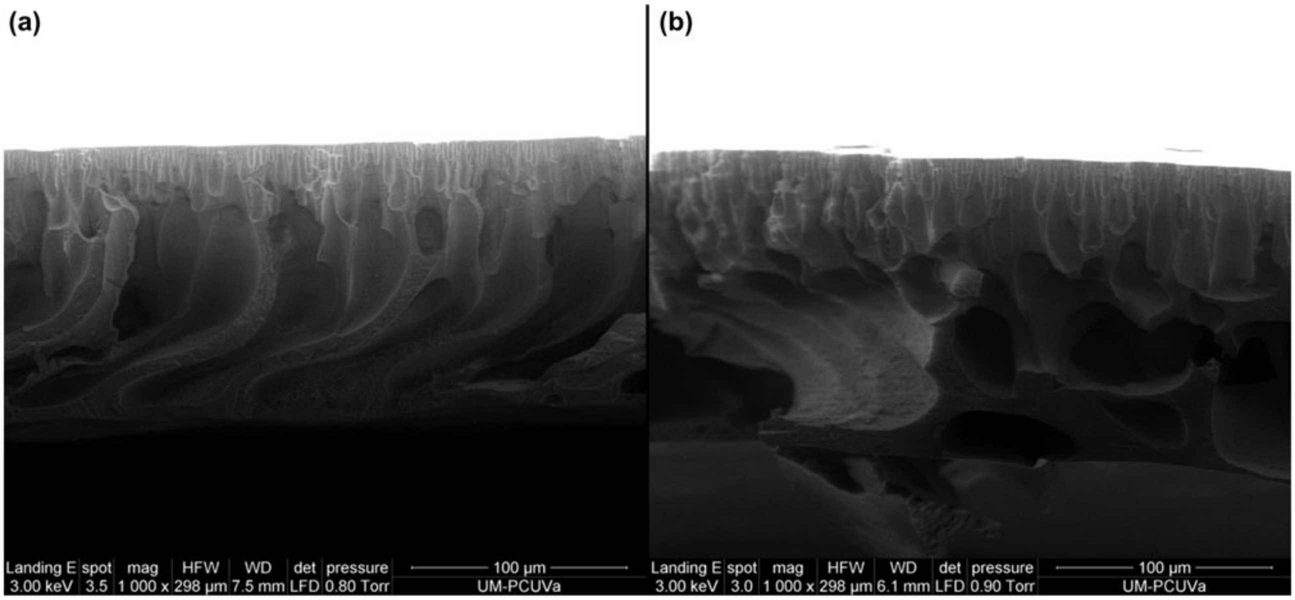

Fig. 2. SEM cross-sectional images of membranes PAN (a), PAN 1% SWCNT (b).

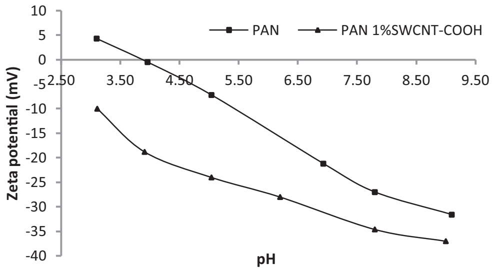

Fig. 3. Zeta potential of membranes.

surface. The unmodified PAN membrane exhibited an initial contact angle of 65.8˚, while it was slightly lower for PAN 0.2% SWCNT (64˚) and PAN 0.5% SWCT (63˚), which means that modification of membrane with low amount of nanotubes was not significantly dependent on the addition of SWCNT. On the contrary, the membranes with high nanotubes content i.e. PAN 1% SWCNT and PAN 1% SWCNT-COOH exhibited different tendency. Firstly, PAN 1% SWCNT had lower contact angle (53˚), while contact angle of the PAN 1% SWCNT-COOH reached 70˚. This divergence could be caused by high concentration of CNTs and their accumulation in comparison with the other membranes, which results in uneven distribution of nanotubes in the membrane structure. It can lead to the lack of nanotubes in some parts of the membrane, and their very high concentration in another part. Due to high concentration of CNTs and their accumulation in some parts of membrane, measured contact angle is not completely real.

