

# Characterization and performance of post treated PVDF hollow fiber membrane

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**Abstract.** Modification of Polyvinylidene fluoride (PVDF) hollow fiber membranes (HFMs) characteristics and performance were investigated via post treatment using different oxidants. sodium hypochlorite (NaOCl), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and potassium persulfate (KPS). Fourier transform infrared (FTIR) and Proton nuclear magnetic resonance (<sup>1</sup>H-NMR) results revealed no structural differences after post treatment. Cross-sectional micrographs show finger-like structures at the outer and inner walls of the HFMs and sponge-like structures in middle, where NaOCl and KPS post treated fibers exhibited a decrease in finger-like structures in addition to aggregates appearing on the surface, consequently leading to an increase in the surface roughness (Ra) from 48 nm to 52.8nm and 56 nm, respectively. Hydrogen peroxide post treatment only was observed to decrease the water contact angle from 98° to 81.4°. It was also observed that the elongation at break and the modulus decreased after NaOCl post treatment from 34.5 to 28.5% and from 19.3 Mpa to 16.6 Mpa, respectively. Moreover, pure water flux after H<sub>2</sub>O<sub>2</sub> post treatment increased from 87.8 LMH/bar to 113 LMH/bar at 0.45 bar, while no changes were detected for the methylene blue dye rejection (74%) between raw and hydrogen peroxide post treated fibers at the same pressure. According to the findings hydrogen peroxide post treated PVDF HFMs have the most uniform surfaces, with almost no alterations in structural and mechanical properties or porosities with enhanced hydrophilicity and pure water flux maintaining appropriate rejection. Therefore, it is considered an efficient surface modifying agent for UF/NF membranes or low-pressure separators.

**Keywords:** characterization; performance; post treatment; PVDF hollow fiber membrane

## 1. Introduction

Development of polymer modifications in membrane separation is essential for the wide variety of membrane applications including water treatment and gas separation (Alkindy *et al.* 2020, Matsuyama *et al.* 2017, Yang *et al.* 2018, Tavangar *et al.* 2020). Hollow fiber membranes (HFMs) are the most effective configuration due to their high active area to volume ratio, mechanical self-supporting construction and ease of processing (Goh *et al.* 2015, Turken *et al.* 2019, Sorour *et al.* 2021). Recently, numerous research endeavours have been carried out concerned with surface modification of reverse osmosis (RO), nanofiltration (NF) and ultrafiltration (UF) membranes using the most common polymeric materials include cellulose acetate, polysulfone (PS), polyethersulfone (PES) and polyvinylidene fluoride (PVDF) (Matsuyama *et al.* 2017, Fatima *et al.* 2023). Polyvinylidene fluoride (PVDF) membranes are among a variety of materials that are widely employed in several applications due to their exceptional mechanical, chemical, and thermal resistance (Bonyadi an Chung 2009, Sorour *et al.* 2021, Xu *et al.* 2021). However, PVDF is hydrophobic in nature and has a low surface free energy,

which leads to poor wettability and organic fouling in aqueous solution applications (Liang *et al.* 2013). Modifying the PVDF surface using surface coating and surface grafting has been found to be efficient and simple method to increase the surface hydrophilicity and antifouling characteristics of PVDF membranes (Hernández *et al.* 2016, Vatanpour *et al.* 2016, Ling *et al.* 2017). Surface coating techniques are the simplest to use but, the coated layer is frequently unstable. On the other hand, surface grafting copolymerization using monomers of functional molecules onto the existing PVDF membrane increase membrane stability (Ying *et al.* 2003). Surface treatment agents for membranes includes: acids, bases, oxidants, surfactants or complexing agents (Mukherjee *et al.* 1996, Jung *et al.* 2006, Regula *et al.* 2014). Other oxidizing agents include for example acidic, alkaline solutions with Ethylenediaminetetraacetic acid (EDTA), citric acid (CA) (Gan *et al.* 2021), ethyleneglycol monobutyrate (EGMB), hydrofluoric acid (HF), fluosilicic acid (FSA) and isopropyl alcohol (IPA) (Mukherjee *et al.* 1996, Jung *et al.* 2006, Hernández *et al.* 2016). Oxidizing agents like hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) are environmentally friendly oxidants, while sodium hypochlorite (NaOCl) is a low-cost oxidant and potassium persulfate (KPS) is a cross-linking agent which provides non-hazardous decomposition products.

Several investigations reported increased surface

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roughness and pore size of PVDF membrane after the treatment with NaOCl, however, its surface hydrophilicity were either increased or decreased with the NaOCl (Puspitasari *et al.* 2010, Abdullah and Bérubé 2013, Gao *et al.* 2016, Zhang *et al.* 2017, Ren *et al.* 2021). Zhang *et al.* (2017) observed significant increase in surface hydrophilicity and pore diameter of PS and PVDF ultrafiltration (UF) membranes with the treatment of 4000 ppm of NaOCl within time range (10-200 hrs) at pH around 10. Ravereau *et al.* (2016) concluded that the pH of the ageing solution has no effect on the PVDF membrane's characteristics or functionality using NaOCl. Although the PVDF degradation rate was high between pH 6 and 7.5, there were no differences in porosity (73.9%) and hydrophilicity after ageing with NaOCl. It was concluded that the pH of the ageing solution has no effect on the PVDF membrane's characteristics or functionality. On the other hand, Li *et al.* (2019) reported that ageing PVDF membrane using NaOCl at pH 3–11 caused a moderate increase in permeability and decreased rejection due to the oxidation and release of PVP whereas the membrane's tensile strength decreased only at pH 11 due to PVDF molecules defluorination. Yu *et al.* 2018 studied the modification of commercial PVDF HFMs through a two-step surface grafting method using (5 wt.%) PVP and (0.4 wt.%) KPS as a cross-linking agent at 90 °C for 6 hrs. It was concluded that flux was enhanced from 130 to 171 L m<sup>-2</sup> h<sup>-1</sup> and hydrophilicity decreased from 93° to 83°. Bi *et al.* (2013) studied the effect of PVP and KPS on the performance of the PVDF/PVP HFMs. The results showed an increase in the hydrophilicity and flux at 5% PVP was 600 LMH. Laizhou *et al.* (2007) studied the modification of PVDF HFMs from a novel thermally induced chemical graft polymerization with a blend solution of acrylic acid (AA), acrylamide (AM), N, N'- dimethylacetamide (NMBA), and KPS to enhance the hydrophilic and adsorption properties of heavy metals. Few researches focused on post treatment of PVDF HFMs with H<sub>2</sub>O<sub>2</sub>. Several studies demonstrated the effect of H<sub>2</sub>O<sub>2</sub> on PES and PS for UF membranes (Zhang *et al.* 2017, Özay *et al.* 2022).

