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Modification of Polyvinylidene Fluoride (PVDF) Membrane by Polymer Blending with Phase Inversion Method

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Abstract

The enhancement of membrane performance often relies on straightforward methods, and among them, increasing membrane hydrophilicity stands out. This article delineates the fabrication of modified polyvinylidene fluoride (PVDF) membranes through the incorporation of polyvinylpyrrolidone (PVP) and chitosan as organic additives, with a primary objective of augmenting membrane hydrophilicity. Various formulations were prepared by introducing 1%wt of PVP and 1%, 2%, and 3%wt of chitosan into three distinct PVDF polymer solutions. The impact of these additives on the membrane was comprehensively assessed through the analysis of functional chemical groups using ATR-FTIR, examination of morphological changes employing SEM equipment, and evaluation of filtration performance. SEM images clearly depict alterations in the membrane's morphological structure attributable to the presence of additives. This structural transformation significantly influenced membrane performance, as evidenced by heightened permeability to pure water solutions and increased removal of dissolved humic acid. In summary, the incorporation of 1%wt of PVP and 1%, 2%, and 3%wt of chitosan into PVDF membranes resulted in markedly improved permeability compared to unmodified PVDF membranes. This enhancement can be attributed to the exceptional hydrophilicity conferred by the additives.

Keywords: Polyvinilidene fluoride (PVDF), Polyvinyl Pirrolidone (PVP), Chitosan, fouling, hidrophilicity

1. Introduction

Clean water is essential for survival, industrial and economic development. The need for clean water has increased exponentially over the last decade. This is mainly due to population growth and rapid industrialization in many developing countries (Baten and Stummeyer 2013)(Goh et al. 2018).

Presently, ultrafiltration (UF) technology is garnering significant attention not only in water treatment but also in the fields of medical purification, food product manufacturing, and paper production, proving to be an efficacious method for industrial separation processes (Z. Wang et al. 2012). Ultrafiltration processes are among the most widely used membrane separation processes for water treatment, particularly in the removal of unwanted constituents such as colloids, viruses, pathogens, and proteins (Wahab et al. 2019). Membrane separation technologies, such as ultrafiltration (UF), reverse osmosis (RO), and nanofiltration (NF), have emerged as competitive methods for producing purified water due to their advantages in low energy consumption, ease of operation, and high efficiency (Mi et al. 2017). Despite the development and successful application of membrane systems in various industries, the decline of membrane performance over time due to fouling remains a significant challenge. Proper management is crucial, as fouling can lead to a decrease in permeate flow, impact separation characteristics, and elevate operating pressure (Teow, Ooi, and Ahmad 2017).

Poly (vinylidene fluoride) (PVDF) polymer is commercially utilized in the manufacture of ultrafiltration and microfiltration membranes due to its good resistance of chemical, high strength of mechanical, and good stability of thermal (Dong et al. 2012). However, its hydrophobicity makes PVDF more susceptible to fouling (Balta et al. 2012). This is a significant drawback for various water treatment applications (Kang and Cao 2014). Due to the hydrophobic nature of PVDF

ultrafiltration membranes, they are susceptible to protein adsorption and other contaminants in water and wastewater. This susceptibility can lead to a significant decrease in water flux through the membrane (Z. Wang et al. 2012). Hydrophobic PVDF membranes are prone to fouling during the filtration process of solutions containing natural organic matter (X. Huang et al. 2015).

Fouling, a persistent challenge in the prolonged use of PVDF membranes, poses a significant drawback and hampers advancements in wastewater treatment applications. Rapid declines in water flux, diminished membrane efficiency, heightened energy consumption, increased operating costs, and a shortened membrane lifespan are some of the undesirable consequences associated with fouling (Nikooe and Saljoughi 2017). Membrane fouling can occur on the surface's top layer and within the pores of the membrane due to the accumulation or adsorption of foulants (organic or inorganic matter) present in the feed solution (Saqib and Aljundi 2016), (S. Jiang, Li, and Ladewig 2017). The properties of the membrane surface are the most significant factors influencing the primary performance of membranes, including permeability and antifouling characteristics (Mi et al. 2017), (Ishigami et al. 2012), (Liu et al. 2015). The fouling phenomenon of the membrane is heavily influenced by the interaction between the foulant and the membrane material. Typically, this interaction involves hydrophobic-hydrophobic interactions on the surface. Consequently, pure polymer-based membranes exhibit excellent mechanical and flexible properties but are susceptible to fouling due to their inherent hydrophobic nature (Fahrina et al. 2020).

The adsorption of water molecules by hydrophilic segments or molecules on the membrane's surface can form a protective layer of hydration. This layer acts as a barrier, preventing foulants from coming into direct contact with the membrane material and being adsorbed onto its surface (Kobayashi et al. 2012).

Hence, various methods have been developed to enhance the hydrophilicity of PVDF membranes, categorized into two main types: surface modification (via coating or grafting) and blending modification with hydrophilic polymers or nanoparticles. The blending modification method is considered a more practical approach for commercial development compared to surface modification (Oikonomou et al. 2017). Blending polymers not only enhances hydrophilicity but also imparts membrane films with excellent pore properties, high flux, and outstanding antifouling characteristics. Researchers have experimented with the impact of incorporating small amounts of various additives on the membrane's structure. These additives often exhibit specific interactions with other substances (Susan et al. 2017). Previous studies have demonstrated that the addition of hydrophilic additives, such as Pluronic F127, polyethylene glycol (PEG), polydopamine, and chitosan, to the dope solution enhances the antifouling properties of the resulting membranes (Fathanah et al. 2020). Blending modification with biopolymers has especially garnered significant attention in recent years due to its positive impact on membrane properties (Fathanah et al. 2020).

Polyvinyl pyrrolidone (PVP), typically a hydrophilic polymer, is employed in doped solutions to enlarge pore size and membrane porosity while suppressing macropore formation. Its excellent non-toxicity, solubility, and water biocompatibility make PVP a widely used additive in polymeric membrane production, enhancing compatibility and antifouling capabilities. PVP, as a hydrophilic membrane material, can be blended with both organic and inorganic compounds. The amide and carbonyl groups in PVP facilitate hydrogen bond formation between the membrane and water. The addition of PVP as an additive reduces the crystallinity of the polymer mixture and increases membrane free volume, impacting separation efficiency by enhancing membrane swelling. While numerous studies in the literature focus on PVP's application in processes like pervaporation for organic solvent dehydration, azeotropic separation, and desalination, ensuring the mechanical and chemical stability of PVP membranes requires compatible polymers due to their inherently brittle structure (Ozekmekci, Unlu, and Copur 2021).

