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Microporous Organic Nanotube Assisted Design for High Performance Nanofiltration Membranes

Muhammad Raheel Ahsan [1], Muhammad Jamal [2], Aneela Bashir [3], Muhammad Tehseen [4]
[1] Comsats University, Pakistan Email: raheelahsan21@163.com*
[2]University of Malakand, Pakistan Email: muhammadjamal.3866.mj@gmail.com*
*[3, 4 *]Chongqing University, China Email:aneelabashir19@gmail.com*

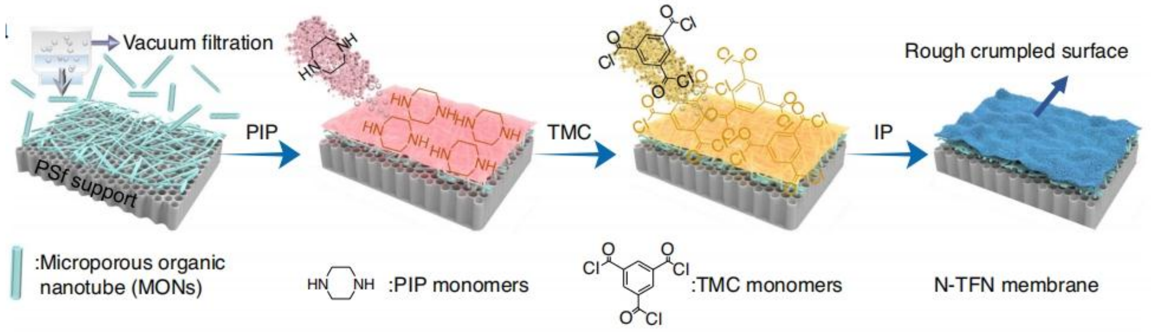
Abstract:
Water scarcity and pollution have become pressing global issues, necessitating the development of advanced filtration technologies capable of addressing these challenges. Nanofiltration (NF) membranes, known for their ability to separate divalent and monovalent ions, have shown great promise in water purification. However, traditional NF membranes face significant limitations in terms of water permeability, ion selectivity, and fouling resistance, which restrict their efficiency in real-world applications. This study presents a novel approach that incorporates microporous organic nanotubes (MONs) derived from covalent organic frameworks (COFs) to enhance the performance of polyamide-based NF membranes, providing a potential solution to these limitations. The integration of COF-derived MONs into the membrane structure improves the morphology, permeability, and separation efficiency of the polyamide selective layers. By acting as an interlayer in the interfacial polymerization (IP) process, MONs help to fine-tune the polyamide formation, resulting in thinner, more uniform membranes with enhanced porosity. This modification not only improves the water flux but also increases ion selectivity and fouling resistance, making the membranes more durable. The MONs' high surface area and tunable pore sizes provide additional channels for water transport, allowing for improved membrane performance without compromising its selective capabilities.

The experimental results demonstrate that the MON-modified thin-film nanocomposite (N-TFN) membranes exhibit significantly higher water permeability (41.7 Lm−2 h−1 bar−1) and excellent retention of ions like **boron** *(78%) and* **phosphorus** *(96.8%) under alkaline conditions. These membranes also show high rejection for sulfate ions, offering superior ion selectivity. The introduction of MONs leads to enhanced membrane stability and long-term performance, even under challenging filtration conditions. The findings suggest that MON-modified NF membranes could serve as highly effective materials for water purification, desalination, and wastewater treatment applications.*

Keywords*: Nanofiltration membranes, microporous organic nanotubes, covalent organic frameworks, water permeability, ion selectivity, fouling resistance, interfacial polymerization, membrane modification, boron removal, phosphorus removal.*

Introduction to Microporous Organic Nanotubes (MONs) and Nanofiltration (NF) Membranes:

