



Rice husk ash and Zr-MOF nanoparticles improve the properties and ultrafiltration performance of PVDF nanomembranes

Akarapan Rojjanapinun, Sheree A. Pagsuyoin *

Civil and Environmental Engineering, University of Massachusetts Lowell, Lowell, MA, USA

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ABSTRACT

Herein we demonstrate the effects of rice husk ash (RHA) and two Zr-metal organic frameworks (MOFs; OPA-Uio-66 and OPA-Uio-66-SO₃H) nanoparticles on the properties and performance of polyvinylidene fluoride (PVDF) composite membranes. The nanoparticles and PVDF dope were pre-blended and fabricated as thin-film nanomembranes via soft lithography. The new membranes had uniform pore structures and demonstrated high permeability and durability. Improved tensile strength was associated with increased β crystalline formation of the PVDF, with the greatest increase observed for PVDF/RHA due to the high silica content of the RHA. RHA increased membrane hydrophilicity whereas the MOFs increased hydrophobicity. In ultrafiltration, the new membranes exhibited superior performance compared to conventional PVDF composite membranes made with titanium oxide and nanoclay. High rejection rates and significantly improved antifouling properties were achieved in both PVDF/RHA and PVDF/MOF membranes for high concentration aqueous solutions of sulfamethoxazole, bovine serum albumin, and SARS-CoV-2. This improved performance was attributed to multiple functional groups in RHA and MOFs that promote various surface interactions between contaminants and PVDF membranes. The new high-performance nanomembranes have potential applications in separation and purification processes, biosensing, and in personal protective equipment.

1. Introduction

Polymer membranes are used in many separation processes due to their excellent mechanical, thermal, and chemical stability [1]. However, some membranes may be less effective, for instance, only about 50–60% of sulfamethoxazole [2] and 15–30% of amoxicillin and naproxen [3] can be removed from water via ultrafiltration. Improving membrane properties and rejection rates and can be achieved via chemical surface modification post fabrication [4], use of fabrication techniques that enhance structural integrity [5], and incorporation of additive materials that impart novel functionalities for specific applications [1,6–8]. Nanoparticles such as nanoclay [1], silicon dioxide [6] and titanium dioxide (TiO₂) [7] have been successfully used as additives for polymer membranes but these may give rise to unintended problems such as particle aggregation [6,7] poor additive dispersion [9], creation of nonselective interface voids [1], and reduced membrane durability [4]. For example, montmorillonite nanoclay increased the hydrophilicity, porosity, and antifouling properties of polyvinylidene fluoride (PVDF) membranes but these became brittle beyond 6 wt % nanoclay

composition [10].

As an additive, TiO₂ is inexpensive and imparts catalytic properties [7] and increased hydrophilicity and permeate flux [9] to polymer membranes. Nanoclay is also low-cost and increases the mechanical strength [1] and thermal resistance of polymer membranes, resulting in improved reusability and durability against biofouling [10]. Biowaste materials such as rice husk ash (RHA) have also been used as additives [6]. RHA is made from calcined rice husk and has high silica (~90%) and carbon content [11]. By itself, it exhibits high mechanical strength [11] and adsorption capacity [12], making it ideal for many purification applications such as in the removal of heavy metals from water [13]. When used as a polymer additive, it has been shown to improve the ion exchange capacity of sulfonated polyamide membrane [14] and the removal of chromium by polymethylmethacrylate/polypyrrole membranes [12].

Interest in metal-organic frameworks (MOFs) [15] have increased significantly in recent years due to the high tunability of MOF pore structures and surface properties [16] for targeted applications in catalysis [8], separation [16] and drug delivery [16]. The intrinsic

* Corresponding author. Department of Civil and Environmental Engineering, University of Massachusetts Lowell, 1 University Avenue, Lowell, MA, 01854, USA.
E-mail address: Sheree.Pagsuyoin@uml.edu (S.A. Pagsuyoin).

fragility of MOF structures may limit their performance but engineered MOF-based polymer composites have potential industrial-scale applications such as in water remediation [17]. Compared with traditional inorganic material additives, the main advantage of MOFs lies in their greater compatibility with polymer matrices due to the presence of organic ligands in their structure [8,14], which results in the superior properties of MOF composites. Thin film membranes made from polyamide infused with zeolitic imidazolate frameworks-8 have been demonstrated to be highly effective in desalination compared to pristine polyamide membranes [17]. Electrospun nanofibers made from Zn-based MOF and polyacrylonitrile have been shown to efficiently remove cationic dyes in solution even over five treatment cycles, demonstrating potential robustness for long-term use [18]. Furthermore, Zr-based MOFs such as OPA-UiO-66 and OPA-UiO-66-SO₃H have attracted interest due to their superhydrophobicity, highly stability, and low toxicity, making them suitable for many biological and separation applications [15].

The present study evaluated the impacts of TiO₂, nanoclay, RHA, OPA-UiO-66, and OPA-UiO-66-SO₃H nanoparticles on the properties of polyvinylidene fluoride nanomembranes. The PVDF membranes were fabricated as isoporous thin films with nominal pore sizes of 100 nm and 20 nm using soft lithography [19]. The membrane performance was evaluated via filtration of high concentration aqueous solutions of sulfamethoxazole (SMX), bovine serum albumin (BSA), and heat-inactivated SARS-CoV-2.

