PROPERTIES AND PERFORMANCE OF POLYETHERSULFONE MEMBRANES MODIFIED WITH HALLOYSITE AND TITANATE NANOTUBES

M.Sc. Eng. Grylewicz A.[1], Prof. Dr. Hab. Eng. Mozia S.
West Pomeranian University of Technology in Szczecin, Faculty of Chemical Technology and Engineering, Institute of Inorganic Chemical Technology and Environment Engineering, ul. Pułaskiego 10, 70-322 Szczecin, Poland

amanda.grylewicz@zut.edu.pl[1]

Abstract: *Ultrafiltration polyethersulfone (PES) membranes were prepared by wet phase inversion method. Halloysite nanotubes (HNTs), hydrothermally synthesized titanate nanotubes (TNTs) or their mixture (HNTs/TNTs, weight ratio 50/50) were applied as nanofillers (NFs). N,N – dimethylformamide was used as a solvent, and deionized water was applied as a non-solvent. Some well dispersed aggregates as well as larger agglomerates of the NFs were observed on the surface of the membranes examined by atomic force microscopy. The retention of poly(ethylene glycol) (20 kDa) applied as a model organic compound, by the modified and unmodified membranes was similar and did not exceed 10%. The rejection of 500 kDa dextran ranged from 84 to 92%, and was the highest for the membrane modified with HNTs. A 71% improvement of pure water flux, compared to the neat membrane, was observed in the case of the membrane modified with the HNTs/TNTs. The best antifouling performance during bovine serum albumin filtration exhibited the HNTs-modified membrane.*

Keywords: POLYETHERSULFONE, MEMBRANE, HALLOYSITE NANOTUBES, TITANATE NANOTUBES, FOULING, SEPARATION

1. Introduction

The membranes used in pressure-driven membrane techniques are usually made of polymers, mainly due to simple procedure of their fabrication at various characteristics as well as low price of their manufacturing [1]. Polyethersulfone (PES) is one of the polymers used to prepare ultrafiltration (UF) and microfiltration (MF) membranes. However, PES membranes have relatively low hydrophilicity which can lead to membrane fouling [2]. Fouling is one of the major problems in membrane processes. The colloids, particles and organic solutes present in feed can be deposited on the membrane surface or within its pores which leads to a decrease of permeability or damage of the membrane [3,4]. To reduce fouling and improve membrane properties, various modifications are used. One of the very common attempts is the introduction of a filler into a casting solution. In case of PES membranes the nanofillers as halloysite nanotubes (HNTs), carbon nanotubes (CNTs), TiO_2, SiO_2, Al_2O_3, silver and copper nanoparticles (NPs) and titania/titanate nanotubes (TNTs) have been proposed for the modification purpose [5,6].

Halloysite nanotubes are natural inorganic aluminasilicates with the general formula $Al_2Si_2O_5(OH)_4 \bullet nH_2O$ [7]. HNTs have natural tubular structure, large surface, porous microstructure, chemically active internal and external surface, high ion exchange capacity, and possess hydrophilic groups on the surface [8,9]. TNTs can be synthesized by hydrothermal method, electrochemical oxidation or soft chemical method. The titanate nanotubes derived from the hydrothermal method have ion exchange properties, high surface area and pore volume and possess hydrophilic –OH groups on their surface [10]. The literature reports show that both HNTs and TNTs have positive influence on hydrophilicity of membranes, they can improve water flux and separation properties [5,6].

The main aim of the present study was to examine the effect of HNTs and TNTs on physicochemical properties, pure water flux, separation properties and antifouling performance of mixed matrix membranes. The PES membranes and modified membranes were prepared by wet phase inversion method using *N,N*-dimethylformamide as a solvent. The membranes were characterized based on contact angle (CA), atomic force microscopy (AFM), scanning electron microscopy (SEM) and pure water flux measurements. Membrane fouling resistance was evaluated using bovine serum albumin (BSA). Separation properties were examined by separation of poly(ethylene glycols) (PEGs) and dextrans.

