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The influence of graphene addition on the properties of composite membranes RG / PAN and their potential application

Fryczkowska B.[1,*]

[1] University of Bielsko-Biala, Faculty of Materials, Civil and Environmental Engineering, Institute of Textile Engineering and Polymer Materials, Willowa 2, 43-309 Bielsko-Biala, Poland,

*corresponding author: e-mail: bfryczkowska@ath.bielsko.pl

Abstract

PAN is an inexpensive and popular engineering polymer, which is widely used in membrane techniques: ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO) and pervaporation (PV). It is characterized by good thermal stability, high thermal conductivity, chemical resistance, solubility in many classic solvents, resistance to UV radiation and good mechanical properties. It can be easily modified both chemically and physically.

The paper describes the method of obtaining composite membranes by the phase inversion method of homogeneous dispersion of graphene (RG) in a solution of polyacrylonitrile (PAN) dissolved in N, N-dimethylformamide (DMF). The influence of RG concentration on physicochemical properties, transport and separation properties (removing microplastic), and resistance to fouling of composite was investigated.

Keywords: graphene, polyacrylonitrile, composite membranes, microplastic

1. Introduction

The use of plastics in all areas of human life has caused a new pollution, called microplastics, to appear in the surrounding environment.

The simplest method of removing microplastics from water is the gravitational method, which uses the difference in density between the plastic and water (Prata et al., 2019). Larger microplastic particles can be separated on different types of filters (Rowe et al., 2018). Small polymer molecules are removed by coagulation / flocculation and sand filtration processes (Cermakova et al., 2018). Commonly employed method to remove organic matter is wet peroxidation (H2O2, NaClO, Fenton reagents) (Sun et al., 2019). Microplastic can also be removed in the membrane bioreactor process (Talviti et al., 2017) and in the ultrafiltration process (Ma et al., 2019).

The paper presents a new method of obtaining composite membranes RG / PAN and the possibility of their use for removing microplastics from industrial wastewater.

2. Materials and Methods

2.1. Reagents

Polyacrylonitrile (PAN) (Mw=85,000) was purchased from GoodFellow. N,N-dimethylformamide (DMF) was purchased from Avantor Performance Materials Poland S.A.

Graphene oxide was obtained according to modified Hummers method (Fryczkowska et al., 2015). Graphene (RG) was obtained from graphene oxide powder by thermal reduction. For this purpose, graphene oxide was heated in nitrogen to approx. 180°C, at which point explosion occurred, during which GO was reduced to graphene.

Real wastewater (WW) came from the company in the Silesian province dealing with polyester (PET) recycling.

2.2. Membrane forming

Membranes were obtained using phase inversion method. First, a 12% w/w solution of PAN in DMF was prepared (A0). Identical solutions (12% w/w of PAN in DMF) were prepared, but this time they contained 0.0135 (A1); 0.027 (A2); 0.054 (A3) and 0.1% (A4) w/w of RG, respectively. Then, PAN solution and well-dispersed RG / PAN solution were rapidly coagulated in distilled water and dried in air.

2.3. Transport and separation properties of the membranes

The transport and separation properties of the obtained membranes were tested using a 350 cm^3 AMICON 8400 ultrafiltration cell (Millipore), designed for flat membranes. Permeate flux (J_v) was calculated using the following formula:

$$J_v = \frac{V}{F \times s}$$

where: J_v - volume permeate flux (L/m^2h), V - permeate volume (L), F - membrane surface (m^2), s - discharge time (h).

3. Discussion of the Results

As a result of the research, composite membranes RG / PAN were obtained, which differed from one another in physicochemical and transport properties.

The introduction of RG into the PAN matrix resulted in the reduction of the contact angle from 52 ° (A0) to 50 ° (A1); 47 ° (A2); 43 ° (A3); 40 ° (A4). At the same time, it was observed that the increase in the amount of RG additive increases the water sorption: 244% (A0); 254% (A1); 269% (A2); 307% (A3); 321% (A4).

As a result of the experiment composite membranes (Table 1) were obtained, characterized by good transport properties (PW). During the ultrafiltration of real wastewater (WW) containing microplastics, a reduction in the volume permeate flux was observed for RG / PAN membranes by about half. However, for the A0 membrane, the flow decreases by about 85%.