Chitosan is one of the most commonly used additives. It is a cost-effective, non-toxic, and environmentally friendly material, often derived from industrial waste. Chitosan is a linear polysaccharide with NH and OH groups in its structure, which can be further modified. The NH and OH groups enhance the binding between metal ions and chitosan. In acidic solutions, chitosan exhibits a highly positive charge density and can bind to

glucosamine groups in molecular chains. As a biopolymer, chitosan is naturally derived from renewable raw materials, is highly hydrophilic, and possesses excellent biocompatibility (Fathanah et al. 2020).

Recognizing the beneficial effects of chitosan and PVP as additives, this research was conducted to combine both for enhanced performance of the PVDF membranes. The addition of the hydrophilic polymer PVP serves as a pore agent, while chitosan, with its hydroxyl group, acts as a carrier for hydrophilic properties, thereby improving membrane hydrophilicity and pore characterictics.

2. Methodology

2.1. Materials

The polymer material used for the membrane preparation was Polyvinylidene fluoride (PVDF) with a molecular weight of 534,000 Da, sourced from Sigma Aldrich (USA). Dimethylacetamide (DMAc) from Wako Pure Chemical Industries (Japan) served as the solvent. Additives included PVP from Merck KgaA in Darmstadt, Germany, and chitosan from Sigma Aldrich. The foulant compound, humic acid, was procured from Sigma Aldrich in Germany. Deionized water (DI) was utilized as a non-solvent material for membrane production and as the feed material during the membrane filtration process to determine pure water flux.

2.2. Chitosan solution preparation

The chitosan solution was prepared by dissolving 1 gram of chitosan compound in 100 ml of acetic acid. Subsequently, the chitosan solution was stirred for 24 hours until achieving homogeneity. The solution was then stored at room temperature and utilized as an additive for membrane production (Fathanah et al. 2020).

2.3. Flat sheet membrane preparation

Four types of flat sheet membranes were produced. The PVDF-DMAc solution was synthesized with a PVDF content of 17%wt, and modifications were made by incorporating PVP and chitosan as additives. The polymer, additives, and solvent were stirred and mixed in an Erlenmeyer flask, hereinafter referred to as the dope solution. Once homogenous, the dope solution was poured onto a glass plate and smoothed with an applicator. Subsequently, the glass plate was immersed in water as a non-solvent contained in a coagulation bath. The resulting membrane (refer to Table 1) was then stored in a container filled with water for further use.

Table 1. Dope solutions composition and code names of membrane

Membrane name	PVDF (%)	PVP (%)	Chitosan (%)	DMAc (%)
C-0	17	0	0	83
C-1	17	1	1	81
C-2	17	1	2	80
C-3	17	1	3	79

2.4. Membrane characterization

Various instrumental analyses were employed to characterize the membranes. Specifically, the FTIR-8100A equipment from Shimadzu (Kyoto, Japan) was utilized to analyze the chemical functional groups present in the membrane. Changes in membrane morphology were investigated using a scanning electron microscope (FESEM, JSF7500F, JEOL Ltd., Japan). The gravimetric method (Equation (1)) was then employed to determine the membrane porosity (ε). The porosity was obtained through the gravimetric method (Y. W. Huang et al. 2017) (Panda and De 2013).

$$\varepsilon\,(\%) = \left(\frac{\omega_W - \omega_d}{\rho \times A \times l}\right) \times 100 \qquad (1)$$

ω_w and ω_d indicate the weight of sample in wet and dry form (kg), ρ indicates the water density, A and l indicate the area of surface (m^2) and thickness of membrane sample (m), respectively.

2.5. Membrane Performance

2.5.1 Ultrafiltration of dead-end

The filtration test was conducted using the dead-end ultrafiltration module, as depicted in Figure 1. This module has a capacity of 300 mL for each filtration process. The membrane's performance was evaluated based on the permeability of pure water and the removal of humic acid solutions. Prior to the filtration test, the membrane sample was compacted until a steady flow rate was achieved.

The Permeability of Pure Water (PWP) was tested using deionized water as the feed. Permeate was collected and weighed every 10 minutes using a digital scale. Subsequently, PWP ($L/m^2.h.bar$) was

calculated using the data obtained with equation (2) (Fathanah et al. 2020).

$$PWP = \frac{Q}{A \times \Delta t \times \Delta P} \times 100\% \quad (2)$$

Q is the permeate (L) produced in a certain time of filtration, t, (h), A is area of surface of the membrane (m^2), and P is the pressure (bar) used during filtration process.

To assess the membrane's selectivity, a filtration experiment was conducted using a 50 ppm solution of humic acid as the feed. The feed solution was prepared by dissolving 0.05 g of humic acid in 1 liter of deionized water. The membrane separation performance was evaluated using the Rejection coefficient (R), calculated according to Eq. (3) (He et al. 2017) (Sadeghi et al. 2013):

$$R(\%) = (1 - \frac{C_p}{C_f}) \times 100 \quad (3)$$

Cf and Cp are concentrations of acid of humic in feed and permeate, respectively.

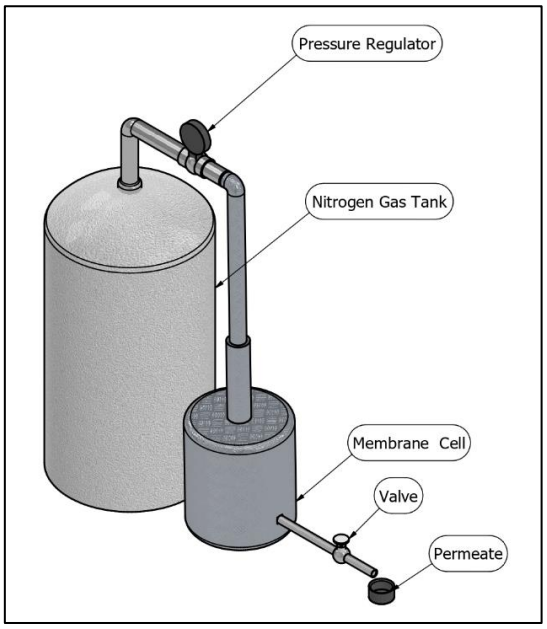

Figure 1. Dead-end ultrafiltration module

3.2. Antifouling Performance

The antifouling performance of the membrane was assessed through the following method. Initially, a flux of pure water (J_{w1}) was measured at 1 bar pressure for 1 hour. Subsequently, the feed was switched to humic acid (J_{HA}), and the procedure was repeated under the same conditions. The membrane sample was then inverted, allowing deionized water to be used as feed for backwashing. Following the backwashing, the membrane was inverted again for the PWP test (J_{w2}). With these data in hand, the Flux Recovery Rate (FRR) was calculated using equation (4) (J. H. Jiang et al. 2014):

$$FRR\ (\%) = (\frac{J_{W2}}{J_{W1}}) \times 100 \quad (4)$$

3. Results and Discussion

3.1. Chemical Structure

The IR spectra of the C-0, C-1, C-2, and C-3 membranes in Figure 2 reveal intriguing chemical structure transformations. Overall, all the manufactured membranes exhibit several identical peaks in their spectra, which are associated with the characteristic peaks of PVDF. The two peaks at 2978 cm^{-1} and 1930 cm^{-1} correspond to the stretching and bending modes of CH_2, respectively, while the peak at 1180 cm^{-1} can be attributed to the stretching mode of CF_2 (Nikooe and Saljoughi 2017) (Saini, Sinha, and Dash 2019).

