SUPERHYDROPHILIC SURFACE MODIFICATION OF PTFE HOLLOW-FIBER MEMBRANE WITH ADVANCED BIOFOULING PROPERTIES FOR WATER PURIFICATION

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Abstract

Irrespective of all affirmative physiochemical properties of polytetrafluoroethylene (PTFE) hollow fiber (HF) membrane, its promotion to be served for water purification function is significantly threatened by biofouling which is known as the primary problem in the membrane technology. The hydrophobic nature of PTFE attracts biofoulants leading to the pore blockage and lowering of the flux and functional life. Thus, this investigation aimed to devise an innovative silan-mediated polydopamine (PDA) coating incorporated with ZnO nanoparticles (NP) to trim the surface of the PTFE HF membrane and subsequently increase its functional property and biofouling resistivity. SEM images and EDX spectroscopies showed the time-dependent growth of PDA coating and elemental analysis on the surface, respectively. The water contact angle results illustrated the successful transformation of the surface characteristics of the PTFE HF membrane from hydrophobic (app. 130°) to superhydrophilic (0°) after surface modification. An exclusive dead-end cell was devised to comparatively evaluate the permeation and protein separation of surface-modified and pure PTFE HF membranes under constant pressure. Filtration tests' results, alongside the microbial assessments, revealed that the modified membranes showed a lower tendency towards biofouling. The outcomes of this study shed light on addressing the key challenges of today's demands for harnessing membrane biofouling and remarkably expand the PTFE HF membrane's potential to be utilized in advanced water treatment technology.

Keywords: Superhydrophilicity, polytetrafluoroethylene, zinc oxide nanoparticle, hollow fiber membrane, surface treatment, biofouling resistivity

1. INTRODUCTION

Organic hollow fiber (HF) membranes are unanimously considered the promising separation approach in water treatment due to its cost effective, cost effective, higher efficiency during the water filtration process, and space-saving which then ensure cleaner water purification [1-2]. However, the hydrophobic nature of these HF membranes are prone to the adsorption of biofoulants which consist of proteins, humic acids, and microorganisms which will then lead to membrane blockage [3-4]. Although polytetrafluoroethylene (PTFE) hollow fiber (HF) membrane contains comparatively higher chemical, thermal and mechanical properties than all other HF membranes [5], its widespread promotion in water application is affected by the feasible, permanent and efficient surface modification [6-7]. However, there is still a knowledge gap in the long-lasting and biofouling resistant modified coating for PTFE HF membrane to meet the requisites of the water treatment technologies. Accordingly this study tries to introduce the promising surface modification on the basis of a nature-inspired polydopamine (PDA) coating due to its remarkable properties [8-9] and incorporation with zinc oxide nanoparticles (ZnO NPs) as an advanced biofouling resistant approach for PTFE HF membranes.

2. MATERIALS AND METHODS

2.1. Surface modification method

The surface modification method of the PTFE HF membrane was based on the hierarchical steps of surface polymerization of PDA and immobilization of ZnO NPs on the surface, respectively. PDA coating initiated by immersion of PTFE HF (Dongyang Hanchen Membrane Technology) membranes in the Tris-base (Tris(hydroxymethyl)-aminomethane, Penta) buffer solution and In-Situ polymerization of dopamine hydrochloride (99%, Alfa Aesar) at a certain adjusted pH = 8.5. Then, the membranes were washed intensively three times with deionized water (DW) to remove non-reacted monomers. ZnO NPs immobilized on the membranes‘ surface followed by dispersion and ultrasonication in Ethanol, and addition of (3-Aminopropyl)triethoxysilane (APTES, TCI) 2% v/v to the solution. The specimens were gently washed three times again and kept in DW for further analysis.

2.2. Surface characterization

Scanning electron microscopy (SEM) images were used to analyze the surface morphology of the treated PTFE HF membranes. Simultaneously, energy Dispersive X-ray Spectroscopy (EDX) analysis was carried out to quantitatively measure the elemental composition on the surface area of specimens after modifications. Water contact angle measurement was performed to evaluate the surface hydrophilicity of PTFE HF membranes before and after surface treatment. ATR-FTIR spectrophotometer was utilized to assess the spectra of the chemical bonds for pristine and surface-treated membranes.

