Electrified membranes for microplastic fouling mitigation

Ouda M.[1], Banat, F.[1], Naddeo V.[2], Hasan, S. W.[1],*

[1]Center for Membranes and Advanced Water Technology (CMAT), Department of Chemical Engineering, Khalifa University of Science and Technology, P.O. Box 127788, Abu Dhabi, United Arab Emirates
[2]Sanitary Environmental Engineering Division (SEED), Department of Civil Engineering, University of Salerno - Via Giovanni Paolo II #132, 84084 Fisciano (SA), Italy

*corresponding author: Hasan, S. W.
e-mail: shadi.hasan@ku.ac.ae

Abstract. The excessive use of plastics has created a route for microplastics into our water and wastewater treatment plants. Coupled with the on-going water crises, this creates a threat to fresh water availability as microplastics disrupt the operation of these plants. Microplastics result in severe fouling to low pressure membrane technologies, such as ultrafiltration. Electrified membranes are suggested as an alternative microplastic fouling mitigation strategy. In this study, polyethersulfone (PES) pellets were sulfonated to create sulfonated polyethersulfone (SPES), resulting in an additional layer of negative charge for microplastic repulsion. PES and SPES membranes were then fabricated using non-solvent induced phase inversion, and tested under DC electric field as a fouling mitigation strategy. Additionally, several characterization techniques were utilized to confirm the sulfonation and study the morphology and structure of the fabricated membranes. These include Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDS), X-ray diffraction (XRD), Raman Spectroscopy, and Fourier Transform Infrared Spectroscopy (FTIR). Finally, the microplastic flux, pore characteristics, hydrophilicity and charge of the fabricated membranes were determined experimentally. The microplastic flux increased by 16% in SPES compared to PES at 0 V. Additionally, the microplastic flux increased from 22.7 ± 0.9 L/m2.h in PES at 0 V to 34.0 ± 0.9 L/m2.h in SPES at 5 V, which reflects a 49% increase. This study lays basic foundations for this system as a microplastic fouling mitigation strategy, and creates a route for future studies on suitable membrane materials to enhance the system.

Keywords: Microplastics; membrane fouling; ultrafiltration; electrochemical system

1. Introduction

Microplastics (MPs) are plastic debris of sizes less than 5 mm. Their excessive use has made them more abundant in the ecosystem, specifically in our water bodies and water systems. Their slow degradation and toxicity cause significant harm to biotic organisms once they reach water bodies [1]. Conventional water and wastewater treatment plants were proven as non-effective for MP handling [2]. Membrane-based processes are rising as an alternative to conventional processes due to their compactness, ease of operation, and sustainability aspects. However, membranes are susceptible to severe fouling from MPs due to their size and specific surface properties [1], [2]. Several fouling mitigation strategies such as hybrid systems, surface modification techniques, and effective cleaning procedures have been considered [1]. In this work, an electrified membrane hybrid system, in combination with surface modification is suggested for MP fouling mitigation. First, polyethersulfone (PES) pellets were sulfonated to create more hydrophilic functional groups. As a result, a membrane with a more hydrophilic surface was fabricated. The properties of the fabricated membranes were analyzed in details and compared to the pristine PES membrane. Finally, the membranes were tested in a custom-made electrified system, where electric field is applied directly to the membrane as an additional fouling mitigation strategy. The effect of sulfonation, in addition to the electric field was studied, and the mechanism was analyzed.

2. Methodology

The sulfonation begins by drying the PES pellets overnight at 60°C. Subsequently, 15 g of PES was dissolved in 200 ml H2SO4. The solution was left to reaction in an oil bath under reflux at a temperature of 55°C for 4 hr. The solution is then placed in a separation funnel and added drop wise to an ice-cold DI water bath. The sulfonated PES (SPES) pellets are formed upon contact with the DI water bath. The SPES pellets were thoroughly washed using DI water to get rid of the excess acid. Finally, the pellets were dried under vacuum overnight at 60°C. The obtained SPES pellets were used for the membrane fabrication process. PVP was added to the NMP solvent and sonicated for an hour. Subsequently, 16 wt% PES or SPES are added, and the suspension was left to stir for 24 hr until homogeneity is obtained. The suspension was then degassed for an additional 1 hr to minimize the formation of macropores

on the membrane surface. Finally, suspension was casted on a glass plate using a 200 μm casting knife. The casted dope solution was finally placed in a DI water coagulation bath at 25 °C.

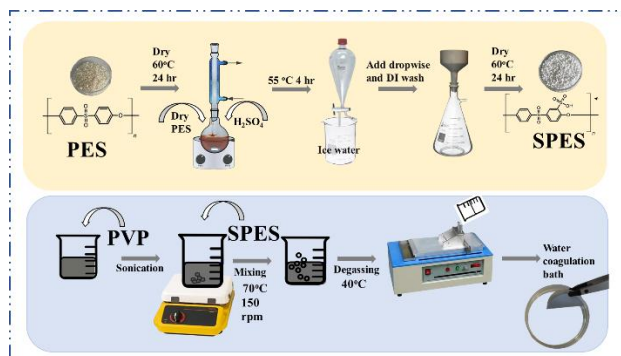**Figure 1**. PES sulfonation and membrane fabrication schematic.

