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The application of ultrafiltration composite GO/PAN membranes for removing dyes from textile wastewater

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ABSTRACT

Wastewater produced by the textile industry is a large percentage of total wastewater subjected to treatment processes. This paper presents the results of research on the use of ultrafiltration composite graphene oxide (GO)/polyacrylonitrile (PAN) membranes (containing 0.8% (membrane A), 4.0% (membrane B), 7.7% w/w (membrane C) of GO in PAN matrix) for removal of dyes from synthetic sewage and real laundry wastewater. Cationic dyes (Indigo synthetic – IS; Methylene blue – MB) and anionic dyes (Thymol blue – TB; Congo red – CR) were selected for the study. During testing of the flow of synthetic sewage through membranes, it was shown that TB and CR did not impair the transport properties of GO/PAN membranes, which for subsequent GO/PAN membranes were: ~24, ~35, and ~58 L/m^2 h bar, respectively. On the other hand, decrease of permeate flux was noted for synthetic sewage containing the IS and MB cationic dyes. The investigation of actual laundry wastewater showed a reduction in volumetric permeate flux by: 35% (membrane A), 61% (membrane B), and 50% (membrane C). The GO/PAN composite membranes could be used to remove anionic dyes, because they effectively (in nearly 100%) removed TB and CR, while cationic dyes (IS and MB) were separated in 60% ÷ 95%.

Keywords: Graphene oxide; Polyacrylonitrile; Composite membranes; Dye separation

1. Introduction

Dyes are found in many areas of our lives and they are used in the food, cosmetics, pharmaceutical, chemical, plastics, construction and textile, rubber, paper, and tannery industries [1,2].

The textile industry is considered as one of the world's largest industries that intensively uses water (2–180 L of water per 1 kg of textiles) and produces huge amounts of wastewater. Wastewater produced by the textile industry is usually polluted with contaminants consisting of used textile dyes, suspended solids, dispersants, bases, acids, detergents, salts, oxidants, surfactants, inhibitory compounds, grease and oil, toxicants, etc. [3,4]. Dyes used in the textile industry can be classified according to their chemical structure (azo, anthraquinone, indigoid, phthalocyanine, sulfur, nitro, and nitrozo dyes) and application (reactive, disperse, acid, basic, direct, and vat dyes) [5].

From the point of view of water and sewage management of industrial plants, dyes are only one of the pollutants in generated wastewater. Environmental protection regulations require companies to remove colored substances from wastewater. There are many methods for treatment of wastewater containing dyes, including biological, chemical, and physical methods [6]. Among the biological methods of removing dyes, decolorization by white-rot fungi and other microbial cultures [7], adsorption by living/dead microbial biomass, anaerobic textile-dye bioremediation systems [6] may be mentioned. The chemical methods of removing colored substances include: Fenton's reagent, ozonation, photochemical, sodium hypochloride (NaOCl), cucurbituril, or electrochemical destruction [5]. The physical methods

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used to decolorize wastewater are the adsorption methods (on activated carbon, peat, wood chips, and silica gel), ion exchange, irradiation, electrokinetic coagulation, and membrane methods [6].

The most common methods used to remove dyes are combinations of different processes into hybrid systems. Jana et al. [8] used Fenton's reagent, followed by microfiltration (MF) on a ceramic membrane to remove Crystal violet. The hybrid photodegradation process (TiO_2 nanotube) combined with MF on a polyamide membrane (PA6) was used to remove Reactive brilliant blue [9]. Other researchers observed that applying a layer of ZnO nanoparticles to polypiperazine amide membrane prevented fouling of the membrane and lead to complete removal of Congo red (CR) [10]. Zhang's team [11], on the other hand, performed Reactive brilliant red removal in the hybrid process of photocatalysis/ultrafiltration (UF). A technique for removing azo dyes by combining photocatalysis and membrane distillation was also developed [12]. Hayat et al. [4] and Punzi et al. [13] combined the biological method for the treatment of textile wastes containing dyes with a chemical method based on Fenton's reagent. In another case, the treatment and decolorization of textile sewage were carried out in two stages: by biological purification, followed by the ozonation process [14]. Other researchers used a membrane bioreactor in which the dye removal process took place on a granular activated carbon-coated hollow fiber module [15]. Yao et al. designed an alumina/polyethyleneimine (PEI) hollow fiber membrane, on which both the addition and oxidation of Reactive black dye occurred simultaneously [16].

Composite membranes can also be used to remove color substances. Lin et al. [17] used a composite MF membrane made of polyethersulfone (PES) with plant pulp addition for dye adsorption. Ultrathin nanofiltration (NF) composite membranes based on PES, modified with lysozyme, were obtained by Wang et al. [18] and used to remove dyes; the obtained membranes also showed antibacterial properties. Dyes were also removed on UF membranes of polysulfone modified with diallyl dimethyl ammonium chloride [19]. Textile industry wastewater was treated by Ong et al. [3] using polyamide-imide hollow fibers, while separation layer was made of PEI.

One of the well-known membrane polymers is polyacrylonitrile (PAN), from which UF, NF, reverse osmosis, and pervaporation (PV) membranes are obtained [20–23]. The literature reports the possibility of using PAN-based composite membranes to remove color substances. Zhu et al. [24] used a reactive composite membrane to remove the dye, where separation layer was a mixture of reduced graphene and halloysite nanotubes, while the carrier layer was PAN membrane. The Indigo dye was removed using composite membranes consisting of three layers: polypropylene nonwoven, PAN nanofibers, and dispersions from modified multiwalled carbon nanotubes [25].