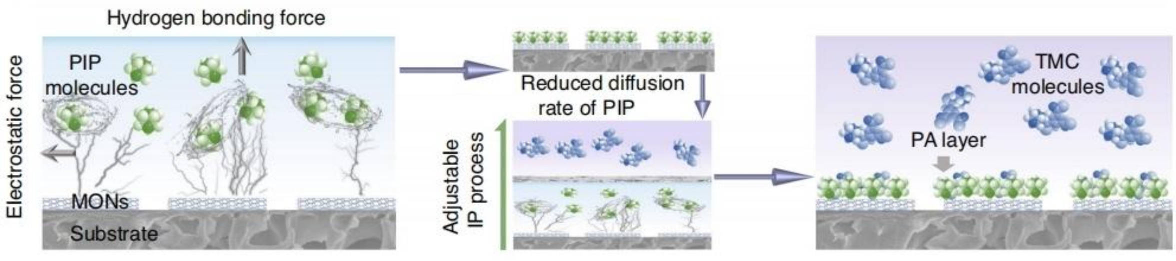
The growing global concerns of water contamination, resource scarcity, and wastewater treatment have necessitated the development of advanced filtration technologies to ensure sustainable water management[1]. Clean water is increasingly becoming a precious resource, with industrial processes, agriculture, and domestic use placing immense pressure on freshwater supplies. Traditional water treatment methods, including reverse osmosis and activated carbon filtration, have been widely used for desalination and wastewater treatment[2-10]. However, these methods often suffer from high energy consumption, large-scale infrastructure requirements, and limited selectivity [11], especially when dealing with complex mixtures containing ions, organic molecules, and micro-pollutants. Nanofiltration (NF) membranes have emerged as an alternative solution for efficient water purification due to their ability to selectively remove ions, small organic molecules, and pollutants[12-19]. NF membranes operate by sieving solutes based on their size and charge, making them suitable for a range of applications including desalination, softening, wastewater reuse, and food and beverage processing. Despite their versatility, traditional NF membranes face significant limitations, particularly in terms of low permeability, inadequate selectivity for specific ions, and a tendency to foul over time due to organic and inorganic deposition on their surfaces. These challenges hinder the efficiency and cost-effectiveness of NF technology in large-scale water treatment applications [20].



1. preparation process of N-TFN membrane

To address these issues, researchers have focused on developing new materials and modifying existing membrane structures. One promising approach is the incorporation of functional nanomaterials into the membrane matrix to enhance their performance[21]. These materials can improve various properties of NF membranes, such as permeability, selectivity, fouling resistance, and mechanical stability. Microporous organic nanotubes (MONs), a class of materials derived from covalent organic frameworks (COFs), are one of the most promising candidates for membrane modification. MONs are nanostructures formed by organic building blocks linked via stable covalent bonds, which provide them with unique properties such as high surface area, tunable pore size, excellent chemical stability, and superior polymer affinity. These characteristics make MONs highly attractive for enhancing membrane performance in filtration applications. Unlike traditional inorganic nanomaterials, MONs offer the advantage of being lightweight, flexible, and chemically versatile, with their pore size and surface chemistry adjustable to suit specific separation requirements[22].

The structural integrity of MONs ensures that they remain stable under harsh operational conditions, such as high pressure and diverse pH environments, commonly encountered in water filtration. The high surface area of MONs also creates additional nanoscale channels within the membrane, improving water flux while maintaining precise solute separation. Their high polymer affinity is a key feature that allows for seamless integration with the polymeric matrix of polyamide NF membranes[23]. This affinity reduces the risk of defects and enhances the interfacial adhesion between the membrane's selective layer and the underlying support, leading to a more uniform and stable membrane structure. By incorporating MONs into polyamide NF membranes, it is possible to achieve membranes that exhibit improved selectivity, higher water permeability, and fouling resistance compared to conventional polyamide membranes[24]. This work explores the incorporation of COF-derived MONs into polyamide NF membranes, demonstrating their potential for optimizing membrane performance for precise solute separation, specifically targeting challenging contaminants like boron, phosphorus, and other trace ions that are difficult to remove with traditional NF membranes [25].