In the modified membranes equipped with chitosan and PVP (C-1, C-2, and C-3), the appearance of broad peaks at wavelengths 3412 cm^{-1} and 3410 cm^{-1} indicates the vibrational strain of the hydroxyl (OH) group of chitosan. Additionally, the strong band from 3200 to 3600 cm^{-1} signifies the presence of OH and –NH groups. An important exception is observed in membranes containing 1% chitosan (C-1), where peaks of chitosan are not clearly evident. This phenomenon can be correlated to previous studies suggesting that a small concentration of hydrophilic particles added to the PVDF membrane may not attract the particles to the surface layer due to hydrogen bonding interactions between water molecules and hydrophilic OH groups. This indicates that particles of hydrophilic moieties tend to remain within the membrane. With this low concentration, the absence of particle movement to the surface layer results in less obvious absorption peaks in the FTIR analysis, which is a surface characterization method (Elizalde et al. 2018).

The peak characteristic of PVP occurred at 1666 cm^{-1} which was indicated by strain oscillations of C=O (Ozekmekci, Unlu, and Copur 2021). This indicates that PVP and chitosan have successfully bonded to the PVDF membrane.

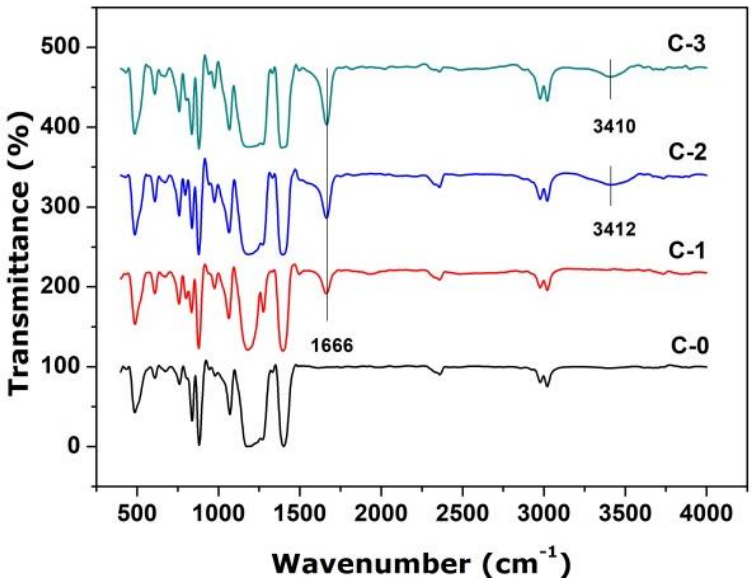

Figure 2. FTIR spectra of the four membrane samples.

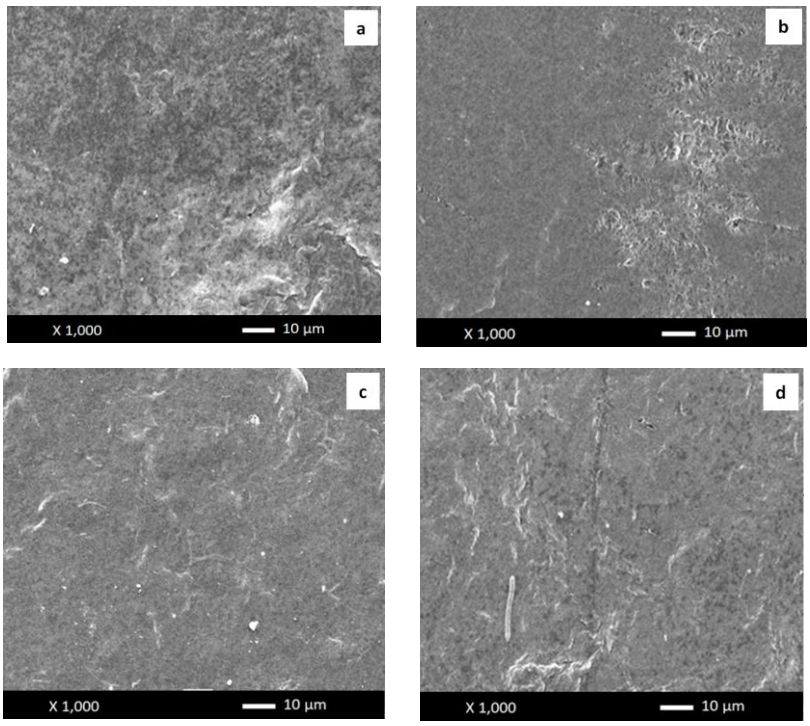

Figure 3. Surface morphology of membranes; (a) C-0, (b) C-1, (c) C-2, (d) C-3

3.3. Membrane Morphology

SEM micrographs of all prepared membranes are illustrated in Fig. 3 and Fig. 4 to examine the membrane's morphology and sublayer structure. The dense layer of the membrane serves as a separation layer and provides mechanical strength to the membrane, acting as a support layer (Panda and De 2013).

