

Fabrication of Polyphenylsulfone Nanocomposite Membranes with SiO₂ Nanoparticles Used in Pharmaceutical Industry

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Abstract: SiO₂ nanoparticle were used in aPolyphenylsulfone (PPSU) matrix to obtain nanofiltration membranes used in the pharmaceutical sector to remove pollutants from the water processes. In this study was investigated the influence of SiO₂ nanoparticles on the PPSU membranes performance at different concentration of polymer and at six different concentrations of SiO₂. Adding SiO₂ like additive in the PPSU membrane matrix, the permeability increases due to the higher porosity. Increasing the polymer concentration, the pores are smaller and the permeation properties are decreasing. The affinity for water of membrane surface is higher when nanoparticles are added in the polymer matrix. Adding 0.3 wt.% SiO₂ the permeation properties are increasing with more than 10% in comparison with membranes without nanoparticles.

Keywords: membranes, SiO₂ nanoparticles, pharmaceutical

1. Introduction

In the pharmaceutical industry water is used for a variety of processes like washing of solid cake, extraction of different substances or to wash the equipment. The waste water from the pharmaceutical and drugs industry has a wide variety of pollutants which are very dangerous for humans and environment. The treatment of pharmaceutical waste water is realized from many methods, from aeration, flocculation-coagulation, biological degradation to the filtration process. In the filtration processes the most use technique is nanofiltration due to the low pressure needed and high rejection rate. The main problem in the filtration processes in general are the membrane properties in view of life cycle, permeability and rejection capacity. In view to improve the membranes properties many studies were made to establish the optimal condition of fabrication [1-5], the polymer [6-9] and the additive influence [10-14]. In general, researches are focused on the use of nanoparticles like additive in the membrane structure, or on the membrane surface. The optimum nanoparticles concentration is challenge due to the variety of the nanoparticles type, size and concentration [15-18]. In this paper, SiO₂ nanoparticles were used in a PPSU matrix membrane at different concentration. The influence of the SiO₂ nanoparticles on the membrane properties [19-22] is less studied in comparison with others type on nanoparticles. Was studied the influence of the polymer and nanoparticles concentration on the permeation properties.

2. Materials and methods

2.1. Materials

Polyphenylsulfone (Figure 1) is a high performance polymer with a good chemical and heat resistance used for different application like automotive, aerospace but and for membranes used in waste water treatment.

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Figure 1. Polyphenylsulfone

SiO₂ nanoparticles are used on a large scale in biomedical research due to their stability and low toxicity. SiO₂ nanoparticles have a density of 2.4 g/cm³ and a molar mass of 59.96 g/mol.

2.2. Preparation of nanocomposite membrane

Membranes were obtained by immersion precipitation method (Figure 2).

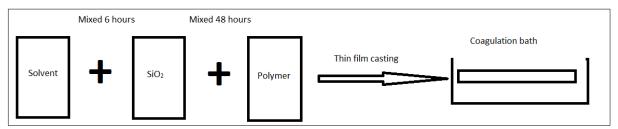


Figure 2. Membranes preparation

SiO₂ nanoparticles were added in the solvent and mixed for 6h. The polymer was gradually added and mixed for 4h. Resulted composite solution was casted on a support layer and immersed in deionized water.

All the membranes were obtained by adding nanoparticles in the solvent and mixed for 4hat room temperature. The polymer was added gradually and mixed for 24h to obtain a homogeneous solution.

3. Results and discussions

3.1. Permeability

In Figure 3 in presented the permeability evolution at different concentration of PPSU.

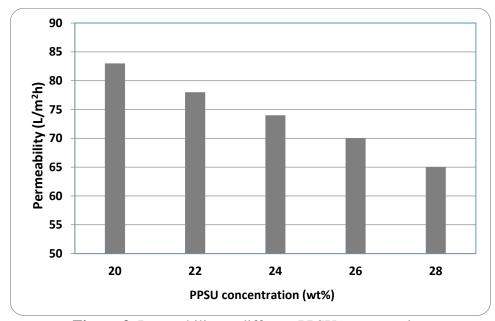


Figure 3. Permeability at different PPSU concentration



Increasing the polymer concentration, the porosity and the pore size are decreasing. Increasing the polymer concentration from 20 wt.% to 28 wt.% the permeability decrease with more than 13%, from 83 L/m²h to 65 L/m²h. Adding nanoparticles in the membrane with 20 wt.% polymer (Figure 4) the permeability increases even at small concentration of SiO₂. This aspect show that the nanoparticles increase the porosity of membranes without increasing and the pore size.