To prepare for the fouling tests, 1000 μg/L MP solution was prepared in 1000 ppm NaCl. A MP-rich solution is pumped into a cross-flow cell and recycled back into the feed, with a pressure gauge at the inlet and at the recycle stream. The cell is composed of 2 acrylic sheets, with a hollow compartment in the middle to provide distance between the electrodes. The anode is a 25 mm diameter aluminum mesh disc, and the cathode consists of the fabricated membrane fixed by a stainless-steel mesh for enhanced electrical conductivity. The applied pressure is adjusted via a needle valve at the recycle stream, and set to 1 bar throughout all experiments and monitored. The permeate is collected and mass is collected. The applied voltage was varied from 0 to 5 V, and the MP flux was calculated from the permeate mass.
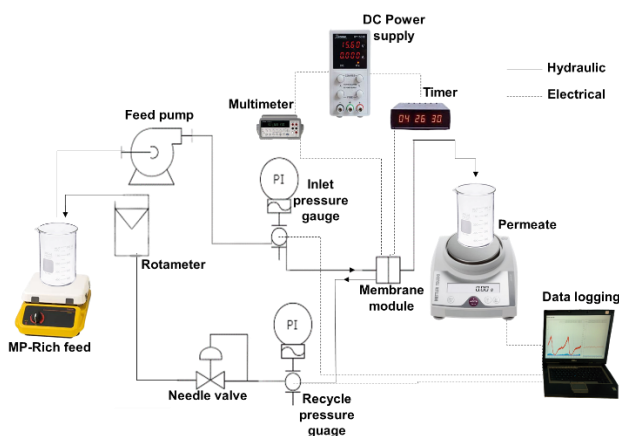

Figure 2. Schematic of cross-flow electrified filtration set-up.

3. Results and Discussion

The physiochemical, thermal and mechanical properties of the fabricated membranes were analyzed in details and are shown in Figure 3. It is first noted from Figure 3 (a) that the pure water permeability (PWP) increased by 15.6 % as a result of sulfonation. This can be attributed to the additional -SO3H groups formed in the membrane structure. The additional -SO3H groups resulted in a more hydrophilic polymer, which in turn lead to two effects (1) A drop in the water contact angle and (2) A faster phase inversion processes, resulting in additional pores. The contact angle shown in Figure 3 (b) dropped from $78 \pm 4°$ to $73 \pm 1°$, and as a result the surface energy increased from 88 ± 5 to 94 ± 1 MJ/m2. A higher surface energy leads to the formation of a thicker hydration later, allowing higher mass transfer of water across the membrane. Additionally, the contact angle variation is depicted in Figure 2(c), which shows that sulfonation results in a faster drop in the contact angle with time, reflecting improved hydrophilicity. Furthermore, the additional hydrophilicity as a result of the SO3H groups caused a faster exchange rate between the non-solvent (NMP), and the solvent (water) during phase inversion, as the -SO3H groups draw the solvent (water), into the membrane faster creating larger pores and a higher porosity. The improved pore size and porosity are shown in Figure 2 (d).

Thermogravimetric analysis (TGA) and the derivative thermogravimetric (DTG) analysis results on the membranes is shown in Figure 3 (e) and Figure 3 (f). From the TGA plots, we can see the temperature at 5 wt% weight loss is 453°C for PES compared to 418°C for SPES. However, the maximum weight loss is reported to be at 537°C for PES compared to 568 for SPES. Hence, it can be concluded that the thermal stability was maintained or slightly increased as a result of the sulfonation. Similarly, there was no significant difference in the tensile strength or the elongation at break before and after sulfonation. Hence, it can be concluded that the sulfonation maintained the structural properties of the polymer chains, reflected by minimal changes in the thermal and mechanical properties of the membrane.