2. Materials and methods

Polyethersulfone (Ultrason E6020P) was supplied by BASF SE (Germany). *N,N*-dimethylformamide (DMF) was provided by Avantor Performance Materials Poland S.A. Halloysite nanotubes were purchased from Sigma Aldrich. Titanate nanotubes were prepared using hydrothermal treatment [6] from TiO_2 powder (Aeroxide®TiO_2 P25, Evonik Industries). Bovine serum albumin (Probumin) was obtained from Merck, poly(ethylene glycols) were provided by Sigma Aldrich. In all experiments pure (deionized) water (type 2, 0.006 μS/cm) from Elix 3 (Millipore) was applied.

The membranes were prepared by wet phase inversion method. In case of the unmodified membrane (NM) the 15 wt% of PES were dissolved in DMF. The casting dope was casted on a glass plate using an automatic film applicator (Elcometer 4340) with the knife gap of 0.1 mm, and immersed in pure water bath to complete the phase inversion process. The modified membranes were prepared by mixing a dispersion containing 1 wt% of HNTs, TNTs or their mixture (Table 1) in 10 cm^3 of DMF with previously prepared solution of polymer in DMF (40 cm^3). The NPs dispersion was prepared by sonication for 30 min using ultrasonic probe (Vibra-cell VCX-130, Sonic, USA, amplitude 80%). After addition of the NPs dispersion to PES solution, the casting dope was mixed alternately (15 min by turns) using a magnetic stirrer and sonication in ultrasonic bath (Sonic-6D, Polsonic, Poland) for 2h.

Table 1:*.Weight ratio of HNTs and TNTs in casting solutions.*

Membrane	HNTs	TNTs
NM	0	0
PES/HNTs	100	0
PES/TNTs	0	100
PES/HNTs/TNTs	50	50

The morphology of HNTs and TNTs was analyzed using transmission electron microscope (TEM) FEI Tencai F20.

Topography of the membranes was analyzed using atomic force microscope (AFM, NanoScope V Multimode 8, Bruker Corp.) with silicon nitride probe in the ScanAsyst mode. Roughness of membranes (R_a) was calculated using the NanoScope Analysis Software. The hydrophilicity of membranes surface was determined by water static contact angle measurement using goniometer (type 260 ramé-hart instruments co.) by the sessile drop method. The volume of the water drop was 10 μl, and the results are mean values of 10 measurements. Morphology of membranes was analyzed using ultra-high-resolution field-emission scanning electron microscope (UHR FE-SEM Hitachi SU8020) in the secondary electrons mode (SE, accelerating voltage 5kV) and dispersive X-ray spectroscope EDX NSS 312 (Thermo Scientific). A small piece of a membrane (dehydrated in ethanol) was broken in liquid nitrogen

and sputtered with a chromium layer before SEM analysis. The pure water flux was determined with application of a laboratory scale cross-flow unit by ultrafiltration of pure water at transmembrane pressure of TMP = 1, 2 and 3 bar. The membrane (0.0025 m^2) was mounted in a stainless steel membrane module with a 1.19 mm feed spacer. Antifouling properties were determined by ultrafiltration of BSA solution (1g/dm^3) at TMP = 2 bar and feed cross flow velocity of 1 m/s. Separation properties were evaluated on a basis of rejection of model organic compounds: PEGs (4, 10, 20, 35 kDa) and dextrans (70, 110, 200, 500 kDa) at TMP = 1 bar. The concentration of the model solutions was 0.5 g/dm^3. Concentration of PEGs and dextrans were measured using HPLC LaChrom Elite (Hitachi, Japan).

3. Results and discussion

2.1 Characteristics of HNTs and TNTs

HNTs and TNTs were characterized using TEM technique, and the results are presented in Fig. 1.

