

## The application of composite GO/PAN membranes for removing surfactants from laundry wastewater

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### ABSTRACT

The paper presents the results of research on the use of ultrafiltration composite graphene oxide/polyacrylonitrile (GO/PAN) membranes (containing 0.8% (membrane A), 4.0% (membrane B), and 7.7% (membrane C) w/w of GO in PAN matrix) for removing surfactants from synthetic sewage and real laundry wastewater (LWW). For the preparation of synthetic sewage, anionic surfactants (dodecylbenzenesulfonic acid (DBSA), white sodium soap (SS)) and nonionic surfactants (Triton X-100, Mulan Citro) were selected. Real wastewater came from two different laundries, which used a mixture of nonionic and anionic surfactants (LWW 1) and only nonionic surfactants (LWW 2) in the washing process. The research demonstrated that anionic surfactants positively influenced the functionality of the membranes, increasing the volumetric permeate flux, which for DBSA was  $\sim 418 \text{ L m}^{-2} \text{ h}^{-1}$  (membrane A),  $\sim 212 \text{ L m}^{-2} \text{ h}^{-1}$  (membrane B), and  $\sim 245 \text{ L m}^{-2} \text{ h}^{-1}$  (membrane C) and had slightly lower values for SS. The GO/PAN composite membranes are characterized by a rejection rate of 100% for SS and more than 90% for DBSA and therefore can be used to remove anionic surfactants of LWW 1 ( $R = 90\text{--}99\%$ ).

*Keywords:* Graphene oxide; Polyacrylonitrile; Composite membranes; Surfactant; Laundry wastewater

### 1. Introduction

Domestic and industrial laundry wastewaters (LWWs) are gray water sources that could be refined, recycled, and reused [1]. In industrial washing laundries, nearly 15 L of water is used for washing 1 kg of clothes, which produces on average 400 m<sup>3</sup> of wastewater daily [2]. Domestic and industrial LWWs are relatively 'clean' in comparison with other industrial effluents, but it does not mean that there is no need to process it. If there are huge amounts of surface-active compounds in LWW, they highly increase total organic carbon (TOC). LWW is not very toxic; the problems are its bioaccumulation in water organisms, foaming, decreasing

oxygen dissolution in water, and increasing solubility of toxic substances [3].

LWW treatment methods use, among others, processes of coagulation, flotation, adsorption combined with sedimentation, as well as biological processes [4], such as membrane bioreactor processes [5,6]. Cleaning of LWW is very often carried out in several different successive processes. Ge et al. [7] developed combinative bipolar electrocoagulation (EC)-electroflotation process to treat LWW. Treatment of LWW by biological and EC methods was recently described by Ramcharan and Bissessur [8]. Advanced oxidation processes (photolysis, photocatalysis, and ozonation under ultraviolet (UV) irradiation) were used in the second stage of LWW treatment by Kuzminski et al. [9]. Organic compounds in LWW were degraded by photoelectrochemical (PEC) and electrochemical (EC) processes on a mesoporous

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$\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanostructured film by Nguyen et al. [10]. Bautista-Toledo et al. [11] analyzed the bioadsorption/biodegradation kinetics of the sodium dodecylbenzenesulfonate surfactant on commercial activated carbons and on activated carbons prepared in the laboratory by activation of almond shells. Terechov's team removed anionic surface-active agent in combined chemical coagulation-flocculation/UV photolysis [12], while Mohan proposed a treatment system that consisted of coagulation-flocculation, sand filtration (SF), and granular activated carbon adsorption [13].

Membrane processes are highly suitable for LWW treatment. Sumisha et al. used hydrophilic polyvinylpyrrolidone (PVP) modified polyethersulfone (PES) membranes for ultrafiltration (UF) process of LWW. They discovered that modified PES membranes were suitable for removing surfactants and oil from LWW [14]. Ciabatti et al. [2] and Shang et al. [15] employed an UF polyvinylidene fluoride (PVDF) membrane and achieved an effective removal of contaminants in laundry effluent. Commercial PVDF membrane was also used for microfiltration (MF) by Kim et al. [16], while Guilbaud et al. [17] employed nanofiltration membrane (AFC80 membrane) to treat ship LWW and obtained a 93% chemical oxygen demand (COD) rejection. Kowalska demonstrated that polysulfone (PS) and PES membranes can be successfully used to remove anionic surfactants from water solutions [18]. Manoucheri treated domestic LWW in a membrane process using a mixed cellulose ester MF membrane [19].

