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Structural Studies and Applications of Sulfobetaine-Based Polybetaines at Interfaces

The main goals of this research endeavor are to enhance the hydrophilic properties and water permeability of a nanofiltration membrane. This is achieved by incorporating a Zeolitic imidazolate framework (ZIF-8) layer that has been stabilized utilizing a redox-grafted methacrylate hydrogel. The decision to use polyacrylonitrile (PAN) as the substrate material was motivated by its intrinsic hydrophilic properties, which contribute to its ability to resist fouling and promote water permeability. The shift of the surface from hydrophilic to superhydrophilic was confirmed using physicochemical evaluations, including scanning electron microscopy (SEM) and contact angle measurements. Hydrolyzed Polyacrylonitrile Zeolitic imidazolate framework grafted (HPANZifG) membrane exhibited a remarkably high-water flux of 82.3 L/m^2 Bar hour, which is an achievement of notable significance. This study makes a valuable contribution to the advancement of nanofiltration technology by proposing potential solutions to the challenges faced in the field of water purification and treatment.

Keywords: Sulfobetaine, Zwitterionic polymer, membrane modification, nanofiltration, Metal-Organic Framework (MOF), ZIF-8 layer, redox grafting, water flux, polyacrylonitrile (PAN).

Introduction

Water is an essential requirement for the sustenance of both human societies and ecological systems that exist within the confines of the planet Earth. The fraction of freshwater within the Earth's total water resources is estimated to be around 2.5 %. This percentage has undergone a decline due to several factors, including contamination and the impacts of climate change [1, 2]. According to recent research conducted by the World Health Organization (WHO), a considerable segment of the global population, comprising more than 1.6 billion individuals, confronts the issue of insufficient access to water sources that adhere to the necessary safety criteria [3–6]. It is anticipated that by the year 2025, almost 50 % of the global population would inhabit areas that are confronted with substantial water scarcity issues [7].

Currently, there are three viable strategies that show potential in enhancing clean water resources and effectively addressing the issue of water scarcity. The first approach involves facilitating the reuse of water obtained from wastewater and other sources of degraded water. The second approach entails extracting freshwater from seawater through the process of desalination. Lastly, the third approach involves the collection of moisture from the atmosphere [8].

At present, the issue has become an urgent matter for scientists to solve worldwide. The current technology used includes thermal, chemical, and membrane. Among them, the membrane technology is the most popular for desalination of water. Membrane technology is divided in two: reverse osmosis and electrodialysis.

Electrodialysis method is economical, operational at room temperature and continuous process. Nevertheless, the disadvantages include the removal of colloidal impurities, and the consumption of a huge amount of electricity. On the contrary, the reverse osmosis semipermeable membrane is a robust technology, easily eliminating colloidal and suspended impurities. A sustainable water supply system is feasible with this type of method due to its cost-effectiveness. The membrane-based advanced technologies could potentially offer a sustainable technical solution to global resource shortages. However, the establishment of sustainable membrane technologies with energy-efficient, eco-benign and scalable separation in comparison with conventional processes is still challenging [9].

Zwitterions are molecular entities characterized by an equal number of positive and negative charges that are connected by covalent bonds. These molecules possess remarkable resistance to fouling, which can be attributed to their significant level of hydration. Numerous studies have utilized the characteristic of zwitterionic groups to improve resistance against fouling [10, 11]. This has been achieved through two main approaches: altering the surface chemistry of the membrane to incorporate zwitterionic moieties [12–15], or applying zwitterionic hydrogels as coatings on the membranes. Zwitterions exhibit a high degree of polarity, hence inducing microphase separation in many copolymer systems containing zwitterionic moieties [16, 17].