Vatanpour *et al.* (2022) reported that fouling was reduced for TiO<sub>2</sub>/ PVDF nanocomposite membrane, in addition to increase in rejection of reactive green 19 dye after UV/ H<sub>2</sub>O<sub>2</sub> advanced oxidation as a pre-treatment process. Özay *et al.* (2022) studied the H<sub>2</sub>O<sub>2</sub> treatment of PES membrane where the permeability significantly increased by 2.3 folds using 5 mM H<sub>2</sub>O<sub>2</sub> and temperature of 100 °C. Additionally, at 2.5 mM H<sub>2</sub>O<sub>2</sub>, the largest pore size of 161.23 nm, contact angle (54.76°) and porosity (61.88%) were obtained.

In this study, the effect of post treatment on PVDF HFMs using different chemical oxidants such as sodium hypochlorite, hydrogen peroxide and potassium persulfate was investigated. PVDF HFMs properties including, surface morphology, roughness, mechanical properties, porosity and contact angle were studied for the raw and post-treated PVDF HFMs. Consequently, the permeability and rejection of methylene blue dye was measured for the best investigated oxidant, selected based on membrane characteristics, was compared with untreated membrane.

## 2. Materials and methods

### 2.1 Materials

Polyvinylidene fluoride (PVDF), used as the base polymer, was purchased from Alfa Aeser, Germany. Dimethylacetamide (DMAc) used as the solvent was supplied from Carl-Roth. Polyvinyl pyrrolidone (PVP M.wt. 90k) and Polyvinylidene fluoride-co-hexafluoropropylene (PVDF-CO-HFP average M.wt. 400000-130000) were purchased from Sigma Aldrich used as pore former and a non-solvent additive, respectively. Sodium hypochloride (NaOCl available chlorine 12–14%) was purchased from Alpha Chemika, India. Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub> 9%) was provided by Luna Co., Ltd, Egypt. Potassium persulfate (KPS; K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> ≥ 97.0%) was provided by SRL Chem. HCl and NaOH (7%) solutions were used to adjust the pH of NaOCl, KPS and H<sub>2</sub>O<sub>2</sub> aqueous solutions. Methylene blue dye (MB M.wt. 319.86) was used as feed solution for synthetic dye, purchased from S.d.fine - Chem LTd.

### 2.2 PVDF HFMs preparation and post-treatment

PVDF HFMs were prepared via the dry/wet spinning technique described elsewhere (Tewfik *et al.* 2018). Briefly, the polymeric dope was prepared by dissolving PVDF in DMAc as a solvent and PVP K-90, PVDF-CO-HFP as a pore former and a non-solvent additive, respectively. The produced PVDF HFMs were soaked in a solution of 3 % NaCl and 0.5% formalin for four days then rinsed thoroughly with RO water. All post treatment experiments with NaOCl, H<sub>2</sub>O<sub>2</sub> and KPS were carried out at 45°C for 3 hrs in a water bath (Scifinetic water bath). After post treatment, fibers were taken out on a filter paper, then washed and rinsed till next day for characterization. Samples were named (PVDF, PVDF<sub>raw</sub>, PVDF<sub>NaOCl</sub>, PVDF<sub>H<sub>2</sub>O<sub>2</sub></sub> and PVDF<sub>KPS</sub>) for powder, raw, post-treated samples with NaOCl, H<sub>2</sub>O<sub>2</sub> and KPS, respectively.

### 2.3 Characterization

#### 2.3.1 Chemical analysis

##### 2.3.1.1 FTIR

FTIR analysis was used to identify the chemical structure of PVDF powder and PVDF HFMs samples before and after post treatment. FTIR spectra was obtained using (Burukr) with KBr in the range of 500–4000 cm<sup>-1</sup>.

##### 2.3.1.2 1H- NMR

1H-NMR (300 MHz) spectra was conducted obtained on a (Burukr) of PVDF HFMs before and after post treatment dissolved in dimethyl sulfoxide (DMSO).

#### 2.3.2 Surface morphology

##### 2.3.2.1. SEM & EDS

The surface morphology of the outer surfaces and cross sections of five PVDF HFMs samples before and after post treatment were analysed by a scanning electron microscope

JOEL JCM-6000 Neoscope desktop apparatus at high vacuum of 15 kV. The samples were coated with gold before the SEM analysis. Also, elemental dispersion spectroscopy (EDS) measurements were carried out using the same device to identify elemental peaks in the sample surface.

### 2.3.2.2 Surface roughness

The average surface roughness ( $R_a$ ) and mean average surface roughness ( $R_{ms}$ ) of raw and post-treated PVDF HFMs samples were investigated by an atomic force microscope (5 micron resolution TT-AFM workshop, equipped with a video optical microscope with up to 400X zoom). Vibrating scan mode was used for testing with a scan area of  $5\mu\text{m}\times 5\mu\text{m}$ . Roughness parameters were calculated using “Gwyddion” software. An average of five samples were carried out.