Graphene oxide (GO) is one of many additives used as a component of composite membranes. The diversity of oxygen functional groups (hydroxyl, carbonyl, carboxyl, and ether) arranged on the GO surface makes it easy to be dispersed in polymer with functional groups to form durable bonds [26,27]. Zhu et al. [28] studied the polyvinylidene difluoride/GO/LiCl composite membrane to Rhodamine B adsorption. Chen et al. [29], on the other hand, presented NF multilayer membranes, containing a film (GO) to separate dyes such as CR, Victoria blue, and Brilliant green. The work of Zhan et al. [30] presented the possibility of removing anionic dyes on a composite membrane, in which the separation layer consisted of polydopamine-modified GO, while the support layer was made of poly(arylene ether nitrile) nano-nonwoven.

In this work, the possibility of removing dyes using PAN-based composite membranes containing GO additions was investigated. The GO/PAN membranes were obtained in a very simple, one-step manner, which was described in our earlier article [31], including the preparation of a homogeneous GO/PAN mixture in *N*,*N*-dimethylformamide (DMF). The literature describes a much more labor-intensive method of obtaining membranes from GO/PAN, in which thin layers of GO dispersed in poly(allylamine hydrochloride) were applied on the PAN membrane (layer-by-layer method) [32]. The membranes obtained in our experiment were tested for the separation of dyes, which varied in their molecular weight and charge (cationic and anionic). Four dyes were selected for the study: Indigo synthetic (IS), Methylene blue (MB), Thymol blue (TB) and CR. The investigation of the separation properties of GO/PAN membranes included the purification of synthetic sewage and actual washing wastewater (which had a blue color caused by Indigo). The studies showed that GO/PAN composite membranes could be used to remove both anionic and cationic dyes.

2. Materials and methods

2.1. Materials

PAN (MW = 85,000) – copolymer (93.9% acrylonitrile/5.8% methyl acrylate/0.3% methallyl sulfonate) was purchased from Goodfellow Cambridge Ltd, England. The dyes used for experiment were: IS ($C_{16}H_{10}N_2O_2$; 262.26 Da), MB ($C_{16}H_{18}ClN_3S$; 319.85 Da), TB ($C_{27}H_{30}O_5S$; 466.59 Da), and CR ($C_{32}H_{22}N_6Na_2O_6S_2$; 696.68 Da). All four dyes, graphite powder <20 μm and 4-dodecylbenzenesulfonic acid (DBSA; >95%) were purchased from Sigma-Aldrich, Poland. DMF, min. 95% H_2SO_4, 30% H_2O_2, $KMnO_4$, $NaNO_3$, Na_2SO_4, NaCl were purchased from Avantor Performance Materials, Poland S.A.

2.2. Synthesis of GO

GO was synthesized by the modified Hummers method, as described in our previous work [33].

GO, which was used to prepare GO/PAN composite membranes, was studied using X-ray diffraction (XRD), differential scanning calorimeter (DSC) thermal analysis, and Fourier transform infrared (FTIR) spectroscopy. The analysis results were very similar to the ones obtained in our earlier work [33].

2.3. Formation of PAN membranes and GO/PAN composite membranes

At the beginning, 12% w/w solution of PAN in DMF was prepared and afterwards used to form membranes "0."

Solutions necessary for the formation of GO/PAN composite membranes were also prepared. The appropriate amounts of 3.7% GO/DMF dispersion were batched and then adequate amounts of DMF were added and mixed thoroughly. 12 g of PAN was then added and mixed until the polymer was dissolved and 100 mL of a homogeneous GO/PAN/DMF dispersed solution was obtained.

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 detached from the glass. Precipitated PAN membranes (membrane "0") and composite membranes A, B, and C were air dried, and their quantitative composition is summarized in Table 1.

2.4. General characterization

The studies of physicochemical properties of the membranes allowed to specify such parameters as: thickness (l), mass per surface area (W_s), apparent density (d_m), water absorption (U), and porosity (ε), and the obtained results are summarized in Table 2.

The mass per unit area (W_s) (g/cm^2) and the apparent density (d_m) (g/cm^3) of the membranes were calculated using Eqs. (1) and (2), respectively:

$$W_s = \frac{w}{s} \tag{1}$$

$$d_m = \frac{w}{s \times l} \tag{2}$$

where w is the mass of a membrane with an area of 1 cm^2, s is the membrane surface area (cm^2), and l is the membrane thickness (cm).

The sorption of water (U) was measured as follows: dry membrane samples (W_d) with dimensions of 1 × 1 cm were weighed on an analytical scale with an accuracy of 0.0001 g and then immersed in distilled water for 10 s. The membranes were then blotted on filter paper and weighed again in the wet state (W_w). The sorption of water was calculated according to Eq. (3) as follows:

$$U = \frac{W_w - W_d}{W_d} \times 100\% \tag{3}$$

The porosity of the membranes (ε), that is, the ratio of pore volume to the volume of the membrane, was calculated using Eq. (4) as follows:

$$\varepsilon = \frac{\left(W_w - W_d\right)/d_w}{\left(W_w - W_d\right)/d_w + W_d/d_p} \times 100\% \tag{4}$$

where d_w is the density of distilled water (0.998 g/cm^3) and d_p is the polymer density (1.184 g/cm^3) [34].

