EXTERIOR SURFACE CHARACTERIZATION OF THE NOVEL SURFACE MODIFIED PES HOLLOW FIBER MEMBRANE APPLICABLE IN BIOREACTOR

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Abstract

Exterior surface characteristics of the submerged hollow fiber (HF) membranes are believed to have a significant impact on the fouling rate within the filtration process in a bioreactor used for wastewater treatment. Most of the interactions among the organics, particulate particles, and microorganisms occur at the interface of the membrane surface and activated sludge (AS). Despite the numerous advantages exhibited by polyethersulfone (PES) hollow fiber (HF) membranes, their extensive utilization in wastewater treatment applications is substantially hindered by the prevalent issue of biofouling, which stands as the primary challenge in membrane bioreactors (MBR). Accordingly, the aim of this investigation is to characterize the exterior surface of the PES HF membrane after a two-step modification process involving the biomimetic-based polydopamine nanospheres and *in situ* synthesis and immobilization of zinc oxide nanoparticles (ZnO NPs), and to assess its impact on the permeability and fouling rate of the membrane in an MBR.

The surface morphology and elemental analysis of the surface functionalized PES HF membranes were assessed by scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX). Antimicrobial properties of the surface-modified PES HF membranes were tested under dynamic contact conditions based on the ASTM E2149 after inoculation with *Staphylococcus spp.* strain CCM 2446 and *Escherichia coli* strain CCM 7395 (supplied by Masaryk University in Brno). Finally, the permeability of the membranes beneath deionized (DI) water and activated sludge was evaluated as well. The results of this study can aid in the development of PES HF membrane performance used for wastewater treatment applications.

Keywords: Polyethersulfone, hollow fibre membrane, biofouling, zinc oxide nanoparticle, surface modification

1. INTRODUCTION

Submerged hollow fiber membranes in bioreactors are widely recognized for their prominent role in water treatment, offering cost-effectiveness, enhanced wastewater treatment efficiency, and a small foot-print, ensuring cleaner water treatment [1]. Polymeric hollow fiber membranes in bioreactors combine biological treatment with selective separation, making membrane bioreactors (MBRs) increasingly popular in wastewater treatment [2] due to their capability in wastewater reuse, smaller foot-print demand and cost savings in installation and operation [2]. They provide numerous advantages over traditional activated sludge processes, including high biomass operational concentration, reduced sludge production, pathogen and virus retention, and high-quality effluent production [2]–[4].

Despite their benefits, MBR technology expansion faces limitations, primarily membrane fouling, including surface fouling and pore clogging, resulting in increased hydraulic resistance, reduced permeate flux, or elevated transmembrane pressure (TMP) [3]. Regular physical and chemical cleaning is necessary to maintain their performance. MBR fouling is a complex issue influenced by membrane properties, biomass

characteristics, and operating conditions [3,4]. Practical applications minimize MBR membrane fouling by implementing sub-critical flux operation, which restricts flow rates through the membrane and mitigates fouling problems [5]. This investigation aims not only to surface functionalized PES HF membranes with ZnO NPs to enhance the exterior surface resistance against biofouling but also to determine the critical flux of those membranes. When the membranes are operated under this critical flux, the fouling rate should be limited.

2. MATERIALS AND METHODS

2.1 Surface modification

The PES HF membrane underwent surface modification using a two-step process similar to the last published method [6]. First, PDA surface polymerization was initiated by immersing PES HF membrane modules (Shandong Jinhuimo Technology Co.) in a 10 mmol·L^{-1} Tris(hydroxymethyl)aminomethane (Penta) buffer solution. Dopamine hydrochloride (Alfa Aesar) was polymerized at a pre-adjusted pH of 8.5 for 1.0, 2.5, and 4.0 hours, respectively. The membranes were then thoroughly washed three times with DI water to remove unreacted monomers. Subsequently, the PDA-coated PES HF membranes were immersed in a ZnO seed solution prepared by dissolving zinc acetate in DI water (0.02 mol·L^{-1}). In-situ synthesis and immobilization of ZnO NPs were initiated by vigorously stirring the solution at 80°C while gradually adding 2.0 mol·L^{-1} Tris buffer until the pH reached 9. The membrane modules were left in the solution for an additional one hour. The resulting PDA-coated PES HF membranes with incorporated and immobilized ZnO NPs were then immersed in DI water to eliminate unattached particles, and stored in DI water for further experimentation.