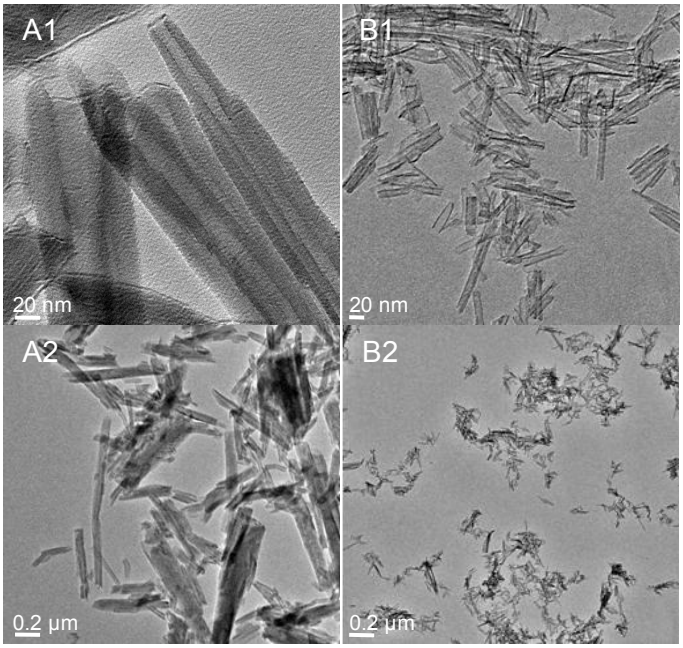

Fig. 1 *TEM images of HNTs (A1-2) and TNTs (B1-2)*

The commercial HNTs and the hydrothermally synthesized TNTs are multi-walled and open-ended. The length of HNTs was in the range of 15-1250 nm, the internal diameter and wall thickness changed from 11 to 28 nm and from 5 to 23 nm, respectively. The length of TNTs was in the range of 29–164 nm, the internal diameter changed from 4 to 8 nm and external from 8 to 13 nm.

2.2 Contact angle

Fig. 2 shows results of contact angle measurement.

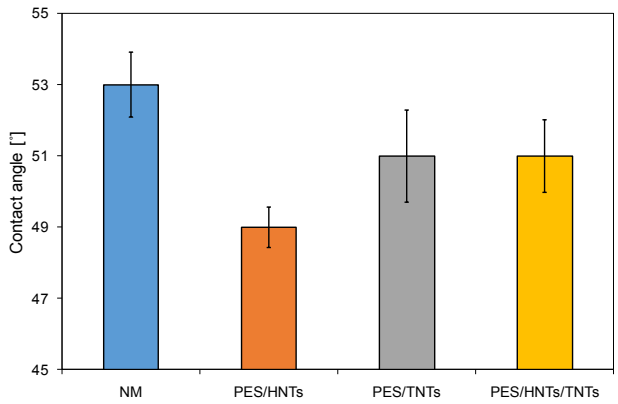

Fig. 2 *Contact angle of obtained membranes.*

The introduction of HNTs and TNTs into membrane matrix affected hydrophilicity of membranes. The contact angle value was in the range of 49 to 53˚ being the highest for the unmodified membrane and the lowest for membrane modified with HNTs. The increase in hydrophilicity of the modified membranes was attributed to the presence of –OH groups in the structure of both HNTs and TNTs nanoparticles. A positive influence of the introduction of the nanofillers on hydrophilicity of membranes was also reported by Buruga et al. [11] in case of polystyrene membranes modified with HNTs and Padaki et al. [12] in case of polysulfone membrane modified with TNTs.

2.3 Topography and morphology of membranes

Fig. 3 shows AFM images of membranes surface visualized in 2D mode.