From Figure 3, the membrane's morphology reveals that the pore size increased when chitosan and PVP were added. Additionally, the SEM results in Figure 4 demonstrate the presence of an upper layer with higher density (dense layer). All membranes (C-0, C-1, C-2, and C-3) exhibit an asymmetrical structure characterized by the presence of

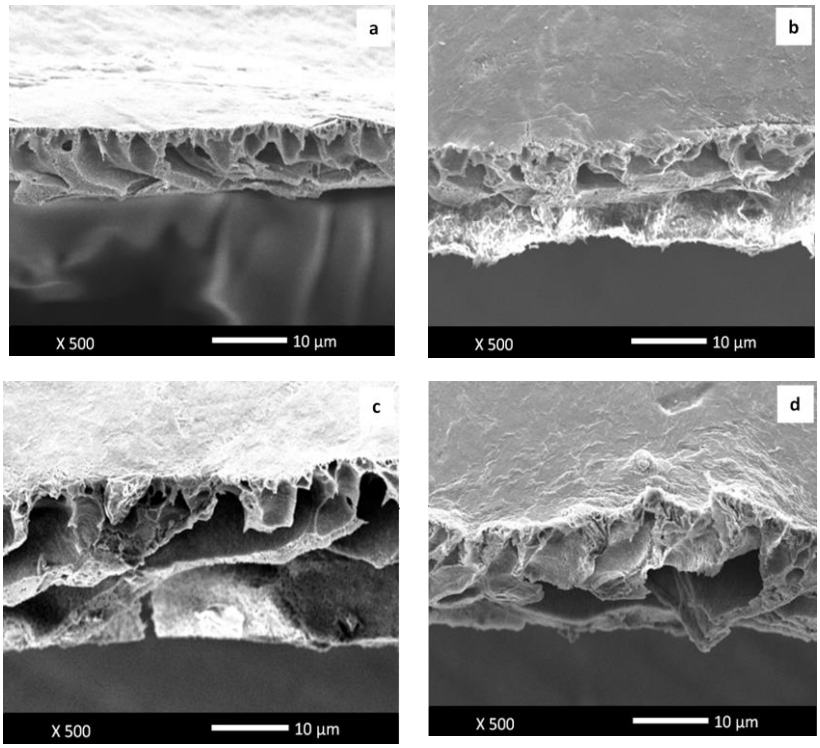

Figure 4. Cross-section SEM imaging of the membrane; (a) C-0, (b) C-1, (b) C-2, and (b) C-3

support at the bottom—the bottom layer shows pores resembling a finger-like structure. A similar result was reported in a study conducted by Chakrabarty et al. focused on the PSF system as the base polymer using NMP and DMAc as solvents separately, with the addition of PVP. Due to the high affinity of NMP for water, separation occurs rapidly, forming a finger-like structure in the lower layer of the prepared membrane (Chakrabarty, Ghoshal, and Purkait 2008), (Sinha and Purkait 2013).

The morphology of asymmetric membranes is commonly observed in membranes obtained through the NIPS process. It was noted that the C-0 membrane exhibited a dense upper layer with finger-like or macro-void support in Fig. 4a. However, significant morphological changes were observed in membranes with the addition of 1% by weight of PVP and 1%, 2%, and 3% by weight of chitosan. A comparison of the C-0 membrane's morphology with that of the C-1, C-2, and C-3 membranes reveals an asymmetrical structure, where the addition of chitosan and PVP creates a wider channel in the macro-void layer. This structural change can be explained by the increase in pores due to more water intrusion as a non-solvent into the membrane with the increasing concentration of the hydrophilic chitosan compound (Elizalde et al. 2018). In addition, macrovoids are more aligned and straight on the C-1, C-2, and C-3 membranes which helps to increase the permeability of the membrane (Ghaemi, Daraei, and Akhlaghi 2018).

3.4. Porosity of membrane

Figure 5 illustrates the modification effect of PVP and chitosan on the porosity of the resulting membranes. C-1, C-2, and C-3 membranes exhibit higher porosity than C-0. The porosity increased with the increase in additive content in the casting solution for all modified membranes. This trend can be explained by the film formation mechanism during the phase inversion process in a coagulation bath (Nikooe and Saljoughi 2017).

As seen in Figure 5, the C-0 membrane exhibited the lowest porosity at 33%, whereas the C-1, C-2, and C-3 have a more increased porosity of 38%, 45%, and 49%, respectively. In this study, the presence of hydrophilic additives, chitosan and PVP, in the casting solution facilitated the entry of non-solvent (water) into the casting solution. This led to an exchange between the solvent

and non-solvent during membrane formation. The rapid exchange between solvent and non-solvent promoted the rapid deposition of the casting solution in the coagulation bath, facilitating instantaneous separation. This mechanism contributed to the production of highly porous membranes (Z. Wang et al. 2012).

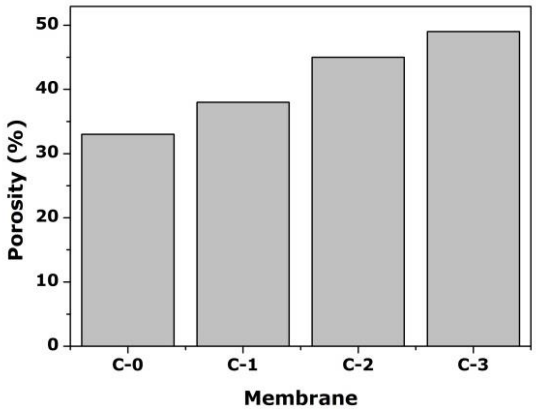

Figure 5. The effect of adding PVP and chitosan as additives to the porosity in the PVDF membrane

3.5. filtration Performance

Figures 6 and 7 depict the impact of adding a combination of PVP and chitosan to PWF and PWP on the membrane. PWP is a crucial and fundamental property of membranes, especially when employed in water treatment processes (Muchtar et al. 2019). All membranes modified with the addition of chitosan at 1%, 2%, and 3%wt exhibited higher PWF and PWP compared to C-0 membranes.

Figure 6 illustrates that the modified membrane PWF increased with higher amount of chitosan additives. The membrane PWF with 1%, 2%, and 3%wt of chitosan increased more rapidly than the C-0 membrane. This heightened permeability is a result of the increased hydrophilicity of the membrane induced by the adsorption of the chitosan particles into the casting solution (Gao, Sun, and Gao 2017), (Moslehyani et al. 2015). Indeed, in addition to the hydrophilicity factor, the flux of pure water also increases with the growing average pore size of the membrane. The larger pore size facilitates the flow of water through the membrane, contributing to the enhanced flux (Ngang et al. 2017) (Zhang et al. 2013).