2.3. Filtration performance

The particular homemade dead-end cell specially devised for HF membranes was conducted to determine membrane hydraulic performance. The pressure-driven cell coupled with PTFE HF membrane modules (34 cm^2) was fed by DW. The measurements were performed at 1 bar, and room temperature. Meanwhile, the flux (J) and flux recovery ratio (FRR) before and after modification against filtration of deionized water (DW) and bovine serum albumin (BSA) were determined by using the below equations:

$$J\left(\frac{L}{M^2.H}\right) = \frac{V}{A\,.\,t} \quad (1), \qquad FRR = \left(\frac{J_{w2}}{J_{w1}}\right) * 100 \quad (2)$$

Initial filtration of DW was performed to determine the flux, J_{w1}, at 1 bar for 1 h. Then, the cell was emptied, refilled with BSA, and filtrated for 1 h at 1 bar. Subsequently, the flux recovery ratio (FRR) was determined after gently three times washing the membranes and refilter the DW for another 1 h to measure J_{w2}.

2.4. Antimicrobial assessments

Surface modified PTFE HF membranes incorporated with different concentrations of ZnO NPs (0.5 mg/mL, 1 mg/mL, and 1.5 mg/mL) were qualitatively tested under static contact condition according to the AATCC method 147 [10] and quantitatively under dynamic contact condition according to the standard ASTM E2149 by inoculation with gram-positive *Staphylococcus spp.* CCM 2446 and gram-negative *Escherichia coli* CCM 7395 (obtained from the Czech Collection of Microorganisms, Masaryk University in Brno, Czech Republic).

2.4.1. Antimicrobial activity under static contact conditions

To evaluate the inhibition zone of surface-modified PTFE HF membranes an initial concentration of 10^5 cells inoculum/1ml of bacteria suspensions were prepared by using a Densi-La-Meter® II densitometer (Erba Lachema). Then, four lines of the given bacterial suspensions ranging from non-diluted, 10 times, 10^2, and 10^3 times dilution were prepared in parallel on the agar plates (PCA). Tested HF membranes were placed perpendicularly with the bacteria lines on the agar plates.

Sample plates were cultivated beneath 37 °C for 48 h. After incubation, the contact area between the tested membranes and bacteria lines were qualitatively assessed based on three factors: growth of bacteria under the HF membrane, leaking from the modified HF membrane into the agar plates, and reduction zones between the edge of the bacteria lines and samples. Consequently, the reducing inhibition zones sign a qualitative degree of antimicrobial activity.

2.4.2. Antimicrobial activity under dynamic contact conditions

The quantitative measurements of each specimen was carried out at the certain contact time based on the following steps. The initial suspension solutions of the test organisms were prepared in sterile saline solution (8.5 g NaCl / 1l H2O), and the concentration of bacteria equal to the 10^5 colony-forming-unit (CFU) / 1 ml was obtained. CFU were determined after 0, 1, 3, 6, and 24 hours contact times.

Each sample piece (0.5 g) was put in the 25 ml bacterial inoculum solution and thoroughly agitated on a shaker at 120 rpm. Subsequently, for the specified time intervals of 0, 1, 3, 6, and 24 hours, samples were pipetted into Petri dishes and poured with tempered PCA agar (BioRad). The same procedures were repeated for 10 times and 100 times dilutions of each sample. The samples-contained-agar Petri dishes were incubated at 37 ˚C for 48 hours. Finally, individual colonies of microorganisms were counted and recorded in.

3. RESULTS AND DISCUSSION

3.1. Surface characterization

The SEM images of the PTFE HF membranes before and after treatment illustrated that thickness of the PDA layer is time-dependent in a way that by increasing the polymerization time, PDA coating significantly increase **(Figure 1)** util it uniformly cover whole of the membrane‘s surface after 24 h **(Figure 1, d)**. It was also deduced that PDA coating is not a practicable technique to immobilize NP on the surface, and as it does, APTES was successfully exploited to immobilize ZnO NPs on the PTFE@PDA 24h HF membranes **(Figure 1, e)**.

EDX analysis was also performed to distinguish various amounts of immobilized ZnO NPs on the membrane surface. Accordingly, samples containing ZnO = (0.5 mg/mL, 1 mg/mL and 1.5 mg/mL) showed homogenous elemental distribution on the surface with the values equal to 1.72 %wt, 8.44 %wt and 18.95 %wt, respectively.