### 2.3.3 Water contact angle (CA°)

Surface hydrophilicity for raw and post-treated PVDF HFMs samples were characterized by manipulating water drop shape on the samples and through a digital video image of the drop on the dried surface of the HFMs at 25 °C using the CA 15EC Contact angle model produced by the company of Data Physics Instrument GmbH. All the samples were tested for five different positions and the final results presented are an average of the measured values.

### 2.3.4 Porosity and Mean pore size

Total membrane porosity was determined according to its dry-wet weight. Firstly, raw (PVDF HFMs) and post-treated sample (PVDF<sub>H<sub>2</sub>O<sub>2</sub></sub>) were dried at 60°C and weighed with a precision balance, then impregnated with kerosene for about 24 h and weighed again after wiping the excess kerosene with filter paper 11. The porosity ( $\epsilon$ ) of the raw and post treated HFMs was calculated using the following Eq. (1): (Simone *et al.* 2010, Drioli *et al.* 2013).

$$\epsilon(\%) = \frac{\frac{w_w - w_D}{D_{kerosene}}}{\frac{w_w - w_D}{D_{kerosene}} + \frac{w_D}{D_{polymer}}} * 100 \quad (1)$$

where  $\epsilon$  is the membrane porosity (volume %),  $w_w$  is the weight of the wet membrane (g),  $w_D$  the weight of the dry membrane (g),  $D_{kerosene}$  the density of kerosene (0.82 g/cm<sub>3</sub>),  $D_{polymer}$  is the density of polymer (PVDF) (1.78 g/cm<sub>3</sub>).

Mean pore size for the raw (PVDF HFMs) and post-treated sample (PVDF H<sub>2</sub>O<sub>2</sub>) were determined using pore size distribution analyzer Belsorp Max apparatus (Microtrac Bel. Corp.). Adsorptive nitrogen was used at 77 K. Vacuum degree before measurement was 6.95E-4 Pa and standard vapor pressure was 108 kPa

### 2.3.5 Mechanical properties

Mechanical properties of raw and post-treated PVDF HFMs samples were analysed using a bench top tensile testing machine, Tinius Olsen H5kS, equipped with a 5N load cell. Testing was undertaken at 50 mm/min speed and gauge length of 100 mm. Tensile strength, elongation at break and fiber’s Young’s modulus were measured. An average of five samples were calculated.

### 2.3.6 Membrane performance tests

The performance of the raw and post treated PVDF HFMs samples have been assessed by permeability measurements. For each sample, about 14-20 hollow fibers were potted in a suitable connection using epoxy resin to form testing modules. The pure water permeability and flux were measured using a permeability test set up provided by “PHILOS Co., Ltd”. The pure water flux of the membranes samples was determined using RO water while, rejection was measured using methylene blue dye solution (50 ppm). The pure water flux or permeate flux was subsequently calculated according to the following Eq. (2):

$$F = V/A * \Delta t \quad (2)$$

where V is the volume of the water or solution permeated during the experiment, A represents the effective HF membrane surface area (m<sup>2</sup>), and  $\Delta t$  denotes the operation time (h). The rejection (%) is calculated using the following Eq. (3):

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

where,  $C_f$  and  $C_p$  are the dye concentration in feed and permeate solutions, respectively. The concentration of dye was determined by UV spectrophotometer (TW80) is a high performance double beam spectrophotometer available with a fixed (2nm) or variable (0.5, 1, 2, 5nm) spectral bandwidth.

## 3. Results and discussions

### 3.1 Chemical structure

#### 3.1.1 FTIR

The chemical structure of PVDF, PVDF<sub>raw</sub> and post treated PVDF samples (PVDF<sub>NaOCl</sub>, PVDF<sub>KPS</sub> and PVDF<sub>H<sub>2</sub>O<sub>2</sub></sub>) is presented in Fig. 1. The peaks at 3022 cm<sup>-1</sup> and 2980 cm<sup>-1</sup> are related to the CH<sub>2</sub> asymmetric and symmetric vibration of PVDF<sub>raw</sub>. The stretching vibrations of CF<sub>2</sub> and CH<sub>2</sub> appeared at peaks 1173 cm<sup>-1</sup> and 1401 cm<sup>-1</sup>, respectively (Puspitasari *et al.* 2010, Xu *et al.* 2012). The band at 879 cm<sup>-1</sup> is indicative of symmetric CF<sub>2</sub> stretching (Eleshmawi 2008). These peaks represent the typical peaks for PVDF. Spectra at 761 cm<sup>-1</sup> was created from PVDF skeletal bending, while, 795 and 839 cm<sup>-1</sup> resulted from CH<sub>2</sub> rocking Mohammadi *et al.* (2007). A new band can be seen in the curve for PVDF<sub>raw</sub> at wavelength 1658 cm<sup>-1</sup>, proving that PVP exists in the PVDF HFMs Purnawan *et al.* (2021). After post treatment using NaOCl and KPS, the main characteristic peaks of PVDF did not change significantly, and there were no new peaks, that post treatment indicating no change in chemical properties of PVDF HFMs. These results agreed with Gan *et al.* (2021) treating PVDF membrane using 200 ppm NaOCl for 48 hr. On the other hand, Puspitasari *et al.* (2010) concluded that the treatment of PVDF membrane with NaOCl solutions showed chemical changes in membrane functional groups after 6 days of treatment. As for H<sub>2</sub>O<sub>2</sub> treatment, there was a peak at 3390 cm<sup>-1</sup> and 1658 cm<sup>-1</sup> with high intensity than

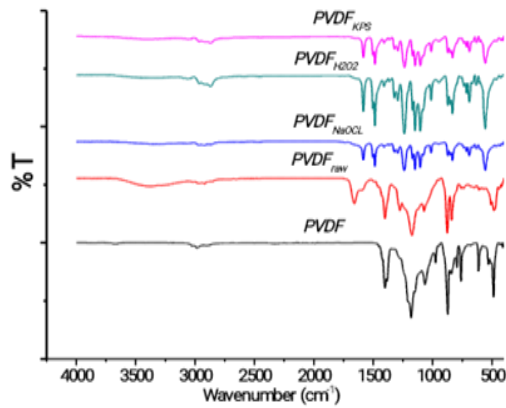


Fig. 1 FTIR spectra for PVDF, PVDF<sub>raw</sub>, PVDF<sub>KPS</sub>, PVDF<sub>H<sub>2</sub>O<sub>2</sub></sub> and PVDF<sub>NaOCL</sub> samples