2.2 Exterior surface characterization

Exterior surface characterization of the modified PES HF membrane started by analysis of field emission-SEM (Fe-SEM, Zeiss, Germany) images to observe the surface morphology and aestetic analysis of the surface modified membranes. The Energy Dispersive X-ray Spectroscopy (EDX) was emploeyd to measure the exterior surface elemental composition after modifications and provide high elemental contrast images.

2.3 Filtration characteristics

First, the permeabilities of the pristine and surface-modified membranes were measured by incrementally increasing flux and collecting the permeate while recording the transmembrane pressure (TMP) at 4-minute intervals. The test was repeated three times, and the slope of the regression fitting line of flux versus TMP enabled the assessment of the membrane's permeability, and provided valuable data for further analysis of membrane fouling after filtration of activated sludge (AS).

The critical flux of pristine and surface-modified membranes was determined initially using a flux-step experiment [7]. The critical flux is defined as the point at which the fouling rate (FR) exceeds a threshold of 0.5 mbar·min^{-1} [5]. The fouling rate (FR) indicates the instantaneous change of TMP in time [7] (as shown in eq. 1).

$$FR = dTMP/dT \quad (1)$$

The critical flux was evaluated using the flux-steps method with 10-minute intervals per cycle. It started with steps of around 13 LMH ($l.m^{-2}.h^{-1}$) and gradually increased to a maximum flux of approximately 40 LMH. Each step in the flux-step process was duplicated, resulting in a total permeate extraction time of 20 minutes for each step.

2.4 Antimicrobial analysis

The antimicrobial properties of the surface-modified PES HF membranes containing ZnO NPs were assessed under dynamic contact conditions following ASTM E2149 standards [8]. Bacterial stocks (Gram-positive *Staphylococcus spp.* CCM 2446 and Gram-negative *Escherichia coli* CCM 7395, sourced from the Czech

Collection of Microorganisms in Brno, Czech Republic) were cultured to reach the mid-log exponential growth phase (approximately 1 × 10^5 cells·mL^{-1}). The membranes' samples of 0.5 g were immersed in 25 mL of bacterial culture and thoroughly homogenized at 120 rpm. Following immersion, 1.0 mL of the solution was taken and pipetted onto PCA agar plates (Bio-Rad, France) at 0, 2, 5, and 24 hours, respectively. All samples were subjected to the 10-fold, and 100-fold dilution up to the 10^4, and 10^3 dilution using physiological sterile saline solution (8.5 g·L^{-1} NaCl in DI water). Subsequently, the cells were harvested beneath incubation at 37 °C for 48 hours. The colony-forming units (CFU) of bacteria were determined through the cultivation method, and the total CFU count was expressed in $\log_{10}$ scale (CFU·mL^{-1}).

3. RESULTS AND DISCUSSION

3.1. Exterior surface characterization

The SEM images of the PES HF membranes before and after treatment illustrate that the growth of the PDA nanolayer is time-dependent. With increasing polymerization time, PDA nanospheres exhibit increased coverage on the membrane's surface after various time intervals of 1.0, 2.5, and 4.0 hours (**Figure 1**). Furthermore, it was demonstrated that as the polymerization time increased, the growth of PDA nanospheres resulted in a reduction in the pore size and porosity of the PES membrane. SEM images coupled with EDX enhance image contrast, facilitating a better distinction of immobilized ZnO NPs and PDA nanospheres on the PES HF membrane surface (**Figure 1e**). Additionally, EDX analysis confirmed the successful immobilization of ZnO NPs on the membrane surface. The homogeneous and non-agglomerated dispersion of ZnO NPs indicates a promising methodology for in situ synthesis and immobilization of ZnO NPs on the PES HF membrane surface.