2.5. Dyes adsorption studies

Sorption tests of individual dyes on membranes were carried out. For this purpose, solutions of IS, MB, TB, and CR at concentrations of 1 ppm were prepared. 1 × 1 cm membrane samples were cut out. A 10 mL of a dye solution was placed on a Petri dish containing a membrane sample and left for 24 h. The sample was then removed and the absorbance of the solution was measured using Perkin Elmer Lambda 35 UV-Vis spectrophotometer. Wavelengths for individual dyes were as follows: 690 nm (for IS), 663 nm (for MB), 432 nm (for TB), and 500 nm (for CR). Based on the calibration curve, the concentrations of the dye in each solution sample were measured. Sorption of dyes (S_d) was calculated according to Eq. (5) as follows:

$$S_d = \frac{C_1 - C_2}{C_1} \times 100\% \tag{5}$$

where $C_1$is the initial concentration of the test solution (g/cm^3) and C_2 is the concentration of solution after examining sorption properties (g/cm^3).

2.6. 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 was equipped with an equalizing tank of a capacity of 800 mL. First, dry membranes were immersed in distilled water for 1 h. Then, they were treated with distilled water for an additional 2 h under a pressure of 0.2 MPa to improve the membrane stability. UF tests were performed at operational pressures of

Table 1
Quantities of components in membranes

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

Table 2
Physicochemical properties of membranes

Property	l (μm)	W_s (g/cm^2)	d_m (g/cm^3)	U (%)	ε (%)	r_m (nm)
Membrane "0"	138.6 ± 3.1	0.0027 ± 0.0004	0.195 ± 0.027	354.8 ± 23.7	80.88 ± 3.7	63.4 ± 2.9
Membrane A	152.5 ± 6.7	0.0029 ± 0.0003	0.190 ± 0.025	292.8 ± 23.4	77.84 ± 4.8	55.8 ± 3.1
Membrane B	177.4 ± 7.3	0.0033 ± 0.0003	0.186 ± 0.008	275.5 ± 26.1	76.41 ± 3.3	74.4 ± 4.5
Membrane C	197.7 ± 5.2	0.0036 ± 0.0003	0.167 ± 0.020	268.8 ± 64.6	73.84 ± 4.0	103.9 ± 4.2

0.1, 0.15, or 0.2 MPa. Permeate flux (J_v) was calculated using Eq. (6) as follows:

$$J_v = \frac{Q}{A \times t} \tag{6}$$

where J_v is water flux (L/m^2 h), Q is the permeate volume (L), A is the effective membrane area (m^2), and t is the permeation time (h).

Pore size (r_m) was calculated on the basis of the specific permeate flux and porosity using the Guerout–Elford–Ferry equation [35] (Eq. (7)).

$$r_m = \sqrt{\frac{(2.9 - 1.75\varepsilon) \times 8\eta l Q}{\varepsilon \times A \times \Delta P}} \tag{7}$$

where η is the water viscosity (8.9 × 10^{-4} Pa s), l is the membrane thickness (m), Q is the volume of permeated pure water per unit time (m^3/s), A is the effective membrane area (m^2), and ΔP is the operational pressure.

2.7. Measurements of rejection

The separation properties of PAN and GO/PAN membranes with respect to dye solutions were investigated. Two different types of synthetic wastewater solutions were prepared for this purpose. The first ones were aqueous solutions containing individual dyes (IS, MB, TB, and CR), each with a concentration of 1 ppm. The second one was a mixture of synthetic dye wastewater (IS+, MB+, TB+, CR+) containing: 1 ppm of the individual dye and 0.01 g/L of NaCl, 0.01 g/L of Na_2SO_4 and 1 ppm of DBSA. Next, 300 mL of individual solutions were placed in the UF cell equipped with the test membrane. The permeation process was carried out at a working pressure of 0.2 MPa and 30 mL doses of permeate were tapped, simultaneously measuring the time of the permeate discharge from the test tank. Volumetric permeate flux (J_v) was calculated using Eq. (6), assuming that in this case Q is the permeate volume of each specific test solution.

The concentrations of dyes were determined indirectly by measuring the absorbance of subsequent permeates using Perkin Elmer Lambda 35 UV-Vis spectrophotometer, and then, by means of Eq. (8), the rejection coefficient (R) was calculated as follows:

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \tag{8}$$

where R is the rejection performance of the membrane (%) and C_p and C_f are the concentrations of dyes in the permeate and feed solution (g/L), respectively.

Textile wastewater (TW) flux and its purification on PAN membranes and GO/PAN composite membranes were also studied. TW was obtained from an industrial laundry in the Silesian Voivodeship, dealing with the washing of denim fabrics. They were characterized by a blue color that originated from Indigo.

3. Discussion of the results

3.1. Physicochemical properties of membranes

GO/PAN composite membranes were studied using scanning electron microscope, XRD, DSC, Raman spectroscopy and FTIR spectrometer with an attenuated total reflectance accessory equipped. The analysis results were very similar to the ones obtained in our earlier work [31].

As a result of the experiment, the membranes were obtained and studied in terms of the following physicochemical properties: thickness, mass per surface area, apparent density, water absorption (Table 2), and sorption of dyes (Fig. 1).

Membrane "0" characterized with the lowest thickness ~138 μm and the highest density ~0.195 g/cm^3 (Table 2). These results indicated that the PAN coagulation process proceeded quickly, and the obtained membrane had hydrophilic properties, which were confirmed by the water absorbency result (~350%). In contrast, GO/PAN composite membranes were characterized by higher thickness (Table 2), which, for consecutive membranes, was: ~153 μm (membrane A), ~177 μm (membrane B), and ~198 μm (membrane C). The obtained results suggested that the addition of GO to the PAN matrix delayed the coagulation process of the membranes, resulting in their lower density: ~190 g/cm^3 (membrane A), ~186 g/cm^3 (membrane B), and ~167 g/cm^3 (membrane C). For membranes A, B, and C, a decrease in water absorption was also recorded and resulted in values of 18%, 23%, and 24% respectively, against the pure PAN membrane.