2. Experimental

2.1. Materials and chemicals

For the nanomembrane fabrication, PVDF (530 kDa), polydimethylsiloxane, and N-methyl-2-pyrrolidone (NMP) were purchased from Sigma-Aldrich. For the preparation of nanoparticle additives, ethyl alcohol (>99.5%), methanol (99.8%), titanium oxide, bentonite clay, sodium persulfate, zirconium tetrachloride tetrahydrofuran (ZrCl₄), terephthalic acid (98%), monosodium 2-sulfoterephthalic acid (BDC-SO₃Na), dimethylformamide (99%), n-octadecylphosphonic acid, hydrochloric acid, and acetic acid were purchased from Sigma-Aldrich. Rice husk was kindly provided by a farm from the Philippines. For the membrane performance evaluation, sulfamethoxazole and BSA were purchased from Sigma-Aldrich, while heat-inactivated SARS-CoV-2 samples were provided by a core laboratory facility at the University of Massachusetts Lowell. Ultrapure water was produced onsite and was used in all experiments.

2.2. Preparation of nanoparticle (NP) additives

TiO₂ (mean particle size <5 μm) and bentonite clay (mean particle size <25 μm) were ground using a mortar and pestle to reduce particle size, with intermittent dropwise addition of water to prevent particle dispersion in air. Ground particles were stirred into 10 mL DI water in a beaker to induce gravity separation. The resulting colloidal solution was passed through a 0.02 μm PTFE filter; the particles retained on the filter were dried overnight at 40 °C and examined under a scanning electron microscope (SEM) to qualitatively check particle size.

To prepare the RHA nanoparticles, 100 g of rice husk was thoroughly rinsed with tap water to remove adhering soil and dirt, and then soaked in 1 M hydrochloric acid for 1 h to remove metallic impurities. Afterwards, the acid was removed, and the husk was rinsed thrice with DI water and then dried overnight at 110 °C. The dried husk was calcined in a muffle furnace at 700 °C for 2 h under a gentle stream of nitrogen, cooled to room temperature, ground by hand as with the TiO₂ and nanoclay, and analyzed for particle size under SEM.

UiO-66 nanoparticles were synthesized using a modified solvothermal method [15]. Briefly, 90 mg of zirconium tetrachloride (ZrCl₄) and 128.25 mg of terephthalic acid were dissolved in 15 mL of

dimethylformamide (DMF) and 400 μL of DI water in a 20 mL Teflon vial and then placed in a sealed stainless vessel. The mixture was heated at 110 °C for 24 h, cooled to room temperature, transferred to 2 mL propylene microcentrifuge vials, and centrifuged at 8500 RPM for 10 min. The resulting supernatant was decanted, and the settled powder was soaked in 2 mL DMF for 72 h, replacing the solvent every 24 h. This was followed by a similar washing procedure with methanol, after which the remaining powder was dried under flowing nitrogen and dried at 100 °C for 48 h.

UiO-66-SO₃H nanoparticles were prepared via hydrothermal synthesis based on [15]. Briefly, 1.3 g BDC-SO₃Na and 1.2 g ZrCl₄ were dissolved in 50 mL water/acetic acid (30:20, v/v) in a Teflon vial, sealed, and then heated at 80 °C for 24 h to yield UiO-66-SO₃H powder. The powder was cooled to room temperature, washed thrice with DI water, and soaked in 2 mL methanol for 3 days at room temperature, during which time the methanol was replaced daily with fresh methanol. After decanting the final methanol soak, the powder was dried in a vacuum oven (10 mm Hg) at 150 °C for 24 h.

To prepare the OPA-UiO-66 (MOF1) and OPA-UiO-66-SO₃H (MOF2) nanoparticles [15], UiO-66 and UiO-66-SO₃H were each immersed in 5 mM n-octadecylphosphonic acid ethanol solution for 24 h at room temperature during which time the mixture was stirred once every 2 h for 5 min. The solution was then decanted, and the remaining solid material was washed thrice with ethanol. The washed material was activated under dynamic vacuum (0.01 mmHg) for 24 h at room temperature and then at 120 °C for 24 h.

The mean zeta potential of the nanoparticles was analyzed using a Horiba SZ-100 dynamic light scattering instrument. The nanoparticles were diluted in DI water (1% w/w) and loaded onto a pre-rinsed folded capillary cell for potential measurement [20]. Measurements were taken from duplicate samples for each nanoparticle type.

2.3. Membrane fabrication via hybrid lithography

The nanocomposite membranes were fabricated according to previous methods [19], with some modifications. Briefly, the PVDF dope solution (PVDF and N-methyl-2-pyrrolidone) and NP additive were blended at 95:5 ratio (w/w), resulting in five dope blends. PVDF pellets were first dissolved in NMP, and the solution was continuously stirred for 24 h at 85 °C, after which the NPs were added, and the solution was again stirred for another 24 h. The resulting dope solution was sonicated for 30 min to remove dissolved gases, and then kept at room temperature prior to spin coating in the polydimethylsiloxane molds (4 cm × 4 cm membrane area). When casting the dope solution onto the molds, the spin coating parameters (speed and duration) were varied for each dope composition to ensure uniform pores with minimal residues (excess dope) in the final membrane product.

2.4. Characterization of the dope solution and nanocomposite membranes

The viscosity of the dope solution was evaluated by determining the terminal velocity of a 0.5 cm glass bead dropped into a 1-cm diameter cylinder filled with solution to a 2-cm height [21]. The viscosity (μ) was calculated using Equation (1),

$$\mu = \frac{2(\rho_s - \rho_f)gr^2}{9v_s} \quad (\text{Equation 1})$$

where ρ_s and ρ_f are the densities of the bead and fluid, respectively, g is gravity, r is the radius of the bead, and v_s is the terminal velocity of the bead.