We decided to apply our new graphene oxide/polyacrylonitrile (GO/PAN) membranes [20] for treatment of both model and real LWW. The LWW contains detergents which are mainly anionic or nonionic surfactants or both. The efficiency of the LWW treatment using our method was assessed by determination of concentration of both types of surfactants. In all cases, COD, pH, conductivity, and oxidative reductive potential were also measured.

## 2. Materials and methods

### 2.1. Materials

PAN (molecular weight = 85,000), copolymer (93.9% acrylonitrile/5.8% methyl acrylate/0.3% methallyl sulfonate), was purchased from Goodfellow Cambridge Ltd, England. GO was synthesized by modified Hummers method, as described in our previous work [21].

Analytical grade methylene blue, dodecylbenzenesulfonic acid (DBSA), and Triton X-100 (TX) were purchased from Sigma Aldrich, Poland. Analytical grade *N,N*-dimethylformamide (DMF), chloroform, methylene chloride, ammonium thiocyanate, cobalt nitrate, and sodium tetraborate were purchased from Avantor Performance Materials, Poland, S.A. White sodium soap (SS) was delivered from Pollena-Ostrzeszow, Poland. Mulan Citro (MC) of Christeyns NV was a kind gift from the laundry no. 2.

LWW from the laundry no. 1 (LWW 1) contained both anionic and nonionic detergents, LWW from the laundry no. 2 (LWW 2) contained the nonionic surfactants only as the anionic ones are not used there. Both real LWW are situated in the Silesian voivodship, Poland; parameters of their wastewaters are presented in Table 1. Prior to testing, the LWW was pre-filtered through a filter paper.

Typical LWW contains 1–10 mg L<sup>-1</sup> of nonionic surfactants and 1–15 mg L<sup>-1</sup> of anionic surfactants [2]. Therefore, aqueous solutions of synthetic wastewater with the lowest possible concentrations were prepared. Anionic surfactants (DBSA, SS) and nonionic surfactants (TX, MC) were selected for the study, and then their 1 ppm solutions were prepared.

### 2.2. Formation of PAN membranes and GO/PAN composite membranes

Membranes were formed by the phase inversion method, as described in our earlier work [20].

Initially, a solution was prepared, which was then used to form membranes from pure PAN (membrane "0"). For this purpose, a 12% w/w solution of PAN in DMF was prepared.

Next, a GO dispersion in DMF at a concentration of 3.7% w/w was formulated and then used to obtain a homogeneous GO/PAN/DMF mixture. For this purpose, appropriate quantities of PAN and DMF were introduced into the GO/DMF dispersion until solutions containing the appropriate amounts of individual components were obtained (Table 2).

The membrane-forming solutions were next poured onto a clean glass plate and spread using a casting knife with an adjustable thickness fixed at 0.2 mm. Finally, they were rapidly coagulated in distilled water at room temperature until the membrane was detached from the glass. Precipitated PAN membranes (membrane "0") and composite membranes A, B, and C were air dried.

### 2.3. Measurements of water flux

The transport properties of the formed membranes were tested using a Millipore Amicon 8400 UF cell with a capacity of 350 mL and a 7.6-cm membrane diameter that

Table 1  
Parameters of the studied LWWs (*P*-conductivity, ORP-Oxidation/Reduction Potential, COD-Chemical Oxygen Demand).

Parameters	pH	<i>P</i> [μS cm <sup>-1</sup> ]	ORP [mV]	COD [mg O <sub>2</sub> L <sup>-1</sup> ]
LWW 1	8.14	148	-39.9	1,385
LWW 2	10.14	245	-186.9	1,630

Table 2  
Quantities of components in membranes [22]

Type of membrane	Concentration of GO (% w/w)	Concentration of PAN (% w/w)
"0"	0.0	100.0
A	0.8	99.2
B	4.0	96.0
C	7.7	92.3

was equipped with an equalizing tank with a capacity of 800 mL. First, dry membranes were immersed in distilled water for 1 h. Then, they were treated with distilled water for additional 2 h under a pressure of 0.2 MPa to improve the membrane stability. UF tests were performed at operational pressures of 0.1, 0.15, or 0.2 MPa. Permeate flux ( $J_v$ ) was calculated using Eq. (1):

$$J_v = \frac{Q}{A \times t} \quad (1)$$

where  $J_v$  is water flux ( $\text{L m}^{-2} \text{h}^{-1}$ ),  $Q$  is the permeate volume (L),  $A$  is the effective membrane area ( $\text{m}^2$ ), and  $t$  is the permeation time (h).