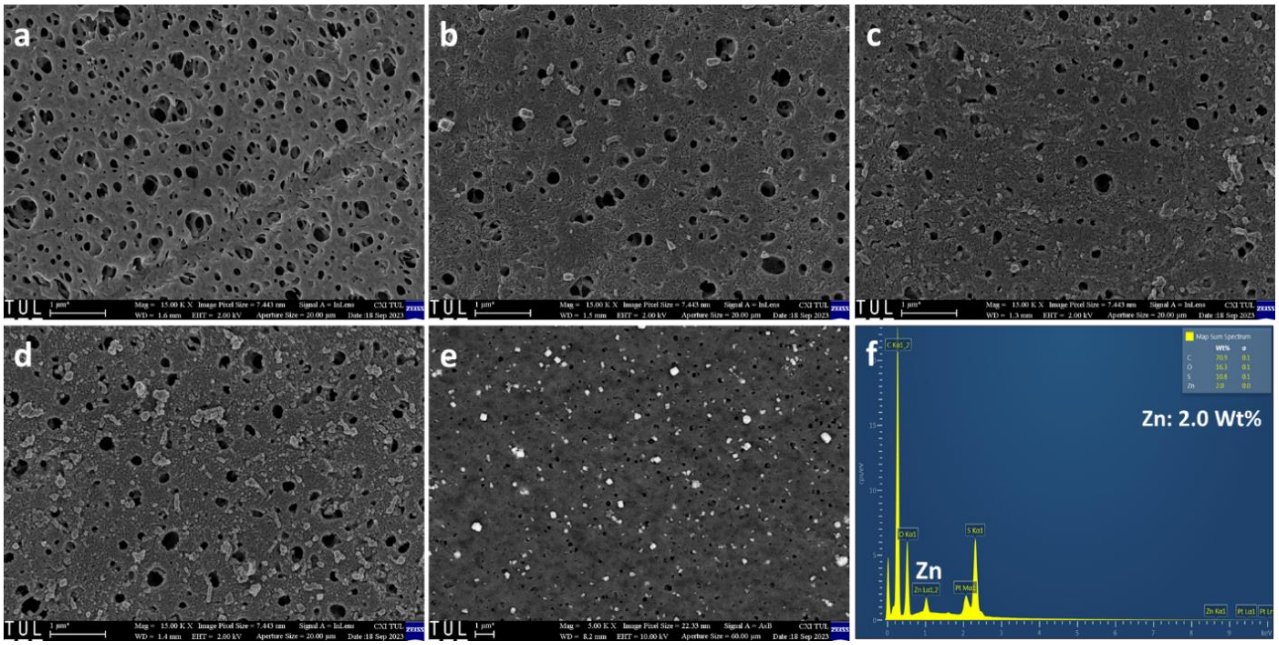

Figure 1 SEM analysis of: a) pristine PES HF membrane, b) PDA {1.0 h}, c) PDA {2.5 h}, d) PDA {4.0 h} incorporated ZnO NPs modified PES HF membrane, and EDX-coupled e) high contrast image and f) elemental analysis of PDA (1.0 h) incorporated ZnO NPs modified PES HF membrane.

3.2. Filtration characteristics of membrane

The **Figure 2** presents the permeability of the pristine and surface-modified membranes with DI water determined before filtration of AS by assessing the curve fitting of flux versus transmembrane pressure (fitted curves showed R^2 values as high as 0.99, indicating the promising accuracy of the permeability measurement).

