Production, characterization and water filtration performance of polyvinylidene fluoride-based membranes performance of polyvinylidene fluoride membranes

Seren Acarer Arat, İnci Pir, Mertol Tüfekci & Neşe Tüfekci

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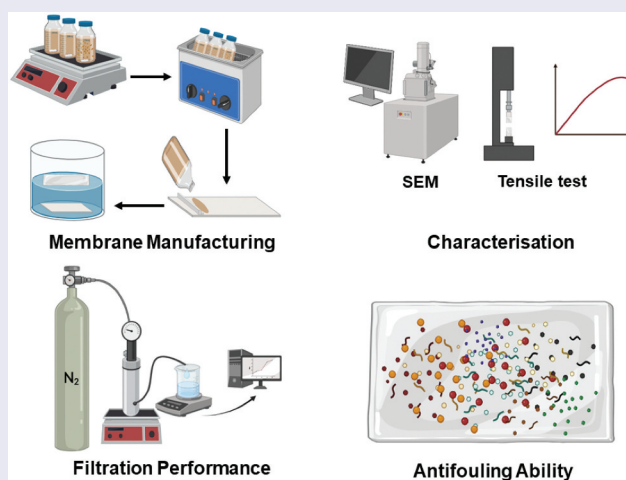Seren Acarer Arat[a], İnci Pir[b], Mertol Tüfekci[c,d], and Neşe Tüfekci[a]

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ABSTRACT

PVDF, PVDF/PVP and PVDF/PVP/CNC membranes were prepared using the phase inversion method using polyvinylidene fluoride (PVDF), polyvinylpyrrolidone (PVP) and cellulose nanocrystal (CNC). The morphologies of the membranes and CNC were determined by scanning electron microscopy (SEM), and the mechanical properties of the membranes were determined by tensile tests. After lake water filtration, the fouled membranes were subjected to physical cleaning for 15 min, and then pure water fluxes of fouled-cleaned membranes were determined. The antifouling abilities of the membranes were investigated by calculating the total fouling ratio (Rt), reversible fouling ratio (Rr), irreversible fouling ratio (Rir), and flux recovery ratio (FRR) of the membranes. Moreover, antifouling abilities were further investigated by SEM. With the addition of 6 wt% PVP to 12 wt% PVDF-based membrane, the water content, pure water flux, elastic modulus and tensile strength of the membrane decreased by 25.5%, 16.6%, 34.3% and 31.3%, respectively. As a result of 0.5 wt% CNC reinforcement of PVDF/PVP, pure water flux, water content, elasticity modulus, tensile strength and FRR value of the membrane increased by 5%, 5.5%, 17.6%, 5.8% and 3%, respectively. The turbidity and electrical conductivity removal efficiencies of the membranes from lake water ranged between 38.22–74.76% and 19.32–34.62%, respectively.

HIGHLIGHTS

- The addition of 6% wt. PVP to pure PVDF membrane significantly changed the surface morphology.
- The addition of 6% wt. PVP to the pure PVDF membrane contributed to reducing the flux performance and mechanical stability of the membrane and improving its antifouling ability.
- The addition of CNC to the PVDF/PVP membrane improved the water flux, treatment performance, mechanical strength, and antifouling ability.

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1. Introduction

Polymeric membranes are widely used in water/wastewater treatment plants for water and wastewater filtration due to their low production cost, easy preparation, easy modification, and high chemical, thermal stability and mechanical properties.[1] Polymers such as polyvinylidene fluoride (PVDF), polyvinyl chloride (PVC), polyethersulfone (PES), polysulfone (PSf), cellulose acetate (CA) are widely used in the preparation of polymeric membranes for water/wastewater filtration purposes.[2–6] PVDF is widely used in the preparation of microfiltration (MF), ultrafiltration (UF), and nanofiltration (NF) membranes due to its good membrane formation ability, flexibility, mechanical properties, and superior resistance to chemicals.[7] However, the high surface hydrophobicity of PVDF membranes makes them more prone to fouling during water/wastewater filtration.[8] Since the surface and pores of dirty membranes are blocked, the membrane's resistance to water increases, and the passage of water becomes difficult. This phenomenon leads to the flux reduction problem that is very common in membranes.[1] Applying physical and especially chemical cleaning processes to remove contaminants accumulated in the membrane interrupts the filtration process, reduces the membrane's life, and increases operating costs.[9,10] In addition, exposing membranes that have a high tendency to fouling to excessive cleaning reduces their durability. In addition, exposing membranes that have a high tendency to fouling to excessive cleaning reduces their durability. A study conducted by[11] revealed that plastic particles (microplastics) from the structure of the membrane are released into the water due to exposure of the PVDF membrane to different cleaning agents.

In order to improve the properties of polymeric membranes, increase their flux performance and enhance their antifouling abilities, researchers have used various methods, such as blending with hydrophilic and/or pore-forming polymers,[12–14] incorporating various nanomaterials,[12,15] surface coating[16] and plasma treatment.[17] Among these membrane modification methods, the incorporation of hydrophilic polymers and/or nanomaterials into polymeric membranes significantly improves the water flux performance, separation performance, and fouling resistance of the membranes.[12,18–20] Cellulose nanocrystals (CNCs) are nanomaterials with the renewable and degradable properties of natural cellulose. The small size, large surface area, high crystallinity, and high mechanical properties of CNCs make them an ideal material for producing nanocomposite

membranes.[21][22] reported that the surface hydrophilicity of the membrane gradually increased with increasing the ratio of CNC (0.06%-0.1%) added to the PA layer of the thin film composite membrane consisting of PSf substrate and PA top layer and the water flux of the membrane increased up to 0.05 wt% CNC reinforcement (up to 106.9 L/m^2.h).[23] reported that the surface hydrophilicity, porosity, average pore size and water flux of 0.7–4.2 wt% CNC reinforced PVDF/CNC nanocomposite membranes were higher than those of pure PVDF membrane.[24] found that the surface hydrophilicity, water content, water flux and porosity of the membrane increased, and the skin layer thickness decreased after CNC reinforcement of the membrane containing 20 wt% PES and 1 wt% PVP.

Polyvinylpyrrolidone (PVP) is a polymer that is hydrophilic, soluble in water and many organic solvents, heat resistant, and of low toxicity to humans.[25] PVP is used as a pore-forming agent in the preparation of polymeric membranes via phase inversion. Studies have shown that the porosity, water flux and surface hydrophilicity of membranes increase with the inclusion of PVP in polymeric membranes.[26–28] It has been reported that membrane properties are affected by both the amount[27] and the molecular weight[26] of PVP added to the PVDF membrane.

In this study, pure PVDF, PVDF/PVP blend, and CNC-added nanocomposite PVDF/PVP (PVDF/PVP/CNC) membranes were produced using the phase inversion method. In the characterization stage, the surface morphologies of the membranes were examined, and their mechanical properties were investigated. Then, pure water flux and surface water (lake water) flux values of clean membranes were determined using the dead-end filtration system. After lake water filtration, the fouled membranes were cleaned by physical cleaning with pure water, and then the pure water flux values of the fouled-cleaned membranes were determined. Parameters showing the resistance of membranes to fouling were calculated using all membrane flux values. In addition, fouling on the surface of fouled-cleaned membranes was revealed by scanning electron microscope (SEM). Finally, prepared membrane samples were exposed to tensile testing to determine the mechanical behavior. To the best of our knowledge, this is the first study to investigate the effect of CNC on the microstructure, crystallinity, mechanical properties, flux performance and fouling resistance of a membrane composed of 12 wt% PVDF and 6 wt% PVP. In addition, the fouling behavior and antifouling ability of PVDF, PVDF/PVP and PVDF/PVP/CNC membranes composed of 12 wt% PVDF after filtration of surface water

(Terkos Lake water) were extensively investigated for the first time in this study.

2. Materials and methods

2.1. Materials

PVDF (average molecular weight ~534000 g/mol) and PVP (average molecular weight = 40000 g/mol) were purchased from Sigma-Aldrich. DMF, which was used as a solvent to dissolve the polymer(s), was obtained from Carlo Erba Reagents. CNC in powder form (width:10–20 nm, length:300–900 nm) was obtained from Nanografi.

2.2. Preparation of membranes

In this study, the phase inversion method, which is widely used by researchers in membrane preparation studies and commercial membranes, was used in the preparation process of membranes. First of all, the materials were kept in an incubator at 45°C (Nuve EN 500) for 2 h to remove moisture potentially present in the glass bottles, PVDF, PVP, and CNC. Following this process, the required amount of DMF was added into a 250 mL glass bottle containing a dry and clean stir bar. In preparing the casting solution of the PVDF membrane, 12 wt.% PVDF was gradually added to the membrane casting solution to prevent agglomeration. While preparing the casting solution of the PVDF/PVP membrane, after adding the required amount of DMF to the glass bottle, the first 12% wt. PVDF and then 6% wt. PVP were added. Finally, to prepare the PVDF/PVP/CNC membrane casting solution, 0.5% wt. CNC was added to DMF, followed by 12% wt. PVDF and 6% wt. PVP. The compositions of the prepared membrane casting solutions are given in Table 1.

The glass bottles containing membrane casting solutions were capped and mixed on a heated magnetic stirrer (WiseStir MSH-20A) at 60°C for 48 h until a homogeneous mixture was obtained. Then, the bottles were kept in a 25°C ultrasonic water bath (Weightlab Instruments) in degassing mode for 30 min to remove air bubbles in the solutions and reduce the temperature of the solutions. After pouring the solutions onto a clean and dry glass plate, they were spread on the glass plate with a thickness of 200 μm using a casting knife (TQC Sheen, VF2170–261). Immediately afterward, the glass plate was immersed in a 25°C water bath (coagulation bath) containing only pure water. In the water bath, the polymer was solidified by the exchange between solvent (DMF) and non-solvent (pure water), and flat sheet membranes were obtained for use in filtration applications. Similar to previous studies, mixing, degassing in an ultrasonic water bath, casting and immersion processes were carried out in the membrane production studies, respectively.[13–15]

2.3. Characterisation of membranes

The surface morphologies of CNC and prepared membranes were examined using SEM (Philips XL 30S FEG). The membranes were dried at room temperature for 48 h before examination with a SEM. In order to make the membranes and CNC conductive, the surfaces were coated with gold at 10 mA for 90 sec using a coating device (Quorum SC7620). While the SEM surface view of CNC agglomerates was obtained at a magnification of 5000×, the surface views of clean membranes were obtained at a magnification of 5000×, 10000×, and 20,000 ×. After filtering pure water and lake water, respectively, the fouled membranes were physically cleaned with pure water. After filtering pure water from these fouled-cleaned membranes again, the contaminants on the surfaces of the membranes were examined with SEM. SEM surface views of fouled-cleaned membranes were examined under 5000× magnification.