The transport properties of membranes are presented in Fig. 1.

#### 2.4. Measurements of concentration of surfactants

The contents of anionic and nonionic surfactants were analyzed in model and real LWWs before and after membrane processes. Determination of anionic surfactants was performed by measuring MBAS (methylene blue active substances) index according to the slightly modified PN-EN 903 standard procedure [23]. In our procedure, a sample of 5 mL was introduced into a 10-mL sample tube (made of a spectrophotometric glass and tightly closed) and was alkalinized by addition of 50 mM solution of borate buffer in the presence of phenolphthalein. Then, 0.1 mL of 0.01% methylene blue solution was added, and the solution was mixed with 4 mL of chloroform. It was shaken for 30 s and then left for 5 min to allow phase separation. Absorbance of a lower chloroform part was measured using 650 nm wavelength.

For a preparation of a calibration curve, we used DBSA solutions. The nonionic surfactants were determined by measuring CTAS (cobalt thiocyanate active substances) according to Standard Methods procedure no. 5540 D [24], modified by us to increase absorbance. We changed amounts of reagents when preparing a cobalt thiocyanate solution: 2.8 g of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and 6.2 g of  $\text{NH}_4\text{SCN}$  were dissolved in

10 mL of water. We used TX for the preparation of the calibration curves for LWW 1 and MC in the case of LWW 2. Absorbance of a lower chloroform part was measured using 620 nm wavelength.

HACH DR/4000U spectrometer was used for Vis analyses.

#### 2.5. Measurements of rejection

After the determination of MBAS and CTAS indices in raw LWWs, we subjected them to UF using GO/PAN composite membranes.

The separation properties of PAN and GO/PAN membranes with respect to surfactant solutions were investigated. Model and real LWWs were filtrated through each membrane type at a working pressure of 0.2 MPa; 30 mL of permeate was collected each time. Volumetric permeate flux ( $J_v$ ) was calculated using Eq. (1) and presented in Fig. 2.

The concentrations of surfactants were determined indirectly by measuring the absorbance of subsequent permeates using HACH DR/4000U spectrometer for Vis analyses, and then, by means of Eq. (2), the rejection coefficient ( $R$ ) was calculated:

$$R = \left( 1 - \frac{C_p}{C_f} \right) \times 100\% \quad (2)$$

where  $R$  is the rejection performance of the membrane (%), and  $C_p$  and  $C_f$  are the concentrations of surfactants in the permeate and feed solution ( $\text{g L}^{-1}$ ), respectively.

### 3. Results and discussion

#### 3.1. Physicochemical properties of membranes

GO/PAN composite membranes were studied using scanning electron microscope (SEM), X-ray diffraction, differential scanning calorimetry (DSC), Raman spectroscopy, and Fourier transform infrared (FTIR) spectrometer equipped with an attenuated total reflectance accessory. The analysis results were very similar to the ones obtained in our earlier work [20].

The studies carried out using SEM show that asymmetric membranes were obtained. SEM photomicrographs showed that the GO/PAN composite membranes, unlike the pure PAN membrane, are built of a thin and porous skin layer. Wide-angle X-ray scattering structural study did not indicate GO phase separation in the PAN matrix, but its good dispersion. Raman spectroscopy and FTIR studies confirmed the possibility of formation of coordination bonds between PAN chains and GO functional groups, which affects the good dispersion of the addition in the polymer matrix. Thermal analysis (DSC) also confirmed good dispersion of GO in the PAN matrix and the effect of GO on the reduction of polymerization cyclization temperature.

#### 3.2. Transport properties

At the beginning of our studies, we measured transport properties of the analyzed membranes; they are presented in Fig. 1. The volumetric permeate flux for membrane "0" was  $\sim 120$ ,  $\sim 161$ , and  $\sim 174 \text{ L m}^{-2} \text{h}^{-1}$ , respectively, for working

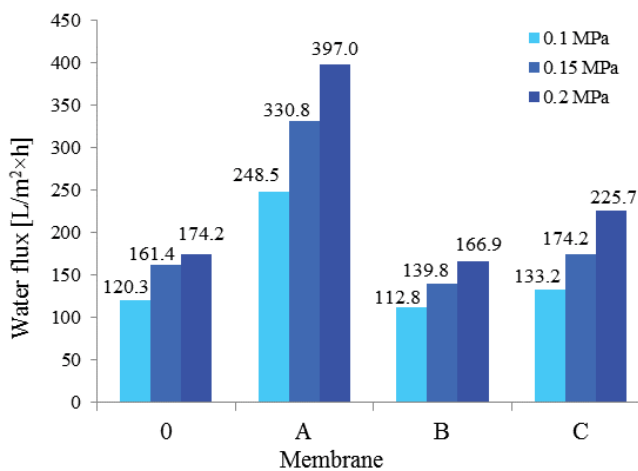


Fig. 1. Water flux for pure PAN membrane (membrane "0") and GO/PAN composite membranes (membranes A–C).