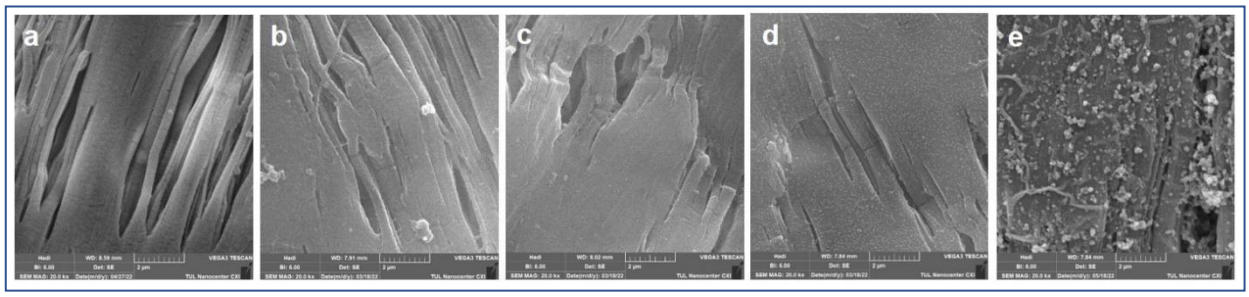

Figure 1 SEM surface images of: a) Pure PTFE HF membrane, b) PTFE@PDA 4h, c) PTFE@PDA 14h, d) PTFE@PDA 24h and e) PTFE@PDA 24h incorporated ZnO = 1 mg/mL.

3.2. Water contact angle

Water contact angle results of the pristine and surface-treated PTFE HF membranes are shown in the **Figure 2**. It was deduced that the transformation of the surface characteristics of the PTFE HF membrane from hydrophobic to superhydrophilic can be accessible by decreasing the water contact angle from (app. 130˚) to (0˚), followed by increasing the PDA polymerization time up to 24 h and uniform growth of PDA NP on the surface. Time-dependency of the surface hydrophilicity of the membrane to PDA polymerization time was

also proved by considering the reduction of the water contact angle degrees from (app. 89˚), (app. 68˚), and (0˚) after increment in PDA polymerization time from 4 h, 14 h, and 24 h.

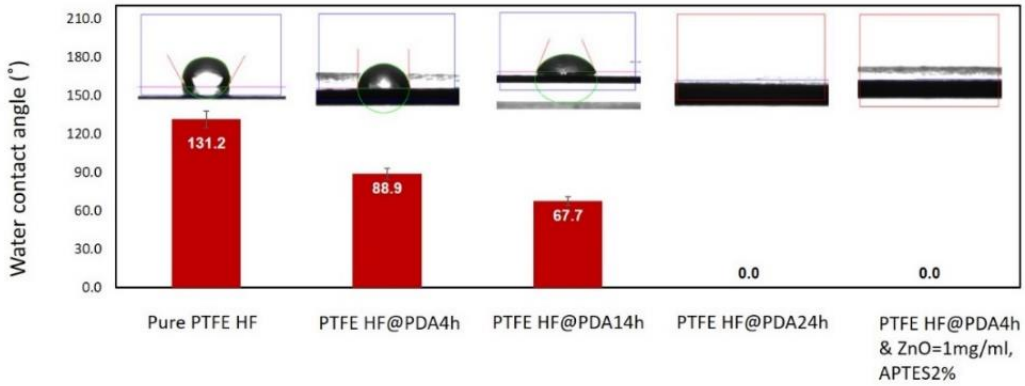

Figure 2 Effects of polymerization time and surface treatment on water contact angle degrees

3.3. ATR-FTIR spectroscopy

Successful polymerization of PDA and also APTES-aided immobilization of ZnO NPs on the surface of PTFE HF membranes were proved by comparing the obtained spectra of FT-IR. As it is shown in the **Figure 3, a)**, two peaks at 1140 cm^{-1} and 1200 cm^{-1} attributed to the C-F bond of the PTFE. New spectra appeared on the modified membranes between 1300 cm^{-1} to 1700 cm^{-1}, and 2400 cm^{-1} to 3600 cm^{-1} assigned to the O-H, N-H, and C-H bonds and hydrogen bonds of PDA, respectively. The broad peak at 1010 cm^{-1} is related to the vibration of Si-O bonds of the APTES crosslinking agent. These results indicated the successful modification of the membranes through PDA coating and ZnO NPs incorporation on the surface of PTFE HF.

3.4. Flux recovery measurement

Fluxes of pristine and modified PTFE HF membranes during DW and BSA filtration operation are shown in the **Figure 3, b)**. The initial DW fluxes at the first 1 h (J_{w1}) for pure PTFE HF and PTFE@PDA24 incorporated 1mg/mL ZnO NPs are app. 1854 (L/m2.h) and app. 226 (L/m2.h), respectively. The secondary DW fluxes after filtration of BSA are always lower than the initial one owing to the adsorption and deposition of some protein molecules on the membrane surface, contributing to the increment of the fouling rate. However, as it is shown in the **Figure 3, b)**, the FRR for the treated membrane is significantly improved by recovering the app. 46 % of the initial flux compared to the non-treated membrane, with an 8 % recovery ratio.

