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# THE EFFECT OF THE TYPE OF ADMIXTURE ON THE PROPERTIES OF POLYACRYLONITRILE MEMBRANES MODIFIED WITH NANOTUBES, GRAPHENE OXIDE AND GRAPHENE

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**ABSTRACT**

This paper presents the results of research on the production of composite polyacrylonitrile (PAN) membranes with nanotubes (MWCNT), graphene (RG) and graphene oxide (GO) addition. All of the specified additions differ diametrically in terms of properties, starting from the spatial structure of the particles, to the chemical properties. The membranes were obtained using phase inversion method from a solution of N,N-dimethylformamide (DMF). Subsequently, the impact of the nano-addition on the transport and separation properties of the membranes was investigated using Millipore AMICON ultrafiltration kit. Membranes with graphene addition (PAN/RG) are characterized by the best transport properties and the highest specific permeate flux values in the range of ~913÷1006 $dm^3/m^2 \times h$ for the working pressure of 2.0 MPa. In order to test the separation properties, electroplating wastewater generated in one of the Silesian galvanizing plants was used. The qualitative and quantitative composition of the wastewater was tested by means of UV-Vis spectrophotometer (HACH) and absorption atomic spectrometry (AAS). The ultrafiltration process carried out on composite membranes allows for the complete removal of phosphate ions and ~88÷94% removal of iron from the waste water. The rejection coefficient of the remaining metals is high: ~35÷85% for copper and ~17÷100% for cadmium.

**Keywords:** composite membranes: PAN/GO, PAN/RG, PAN/MWCNT, ultrafiltration, electroplating waste water

## INTRODUCTION

Polyacrylonitrile (PAN) constitutes one of the polymers used to make the membranes. PAN is an inexpensive and popular engineering polymer that is widely used in membrane techniques: ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO) and pervaporation (PV) [Mori et al. 2007, Arai et al. 2002, Kim et al. 2002, Huang et al. 2011]. It is a polymer with good thermal stability [Lee et al. 2012], high thermal conductivity, UV resistance and chemical resistance as well as good mechanical properties [Wypych 2012]. PAN is soluble in many solvents, so it can be easily formulated from the solution [Wypych 2012, Iovleva et al. 2001]. The morphology of the membranes obtained with this technique, and thus their properties, are influenced by the factors such as the polymer concentration, the type of solvent and coagulant used, and the solvent evaporation time [Kim et al. 2002, Lohokare et al. 2012, Wang et al. 2012]. Polyacrylonitrile can be easily modified by giving new properties to this polymer. One of the ways to modify the PAN membranes is to introduce particles of another substance in order to obtain composite membranes. For polymers, such additions may in-

clude nanoparticles such as allotropic carbon varieties: carbon nanotubes (MWCNT), graphene (RG) and graphene oxide (GO).

Carbon nanotubes are supramolecular structures resembling hollow cylinders composed of rolled graphene layers: single-walled carbon nanotubes (SWCNT) and multi-walled carbon nanotubes (MWCNT) [Noy et al. 2007]. Nanotubes are characterized by excellent mechanical, thermal and electrical properties [Saito et al. 1998], which result from their length-to-diameter ratio, surface smoothness and hydrophobicity [Noy et al. 2007, Kar et al. 2012]. These properties allow the use of nanotubes in the production of unique composites, including polyacrylonitrile composites [Palade et al. 2015]. The membranes containing nanotubes are obtained in two forms: vertically aligned (VA) and mixed matrices (MM) [Ahn et al. 2012]. You et al. [2013] obtained composite membranes from PAN nanofibers that constituted the carrier layer on which they applied a layer of Polyvinyl alcohol (PVA) nanofibers, with MWCNT addition. Then, by washing in the solvent mixtures, PVA swelled and formed a skin layer containing nanotubes. Majeed et al. [2012] obtained PAN/MWCNT composite membranes from 14% PAN solution in DMF, using 0.5; 1; 2% w/w functionalized [Goh et al. 2013] carbon nanotubes. The membranes containing carbon nanotubes are widely used in membrane cleaning and desalination [Das et al. 2014, Goh et al. 2013, Hinds et al. 2004] as well as decontamination techniques [Elimelech et al. 2011].