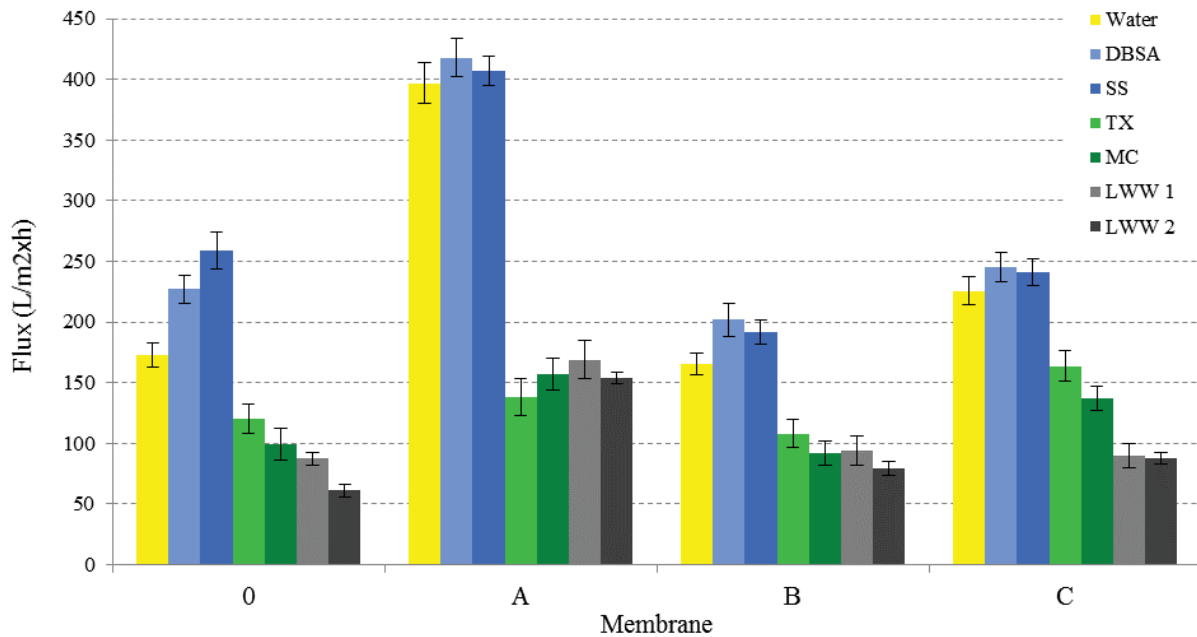


Fig. 2. The volumetric permeate flux for surfactant solutions (DBSA, SS, TX, MC) and laundry wastewaters (LWW 1, LWW 2) determined for subsequent membranes operated at a working pressure of 0.2 MPa.

pressures of 0.1, 0.15, and 0.2 MPa. Composite membrane B was characterized by volumetric permeate flux values close to those obtained for the pure PAN membrane, namely  $\sim 113$ ,  $140$ , and  $167 \text{ L m}^{-2} \text{ h}^{-1}$  (for pressures of 0.1, 0.15, and 0.2 MPa, respectively). The membrane with the highest (7.7% w/w) content of the GO addition (membrane C) displayed an increase of 8%–30% in the permeate volumetric flux in relation to membrane “0”, which for subsequent working pressures 0.1, 0.15, and 0.2 MPa is  $133$ ,  $174$ , and  $226 \text{ L m}^{-2} \text{ h}^{-1}$ , respectively.

Membrane A (0.8% of GO to the PAN matrix) displayed more than twofold increase in transport properties in comparison with the pure PAN membrane. The volumetric permeate flux values for membrane A, for subsequent working pressures, were  $\sim 286 \text{ L m}^{-2} \text{ h}^{-1}$  (0.1 MPa),  $\sim 331 \text{ L m}^{-2} \text{ h}^{-1}$  (0.15 MPa), and  $\sim 397 \text{ L m}^{-2} \text{ h}^{-1}$  (0.2 MPa).