To determine the water content of the membrane samples, the samples were placed in aluminum weighing dishes and dried in an oven (Nuve EN 500) at 45°C for 60 hours. The weights of the dried membrane samples were determined with a precision balance (Precisa XB 220A). Then, dried membranes were immersed in distilled water using pens. The membranes were removed from the water after 30 seconds using pens. Excess water was immediately removed from the membranes using a blotting paper. Immediately afterward, the wet weights of the membranes were determined with a precision balance (Precisa XB 220A). The water content of the membranes was calculated using Equation 1. Water content experiments were performed three times for each membrane.[15]

Table 1. Composition of membrane casting solutions.

	PVDF (wt%)	DMF (wt%)	PVP (wt%)	CNC (wt%)
PVDF	12	88	-	-
PVDF/PVP	12	82	6	-
PVDF/PVP/CNC	12	81.5	6	0.5

$$Watercontent(\%) = \frac{Ww - Wd}{Ww} x100 \qquad (1)$$

where Ww (g) and Wd (g) are the wet and dry weights of the membranes respectively.

The porosity of the membranes was determined by the gravimetric method. Equation 2 was used to determine the porosity of the membranes.[15]

$$P(\%) = \frac{m_w - m_d}{At\rho} x100 \qquad (2)$$

P represents the porosity of the membrane (%). m_w and m_d are the wet and dry weights (g) of the membrane, respectively. A is the membrane area (cm²). t is the membrane thickness (cm), ρ represents the density of water (0.998 g/cm³).

Tensile testing was used to characterize membranes mechanically. A quasi-static strain rate of 1% strain per minute was chosen to represent a static loading state. Tests were performed three times for each membrane combination. The ASTM D882 standard was followed when conducting tests.[29] Tensile tests were conducted in ambient conditions with a Shimadzu AG-IS 50 kN universal testing machine.

X-ray diffraction (XRD) patterns of the membranes were analyzed using an X-ray diffractometer (Bruker D8 Advance). The XRD patterns of the membranes were analyzed at 40 kV and 40 mA in an instrument equipped with Cu Kα (k = 1.54 Å) radiation. The XRD patterns of the membranes were recorded at diffraction angles ranging from 2θ = 3–70°.

2.4. Determination of flux and treatment performances of membranes

Pure water and lake water flux tests of the membranes were determined with the dead-end filtration system (Tin Mühendislik). In this study, the lake water sample was collected from Durusu Lake, also known as Terkos Lake, located in Istanbul, Turkey, in 2023. Lake water was filtered through membranes with a dead-end filtration system. The schematic diagram of the experimental setup used to determine the fluxes of membranes is shown in Figure 1. Samples cut from the membranes with a diameter of 5 cm were placed in the filtration system, and the filtration cell was filled with pure water or lake water. Nitrogen gas (N_2) was used to provide the pressure required to filter water through the membrane. All flux tests were carried out under 3 bar. The water filtered through the membranes that is, the permeates, were collected in a 250 mL beaker on a precision balance (AND EJ-610). Time-weight data were transferred to the computer for 15 minutes using WinCT-RSWeight software. Pure water/lake water fluxes of the membranes were calculated using Equation 3.

Pure water flux of clean membranes (J_{w1}) and lake water flux of clean membranes (J_{lake}) were calculated. The front and back surfaces of the membranes fouled with lake water were cleaned by washing with pure water for 10 sec, and the membranes were kept in a container containing pure water for 15 minutes. Pure water flux of physically cleaned membranes (fouled-cleaned membranes) (J_{w2}) was calculated. Flux tests of
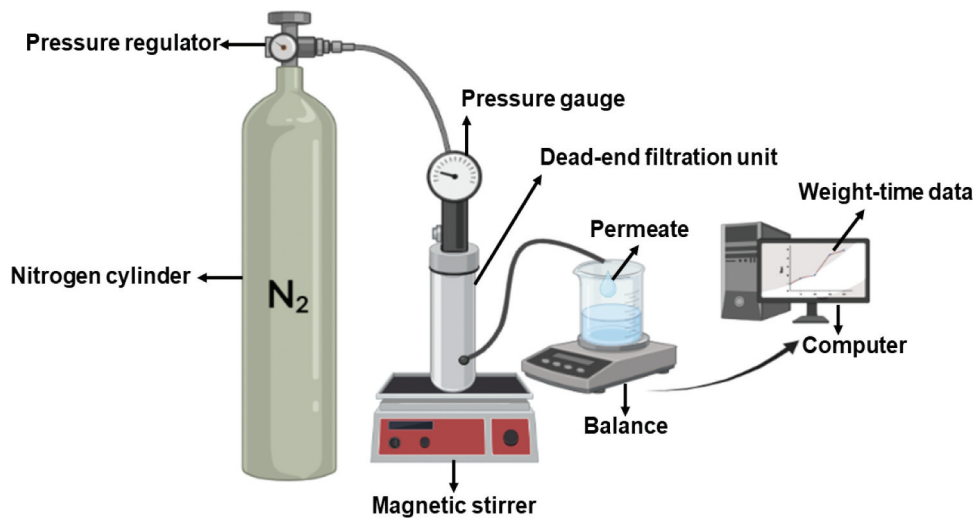
Figure 1. Schematic diagram of the dead-end filtration system used to determine the flux performance of membranes.

the membranes were carried out in duplicate, and the flux values are given as average values.

$$J = \frac{V}{Ax\Delta t} \tag{3}$$

where, J is flux (L/m^2.h), V is permeate volume (L), A is membrane area (m^2), and Δt is time (h).

In order to determine the turbidity and electrical conductivity removal performance of membranes from Terkos Lake water, membrane permeates were collected using a dead-end filtration setup at 3 bar. Turbidity measurements were performed with a HACH 2100P Turbidimeter. Electrical conductivity measurements were performed with the HACH HQ40d device. The turbidity and electrical conductivity removal efficiency of the membranes from surface water was calculated using Equation 4.

$$R(\%) = \frac{Cf - Cp}{Cf} x100 \tag{4}$$

where, Cf and Cp were the pollutant concentrations in the feed and membrane permeate, respectively.

2.5. Calculation of fouling ratio and flux recovery ratio of membranes

In order to investigate the fouling of membranes after lake water filtration and to compare the resistance of membranes to fouling, the total fouling ratio (Rt), reversible fouling ratio (Rr), irreversible fouling ratio (Rir) and flux recovery ratio (FRR) values of membranes were calculated. The parameters showing the antifouling ability of the membranes were calculated using the data obtained from the flux tests performed in the dead-end filtration system and the equations below (Equation 5–8),

$$R_t(\%) = \frac{j_{w1} - j_{lake}}{j_{w1}} x100 \tag{5}$$

$$R_r(\%) = \frac{j_{w2} - j_{lake}}{j_{w1}} x100 \tag{6}$$

$$R_{ir}(\%) = \frac{j_{w1} - j_{w2}}{j_{w1}} x100 \tag{7}$$

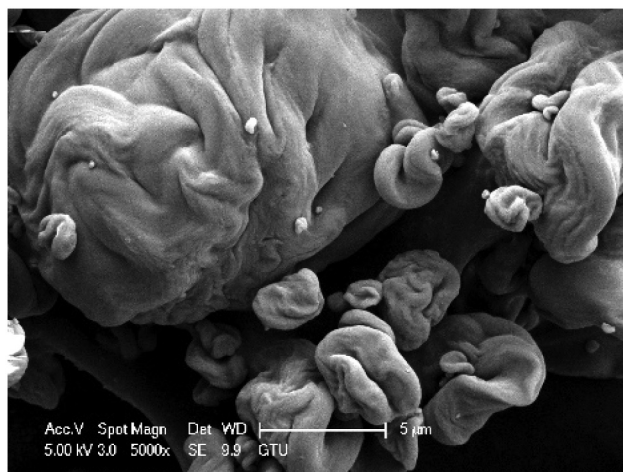$$FRR(\%) = \frac{j_{w2}}{j_{w1}} x100 \tag{8}$$

**Figure 2.** SEM view of CNC agglomerates.

3. Results and discussion

3.1. Surface morphology of CNC agglomerates

The surface of the CNC-doped membrane was examined with SEM. Figure 2 shows the SEM surface view of CNC agglomerates. The CNC agglomerates had irregular shapes and were wrinkled. In previous studies in the literature, SEM views very similar to the SEM surface view of CNC agglomerates obtained in this study were presented, and similar findings were reported.[30,31]

3.2. Surface morphology of membranes

The surface properties of membranes significantly affect the water flux and rejection performance of membranes. Figure 3 shows the SEM surface views of the membranes at 5000×, 10000×, and 20,000× magnification. It was observed that the surfaces of all membranes had a porous structure. Pores larger than 100 nm formed on the surface of the PVDF membrane indicate that the membrane is an MF membrane (Figure 3(a)). The addition of 6% wt. PVP to the PVDF membrane resulted in a significant reduction in the size of the pores on the membrane surface and an increase in surface roughness (Figure 3(b)). The fact that most of the pores on the surface of the PVDF/PVP membrane were in the range of 1–100 nm showed that the membrane was a UF membrane (Figure 3(b)). PVP can increase or decrease the porosity of the membrane. The change in membrane porosity and/or pore size also depends significantly on the molecular weight of PVP,[32] the amount of PVP in the casting solution,[33] and the viscosity of the casting solution.[14] During phase inversion, PVP can increase the exchange rate between solvent and non-solvent due
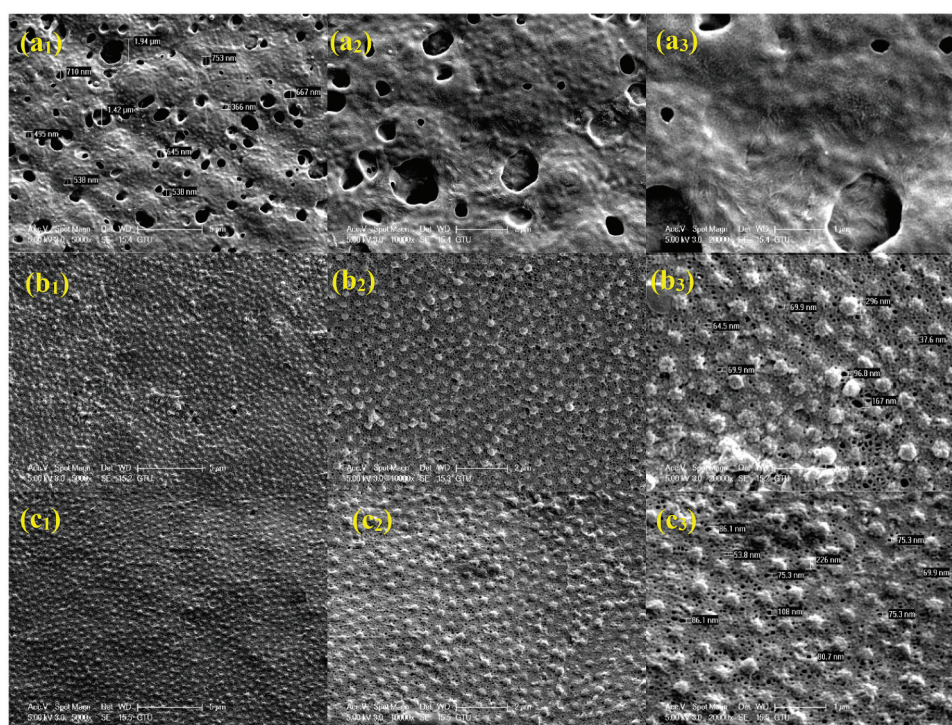
Figure 3. SEM surface views of clean membranes (a$_1$-a$_3$) PVDF, (b$_1$-b$_3$) PVDF/PVP, (c$_1$-c$_3$) PVDF/PVP/CNC. ((a$_1$, b$_1$, c$_1$) 5000x, (a$_2$, b$_2$, c$_2$) 10000x, (a$_3$, b$_3$, c$_3$) 200000x)).