Polymers possess favorable characteristics in terms of their ability to create membranes and their cost-effectiveness as resources [18]. Various efficient techniques, including non-solvent induced phase separation (NIPS), interfacial polymerization, and solution coating, have been widely adopted for the fabrication of polymer membranes, which currently hold a prominent position in the membrane market [19]. However, in typical cases, dynamic polymer chains are commonly interwoven and densely packed, leading to limited available spaces with varying diameters. These features not only increase the difficulty to mass movement over the membrane, but also decrease the precision of separation. Consequently, the implementation of nanofluidics transport in traditional polymer membranes has been limited. In recent studies, it has been discovered that the incorporation of twisted monomers [20] and crystalline porous organic frameworks [21] can significantly improve the structural stiffness and microporosity of polymer membranes. Metal-organic frameworks (MOFs) are a novel class of porous crystalline materials that combine organic and inorganic components. These materials possess a large surface area and can be tailored to have specific pore structures. They have been extensively employed in the production of separation membranes using different techniques such as physical blending, direct/secondary growth, layer-by-layer assembly, and contra-diffusion methods [22]. While MOF-based membranes do demonstrate enhanced water penetration, the formation of continuous nanochannels in the membrane without intercrystallite cracks remains a significant challenge. Furthermore, it should be noted that the water permeability of these membranes is currently subpar when compared to state-of-the-art nanofluidic membranes. Additionally, the synthetic process for these membranes is somewhat complex. Hence, the development of efficient polymeric nanofluidic membranes continues to be a complex and unresolved task in the field of advanced molecular separation [23].

The main goal of this research was to establish a chemical method for stabilizing a ZIF-8 layer on an ultrafiltration membrane using a redox-grafted methacrylate hydrogel. This approach aimed to enhance the water flux and hydrophilicity of the membrane. The selection of the polyacrylonitrile (PAN) membrane as the porous support was based on its hydrophilic properties, which contribute to improved antifouling effects and water permeability. The confirmation of the chemical structure of the membrane was achieved by the utilization of attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy. The membranes were subjected to physicochemical evaluation using scanning electron microscopy (SEM) and contact angle measurements. The membrane's performance in terms of pure water permeance was assessed in order to showcase the effectiveness of the synthesized membrane in water treatment applications.

Experimental

Materials

Polyacrylonitrile (PAN) powder with a weight-average molecular weight (Mw) of 150 000 g/mol was purchased from Sigma-Aldrich, Polyvinyl pyrrolidone (PVP) 29 000 g/mol, [2 (Methacryloyloxy)ethyl] dimethyl-(3-sulfopropyl) ammonium hydroxide (SBMA, ~95%), N,N'-methylenebisacrylamide (MBA, ~99 %), zinc nitrate hexahydrate (~99 %), N,N-Dimethylformamide (DMF,~99.8%), 1-vinylimidazole (1-VIM ~99 %).

Fabrication of the membranes

Figure 1 illustrates the schematic preparation of the zwitterionic PAN membrane. To enhance membrane porosity, we introduced PVP as a pore-forming agent, guided by previous studies [24]. PVP, recognized for its CH_2, C–O, and C–N functional groups, serves as an effective pore-forming agent, increasing the number of pores per unit surface area without altering their size or distribution, as documented in the literature [25]. For the preparation of a homogeneous casting solution, 11 wt. % PAN powder and 5 wt % PVP were dissolved in DMF. This polymer ratio of PAN to PVP was meticulously selected to pursue optimal membrane properties, capitalizing on the unique advantages associated with PVP in membrane synthesis. The mixture was dropped onto a clean glass plate and then was cast with a knife (150 μm). The liquid PAN membrane was solidified in a pure water bath. The hydrolyzed membrane (PAN-COOH) was prepared by immersing the pure PAN membrane samples in a NaOH solution (2 mol/L) at 60 °C for 1.5 hours. It was then extensively washed with distilled water until pH neutrality. The hydrolyzed membrane is referred to here as the HPAN.

The synthesis of ZIF-8 nanoparticles within the HPAN membrane.