Analyzing the results of porosity (Table 2), it was observed that the admixture of GO in membranes led to their porosity decreased. Membrane "0" was characterized by a porosity of ~81% and a pore size of ~63 nm. Porosity ~78%, pore size ~56 nm could indicate on a large number of small pores in membrane A. However, composite membranes B and C had a porosity of ~76% and ~74% and a pore diameter of ~74 and ~104 nm. The obtained research results: porosity, pore size, thickness, and density suggested that the introduction of subsequent portions of the GO addition resulted in the formation of GO/PAN membranes with increasing size of pores.

3.2. Sorption properties

Investigating the possibility of using membranes obtained in the experiment for removal of dyes from TW, we examined the sorption of individual dyes on subsequent membranes (Fig. 1). Dyes selected for the study differed in molecular weight, increasing from ~262 Da (IS), ~320 Da (MB), ~467 Da (TB), to ~697 Da (CR). In addition, these dyes differed in chemical nature. IS and MB belong to the group of cationic dyes and are electropositive, in contrast to TB and CR, which are electronegative, anionic dyes.

The results of the studies (Fig. 1) demonstrated that the dyes endowed with a positive (cationic) charge – IS and MB – were adsorbed on membrane "0," which was the result of electrostatic interactions between the pure PAN membrane and the electropositive dyes. Studies of sorption of dyes on GO/PAN membranes indicated on lower sorption, which for membranes A, B, and C was: ~12%, 7%, and 2% for IS, and for MB ~10%, 6%, and 1%, respectively. The obtained results demonstrated that the GO addition changed the electrical properties of composite membranes, which resulted in a decrease in the sorption of cationic dyes in the direction: 0.8%, 4.0%, and 7.7% GO content in the composite membrane.

In the case of anionic dyes, the sorption on membrane "0" was negligible and amounted to ~1% for IS and ~0.1% for MB

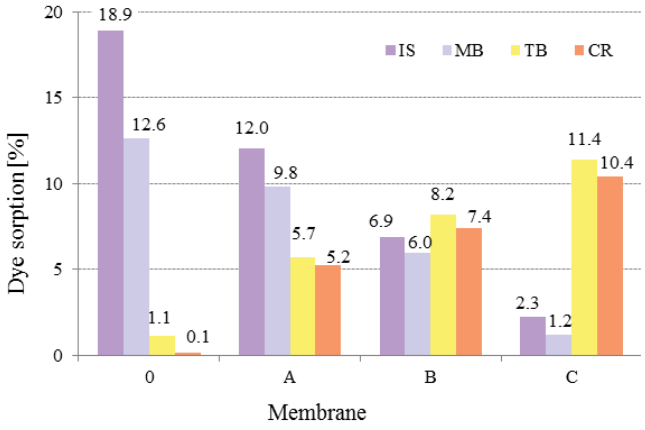

Fig. 1. Sorption of dyes (IS, MB, TB, and CR) on membranes made of pure PAN (membrane "0"), and composite GO/PAN membranes (membranes A, B, and C).

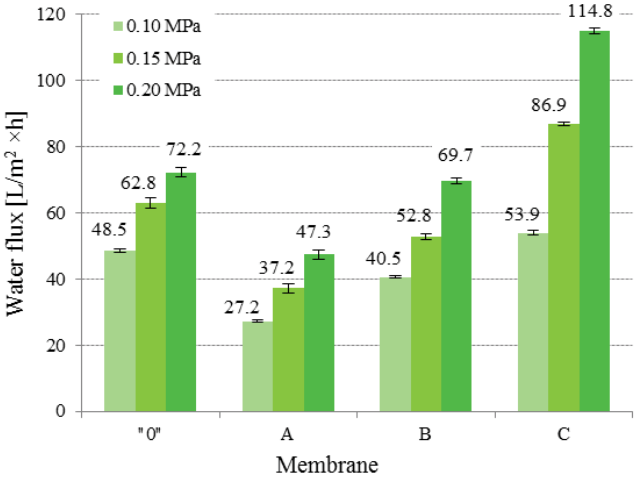

Fig. 2. Deionized water flux for pure PAN membrane (membrane "0") and GO/PAN composite membranes (membranes A, B, and C).

(Fig. 1). The observed phenomenon was the result of repelling of electronegative dyes from the pure PAN membrane. In the case of GO/PAN composite membranes, an increase in the sorption of anionic dyes was observed, along with an increase in GO concentration in the PAN matrix. The dyes sorption values on the subsequent membranes A, B, and C were: ~6%, 8%, and 11% for TB and ~5%, 7%, and 10% for CR, respectively. The sorption results of anionic dyes on GO/PAN membranes confirmed that the GO addition changed the electric charge value of these membranes.

The conclusion from the study could be that during the formation of composite membranes, interactions between PAN molecules and oxygen groups on GO occurred and resulted in change of the electrical properties of the GO/PAN composite. Changes in the structure of composite membranes also caused their hydrophobization, which resulted in a decrease in water absorption (Table 2), as described in our previous publication [31].

The phenomena of interactions between electronegative and electropositive dyes were described by Liu et al. [36], who investigated composite membranes built of GO in the skin layer. In our studies, we observed similar interactions that formed between the dye and the GO/PAN composite membrane.