Graphene (RG) is another nanoadditive that is increasingly used in membrane processes. RG is most commonly used in the form of thin, nanoporous films. Obtaining composite membranes containing single layers of graphene introduced into the polymer matrix is a difficult task. Wang et al. [2015] described the process of obtaining graphene containing cellulose membranes. Their method consisted in combining the GO dispersion with never-dried cellulose in the presence of an organic base and then filtering under reduced pressure. The team of Ye [2016], on the other hand, obtained cellulose composites containing graphene by exfoliation of graphite dissolved in a cellulose solution that was dissolved in the ionic liquid. Graphene is used in such membrane techniques as gas separation [Kim et al., 2013], selective transport of ions [O'Hern 2014, Tian 2017] and desalination [Wang et al. 2017].

Graphene oxide is increasingly used as a component in membranes. It allows for easy preparation of thin, monolayer films that can be used for desalination and purification [Sun et al. 2013, Mahmoud et al. 2015, Han et al. 2013, Goh et al. 2015, Nair et al. 2012] and membrane distillation [Bhadra et al. 2016]. There are many techniques, reported in literature, for obtaining polymer membranes with GO addition resulting in the creation of layer membranes. The "layer-by-layer" method with partial hydrolysis of PAN is described by Hu et al [2014]. Zhu et al. [2016] prepared GO/PAN membranes by electrospinning from GO/PAN/DMF solution. On the other hand, Zhang et al. [2017] obtained them from the PAN solution in DMF nanofibres, which were chemically modified, and then a GO dispersion was applied in a strongly acidic environment.

The purpose of the study was to compare the transport and separation properties of polyacrylonitrile (PAN) doped with three different nano-additions: carbon nanotubes (MWCNT), reduced graphene (RG) and graphene oxide (GO). Membranes were prepared from a solution in N, N-dimethylformamide (DMF) and coagulated in water resulting in composite membranes. These membranes differed diametrically in the specific permeate flux for distilled water, which varied in the specific way for each membrane under the influence of the electroplating waste water. The common feature of all membranes obtained in the experiment is the complete removal of phosphate ions and ~ 90% removal of iron from the electroplating waste water.

## MATERIALS AND TEST METHODS

Polyacrylonitrile (PAN) ($M_w$=85,000) – copolymer purchased from GoodFellow. Graphite powder <20 microns, purchased from Sigma-Aldrich. Carbon nanotubes NC 700 (MWCNT) were purchased from Nanocyl. N,N-dimethylformamide (DMF), $NaNO_3$, 98% $H_2SO_4$, $KMnO_4$, 30% $H_2O_2$ were purchased from Avantor Performance Materials Poland S.A.

Graphene oxide was obtained according to a modified Hummers method [1958]. The process of obtaining GO is the same as the one described in our previous paper [Fryczkowska et al. 2015]. The resulting GO powder was dispersed in DMF using an ultrasonic bath. As a result of the experiment, 3.7% GO/DMF mixture was obtained.

Graphene was obtained from graphene oxide powder through thermal reduction. For this pur-

pose, graphene oxide was heated in nitrogen to approx. 180°C, until an explosion occurred, resulting in the reduction of GO to graphene.

### Forming of PAN membranes

Polyacrylonitrile membranes were obtained using the phase inversion method. First, a 12% solution of PAN in N, N-dimethylformamide (DMF) was prepared. The PAN solution was then poured onto a clean glass plate and spread using a casting knife with an adjustable thickness fixed at 0.2 mm. Finally, the polymer film was rapidly coagulated in distilled water at room temperature until the membrane detached from the glass. The precipitated membranes (membrane "0") were dried in air (Table 1).

### Forming of composite PAN/MWCNT membranes

Solutions containing 12% w/w of PAN in DMF containing 0.1; 0.5 and 1.0% w/w of MWCNT, respectively, were prepared. To this end, appropriate amounts of MWCNT, 12 g of PAN were batched and then the amounts were added to DMF and mixed thoroughly (Table 1). Then, a well-dispersed PAN/MCWNT solution was poured onto a clean glass plate and spread using a casting knife with an adjustable thickness fixed at 0.2 mm. Finally, it was rapidly coagulated in distilled water at room temperature until the membrane detached from the glass. Precipitated membranes (A-MWCNT, B-MWCNT, C-MWCNT) were dried in air.

