

# NOVEL NANOFIBER MEMBRANES FOR SAFE AND SUSTAINABLE WATER MANAGEMENT

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## **Summary of Scientific Research**

Polymeric membranes are used in water treatment and separation processes. Polyethersulfone (PES) is a preferred choice due to its thermal and mechanical properties, and ease of use, yet faces microbial and biofouling attacks reducing its lifetime. Nanotechnology offers new avenues to improve the performance of these membranes. In this research work, PES nanofibrous membranes were blended with different nanomaterials for wastewater treatment purpose.

The scientific research began by studying the photocatalytic bacterial removal and dye degradation by polyethersulfone (PES) fibers under visible light as reported here. PES fibers were arranged in a random mesh structure using electro-spinning technique that allows utilization of maximum surface area of the fibers. The influence of concentration of PES polymer, type of solvent and surface chemistry of the fibers on their mechanical properties and photocatalytic activities was investigated. The ratio of solvent (DMF (Dimethylformamide) to NMP (N-Methyl-2-pyrrolidone) while preparing the PES fibers was found to be crucial in terms of the PES fiber thickness, fluid flux, mechanical strength and hydrophobicity of the fibers. The as-prepared PES fibers showed considerable amount of OH<sup>•</sup> radical generation under visible light excitation resulting in efficient degradation of model dye contaminant methylene blue (MB) and disinfection of model bacterium Escherichia coli (E. coli). However, increased hydrophilicity of the fibers using oxidation treatment resulted in reduction in the generation of OH<sup>•</sup>

radicals showing less photocatalytic activity by the PES fibers. FTIR investigations confirmed no self-destruction of the PES fibers due to the generation OH% radicals indicating potential application of PES fibers as a useful photocatalytic polymer material for bacterial removal and decontamination of water.

There was an emerging interest in applying the fabricated nanofiber membrane in oil/water separation application to study their fixability. In this work, a new type of ultrafiltration (UF) electrospun nanofibrous membranes (ENMs) incorporating hydrous manganese dioxide (HMO) nanoparticles was fabricated with the objective of improving properties of polyethersulfone (PES)-based membrane for synthetic oily solution treatment. Two treatments were carried out to improve the mechanical property and hydrophilicity of the PES-based membrane without compromising its porosity and water permeance. The first treatment involved the use of mixed solvents – dimethylformamide and n-methylpyrrolidinone (DMF/NMP) in which NMP is a high vapor pressure component that could enhance the mechanical properties of the nanofibrous membrane by improving solvent-induced fusion of inter-fiber junction points. The second treatment involved the incorporation of specific amount of HMO nanoparticles in PES dope solution to enhance membrane hydrophilicity. Heat treatment was also adopted as an effective approach to strengthen and prevent delamination of the nanofibrous mat during UF process. The HMO-incorporated ENMs exhibited an excellent oil rejection (97.98% and 94.04%) and a promising water flux recovery (89.29% and 71.10%) when used to treat a synthetic oily solution containing 5000 or 10,000 ppm oil, respectively. The best promising HMO-incorporated ENM exhibited much higher magnitude of water productivity ( $> 7000 \text{ L/m}^2 \cdot \text{h}^{-1}$ ) without sacrificing oil removal rate. Most importantly, this nanofillers-incorporated membrane showed significantly lower degree of flux decline as a result of improved surface resistance against oil fouling and is of potential for long-term operation with extended lifespan. The promising mechanical and anti-fouling properties of the ENMs is potentially applicable in the efficient industrial oily effluents treatment when challenged with oil-in-water emulsions.

Later, the research team decided to study the effect of different nanomaterial/PES nanofibers in oil/water separation application. This work reports the synthesis and characterization of novel ultrafiltration (UF) electrospun nanofibrous membranes (ENMs) incorporated with iron oxide (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles (NPs) for effective oily solution treatment. Three strategies were employed to improve the physiochemical properties of the resultant ENMs. First, n-methyl-pyrrolidinone (NMP) was added to dimethylformamide (DMF) wherein the solvent stimulated fusion of the inter-fiber junctions was enhanced. Second, Fe<sub>3</sub>O<sub>4</sub> NPs were introduced into the ENMs to improve their hydrophilicity and anti-fouling resistance against oil molecules. Third, hot pressed technique was adopted to strengthen the electrospun mat, avoiding delamination of the ENMs layer during liquid filtration processes. The findings indicated that the developed Fe<sub>3</sub>O<sub>4</sub> NPs incorporated ENMs exhibited outstanding oil elimination (94.01%) and excellent water flux recovery (79.50%) when tested with synthetic oil solution (12,000 ppm). Water productivity of over 3200 L/m<sup>2</sup> .h<sup>-1</sup> was achieved without forfeiting the rate of oil removal under gravity. Extraordinarily low flux declination disclosed by the proposed ENMs was attributed to their tailored surface resistance mediated oil anti-fouling character. The enhanced mechanical and oil anti-fouling traits of the prepared ENMs were established to be potential for the treatment of diverse oily effluents (especially emulsions of oil–water) in the industries. Polymeric membranes are used in water treatment and separation processes. Polyethersulfone(PES) is a preferred choice due to its thermal and mechanical properties, and ease of use, yet faces microbial and biofouling attacks reducing its lifetime. Nanotechnology offers new avenues to improve the performance of their membranes.