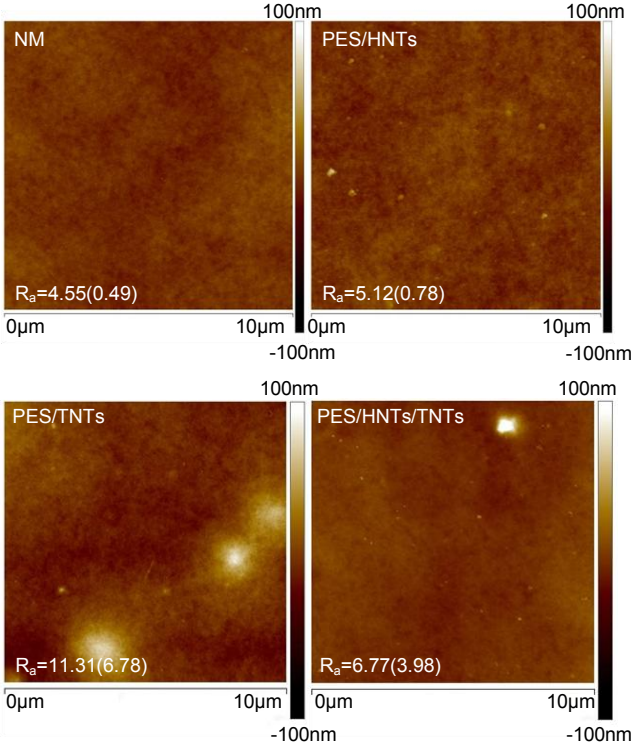

Fig. 3 *AFM images of the surface of the obtained membranes.*

In case of the membranes containing only halloysite nanotubes some well dispersed NPs agglomerates with diameters in the range of ca. 30-270 nm are present. On the skin layer of the PES/TNTs membrane the small NPs aggregates possess diameters in the range of ca. 15-100 nm, however, also larger agglomerates with diameters even up to 2.5 µm are observed. Similar results were obtained previously [6] in case of Ag-TNTs modified membranes. On the surface of the membrane containing both HNTs and TNTs nanoparticles, the diameters of the small aggregates are in the range of ca. 15-150 nm, while some larger agglomerates with diameters up to 1 µm are also present. The obtained results show that when a mixture of HNTs/TNTs was used, the diameters of agglomerates formed on the membrane surface were reduced compared to PES/TNTs membrane. This can be attributed to a lower weight loading of TNTs in the PES/HNTs/TNTs membranes compared to PES/TNTs one (Table 1), resulting in a lower NPs agglomeration.

Based on AFM images, the surface roughness of the prepared membranes was determined. The R_a value calculated for the NM membrane was 4.55(0.49) nm. The highest surface roughness was observed in case of PES/TNTs membrane (11.31(6.78) nm). The application of a mixture of HNTs and TNTs resulted in a decrease of surface roughness to 6.77(3.98) nm compared to PES/TNTs membranes. The lowest R_a amongst the mixed matrix membranes exhibited the PES/HNTs (5.12(0.78)).

SEM images of the membranes cross section taken using SE mode are shown in Fig. 4. All of the membranes exhibit asymmetric

structure with a dense thin separation layer in the top of the membrane, narrow finger-like pores in the middle part and spongy structure in the bottom part of the membrane and between the finger-like pores. In case of the modified membrane some clusters of NPs can be observed (circles in Fig. 4).

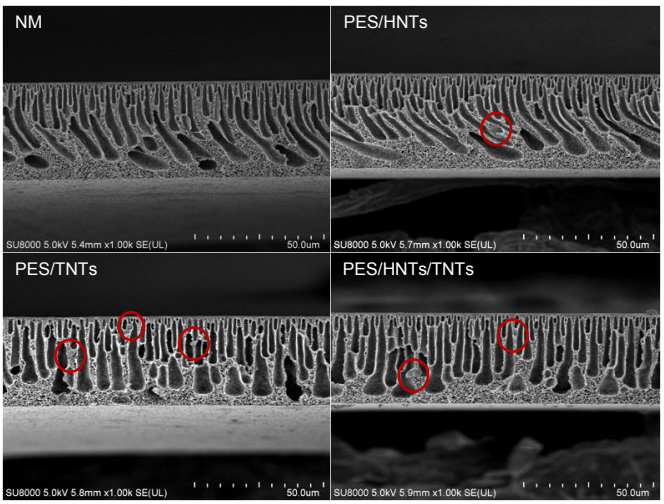

Fig. 4 *SEM images of membranes cross-section. The NPs agglomerates are marked with circles.*

Furthermore, the membrane modified with a mixture of HNTs and TNTs nanoparticles was analyzed using SEM-EDX method. The results are presented in Fig. 5.