### Forming of composite PAN/RG membranes

Solutions containing 12% w/w of PAN in DMF containing 0.1; 0.5 and 1.0% w/w of RG, respectively, were prepared. For this purpose, appropriate amounts of RG, 12 g of PAN were batched and then the amounts were added to DMF and mixed thoroughly (Table 1). Then, a well-dispersed PAN/RG solution was poured onto a clean glass plate and spread using a casting knife with an adjustable thickness fixed at 0.2 mm. Finally, it was rapidly coagulated in distilled water at room temperature until the membrane detached from the glass. Precipitated membranes (A-RG, B-RG, C-RG) were dried in air.

### Forming of composite PAN/GO membranes

Solutions containing 12% w/w of PAN in DMF containing 0.1; 0.5 and 1.0% w/w of GO, respectively, were prepared. To this end, appropriate amounts of 3.7% GO/DMF dispersion were batched and then the amounts were added to DMF and mixed thoroughly (Table 1). Then, 12 g of PAN was added and stirred until the polymer dissolved. Just before the membrane was formed, the PAN/GO solution was sonicated shortly. Subsequently, the well dispersed solution was poured onto a clean glass plate and spread using a casting knife with an adjustable thickness fixed at 0.2 mm. Finally, it was rapidly coagulated in distilled water at room temperature until the membrane detached from the glass. Precipitated membranes (A-GO, B-GO, C-GO) were dried in air.

## TRANSPORT AND SEPARATION PROPERTIES OF THE MEMBRANES

The transport properties of the obtained membranes were tested using a 350 $cm^3$ AMICON 8400 ultrafiltration cell (Millipore), designed for flat membranes. The membrane working surface was 45.4 $cm^2$. The ultrafiltration cell was

**Table 1**. The composition of the solutions for the preparation of membranes

| Type of the membrane | Symbol | Amount of PAN [g] | Amount of DMF [g] | Amount of addition (MWCNT; RG; GO) [g] |
|---|---|---|---|---|
| PAN membranes | "0" | 12 | 88 | - |
| PAN/MWCNT membranes | A-MWCNT | 12 | 87.9 | 0.1 |
| | B-MWCNT | 12 | 87.5 | 0.5 |
| | C-MWCNT | 12 | 87 | 1.0 |
| PAN/RG membranes | A-RG | 12 | 87.9 | 0.1 |
| | B-RG | 12 | 87.5 | 0.5 |
| | C-RG | 12 | 87 | 1.0 |
| PAN/GO membranes | A-GO | 12 | 85.3 | 2.7 (GO/DMF) |
| | B-GO | 12 | 74.5 | 13.5 (GO/DMF) |
| | C-GO | 12 | 61 | 27 (GO/DMF) |

equipped with a mixing element, a magnetic stirrer and an additional 800 $cm^3$ equalizing tank. The device operated in a dead-end system in which the feed was perpendicular to the surface of the membrane.

At the beginning, dry membranes were immersed in distilled water for 1 hour. Then, they were treated with distilled water for 2 hours under a pressure of 0.2 MPa. Studies on the transport properties of the membranes were carried out for the working pressures of 1.0; 1.5; 2.0 MPa. Permeate flux (Jv) was calculated using the formula (1) below. The results are presented in Figury 1.

$$J_v = \frac{V}{F \times s} \quad (1)$$

where: $J_v$ – volume permeate flux ($dm^3/m^2\times$ h),
$V$ – permeate volume ($dm^3$),
$F$ – membrane surface ($m^2$),
$s$ – discharge time (h).

In order to test the separation properties of the obtained membranes, the electroplating waste water, pre-treated in accordance with the previously developed procedure [Fryczkowska et al. 2017] was used. Its properties are summarized in Table 2. Wastewater in the amount of 250 $cm^3$ was fed into the ultrafiltration cell equipped with a suitable membrane. The ultrafiltration process was carried out at constant pressure (0.2 MPa), collecting 10% of permeate (25 $cm^3$). The specific permeate flux for the tested waste water was calculated using the formula (1). The results are presented in Figure 2.