As a consequence of the time-dependent growth of the PDA layer on the PES HF membrane, an increase in polymerization time led to a reduction in pore size, resulting in a decrease in permeability of the modified membranes. Specifically, permeability decreased from 394 LMH·bar^{-1} for pristine PES to 342, 284, and 272 LMH·bar^{-1} for 1.0 h, 2.5 h, and 4.0 h PDA treatments (incorporating the same amount of ZnO NPs), respectively. Nevertheless, it is noteworthy that even with these reductions in permeability, the modified membranes still exhibited ample permeability levels suitable for wastewater treatment and can effectively serve as submerged membrane modules in the MBRs.

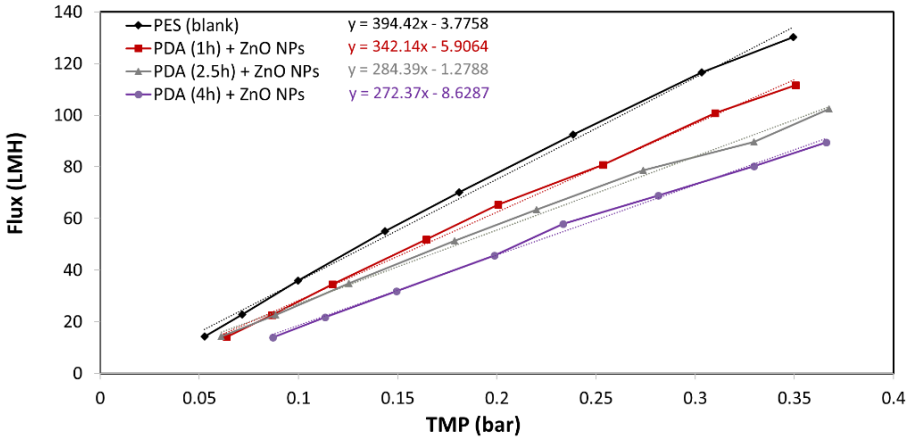

Figure 2 Permeability of the pristine PES HF membranes and surface-modified membranes with DI water: TMP - transmembrane pressure, flux in LMH (l.m^{-2}.h^{-1})