The HPAN membrane was incubated in an aqueous solution of $Zn(NO_3)_2{\cdot}6H_2O$ (1.25 g in 50 mL) for 12 hours with shaking. The $Zn(NO_3)_2{\cdot}6H_2O$ aqueous solution was discarded, the membrane was washed with distilled water for 15 seconds, treated with an aqueous solution of 1-VIM (2.75 g in 50 mL) for 1 hour with shaking, then gently washed three times with 50% aqueous methanol. The HPAN membrane with in situ-grown ZIF-8 nanoparticles is referred to as the HPANZif membrane.

Redox-initiated graft polymerization on the membrane

The membrane was initially treated with an aqueous solution of 1.0 M SBMA (40 mL) containing 5 wt% MBA (as a crosslinker) and shaken for 10 minutes before adding 0.2 M $K_2S_2O_8$ aqueous solutions (10 mL) in sequence and shaking for 40 minutes. The reaction was stopped by removing the reaction mixture and washing the membrane thoroughly with distilled water. The HPANZif membrane corresponds to the HPANZif-Grafted membrane.

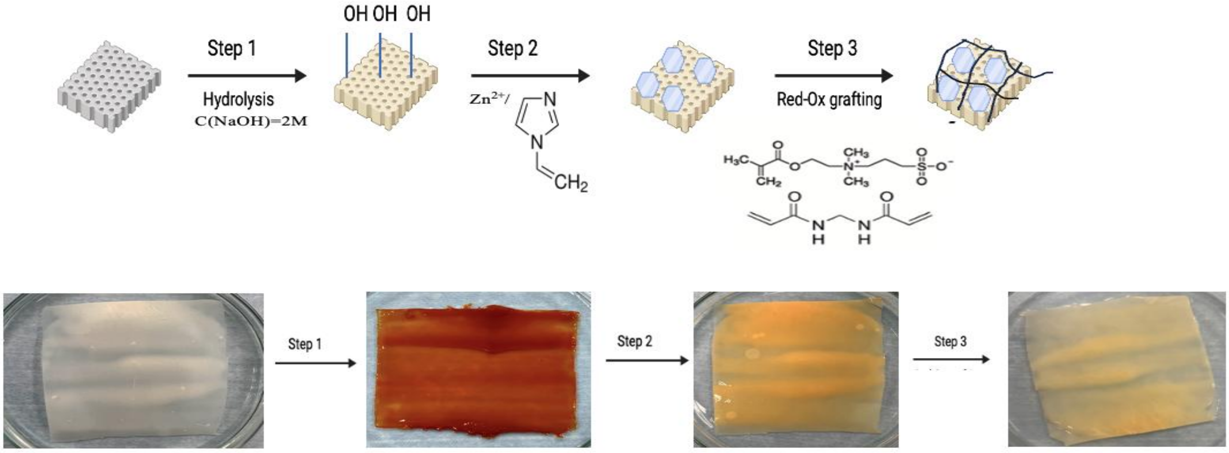


Figure 1. Preparation of HPANZif-grafted membrane

Characterization

Fourier transform infrared spectroscopic investigation was carried out using the Nicolet iS10 FT-IR spectrometer. In the FTIR analysis of polymers, a small amount of the sample was placed at the center of the ATR plate's diamond crystal. Gentle pressure was applied to ensure contact. A background spectrum was recorded for reference. The FTIR spectrum was recorded using a calibrated instrument. The ATR plate was cleaned to prevent contamination. These steps ensured accurate polymer characterization.

Scanning electron microscopy ZEISS, Crossbeam 540 was used to observe the surface and cross-section structure. In SEM analysis of membranes, a 10 nm gold coating is applied using a high-vacuum coater for enhanced conductivity and sample detail preservation. A 15 kV electron beam was used for all the membrane samples.

Automatic Sputter Coater Q150T was employed to coat the surfaces of the samples. The water contact angle (WCA) of membrane was evaluated by a water contact angle instrument Dataphysics OCA 15Pro. To ascertain contact angle values, a 5μL droplet volume was utilized, and contact angle measurements were conducted immediately after the droplet was dispensed onto the membrane surface.