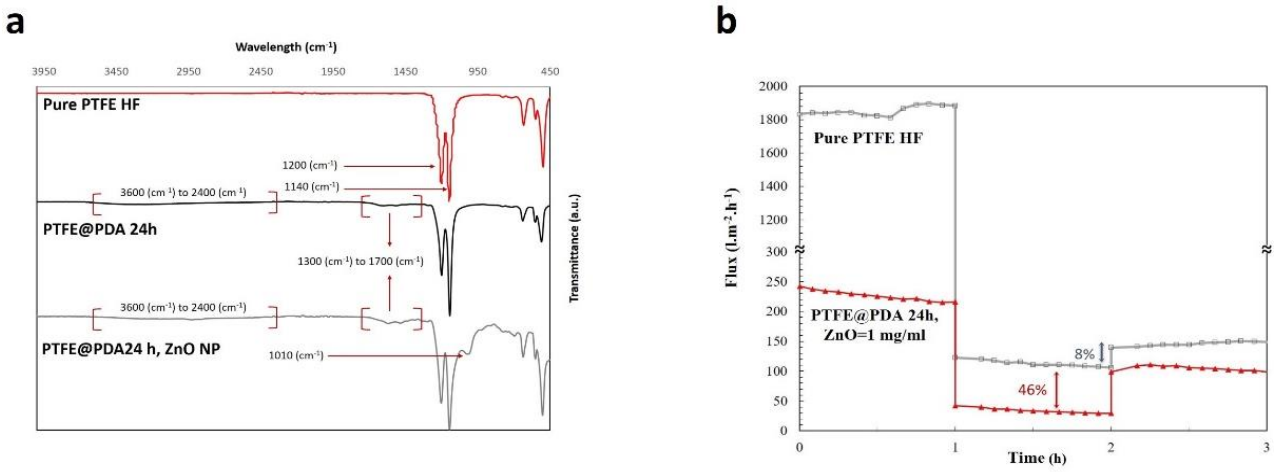

Figure 3 a) FT-IR spectra of pure and treated membranes. b) Flux Vs process time diagrams

3.5. Antimicrobial assessments

Qualitative analyses of the PTFE HF membranes after 48 h at 37 ˚C incubation sign the non-activity of both pure PTFE and PTFE@PDA 24h, and also low antimicrobial activity of the surface treated PTFE HF membranes. Samples containing ZnO = 0.5 mg/mL did not show inhibition properties; nonetheless, those treated samples which incorporated with ZnO = 1mg/mL and ZnO=1.5 mg/mL showed low inhibition zone for both tested bacteria of *E. coli* and *Staphylococcus spp*. (**Figure 4**).

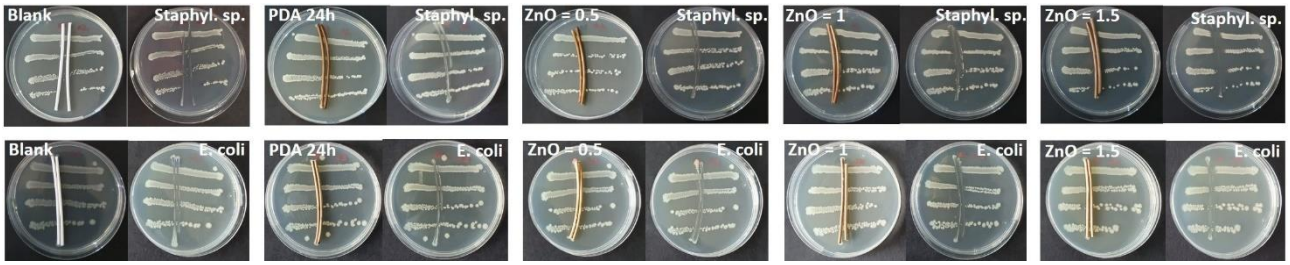

Figure 4 Inhibition zones of specimens against different concentrations of bacterial suspensions

According to the dynamic contact procedure, it can be deduced that the surface-treated PTFE HF membranes by ZnO NPss (containing 0.5 mg/mL, 1 mg/mL, and 1.5 mg/mL) showed favorable antimicrobial activities compared to the blank sample (**Figure 5**). Besides, samples containing 1 mg/mL and 1.5 mg/mL ZnO NPs showed the highest antimicrobial activity. Our observations, even after three times repetitions of experiments, proved the non-antibacterial properties of PDA coating.