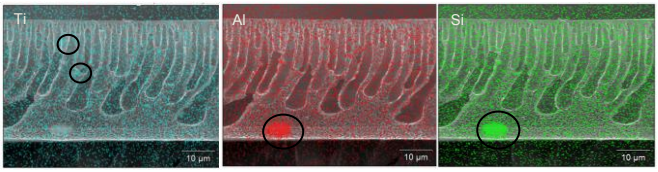

Fig. 5 *Results of SEM-EDX analysis for PES/HNTs/TNTs membranes.*

Despite application of thorough sonication and mixing at the stage of preparation of the casting dope, both types of NPs did not form joint agglomerates. Separate spots of halloysite nanotubes and titanate nanotubes are visible in the cross-section of the membrane.

2.4 Permeability and fouling resistance of the membranes

A comparison of pure water flux (PWF) measured for the prepared membranes is presented in Fig. 6.

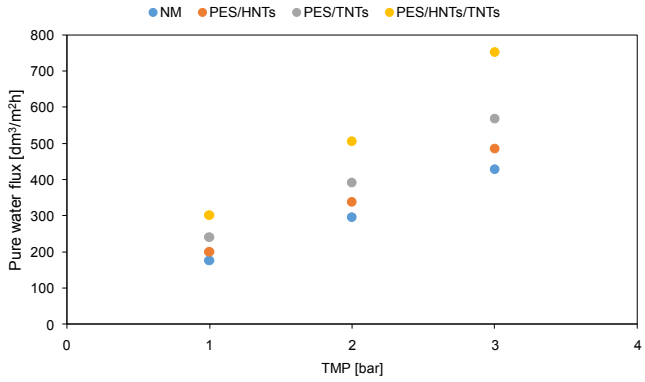

Fig. 6 *The influence of transmembrane pressure on the pure water flux through the prepared membranes.*

The introduction of different types of the nanofillers affected the PWF values of the modified membranes to a various extent. The least improvement of permeability compared to the unmodified membrane was found in case of PES/HNTs sample. That did not correspond with the hydrophilicity, which was in case of this membrane the highest (Fig. 2). A more significant increase of PWF values was found in case of PES/TNTs membrane. The increase in PWF may be related to the distribution of nanoparticles. The NPs can create additional pores which could increase the permeability of membranes [5]. In addition, some additional pores are present due to the tubular structure of TNTs, which also contributes to the improved PWF of the membrane. The use of a mixture of halloysite and titanate nanotubes caused an increase in PWF by 71% in relation to the unmodified membrane and by 55 and 33%, respectively, in relation to PES/HNTs and PES/TNTs membranes. The increase in the permeate flux may be associated with an increase in the dispersion of the particles in the membrane matrix that can be seen in Fig. 3.

The influence of the NPs on fouling of the membranes was determined using bovine serum albumin as a model foulant (Fig. 7). After 2h of the BSA ultrafiltration the decrease of permeate flux through the NM membrane in comparison to PWF reached 54%. The introduction of 1 wt% of HNTs led to an improvement of the antifouling properties of the PES membrane resulting in a 46% decrease in permeate flux compared to PWF. On the opposite, the application of TNTs caused a deterioration of the antifouling performance in comparison to the unmodified membrane, and the permeate flux declined for 70% with reference to PWF. The sample containing a mixture of HNTs and TNTs was characterized by better antifouling properties compared to PES/TNTs, however, the flux decline was more severe (64%) than that observed for PES/HNTs membrane (46%).

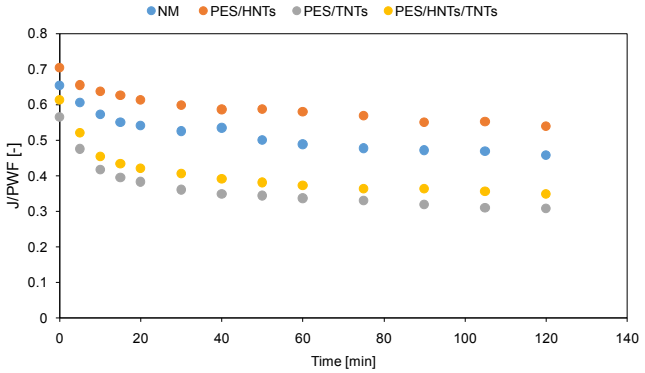

Fig. 7 *The effect of HNTs and TNTs on BSA fouling of the PES membranes. Initial BSA concentration: 1 g/dm^3; TMP = 2 bar.*