All membrane samples were dried overnight before characterization.

Water Flux in Membrane Systems

The membranes' pure water flux was evaluated at 1 bar using dead- end stirred cell filtration experiments. After achieving a steady flow with at least 30 minutes of filtration, the pure water flux of each membrane was calculated using Equation (1):

$$\text{Pure water flux} = \frac{V}{A \times P \times t}, \tag{1}$$

where V is the volume of permeate water (L), A is the effective membrane area, and t is the time length (h). For each membrane, at least three readings were collected.

Results and Discussion

The central objective of this research project was to develop a specialized membrane that had been modified with the zwitterionic ZIF-8. This tailored membrane was envisioned to exhibit significantly enhanced water permeability, exceptional resistance to salt, and an outstanding ability to effectively remove salt during the treatment of seawater. The goal was to address the critical need for more efficient and robust membranes in the fields of desalination and seawater treatment, ensuring a sustainable and reliable source of freshwater in regions with limited access to clean water resources.

Figure 2 shows the FTIR spectra of the changed membranes, which are presented in comparison to the pristine PAN membrane. The FTIR spectrum of the pristine PAN membrane had peaks at 1451 $\text{cm}^{-1}$and 2243 cm^{-1}, corresponding to the C–N stretching of the –C≡N group. Hydrolysis of the PAN membrane (HPAN membrane) resulted in prominent peaks at (3369 cm^{-1}) corresponded to the O–H moieties of carboxyl groups on the membrane surface. The appearance of the peak confirmed partial hydrolysis of the PAN membrane. In situ growth of ZIF-8 nanoparticles on the HPAN membrane provided HPANZif membrane, which showed peaks characteristic of ZIF-8 nanoparticles (652cm^{-1}), corresponding to the stretching vibrations of the ZnO bond in octahedral coordination, the bending vibration of the imidazole ring, the bending vibration of the $–\text{CH}_2$ (757 cm^{-1} group in 1-vinyllimidazole respectively. The appearance of these peaks confirmed the presence of ZIF-8 nanoparticles on the membrane surface. Grafting poly (methacrylate) hydrogel on HPAN membrane provided HPANZifG membrane with peaks at 1043 cm^{-1} (sulfonate S=O stretch), 3188 cm^{-1}, 1563 cm^{-1} (CO–NH) stretching vibration of the amide group, corresponding to the stretching vibration of N–H in the amide groups of poly(MBA-co-SBMA). The appearance of these peaks confirmed the presence of grafted methacrylate hydrogel on the membrane surface. The FITR spectrum of the HPANZifG membrane had peaks characteristic of the ZIF-8 nanoparticles (observed in the FTIR spectrum of the HPANZif membrane) and from grafted methacrylate hydrogel, confirming modification of the membranes with the ZIF-8 nanoparticles and grafted hydrogel. These various groups on the surface of the membranes affect the surface properties of the membranes.