3.4. Sorption capacity of membranes

Several studies have showed that membrane polymers can act as an active sorbents which "capture" the impurities present in the feed passing through the membrane. It is occasionally a very intensive phenomenon and guarantees almost complete removal of pollutants from the solution [25–27]. However, over time, sorption sites of the membrane would be saturated. A regeneration of membrane by means of ultrasonication method or chemical cleaning could restore the pristine properties to further use [28].

It was found that SWCNT content in the range of 0–1% (i.e. membranes: PAN—PAN 1% SWCNT) caused an increase in the quantity of adsorbed BPA (Fig. 5). This effect is related to an increase in sorption sites in the membranes. However, sorption capacity of the PAN 1% SWCNT was not significantly higher than for the PAN 0.5% SWCNT, which contained twofold higher CNTs content. This can be caused by low hydrophobicity (Fig. 4), which means that its surface attracted pollutants to a lesser extent than the other membranes. Thus, lower quantity of BPA is obvious. The second reason can be a fact that at high concentration of nanotubes, a common phenomenon is the aggregation of CNTs leading to the formation of CNTs-clusters, which can cause locking of the adsorption surface and a decrease of adsorption capacity. In this case, the real specific surface area of nanotubes can be significantly lower than the theoretical one [20]. The aggregation effect could be also the reason of lower sorption capacity of the PAN 1%

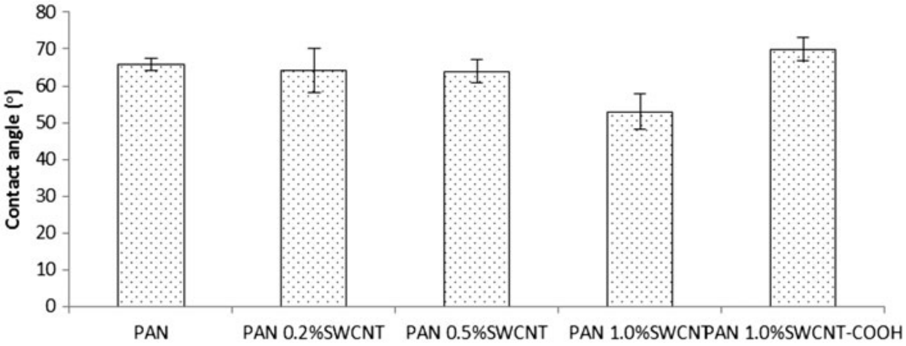

Fig. 4. Surface contact angle of prepared membranes as a function of SWCNT content and type.

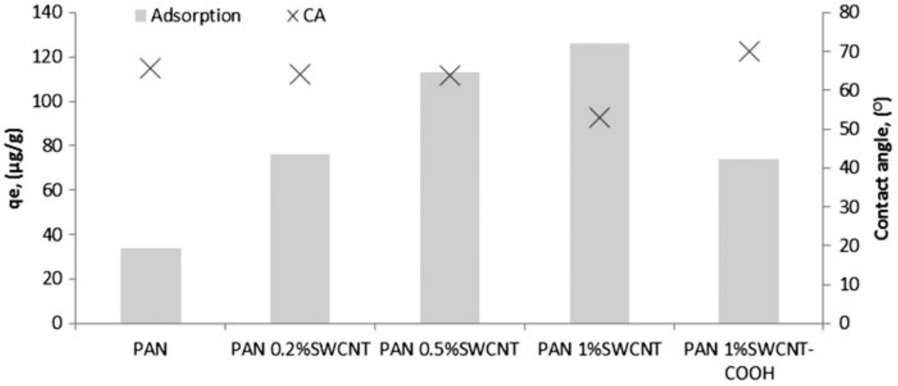

Fig. 5. Adsorption of BPA on the membranes.