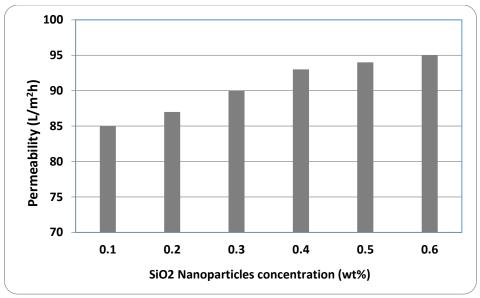


Figure 4. Pure water permeability of 20% PPSU membranes at different SiO₂ concentration

Adding 0.1 wt.% SiO₂ nanoparticles the permeability increase from 83 to 85 L/m²h. For higher SiO₂ nanoparticles concentration the permeability is increasing more, reaching 95 L/m²h for membranes with 0.6 SiO₂ concentration. The nanoparticles concentration has an important influence on the permeation properties, due to the modification of membrane structures. Increasing the concentration the porosity is higher and the permeation properties are increasing.

Adding 0.3 wt.% SiO₂ nanoparticles (Figure 5) the permeability is improved for every polymer concentration.

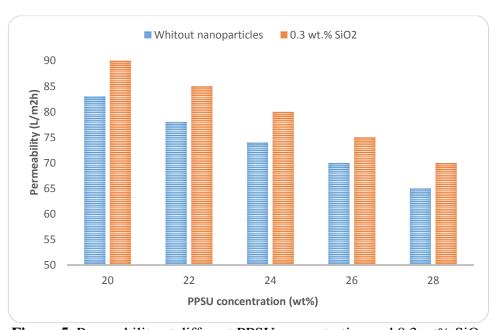


Figure 5. Permeability at different PPSU concentration and 0.3 wt% SiO₂



In Figure 5 is presented the influence of 0.3 wt.% SiO₂, which improve with more than 10% permeability for all types of membranes, showing that the influence of nanoparticles is the same regardless of the polymer concentration.

3.2. Pure water flux

To establish the permeation properties, all the membranes were tested at different pressure (Figure 6) for 50 mL of water, and at a constat pressure (Figure 7) for 300 mL of water.

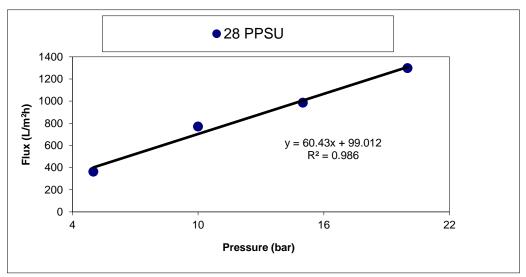


Figure 6. Flux for membranes at 28 wt% PPSU

In Figure 6 is presented the water flux for a membrane with a 28 wt.% PPSU without nanoparticles, at pressures between 6 and 20 bars.

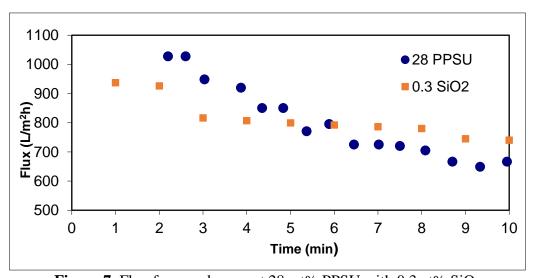


Figure 7. Flux for membranes at 28 wt% PPSU with 0.3wt% SiO₂

In Figure 7 is presented the comparison between water flux of a membrane with 28 wt.% PPSU without nanoparticles and one with 0.3 wt.% SiO₂ nanoparticles. Adding nanoparticles, the membrane stability is increasing and the water flux, after the membrane compaction, is higher. This effect of nanoparticles on membranes properties is due to the reducing the macropores which give more stability and reduce the precompactation value. In the same time, increasing the porosity the permeation is higher after precompactation period.



3.3. Hydrophilicity

The membrane surface affinity for water is increasing by adding nanoparticles.

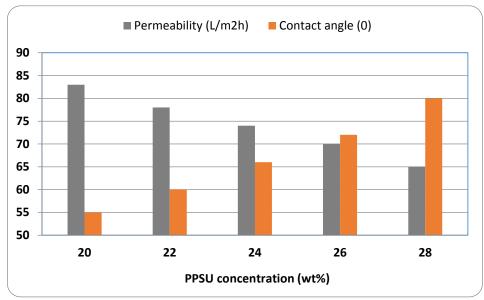


Figure 8. Permeability versus contact angle for membranes at different concentration of PPSU

In Figure 8 is presented the comparison between evolution of permeability and contact angle for membranes at different concentration of polymer. Increasing the polymer concentration permeability is decreasing and the contact angle is increasing.