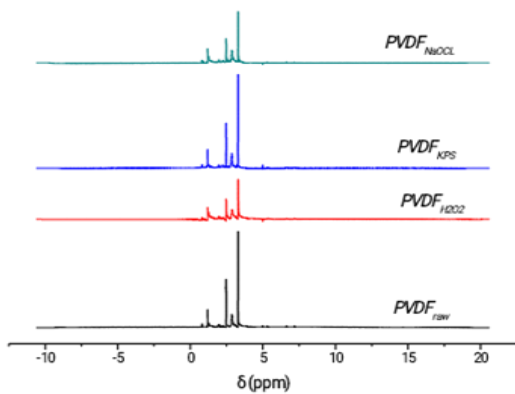


Fig. 2 <sup>1</sup>H-NMR for PVDF<sub>raw</sub>, PVDF<sub>KPS</sub>, PVDF<sub>H<sub>2</sub>O<sub>2</sub></sub> and PVDF<sub>NaOCL</sub> samples

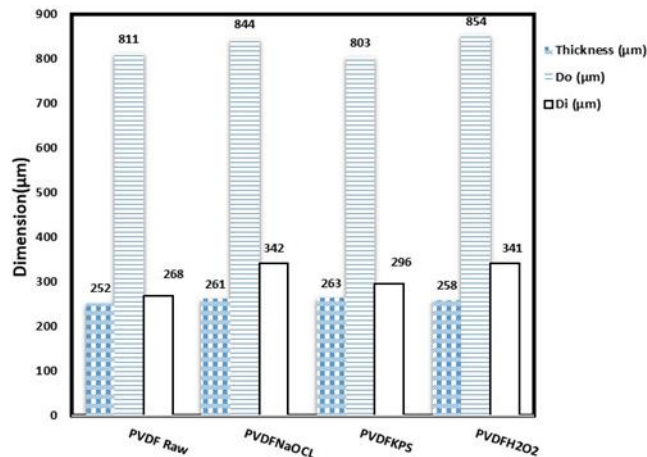


Fig. 3 Inner, outer diameters and wall thickness for PVDF<sub>raw</sub> and PVDF<sub>KPS</sub>, PVDF<sub>H<sub>2</sub>O<sub>2</sub></sub>, PVDF and PVDF<sub>NaOCL</sub> samples

NaOCl and KPS, representing the O-H and carbonyl groups, which could be derived from PVP as additives during membrane preparation which increase the membrane hydrophilicity and this agrees with Ross *et al.* (2000).

### 3.1.2 <sup>1</sup>H-NMR analysis

The chemical structure for PVDF<sub>raw</sub>, PVDF<sub>NaOCL</sub>, PVDF<sub>H<sub>2</sub>O<sub>2</sub></sub> and PVDF<sub>KPS</sub> samples were confirmed using

<sup>1</sup>H-NMR spectroscopy as shown in Fig. 2. For all samples, the peaks of the DMSO solvent appeared at 2.6 ppm, respectively. <sup>1</sup>H-NMR spectrum displayed signals at δ 1.2 and 1.97 equivalent to CH<sub>2</sub> (chain) and CH<sub>2</sub> (ring) Golcuk *et al.* (2013). Also, it showed a signal at δ 2.25 corresponding to CH<sub>2</sub> (chain) and CH<sub>2</sub> (hh). The peaks at δ 2.85 and 2.88 attributed to CH<sub>2</sub> (ht), CH<sub>2</sub> (ring) and CH (ring), respectively. <sup>1</sup>H-NMR spectrum for post treated PVDF HFMs PVDF<sub>NaOCL</sub>, PVDF<sub>H<sub>2</sub>O<sub>2</sub></sub> and PVDF<sub>KPS</sub> using different oxidant NaOCL, H<sub>2</sub>O<sub>2</sub> or KPS showed no effect on membrane.

## 3.2 Surface morphology

### 3.2.1 SEM and EDS

The SEM images of PVDF<sub>raw</sub> and post treated samples (PVDF<sub>NaOCL</sub>, PVDF<sub>KPS</sub>, PVDF<sub>H<sub>2</sub>O<sub>2</sub></sub>) are showed in Fig. 4. Cross-sectional micrographs show that finger-like structures are present at the outer and inner walls of the HFMs and sponge-like structures are present in the fiber's centre. When compared to the raw PVDF sample, post treated samples (PVDF<sub>NaOCL</sub> and PVDF<sub>KPS</sub>) exhibited a decrease in finger-like structures in addition to agglomerates appearing on the surface. These agglomerates showed increased number upon post-treatment with NaOCl and KPS than with H<sub>2</sub>O<sub>2</sub> treatment, consequently leading to an increase in the membrane surface roughness as reported by AFM analysis Gan *et al.* (2021). The change in fibers dimensions are depicted in Fig.3. The cross-sectional outer diameter of the raw and post treated samples (PVDF, PVDF<sub>NaOCL</sub> and PVDF<sub>H<sub>2</sub>O<sub>2</sub></sub>) were increased to 844 μm and 854 μm, as compared to the raw sample (811 μm), respectively. While, the inner diameter increased to 342, 341 μm of the post treated samples (PVDF<sub>NaOCL</sub> and PVDF<sub>H<sub>2</sub>O<sub>2</sub></sub>), as compared to raw sample (268 μm), respectively. Some slight differences at the EDS values are noticeable in Table 1. The EDS spectrum of PVDF<sub>raw</sub>, PVDF<sub>H<sub>2</sub>O<sub>2</sub></sub>, PVDF<sub>NaOCL</sub> and PVDF<sub>KPS</sub> C, N, O and F as major components, of PVDF and PVP during PVDF HFMs preparation. Also, the EDS values showed slight changes include presence of Na, Cl and K element due to the post treatment by NaOCl and KPS.