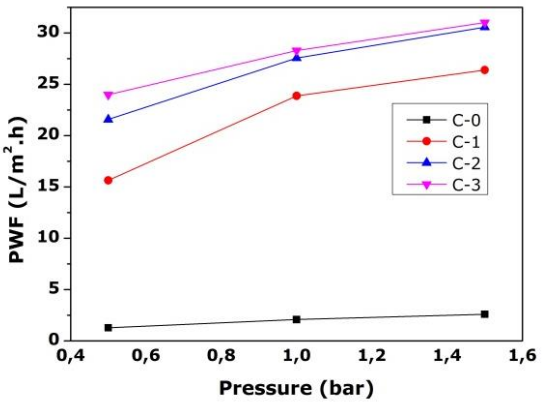

Figure 6. PWF of the membranes

From Figure 7, it is observed that the lowest PWP of the C-0 membrane was 0.9461 L/m^2.h.bar. By adding chitosan at 1%, 2%, and 3%wt to the dope solution, the PWP of each membrane increased to 10.183 L/m^2.h.bar, 12.026 L/m^2.h.bar, and 12.401 L/m^2.h.bar for the C-1, C-2, and C-3 membranes, respectively. The increase in PWP was directly related to the membrane morphology (Figure 3). The PWP values for C-1, C-2, and C-3 membranes were larger than the PWP for C-0, attributed to their macro-void and finger-like structure, which increased water permeation through the membrane. The highest PWP was observed for C-3 at 12.401 L/m^2.h.bar which is the membrane modified with 3% chitosan. The increase in additive amount enhances the hydrophilic nature of the membrane, attracting water molecules and facilitating water passage through the membrane (Munnawar et al. 2017). This increase may be attributed to the hydroxyl groups spontaneously migrating to the surface of the membrane during the phase-inversion preparation (Xia and Ni 2015), (Balta et al. 2012), (Shen et al. 2012)

The increase in the number of macrovoids in the support layers of the C-1, C-2, and C-3 membranes was attributed to the presence of hydrophilic compound groups in the polymer solution. These groups enhanced the rate of separation during the phase inversion process. Furthermore, the straight and parallel form of the macrovoids contributes to an increase in membrane permeability (Daraei, Ghaemi, and Sadeghi Ghari 2017).

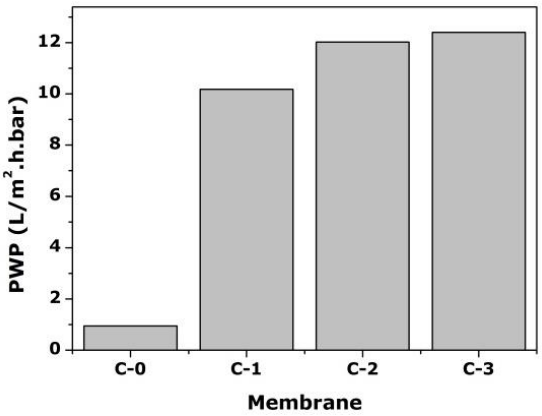

Figure 7. PWP of the membranes

Besides PWF, solute rejection is considered as another important characteristic factor for ultrafiltration membranes, especially those specialized for water treatment (P. Wang et al. 2012). The impact of chitosan and PVP as additives on the membrane selectivity performance was experimentally investigated, and the rejection performance results are shown in Fig. 8.

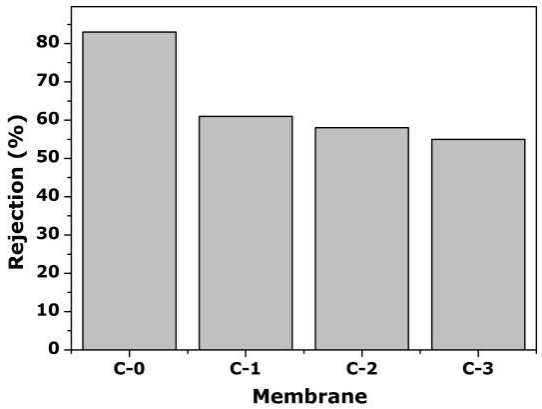

Figure 8. Effect of additives on humic acid rejection from prepared membranes

From Fig. 8 it is observed that the nonmodified membrane showed the highest rejection performance of >80%. However, after the addition of chitosan at 1%, 2%, and 3%, the membrane rejection rates of C-1, C-2, and C-3 decreased to 61%, 58%, and 55%, respectively. This is attributed to the formation of membrane pores and/or an increase in pore size after being modified with PVP and chitosan. Membrane modification with the addition of 1% PVP and 1%, 2%, and 3% chitosan decreased humic acid rejection because the combination of additives caused a larger pore size in the surface layer of the membrane, as represented in the SEM results (Figure 3), and increased porosity (Figure 5).

3.6. Antifouling Performance

The main problem of filtration with membranes is the decreased permeability and selectivity due to membrane fouling (Zhao et al. 2013). Pore clogging and the formation of a cake generally occur simultaneously during the membrane filtration process (Deng et al. 2014) (Luo et al. 2015). To study the properties of antifouling of the prepared membranes, humic acid solutions were used as a feed in a three-step filtration operation as described in the experimental section.

The ultrafiltration process and antifouling capacity of membranes modified with additives were analyzed by filtering a 50 ppm humic acid solution under a constant pressure of 1 bar. Figure 9 illustrates the flux of pure water at the beginning of filtration experiment (J_{w1}), the flux of humic acid (J_{HA}), and the flux of pure water after backwashing (J_{w2}). In all ultrafiltration experiments, the modified membrane exhibited a higher PWF compared to the unmodified membrane (Saini, Sinha, and Dash 2019).

Figure 9 shows a decrease in flux in permeation of acid of humic (J_{HA}). In the humic acid ultrafiltration process, it was reported that humic acid molecules usually are crosslinked to form a mesh-like porous gel sheet on the membrane surface and blocking the flowing of mater molecule to pass through, hence, the flux is lower than that of the PWF (Saini, Sinha, and Dash 2019), (Sinha and Purkait 2015). However, the PWF on the third step of filtration experiment showed an increase, which is due to backwash procedure that cleaned the fouled surface of the membrane (Ma et al. 2016).

Figure 10 displays the recovery ratio of flux (FRR) on the modified membrane. The FRR was determined to assess the level of foulant removal on the surface of the membrane. A higher permeation of water flux and FRR indicates greater resistance of the membrane to fouling (P. Wang et al. 2012). In Fig. 10, we can see that the addition of PVP and chitosan as additives and their concentraions increased the membranes FRR. The original PVDF membrane (C-0) owns a FRR of 27.89%, meanwhile after modification, the FRR increased to 60.99%, 93.95%, and 97.43% on C-1, C-2, and C-3 membranes, respectively.