The observed results revealed much better antifouling properties of the membrane containing HNTs compared to the other types of the fabricated mixed matrix membranes. One reason can be its higher hydrophilicity (Fig. 2) compared to the other samples. Another factor can be its relatively low permeability in comparison to the PES/TNTs and PES/HNTs/TNTs membranes. At higher flux, the enhanced transport of BSA molecules towards the membrane occurs during initial stages of filtration, which contributes to the intensity of the fouling phenomenon [14]. Other reason can be surface roughness. In case of PES/HNTs membrane the R_a value was the lowest amongst the mixed matrix membranes what was reflected by the best fouling resistance of this sample. Moreover, the roughness of PES/HNTs/TNTs membrane was lower compared to that of PES/TNTs which also resulted in its better antifouling performance. Both Liu et al [15] and Hobbs et al [16] reported that relatively smooth surfaces were more resistant to fouling. Incorporating HNTs into membrane containing TNTs results in higher dispersion of NPs and decrease in surface roughness what affects the fouling resistance of that membrane.

2.5 Separation properties

Fig. 7 shows the rejection of model organic compounds by the obtained membranes. The introduction of HNTs and TNTs into the membranes improved their separation properties. The highest influence of the modification was found in the case of the PES/HNTs membrane. The retention of dextran 110 kDa increased from 50% for the unmodified membrane to 69% after modification with halloysite. In the case of PEGs, the average increase in retention was 4 percent points (p.p.), being the lowest for PEG 35 kDa (2 p.p.) and the highest for PEG 20 kDa (6 p.p).

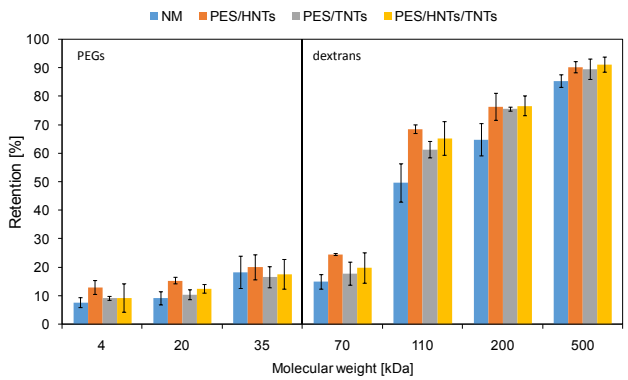

Fig. 7 *Separation properties of the obtained membranes.*

The use of the mixture of halloysite and titanate nanotubes resulted in an improvement of the separation properties of the membrane compared to the membrane containing TNTs only. The lowest effect was observed for PEGs. More significant changes can be seen in case of dextrans, e.g. the retention of dextran 110 kDa increased by 15 p.p compared to the unmodified membrane.

3. Conclusions

The incorporation of halloysite nanotubes, titanate nanotubes or their mixture into PES membrane matrix affected its physicochemical properties, water permeability, fouling resistance and separation characteristics. The use of both HNTs and TNTs nanofillers caused an increase of hydrophilicity and pure water flux of the PES membrane. The membrane prepared using TNTs as a filler exhibited higher pure water flux than the membrane prepared with HNTs. The highest water permeability was observed for PES/HNTs/TNTs membrane. Application of HNTs resulted in an improvement of the fouling resistance and separation properties of the membranes. However, the membranes modified with TNTs and HNTs/TNTs mixtures were more prone to BSA fouling compared to the unmodified membrane. Nonetheless, the PES/HNTs/TNTs was less fouled than the PES/TNTs membrane confirming a positive effect of HNTs on membrane fouling mitigation. The highest improvement of separation properties of the membranes was obtained by application of HNTs nanofiller.

Acknowledgements

This work was supported by the National Science Centre, Poland under project No. 2016/21/B/ST8/00317.