to its hydrophilic nature and make the membrane more porous and/or have larger pores.[12, 34, 35] On the other hand, PVP causes an increase in the viscosity of the membrane-casting solution, reducing the exchange rate between solvent and non-solvent and causing the membrane to have a less porous and/or smaller porous structure.[36,37] In this study, PVP additive significantly reduced the size of the pores on the surface of the membrane, but many small-sized pores were formed on the membrane surface. This phenomenon can be attributed to the diffusion of PVP into water during phase inversion.[38] In the study of,[39] similar to the results of this study, it was observed that smaller sizes but more pores were formed on the surfaces of the membranes with the addition of 2%wt. PVP to 23%-30% PSf-based membranes.

Since most of the pores on the surface of the PVDF/PVP/CNC membrane are in the range of 1–100 nm, it was determined that the membrane is a UF membrane (Figure 3(c)). With 0.5% wt. CNC contribution to the PVDF/PVP membrane, no agglomeration was detected on the membrane surface even under high magnification (Figure 3(c)). The absence of agglomerate in the PVDF/PVP/CNC membrane is explained by the fact that 0.5% wt. is well distributed in the membrane. The homogeneous distribution of nanomaterials in membrane structures is of great importance in improving membrane properties and performance. Otherwise, agglomerates formed by nanomaterials worsen/decrease membrane properties and/or filtration performance instead of improving it. In the study of,[40] it was reported that CNCs exhibit poor dispersion in the polymer matrix at high concentrations, which leads to membrane defects.

3.3. Porosity and water content of membranes

Figure 4 shows the porosity and water content of membranes. While the porosity of the PVDF membrane was 54.57%, the porosity increased to 71.32% with the addition of PVP to the PVDF membrane. When 0.5 wt% CNC was added to the PVDF/PVP membrane, the porosity of the membrane decreased to 67.78%. Although the addition of PVP to the PVDF membrane increased the porosity, it significantly reduced the pore sizes on the surface of the membrane. The addition of 6% PVP to 12 wt% PVDF membrane resulted in a membrane corresponding to the pore size of the UF membrane. Adding CNC to the PVDF/PVP membrane slightly decreased the membrane porosity. The increase in viscosity with the addition of CNC to the membrane casting solution may have caused a decrease in the porosity of
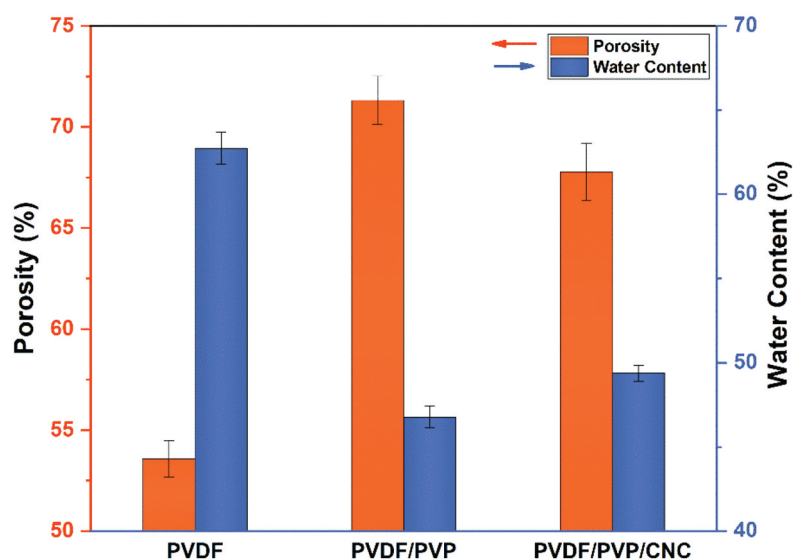
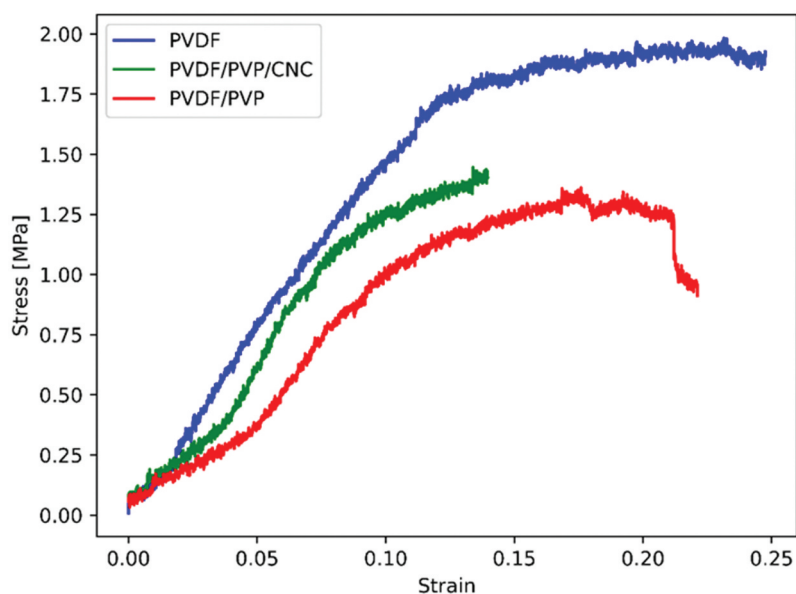**Figure 4.** Porosity and water content of membranes.

Figure 5. Stress-strain curves of membranes.

the membrane. The change in porosity caused by PVP or CNC addition to the membranes was consistent with the SEM surface images of the membranes.

The water content of PVDF, PVDF/PVP and PVDF/PVP/CNC membranes were 62.74%, 46.77% and 49.33%, respectively (Figure 4). The microstructure and hydrophilicity of the membranes significantly affect the water content of the membranes. High porosity, large pore sizes, and high hydrophilicity facilitate the passage of water into the internal structure when the membrane comes into contact with water, affecting the water retention capacity of the membrane. The large pore size of the PVDF membrane (MF membrane) allowed it to retain a greater volume of water within its internal structure. The pore sizes of PVDF/PVP and PVDF/PVP/CNC membranes (UF membranes) were smaller than those of PVDF membranes, which caused these membranes to retain less water in their internal structure when in contact with water. After the CNC addition to the PVDF/PVP membrane, the water content of the membrane increased. This is due to the fact that CNC, which has an abundance of -OH groups in its
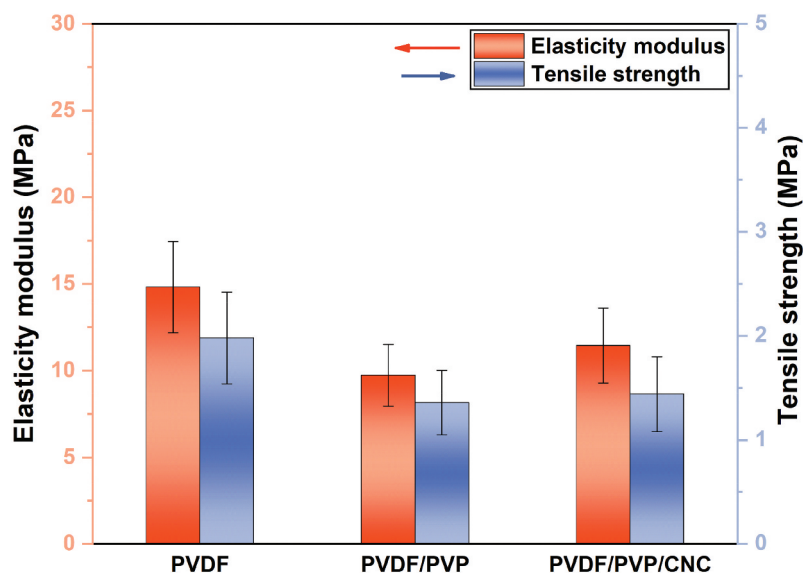
Figure 6. Elasticity modulus and tensile strength of membranes.

3.4. Mechanical properties of membranes

It is important for membranes to have improved mechanical properties so that they are resistant to pressure, hydraulic blow, and contaminants such as solids with sharp corners in water during filtration. The stress-strain curves of the membranes are shown in Figure 5. All membranes with polymeric structures exhibited elastic behavior followed by plastic behavior (Figure 5). When the slopes in the elastic region, which represents the elasticity modulus of the material, were ranked from high to low, an order was obtained as follows: PVDF > PVDF/PVP/CNC > PVDF/PVP.

The elasticity modulus and tensile strength values of the membranes are shown in Figure 6. The elasticity modulus, an indicator of the rigidity of the membranes, was calculated from the slopes of the elastic regions of the stress-strain curves. The elastic modulus of PVDF, PVDF/PVP and PVDF/PVP/CNC membranes were determined as 14.82, 9.73 and 11.45 MPa, respectively. The tensile strength of membranes refers to the maximum stress that the membrane can withstand until the membrane ruptures during the tensile test. The tensile strengths of PVDF, PVDF/PVP and PVDF/PVP/CNC membranes were determined as 1.98, 1.36 and 1.44 MPa, respectively. The lower elasticity modulus and tensile strength values of PVDF/PVP and PVDF/PVP/CNC membranes compared to pure PVDF membranes can be attributed to the presence of many small pores on

the membrane surfaces. Since the elasticity modulus of CNC (100–150 GPa)[42] is higher than polymers, the elasticity modulus of the nanocomposite membrane (PVDF/PVP/CNC) was higher than the elastic modulus of PVDF/PVP. With the addition of 0.5% wt. CNC to the PVDF/PVP membrane, the elasticity modulus and tensile strength of the membrane increased by ~ 18% and ~ 6%, respectively.