The volumetric permeate flux values obtained in the experiment for all membranes are many times higher than those obtained by Sumisha et al. [14] who studied PES/PVP composite membranes and commercial PES membranes. The researchers showed that the permeate volumetric flux for the working pressure of 0.5 MPa is  $\sim 55$  to  $59 \text{ L m}^{-2} \text{ h}^{-1}$  for PES/PVP composite membranes and  $\sim 108 \text{ L m}^{-2} \text{ h}^{-1}$  for the commercial PES membrane, respectively.

The next stage of the research was checking how the volumetric permeate flux changes under the influence of anionic (DBSA, SS) and nonionic (TX, MC) surfactants and LWW (LWW 1, LWW 2) flow through successive membranes (Fig. 2).

Aqueous solutions containing anionic surfactants improved the transport properties of subsequent membranes. In the case of DBSA solution flow, the observed volumetric permeate flux values were  $226.85 \pm 12.1 \text{ L m}^{-2} \text{ h}^{-1}$  (membrane “0”),  $417.9 \pm 15.8 \text{ L m}^{-2} \text{ h}^{-1}$  (membrane A),  $201.7 \pm 14.0 \text{ L m}^{-2} \text{ h}^{-1}$

(membrane B), and  $245.1 \pm 12.4 \text{ L m}^{-2} \text{ h}^{-1}$  (membrane C). For a solution containing SS, on the other hand, the volumetric permeate flux values for subsequent membranes (“0,” A, B, C) were  $258.6 \pm 14.8$ ,  $407.3 \pm 12.2$ ,  $191.3 \pm 10.7$ , and  $240.6 \pm 11.6 \text{ L m}^{-2} \text{ h}^{-1}$ .

The results may suggest that in the case of anionic surfactants, the phenomenon of repulsion of these compounds from negatively charged membranes is observed. This phenomenon positively affects the operation of the membranes, causing an increase in permeate flux. Higher volumetric permeate flux values are observed for membrane “0” which contains pure PAN. This polymer accumulates negative charges on its surface which results in a significant improvement of permeate flux through membrane “0” and an increase in the flux by  $\sim 30\%$  (DBSA) and  $\sim 48\%$  (SS).

GO/PAN composite membranes, on the other hand, as shown in our earlier studies [20], have a smaller surface charge which results in an increase in the volumetric permeate flux values during the flow of anionic surfactants. In the case of DBSA, the increase in flux values through subsequent membranes (A, B, C) are  $\sim 5\%$ ,  $\sim 20\%$ , and  $\sim 8\%$ , respectively. While the flux values of SS through the GO/PAN membranes, as compared with distilled water, also increase to  $\sim 3\%$  (membrane A),  $\sim 14\%$  (membrane B), and  $\sim 6\%$  (membrane C).

It was observed that nonionic surfactants significantly deteriorate the transport properties of all membranes. The values of the volumetric permeate flux for TX were successively  $120.6 \pm 9.5 \text{ L m}^{-2} \text{ h}^{-1}$  (membrane “0”),  $137.9 \pm 15.1 \text{ L m}^{-2} \text{ h}^{-1}$  (membrane A),  $108.1 \pm 12.4 \text{ L m}^{-2} \text{ h}^{-1}$  (membrane B), and  $163.8 \pm 12.9 \text{ L m}^{-2} \text{ h}^{-1}$  (membrane C). For the MC solution, the volumetric permeate flux values were  $99.0 \pm 13.2$ ,  $157.0 \pm 12.7 \text{ L m}^{-2} \text{ h}^{-1}$ ,  $92.1 \pm 10.2$ , and  $137.0 \pm 9.8 \text{ L m}^{-2} \text{ h}^{-1}$ , respectively, for subsequent membranes “0,” A, B, and C.

These results may indicate that there is no repulsion of nonionic surfactants from membranes, both made of pure PAN as well as composite ones, which results in clogging of the membranes due to fouling and reduction of permeate flux. For pure PAN membrane, the permeate flux is reduced by ~40% for TX and ~43% for MC. And for GO/PAN composite membranes, the highest decrease in volumetric permeate flux is observed in membrane A and is ~65% for TX and ~73% for MC. Membranes B and C are characterized by smaller differences in flux values. The flow of nonionic surfactants through membrane B causes a decrease in the volumetric permeate flux by ~35% (for TX) and ~45% (for MC). On the other hand, for membrane C, these drops are ~27% (for TX) and ~40% (for MC).