### 3.2.2 AFM

AFM values for (Ra) and root mean square (Rms) surface roughness and 3D images surface have been obtained and presented in Fig. 5-6 for raw PVDF HFMs sample (PVDF<sub>raw</sub>) and post treated samples (PVDF<sub>NaOCL</sub>, PVDF<sub>KPS</sub> and PVDF<sub>H<sub>2</sub>O<sub>2</sub></sub>). For PVDF, PVDF<sub>NaOCL</sub> and PVDF<sub>KPS</sub> samples after post treatment, surface roughness values (Ra) increased to 52.8nm and 56 nm, respectively as compared with raw PVDF (48nm) which explains the aggregates shown in SEM changes for post treatment samples also, water contact angle. These results agree with (Jung *et al.* 2006) which large particles appeared on the membranes surface before and after acid or alkaline cleaning or treatment using HCl, NaOH and EDTA. For PVDF<sub>H<sub>2</sub>O<sub>2</sub></sub> sample, it showed no change in surface roughness (Ra) and root mean square (Rms) is noticed which is confirmed by contact angle results. Naim *et al.* (2013) reported that the contact angle decreased as the

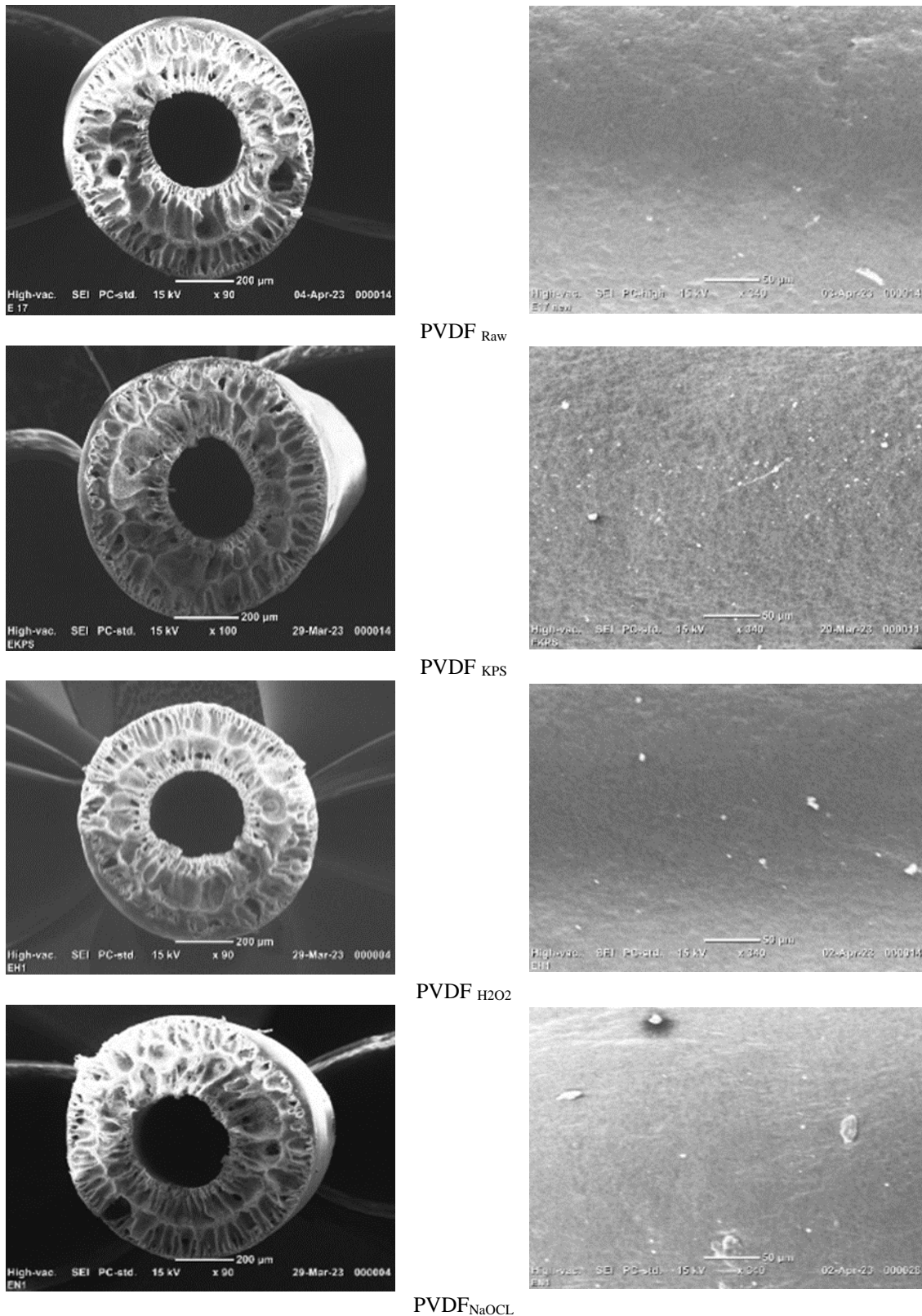


Fig. 4 SEM and surface images for PVDF<sub>raw</sub> and PVDF<sub>KPS</sub>, PVDF<sub>H<sub>2</sub>O<sub>2</sub></sub>, and PVDF<sub>NaOCL</sub> samples

roughness decreased. It is concluded that, treatment using KPS increase high contact angle and surface roughness.