The surface morphology of the membranes was examined under a scanning electron microscope (JEOL 6390). All samples were pretreated with silver under a vacuum. The chemical compositions and crystalline structure of nanomembranes were analyzed using attenuated total reflectance Fourier transform infrared spectroscopy (Shimadzu H8400

equipped with an ATR KRS-5 crystal cell). The β fraction (F_β) of the crystalline phase, which is the mass fraction of the β -phase in the PVDF crystal, was calculated using Equation (2) [19],

$$F_\beta = \frac{A_\beta}{\left(\frac{k_\beta}{k_\alpha}\right)A_\alpha + A_\beta} \quad (\text{Equation 2})$$

where A_α and A_β are absorbance of the characteristic peaks of α -phase

and β -phase at 779 cm^{-1} and 840 cm^{-1} , respectively. Absorption coefficients of the α -phase (k_α) and β -phase (k_β) were taken as $6.1 \times 10^4 \text{ cm}^2/\text{mol}$ and $7.7 \times 10^4 \text{ cm}^2/\text{mol}$, respectively [1].

Membrane hydrophobicity was determined via contact angle measurements of a $5 \mu\text{L}$ water deposited onto the membrane surface as captured by a high-speed camera. Tensile strength was measured with a universal testing machine (Instron 5944) using $2 \text{ cm} \times 4 \text{ cm}$ membranes clamped at both ends and pulled at a crosshead speed of 0.1 mm/s .

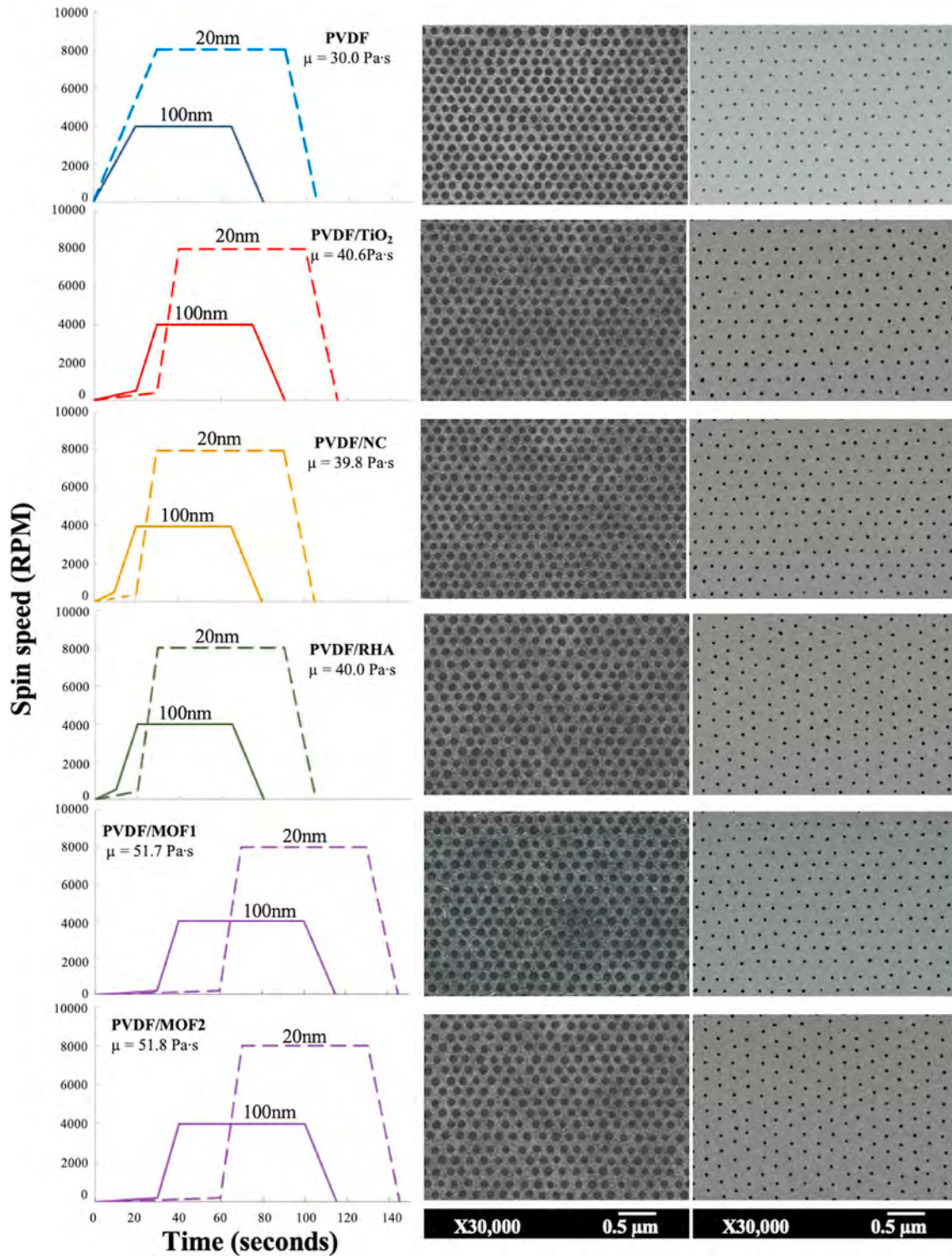


Fig. 1. Spin patterns (speed and duration) used in fabricating nanocomposite PVDF membranes (left column), and corresponding SEM images of 100 nm (center) and 20 nm (right) product membranes.