Subsequently, the physical and chemical properties as well as the composition of permeates were examined. The reaction and conductivity of the solution was tested using Elmetron CPC 511 laboratory pH/conductivity meter. Chlorides, sulphates, phosphates, iron were determined using ready HACH cuvette test sets on HACH DR4000 spectrophotometer (according to current standards). The content of heavy metal ions was determined by atomic absorption spectrometry using Perkins-Elmer AAS Analist 100 spectrometer. The results are summarized in Table 3. Afterwards, the rejection coefficient (R) of each waste water component was calculated using formula (2), and the results are summarized in Figures 3 and 4.

$$R = \frac{C_p}{C_n} \times 100\% \quad (2)$$

where: $C_p$ – concentration of the component in the permeate;
$C_n$ – concentration of the component in the feed

## RESULTS AND ANALYSIS

The results of specific permeate flux tests (Fig. 1) indicate that membranes "0" are characterized by good transport properties, which are:

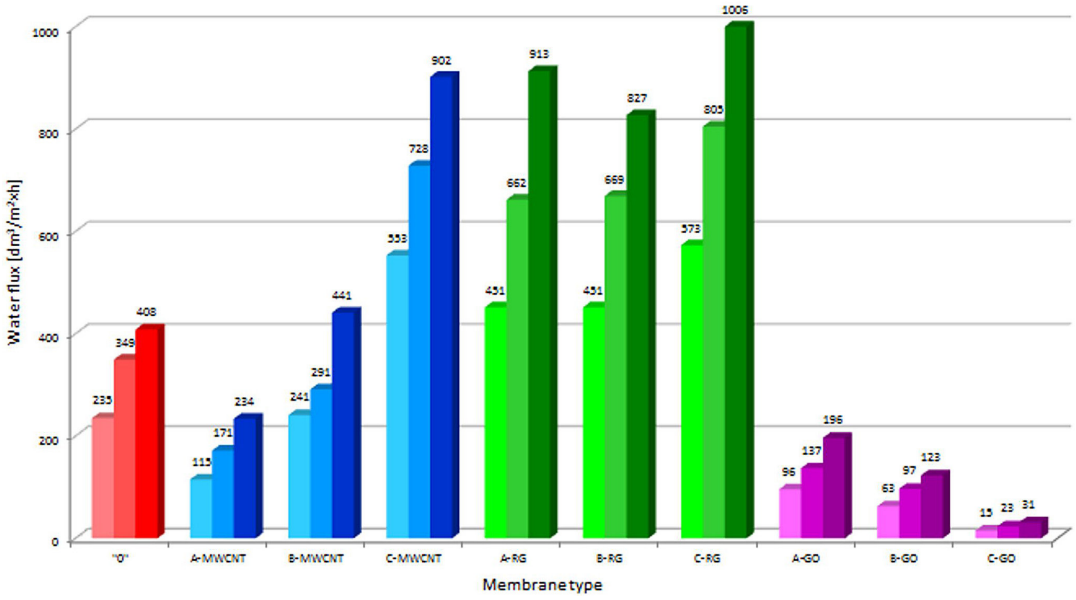


**Fig. 1**. Transport properties of pure PAN and composite membranes (values of specific permeate flux for pressures: 0.1 (light bar); 1.5 and 2.0 MPa (dark bar)

**Table 2**. Selected physical and chemical properties of electroplating waste water

| Designation | pH | Conductivity [µS/cm] | Sulphates [mg/dm$^3$] | Chlorides [mg/dm$^3$] | Phosphates [mg/dm$^3$] | Fe [mg/dm$^3$] | Cu [mg/dm$^3$] | Cd [mg/dm$^3$] |
|---|---|---|---|---|---|---|---|---|
| Numeric value | 7.38 | 1530 | 80 | 1820 | 0.06 | 1.02 | 0.61 | 0.06 |