SWCNT-COOH. Furthermore, its worse sorption potential could be also caused by lower specific surface area of functionalized SWCNT-COOH in comparison with pristine SWCNT (Table 1).

Additionally, the impact of synthetic wastewater pH on the adsorption of BPA was studied (Fig. 6). This examination was performed only for the PAN 1% SWCNT-COOH, because pH has an impact on the chemical form of carboxyl group in functionalized SWCNT and zeta potential of this membrane and thereby influencing interaction between pollutants in the feed and the membrane and affecting the intensity of the sorption. The quantity of adsorbed BPA was at similar levels between pH 3 and 7. The slightly lower sorption capacity at pH 3 was due to the limited solubility of BPA in an acid medium. However, BPA adsorption decreased significantly when the solution pH reached 9. It is well known that BPA is a weak acid (Table 2). Therefore, in alkaline wastewater, BPA molecules released a proton and formed bisphenolate anions. On the other hand, in pH 9, the PAN 1% SWCNT-COOH membrane is negatively charged. Reduction of adsorption when pH reached 9 was obvious because of growing repulsion forces between BPA anions and negatively charged membrane surface.

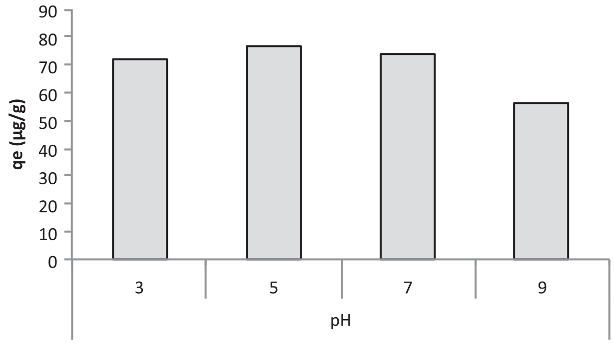

Fig. 6. The effect of wastewater pH on the adsorption of BPA on the PAN 1% SWCNT-COOH.

3.5. Effectiveness and performance of micropollutants removal

Fig. 7 illustrates the changes in the effectiveness of micropollutants removal (BPA and 4-NP) and permeate fluxes depending on the content of CNTs in the

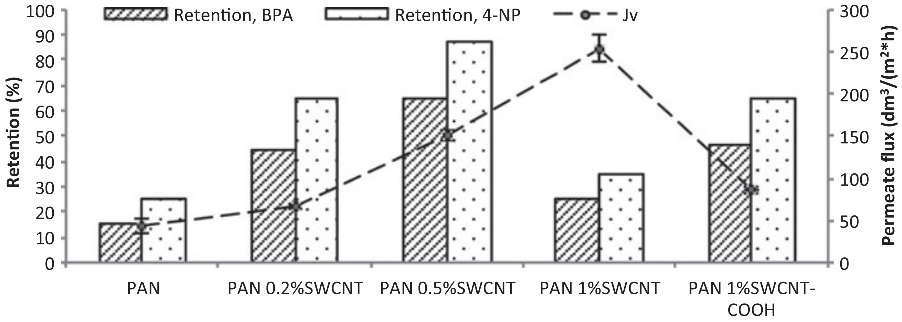

Fig. 7. Effect of SWCNT loading on wastewater flux (at 0.5 bar) and the removal of micropollutants.

membranes. The membrane capacity, excluding PAN 1% SWCNT-COOH, tended to increase with increasing CNTs loading in PAN matrix. The permeate flux of PAN 1% SWCNT was about 80% higher than for unmodified PAN. Generally, modification of membranes with CNTs induced two major effects on the membrane properties. One, very evident, is a change in the membrane structure, and the other one is a change of hydrophilicity of membranes. Both factors can influence membrane capacity. In fact, the structure of PAN 1% SWCNT was looser and more porous than the unmodified membrane (Fig. 2), consequently leading to the higher permeate flux. In contrast, lower membrane capacity of PAN 1% SWCNT-COOH could be caused by another type of CNTs and their density, as well as it could be a consequence of higher hydrophobicity of that membrane (Fig. 4).