2.5. Membrane performance

Membrane permeability was evaluated via water flux test in a dead-end ultrafiltration set-up using membranes cut to fit a filter holder with a 1 cm flow diameter. Tests were performed in five replicates over 1 h, using a new membrane for each test run. Water was fed through the filter using a peristaltic pump and permeate was collected over time. The permeate flux was calculated using Equation (3):

$$J_w = \frac{V_p}{AT} \quad (\text{Equation 3})$$

where J_w is the permeate flux, V_p is the volume of collected permeate, A is the membrane area, and T duration of sample collection.

To evaluate chemical rejection performance, dead-end filtration tests were carried out for each membrane using aqueous SMX solution (500 µg/L) as feed. Tests were performed in duplicate runs at room temperature, using a new membrane for each test run, and with each run lasting 3 h. The permeate was collected every 30 min for chemical analysis. SMX concentrations were measured in a high-performance liquid chromatograph (Agilent 1260 Infinity II) using a mobile phase consisting of 20 mM ammonium acetate and methanol (95:5, v/v) pumped isocratically at 0.7 mL/min. Limits of detection (LOD) and quantification (LOQ) were taken as concentrations with S/N = 3 and S/N = 10, respectively.

To evaluate biological rejection rates, dead-end filtration tests were carried out for the best best-performing membranes from the SMX tests, using pristine PVDF membrane as control, and aqueous solutions spiked with BSA (5 g/L) and heat-inactivated SARS-CoV-2 (10^5 gene copies/L) as feeds. Filtration tests were performed in duplicates at room temperature for BSA and at 20 °C for SARS-CoV-2, using a new membrane for each test run, and with each run lasting 3 h. The BSA and SARS-CoV-2 concentrations in the feed were also measured at the start and end of the tests. The permeate was collected for flux and concentration analysis at 30-min intervals. The BSA concentration was quantified in a UV-vis spectrophotometer at $\lambda = 278$ nm [22]. For SARS-Cov-2, 80 µL of viral RNA was isolated from the permeate using QIAamp Viral RNA kit following manufacturer instructions, and quantified via RT-qPCR by targeting the N1 gene [23].

3. Results and discussion

3.1. Nanoparticle effects on PVDF dope properties and crystallization

The addition of 5% nanoparticle additives increased the viscosity of the PVDF dope by 33%–73%, with the highest increase observed for PVDF-MOF blends (Fig. 1). These results are consistent with prior findings of increased viscosity of PVDF dope due to the addition of TiO₂ [7] and nanoclay [1]. Furthermore, RHA has also been found to increase the viscosity of polysulfone (PSF)-RHA dope mixtures [11]. With respect to OPA-UiO-66 (MOF1) and OPA-UiO-66-SO₃H (MOF2), to the authors' knowledge, these MOFs have not been previously studied as polymer additives and the present study is the first to report on their effect on PVDF dope viscosity.

Previously, we successfully fabricated thin film isoporous PVDF nanomembranes through soft lithography using cyclic ramp up-hold-deceleration speeds in the spin coater [19]. As the dope settles and coalesces into the mold channels, these repeated but brief spin cycles promote better nucleation and β -phase formation of the PVDF. In the present work, the increase in dope viscosity is accompanied by changes in the ramp up phase for the spin coater speed, notably, the addition of slower initial acceleration period to spread the initially viscous dope onto mold channels, followed by rapid acceleration faster than that of the pristine PVDF when the viscosity has reduced. Higher initial dope viscosity is associated with longer initial acceleration periods (e.g., 30 and 60 s for the 100 nm and 20 nm PVDF/MOF membranes, respectively). This phenomenon is attributed to changes in the rheology of the

polymer blends. Additives can shift the rheological properties of PVDF from Newtonian to non-Newtonian [7], and the faster spin speeds are necessary when making ultrathin films from initially viscous polymer dope solutions that exhibit non-Newtonian shear thinning behavior [24]. The product nanomembranes have a smooth surface and uniform pores (Fig. 1). Further investigations into higher initial acceleration yielded membranes with non-uniform thickness and evidence of tearing (Fig. S1, Supporting Information) while slower spin speeds resulted in membranes with uneven thickness and polymer residues in the pores (Fig. S2).

PVDF has five crystalline forms (α , β , γ , δ and ϵ), of which the β fraction is associated with greater mechanical and piezoelectric properties [25]. FTIR-ATR measurements (Fig. 2) indicate that PVDF-NP membranes exhibit decreased α -phase and increased β -phase absorption peaks, resulting in higher β fractions compared to pristine PVDF. β fraction values are in the order PVDF/RHA & PVDF/NC > PVDF/TiO₂ > PVDF/MOF1 & PVDF/MOF2 > PVDF. FTIR spectra also indicate successful blending of nanoparticles into the PVDF composites. In PVDF/TiO₂, new absorption peaks indicative of TiO₂, TiOH, and CH stretching were identified [26]. The absorption peaks for SiO and SiOH [26] were observed in PVDF/RHA and PVDF/NC while the vibration bands for AlO and AlOH [27] were found in PVDF/NC. For PVDF/MOFs, spectral bands corresponding to C=C vibration, C=O stretching, C-C stretching and OH were identified [26]. The vibrations of C-H and COOH from the OPA molecule were also noted (2850 cm⁻¹ and 2920 cm⁻¹, respectively [15] for both PVDF/MOFs. Furthermore, absorption peaks attributed to SO₃H and SO₂ were found for PVDF/MOF2.