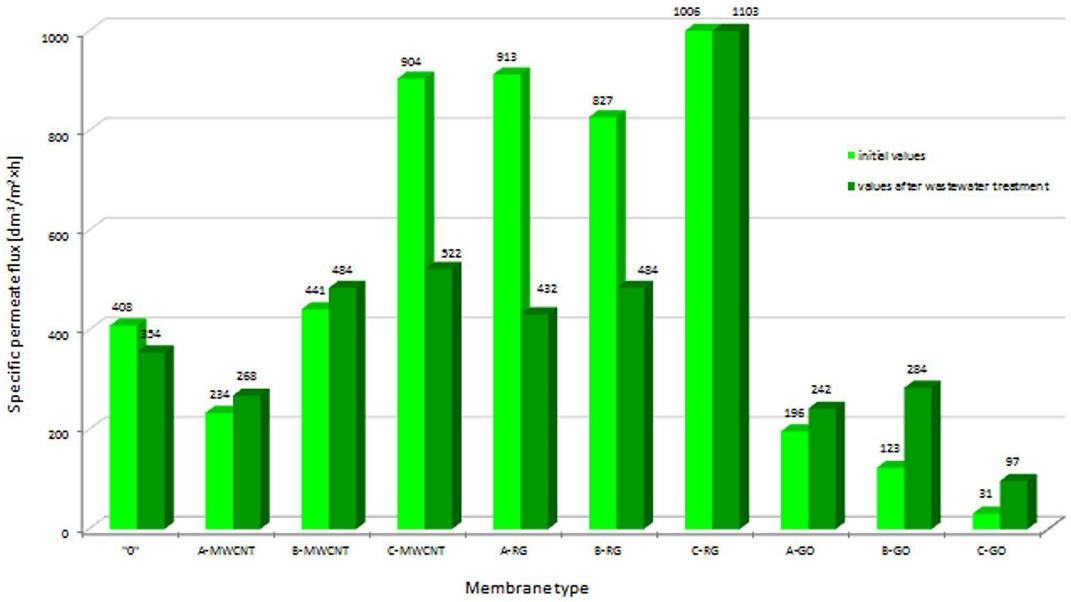


**Fig. 2**. Specific permeate flux of pure PAN and composite membranes before and after ultrafiltration (for working pressure of 0.2 MPa)

~240; ~350; ~408 [dm$^3$/m$^2$×h], respectively, for successive working pressures (0.5; 1.0; 2.0 MPa).

Introduction to the graphene (RG) into the polyacrylonitrile matrix enables obtaining composite membranes characterized by very good transport properties (~450÷1000 dm$^3$/m$^2$× h). For A-RG and B-RG membranes, water transport through PAN/RG membranes is comparable for the same operating pressures. The values of specific permeate flux, on the other hand, increase slightly for the C-RG membrane which contains the highest amount of graphene oxide in the polymer matrix.

Conversely, A-MWCNT and B-MWCNT composite membranes have worse transport properties than the membrane "0." The water flow through the C-MWCNT membrane is ~550 (for 0.1 MPa), ~730 (for 1.5 MPa) and ~900 dm$^3$/m$^2$×h (for 2.0 MPa), respectively. At the same time, it can be observed that the values of the specific permeate flux are twice as high for further nanotube concentrations in the polymer matrix.

PAN/GO composite membranes, on the other hand, exhibit the worst transport properties as compared to the others. The specific permeate flux values range from 15÷196 dm$^3$/m$^2$×h and decrease as the concentration of GO additive in the polymer matrix increases.

The analysis of the specific permeate flux (Fig. 1) leads to the conclusion that the addition of various dopants into the polyacrylonitrile matrix has a direct effect on the transport properties of the resulting composite membranes.

The studies on transport properties carried out using electroplating wastewater have shown that they behave differently under the influence of the ions which flow through them. The permeate flux for the membrane "0" drops by ~13%, which slightly reduces the performance of this membrane.

For the nanotube-doped composite membranes, the transport properties are observed to increase for A-MWCNT and B-MWCNT membranes by ~15 and ~10%, respectively. The C-MWCNT membrane, on the other hand, behaves differently because the specific permeate flux drops by as much as ~47%. The resulting outcome may be a consequence of the morphological construction of this membrane, resulting in the phenomenon of fouling.

While analysing the waste water flow through the graphene-doped composite membranes, a decrease in the specific permeate flux of ~53% is observed for A-RG membrane and of ~42% for the B-RG membrane. The observed decreases may

result from the occurrence of fouling, which hinders the flow through the membrane. Composite membrane C, on the other hand, which contains the highest concentration of RG in the polymer matrix, behaves differently from the others under the influence of the wastewater flow. In the case of the C-RG membrane, a slight improvement (~10%) of the transport properties is observed.