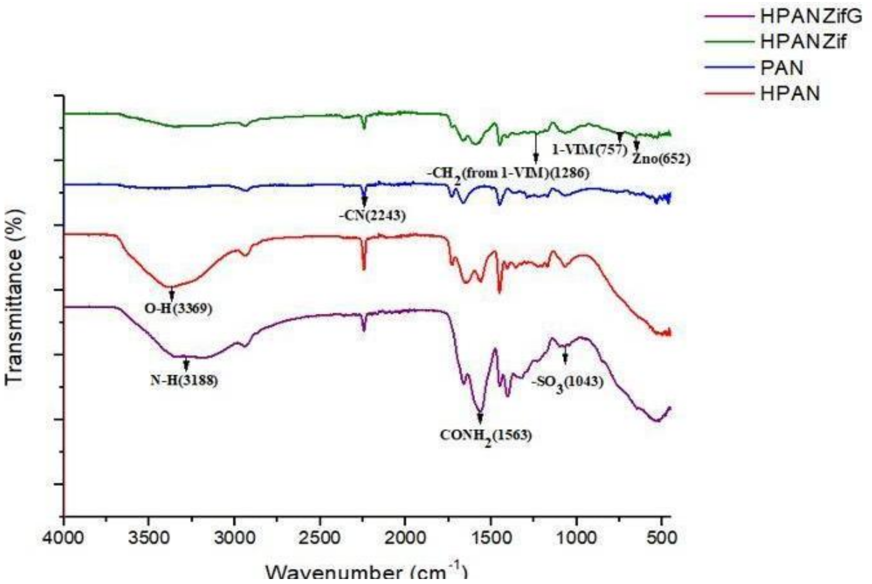
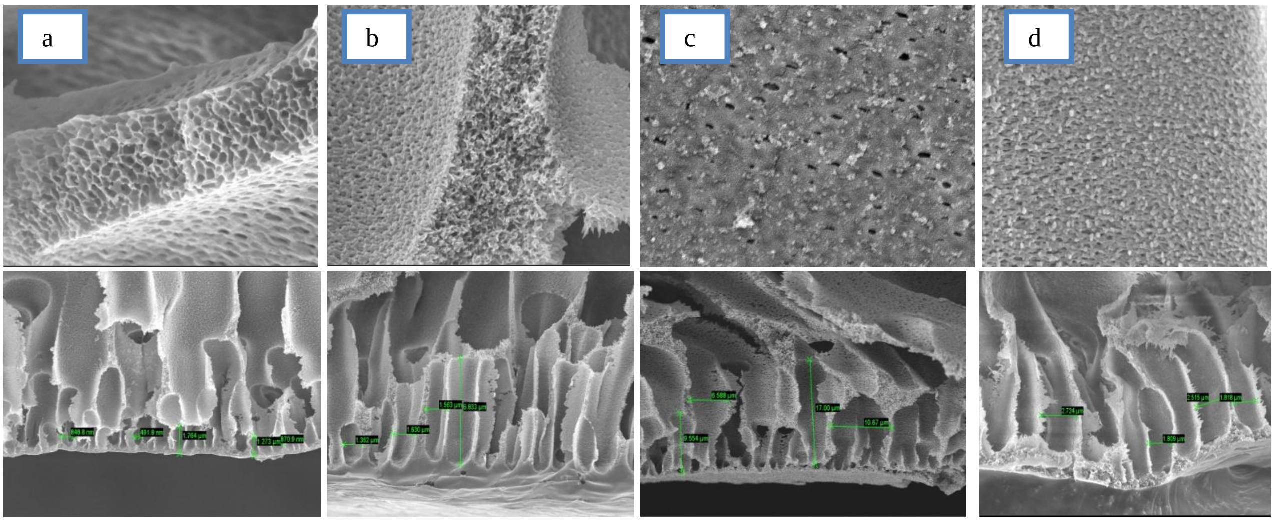


Figure 2. FTIR spectra of prepared membranes.
The presence of characteristic functional groups on the membranes confirmed the modifications

Morphological Analysis of the Membranes

SEM was used to examine the morphology of the produced membranes. The formed membrane's cross-sectional morphology, as shown in Figure 3 consists of a skin layer and a porous sublayer, which result from the instantaneous phase separation of the PAN casting solution during manufacture. It should be noted that the surface grafting of PSBMA chains had no influence on the cross-sectional morphology of the membranes. Figure 3 depicts the surface structures of the membranes PAN (surface: 300 nm, cross-section: 1 μm), HPAN (surface: 300nm, cross-section: 1μm), HPANZif (surface: 1μm, cross-section: 3μm), and HPANZifG (surface: 300nm, cross-section: 1μm). Micropores form on the PAN membrane surface, whereas new, larger holes form on the PAN-COOH membrane due to pore formation during C≡N hydrolysis.



a — PAN (surface: 300 nm, cross-section: 1 μm); *b* — HPAN (surface: 300 nm, cross-section: 1 μm);
c — HPANZif (surface: 1 μm, cross-section: 3 μm), *d* — HPANZifG (surface: 300 nm, cross-section: 1 μm)

Figure 3. Surface and Cross-Section SEM Images of Zwitterion Modified PAN Membranes

The cross-sectional images of these membranes provide unambiguous visual evidence of the sizes of the continuous water channels, which displayed an average size.