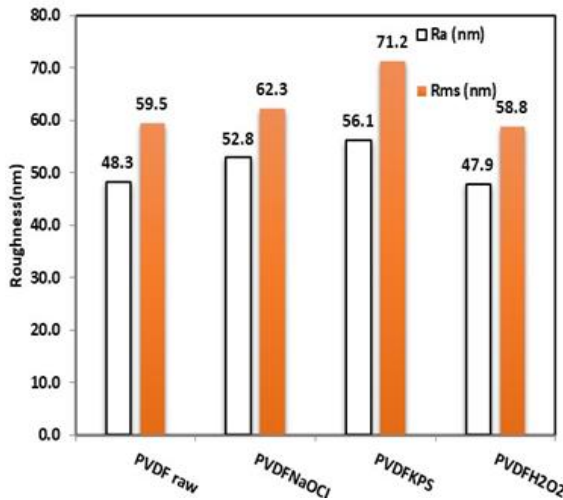
### 3.2.3 Water contact angle

The water contact angle of the PVDF<sub>raw</sub> and post treated

samples PVDF<sub>NaOCL</sub>, PVDF<sub>KPS</sub> and PVDF<sub>H<sub>2</sub>O<sub>2</sub></sub> are demonstrated in Fig.7. it is obvious that the contact angle for PVDF<sub>H<sub>2</sub>O<sub>2</sub></sub> was decreased, which indicates that surface hydrophilicity was increased. This is attributed to the formation of aldehydic carbonyl groups at the carbon chains

Table 1 EDS elemental values for PVDF<sub>raw</sub> and PVDF<sub>KPS</sub>, PVDF<sub>H2O2</sub> and PVDF<sub>NaOCl</sub> samples

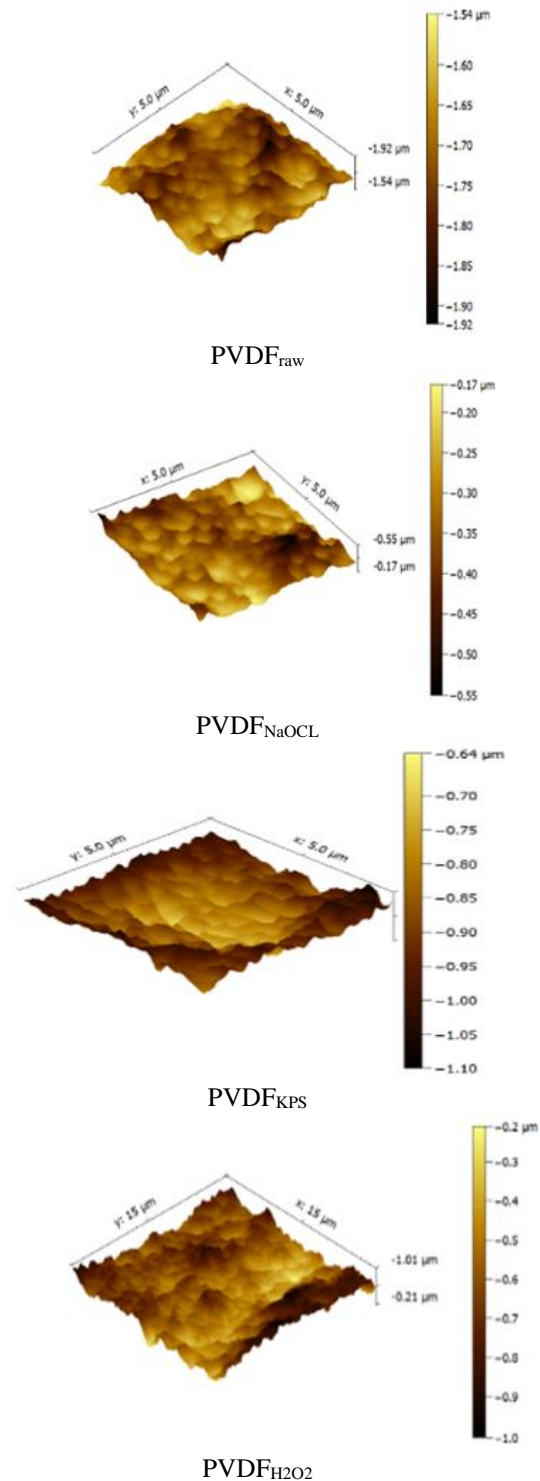
Sample	EDX (mass %)						
	C	N	O	F	K	Na	CL
PVDF <sub>raw</sub>	35.5	14.17	7.54	42.77	0	0	0
PVDF <sub>NaOCl</sub>	35.0	14.2	8.6	41.3	0	0.5	0.4
PVDF <sub>H2O2</sub>	34.5	14.8	7.5	43.3	0	0	0
PVDF <sub>KPS</sub>	30.5	13.7	7.4	48.3	0.1	0	0

Fig. 5 Surface Roughness for PVDF<sub>raw</sub> and PVDF<sub>KPS</sub>, PVDF<sub>H2O2</sub>, PVDF<sub>NaOCl</sub> samples

through the oxidation of PVP a pore forming agent during membrane preparation, which led to a decrease in contact angle as described by (Ross *et al.* 2000, Puspitasari *et al.* 2010, Gan *et al.* 2021), which confirmed by FTIR results. Further, these trends were also confirmed by Naim *et al.* (2013) who, reported that the contact angle decreased as the roughness decreased. These results agree with Özay *et al.* (2022) which used 2.5 mM H<sub>2</sub>O<sub>2</sub>/UV treatment and contact angle (54.76°) of polyether sulfone membrane. Also, there is no change in the water contact angle of the post treated PVDF HFMs with (NaOCl), while, minor change occurred in treatment with PVDF<sub>KPS</sub> sample.