3.3. Transport properties

The transport properties of the membranes are presented in Fig. 2. The volumetric permeate flux for membrane "0" was: ~49, ~63, and ~72 L/m² h, respectively, for working pressures of: 0.1, 0.15, and 0.2 MPa. In case of composite membranes, it was observed that the addition of 0.8% and 4.0% of GO to the PAN matrix caused a decrease in transport properties, which for the working pressure of 0.2 MPa were ~47 L/m² h (for membrane A) and ~70 L/m² h (for membrane B), respectively. The permeate flux, on the other hand, increased to: ~54, 87, and 115 L/m² h (for subsequent pressures 0.1, 0.15, and 0.2 MPa) only at 7.7% w/w of GO addition to GO/PAN membranes. The results obtained in the experiment were probably caused by two different phenomena. On the one hand, it was observed that the GO addition resulted in the formation of GO/PAN composite membranes with lower density and porosity. On the other hand, subsequent portions of GO admixture (membranes A and B) affected the decrease of water absorption resulting of the increase of hydrophobic properties and increase in the average pore size.

The transport properties of membranes were also investigated (Fig. 3) in the environment of synthetic and actual wastewater–TW. Synthetic wastewater solutions were prepared in two ways. The first were water solutions of individual dyes (IS, MB, TB, CR). The second were wastewater solutions (IS+, MB+, TB+, and CR+), which, except for the corresponding dye, contained NaCl, Na_2SO_4, and DBSA, which often accompanied textile processes such as washing or dyeing as auxiliary substances.

During studies of transport properties on membrane "0" (Fig. 3), small differences in the volumetric permeate flux were observed. The flow of IS through membrane "0" was 63.1 L/m² h, while the IS+ wastewater flux grew slightly to 75.2 L/m² h. The value of the permeate flux obtained for IS dye solution filtration flux was slightly lower than for the distilled water, which could be related to the sorption of IS dye on membrane "0." In the case of IS+ solution, it was observed that the permeate flux characterized with similar values as distilled water flux (~72 L/m² h). In addition, it was slightly higher than the permeate flux of synthetic water containing IS. The value of the volumetric permeate flux of IS+ could be the result of the presence of DBSA in the wastewater solution. This compound belongs to the group of surfactants, therefore it could have combined with the dye, which prevented its sorption on the PAN membrane.

Very similar values of the flux were obtained during the study of transport properties of membrane "0" during filtration of synthetic wastewater containing MB. The volumetric permeate flux were: 69.2 L/m² h (MB) and 76.7 L/m² h (MB+), respectively. MB is also a cationic dye, therefore the results of the volumetric permeate flux were similar to the results obtained for IS.

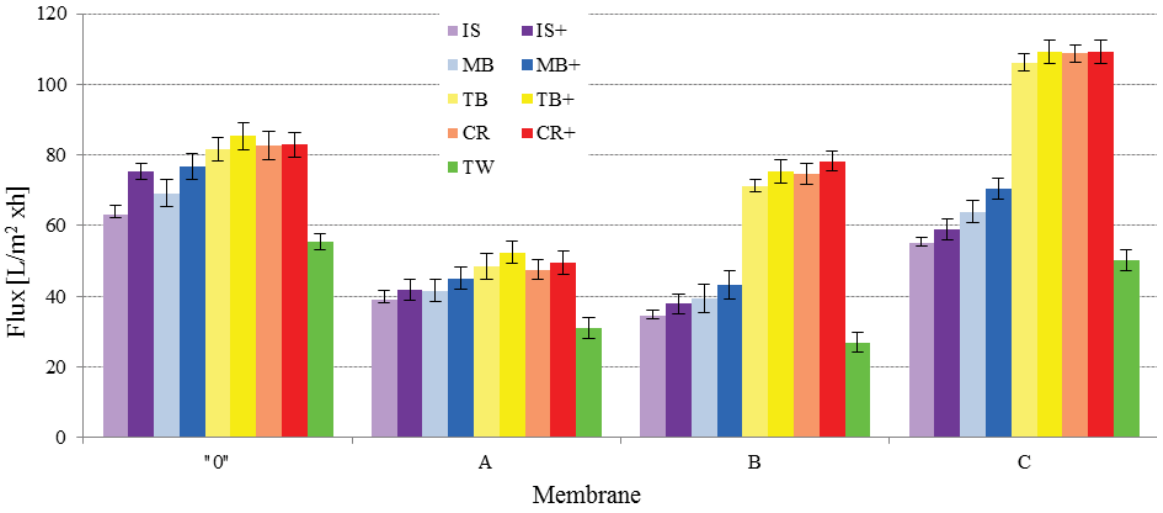

Fig. 3. The volumetric permeate flux for dye solutions (IS, MB, TB, and CR) and for synthetic dye wastewater (IS+, MB+, TB+, and CR+) and textile wastewater (TW) determined for subsequent membranes operated at a working pressure of 0.2 MPa.

On the other hand, studies of transport properties of membrane "0" during filtration of anionic dyes solutions (TB, CR) showed that the volumetric permeate flux were 81.7 and 85.3 L/m² h (for TB and TB+) and 82.6 and 82.9 L/m² h (for CR and CR+). The obtained results confirmed that no interaction of TB and CR with membrane "0" took place. In addition, like with previous results, a slight increase in the value of the volumetric permeate flux during filtration of synthetic wastewater that contained salts and DBSA was observed.

The tests showed that the permeates obtained during operation of membrane "0" were colorless (Fig. 4), thus the separation of both cationic and anionic dyes was effective.