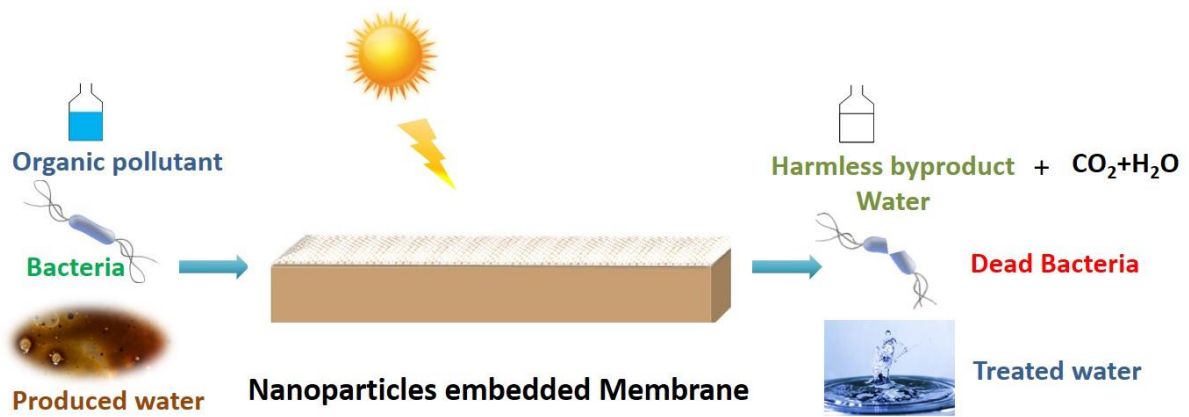


Figure 1. Schematic diagram of wastewater and oily water treatment process using membrane-based nanoparticles under sun irradiation