### 3.2.4 Mechanical properties

Results of the mechanical properties for raw PVDF HFMs sample (PVDF<sub>raw</sub>) and post treated samples (PVDF<sub>NaOCl</sub>, PVDF<sub>KPS</sub> and PVDF<sub>H2O2</sub>) are presented in Table 2. There was no significant difference in the tensile strength and the elongation at break for PVDF<sub>raw</sub>, PVDF<sub>H2O2</sub> and PVDF<sub>KPS</sub> HFMs treated with H<sub>2</sub>O<sub>2</sub> and KPS. It is clear that the mechanical properties after treatment with NaOCl post treatment were decreased since the elongation at break for PVDF HFMs membrane decrease from 34.5% to 28.5%. Also, Modules decreased from 19.3 Mpa to 16.6 Mpa for PVDF and PVDF<sub>NaOCl</sub> HFMs, respectively. This is due to the cross-linking or partial degradation of the PVDF through a dehydrofluorination reaction. According to (Wienk *et al.* 1995, Pellegrin *et al.* 2013, Zhang *et al.* 2017), the PVP was unstable in hypochlorite solutions with increased dislodgment from the polymer matrix and radical

Fig. 6 Surface roughness 3D images for PVDF<sub>raw</sub> and PVDF<sub>KPS</sub>, PVDF<sub>H2O2</sub>, PVDF<sub>NaOCl</sub> samples

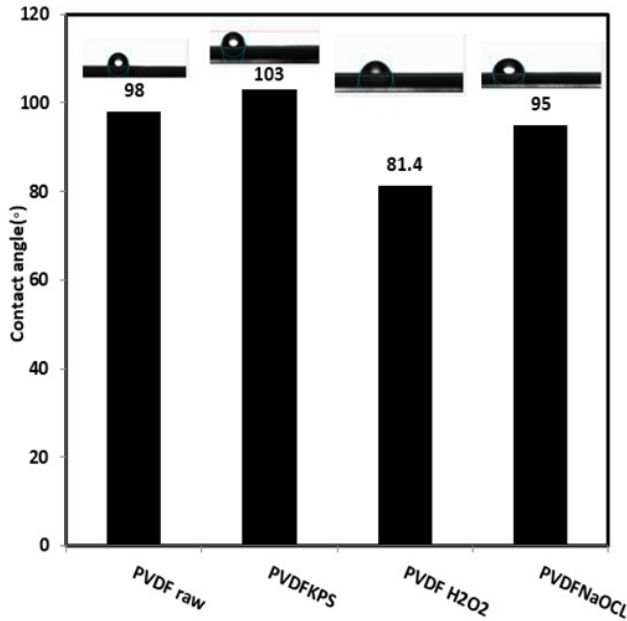


Fig. 7 Water Contact angles for PVDF<sub>raw</sub>, PVDF<sub>KPS</sub>, PVDF<sub>H<sub>2</sub>O<sub>2</sub></sub>, and PVDF<sub>NaOCL</sub> samples

Table 2 Mechanical properties for PVDF<sub>raw</sub> and post treatment samples PVDF<sub>KPS</sub>, PVDF<sub>H<sub>2</sub>O<sub>2</sub></sub> and PVDF<sub>NaOCL</sub>

Sample	Break Force (N)	Tensile strength (MPa)	Elongation at break (%)	Modulus (Mpa)
PVDF <sub>raw</sub>	0.532	1.13	34.5	19.3
PVDF <sub>NaOCL</sub>	0.418	0.873	28.5	16.6
PVDF <sub>H<sub>2</sub>O<sub>2</sub></sub>	0.501	1.03	34.8	22
PVDF <sub>KPS</sub>	0.436	0.972	34.3	17

Table 3 Porosity and Mean pore diameter

Sample	Mean pore diameter (nm)	Porosity (%)
PVDF	9.07	90.5
PVDF <sub>H<sub>2</sub>O<sub>2</sub></sub>	10.93	91

degradation, resulting in a reduction in membrane mechanical properties. These results are consistent with (Li *et al.* 2019, Gan *et al.* 2021) reported the mechanical properties of PVDF membrane decreased after treated with NaOCL, NaOH and citric acid due to defluorination.

According to the findings, among the investigated oxidizing agents, hydrogen peroxide treated samples have the most uniform surfaces, and the lowest contact angle. Therefore, further investigations are conducted on these treated fibers (mean pore diameter, porosity and permeability) for comparison with the raw sample in order to further understand its impacts.

### 3.2.5 Membrane porosity and Mean pore diameter

Porosities and mean pore diameter (nm) for the raw and post treated HFMs sample (PVDF<sub>raw</sub>, PVDF<sub>H<sub>2</sub>O<sub>2</sub></sub>) are displayed in Table 3. It was found that the treatment with H<sub>2</sub>O<sub>2</sub> had no effect on porosity of PVDF HFMs as compared

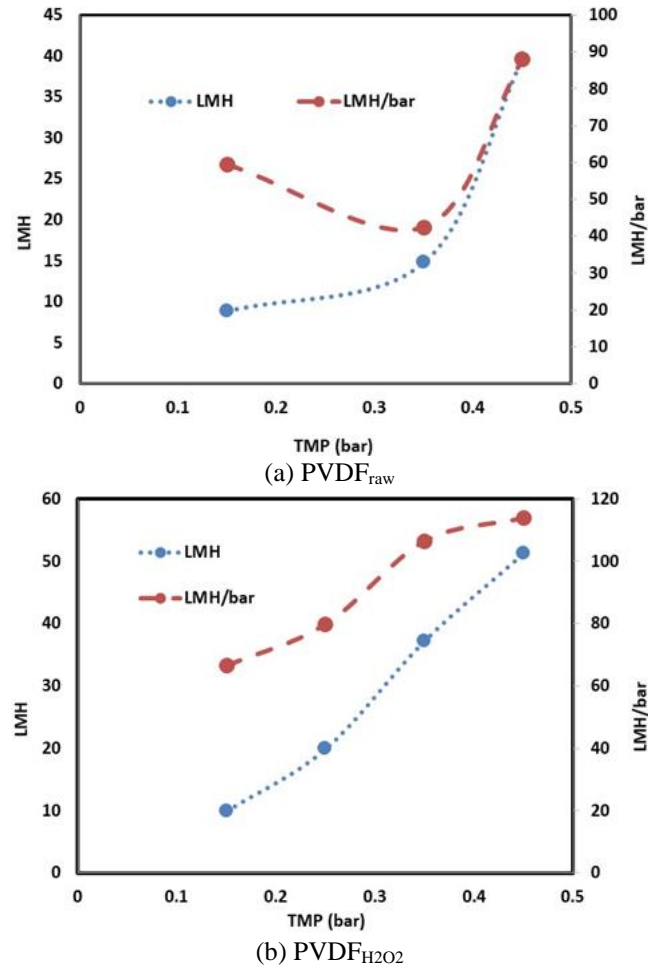


Fig. 8 LMH and LMH/bar for PVDF<sub>raw</sub> (a) and PVDF<sub>H<sub>2</sub>O<sub>2</sub></sub> (b) samples