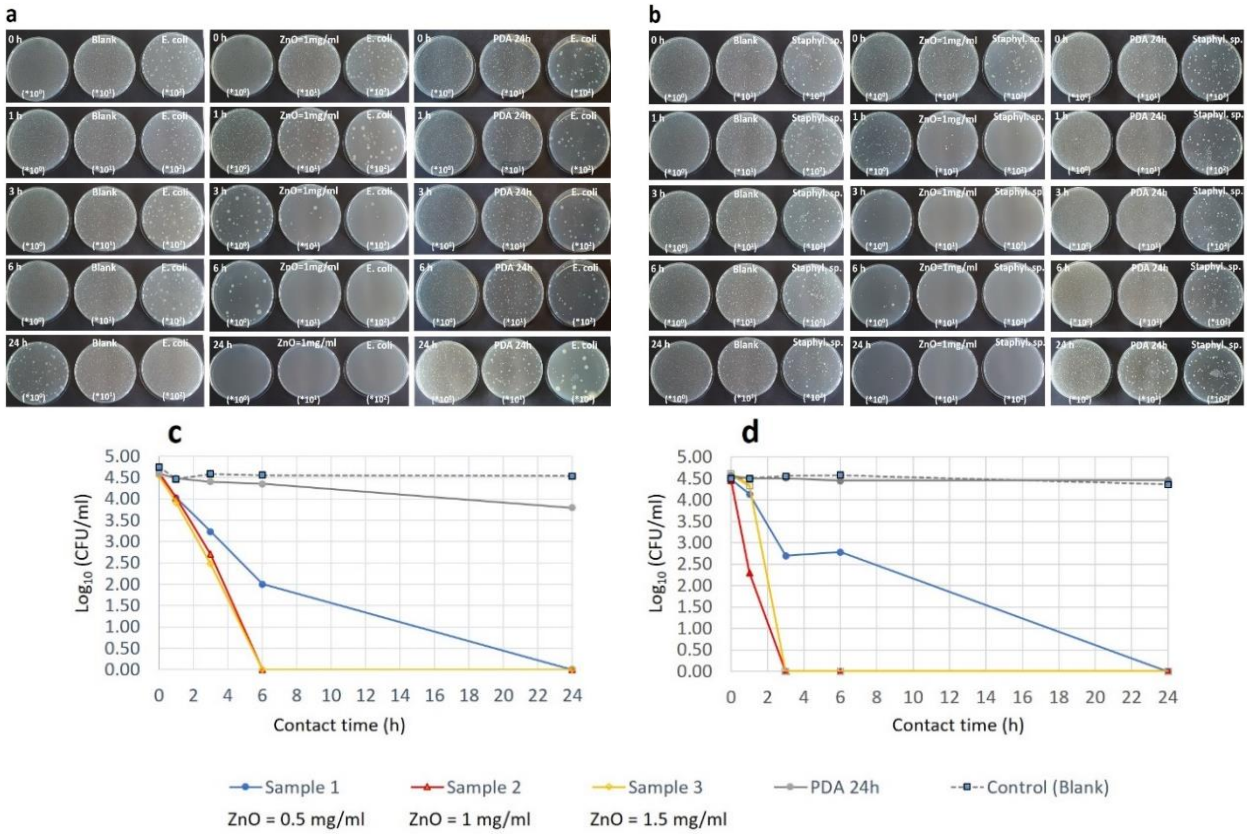

Figure 5 Colony-forming unit (CFU) assays. a) images & c) diagrams of *E. coli* and b) images & d) diagrams of *Staphylococcus spp.* cells grown by inoculation of 10^5, 10^4 and 10^3 cells with blank PTFE HF, PTFE@PDA 24 h, and PTFE@PDA 24 incorporated ZnO=1mg/mL, as the optimum specimen, at various contact time intervals from 0 h to 24 h.

4. CONCLUSION

The surface analysis experiments affirmed satisfactory transformation of the surface characteristics of PTFE HF membrane as one of the most hydrophobic polymers to become super-hydrophilic. In addition, the anti-biofouling capability of the treated membranes was proved by the antimicrobial experiments. Finally, flux and flux recovery filtration tests were performed as a supplement of the experiments to demonstrate the potential capability of the surface-treated PTFE HF membrane to serve in the submerged filtration process.

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