The elongation at break of the membranes is an indicator of how far the membrane can extend before breaking/tearing during the tensile test. The elongation at break values of PVDF, PVDF/PVP and PVDF/PVP/CNC membranes were determined as 0.24, 0.22 and 0.14, respectively (Figure 7). Elongation at break results of the membranes shows the ductility of the membranes. The higher elongation at break values emphasizes the more ductile behavior of the membrane, which reduces the chance of sudden brittle failure.

3.5. Results of XRD

Figure 8 shows the XRD pattern of the membranes. XRD pattern of PVDF/PVP membrane exhibited peaks at $2\theta = 9.40, 14.02, 16.88, 18.46, 19.94, 25.50$ and $28.52°$. XRD patterns of PVDF/PVP/CNC membrane exhibited peaks at 9.39, 14.02, 16.88, 18.46, 19.98, 25.58, 28.56 and 31.64°. The XRD patterns of PVDF/PVP and PVDF/PVP/CNC membranes exhibited sharp peaks in the range $2\theta = 9°$-30°. The XRD patterns of both membranes were quite similar, and both membranes exhibited a major peak at $2\theta = 16.88°$. The intensity of the highest peak in the XRD pattern of PVDF/PVP and
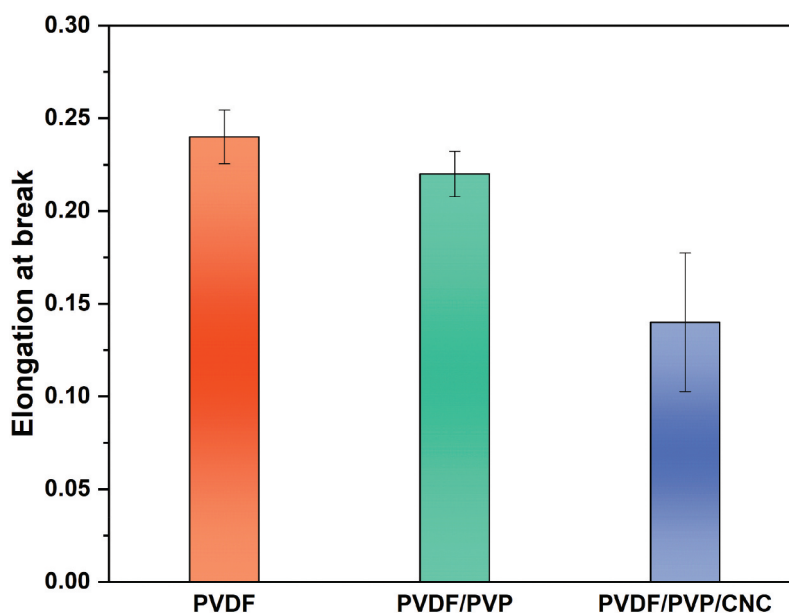
Figure 7. Elongation at break values of membranes.

PVDF/PVP/CNC membrane was 49,966 and 45,172 counts, respectively. The XRD pattern of the PVDF/PVP/CNC membrane had a low-intensity (~3,000 counts) peak at $2\theta = 31.64°$, which was not present in the XRD pattern of the PVDF/PVP membrane. There was no significant difference in the intensity of the peaks in the XRD pattern of the PVDF/PVP membrane after CNC was added to the membrane. The low-intensity sharp peak at 31.64° in the XRD pattern of the PVDF/PVP/CNC membrane showed the presence of CNC in the membrane and its effect on the crystal form of the PVDF/PVP membrane. Similarly,[43] detected a minimal difference in the XRD spectrum with CNC reinforcement in the PVDF membrane, and they reported that the crystallinity index increased with CNC reinforcement in the membrane. In this study, the low amount of CNC in the membrane matrix (0.5 wt.%) may have limited the potential for CNC to enhance the crystallinity of the membrane matrix significantly. It was reported that the low quantity of nanomaterial incorporated into the polymeric membrane matrix did not result in any alteration to the XRD pattern of the membrane.[44]

3.6. Flux performance of membranes

Figure 9 shows the pure water flux values of clean membranes (J_{w1}), lake water flux values of clean membranes (J_{lake}), and pure water flux values of fouled-cleaned membranes (J_{w2}) at 3 bar. The average pure water fluxes of clean PVDF, PVDF/PVP and PVDF/PVP/CNC membranes were determined as 463.88 L/m².h, 389.19 L/m².h and 407.75 L/m².h, respectively. The difference in water flux values of membranes under the same conditions is due to the difference in structural properties of the membranes, such as porosity, pore size, and surface hydrophilicity. In polymeric membranes with large pores, the membrane's resistance to water is lower, and water is filtered by easily passing through the pores under pressure. Due to the absence of PVP and nanomaterials in the casting solution of the pure PVDF membrane, the viscosity of the casting solution is lower than that of other membrane casting solutions, leading to the formation of large pores on the membrane surface during phase inversion. This explains why the PVDF membrane has a higher flux than other membranes. On the other hand, in PVDF/PVP and PVDF/PVP/CNC membranes with smaller pore sizes, it was more difficult for water to pass through the pores, leading to a decrease in pure water flux. It is worth reporting that adding a low amount of CNC (0.5% wt.) to the PVDF/PVP membrane resulted in an approximately 5% increase in pure water flux. Hydrophilic CNC distributed on the surface and internal structure of the membrane increased the affinity of the membrane for water and enabled easier water filtering through the membrane.

Filtration of the produced membranes in real water, surface water, groundwater or wastewater, etc. is necessary to determine their performance under real conditions. When the J_{lake} values of the membranes were listed from high to low, the order was as follows:
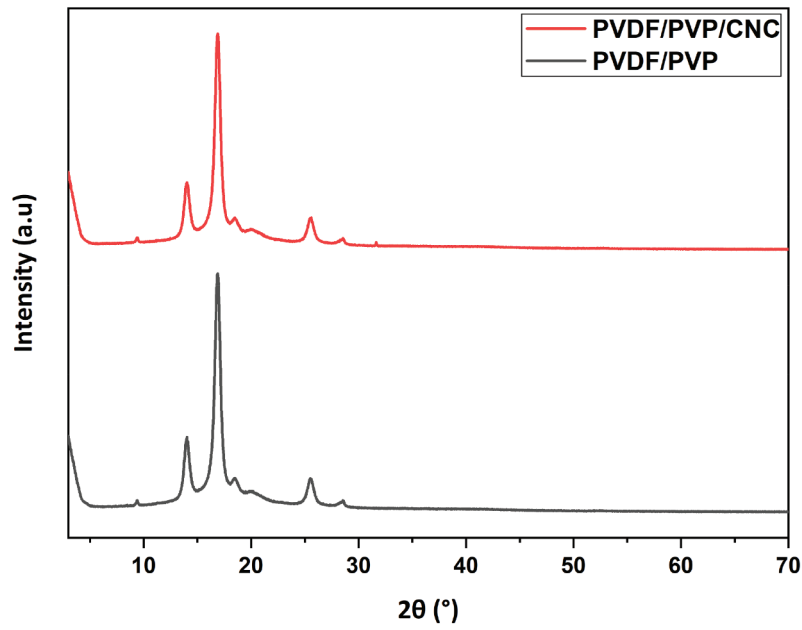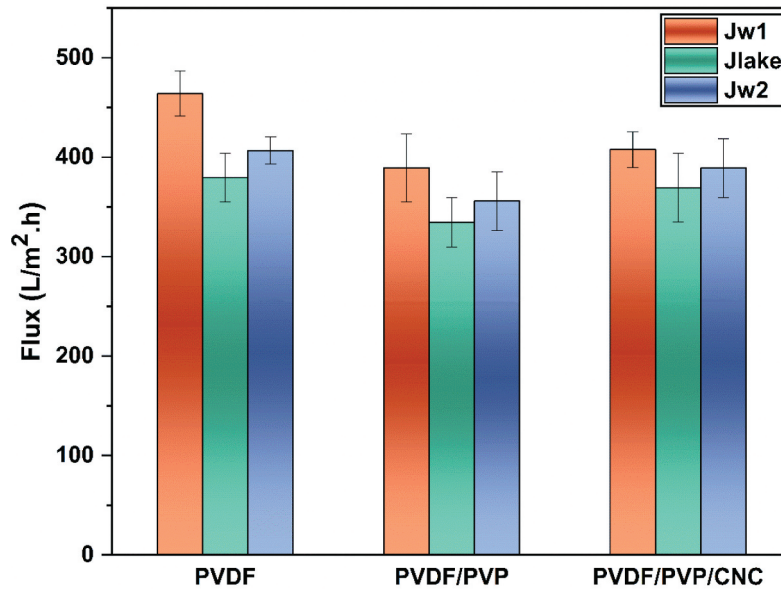
Figure 8. XRD pattern of the membranes.

Figure 9. J_{w1}, J_{lake} and J_{w2} values of membranes at 3 bar.

PVDF (379.50 L/m^2.h) > PVDF/PVP/CNC (369.35 L/m^2.h) > PVDF/PVP (334.53 L/m^2.h). The J_{lake} performances of the membranes were consistent with the J_{w1} performances, and the J_{lake} values of the membranes were lower than the J_{w1} values. It was caused by the accumulation of organic and inorganic contaminants in the lake water on the surface and/or pores of the membrane, which clog them.