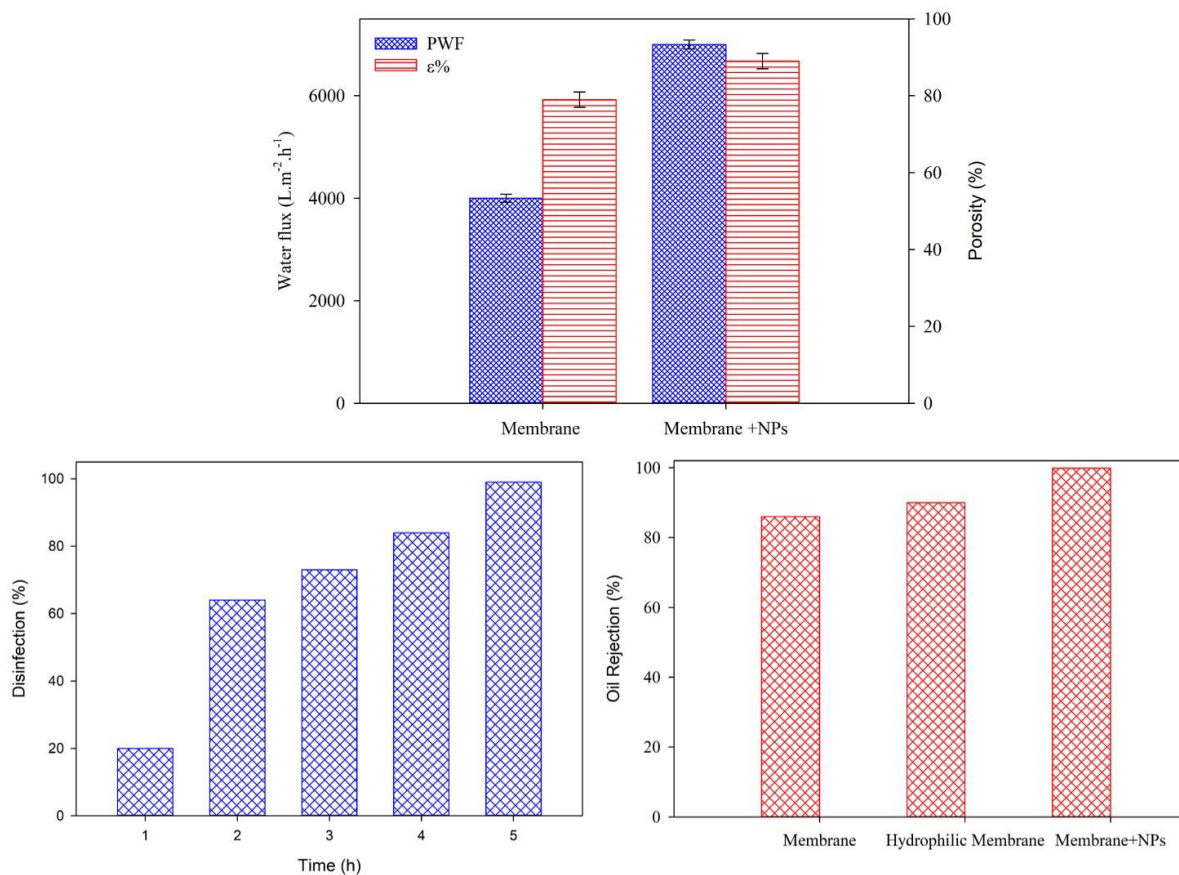


Figure 2: Application of nanocomposite nanofiber membranes in wastewater treatment. a) membrane water flux and porosity, b) disinfection of e-coli bacteria, and c) membrane oil rejection.

In continuation in the same field, the team studied and modified another type of polymer to be used in wastewater application. The main objective of this work is to fabricate and characterize a new type of nanocomposite nanofiber membrane by incorporating photocatalytic

nanomaterials – titanium dioxide (TiO<sub>2</sub>) into a highly porous nanofiber made of UV-resistant polyetherimide (PEI). The nanofiber membrane was fabricated via an electrospinning method using a dope solution containing 15 wt% PEI dissolved in a mixed solvent of dimethylformamide (DMF)/ n-methyl-2-pyrrolidone (NMP). The resultant PEI nanofiber membrane was further modified by coating its surface with TiO<sub>2</sub> (0.2 and 0.6 wt%) using electrospraying method. The properties of the TiO<sub>2</sub>-modified PEI nanofiber membranes were then analyzed using scanning electron microscope (SEM), water contact angle (WCA) goniometer and tensile strength machine. Results showed that 0.2 wt% TiO<sub>2</sub>-modified PEI nanofiber displayed better behaviour by reducing WCA of unmodified nanofiber from 130.25° to 23.35° and improving water flux by 28%. Although the WCA of membrane was further reduced when a higher TiO<sub>2</sub> amount (0.6 wt%) was used, the resultant nanofiber suffered from decreased ultimate strength and significant nanoparticles leaching. Using the best performing 0.2% TiO<sub>2</sub>-modified PEI membrane, significant removal rate of Escherichia coli (99%) and humic acid (~80%) could be achieved along with 85% methylene blue degradation during photocatalytic process. The findings of this work provide an insight into the design of advanced nanocomposite nanofiber membrane for photocatalytic process.

The findings of this research will be able to guide the design of electrospun non-wovens and improve their microbial control in a broad range of application. The nanofiber membranes that can be prepared by the described method exhibit unique porous morphology, and hence feature a number of medical, environmental and energy-related applications. Electrospun nanofibers have drawn considerable attention for application in absorption/filtration of oil/water mixture owing to their high surface to volume ratio. Great achievements made in this field using innovative materials (PES nanofibers/HMO and Iron oxide) and enhanced electrospinning techniques have provided a new future to greatly improve nanofiber membrane performance for oily wastewater treatment. Moreover, the findings have shown that the electrospun nanofiber membranes are promising candidates for oily wastewater treatment in comparison to the conventional ultrafiltration membrane, particularly those incorporating functional nanomaterials. These kinds of

nanofiber membranes exhibited not only extremely high water flux/sorption capacity but also achieved substantial degrees of reuse.

Moreover, the research results reveal that photocatalytic membrane is an emerging technology that is capable of simultaneously separating and degrading organic pollutants (e.g., humic acid (HA) and dyes) present in aqueous solution under visible light or UV-irradiation besides microorganism disinfection. The use of visible light for disinfection purpose is a perfect approach, as almost all Arab countries are rich in solar energy and so low cost.

It can be concluded that the incorporation of electrospun PES nanofiber membrane as part of nanocomposite-based polymer membrane is a promising and interesting development path for the improvement of wastewater treatment via nanotechnology. Moreover, the obtained water needs to follow the required quality of effluent which will depend on the proposed water uses, crops to be irrigated, soil conditions and the irrigation system.

As a recommendation, scaling-up the production of nanofiber membranes is highly required for industrial processes with significantly reduced manufacturing cost.