3.2. Nanoparticle effects on PVDF membrane properties

The average pore sizes, wettability (contact angle), and tensile strength of the nanocomposite PVDF membranes are summarized in Table 1. Except for PVDF/MOFs, the addition of nanoparticles altered the hydrophobicity of the PVDF composite membranes, consistent with the inherent hydrophilicity of TiO₂ [7], nanoclay [1], and RHA [6], and the superhydrophobicity of OPA-UiO-66, and OPA-UiO-66-SO₃H [15]. The increased hydrophilicity of the PVDF/TiO₂ results from the introduction of the hydroxyl [28] from TiO₂ to PVDF, as evident from the FTIR measurements (Fig. 2); whereas in PVDF/NC, this is due to the presence of aluminum silicates in the nanoclay [29]. In PVDF/RHA, the hydrophilicity is due to the high silica content of RHA [12]. The effects of OPA-UiO-66, and OPA-UiO-66-SO₃H on the hydrophobicity of polymer membranes have not been previously studied, though Zhu et al. [8] reported that the addition of UiO-66 significantly increased the hydrophobicity of PVDF composite membranes.

Our results indicate associations between higher β fractions (in Fig. 2) and greater tensile strength (Table 1) in polymer composites, consistent with previous findings [1]. All composite membranes have higher tensile strength than pristine PVDF, with PVDF/RHA membranes exhibiting the highest tensile strength (66% increase vs pristine PVDF) followed by PVDF/NC and then by PVDF/TiO₂. As with hydrophilicity, the mechanical strength of PVDF/RHA is associated with the high silica content of RHA. The addition of nanoclay is known to increase the tensile and flexural strength of nanocomposites and influences the formation of crystalline phases in PVDF [1,10]. The MOF nanoparticles promoted only a slight increase in β crystalline formation and tensile strength of the PVDF composite membranes.

3.3. NP effects on PVDF membrane performance

The pure water permeation flux of membranes is influenced by several factors such as porosity, membrane thickness, and hydrophilicity [10]. In this study, all PVDF composite membranes exhibited high water flux (Fig. 3) due to their highly isoporous uniform structures. Statistically significant improvements (at $p < 0.05$) in water flux were noted for hydrophilic composite membranes compared to the pristine PVDF

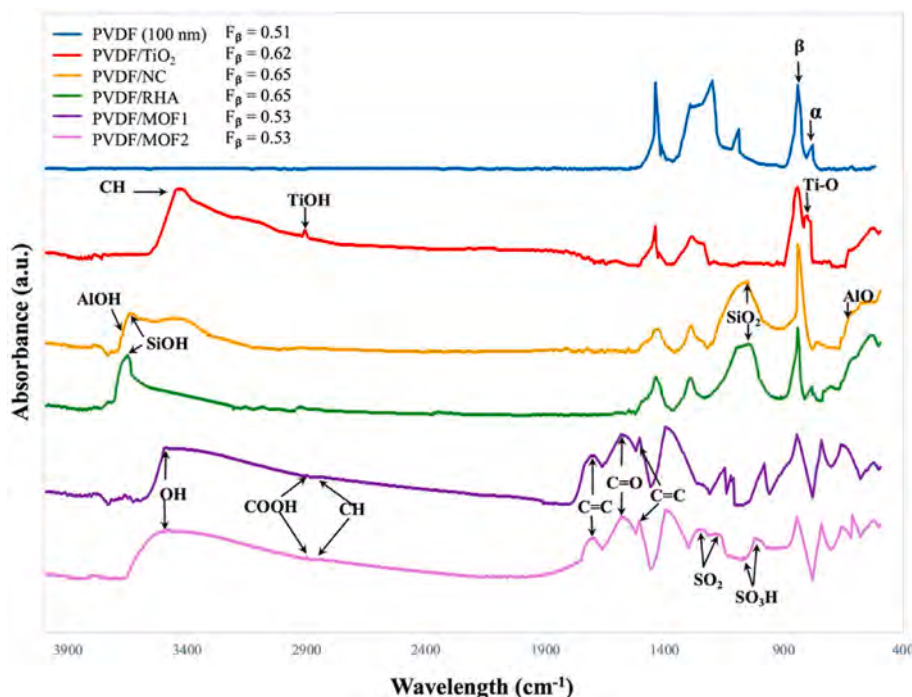


Fig. 2. FTIR-ATR spectra of PVDF nanocomposite membranes (100 nm). The addition of the nanoparticles increases the β phase formation in the PVDF composites, as indicated by the calculated β fractions (F_{β}).

Table 1

Properties of PVDF nanocomposite membranes.

Membrane	Average pore size ^a (nm)	Contact angle ^b (°)	Tensile strength ^c (MPa)
PVDF	100 ± 8	99.1 ± 1.6	8.6 ± 0.3
	20 ± 2	100.8 ± 1.0	8.3 ± 0.0
PVDF/TiO ₂	100 ± 10	77.2 ± 1.1	12.4 ± 0.5
	20 ± 3	77.5 ± 0.7	11.9 ± 0.5
PVDF/NC	100 ± 8	68.0 ± 0.5	14.2 ± 0.7
	20 ± 3	68.8 ± 0.3	14.0 ± 1.2
PVDF/RHA	100 ± 9	88.3 ± 1.6	14.3 ± 0.3
	20 ± 4	89.1 ± 1.2	14.0 ± 0.8
PVDF/ MOF1	100 ± 10	119.5 ± 1.4	9.4 ± 0.3
	20 ± 3	120.4 ± 1.1	9.2 ± 0.0
PVDF/ MOF2	100 ± 10	120.2 ± 0.8	9.4 ± 0.2
	20 ± 2	119.7 ± 1.5	9.0 ± 0.2

^a via SEM.

^b via modified sessile drop test.

^c via ASTM D638.

membranes, for both 100 nm and 20 nm membranes. In contrast, the water fluxes of the hydrophobic PVDF/MOF1 and PVDF/MOF2 membranes were slightly lower than those of the pristine PVDF membranes.