Moreover, all composite membranes with graphene oxide addition improve their transport properties in the environment of wastewater solution. The specific permeate flux for the A-GO membrane increases by ~24%, for the B-GO membrane by ~131%, while for the C-GO membrane the flux increase amounts to ~213%. The studies have shown that PAN/GO membranes significantly increase the specific permeate flux in the presence of electroplating wastewater.

While analysing the results, it was observed that the addition of 0.8% and 4% of nanotubes to polyacrylonitrile membranes improved their transport properties. When 7.7% of graphene is added to the PAN, the resulting membranes are not affected by fouling. On the other hand, PAN/GO composite membranes which are characterized by the lowest values of specific permeate flux for pure water, during electroplating wastewater ultrafiltration, improve the flow parameters, increasing them along with the concentration of GO in the polymer matrix.

Figue 3 presents the results of calculations of the rejection coefficient for the selected anions present in the electroplating wastewater. All membranes, from the membrane "0" to the composite membranes, effectively remove (R = 100%) phosphate ions from the waste water. It seems that the phenomenon is closely related to the concentration of these ions, which is the lowest of the anions determined (Tab. 3).

The chloride and sulphate ion rejection coefficient depends on the type of membrane on which the ultrafiltration was performed. Conducting the membrane process on the membrane "0" results in an increase in the chloride ion concentration by ~ 12% and – at the same time – a decrease in the sulphate ion concentration by ~13%. In the case of PAN/MWCNT composite membranes, the retention of sulphate and chloride ions on the membranes is observed, with a simultaneous increase of the specific permeate flux (Fig. 2). The C-MWCNT membrane behaves differently, i.e. it does not retain sulphate ions (R = 0%) and increases the concentration of chloride ions in waste water by 27%.

The rejection coefficient of sulphate and chloride anions on PAN/RG membranes is in most cases negative. At the same time, it can be observed that the critical concentration of the graphene addition in these membranes is 4%, at which point the chloride ions are removed from the waste water and their concentration drops by

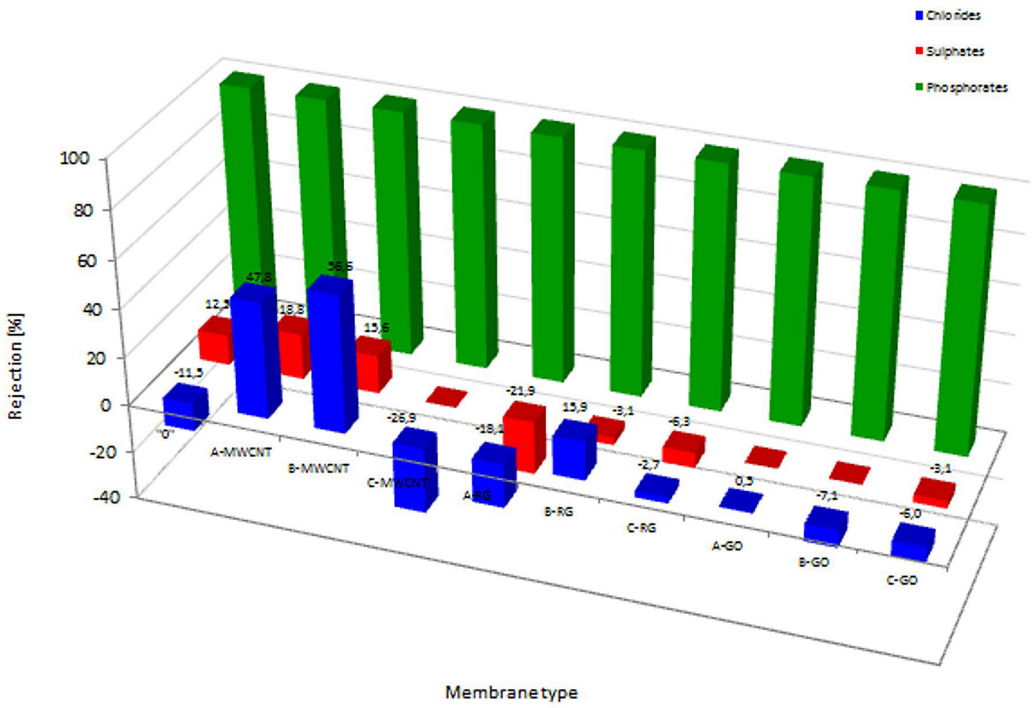


**Fig. 3**. Anion rejection coefficient on composite membranes and pure polyacrylonitrile membrane

**Table 3**. Research results of selected physicochemical properties of waste water after ultrafiltration process conducted on pure PAN membranes and composite membranes