Studies on the effect of IS dye on the transport properties of membranes A, B, and C showed that the permeate flux decreased along with the increase in the amount of GO addition to the GO/PAN composite membrane. The volumetric permeate flux of synthetic wastewater containing IS results were respectively: 39.0 L/m² h (membrane A), 34.5 L/m² h (membrane B), and 55.1 L/m² h (membrane C). Comparing these results with the values obtained for distilled water, the following decrease in the volumetric permeate flux was observed: −17.5% (membrane A), ~50.5% (membrane B), and ~52% (membrane C). The values of the volumetric permeate flux for IS+ synthetic wastewater, on the other hand, were: 41.7 L/m² h (membrane A), 37.9 L/m² h (membrane B), and 58.9 L/m² h (membrane C), that is, slightly higher than the permeate flux for IS wastewater. The decrease in the volumetric permeate flux value was closely related to the partial sorption of IS on the GO/PAN membranes, which resulted in impeded flow through the membrane. Furthermore, it was observed that the permeate color became more and more intense (Fig. 4), as the amount of GO addition increased, because the IS sorption decreased on subsequent membranes (Fig. 1).

The presence of MB in synthetic wastewater led to the reduction of the volumetric permeate flux, characteristic of the individual membranes A, B, and C. The flux values were successively: 41.6 L/m² h (membrane A), 39.4 L/m² h (membrane B), and 63.9 L/m² h (membrane C). The permeate flux was lower than the value for distilled water by: ~12%, ~43%, and ~44%, respectively, for individual membranes A, B, and C. Addition of NaCl, Na_2SO_4, and DBSA to MB+ synthetic wastewater slightly improved the flow of liquid through membranes and for individual GO/PAN composite membranes it was: 45.1 L/m² h (membrane A), 43.2 L/m² h (membrane B), and 70.5 L/m² h (membrane C). The volumetric flux values obtained for the GO/PAN membranes formed in the experiment were 5 ÷ 9 times higher than the results obtained for MB, presented in the paper by Liu et al. [36].

The studies showed that the cationic MB was adsorbed on the membranes, but in a slightly lower amount than IS. This may have resulted of the molecular structure of the dye that had two functional groups symmetrically distributed at both ends of the molecule. Photographs of permeates (Fig. 4) confirmed that as the concentration of GO in the composite membranes increased, the amount of MB passing into the permeate increased as well. The color of permeates observed in Fig. 4 was consistent with the decrease in MB sorption on GO/PAN membranes (Fig. 1).

Anionic dyes, TB and CR, introduced with synthetic wastewater onto GO/PAN composite membranes behaved differently than cationic dyes. Synthetic wastewater solutions containing TB did not substantially change the volumetric permeate flux value, which was: 48.3 L/m² h (membrane A) and 71.2 L/m² h (membrane B). The obtained results confirm strong repulsion of anionic TB from membranes A and B. In the case of membrane C, a 7.5% decrease in the flux to 106.2 L/m² h was observed, which could indicate on the sorption of a small amount of TB on this membrane. Studies on synthetic sewage (TB+) containing NaCl, Na_2SO_4, and DBSA, showed the effect of these auxiliary substances on a slight increase in the volumetric permeate flux. The flow of TB+ wastewater through individual membranes was: 52.4 L/m² h (membrane A), 75.3 L/m² h (membrane B), and 109.2 L/m² h (membrane C).

Similar flow results were obtained for synthetic wastewater containing CR. Membranes A and B were characterized