Fig. 4 shows the dead-end filtration permeate flux and rejection rates in the PVDF composite membranes for high concentration aqueous SMX solutions (500 µg/L) at neutral pH. Throughout the filtration, all composite membranes exhibited improved flux compared to the pristine PVDF, in both 100 nm and 20 nm membranes. The greatest flux improvements were observed for PVDF/MOFs and PVDF/RHA, followed by PVDF/TiO₂ and then by PVDF/NC. After 3 h of continuous operation, membrane fouling was lowest in the PVDF/RHA and PVDF/MOF membranes. In the 100 nm membranes, the average relative flux loss (i. e., flux reduction relative to pure water flux in Table 2) was 10% in pristine PVDF, 5% in PVDF/RHA, and 4% in the PVDF/MOFs. In the 20 nm membranes, the average relative flux loss was 8% in pristine PVDF, 4% in PVDF/RHA, and 3% in the PVDF/MOFs.

SMX rejection rates were also significantly higher in the PVDF/RHA and PVDF/MOF membranes than in the pristine PVDF and other composite membranes. In both 100 nm and 20 nm membranes, notable decreases in rejection rates were observed beginning at the 1.5-h mark for pristine PVDF, and at the 2-h mark for PVDF/NC and PVDF/TiO₂. After 3 h of operation, 96% and 98% rejection rates, respectively, could be achieved in the 100 nm PVDF/RHA and PVDF/MOFs membranes (vs 69% in pristine PVDF, 87% in PVDF/TiO₂, and 83% in PVDF/NC). For the same duration, 98% and 99% rejection rates, respectively, could be achieved in 20 nm PVDF/RHA and PVDF/MOFs membranes (vs 73% in pristine PVDF, 91% in PVDF/TiO₂, and 90% in PVDF/NC). These remarkable rejection rates for PVDF/RHA and PVDF/MOFs membranes can be attributed to several adsorption mechanisms including hydrogen bonding, π - π interactions, and electrostatic interactions between SMX and composite membranes. SMX is a hydrophilic (log K_{ow} of 0.89 [30]) organic with a net negative charge at neutral pH due to amine deprotonation [30]. It has H-acceptors (O and N) in its heteroaromatic structure (see Table S1, Supporting Information) that can interact with the hydroxyl (–OH), carboxylic (–COOH), and phosphonic (–PO(OH)₂) groups in the MOFs (see Fig. S3) and with the hydroxyl and silanol (Si–OH) in the RHA (Fig. 2). SMX also contains amine (–NH₂) groups that function as electron donor in the π - π electron donor-acceptor interactions with the benzene rings of the MOFs. π - π stacking (aromatic interactions) is also present between the benzene rings in SMX and MOFs [31]. Lastly, electrostatic repulsion can contribute to SMX rejection by virtue of the net negative charges of the SMX, PVDF, and nanoparticles at neutral pH. Based on zeta potential measurements, RHA, MOF1, and MOF2, have the most negative zeta potential among all nanoparticles used in this study (Table 2).

Based on the SMX filtration results, further rejection tests were carried out with PVDF/TiO₂, PVDF/RHA, and PVDF/MOF2 using BSA and SARS-CoV-2 solutions as feeds. PVDF/MOF1 was excluded due to the similarity of its performance with PVDF/MOF2. After 3 h, relative flux loss in the composite membranes was lower than in the pristine PVDF. As with the SMX tests, PVDF/RHA and PVDF/MOF2 were the best performing membranes where complete rejection of BSA for both 100 nm and 20 nm membrane were observed (Fig. 5). Rejection rates in

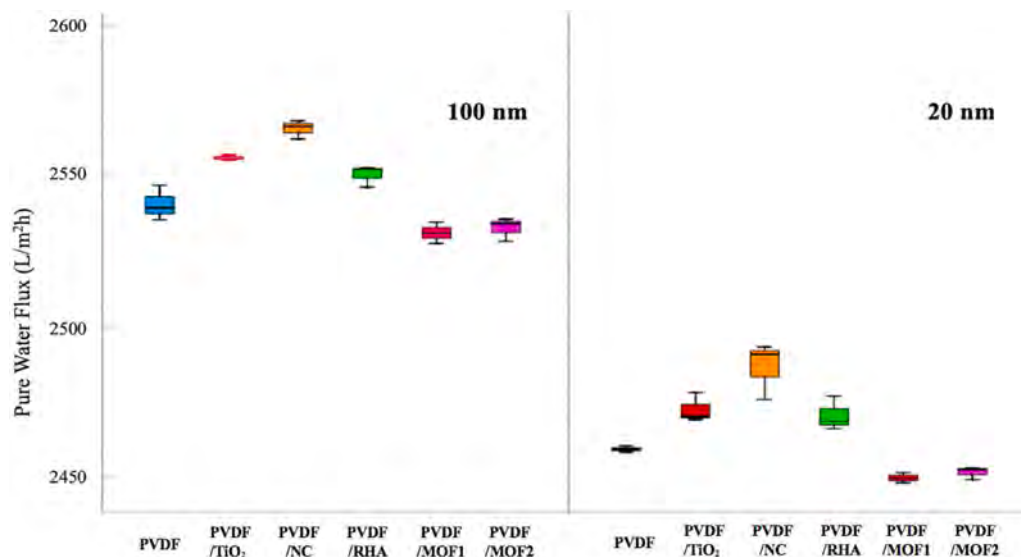


Fig. 3. Pure water permeation flux via dead-end filtration with 100 nm (left) and 20 nm (right) for pristine PVDF and nanocomposite PVDF membranes at 0.15 MPa pressure. For each membrane type, measurements were taken over 5 replicated tests.