| Type of the membrane | PAN | PAN/MWCNT | | | PAN/RG | | | PAN/GO | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | „0" | A-MWCNT | B-MWCNT | C-MWCNT | A-RG | B-RG | C-RG | A-GO | B-GO | C-GO |
| pH | 7.57 | 7.34 | 7.28 | 7.45 | 7.30 | 7.43 | 7.44 | 7.18** | 7.07** | 6.90** |
| Conductivity [µS/cm] | 1538 | 1246 | 1238 | 1436 | 1510 | 1445 | 1526 | 1541** | 1540** | 1539** |
| Sulphates [mg/dm$^3$] | 70 | 65 | 67.5 | 80 | 97.05 | 82.5 | 82.5 | 80** | 80** | 82.5** |
| Chlorides [mg/dm$^3$] | 2030 | 950 | 790 | 2310 | 2150 | 1530 | 1870 | 1810** | 1950** | 1930** |
| Phosphates [mg/dm$^3$] | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0** | 0** | 0** |
| Fe[mg/dm$^3$] | 0.08 | 0.06 | 0.06 | 0.10 | 0.12 | 0.08 | 0.10 | 0.08** | 0.08** | 0.09** |
| Cu*[mg/dm$^3$] | 0.39 | 0.18 | 0.33 | 0.33 | 0.22 | 0.09 | 0.16 | 0.18 | 0.17 | 0.13 |
| Cd*[mg/dm$^3$] | 0.02 | 0.01 | 0 | 0 | 0.01 | 0 | 0 | 0.06 | 0.02 | 0.02** |

* research done on AAS

** results of research in a publication prepared for printing [Turek et al.]

~16%. Moreover, during the ultrafiltration on the B-RG membrane, the sulphate anion concentration in the waste water increases slightly (~3%).

In the ultrafiltration of electroplating wastewater through PAN/GO membranes, improvement of their transport properties is observed (Fig. 2) which simultaneously results in a slight increase in concentration of sulphate ions by ~3% (C-GO membrane) and chloride ions by ~6÷7% in the permeate (B-GO and C-GO membranes).

The separation properties of the obtained membranes for the selected metals present in the electroplating wastewater (Tab. 3) indicated high values of rejection coefficient (Fig. 4). Regardless of the membrane used, iron was removed from the waste water most effectively: ~88÷94%.

The lowest value of rejection coefficient was observed for copper (~35%), which was removed from the waste water on pure PAN membrane (membrane "0"). The same metal is quite well retained on the A-MWCNT membrane (~70%). However, the rejection coefficient on other membranes containing the nanotube addition drops to ~45%. The highest value of the rejection coefficient of ~85% for copper was obtained on the B-RG membrane. In contrast, the composite membranes with graphene oxide addition retain copper, and its amount increases with the addition