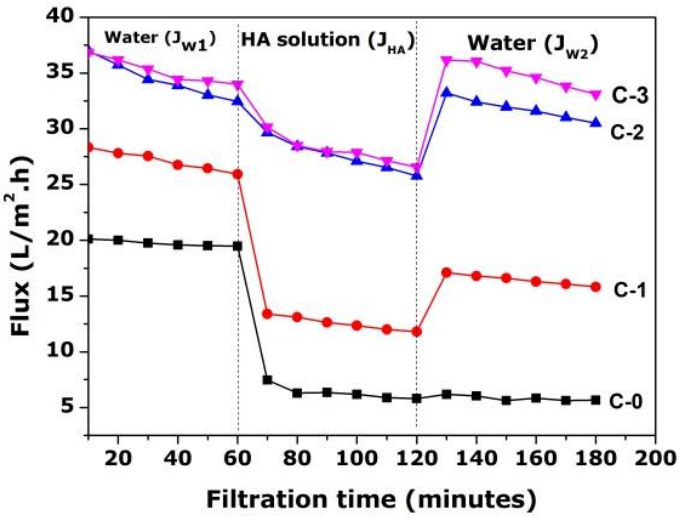

Figure 9. Filtrartion profile of the membranes

This indicates that the addition of hydrophilic additives such as PVP and chitosan can facilitate the removal of humic acid molecules to achieve a high FRR by simple hydraulic washing (Saini, Sinha, and Dash 2019).

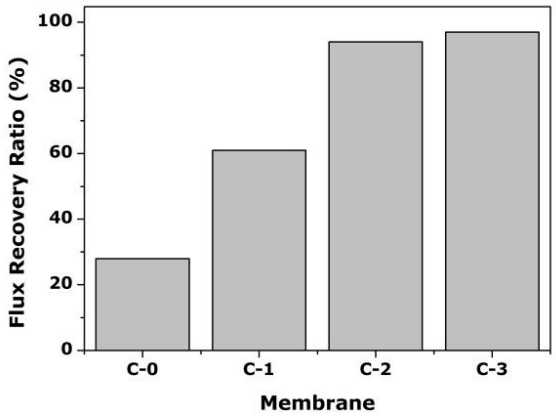

Figure 10. Flux recovery ratio (FRR) on the membrane

4. Conclusion

The successful modification of the PVDF membrane with PVP and chitosan additives is evident from SEM observations, revealing a noticeable change in membrane morphology upon the addition of additives. Chemical interaction between the PVP and chitosan mixture in the manufactured PVDF membrane was confirmed through FT-IR analysis. Membrane permeability demonstrated a substantial increase from 0.9461 (L/m^2.h.bar) for the unmodified C-0 membrane to 10.183 (L/m^2.h.bar), 12.026 (L/m^2.h.bar), and 12.401 (L/m^2.h.bar) for the C-1, C-2, and C-3 membranes, respectively. Selectivity in humic acid rejection indicated a satisfactory level, although further research is essential to evaluate membrane stability over prolonged usage periods. This study lays the foundation for continued investigation into the enhanced performance and long-term reliability of the modified PVDF membrane.

References

Balta, Stefan, Arcadio Sotto, Patricia Luis, Lidia Benea, Bart Van der Bruggen, and Jeonghwan Kim. 2012. "A New Outlook on Membrane Enhancement with Nanoparticles: The Alternative of ZnO." *Journal of Membrane Science* 389: 155–61. https://doi.org/10.1016/j.memsci.2011.10.025.

Baten, Rudolf, and Karen Stummeyer. 2013. "How Sustainable Can Desalination Be?" *Desalination and Water Treatment* 51 (1–3): 44–52. https://doi.org/10.1080/19443994.2012.705061.

Chakrabarty, B., A. K. Ghoshal, and M. K. Purkait. 2008. "Preparation, Characterization and Performance Studies of Polysulfone Membranes Using PVP as an Additive." *Journal of Membrane Science* 315 (1–2): 36–47. https://doi.org/10.1016/j.memsci.2008.02.027.

Daraei, Parisa, Negin Ghaemi, and Hedayatollah Sadeghi Ghari. 2017. "An

Ultra-Antifouling Polyethersulfone Membrane Embedded with Cellulose Nanocrystals for Improved Dye and Salt Removal from Water." *Cellulose* 24 (2): 915–29. https://doi.org/10.1007/s10570-016-1135-3.

Deng, Lijuan, Wenshan Guo, Huu Hao Ngo, Jian Zhang, Shuang Liang, Siqing Xia, Zhiqiang Zhang, and Jianxin Li. 2014. "A Comparison Study on Membrane Fouling in a Sponge-Submerged Membrane Bioreactor and a Conventional Membrane Bioreactor." *Bioresource Technology* 165 (C): 69–74. https://doi.org/10.1016/j.biortech.2014.02.111.

Dong, Chunxu, Gaohong He, Hao Li, Rui Zhao, Yue Han, and Yulin Deng. 2012. "Antifouling Enhancement of Poly (Vinylidene Fluoride) Microfiltration Membrane by Adding Mg (OH) 2 Nanoparticles." *Journal of Membrane Science* 387–388: 40–47. https://doi.org/10.1016/j.memsci.2011.10.007.

Elizalde, Cynthia Noemi Baeza, Samer Al-Gharabli, Joanna Kujawa, Musthafa Mavukkandy, Shadi W. Hasan, and Hassan A. Arafat. 2018. "Fabrication of Blend Polyvinylidene Fluoride/Chitosan Membranes for Enhanced Flux and Fouling Resistance." *Separation and Purification Technology* 190: 68–76. https://doi.org/10.1016/j.seppur.2017.08.053.

Fahrina, Afrillia, Nasrul Arahman, Sri Mulyati, Sri Aprilia, Normi Izati Mat Nawi, Aqsha Aqsha, Muhammad Roil Bilad, Ryosuke Takagi, and Hideto Matsuyama. 2020. "Development of Polyvinylidene Fluoride Membrane by Incorporating Bio-Based Ginger Extract as Additive." *Polymers* 12 (9): 1–11. https://doi.org/10.3390/polym12092003.

Fathanah, Umi, Izarul Machdar, Medyan Riza, Nasrul Arahman, Mukramah Yusuf, Syawaliah Muchtar, Muhammad Roil Bilad, and Nik Abdul Hadi Nordin. 2020. "Enhancement of Antifouling of Ultrafiltration Polyethersulfone Membrane with Hybrid Mg (Oh)2/Chitosan by Polymer Blending." *Journal of Membrane Science and Research* 6 (4): 375–82. https://doi.org/10.22079/JMSR.2020.124107.1365.

Gao, Hongwei, Xiuhua Sun, and Changlu Gao. 2017. "Antifouling Polysulfone Ultrafiltration Membranes with Sulfobetaine Polyimides as Novel Additive for the Enhancement of Both Water Flux and Protein Rejection." *Journal of Membrane Science* 542: 81–90. https://doi.org/10.1016/j.memsci.2017.07.053.