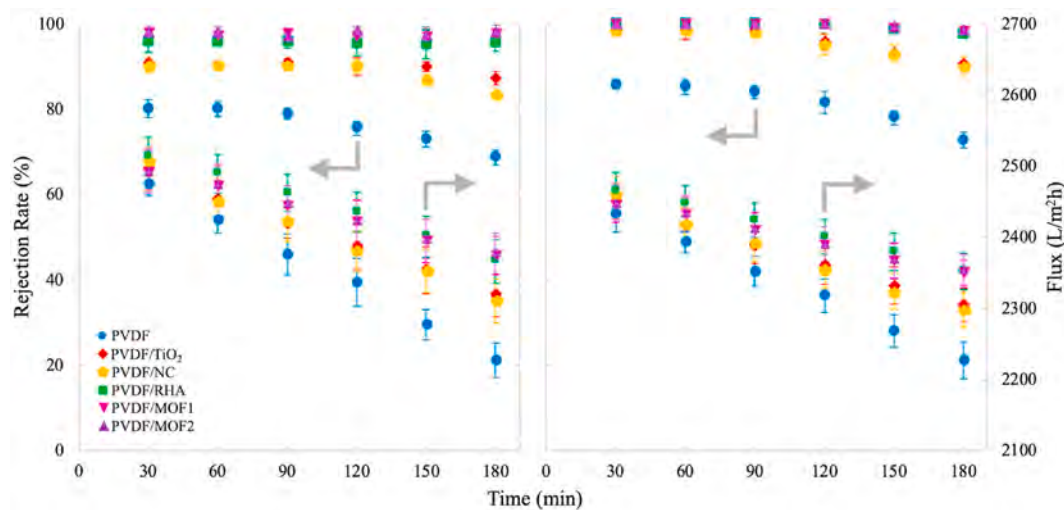


Fig. 4. Rejection rates (top plots) and flux (bottom plots) for sulfamethoxazole in aqueous solutions via dead-end filtration with 100 nm (left) and 20 nm (right) nanocomposite PVDF membranes at 0.15 MPa pressure.

Table 2

Zeta potential values of PVDF and nanoparticles at pH 7.

Material	Zeta Potential (mV)
PVDF	-10.0 ± 2.5
TiO ₂	-13.5 ± 0.7
Nanoclay	-17.0 ± 0.5
Rice husk ash (RHA)	-46.4 ± 2.0
OPA-UiO-66 (MOF1)	-50.3 ± 0.9
OPA-UiO-66-SO ₃ H (MOF2)	-53.0 ± 0.8

PVDF/TiO₂ were 91.0% and 93% for the 100 nm and 20 nm membranes, respectively, after 3 h of continuous operation. These observed trends could be attributed to the combined effects of size exclusion, H-bonding, hydrophobic-hydrophilic interactions, and electrostatic repulsion between BSA and membrane. BSA has a nominal size of 8 nm but may increase particle size up to 300 nm through aggregation [32]. Aggregated BSA can be effectively screened through the highly isoporous structure of the composite membranes. Furthermore, BSA is a globular

protein that has multiple functional groups and binding domains, enabling it to bind to both hydrophilic and hydrophobic surfaces [33]. H-bonding and hydrophilic interactions between the polar groups of BSA and the membranes would be similar to those described in the SMX adsorption mechanisms. The hydrophobic binding of BSA with PVDF composites is driven by the attraction between the nonpolar parts of the BSA and the PVDF surface (i.e., α -phase, which is highest in PVDF/MOF2 than in the PVDF/TiO₂ and PVDF/RHA). Lastly, electrostatic interactions between the negatively charged membranes and the BSA compete with hydrophobic binding. Pristine PVDF membrane is negatively charged in the pH range 3–8 [34]. All nanoparticle additives used in this study are also negatively charged, with the lowest zeta potential measured for RHA and MOFs (Table 2). BSA has an isoelectric point in the pH range of 5.1–5.5 [35] and carries a net negative charge at the neutral pH of the filtration tests. Considering these zeta potential values, the effect of electrostatic repulsion is expected to be highest in PVDF/RHA and PVDF/MOF than in the PVDF TiO₂. Overall, the addition of the nanoparticles in PVDF resulted in improved BSA rejection rates and antifouling performance of the PVDF composite membranes.