The Average J_{w2} values of PVDF, PVDF/PVP, and PVDF/PVP/CNC membranes were determined as 406.68 L/m2.h, 355.81 L/m2.h, and 385.03 L/m2.h, respectively. The membranes' J_{w2} values were lower
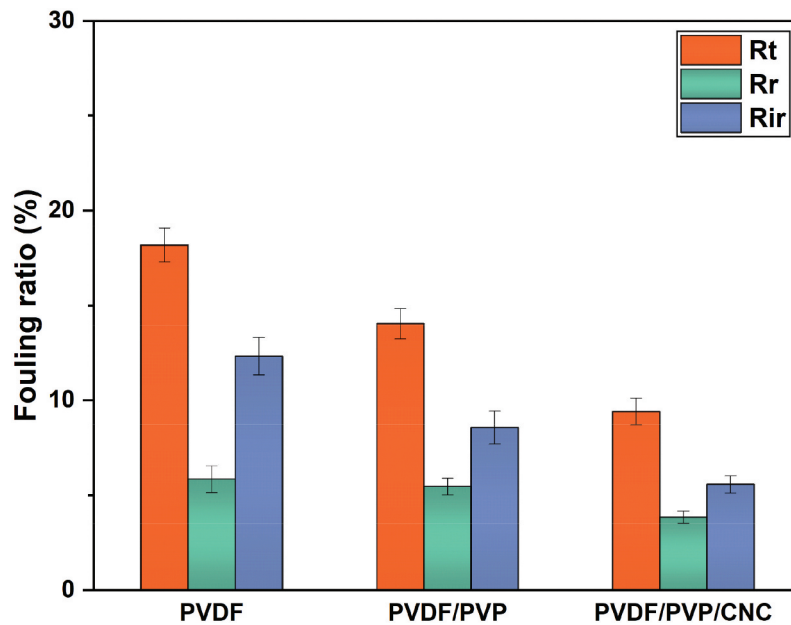
Figure 10. Rt, Rr and Rir values of membranes.

and higher than the J_{w1} and J_{lake} values, respectively. This result showed that 15 minutes of physical cleaning did not remove contaminants accumulated on the surface and/or pores of the fouled membranes with 100% efficiency.

3.7. Antifouling ability and fouling behaviour of membranes

Fouling in membranes is divided into reversible and irreversible fouling. In membranes, the Rr value refers to the fouling ratio caused by contaminants that mostly accumulate on the surface of the membrane and are weakly bound to the membrane. This type of fouling can be removed by simple cleaning methods (e.g. physical cleaning). The Rir value expresses the fouling ratio when the contaminants on the membrane surface and pores cannot be removed by physical cleaning and the contaminants bind more tightly to the membrane. The Rt value is equal to the sum of the Rr and Rir values and expresses the total fouling rate of the membrane. Figure 10 shows the Rt, Rr and Rir values of the fouled
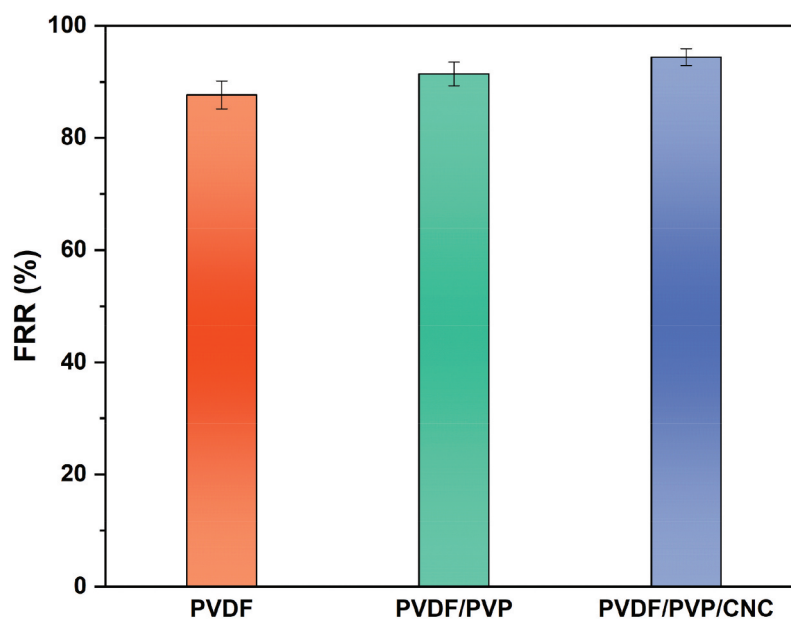

Figure 11. FRR values of membranes.

membranes after lake water filtration. Rt values of PVDF, PVDF/PVP and PVDF/PVP/CNC membranes were determined as 18.19%, 14.04% and 9.41%, respectively. It is desirable for the membranes to have a low Rt value, as less frequent cleaning of the membrane used in water treatment applications interrupts the filtration process less. The Rt value decreased with the addition of PVP to the PVDF membrane and CNC to the PVDF/PVP membrane. The fact that PVP is a hydrophilic polymer and CNC is a hydrophilic nanomaterial improved the antifouling ability of the hydrophobic PVDF membrane by increasing its surface hydrophilicity.

FRR values of membranes indicate their resistance to fouling. While membranes with high FRR values have high fouling resistance, on the contrary, membranes with low FRR values have low fouling resistance. Figure 11 shows the FRR values of the membranes. The membrane with the lowest FRR value was determined as PVDF (87.66%). The FRR value of the PVDF/PVP membrane (91.42%) increased to 94.42% with the addition of CNC. Since PVDF/PVP/CNC is the membrane with the lowest tendency to fouling among all membranes, it is possible to say that PVDF/PVP/CNC membrane may have a longer service life. Since the presence of hydrophilic CNCs in the membrane contributes to improving the surface hydrophilicity of the membrane, it reduces the interaction of hydrophobic contaminants with the membrane surface and

contributes to the prevention of the accumulation of contaminants on the membrane. Since membranes with high surface hydrophobicity become dirty easily during filtration, the use of chemicals is often required to clean these membranes. Using chemical cleaning agents not only increases operating costs in the membrane process but also significantly damages the polymeric membrane structure, causing deformation of the polymeric membrane. Moreover, fouled membranes lead to a poor quality permeate. As a result, it can be predicted that a low amount of CNC additive will extend the service life of the polymeric membrane and reduce operating costs in terms of cleaning.

Figure 12 shows the normalized water flux of the membranes as a function of time during 15 min filtration period. At 15 minutes, the normalized values of fluxes of PVDF, PVDF/PVP and PVDF/PVP/CNC membranes were 0.60, 0.66 and 0.71, respectively. When surface water was filtered through PVDF, PVDF/PVP and PVDF/PVP/CNC membranes, the flux decreased by 40%, 34% and 29% after 15 minutes, respectively. Resistance to fouling increased after the PVP additive was added to the PVDF membrane, and the CNC additive was added to the PVDF/PVP membrane. The normalized flux of PVDF membrane, PVDF/PVP membrane and PVDF/PVP/CNC membrane decreased drastically from the 3rd, 6th and 8th minute, respectively. The PVDF/PVP/CNC membrane had the potential to be used for longer periods of filtration with
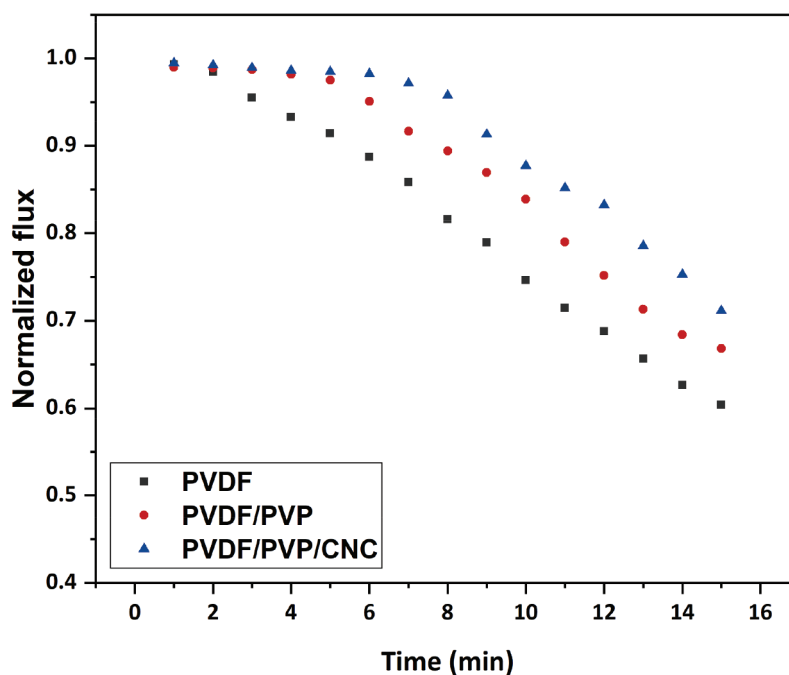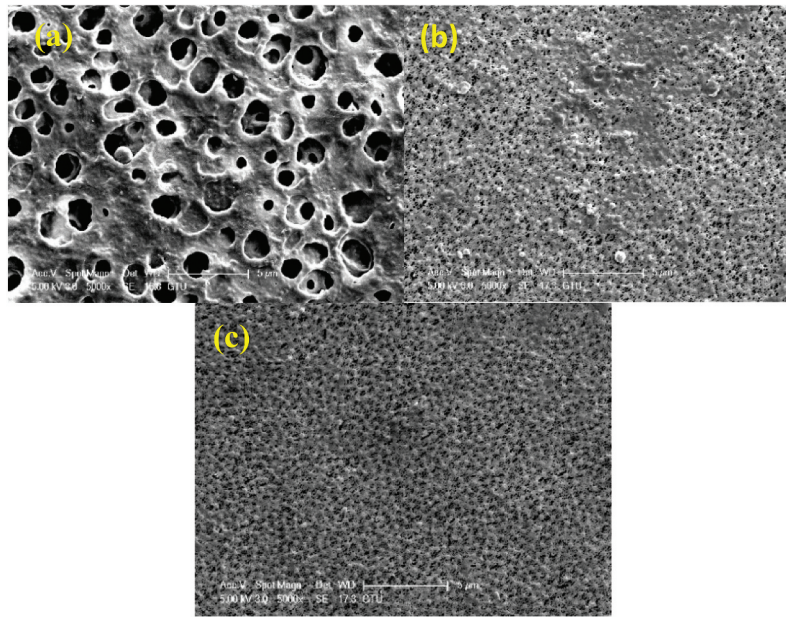

Figure 12. Normalised water flux of membranes.

Figure 13. SEM surface views of membranes after four stages (pure water filtration, lake water filtration, physical cleaning, pure water filtration) (a) PVDF, (b) PVDF/PVP, (c) PVDF/PVP/CNC.

Table 2. Turbidity and electrical conductivity removal performance of membranes.

Membrane	Turbidity removal (%)	Electrical conductivity removal (%)
PVDF	38.22	19.32
PVDF/PVP	71.01	31.28
PVDF/PVP/CNC	74.76	34.62

high flux performance because it is more resistant to fouling than other membranes.