Table 1. Permeate flux for pure water (PW), wastewater (WW), after backflush (AB) (working pressure of 0.2 MPa)

Membrane	**Flux (J_v) [L/m^{2}h]**		
	PW	**WW**	**AB**
A0	281.94	12.16	38.66
A1	222.75	58.32	190.17
A2	253.56	101.36	236.33
A3	286.77	148.15	273.59
A4	305.82	172.97	298.63

At the same time, it was observed that the membrane A0 undergoes fouling in a practically irreversible manner (Fig. 1). Whereas for composite membranes, fouling is reversible and the flow decreases by about 15% (A1); 7% (A2); 4.5% (A3); 3% (A4).

The research shows that the obtained RG / PAN membranes can be successfully used for the treatment of raw industrial wastewater containing microplastics (WW) because they well separate impurities and can be easily cleaned in the process of backflush.

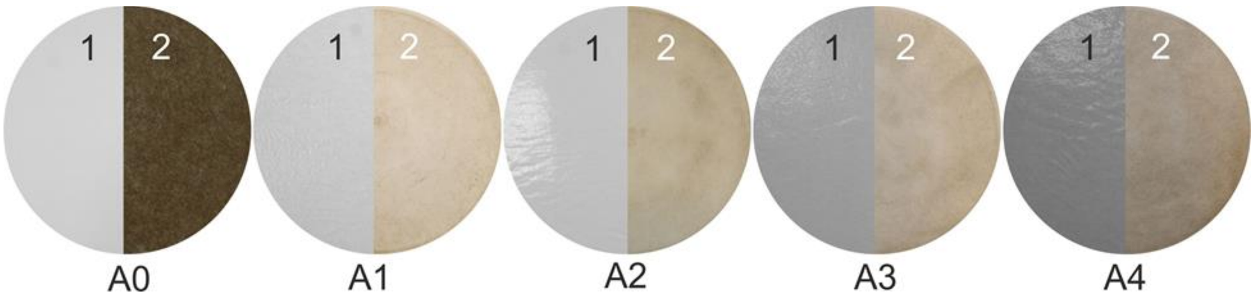

Figure 1. Photographs of PAN and RG /PAN membranes before (1) and after ultrafiltration wastewater (2)

References

Cermakova L., Janda V., Peer P., Cajthaml T., Novotna K., Pivokonsky M. (2018), Occurrence of microplastics in raw and treated drinking water, *Science of The Total Environment*, **643**, 1644–1651.

Fryczkowska B., Sieradzka M., Sarna E., Fryczkowski R., Janicki J. (2015), Influence of a graphene oxide additive and the conditions of membrane formation on the morphology and separative properties of poly(vinylidene fluoride) membranes, *Journal of Applied Polymer Science*, **132** (46).

Ma B., Xue W., Hu C., Liu H., Qu J., Li L. (2019), Characteristics of microplastic removal via coagulation and ultrafiltration during drinking water treatment, *Chemical Engineering Journal*, **359**, 159–167.

Prata J. C., da Costa J. P., Duarte A. C., Rocha-Santos T. (2019), Methods for sampling and detection of microplastics in water and sediment: A critical review, *TrAC - Trends in Analytical Chemistry*, **110**, 150–159.

Rowe L., Kubalewski M., Clark R., Statza E., Goyne T., Leach K., Peller J. (2019), Detecting Microplastics in Soil and Sediment in an Undergraduate Environmental Chemistry Laboratory Experiment That Promotes Skill Building and Encourages Environmental Awareness, *Journal of Chemical Education*, **96** (2) 323-328

Sun J., Dai X., Wang Q., van Loosdrecht M. C. M., Ni, B. J. (2019), Microplastics in wastewater treatment plants: Detection, occurrence and removal, *Water Research*, **152,** 21–37.

Talvitie J., Mikola A., Koistinen A., Setälä O. (2017), Solutions to microplastic pollution – Removal of microplastics from wastewater effluent with advanced wastewater treatment technologies, *Water Research*, **123**, 401–407.