2. Schematic depiction of the IP process modulated by hydrogen bonding and electrostatic interactions.

Furthermore, the integration of MONs into the interfacial polymerization (IP) process, which is used to form the polyamide selective layer, allows for better control over the pore structure and thickness of the membrane [8]. This modification results in the formation of membranes with enhanced microporosity, offering more efficient pathways for water transport[26]. By regulating the IP process using MONs, the membrane's pore size distribution can be finely tuned, allowing for more precise separation of ions based on size and charge. Additionally, the unique ability of MONs to act as fouling-resistant interlayers ensures the longevity and durability of the membranes in real-world applications, where fouling and scaling are major challenges.

This study aims to optimize the use of MONs derived from COFs in polyamide NF membranes, offering a new approach to membrane design that combines advanced nanomaterial properties with practical separation capabilities[27,2]. The results highlight the potential of these modified membranes in improving water treatment efficiency, reducing energy consumption, and enabling the selective removal of both small organic molecules and inorganic ions. By enhancing the structural properties of NF membranes, MONs offers a promising solution for meeting the increasing demands of water purification in an environmentally sustainable and economically feasible manner.

Fabrication and Structural Design of MON-Modified NF Membranes:

The study explores the fabrication of high-performance NF membranes by incorporating COF-derived MONs into the membrane structure using interfacial polymerization (IP). The COFs used in this study are designed to produce organic nanotubes (NT-OEt) upon selective hydrolysis [28], which are then assembled onto a polysulfone (PSf) support via vacuum-assisted filtration. This pre-assembly of the MON layer ensures that the nanotubes are uniformly distributed on the support surface, which is crucial for optimizing the subsequent IP reaction[4].

The IP process is employed to form a thin polyamide selective layer on top of the MON-modified support. The introduction of MONs into the IP process has a significant impact on the morphology and properties of the final membrane[30]. The resulting polyamide membranes, referred to as N-TFN membranes, exhibit a unique Turing structure, characterized by stripe-like patterns that enhance the overall surface roughness. This surface structure is beneficial for increasing membrane hydrophilicity, improving water transport, and reducing fouling tendencies.

Characterization of Membrane Structure and Morphology:

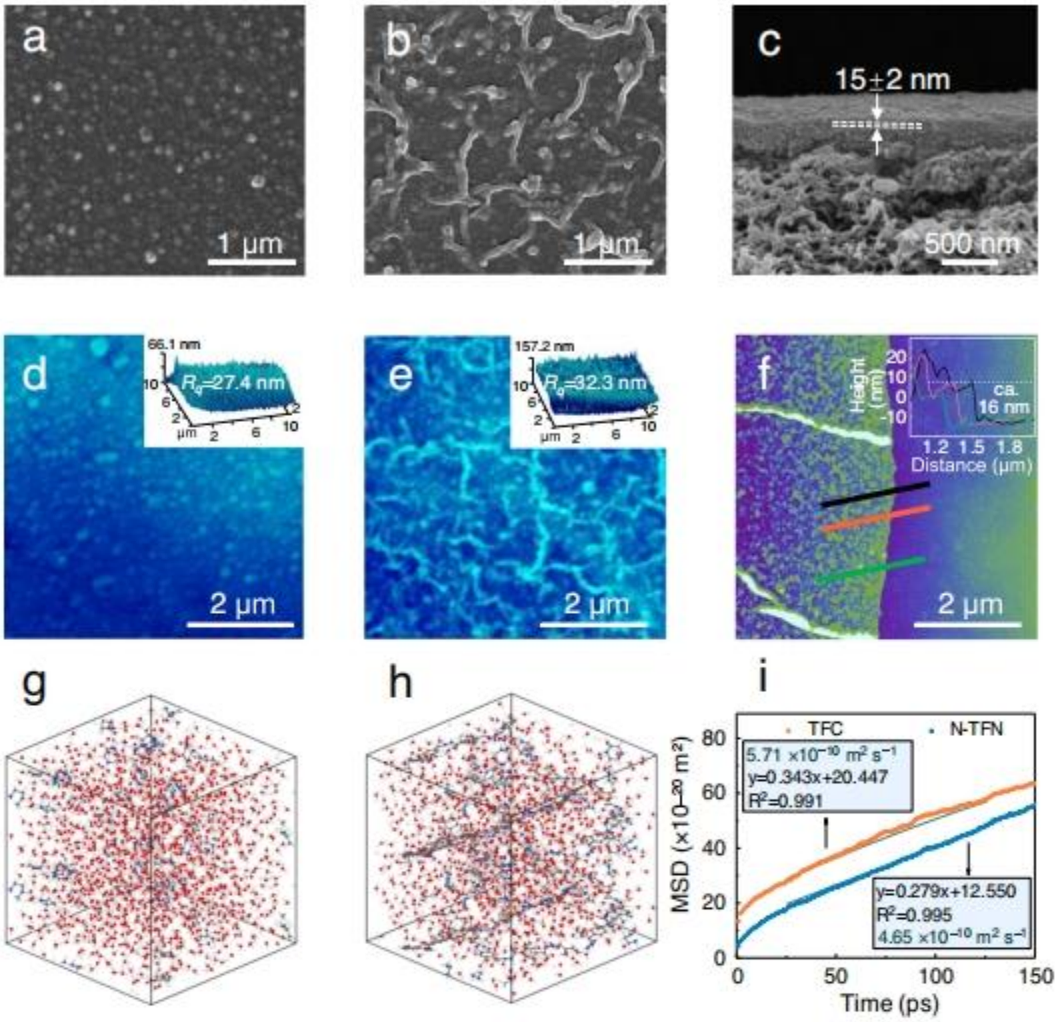
The structural properties of the MON-modified NF membranes are thoroughly characterized using a variety of techniques, including scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS)[2], and Fourier-transform infrared spectroscopy (FTIR) [22]. These analyses reveal that the incorporation of MONs significantly alters the membrane morphology, with the N-TFN membranes displaying increased surface roughness and a distinct Turing structure compared to the traditional thin-film composite (TFC) membranes.

The thickness of the N-TFN polyamide layer is notably reduced to approximately 15 nm, compared to the 118 nm thickness of the traditional TFC membranes. This reduction in thickness contributes to improved water permeability without compromising solute rejection [31]. The high degree of porosity and free volume in the N-TFN membranes, facilitated by the MONs, plays a crucial role in enhancing their separation performance.

Molecular Dynamics Simulations:

To gain further insights into the impact of MONs on the membrane performance, molecular dynamics (MD) simulations are conducted to analyze the diffusion behavior of amine molecules during the IP process. These simulations reveal that the MONs slow down the diffusion of amine monomers (PIP) towards the organic phase boundary, leading to the formation of thinner and more uniform polyamide films[32-35]. This result is consistent with the experimental observations, which show that the incorporation of MONs reduces the thickness of the polyamide layer and improves its microporosity.

The MD simulations also highlight the role of MONs in increasing the density of water molecules around the membrane pores, which contributes to enhanced water transport and permeability. Additionally, the simulations show that the incorporation of MONs improves the interconnectivity of pores in the polyamide membrane, facilitating efficient ion transport.