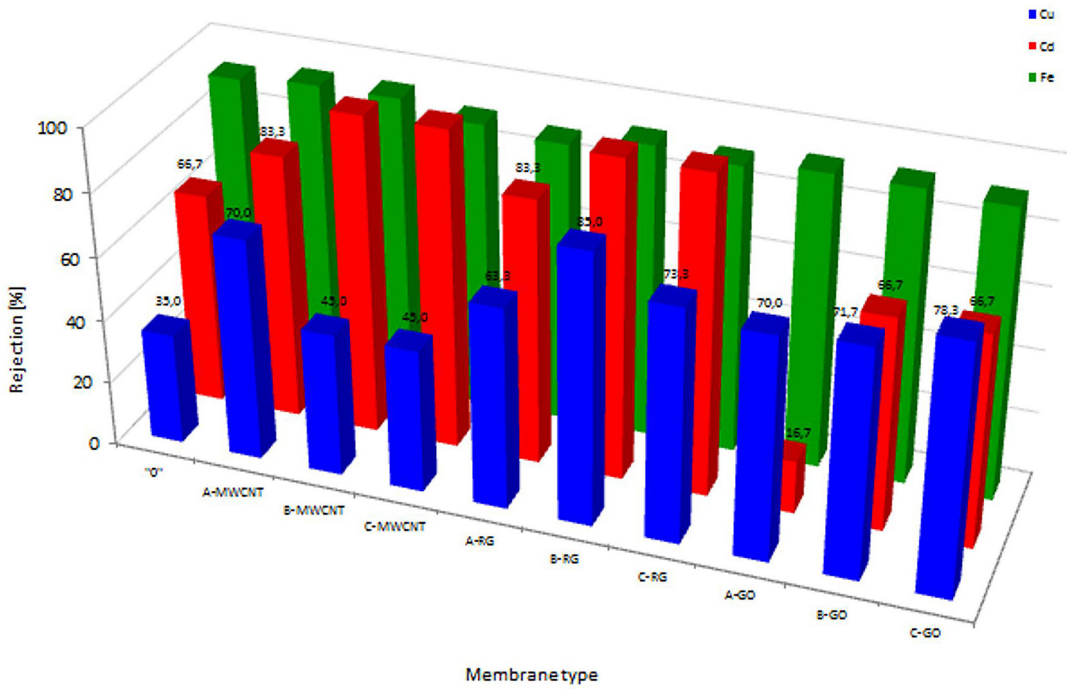


**Fig. 4**. Metal rejection coefficient on composite membranes and pure polyacrylonitrile membrane

of the membrane in the following order: A-GO (~70%), B-GO (~72%), C-GO (~78%).

In the ultrafiltration of electroplating wastewater, a 100% removal of this element is observed on the membranes: B-MWCNT, C-MWCNT, B-RG, C-RG. An equally high rejection coefficient (~83%) was obtained on membranes containing 0.8% nanotubes (A-MWCNT) and 0.8% graphene (A-MWCNT). The A-GO membrane, on the other hand, retains cadmium only in ~17%. It seems that the phenomenon is closely related to the concentration of this metal in waste water, which is the lowest out of the remaining metals (Tab. 3).

The qualitative composition of the analysed waste water is very complicated. Therefore, it was necessary to select only a few sample anions and metals. While analysing the quantitative composition of waste water (Table 2 and Table 3) it can be seen that chloride and sulphate anions as well as iron are the major components. Ultrafiltration almost completely removes a small amount of phosphate ions and results in a very high decrease in iron ions. The imbalance in the wastewater solution, which is accompanied by an increase in the concentration of some ions during the flow through the membranes, is the consequence. In addition, the quantitative and qualitative composition of the waste water after ultrafiltration is closely related to the type of membrane used.

## CONCLUSIONS

Membranes made of polyacrylonitrile are commonly used in membrane processes. This paper presents the results of research on the modification of this polymer with nanotubes (MWCNT), graphene (RG) and graphene oxide (GO) addition. The produced membranes differ radically in terms of transport and separation properties. The membranes with graphene addition (PAN/RG) are characterized by the best transport properties and the highest specific permeate flux values in the range of ~913÷1006 [$dm^3/m^2 \times h$] for working pressure of 2.0 MPa. However, in the waste water environment, the flow through these membranes is reduced by half, which does not deteriorate their separation properties and does not impact high rejection coefficients of Fe (~88÷92%), Cu (~63÷85%) and Cd (~83÷100%). PAN/GO composite membranes, on the other hand, are characterized by the lowest values of a specific permeate flux that grows rapidly (over 200%) during the flow of ions contained in waste water. In the case of nanoparticles addition to PAN, PAN/MWCNT composite membranes are obtained, the transport properties of which change step by step along with the increase of nano-addition concentration. Moreover, these membranes, unlike others, remove the sulphate anions (~16÷19%) and chlorine (~48÷57%) from the waste water most effectively.

The study leads to the conclusion that it is possible to select nano-additions in such a way so as to obtain membranes that will meet the specific requirements. The membranes obtained in the experiment remove the phosphate anions and iron from the waste water in a highly effective way. The studies have also demonstrated that wastewater is a very difficult waste; therefore, the effectiveness of its treatment is varied, and the range of results is the evidence of the many factors that influence the treatment.

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