SEM views of the membranes after exposure to four stages (pure water filtration, lake water filtration, physical cleaning and pure water filtration) are shown in Figure 13. Physical cleaning of the membranes, which was fouled with lake water for 15 minutes and then filtered with pure water at 3 bar for 15 minutes, was not sufficient to remove the contaminants from the membranes with 100% efficiency (Figure 13). The pores on the surface of the PVDF/PVP membrane surface were blocked even after cleaning with pure water and pure water filtration. On the other hand, it was observed that the pores on the surface of the PVDF/PVP/CNC membrane were not clogged. CNC not only reduced the fouling ratio of the PVDF/PVP membrane and increased the flux recovery rate but also contributed to keeping the membrane pores open. As a result, it was determined that PVDF/PVP/CNC was the most resistant to fouling among the prepared membranes, and with the addition of CNC to the PVDF/PVP-based membrane, the membrane's resistance to fouling improved significantly.

3.8. Treatment performance of membranes

Table 2 shows the turbidity and electrical conductivity removal efficiency of membranes from surface water. Substances such as clay, silt, chemical precipitates, organisms and plant particles cause turbidity in water. Turbidity in surface water leads to a decrease in the light transmittance of water. Turbidity in drinking water is undesirable as it creates an unaesthetic appearance. In addition, particles that cause turbidity in water during water treatment provide shelter for microorganisms, reducing disinfection efficiency. It has been reported that there is a negative correlation between water disinfection efficiency and turbidity.[45] In this study, the turbidity of Terkos lake water was 2.3 NTU. The turbidity of surface water filtered through PVDF, PVDF/PVP and PVDF/PVP/CNC membranes decreased by 38.22%, 71.01% and 74.76%, respectively. According to the World Health Organization (WHO), the turbidity value in drinking water should be less than 1 NTU for effective disinfection. Water filtered through the PVDF membrane had turbidity above 1 NTU.[46] However, the turbidity was less than 1 NTU in the permeates of PVDF/PVP and PVDF/PVP/CNC membranes. This can be explained by the fact that the PVDF membrane is an MF membrane with larger pore sizes, while PVDF/PVP and PVDF/PVP/CNC membranes are UF membranes with smaller pore sizes.

The electrical conductivity of water is a function of the dissolved ions in the water, and high conductivity may

indicate the presence of impurities in the water. In this study, the electrical conductivity of the surface water fed to the membranes was 380 μS/cm. The conductivity removal of the produced membranes from water varied between 19.32–34.62%. Nanofiltration and reverse osmosis membranes of much smaller size are generally preferred for removing anions and cations dissolved in water. In this study, it was an expected result that conductivity could not be removed with MF and UF membranes with very high efficiency. However, it should be noted that the decrease in the conductivity of surface water with membranes with larger pore sizes, such as MF and UF, showed that the substances that cause conductivity in water could be retained by membranes by mechanisms such as electrostatic interactions and/or adsorption. The PVDF/PVP/CNC membrane was more efficient in removing turbidity and electrical conductivity from water as CNC reinforcement of the PVDF/PVP membrane caused a decrease in the porosity of the membrane.

3.9. Practical implications of this study

In this study, the flat sheet MF membrane (PVDF) and flat sheet UF membranes (PVDF/PVP and PVDF/PVP/CNC) produced can be used for the treatment of drinking water, domestic wastewater, industrial wastewater, gray water and landfill leachate. PVDF/PVP membrane can remove suspended solids, large particles, microplastics and bacteria from water and wastewater. The UF membranes produced can be used for the removal of suspended solids, bacteria and microplastics, as well as colloids, viruses and macromolecules from water due to their smaller pore size than MF membranes. Although flat sheet membranes require more space due to their flat surface, the flat surface makes them easier to clean and simplifies membrane maintenance. Therefore, the flat sheet membranes produced in this study are also suitable for the filtration of highly contaminated water. PVDF is a widely used membrane material in membrane bioreactors (MBR) due to its high chemical stability, thermal stability, flexible structure, strength, and easy cleanability. The membranes produced in this study can potentially be used in MBR systems. The membranes produced can be used alone in water and wastewater filtration, or they can be used as a pre-treatment process before membranes with smaller pore sizes. Thus, using MF and UF membranes as pre-treatment stages minimizes the fouling and clogging potential of membranes with very small pore sizes, such as nanofiltration and reverse osmosis. Although the production cost of CNC-reinforced mixed membranes was higher than non-CNC reinforced membranes, CNC-reinforced membranes had superior properties and performance. Since the CNC-reinforced membrane with higher flux allows more water to be filtered per unit of time, the CNC-reinforced membrane contributes to reducing energy and operating costs. Time is valuable, especially in large-scale treatment plants that require continuous treatment of water or wastewater. Since the CNC-reinforced membrane can filter more water in a shorter time, it is more suitable for use in large-scale treatment plants.

The properties of the final membrane (porosity, pore size, hydrophilicity, mechanical strength, etc.) and filtration performance (water flux and rejection performance) are influenced by the amounts and properties (structure, size, functional groups, etc.) of the components in the membrane casting solution. Therefore, the effect of different properties and different amounts of CNC on PVDF/PVP membranes should be further investigated in future studies. In addition, under the operating conditions of the membrane (pressure, temperature, chemical cleaning, etc.), whether the CNC mixed into the membrane matrix maintains its presence in the membrane structure (the potential of CNC leaching into water) should be further investigated in future studies.

3.10. Comparison of current study results with other studies

The results of this study and other similar studies in the literature are summarized in Table 3. The properties of the final membrane produced by the phase inversion method depend on the composition of the membrane casting solution and the membrane production conditions (coagulation bath composition, coagulation bath temperature, membrane casting thickness, etc.).[51] It has been reported in previous studies that the amount of PVDF,[52] PVP[27] and CNC[23] in the casting solution affects the properties and performance of PVDF-based composite and nanocomposite membranes. In addition to the amounts of components in the membrane casting solution, the properties of the components also affect the properties and performance of the final membrane. For example,[26] found that the porosity, pore size, hydrophilicity, roughness, mechanical strength, flux performance and bovine serum albumin (BSA) rejection performance of PVDF-based membranes doped with 5 wt% PVP of different molecular weights (10, 24, 40, and 360 kDa) varied depending on the molecular weight of PVP. Therefore, it was an expected result that the properties of membranes

Table 3. Comparing the results of this study with other studies.

Membranes	Water content (%)	Porosity (%)	Water flux (L/m².h)	Elasticity modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	FRR (%)	Reference
PVDF (12%)	62.74	54.57	463.88 (3 bar)	14.82	1.98	24	87.66 (Surface water)	This study
PVDF/PVP (12%/6%)	46.77	71.32	389.19 (3 bar)	9.73	1.36	22	91.42 (Surface water)	This study
PVDF/PVP/CNC (12%/6%/0.5%)	49.33	67.78	407.75 (3 bar)	11.45	1.44	14	94.42 (Surface water)	This study
PVDF/PVP/TiO₂ (16%/2%/1%)	-	85.21	95.84 (1 bar)	14.821	0.00161	15.03	-	[47]
PVDF (15%)	60	~52	~18	0.95	~3.75	~68	~40	[41]
PVDF/CNC (14.5%/0.5%)	~67.5	~73	~25 (1 bar)	~1.3	~3.5	~43	~47 (BSA)	
PVDF	-	20	9	-	~4.1	~75	-	[28]
PVDF/PVP		~22	~15 (3 bar) (oily wastewater)		~4.5	~73		
PVDF (15%)	-	9.23	-64.20	-	-	-	-	[27]
PVDF/PVP (14.9%/0.1%)		32.01	171.60					
PVDF/PVP (14.8%/0.2%)		93.59	(4 bar)					
PES/PVP (15%/3%)		61	185	-	-	-	-	[40]
PES/PVP/CNC (15%/3%/0.75 g)		73	243 (0.6 bar)					
PES (18%)	-	-	25.6	-	21.2	57	97.60	[48]
PES/CNC(18%/1%)			64 (5 bar)		21.7	39	97.80 (Dye)	
PVDF (14%)	-	~30	9.8	-	-	-	~71.60	[23]
PVDF/CNC (12.6%/1.4%)		~40	~50 (1 bar)				~82.50 (BSA)	
PSf/PVP (20%/6%)		50.78	40.13	~15	-	9	57.14	[49]
PSf/PVP/CNC (20%/6%/0.5%)		56.51	63.06 (1 bar)	~13		12	66.67 (BSA)	
PVDF (10%)	-	81.40	-	-	-	-	-	[50]
PVDF/PVP (10%/1%)		83.40						
PVDF (17%)	-	2.21	0	-	-	-	-	[35]
PVDF/PVP (17%/6%)		37.19	11.67 (1 bar)					
PVDF/TiO₂ (18%/2%)	-	81.95	60	-	2.77	351.50	-	[26]
PVDF/PVP/TiO₂ (18%/5%/2%)		85.15	~82		2.18	312		

produced using PVDF and PVP with different molecular weights than the average molecular weights of PVDF (~534,000) and PVP (40,000) in this study would differ. In addition, DMF was used as the solvent in producing all membranes in this study. It has been reported that polymeric membranes with different microstructures were obtained by changing the type of solvent used in the preparation of the membrane-casting solution.[14] The use of different solvents such as N, N-dimethylacetamide (DMAc)[27, 28, 35, 47] and DMF[23] in the production of PVDF-based membranes also affects the final microstructure, flux and rejection performance, and mechanical properties of the membrane.

The flux performance of membranes is affected by the properties of the membrane, such as porosity, pore size, surface hydrophilicity, and surface roughness. In addition, the operating conditions (filtration technique, feed water temperature, and pressure) significantly affect the flux value of the membranes. In this study, the flux performance of the membranes was determined at 3 bar pressure using the dead-end filtration technique. It can be clearly seen in Table 3 that the flux values of the membranes at the filtration performed at pressures lower than 3 bar (0.6 bar and 1 bar) were significantly lower than the flux values of the membranes in this study.

The flux values of PVDF (15%) and PVDF/PVP (14%/0.1% and 14%/0.2%) based membranes at 4 bar were lower than the flux values in this study.[27] The differences in the composition of the membrane casting solutions and the properties of the membranes in the studies can explain this. For example, the pore size and surface structure of the membrane on the surface of the

PVDF membrane in this study were significantly different from the pore size and surface structure of the PVDF membrane in the study of.[27]

The FRR value varies depending on the composition of the feed water, filtration time, operating conditions and membrane cleaning process. In some studies, the FRR value of PVDF and PVDF/CNC membranes was calculated after BSA was filtered from the membrane.[23,41] In this study, for the first time, the FRR value of PVDF-based membranes with and without CNC reinforcement was calculated after surface water filtration (Terkos Lake water filtration). Since surface water differs from synthetic BSA solutions and the membranes were cleaned with distilled water for 15 minutes in this study, the FRR values of the membranes in this study were higher than the FRR values of the membranes in other studies.