Adding nanoparticles the affinity for water is increasing for every type of membrane.

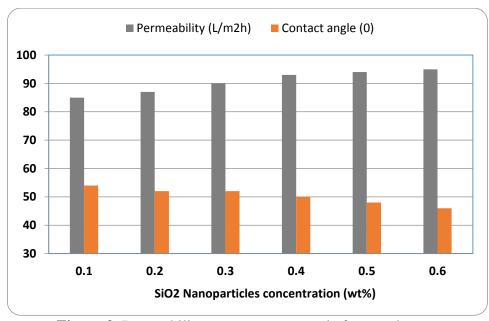


Figure 9. Permeability versus contact angle for membranes at different concentration of SiO₂

In Figure 9 is presented the evolution of permeability for different concentration of nanoparticles and the contact angle for every type of membranes. Increasing the SiO_2 concentration the contact angle is decreasing due to the surface modification of membranes and the permeability is increasing.

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4. Conclusions

In this study the influence of PSSU concentration on the permeation properties was studied. Increasing the polymer concentration the permeability and the water flux is decreasing and this effect in general leads to a better rejection capacity but with mor pressure needed. Adding SiO₂ nanoparticles the permeation properties and the membrane surface affinity for water are increasing. The concentration of nanoparticles have an important impact on the membrane permeability, increasing the SiO₂ concentration from 0.1 to 0.6 wt.%, the permeability is increasing. This effect is due to the membrane structures which is changed when nanoparticles are added. The porosity of membranes increase when nanoparticles are added in the polymeric structure and the pores are uniformly distributed.

References

- 1. WANG, Y., WANG, Z., HAN, X., WANG, J., WANG, S., 2017, Improved flux and anti-biofouling performances of reverse osmosis membrane via surface layer-by-layer assembly. J. Membr. Sci., 539, 403–411:
- 2. ARCADIO SOTTO; ARMAN BOROMAND, ŞTEFAN BALTĂ, JEONGHWAN KIM, BART VAN DER BRUGGEN, Doping of polyethersulfone nanofiltration membranes: antifouling effect observed at ultralow concentrations of TiO₂ nanoparticles, Journal of Materials Chemistry ISSN 0959-9428, 2011, 21, pag. 10311-10320, http://pubs.rsc.org/en/content/articlelanding/2011/jm/c1jm11040c;
- 3.SUN, C., FENG, X., 2017. Enhancing the performance of PVDF membranes by hydrophilic surface modification via amine treatment. Sep. Purif. Technol., 185, 94–102
- 4.ILIYA VALCHEV, ANDREA CORADDU, MILTIADIS KALIKATZARAKIS, RINZE GEERTSMA, LUCA ONETO, Numerical methods for monitoring and evaluating the biofouling state and effects on vessels' hull and propeller performance: A review, Ocean EngineeringVolume 251;
- 5.STEFAN BALTA, DANIELA LAURA BURUIANA, C.S. SIMIONESCU, L.G. TIRON, MARIAN BORDEI, BART VAN DER BRUGGEN, Influence of relative air humidity and casting time on the permeation properties of PSf nanofiltration membranes, 2015, Desalination and Water Treatment, pages 1-6, DOI:10.1080/19443994.2015.1062435
- 6.HALLING-SORENSEN, B., NORS NIELSEN, S., LANZKY, P.F., INGERSLEV, F., HOLTEN LU TZHOFT, H.C., JORGENSEN, S.E., 1998, Occurence, fate and effects of pharmaceutical substances in the environment-a review. Chemosphere 36, 357-393
- 7.JAFARZADEH, Y., YEGANI, R., 2015, Thermal, mechanical, and structural properties of ZnO/polyethylene membranes made by thermally induced phase separation method. J. Appl. Polym. Sci. 132, 42338
- 8. P. LIU, H.X. LIN, X.Z. FU, et al., Preparation of the doped TiO₂ film photocatalyst and its bactericidal mechanism, Chin. J. Catal., 20 (3) (1995) 327-328 (Ch);
- 9.LAURENȚIA GEANINA TIRON, ȘTEFAN CĂTĂLIN PINTILIE, ANDREEA LILIANA LAZĂR, MARIA VLAD, ȘTEFAN BALTĂ, MARIUS BODOR, Influence of Polymer Concentration on Membrane Performance in Wastewater Treatment, *Mater. Plast.*, **55**(1), 2018, 95-98, ISSN: 0025-5289, WOS:000444129500021;
- 10.ERIC M. VRIJENHOEK, SEUNGKWAN HONG, MENACHEM ELIMELECH, Influence of membrane surface properties on initial rate of colloidal fouling of reverse osmosis and nanofiltration membranes, Journal of Membrane Science, 188 (2001) 115-128;
- 11.S.A. AL MALEK, M.N. ABU SEMAN, D. JOHNSON, N. HILAL, Formation and characterization of polyethersulfone membranes using different concentrations of polyvinylpyrrolidone, Desalination, 288 (2012) 31-39;
- 12.YUTAO HU, KUAN LU, FANG YAN, YALAN SHI, PINGPING YU, SANCHUAN YU, SHENGHAI LI, CONGJIE GAO, Enhancing the performance of aromatic polyamide reverse osmosis membrane by surface modification via covalent attachment of polyvinyl alcohol (PVA), Journal of Membrane Science, 501 (2016) 209-219;