4. References

1. Ahmed, Al., Abdulkarim, A.A., Ooi, Bs., Ismail S., Recent development in additives modifications of polyethersulfone membrane for flux enhancement, Chemical Engineering Journal, 223, 2013, 246–267.
2. Qin, J. J., Oo, M. H., Li, Y., Development of high flux polyethersulfone hollow fiber ultrafiltration membranes from a low critical solution temperature dope via hypochlorite treatment, Journal of Membrane Science, 247, 2005, 137–142
3.Zhao, W., Huang, J., Fang, B., Nie, S., Yi, N., Li, B. Su. H., Zhao C., Modification of polyethersulfone membrane by blending semi-interpenetrating network polymeric nanoparticles, Journal of Membrane Science, 369, 2011, 258–266
4. Ciston, S., Lueptow, R.M., Gray, K.A., Bacterial attachment on reactive ceramic ultrafiltration membranes, Journal of Membran Science, 320, 2008, 101–107
5. Mozia, S., Grylewicz, A., Zgrzebnicki, M., Darowna, D., Czyżewski, A., Investigations on the Properties and Performance of Mixed-Matrix Polyethersulfone Membranes Modified with Halloysite Nanotubes, Polymers, 11, 2019, 671
6. Mozia, S., Sienkiewicz, P., Szymański, K., Zgrzebnicki, M., Darowna, D., Czyżewski, A., Morawski, A.W., Influence of Ag/titanate nanotubes on physicochemical, antifouling and antimicrobial properties of mixed-matrix polyethersulfone ultrafiltration membranes, Journal of Chemical Technology and Biotechnology, 94, 2019, 2497-2511
7. Vinokurov, V.A., Stavitskaya, A.V., Glotov, A.P., Novikov, A.A., Zolotukhina, A.V., Kotelev, M.S., Gushchin, P.A., Ivanov, E.V., Darrat, Y., Lvov, Y.M., Nanoparticles Formed onto/into Halloysite Clay Tubules: Architectural Synthesis and Applications, Chemical Reserch, 18, 2018, 858-867
8. Lisuzzo, L., Cavallaro, G., Parisi, F., Milioto, S., Lazzara, G., Colloidal stability of halloysite clay nanotubes, Ceramics International, 45, 2019, 2858-2865
9. Yu, L., Wang, H., Zhang, Y., Zhang, B., Liu, J., Recent advances in halloysite nanotube derived composites for water treatment Enviromental Science: Nano, 1, 2016
10. Liu, R., Yang, W., Chueng, H., Ren, B., Preparation and Application of Titanate Nanotubes on Dye Degradation from Aqueous Media by UV Irradiation, Journal of spectroscopy, 2015, 2015, acticle ID 680183
11. Buruga, K., Kalathi, J.T., Kim, K., Sik, Y., Danil Ok.B., Polystyrene-halloysite nanotube membranes for water purification, Industrial & Engineering Chemistry Research, 61, 2017, 169-180
12. Padaki, M., Emadzadeh, D., Masturra, T., Ismail, A.F., Antifouling properties of novel PSf and TNT composite membrane and study of effect of the flow direction on membrane washing, Desalination 361, 2015, 141-150
13. Zhang, J., Zhang, Y., Chen, Y., Yi, S., Zhang, B., Zhang, H., Liu, J., Preparation and characterization of PES/HNTs hybrid ultrafiltration membranes, Advanced Science Letter, 11,2012,57-62
14. Lin, Che Jen, Rao, P., Shirazi, S., Effect of operating parameters on permeate flux decline caused by cake formation-a model study, Desalination, 171, 2005, 95-105
15. Liu, Z., Mi, Z., Jin, S., Wang, C., Wang, D., Zhao, X., Zhou, H., Chen, C., The influence of sulfonated hyperbranched polyethersulfone-modified halloysite nanotubes on the compatibility and water separation performance of polyethersulfone hybrid ultrafiltration membranes, Journal of Membrane Science, 557, 2018, 13–23
16. Hobbs, C., Hong, S., Taylor, J., Effect of surface roughness on fouling of RO and NF membranes during filtration of a high organic surficial groundwater, Journal of Water Supply Reserch and Technology, 55, 2007, 559-570