4. Conclusion

In this study, PVDF, PVDF/PVP and PVDF/PVP/CNC membranes were prepared using the phase inversion method. As a result of the characterization studies and performance tests of the prepared membranes, the following results were obtained:

The addition of 6% wt. PVP to pure PVDF membrane significantly affected the membrane surface morphology. PVP significantly reduced the pore sizes on the surface of the PVDF membrane and increased its porosity. In relation to the increased porosity, with the addition of PVP, the elasticity modulus, tensile strength, and elongation at the break values of the membrane decreased; that is, the resistance to mechanical loading of the membrane decreased. Additionally, the addition of PVP led to a decrease in the pure water and lake water flux performance of the membrane. On the other hand, the antifouling ability of PVDF/PVP membrane was better than that of pure PVDF membrane. This was due to the very large pores on the surface of PVDF (mostly >100 nm) being ideal places for contaminants to accumulate easily.

With the addition of 0.5% wt. CNC to the PVDF/PVP membrane, no agglomeration occurred on the membrane surface, and CNC was well dispersed in the membrane matrix. The addition of 0.5% wt. CNC did not cause significant changes in the surface morphology of the membrane. On the other hand, compared with PVDF/PVP membrane, the elasticity modulus and tensile strength of PVDF/PVP/CNC were ~ 18% and ~ 6% higher, respectively. Additionally, even low amounts of CNC contributed

to the increase of pure water and lake water flux of the membrane by ~ 5% and ~ 10.5%, respectively. The addition of CNC significantly improved the antifouling ability of the membrane by decreasing the Rt value and increasing the FRR value. SEM analysis results confirmed that PVDF/PVP/CNC nanocomposite membrane has higher antifouling ability compared to PVDF/PVP membrane. The addition of CNC to PVDF/PVP membrane increased the turbidity and electrical conductivity removal of the membrane from lake water.

It can be reported that adding low CNC to PVDF/PVP UF membrane, which is widely used in membrane filtration today, can significantly improve the membrane's mechanical properties, water filtration performance, and fouling resistance. In future studies, it is important to investigate the effect of different CNC amounts on the properties and performance of PVDF/PVP membranes. This enables the optimum amount of CNC to be determined and membranes with improved performance to be used in filtration applications.

Disclosure statement

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Availability of data and materials

No datasets were generated or analyzed during the current study.

References

[1] Acarer, S. A Review of Microplastic Removal from Water and Wastewater by Membrane Technologies. *Water. Sci. Technol.* 2023, *88*(1), 199–219. DOI: 10.2166/wst.2023.186.

[2] Lv, J.; Zhang, G.; Zhang, H.; Yang, F. Graphene Oxide-Cellulose Nanocrystal (GO-CNC) Composite Functionalized PVDF Membrane with Improved Antifouling Performance in MBR: Behavior and Mechanism. *Chem. Eng. J.* 2018, *352*, 765–773. DOI: 10.1016/j.cej.2018.07.088.

[3] Ghazanfari, D.; Bastani, D.; Mousavi, S. A. Preparation and Characterization of Poly(vinyl Chloride) (PVC) Based Membrane for Wastewater Treatment. *J. Water. Process Eng.* 2017, *16*, 98–107. DOI: 10.1016/j.jwpe.2016.12.001.

[4] Wang, L.; Song, X.; Wang, T.; Wang, S.; Wang, Z.; Gao, C. Fabrication and Characterization of Polyethersulfone/Carbon Nanotubes (PES/CNTs) Based Mixed Matrix Membranes (MMMs) for Nanofiltration Application. *Appl. Surf. Sci.* 2015, *330*, 118–125. DOI: 10.1016/j.apsusc.2014.12.183.

[5] Alkhouzaam, A.; Qiblawey, H. Novel Polysulfone Ultrafiltration Membranes Incorporating Polydopamine Functionalized Graphene Oxide with Enhanced Flux and Fouling Resistance. *J Memb Sci.* 2021, *620*, 118900. DOI: 10.1016/j.memsci.2020.118900.

[6] El-Ghaffar, M. A. A.; Elawady, M. M.; Rabie, A. M.; Abdelhamid, A. E. Enhancing the RO Performance of Cellulose Acetate Membrane Using Chitosan Nanoparticles. *J. Polym. Res.* 2020, *27*(11), 337. DOI: 10.1007/s10965-020-02319-7.

[7] Mishra, J. R.; Samal, S. K.; Mohanty, S.; Nayak, S. K. Polyvinylidene Fluoride (PVDF)/Ag@tio2 Nanocomposite Membrane with Enhanced Fouling Resistance and Antibacterial Performance. *Mater. Chem. Phys.* 2021, *268*, 124723. DOI: 10.1016/j.matchemphys.2021.124723.

[8] Sutrisna, P. D.; Mustika, C. P. B. W.; Hadi, R. P.; Caren, Y. E. G. Improved Oily Wastewater Rejection and Flux of Hydrophobic PVDF Membrane After Polydopamine-Polyethyleneimine Co-Deposition and Modification. *S Afr J Chem. Eng.* 2023, *44*, 42–50. DOI: 10.1016/j.sajce.2023.01.006.

[9] Porcelli, N.; Judd, S. Chemical Cleaning of Potable Water Membranes: A Review. *Sep. Purif. Technol.* 2010, *71*(2), 137–143. DOI: 10.1016/j.seppur.2009.12.007.

[10] Alsawaftah, N.; Abuwatfa, W.; Darwish, N.; Husseini, G. A Comprehensive Review on Membrane Fouling: Mathematical Modelling, Prediction, Diagnosis, and Mitigation, Comprehensive Review on Membrane Fouling: Mathematical Modelling, Prediction. *Diagnosis Mitigation.* 2021, *13*(9), 1327. DOI: 10.3390/w13091327.

[11] Gan, X.; Lin, T.; Jiang, F.; Zhang, X. Impacts on Characteristics and Effluent Safety of PVDF Ultrafiltration Membranes Aged by Different Chemical Cleaning Types. *J Memb Sci.* 2021, *640*, 119770. DOI: 10.1016/j.memsci.2021.119770.

[12] Tofighy, M. A.; Mohammadi, T.; Sadeghi, M. H. High-Flux PVDF/PVP Nanocomposite Ultrafiltration Membrane Incorporated with Graphene Oxide Nanoribbones with Improved Antifouling Properties. *J. Appl. Polym. Sci.* 2021, *138*(4), 1–15. DOI: 10.1002/app.49718.

[13] Acarer, S.; Pir, İ.; Tüfekci, M.; Erkoç, T.; Öztekin, V.; Güneş Durak, S.; Özçoban, M. Ş.; Türkoğlu Demirkol, G.; Alhammod, M.; Çavuş, S., et al. Characterisation and Modelling the Mechanics of Cellulose Nanofibril Added Polyethersulfone Ultrafiltration Membranes. *Heliyon.* 2023, *9*(2), e13086. DOI: 10.1016/j.heliyon.2023.e13086.

[14] Acarer, S. Effect of Different Solvents, Pore-Forming Agent and Solubility Parameter Differences on the Properties of PES Ultrafiltration Membrane. *Sakarya Univ. J. Sci.* 2022, *26*(6), 1196–1208. DOI: 10.16984/saufenbilder.1135285.

[15] Acarer, S.; Pir, İ.; Tüfekci, M.; Erkoç, T.; Güneş Durak, S.; Öztekin, V.; Türkoğlu Demirkol, G.; Özçoban, M. Ş.; Temelli Çoban, T. Y.; Cavuş, S., et al. Halloysite Nanotube-Enhanced Polyacrylonitrile Ultrafiltration Membranes: Fabrication. *Charact. Perform. Eval. ACS Omega.* 2023, *8*(38), 34729–34745. DOI: 10.1021/acsomega.3c03655.

[16] Bai, L.; Liu, Y.; Ding, A.; Ren, N.; Li, G.; Liang, H. Surface Coating of UF Membranes to Improve Antifouling Properties: A Comparison Study Between Cellulose Nanocrystals (CNCs) and Cellulose Nanofibrils (CNFs). *Chemosphere.* 2019, *217*, 76–84. DOI: 10.1016/j.chemosphere.2018.10.219.

[17] Salimi, P.; Aroujalian, A.; Iranshahi, D. Graft Copolymerization of Zwitterionic Monomer on the Polyethersulfone Membrane Surface by Corona Air Plasma for Separation of Oily Wastewater. *Sep. Purif. Technol.* 2021, *258*, 117939. DOI: 10.1016/j.seppur.2020.117939.

[18] Mozia, S.; Grylewicz, A.; Zgrzebnicki, M.; Darowna, D.; Czyzewski, A. Investigations on the Properties and Performance of Mixed-Matrix Polyethersulfone Membranes Modified with Halloysite Nanotube. *Polym. (Basel).* 2019, *11*(4), 671. DOI: 10.3390/polym11040671.

[19] Bai, H.; Wang, X.; Sun, H.; Zhang, L. Permeability and Morphology Study of Polysulfone Composite Membrane Blended with Nanocrystalline Cellulose. *Desalin. Water. Treat.* 2015, *53*(11), 2882–2896. DOI: 10.1080/19443994.2013.875944.

[20] Al-Maliki, R. M.; Alsalhy, Q. F.; Al-Jubouri, S.; Abdulrazak, A. A.; Shehab, M. A.; Nemeth, Z.; Hernadi, K.; Majdi, H. S. Enhanced Antifouling in Flat-Sheet Polyphenylsulfone Membranes Incorporating Graphene Oxide – Tungsten Oxide for Ultrafiltration Applications. *Membranes (Basel).* 2023, *13*(3), 269. DOI: 10.3390/membranes13030269.

[21] Yao, A.; Yan, Y.; Tan, L.; Shi, Y.; Zhou, M.; Zhang, Y.; Zhu, P.; Huang, S. Improvement of Filtration and

Antifouling Performance of Cellulose Acetate Membrane Reinforced by Dopamine Modified Cellulose Nanocrystals. *J Memb Sci.* 2021, *637*, 119621. DOI: 10.1016/j.memsci.2021.119621.

[22] Huang, S.; Wu, M.-B.; Zhu, C.-Y.; Ma, M.-Q.; Yang, J.; Wu, J.; Xu, Z.-K. Polyamide Nanofiltration Membranes Incorporated with Cellulose Nanocrystals for Enhanced Water Flux and Chlorine Resistance. *ACS Sustainable Chem. Eng.* 2019, *7*, 12315–12322. DOI: 10.1021/acssuschemeng.9b01651.

[23] Lv, J.; Zhang, G.; Zhang, H.; Zhao, C.; Yang, F. Improvement of Antifouling Performances for Modified PVDF Ultrafiltration Membrane with Hydrophilic Cellulose Nanocrystal. *Appl. Surf. Sci.* 2018, *440*, 1091–1100. DOI: 10.1016/j.apsusc.2018.01.256.