The channels in the unaltered PAN membrane had a diameter of 736 nm, which is a commonly observed dimension for pristine PAN membranes.

Upon undergoing hydrolysis to generate HPAN, the resulting cross-sectional image had a diameter measuring 1,525 μm. The observed increased dimensions are commonly observed in hydrolyzed polyacrylonitrile (PAN) membranes.

The HPANZif membrane, which integrates a Metal-Organic Framework (MOF), exhibited a significant augmentation in channel diameter, reaching a value of 8,629 μm. The significant rise can be attributed mostly to the organized crystal channels present in the MOF substance. These channels provide a clearly defined route for water molecules, hence substantially improving water permeability.

The cross-sectional image of the HPANZifG membrane reveals a significant augmentation in the diameter of water channels as compared to the unmodified PAN membrane. Nevertheless, the precise numerical value for this diameter is not included in the available data. However, it is evident that the incorporation of zwitterions greatly enhances the permeability of water channels, resulting in a membrane that exhibits increased hydrophilicity and facilitates efficient water transportation.

In conclusion, the cross-sectional photographs of the membranes revealed the dimensions of their uninterrupted water channels, and it is worth mentioning that all of the membranes had sizes falling within the average spectrum. The provided information highlights the conventional or customary channel dimensions for each of the individual alterations, which might be significant when assessing their efficacy in diverse applications such as desalination and filtration.

Surface Wettability of the Membranes

The surface wettability of the prepared membranes was characterized based on the dynamic contact angles in pure water. Figure 4 presents a collection of contact angle data that offer a comprehensive analysis of the surface properties shown by PAN, HPAN, HPANZif, and HPANZifG membranes. The initial contact angles provide insight into the wettability of the membranes. The PAN membrane demonstrates an initial contact angle of approximately 60°±2°, indicating a surface that is moderately hydrophilic and promotes the wetting and spreading of water droplets. In contrast, the HPAN, HPANZif, and HPANZifG materials exhibit lower initial contact angles, precisely measuring at 35°±1.5°, 30°±0.8°, and 15.5°±1.1°, respectively. These values indicate a noticeable tendency towards the development of hydrophilic surfaces that facilitate the rapid spreading of water droplets.

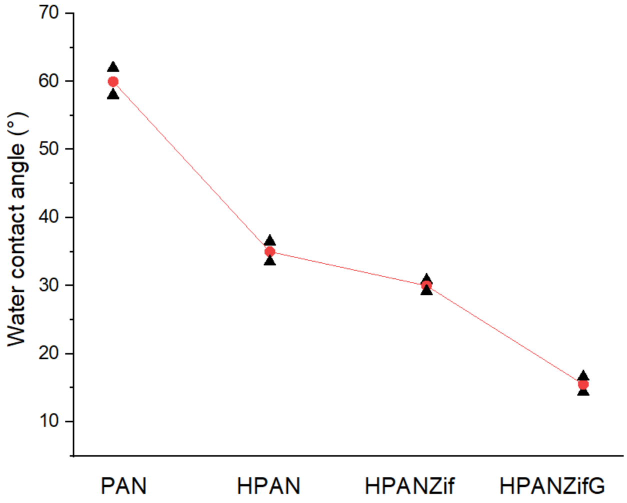


Figure 4. The water contact angles of PAN membranes supplemented by zwitterion

The observed decrease in contact angle across the membranes suggests a significant transition from hydrophilic to super hydrophilic surfaces, which can be attributed to the integration of extremely hydrophilic functional groups. Significantly, in the instance of HPANZif, the incorporation of MOFs results in the formation of crystalline structures with continuous water channels. This introduces a well-organized and porous framework that effectively boosts the membrane's hydrophilic properties. The presence of hydrophilic functional groups, in conjunction with other factors, leads to the observation of remarkably low initial contact angles. This further strengthens the hyper hydrophilic characteristics exhibited by these surfaces.