Ghaemi, Negin, Parisa Daraei, and Farima Sadat Akhlaghi. 2018. "Corresponding Author." *Carbohydrate Polymers*. https://doi.org/10.1016/j.carbpol.2018.03.024.

Goh, P S, W J Lau, M H D Othman, and A F Ismail. 2018. "Membrane Fouling in Desalination and Its Mitigation Strategies." *Desalination* 425 (October 2017): 130–55. https://doi.org/10.1016/j.desal.2017.10.018.

He, Yang, Lihao Xu, Xia Feng, and Yiping Zhao. 2017. "Author ' s Accepted Manuscript." *Journal of Membrane Science*. https://doi.org/10.1016/j.memsci.2017.06.028.

Huang, Xin, Weiping Wang, Yaodong Liu, Hui Wang, Zhibing Zhang, Wenling Fan, and Lei Li. 2015. "Treatment of Oily Waste Water by PVP Grafted PVDF Ultrafiltration Membranes." *Chemical Engineering Journal* 273: 421–29. https://doi.org/10.1016/j.cej.2015.03.086.

Huang, Yuan Wei, Zuo Ming Wang, Xi Yan, Jun Chen, Ya Jun Guo, and Wan Zhong Lang. 2017. "Versatile Polyvinylidene Fluoride Hybrid Ultrafiltration Membranes with Superior Antifouling, Antibacterial and Self-Cleaning Properties for Water Treatment." *Journal of Colloid and Interface Science* 505: 38–48. https://doi.org/10.1016/j.jcis.2017.05.076.

Ishigami, Toru, Kuniaki Amano, Akihiro Fujii, Yoshikage Ohmukai, Eiji Kamio, Tatsuo Maruyama, and Hideto Matsuyama. 2012. "Fouling Reduction of Reverse Osmosis Membrane by Surface Modification via Layer-by-Layer

Assembly." *Separation and Purification Technology* 99: 1–7. https://doi.org/10.1016/j.seppur.2012.08.002.

Jiang, Jin Hong, Li Ping Zhu, Hong Tao Zhang, Bao Ku Zhu, and You Yi Xu. 2014. "Improved Hydrodynamic Permeability and Antifouling Properties of Poly(Vinylidene Fluoride) Membranes Using Polydopamine Nanoparticles as Additives." *Journal of Membrane Science* 457: 73–81. https://doi.org/10.1016/j.memsci.2014.01.043.

Jiang, Shanxue, Yuening Li, and Bradley P. Ladewig. 2017. "A Review of Reverse Osmosis Membrane Fouling and Control Strategies." *Science of the Total Environment* 595: 567–83. https://doi.org/10.1016/j.scitotenv.2017.03.235.

Kang, Guo-dong, and Yi-ming Cao. 2014. "Author ' s Accepted Manuscript." *Journal of Membrane Science*. https://doi.org/10.1016/j.memsci.2014.03.055.

Kobayashi, Motoyasu, Yuki Terayama, Hiroki Yamaguchi, Masami Terada, Daiki Murakami, Kazuhiko Ishihara, and Atsushi Takahara. 2012. "Wettability and Antifouling Behavior on the Surfaces of Superhydrophilic Polymer Brushes."

Liu, Meihong, Qing Chen, Lizhong Wang, Sanchuan Yu, and Congjie Gao. 2015. "Improving Fouling Resistance and Chlorine Stability of Aromatic Polyamide Thin-Film Composite RO Membrane by Surface Grafting of Polyvinyl Alcohol (PVA)." *Desalination* 367: 11–20. https://doi.org/10.1016/j.desal.2015.03.028.

Luo, Nan, Rongle Xu, Min Yang, Xing Yuan, Hui Zhong, and Yaobo Fan. 2015. "Preparation and Characterization of PVDF-Glass Fiber Composite Membrane Reinforced by Interfacial UV-Grafting Copolymerization." *Journal of Environmental Sciences (China)* 38: 24–35. https://doi.org/10.1016/j.jes.2015.04.027.

Ma, Wenzhong, Saeid Rajabzadeh, Abdul Rajjak Shaikh, Yuriko Kakihana, and Yuchen Sun. 2016. "Effect of Type of Poly (Ethylene Glycol) (PEG) Based Amphiphilic Copolymer on Antifouling Properties of Copolymer / Poly (Vinylidene Fl Uoride) (PVDF) Blend Membranes." *Journal of Membrane Science* 514: 429–39. https://doi.org/10.1016/j.memsci.2016.05.021.

Mi, Yi Fang, Feng Yang Zhao, Yao Shen Guo, Xiao Dan Weng, Chun Chun Ye, and Quan Fu An. 2017. "Constructing Zwitterionic Surface of Nanofiltration Membrane for High Flux and Antifouling Performance." *Journal of Membrane Science* 541: 29–38. https://doi.org/10.1016/j.memsci.2017.06.091.

Moslehyani, A., A. F. Ismail, M. H.D. Othman, and T. Matsuura. 2015. "Design and Performance Study of Hybrid Photocatalytic Reactor-PVDF/MWCNT Nanocomposite Membrane System for Treatment of Petroleum Refinery Wastewater." *Desalination* 363: 99–111. https://doi.org/10.1016/j.desal.2015.01.044.

Muchtar, Syawaliah, Mukramah Yusuf Wahab, Sri Mulyati, Nasrul Arahman, and Medyan Riza. 2019. "Superior Fouling Resistant PVDF Membrane with Enhanced Filtration Performance Fabricated by Combined Blending and the Self-Polymerization Approach of Dopamine." *Journal of Water Process Engineering* 28 (February): 293–99. https://doi.org/10.1016/j.jwpe.2019.02.012.

Munnawar, Iqra, Sadia S. Iqbal, Muhammad N. Anwar, Mehwish Batool, Sheraz Tariq, Nosheen Faitma, Asim L. Khan, et al. 2017. "Synergistic Effect of Chitosan-Zinc Oxide Hybrid Nanoparticles on Antibiofouling and Water Disinfection of Mixed Matrix Polyethersulfone Nanocomposite Membranes." *Carbohydrate Polymers* 175: 661–70. https://doi.org/10.1016/j.carbpol.2017.08.036.

Ngang, H. P., A. L. Ahmad, S. C. Low, and B. S. Ooi. 2017. "Preparation of Thermoresponsive PVDF/SiO2-PNIPAM Mixed Matrix Membrane for Saline Oil Emulsion Separation and Its Cleaning Efficiency." *Desalination* 408: 1–12. https://doi.org/10.1016/j.desal.2017.01

.005.