This is obvious that the amount of nanotubes had an important role on the treatment efficiency due to changes in the membrane structure and properties. Thus, the removal of micropollutants was diversified (15–65% for BPA) and (25–87% for 4-NP), depending on the CNTs content in the membranes. Generally, an increase in the CNTs content in the membranes caused a regular increase in the effectiveness of micropollutants removal. Solely, in the case of PAN 1% SWCNT, the reduction of the micropollutants retention to the level similar for unmodified PAN membrane was observed. On the one hand, a membrane with a high content of nanotubes should remove more pollutants due to an increase in sorption sites and enhanced sorption phenomenon. On the other hand, the structure of the PAN 1% SWCNT is evidently more opened and permeable, and it causes that the flow of feed through the membrane was faster and, consequently, contact time between pollutants and the membrane was lower. In this case, when contact time was insufficient for the sorption of pollutants, retention could be lower due to a sieving effect. In other words, filling of PAN membranes with CNTs is favourable only in a certain concentration range of the modifying agent, which should be individually selected for the membrane to be prepared. A similar observation was demonstrated by Vatanpour et al.; the optimal effect in the rejection capability of nanocomposite PES membranes was observed only in specified low quantity of nanotubes [15]. Ghaemi et al. observed the enhancement of retention of nitrophenols with increasing concentration of nanoparticles (only in a certain range) in polyethersulfone membranes [11]. It was also found that the removal of nonylphenol was higher than bisphenol A. Higher removal efficiency of nonylphenol can be considered to be an effect of higher hydrophobicity of this compound, resulting in easy and favourable sorption in nanocomposite membranes. Octanol–water partition coefficient (log K_{ow}) describes the affinity of compounds to the sorption. When the value of log K_{ow} is lower than 2, the compound is hydrophilic, and the higher is the log K_{ow} value is, the more hydrophobic is the substance and it exhibits increasing sorption affinity [29–31]. As it could be seen in Table 2, the value of log K_{ow} for NP is two times higher than for BPA.

Importantly, these results indicate that micropollutants can be removed in low pressure membrane filtration using PAN 0.5% SWCNT to a similar extent as in high-pressure membrane processes [32]. On the other hand, the removal degree of BPA and NP using PAN 0.2% SWCNT I PAN 1% SWCNT and PAN1% SWCNT-COOH is similar to ultrafiltration with commercial ultrafiltration membranes [27].

4. Conclusions

Modified PAN membranes were prepared with the addition of CNTs in the casting solution at different concentration. SEM and AFM analysis proved the change in the topography, morphology and structure of the PAN-SWCNT membranes. The size of pores in support was higher in the PAN 1% SWCNT than in the unmodified PAN. Moreover, the nanomodification caused an increase in surface roughness, which was the effect of a deposition of aggregates of nanotubes in different layers of membrane. It was found that modification with the lower SWCNT content caused a slight increase in hydrophilicity. CNTs affected also the charge of the membrane surface. The addition of carboxyl functionalized CNTs increased their negative zeta potential. Sorption potential of membranes increased with increasing SWCNT content. Accumulation and formation of bigger bundles of nanotubes intensified with an increase in CNTs concentration and blocked the surface available for sorption. In this case, important factors affecting the sorption capacity were also hydrophobicity of the surface and lower specific surface area of the SWCNT-COOH as a result of embedding carboxyl groups in the potential sorption sites.

Overall, these results unequivocally confirm the superiority of the membrane modified with nanotubes in improving the performance and effectiveness of the micropollutants removal. Taking into account the effectiveness and performance of micropollutants removal, the best and most favourable content of SWCNT was 0.5 wt.%. In this case, retention mechanism was based on sorption on nanotubes embedded in the membrane surface and its structure. However, due to saturation of membrane over a period of time and limited sorption potential of CNTs, further studies should focus on regeneration of membranes modified with nanotubes, ensuring their multiple applications.

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