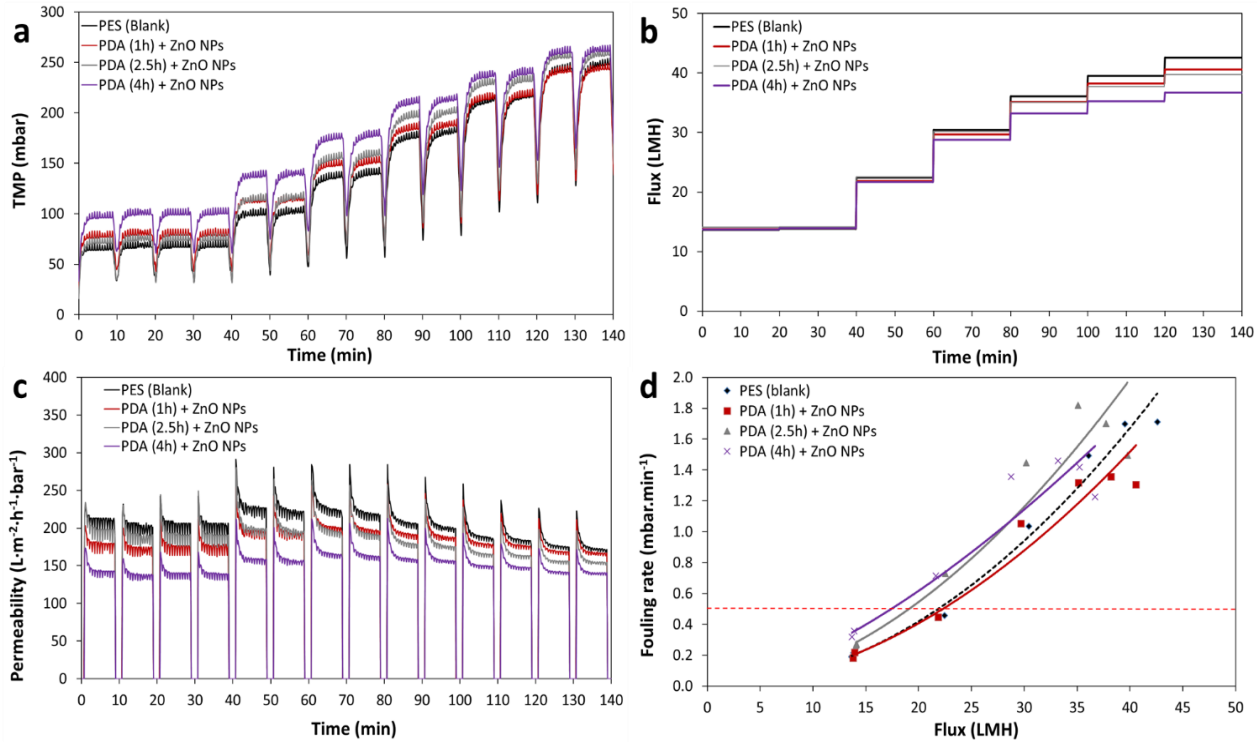

Figure 3 Results of the flux step measurement using pristine and surface modified PES HF membranes

Both pristine and surface-modified PES HF membranes were also assessed through the flux step test. Municipal wastewater was collected from the central WWTP in Liberec, Czechia, and subjected to biological treatment using activated sludge in a lab-scale MBR. In **Figure 3a**, the results depict changes in TMP as the

flux is incrementally increased during 10-minute filtration cycles, with a constant 9-minute filtration time and 1-minute relaxation time per cycle. The previous study demonstrated the time-dependent nature of PDA polymerization on the membrane surface, resulting in an overall decrease in porosity [6].

Similarly, the obtained results indicate that increasing the PDA polymerization time leads to an increase in TMP due to a reduction in the membrane's pore size and porosity. **Figure 3b** and **Figure 3c** display changes in flux steps and alterations in permeability over the time, respectively. Membrane fluxes consistently increased until reaching approximately 30 LMH after 1 hour of filtration, at which point the primary differentiation among membranes became evident. The increase in flux continued until reaching 40.0 LMH, with the pristine PES HF membrane exhibiting the highest flux at around 42.5 LMH and the PES modified with PDA (4.0 h) incorporated ZnO NPs showing the lowest flux at around 36.7 LMH. Evaluation of the membranes' fouling rate (FR) revealed that both pristine and PDA (1.0 h) incorporated ZnO NPs modified membranes exceeded the threshold of 0.5 mbar·min^{-1} at higher fluxes, around 22 LMH, compared to PDA (2.5 h) and PDA (4.0 h) incorporated ZnO NPs modified membranes, which exceeded this threshold at around 19 LMH and 16 LMH, respectively. Consequently, it can be deduced that the PES HF membrane modified with PDA (1 h) incorporated ZnO NPs exhibited the lowest tendency toward fouling in MBR performance.

3.3. Antimicrobial properties of membrane

A quantitative analysis of the PES HF membranes, extracted at various time intervals after microbial assessment through dynamic contact procedures followed by a 48-hour incubation at 37 °C, demonstrated favorable antimicrobial properties of the surface-modified PES HF membranes with ZnO NPs when compared to the pristine membrane, for both tested bacteria, *E. coli* and *Staphylococcus spp.* (**Figure 4**). However, PDA-modified PES did not exhibit any antimicrobial activity, and there was almost no discernible difference in the colony-forming units (CFU) compared to the pristine PES HF membrane.