The top, bottom, and cross-sectional images of the PES and SPES membranes are shown in Figure 3 (h). The top surface shows a dense polymer layer, with minimal pore size for high MP rejection. The bottom layer shows a very porous structure for unobstructed mass transfer of water post MP rejection. The asymmetric structure is clearly shown in the cross section, where a very dense skin layer changes into thin finger-like pores across the cross section. The finger-like pores are followed by larger macropores towards the bottom surface of the membranes. The microporous membrane bulk will allow for a reduced mass transfer resistance post skin layer selectivity, where pure water can pass through the membrane with little flow resistance. By comparing SPES to PES, the transition to the finger like pores are shorter for SPES compared to PES. Additionally, the micro-void layer in SPES is less obstructed compared to PES. These two observations are consistent with the higher PWP reported in SPES.
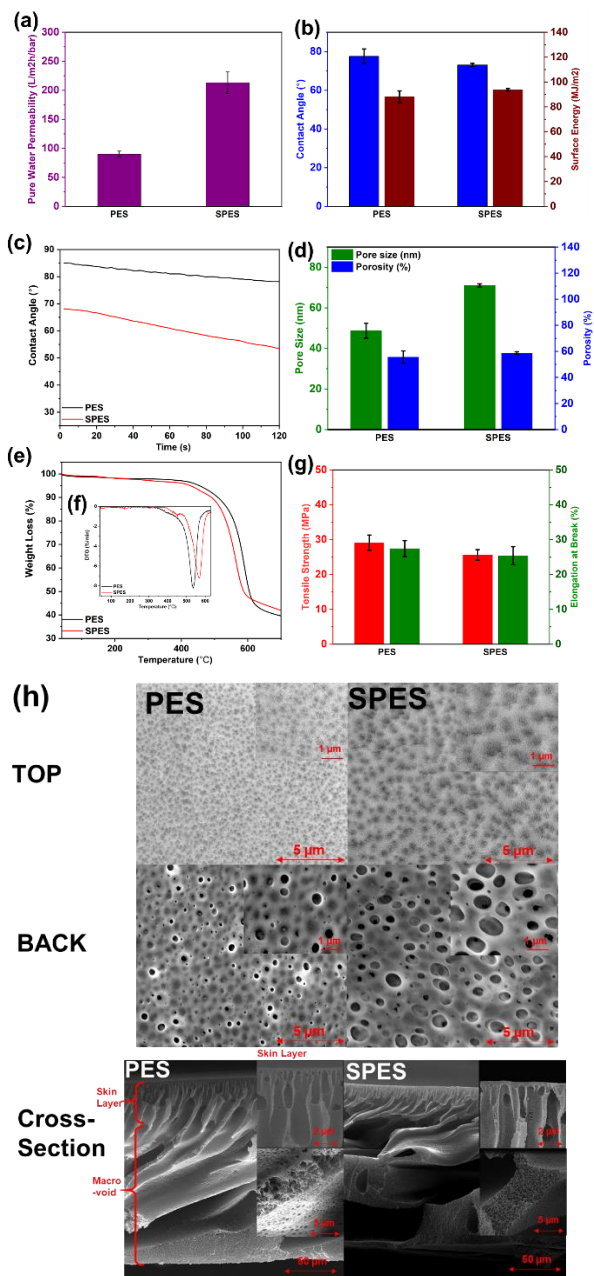
Figure 3. Physiochemical properties of PES and SPES membranes (a) Pure water permeability (b) Static contact angle and surface energy (c) Dynamic contact angle (d) Porosity and pore size (e) TGA analysis (f) DTG analysis (g) Tensile strength and strain at break (h) SEM top, bottom and cross-sectional images.

The performance test results for the electrified membrane system are shown in Figure 4 (a) using a MP-rich suspension. It is first noticed that the trends are consistent with the pure water permeability, where a higher MP flux is recorded at all voltages for SPES compared to PES. Secondly, a steady increase in the flux with increasing voltage for both PES and SPES is observed. Looking at the long-term results in Figure 4 (b), the MP flux of SPES is maintained in the first 30 minutes, and slowly starts to decline after 30 minutes. The increasing initial flux as a result of increasing voltage can be attributed to the higher negative charge that is applied by the DC electric field. The negatively charged MP will repel away from the surface, minimizing concentration polarization on the surface and allowing for a higher flux. Therefore, a higher voltage will result in a higher negative charge, and in turn a higher flux. The drop in the flux overtime can be attributed to the dissociation of the aluminum at the anode, and water at the cathode, where Al^{3+} will combine will OH^- to form an insitu aluminum oxide coagulant. The negatively charged MPs will be attracted to the positively charged coagulants, forming larger flocs that are deposited at the surface. Once these flocs settle overtime, there is a sharp decrease in flux. This is also the reason why higher voltages result in a higher decline in flux over time. These results indicate that applied electric voltage can be an effective fouling mitigation procedure, only if applied in short time intervals.
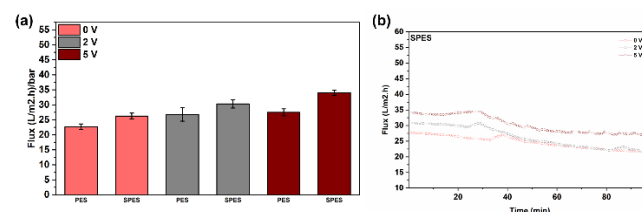

Figure 4. (a) Effect of voltage on the flux of MPs using PES and SPES membranes (b) Long-term effect of voltage on the flux of MPs using SPES membrane.

4. References

[1] Roch, C. Friedrich, and A. Brinker, "Uptake routes of microplastics in fishes: practical and theoretical approaches to test existing theories.," Scientific reports, vol. 10, no. 1, p. 3896, Mar. 2020, doi: 10.1038/s41598-020-60630-1.

[2] M. Ouda et al., "Emerging contaminants in the water bodies of the Middle East and North Africa (MENA): A critical review," Science of the Total Environment, vol. 754, p. 142177, 2021, doi: 10.1016/j.scitotenv.2020.142177.

[3] M. Golgoli et al., "Microplastics fouling and interaction with polymeric membranes: A review," Chemosphere, vol. 283. Elsevier Ltd, Nov. 01, 2021. doi: 10.1016/j.chemosphere.2021.13