Our studies have shown that anionic surfactants improve the transport properties of both pure PAN membranes and all composite membranes (A, B, and C). This phenomenon can be explained by the repulsion of surfactant particles from the negatively charged membrane, which facilitates flow through the tested membranes. In contrast, nonionic surfactants slow down the filtration process and presumably clog the pores in the membranes, hindering the transport of liquids. Similar effects were also observed when using the same membranes for treatment of the wastewater containing dyes. In the presence of anionic dyes, membranes from pure PAN and GO/PAN composite increased permeate flux, as described in our earlier publication [22].

During the study of LWWs (LWW 1, LWW 2), it was observed that the volumetric permeate flux values are definitely decreased. The obtained values may be due to the fact that the actual LWW is a complex mixture of compounds. Apart from the surfactants, they may contain various contaminants, such as dirt, epidermis, and short fibers detached from textiles during washing. Studies have shown that the volumetric permeate flux values for LWW 1, containing anionic and nonionic surfactants, were  $87.3 \pm 5.0$ ,  $168.9 \pm 15.7$ ,  $93.9 \pm 9.1$ , and  $90.2 \pm 12.2$  L m<sup>-2</sup> h<sup>-1</sup>, respectively, for subsequent membranes "0," A, B, and C. On the other hand, LWW 2 wastewater, which contained only nonionic surfactants, showed even lower flux rates:  $60.9 \pm 5.4$  L m<sup>-2</sup> h<sup>-1</sup> (membrane "0"),  $153.9 \pm 15.6$  L m<sup>-2</sup> h<sup>-1</sup> (membrane A),  $79.4 \pm 12.4$  L m<sup>-2</sup> h<sup>-1</sup> (membrane B), and  $87.5 \pm 9.9$  L m<sup>-2</sup> h<sup>-1</sup> (membrane C).

The tests carried out for the LWW confirmed that nonionic surfactants hinder the process of wastewater treatment on the membranes used. Values of the volumetric permeate flux obtained in the process of wastewater treatment are reduced by half (Fig. 2), although they are still higher than those described in the literature [14,19].

### 3.3. Rejection of surfactants

The ultrafiltration (UF) process carried out on the GO/PAN composite membranes allowed to obtain permeates. Then anionic and nonionic surfactants were determined in them using MBAS and CTAS method respectively. Knowing the concentration of surfactants in each permeate, the rejection coefficients were calculated, and the obtained results are collected in Figs. 3 and 4.

The results of the degree of anionic surfactant removal from model wastewater (DBSA, SS) and real wastewater (LWW 1) are summarized in Fig. 3. The research shows that

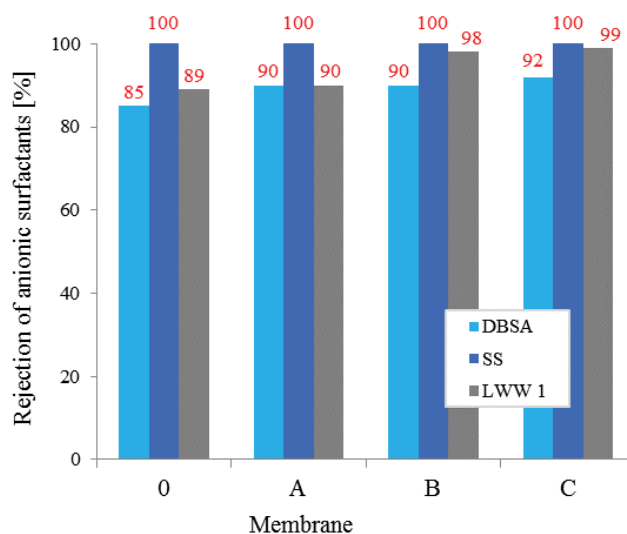


Fig. 3. Rejection coefficients on subsequent membranes for anionic surfactant solutions (DBSA, SS) and laundry wastewater (LWW 1).