Nikooe, Naeme, and Ehsan Saljoughi. 2017. "Preparation and Characterization of Novel PVDF Nanofiltration Membranes with Hydrophilic Property for Filtration of Dye Aqueous Solution." *Applied Surface Science* 413: 41–49. https://doi.org/10.1016/j.apsusc.2017.04.029.

Oikonomou, Evdokia K., Szilvia Karpati, Sana Gassara, André Deratani, François Beaume, Olivier Lorain, Sylvie Tencé-Girault, and Sophie Norvez. 2017. "Localization of Antifouling Surface Additives in the Pore Structure of Hollow Fiber PVDF Membranes." *Journal of Membrane Science* 538: 77–85. https://doi.org/10.1016/j.memsci.2017.05.046.

Ozekmekci, Mehtap, Derya Unlu, and Mehmet Copur. 2021. "Removal of Boron from Industrial Wastewater Using PVP/PVDF Blend Membrane and GO/PVP/PVDF Hybrid Membrane by Pervaporation." *Korean Journal of Chemical Engineering* 38 (9): 1859–69. https://doi.org/10.1007/s11814-021-0845-x.

Panda, Swapna Rekha, and Sirshendu De. 2013. "Role of Polyethylene Glycol with Different Solvents for Tailor-Made Polysulfone Membranes." *Journal of Polymer Research* 20 (7). https://doi.org/10.1007/s10965-013-0179-4.

Sadeghi, Ilin, Abdolreza Aroujalian, Ahmadreza Raisi, Bahram Dabir, and Mahdi Fathizadeh. 2013. "Surface Modification of Polyethersulfone Ultrafiltration Membranes by Corona Air Plasma for Separation of Oil/Water Emulsions." *Journal of Membrane Science* 430: 24–36. https://doi.org/10.1016/j.memsci.2012.11.051.

Saini, Bharti, Manish Kumar Sinha, and Sukanta K. Dash. 2019. "Mitigation of HA, BSA and Oil/Water Emulsion Fouling of PVDF Ultrafiltration Membranes by SiO2-g-PEGMA Nanoparticles." *Journal of Water Process Engineering* 30 (March). https://doi.org/10.1016/j.jwpe.2018.03.018.

Saqib, J, and Isam H Aljundi. 2016. "Journal of Water Process Engineering Membrane Fouling and Modification Using Surface Treatment and Layer-by-Layer Assembly of Polyelectrolytes : State-of-the-Art Review." *Journal of Water Process Engineering* 11: 68–87. https://doi.org/10.1016/j.jwpe.2016.03.009.

Shen, Liguo, Xiaokai Bian, Xiaofeng Lu, Liuqing Shi, Zhongying Liu, Lifang Chen, Zhengchi Hou, and Kai Fan. 2012. "Preparation and Characterization of ZnO/Polyethersulfone (PES) Hybrid Membranes." *Desalination* 293 (2012): 21–29. https://doi.org/10.1016/j.desal.2012.02.019.

Sinha, M. K., and M. K. Purkait. 2015. "Preparation of a Novel Thermo Responsive PSF Membrane, with Cross Linked PVCL-Co-PSF Copolymer for Protein Separation and Easy Cleaning." *RSC Advances* 5 (29): 22609–19. https://doi.org/10.1039/c4ra13863e.

Sinha, M K, and M K Purkait. 2013. "Author ' s Accepted Manuscript." *Journal of Membrane Science*. https://doi.org/10.1016/j.memsci.2013.03.003.

Susan, L. Y., S. Ismail, B. S. Ooi, and H. Mustapa. 2017. "Surface Morphology of Pvdf Membrane and Its Fouling Phenomenon by Crude Oil Emulsion." *Journal of Water Process Engineering* 15: 55–61. https://doi.org/10.1016/j.jwpe.2016.05.013.

Teow, Y. H., B. S. Ooi, and A. L. Ahmad. 2017. "Fouling Behaviours of PVDF-TiO2 Mixed-Matrix Membrane Applied to Humic Acid Treatment." *Journal of Water Process Engineering* 15: 89–98. https://doi.org/10.1016/j.jwpe.2016.03.005.

Wahab, Mukramah Yusuf, Syawaliah Muchtar, Sungil Jeon, Li Feng Fang, Saeid Rajabzadeh, Ryosuke Takagi, Nasrul Arahman, Sri Mulyati, Medyan Riza, and Hideto Matsuyama. 2019. "Synergistic Effects of Organic and Inorganic Additives in Preparation of Composite Poly(Vinylidene Fluoride) Antifouling Ultrafiltration Membranes." *Journal of Applied Polymer Science* 136 (27): 1–10. https://doi.org/10.1002/app.47737.

Wang, Panpan, Jun Ma, Zhenghui Wang,

Fengmei Shi, and Qianliang Liu. 2012. "Enhanced Separation Performance of PVDF/PVP-g-MMT Nanocomposite Ultrafiltration Membrane Based on the NVP-Grafted Polymerization Modification of Montmorillonite (MMT)." *Langmuir* 28 (10): 4776–86. https://doi.org/10.1021/la203494z.

Wang, Zonghua, Hairong Yu, Jianfei Xia, Feifei Zhang, Feng Li, Yanzhi Xia, and Yanhui Li. 2012. "Novel GO-Blended PVDF Ultrafiltration Membranes." *Desalination* 299: 50–54. https://doi.org/10.1016/j.desal.2012.05.015.

Xia, Shengji, and Muzi Ni. 2015. "Preparation of Poly(Vinylidene Fluoride) Membranes with Graphene Oxide Addition for Natural Organic Matter Removal." *Journal of Membrane Science* 473: 54–62. https://doi.org/10.1016/j.memsci.2014.09.018.

Zhang, Jiguo, Zhiwei Xu, Wei Mai, Chunying Min, Baoming Zhou, Mingjing Shan, Yinglin Li, Caiyun Yang, Zhen Wang, and Xiaoming Qian. 2013. "Improved Hydrophilicity, Permeability, Antifouling and Mechanical Performance of PVDF Composite Ultrafiltration Membranes Tailored by Oxidized Low-Dimensional Carbon Nanomaterials." *Journal of Materials Chemistry A* 1 (9): 3101–11. https://doi.org/10.1039/c2ta01415g.

Zhao, Yi Fan, Li Ping Zhu, Zhuan Yi, Bao Ku Zhu, and You Yi Xu. 2013. "Improving the Hydrophilicity and Fouling-Resistance of Polysulfone Ultrafiltration Membranes via Surface Zwitterionicalization Mediated by Polysulfone-Based Triblock Copolymer Additive." *Journal of Membrane Science* 440: 40–47. https://doi.org/10.1016/j.memsci.2013.03.064.