[24] Daraei, P.; Ghaemi, N.; Sadeghi Ghari, H. An Ultra-Antifouling Polyethersulfone Membrane Embedded with Cellulose Nanocrystals for Improved Dye and Salt Removal from Water. *Cellulose.* 2017, *24* (2), 915–929. DOI: 10.1007/s10570-016-1135-3.

[25] Nakada, M.; Ishida, H.; Furushima, Y. Structural and Dynamical Characterisation of Intermediate Water Interacting Polyvinyl Pyrrolidone. *Materialia (Oxf).* 2020, *12*, 100743. DOI: 10.1016/j.mtla.2020.100743.

[26] Ong, C. S.; Lau, W. J.; Goh, P. S.; Ng, B. C.; Matsuura, T.; Ismail, A. F. Effect of PVP Molecular Weights on the Properties of PVDF-Tio2 Composite Membrane for Oily Wastewater Treatment Process. *Sep. Sci Technol.* 2014, *49*(15), 2303–2314. DOI: 10.1080/01496395.2014.928323.

[27] Purnawan, I.; Angputra, D.; Debora, S. C.; Karamah, E. F.; Febriasari, A.; Kartohardjono, S. Polyvinylidene Fluoride Membrane with a Polyvinylpyrrolidone Additive for Tofu Industrial Wastewater Treatment in Combination with the Coagulation – Flocculation Process. *Membranes (Basel).* 2021, *11*(12), 948. DOI: 10.3390/membranes11120948.

[28] Kartohardjono, S.; Salsabila, G. M. K.; Ramadhani, A.; Purnawan, I.; Lau, W. J. Preparation of PVDF-PVP Composite Membranes for Oily Wastewater Treatment. *Membranes (Basel).* 2023, *13*(6), 611. DOI: 10.3390/membranes13060611.

[29] ASTM D 882-02. Standard Test Method for Tensile Properties of Thin Plastic Sheeting. ASTM International, Www.Astm.Org (2002) 1–12. 10.1520/D0882-18.

[30] Esparza, Y.; Ngo, T. D.; Fraschini, C.; Boluk, Y. Aggregate Morphology and Aqueous Dispersibility of Spray-Dried Powders of Cellulose Nanocrystals. *Ind. Eng. Chem. Res.* 2019, *58*(43), 19926–19936. DOI: 10.1021/acs.iecr.9b03951.

[31] Abdallah, W.; Kamal, M. R. Influence of Process Variables on Physical Characteristics of Spray Freeze Dried Cellulose Nanocrystals. *Cellulose.* 2018, *25*(10), 5711–5730. DOI: 10.1007/s10570-018-1975-0.

[32] Bensaadi, S.; Arous, O.; Kerdjoudj, H.; Amara, M. Evaluating Molecular Weight of PVP on Characteristics of CTA Membrane Dialysis. *J. Environ. Chem. Eng.* 2016, *4*(2), 1545–1554. DOI: 10.1016/j.jece.2016.02.003.

[33] Vatsha, B.; Ngila, J. C.; Moutloali, R. M. Preparation of Antifouling Polyvinylpyrrolidone (PVP 40K) Modified Polyethersulfone (PES) Ultrafiltration (UF) Membrane for Water Purification. *Phys. Chem. Earth, Parts A/B/C.* 67–69 (2014, *67-69*, 125–131. DOI: 10.1016/j.pce.2013.09.021.

[34] Anvari, A.; Safekordi, A.; Hemmati, M.; Rekabdar, F.; Tavakolmoghadam, M.; Yancheshme, A. A.; Gheshlaghi, A. Enhanced Separation Performance of PVDF/PAN Blend Membrane Based on PVP Tuning. *Desalin. Water Treat.* 2015, *3994*, 0–9. DOI: 10.1080/19443994.2015.1051123.

[35] Guo, Y. W.; Cui, W.; Xu, W.; Jiang, Y.; Liu, H.; Xu, J.; Gao, Z.; Liu, L. Effect of PVP Hydrophilic Additive on the Morphology and Properties of PVDF Porous Membranes. *Adv Mat Res.* 2014, *981*, 891–894. DOI: 10.4028/www.scientific.net/AMR.981.891.

[36] Anvari, A.; Yancheshme, A. A.; Rekaabdar, F.; Hemmati, M.; Tavakolmoghadam, M.; Safekordi, A. PVDF/PAN Blend Membrane: Preparation, Characterization and Fouling Analysis. *J. Polym. Environ.* 2017, *25*(4), 1348–1358. DOI: 10.1007/s10924-016-0889-x.

[37] Anvari, A.; Safekordi, A.; Hemmati, M.; Rekabdar, F.; Tavakolmoghadam, M.; Azimi Yancheshme, A.; Gheshlaghi, A. Enhanced Separation Performance of PVDF/PAN Blend Membrane Based on PVP Tuning. *Desalin. Water. Treat.* 2016, *57*(26), 12090–12098. DOI: 10.1080/19443994.2015.1051123.

[38] Mavukkandy, M. O.; Bilad, M. R.; Giwa, A. Leaching of PVP from PVDF/PVP Blend Membranes: Impacts on Membrane Structure and Fouling in Membrane Bioreactors. *J. Mater. Sci.* 2016, *51*(9), 4328–4341. DOI: 10.1007/s10853-016-9744-7.

[39] Tiron, L. G.; Vlad, M.; Baltă, Ş. Research on Hydrophilic Nature of Polyvinylpyrrolidone on Polysulfone Membrane Filtration. *IOP Conf Ser Mater Sci Eng.* 2018, *374*, 012059. DOI: 10.1088/1757-899X/374/1/012059.

[40] Bai, L.; Wu, H.; Ding, J.; Ding, A.; Zhang, X.; Ren, N.; Li, G.; Liang, H. Cellulose Nanocrystal-Blended Polyethersulfone Membranes for Enhanced Removal of Natural Organic Matter and Alleviation of Membrane Fouling. *Chem. Eng. J.* 2020, *382*, 122919. DOI: 10.1016/j.cej.2019.122919.

[41] Boruah, P.; Gupta, R.; Katiyar, V. Fabrication of Cellulose Nanocrystal (CNC) from Waste Paper for Developing Antifouling and High-Performance Polyvinylidene Fluoride (PVDF) Membrane for Water Purification. *Carbohydr. Polym Technol. Appl.* 2023, *5*, 100309. DOI: 10.1016/j.carpta.2023.100309.

[42] Faraj, H.; Sollogoub, C.; Guinault, A.; Gervais, M.; Bras, J.; Salmi-Mani, H.; Roger, P.; Le Gars, M.; Domenek, S. A Comparative Study of the Thermo-Mechanical Properties of Polylactide/Cellulose Nanocrystal Nanocomposites Obtained by Two Surface Compatibilization Strategies. *Mater Today Commun.* 2021, *29*, 102907. DOI: 10.1016/j.mtcomm.2021.102907.

[43] Aydemir, D.; Sözen, E.; Borazan, I.; Gündüz, G.; Ceylan, E.; Gulsoy, S. K.; Kılıç-Pekgözlü, A.; Bardak, T. Electrospinning of PVDF Nanofibers

Incorporated Cellulose Nanocrystals with Improved Properties. *Cellulose.* 2023, *30*(2), 885–898. DOI: 10.1007/s10570-022-04948-1.

[44] Ang, M. B. M. Y.; Devanadera, K. P. O.; Duena, A. N. R.; Luo, Z.-Y.; Chiao, Y.-H.; Millare, J. C.; Aquino, R. R.; Huang, S.-H.; Lee, K.-R. Modifying Cellulose Acetate Mixed-Matrix Membranes for Improved Oil–Water Separation: Comparison Between Sodium and Organo-Montmorillonite as Particle Additives. *Membranes (Basel).* 2021, *11*(2), 80. DOI: 10.3390/membranes11020080.

[45] LeChevallier, M. W.; Evans, T. M.; Seidler, R. J. Effect of Turbidity on Chlorination Efficiency and Bacterial Persistence in Drinking Water. *Appl. Environ. Microbiol.* 1981, *42*(1), 159–167. DOI: 10.1128/aem.42.1.159-167.1981.

[46] World Health Organization. WHO-FWC-WSH-17.01, 2017.

[47] Gayatri, R.; Fizal, A. N. S.; Yuliwati, E.; Zailani, M. Z.; Jaafar, J.; Hossain, M. S.; Zulkifli, M.; Taweepreda, W.; Yahaya, A. N. A. Effect of Polyvinylidene Fluoride Concentration in PVDF-Tio2-PVP Composite Membranes Properties and Its Performance in Bovine Serum Albumin Rejection. *Case Stud. Chem. Environ. Eng.* 2024, *9*, 100620. DOI: 10.1016/j.cscee.2024.100620.

[48] Lessan, F.; Karimi, M.; Bañuelos, J. L.; Foudazi, R. Phase Separation and Performance of Polyethersulfone/ Cellulose Nanocrystals Membranes. *Polym (Guildf).* 2020, *186*, 121969. DOI: 10.1016/j.polymer.2019.121969.

[49] Yang, X.; Liu, H.; Zhao, Y.; Liu, L. Preparation and Characterization of Polysulfone Membrane Incorporating Cellulose Nanocrystals Extracted from Corn Husks. *Fiber Polym.* 2016, *17*(11), 1820–1828. DOI: 10.1007/s12221-016-6762-7.

[50] Liu, X.; Duan, J.; Yang, J.; Huang, T.; Zhang, N.; Wang, Y.; Zhou, Z. Hydrophilicity, Morphology and Excellent Adsorption Ability of Poly(vinylidene Fluoride) Membranes Induced by Graphene Oxide and Polyvinylpyrrolidone. *Colloids Surf A Physicochem Eng Asp.* 2015, *486*, 172–184. DOI: 10.1016/j.colsurfa.2015.09.036.

[51] Xu, J.; Tang, Y.; Wang, Y.; Shan, B.; Yu, L.; Gao, C. Effect of Coagulation Bath Conditions on the Morphology and Performance of PSf Membrane Blended with a Capsaicin-Mimic Copolymer. *J Memb Sci.* 2014, *455*, 121–130. DOI: 10.1016/j.memsci.2013.12.076.

[52] Pramono, E.; Simamora, A. L.; Radiman, C. L.; Wahyuningrum, D. Effects of PVDF Concentration on the Properties of PVDF Membranes, IOP Conf. *Ser.: Earth Environ. Sci.* 2017, *75*, 012027. DOI: 10.1088/1755-1315/75/1/012027.