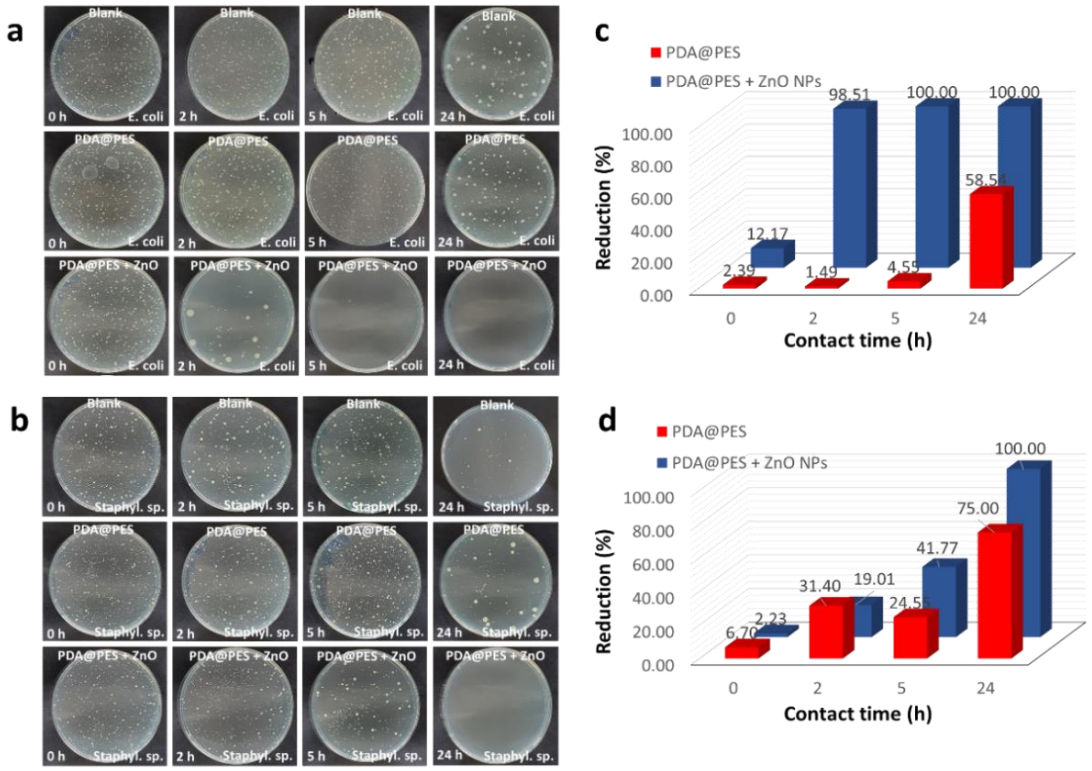

Figure 4 Colony-forming unit (CFU) assays: a) images & c) diagrams of *E. coli* and b) images & d) diagrams of *Staphylococcus spp.* cells grown by inoculation with pristine and surface modified PES at 0.0, 2.0 h, 5.0 h, and 24 h contact time intervals.

4. CONCLUSION

The successful coverage of PDA nanospheres, in addition to the in-situ synthesis and homogeneous (non-agglomerated) distribution of ZnO NPs on the surface of PES HF membranes, was confirmed through surface morphological assessment and elemental analysis. The PDA-modified PES membrane incorporating ZnO NPs exhibited remarkable anti-biofouling properties, achieving a 100% reduction in bacterial cells after 24 h and only 5 hours of exposure with *Staphylococcus spp.* and *E. Coli* bacteria, respectively.

Furthermore, the correlation between membrane performance in MBR and the exterior surface characterization of the membrane was established through permeability with DI water and flux step measurements. An increase in polymerization time led to a reduction in pore size, as indicated by SEM analysis, and a decrease in permeability with DI water. Specifically, the pristine PES HF membrane showed permeability with DI water of 394 $LMH \cdot bar^{-1}$, while the PDA treatments for 1.0 h, 2.5 h, and 4.0 h (containing the same amount of ZnO NPs) resulted in permeabilities of 342 $LMH \cdot bar^{-1}$, 284 $LMH \cdot bar^{-1}$, and 272 $LMH \cdot bar^{-1}$, respectively. Notably, the PDA (1.0 h) modified PES incorporating ZnO NPs exhibited a critical flux similar to that of the pristine membrane (approximately 22 LMH) while concurrently possessing enhanced antimicrobial properties compared to the pristine PES HF membrane, which lacked antibacterial properties.

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