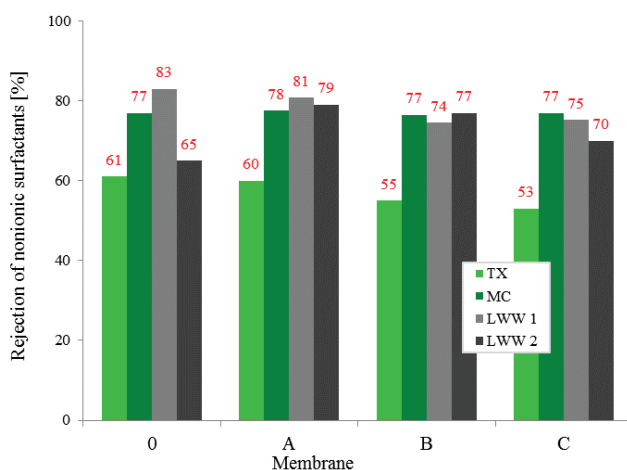


Fig. 4. Rejection coefficients on subsequent membranes for nonionic surfactant solutions (TX, MC) and laundry wastewater (LWW 1, LWW 2).

the degree of DBSA rejection was high and amounted to 85% (membrane "0"), 90% (membrane A, B), and 92% (membrane C). The maximum, 100% of the rejection, was obtained for SS. For LWW 1, on the other hand, the rejection coefficient values were 89%, 90%, 98%, and 99% for consecutive membranes "0," A, B, and C.

The studied membranes are characterized by interesting properties. Membrane "0," obtained from pure PAN, has a negative charge on its surface, which is a characteristic feature for this polymer. In the case of the GO/PAN membranes obtained by us, on the other hand, we have demonstrated that these membranes are also negatively charged, but to a lesser extent than pure PAN. In composite membranes, there are chemical interactions between the GO and PAN functional groups that cause the negative charge accumulating on the

surface of the membranes to decrease. Phenomena occurring at the molecular level have been explained in an earlier publication [20]. The positive effects of these interactions are the properties of GO/PAN membranes consisting in the absence of fouling and an improvement in transport properties with respect to anionic dyes, which are described in our earlier publications [22].

Thus, the pure PAN membrane and the GO/PAN membranes can be successfully used to remove anionic surfactants from aqueous solutions. For real wastewater, on the other hand, we have to deal with a more complicated system. Under these operating conditions, all of the studied membranes remove anionic surfactants; however, during the operation of the membrane, the permeate flux drops considerably (Fig. 2) due to fouling.

It is very difficult to compare the properties of the obtained membranes with those of other researchers. If we compare the research conducted by Kowalska [18], who used, among others, PS and PES membranes to remove anionic surfactants, the results are similar. Studying the PES membranes, the author removed 91% of anionic surfactants, while the rejection rate on PS membranes was 81%.

The results of the degree of nonionic surfactant removal from model wastewater (TX, MC) and real wastewater (LWW 1, LWW 2), on the other hand, are summarized in Fig. 4. The research shows that the rejection coefficient for nonionic surfactants on the GO/PAN composite membranes used in the experiment is unsatisfactory. The rejection values for TX were successively 61% (membrane "0"), 60% (membrane A), 55% (membrane B), and 53% (membrane C). In the case of the second surfactant, MC, the rejection values on the membranes were slightly higher and amounted to ~77%. Equally low rejection values of 65%, 79%, 77%, and 70% were obtained for LWW 2. However, in the case of LWW containing anionic and nonionic surfactants, the rejection rate was slightly higher. Rejection was 83% for membrane "0," 81% for membrane A, and less than 75% for the remaining membranes.

The obtained results of the rejection coefficient (Fig. 4) correlate well with the volumetric permeate flux results (Fig. 2). The PAN-based membrane and GO/PAN composite membranes are not suitable for removal of nonionic surfactants due to the low rejection coefficient and deterioration of transport properties. The research shows that the nonionic surfactants are poorly separated in the UF process, during which the membrane becomes clogged.

### 3.4. Physicochemical properties of LWW after UF process

Important parameters of wastewater include pH, conductivity ( $P$ ), and COD. These parameters were determined for real wastewater, both before (Table 1) and after the UF process (Table 2).

Ciabtti et al. reported that the pH of LWW is between 7 and 9 [2]. According to other authors, pH of wastewater from industrial laundries may be between 9 and 11 [19]. In our case, the initial parameters for the pH of the treated wastewater were 8.14 (for LWW 1) and 10.14 (for LWW 2). Analyzing the results of pH measurement after the membrane process, it can be noticed that for both types of real wastewater these values have decreased (Table 3). For LWW 1, the pH

Table 3

Parameters of the studied LWWs ( $P$ , conductivity; COD, chemical oxygen demand) after UF

Parameters	Membrane	pH	$P$ ( $\mu\text{S cm}^{-1}$ )	COD ( $\text{mg O}_2 \text{L}^{-1}$ )
LWW 1	0	7.78	141	705
	A	7.92	117	705
	B	7.91	115	845
	C	7.77	103	1,015
LWW 2	0	9.79	226	735
	A	9.75	205	338
	B	9.67	211	613
	C	9.66	204	754

values dropped to an average of ~7.8, whereas for LWW 2, they amounted to ~9.7 on average. Analyzing individual pH values obtained for real wastewater, it can be concluded that the UF process carried out on the GO/PAN composite membranes we fabricated removes the components responsible for the alkaline reaction.