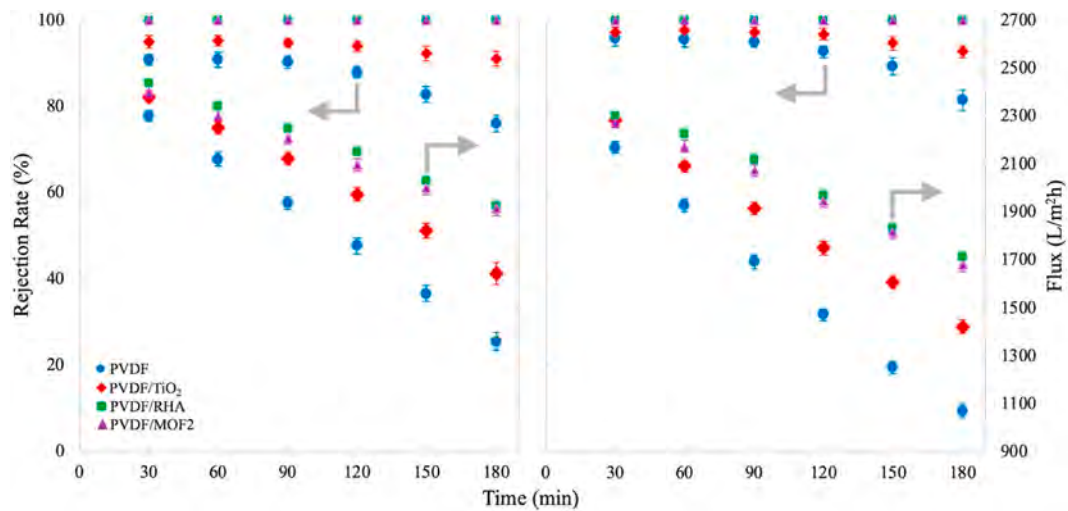


Fig. 5. Rejection rates (top plots) and flux (bottom plots) for BSA via dead-end filtration with 100 nm (left) and 20 nm (right) nanocomposite PVDF membranes at 0.15 MPa pressure.

For SARS-CoV-2, the fluxes for the composite membranes were higher than that of the pristine PVDF in the order PVDF/MOF2 > PVDF/RHA > PVDF/TiO₂ > pristine PVDF for both 100 nm and 20 nm membranes (Fig. 6). After 3 h of continuous operation, relative flux losses in the PVDF/RHA and PVDF/MOF2 were smallest in both membrane sizes (~5%–6% range) and greatest in pristine PVDF membranes (8% and 10% for 100 nm and 20 nm, respectively). Furthermore, complete rejection of SARS-CoV-2 was observed in all membranes likely due to size exclusion; SARS-CoV-2 has an estimated nominal size of 120 nm [36,37]. As with the BSA, electrostatic interactions can also contribute to viral rejection. Most viruses have a negative charge at neutral pH [38]; surface interactions with the composite membranes can also exist due to multiple ionized moieties (e.g., $-\text{NH}_3^+$, $-\text{COOH}$, $-\text{COO}^-$) on the SARS-CoV-2 S-protein [39].

3.4. Potential applications

Integrating nanoparticles into polymer composites provides a facile route for manufacturing engineered membranes with superior properties and performance for applications in separation and purification processes. This simple approach offers an inexpensive and environment-

friendly method for controlling the viscosity of polymer composites. The inherent characteristics of the nanoparticles influence the rheological behavior of the dope and subsequently affect the fabrication and resulting properties of the product membranes. The addition of RHA and superhydrophobic MOF nanoparticles into PVDF dope imparts the inherent characteristics of the nanoparticles that are beneficial for producing isoporous nanomembranes that have superior durability, antifouling, permeation, and rejection performance for a variety of contaminants. The resulting composite membranes are ideal for various specialized applications such as in water treatment, protein separation, biosensing, and in protective equipment and clothing.

4. Conclusion

This study demonstrates that the addition of nanoparticles, particularly rice husk ash and the superhydrophobic metal organic frameworks, OPA-UiO-66 and OPA-UiO-66-SO₃H, significantly improve the durability, permeation, and rejection rates of isoporous PVDF nanocomposite membranes. Compared to pristine PVDF, the new composite membranes are robust, have superior antifouling properties, and are highly effective at removing a variety of chemical and biological contaminants in high-

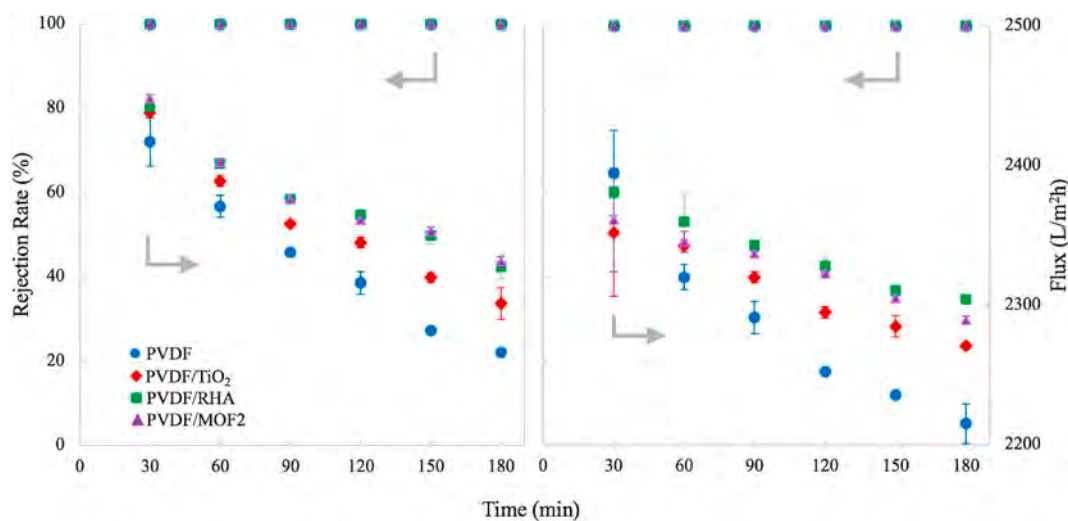


Fig. 6. Rejection rates (top plots) and flux (bottom plots) for SARS-CoV-2 via dead-end filtration test with 100 nm (left) and 20 nm (right) nanocomposite PVDF membranes at 0.15 MPa pressure.

concentration aqueous solutions. These high performance membranes have potential applications in a variety of industrial-scale separation and purification processes.

Author contributions

AR performed the experiments and data analysis, and contributed in manuscript writing. SP supervised this work and contributed in experimental design, data analysis, and manuscript writing and review.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.rinma.2021.100234>.

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