with raw sample indicating the stability of this treated membrane. This result is similar to (Ravereau *et al.* 2016) which use 4000ppm NaOCL at 40 °C at PH 7.5. Other study demonstrated that H<sub>2</sub>O<sub>2</sub> treatment at high temperature 100 °C and treatment time 60 min PES UF membrane resulted in porosity increase from 52 to 84% and 169.58 nm Özay *et al.* (2022). Mean pore diameter increased 18% after post treatment for PVDF<sub>H<sub>2</sub>O<sub>2</sub></sub> sample as compared to raw PVDF. A similar increasing was observed by H<sub>2</sub>O<sub>2</sub> treatment at high temperature 100°C for PES membrane about the largest pore size of 161.23 nm Özay *et al.* (2022).

### 3.2.6 Water permeability and Rejection

The permeability for raw PVDF HFMs sample (PVDF<sub>raw</sub>) and post treated sample (PVDF<sub>H<sub>2</sub>O<sub>2</sub></sub>) are displayed in Fig. 8a and b. It is clear that post-treatment with H<sub>2</sub>O<sub>2</sub> show significant increase of PWF and PWF/bar with increase in pressure (0.1 to 0.5 bar) which approached to 51 LMH and 113 LMH/bar at 0.45 bar while PVDF<sub>raw</sub> was about 39.5 LMH and 87.7 LMH/bar at the same pressure, this may be attributed to decrease of contact angle corresponds to flux increase which is in consistent with mean pore diameter results. (ÖZAY *et al.* 2022) studied the H<sub>2</sub>O<sub>2</sub> treatment of polyether sulfone membrane where the permeability significantly increased by 2.3 folds at 5 mM

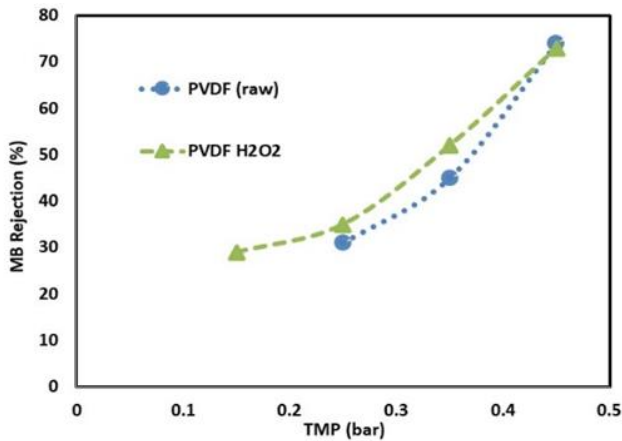


Fig. 9 methylene blue dye rejection for PVDF<sub>raw</sub> and PVDF<sub>H<sub>2</sub>O<sub>2</sub></sub> samples

H<sub>2</sub>O<sub>2</sub> and temperature of 100 °C. Additionally, at 2.5 mM H<sub>2</sub>O<sub>2</sub>, the largest pore size of 161.23 nm, contact angle (54.76°) and porosity (61.88%). Also (Yu *et al.* 2018) concluded that flux was enhanced from 130 to 171 L m<sup>-2</sup> h<sup>-1</sup> after modification of commercial PVDF HFMs through a two-step surface grafting method using 5 wt.% PVP, potassium persulfate and 0.4 wt.% KPS at 90 °C for 6 hours as a cross-linking agent. Also, (Li *et al.* 2019) reported that ageing PVDF membrane using NaOCl caused a moderate increase in permeability due to the oxidation of PVP.

Fig. 9 shows the MB dye rejection% using raw PVDF (PVDF<sub>raw</sub>) and post treated samples (PVDF<sub>H<sub>2</sub>O<sub>2</sub></sub>) at 0.15-0.45 bar. The PVDF raw sample showed 31-74% rejection with increasing pressure from 0.15 to 0.45 bar. As for PVDF and PVDF<sub>H<sub>2</sub>O<sub>2</sub></sub>, both exhibit a similar rejection with increase in pressure from 0.15 bar to 0.45 bar which increased to 74% at 0.45 bar. These results agree with (Vatanpour *et al.* 2022) where, TiO<sub>2</sub>/ PVDF nanocomposite membrane, rejection of reactive green 19 dye didn't change than raw. While, (Li *et al.* 2019) reported decreasing in rejection of PVDF membrane after treatment with NaOCl.

#### 4. Conclusions

Studies of surface and performance modification of PVDF HFMs using some selected oxidants including NaOCl, H<sub>2</sub>O<sub>2</sub> and KPS revealed the following results:

- No noticeable structural differences were detected as evidenced by FTIR and <sup>1</sup>H-NMR investigations.
- The post treatment using NaOCl and KPS exhibited a decrease in finger-like structures and increase in the membrane surface roughness (Ra) from 48 nm to 52.8 nm and 56 nm, respectively.
- In addition, post treatment using H<sub>2</sub>O<sub>2</sub> revealed decreased of the water contact angle from 98° to 81.4°.
- Investigation of mechanical characteristics showed no significant changes except in the case of using NaOCl were decreased the elongation at break and the modulus manifested 17% and 14%, respectively.
- Moreover, H<sub>2</sub>O<sub>2</sub> caused increased of pure water flux by 29 %. Finally no detectable change of MB dye rejection

(74%) was observed under the prevailing experimental conditions.

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