The next parameter of the wastewater was the conductivity, which according to Ciabatti et al. [2] is within the wide range of 1,300–3,000  $\mu\text{S cm}^{-1}$ . Massoumeh et al., on the other hand, provide an even larger range for the conductivity of industrial LWW, amounting to 80–212,000  $\mu\text{S cm}^{-1}$ . In our case, the conductivity of the LWW was low, 148  $\mu\text{S cm}^{-1}$  for LWW 1 and 245  $\mu\text{S cm}^{-1}$  for LWW 2 (Table 1). This means that main detergents used in the washing process did not contain any auxiliary substances such as softeners, oxidants/disinfectants (sodium hypochlorite and hydrogen peroxide), alkali, acetic acid, oxalic acid, and formic acid [2]. The studies have shown that after the membrane process, carried out on pure PAN membranes, the conductivity decrease is low and amounts to 5% and 8% for LWW 1 and LWW 2, respectively (Table 3). In addition, it was observed that for LWW 1, which contained both anionic and nonionic surfactants, the conductivity values decreased by 21%, 22%, and 30% for permeates obtained on the subsequent membranes A, B, and C. The obtained conductivity results confirm the phenomenon discussed in Fig. 3, which consists in stopping the anionic surfactants on the membrane.

In the case of LWW 2, containing only nonionic surfactants, the conductivity dropped only by 14%–17%. The results obtained for LWW 2 can confirm that the membrane process carried out on GO/PAN composite membranes leads to the removal of mainly anionic detergents, while the nonionic surfactants are insufficiently removed from the LWW (Fig. 4).

An important parameter of sewage is COD, which indicates the content of certain chemical compounds (organic and inorganic) that oxidize in the presence of strong oxidants. The literature reports that the COD values for industrial wastewater are in the ranges of 400–1,000  $\text{mg L}^{-1}$  [2] and even 80–212,000  $\text{mg L}^{-1}$  [19]. Analysis of LWW 1 demonstrated that from the initial COD concentration of 1,385  $\text{mg L}^{-1}$  (Table 1), following the process of UF on the PAN and GO/PAN membranes, there is a decrease in COD, which amounts to ~51% (membranes "0" and A), ~39% (membrane B), ~27%

(membrane C), respectively. The obtained results allow to conclude that the COD reduced using GO/PAN composite membranes depends on the type of membrane. The greater the amount of GO in the membrane, the fewer compounds responsible for COD are removed.

In the case of LWW 2, the initial COD values of 1,630 mg L<sup>-1</sup> (Table 1) after the UF process are reduced by ~55% (membrane "0"), ~80% (membrane A), ~63% (membrane B), and ~55% (membrane C). These results lead to a similar conclusion that the COD reduced using GO/PAN membranes decreases as the amount of GO addition in the membrane increases. However, in the case of LWW 2, the removal of COD is greater because nonionic surfactants are retained on the membranes, resulting in a large decrease in the volume permeate flux (Fig. 2).

Comparison of the physicochemical properties of the LWW used in our research with other properties described in the literature is very difficult because compositions of washing baths and types of washed clothes, bed linen, etc. vary laundry to laundry. In addition, the literature reports methods for the treatment of LWW using various membrane techniques (MF, UF, RO), employing other membranes than the ones we used and other pretreatment methods preceding the membrane processes.

#### 4. Conclusion

The GO/PAN composite membranes presented in the article were characterized by good transport properties, which were many times greater than in the case of the LWW treatment membranes described in the literature [14]. The high rejection rates of anionic surfactants on GO/PAN membranes obtained during the studies were similar to those obtained by other researchers [18]. When conducting research on composite membranes, it was observed that the anionic surfactants were well separated, at the same time influencing the improvement of flux parameters on GO/PAN membranes. The observed phenomenon may result from the negative charge of composite membranes, which was described in our previous paper [20] and in the work of Chen et al. [25]. However, in the case of nonionic surfactant studies, it was observed that on the GO/PAN membranes the permeate flux decreased and the separation properties deteriorated. The GO/PAN composite membranes presented in this publication can be successfully applied for the separation of LWW in which anionic surfactants are present.

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