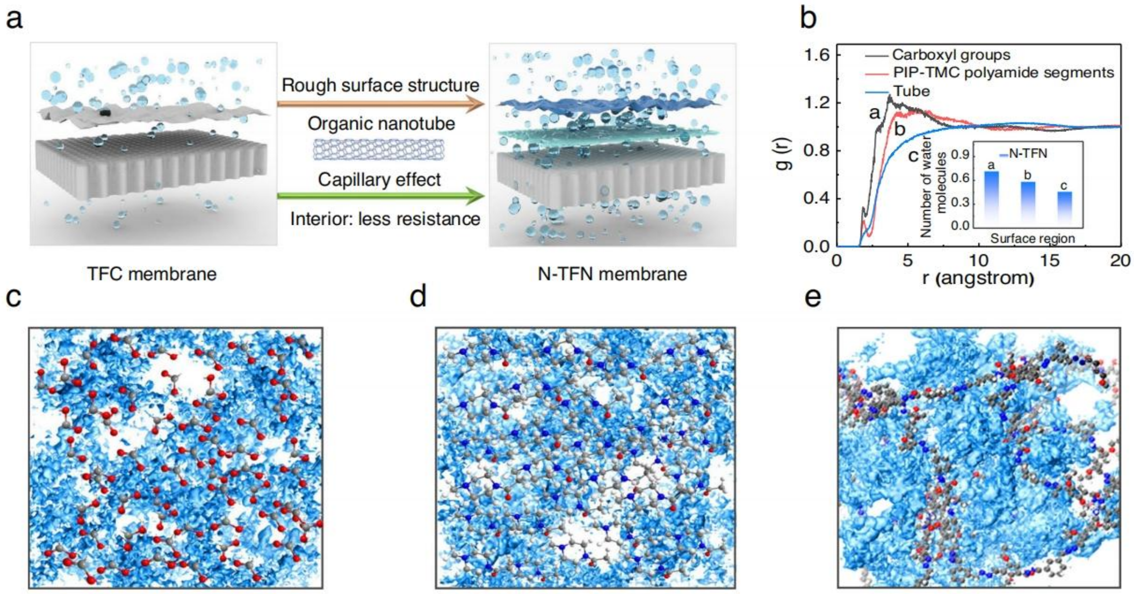
3. Simulations of Membrane morphologies altered by the interfacial polymerization process

Performance Evaluation of the N-TFN Membranes:

The performance of the MON-modified N-TFN membranes is evaluated through a series of filtration tests using different solute solutions. The results demonstrate that the N-TFN membranes exhibit remarkable separation performance, with high water permeability (41.7 Lm−2 h−1 bar−1) and excellent rejection rates for ions such as sodium sulfate (Na2SO4) and magnesium sulfate (MgSO4). The rejection rates for these ions are consistently higher than those observed for traditional TFC membranes[13].

One of the most striking features of the N-TFN membranes is their ability to achieve high retention rates for trace contaminants such as boron and phosphorus, which are typically difficult to remove using conventional NF membranes. The N-TFN membranes demonstrate up to 78% boron removal and 96.8% phosphorus removal at alkaline pH (pH 10), which is significantly higher than the performance of TFC membranes [37-40].

The N-TFN membranes also exhibit excellent long-term stability, with consistent performance over extended filtration cycles. During a 100-hour filtration test, the N-TFN membranes maintain high water permeability and solute rejection rates, showcasing their potential for real-world applications.



4. Water transport properties across the N-TFN membrane

Discussion and Conclusion:

This study presents a novel approach to designing high-performance NF membranes by incorporating microporous organic nanotubes (MONs) derived from COFs. The MON-modified polyamide membranes exhibit enhanced water permeability, improved solute selectivity, and excellent fouling resistance. The unique properties of MONs, such as their high porosity, tunable chemical functionalities, and polymer affinity, enable the precise regulation of the interfacial polymerization process, leading to the formation of thinner, more uniform polyamide layers with enhanced microporosity.

The N-TFN membranes demonstrate superior performance in terms of water permeability and ion selectivity compared to traditional TFC membranes. Additionally, the ability of the N-TFN membranes to remove trace contaminants like boron and phosphorus highlights their potential for addressing critical environmental challenges, such as eutrophication and trace pollutant removal in water treatment.

Overall, the results of this study provide a promising pathway for the development of next-generation NF membranes with tailored properties for precise solute separation . The incorporation of MONs into the membrane structure offers a new approach for enhancing membrane performance, with applications ranging from desalination to wastewater treatment and beyond This work lays the foundation for further research into the use of functional nanomaterials for membrane fabrication and provides valuable insights into the design of advanced filtration technologies.

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