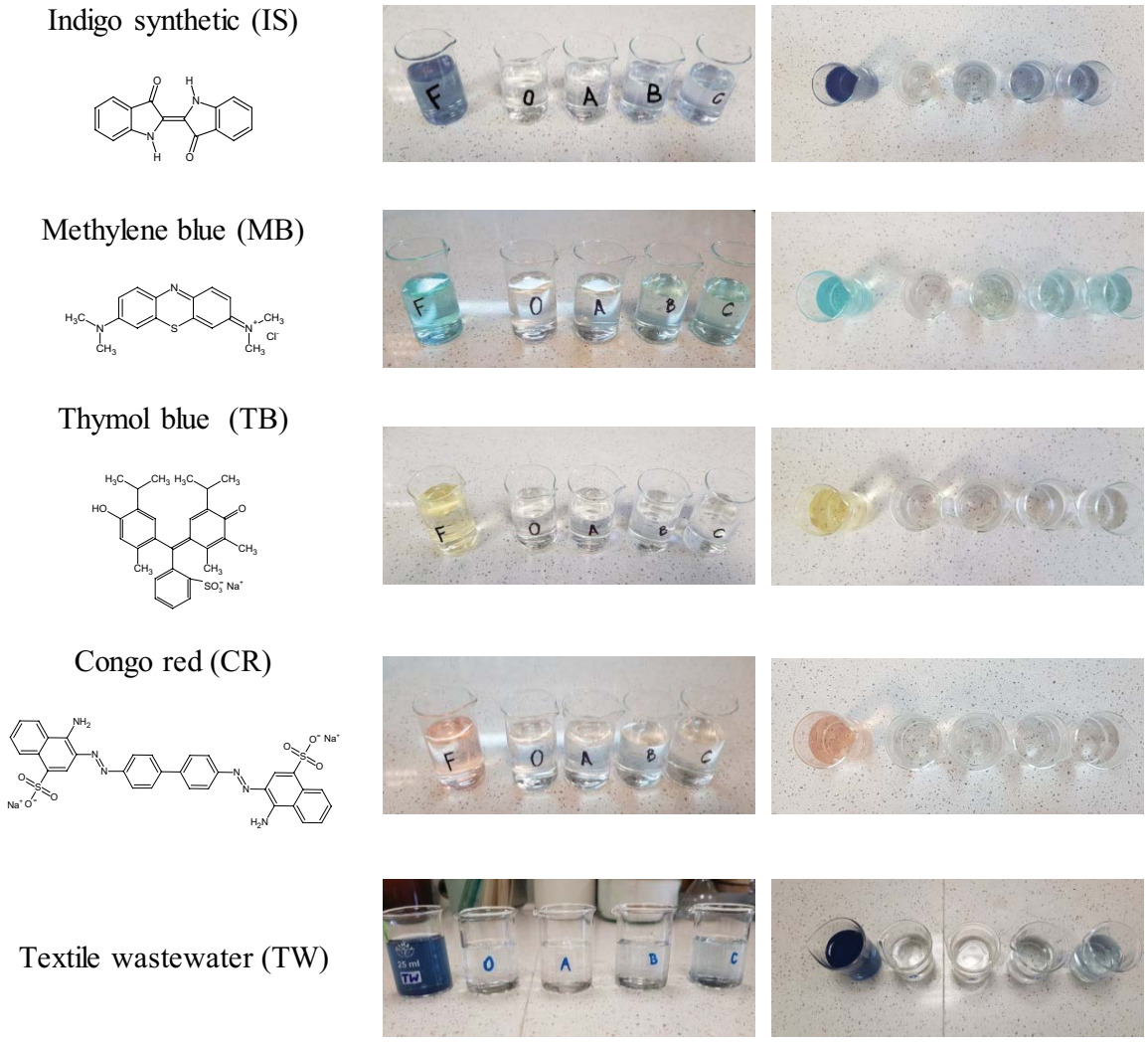

Fig. 4. Photographs of permeates obtained during ultrafiltration of dyes (IS, MB, TB, and CR) and textile wastewater (TW) on individual membranes. Markings: F – feed; 0 – permeate after membrane "0"; A – permeate after membrane A; B – permeate after membrane B; and C – permeate after membrane C.

by a volumetric permeate flux values, which were similar to the ones obtained for distilled water and amounted to: 47.5 L/m^2 h (membrane A) and 74.1 L/m^2 h (membrane B), respectively. The obtained results could also confirm the repulsion of anionic CR from composite membranes A and B. In the case of membrane C, the obtained result indicated on a 5% decrease in the permeate flux, which was 108.7 L/m^2 h. This result confirmed the adsorption of a small amount of CR on membrane C (Fig. 1). In contrast, studies of CR+ wastewater containing auxiliary agents (NaCl, Na_2SO_4, and DBSA) indicated on a slight increase in the volumetric permeate flux, in comparison with the results obtained for CR. Membrane A had a flux value of 49.5 L/m^2 h, membrane B – 78.3 L/m^2 h, and membrane C – 109.2 L/m^2 h. Comparing the obtained results with studies by Liu et al. [36], it was observed that the GO/PAN membranes had 13 ÷ 30 times higher values of the volumetric permeate flux.

Analyzing photographs in Fig. 4 showing samples of synthetic wastewater TB and CR, no permeate color development was observed. This suggested the effective removal of anionic dyes on GO/PAN composite membranes.

The UF tests were carried out on synthetic wastewater and the obtained results allowed us to use the experimental membranes on real laundry wastewater (Fig. 3), which contained Indigo in their composition. TW studies showed that the volumetric permeate flux on membrane "0" dropped by 28% and amounted to 55.3 L/m^2 h. A high decrease in the volumetric permeate flux for all of the tested GO/PAN composite membranes was also observed. TW flow through membrane A dropped by 35% in comparison with distilled water and was 30.9 L/m^2 h. Even lower values of the permeate flux were obtained during TW tests on membrane B. The flow through membrane B was 26.9 L/m^2 h and was lower by ~61% than the volumetric permeate flux for distilled water. In contrast, the TW volumetric permeate flux for membrane C was 50.2 L/m^2 h, which was ~56% of the permeate flux for pure water.

From the conducted research, it can be concluded that in the case of real wastewater, the lowest drop in the volumetric permeate flux was recorded for membrane A, which contained the lowest amount of GO in the PAN matrix (0.8% GO). The remaining GO/PAN composite membranes, containing 4.0% and 7.7% of the GO addition characterized with high decreases in the volumetric permeate flux. The obtained results were caused by many factors. Firstly, TW sewage contained IS, which, as was showed in the first part of the research, could be effectively separated only on membrane A. The confirmation of this conclusion is shown in Fig. 4, in which it can be noticed that TW permeate was colorless only after membrane A. Secondly, another factor that led to the permeate flux decrease was the presence of short fibrils that detached in the course of each washing process, clogging the pores of the membrane.

3.4. Rejection of dyes

The purpose of the research was to analyze the possibility of using GO/PAN composite membranes to remove dyes from wastewater (Fig. 5). Studies on the separation properties of the obtained membranes showed that membrane "0" could be used to remove cationic and anionic dyes from both synthetic and actual wastewater. The degree of removal (rejection) of subsequent dyes on membrane "0" was: 95%–96% (IS), 100% (MB), 97%–99% (TB), 100% (CR), and 98% (TW).

Composite membranes A, B, and C removed anionic dyes (TB and CR) from synthetic wastewater very well (96% ÷ 100%) (Fig. 5) and characterized with good transport properties (Fig. 3). The degree of removal (rejection) of the color substances from actual wastewater (TW) was also high and amounted to 94% ÷ 98%, but it was accompanied by a significant decrease in the volumetric permeate flux (Fig. 3). Comparing the obtained results with studies by Liu et al. [36], who reported that CR rejection had been 90%, it was found that GO/PAN membranes were better in separating their dye.