MATERIALE PLASTICE

https://revmaterialeplastice.ro https://doi.org/10.37358/Mat.Plast.1964



- 13.E.M. VRIJENHOEK, S. HONG, M. ELIMELECH, Influence of membrane surface properties on initial rate of colloidal fouling of reverse osmosis and nanofiltration membranes, J. Membr. Sci., 188 (2001) 115;
- 14.X. ZHU, M. ELIMELECH, Colloidal fouling of reverse osmosis membranes: measurements and fouling mechanisms, Environmental Science Technology, 31 (1997) 3654;
- 15.M. ELIMELECH, X. ZHU, A.E. CHILDRESS, S. HONG, Role of membrane surface morphology in colloidal fouling of cellulose acetate and composite aromatic polyamide reverse osmosis membranes, J. Membr. Sci., 127 (1997) 101-109;
- 16.VAHID VATANPOUR, SAYED SIAVASH MADAENI, LALEH RAJABI, SIRUS ZINADINI, ALI ASHRAF DERAKHSHAN, Boehmite nanoparticles as a new nanofiller for preparation of antifouling mixed matrix membranes, Journal of Membrane Science, 401-402 (2012) 132–143;
- 17.AHMAD RAHIMPOUR, SAYED SIAVASH MADAENI, MOHSEN JAHANSHAHI, YAGHOUB MANSOURPANAH, NARMIN MORTAZAVIAN, Development of high performance nano-porous polyethersulfone ultrafiltration membranes with hydrophilic surface and superior antifouling properties, Applied Surface Science, 255 (2009) 9166–9173;
- 18.JORGE GARCIA-IVARS, MARIA-ISABEL ALCAINA-MIRANDA, MARIA-ISABEL IBORRA-CLAR, JOSÉ-ANTONIO MENDOZA-ROCA, LAURA PASTOR-ALCAÑIZ, Enhancement in hydrophilicity of different polymer phase-inversion ultrafiltration membranes by introducing PEG/Al₂O₃ nanoparticles, Separation and Purification Technology, 128 (2014) 45-57;
- 19.MOAU JIAN TOH, PEI CHING OH, THIAM LENG CHEW, ABDUL LATIF AHMAD, Antiwettability enhancement of PVDF-HFP membrane viasuperhydrophobic modification by SiO₂ nanoparticles, C. R. Chimie 22 (2019) 369-372;
- 20.EKATERINA YU. SAFRONOVA, POLINA A. YUROVA, AMIR M. ASHRAFI, ALEKSANDR V. CHERNYAK, ANDREY V. KHOROSHILOV, ANDREY B. YAROSLAVTSEV, The effect of ultrasonication of polymer solutions on the performance of hybrid perfluorinated sulfonic acid membranes with SiO₂ nanoparticles, Reactive and Functional Polymers, 165 (2021) 104959;
- 21.QIANG HUANG, MEIYING LIU, JUNYU CHEN, QING WAN, JIANWEN TIAN, LONG HUANG, RUMING JIANG, FENGJIE DENG, YUANQING WEN, XIAOYONG ZHANG, YEN WEI, Marrying the mussel inspired chemistry and Kabachnik-Fieldsreaction for preparation of SiO₂ polymer composites andenhancement removal of methylene blue, Applied Surface Science, 422 (2017) 17–27; 22.DUSADEE TUMNANTONG, KUACHON SRISAMRID, SIRILUX POOMPRADUB, PATTARAPAN PRASASSARAKICH, Preparation of poly(methyl methacrylate)-silica nanocomposites viaDMP-assisted RAFT poly-merization and NR/PMMA-RAFT-SiO₂ hybridmembrane for pervaporation, European Polymer Journal, 168 (2022) 111088.

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