The utilization of zwitterionic functional groups and MOF structures to improve surface wettability has significant ramifications in various scientific and industrial applications. This is particularly important in situations where efficient water transport and strong interactions with material surfaces are crucial.

The differences in pure water flux among PAN, HPAN, HPANZif, and HPANZifG membranes, as shown in Figure 5, are significant. These values represent the average pure water permeances, with respective measurements of 60.32, 65.89, 76.05, and 82.3L/h·bar·m^2.

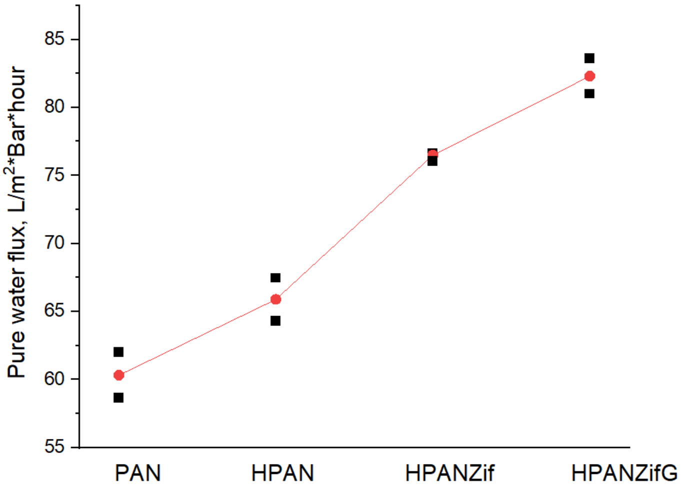


Figure 5. Pure water permeance of the prepared membranes

The HPANZifG material exhibits the maximum water flux due to the presence of uninterrupted water channels and the grafting of zwitterions. The alterations made facilitate an atmosphere that is favorable for efficient water transportation, leading to the notable increase in water permeance reported in HPANZifG.

In summary, there exists a positive correlation between a decrease in water contact angle and an increase in water flux. The aforementioned relationship highlights the correlation between reduced contact angles and the improved wettability and efficiency of water transport on surfaces.

Conclusions

In conclusion, the present study effectively accomplished its main objective of augmenting the hydrophilic properties and water permeability of the nanofiltration membrane. The incorporation of a ZIF-8 layer that has been stabilized using a redox-grafted methacrylate hydrogel, specifically in the HPANZifG membrane, led to a noteworthy water permeance of 82.3 L/m^2 Bar hour. The selection of polyacrylonitrile (PAN) as the substrate material, renowned for its hydrophilic capabilities, had a significant role in enhancing water permeability and mitigating fouling tendencies.

The alteration of the membrane's surface from hydrophobic to super hydrophilic was established through comprehensive physicochemical tests. The aforementioned results establish the synthesized membrane as a highly viable option for water treatment purposes, as it demonstrates commendable efficacy in water transportation and exhibits notable resistance against fouling. This study introduces novel prospects in the field of nanofiltration technology, which holds considerable ramifications for the advancement of water purification and treatment.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. CRediT: **Arshyn Zhengis** and **Yenglik Amrenova** conceptualization, data curation, investigation, methodology, validation, visualization, writing-original draft, writing-review & editing; **Arailym Yergesheva, Dana Kanzhigitova,** and **Gulim Imekova** formal analysis, visualization; data curation, formal analysis; **Zhexenbek Toktarbay** and **Olzat Toktarbaiuly** conceptualization, data curation; **Munziya Abutalip** and **Nurxat Nuraje** funding acquisition, resources, supervision, validation, writing-review & editing.

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Conflicts of Interest

The authors declare no conflict of interest.

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