In the case of synthetic wastewater, containing cationic dyes, slightly lower values of the degree of rejection were observed, in comparison with other types of wastewater. The degree of rejection of IS was the highest on membrane A and amounted to 82% ÷ 87%. In the case of other composite membranes, their IS separation properties decreased along with the increase in the amount of GO addition in the PAN matrix. The degree of rejection was 64% ÷ 65% (membrane B) and 61% ÷ 62% (membrane C), and it was closely related to the decrease in the volumetric permeate flux (Fig. 3). A similar tendency was observed for MB, for which the degree of rejection was successively: 96% ÷ 98% (membrane A), 78% ÷ 80% (membrane B), and 75% ÷ 76% (membrane C). In the case of synthetic wastewater containing cationic dyes, it could be noted that the degree of rejection increased with increasing molecular weight of the dye (IS ~ 260 Da, MB ~ 320 Da). A comparative analysis of the results obtained for MB with those described in the literature [36] showed that GO/PAN composite membranes were equally effective in separating this dye.

Research on the basic parameters of TW wastewater, such as: pH, conductivity, and chemical oxygen demand (COD) showed a change in their value after the UF processes carried out on the individual membranes obtained in the experiment (Table 3). The test results showed that after the process, carried out on GO/PAN membranes, all TW parameters were reduced, which meant that the process was effective. In the case of permeate obtained on membrane "0," on the other hand, the COD value was high and amounted to 1,385 mg/L, indicating on poor wastewater purification, despite removing the color in ~100% (Figs. 4 and 5).

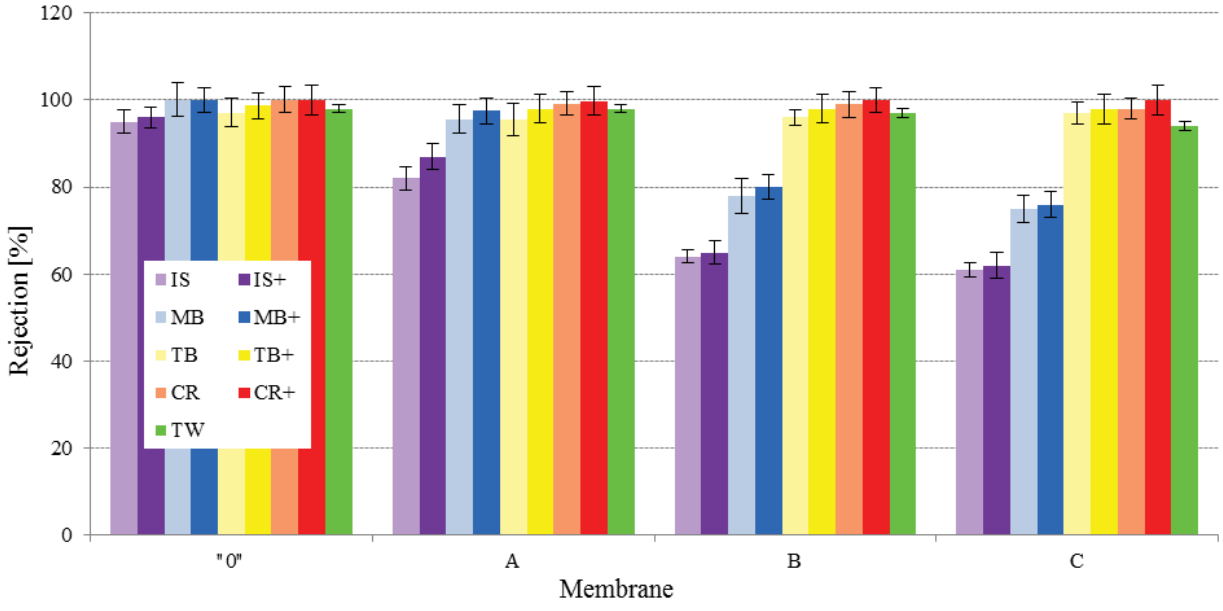

Fig. 5. Rejection coefficients on subsequent membranes for dye solutions (IS, MB, TB, and CR), synthetic dye wastewater (IS+, MB+, TB+, and CR+) and textile wastewater (TW).

Table 3
Properties of textile wastewater (TW) before and after the ultrafiltration process carried out on individual membranes "0," A, B, C

Parameter	pH	*P* (μS)	COD	SO_4^{2-} (mg/L)	NH_4^+ (mg/L)	PO_4^{3-} (mg/L)
TW	8.14	148	1,515	130	14	0.7
"0"	7.87	141	1,385	0	1.6	0.7
A	7.92	117	705	0	1.4	0.4
B	7.91	115	705	0	1.7	0.1
C	7.77	103	845	0	1.7	0.4

4. Conclusion

The GO/PAN composite membranes presented in the article characterized with good transport properties, which were many times greater than those described in the literature [36–38] for membranes made of GO in the skin layer. The advantage of GO/PAN membranes was a simple, one-step method of preparation, which distinguished them from the works of other discussed researches cited.

The high rejection rates of dyes on GO/PAN membranes obtained during the study were similar to those obtained by other research teams [19,30,36,37,39]. When conducting research on composite membranes, it was observed that the anionic dyes were well separated, without impairing the flux parameters on individual membranes. However, in the case of cationic dyes, their sorption, leading to reduction of the permeate flux and to affection of separation properties were observed for GO/PAN membranes, along with the increase in the GO amount in composite membranes. The interactions between anionic and cationic dyes observed in our studies are similar to those described in detail by Chen et al. [38].

The GO/PAN composite membranes presented in this publication may find application for the treatment of TW contaminated with organic dyes, both anionic and cationic.

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