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Tailored PVDF/FTPs Tri-Bore Fibers for successful Phenol Removal via Vacuum Membrane Distillation

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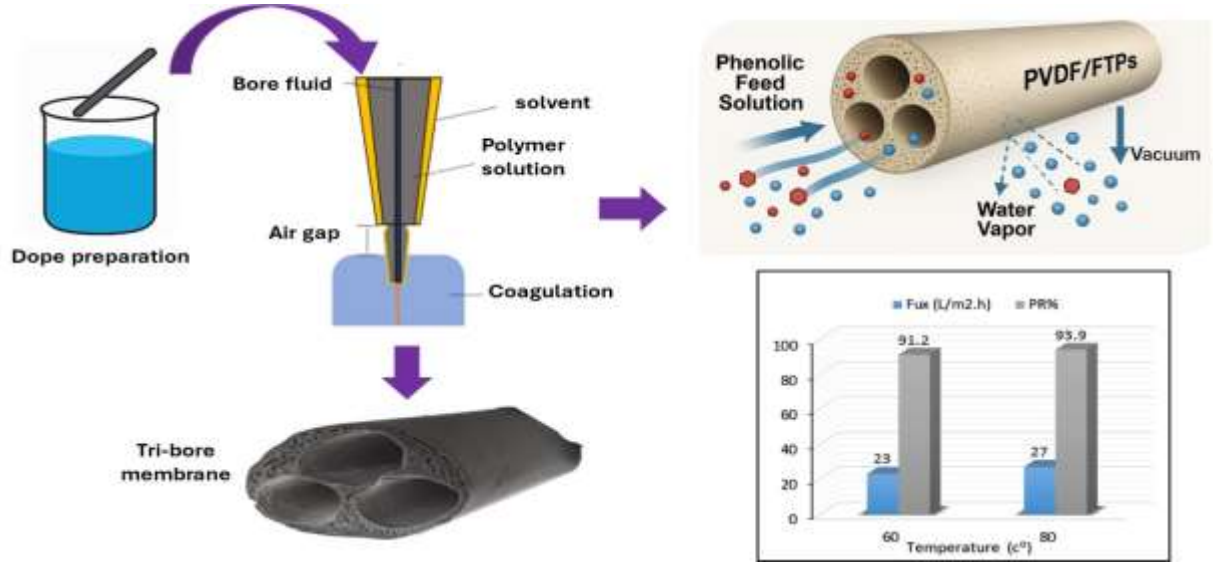
Abstract: The removal of phenol (Ph) from industrial wastewater is a top concern due to its toxicity to ecosystems. Vacuum membrane distillation (VMD) concerns a promising technique for phenol removal. PVDF membranes represent potential application in area of wastewater treatment. In order to improve PVDF membrane's capabilities for the treatment of phenol-containing wastewater, this study incorporated fluorinated titania nano particles (FTPs) into PVDF membrane. A specially developed spinneret and ideal spinning operating conditions used to prepare a Tri Bore Hollow Fiber Membrane (TBHFM). The produced membrane was characterized and tested for phenol removal at a temperature range from 60°C to 80°C using VMD process. The suitability of the VMD process, was investigated to eliminate phenol from industrial wastewater. The phenol removal percentage (PhR %) was found to be 91.2 %, and the permeation flux reached to 23 l/m^{2}h at 60^{o}C. The removal percentage and permeation flux were increased by increase the operating temperature, reaching about 93.9 % at 80°C, while the flux was 27 l/m^{2}h.

Keywords: phenol removal, triple orifice**,** tri-bore hollow fibers, membrane distillation.

Graphical abstract



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Highlights

- Fabrications of PVDF/FTPs Composite tri-bore hollow fiber membrane using a specially developed triple orifice spinneret
- Performance of PVDF/FTPs Composite tri-bore hollow fiber membrane was investigated for phenol removal using VMD.
- The developed PVDF/FTPs Composite tri-bore hollow fiber membrane was superior in terms of phenol rejection.
- At optimum conditions the permeate flux reached 27 L/m2h, where the phenol rejection was 93.9%

1 Introduction

The phenolic compounds consist of an aromatic hydrocarbon group attached to a hydroxyl group. Phenolic compounds and its derivatives are considered moderately water-soluble pollutants common in wastewater of various industries, including oil and gas, paint production, phenolic resin production, pulp and paper mills, and pharmaceutical industries [1]. Many international organizations, including the Environmental Protection Agency (EPA) in the United States and the National Pollutant Release Inventory (NPRI) in Canada, have set strict limits for the discharge of phenols (usually less than 0.5 mg/L) due to the danger of phenolic compounds and their severe toxicity to human health, plants, and animals in general, as well as to the aquatic environment in particular.

At concentrations ranging from 10 to 240 mg/L, prolonged ingestion of the phenols caused oral discomfort, diarrhea, dark urine excretion, and visual problems [2]. Therefore, wastewater containing phenolic compounds should be treated before being released into the environment due to their high toxicity. Hence several procedures, such as total chemical oxidations, membrane separation techniques, biodegradation, extraction, distillation, and adsorption, have been suggested for removal of phenolic compounds from wastewater [3,4].

Membrane-based purification methods have emerged as some of the most innovative and versatile ones available for desalination, water recycling, wastewater treatment, and the production of potable and ultrapure water [5].

Vacuum membrane distillation (VMD) is investigated as an energy-efficient method of recovering phenols compounds from wastewater, as other membrane separation processes require high pressure.

A microporous membrane with high hydrophobicity serves as the feed solution's barrier. With the aid of a partial vapour pressure difference, water in the vapor phase can pass through the membrane pores [6,7]. PVDF (polyvinylidene fluoride) membranes are widely used in the MD process and have a high solubility in a variety of solvents, which makes them useful for membrane distillation. Nanoparticles like ZnO, SiO_2, and TiO_2 have been impregnated into PVDF polymer solution to achieve high mechanical properties and separation efficiency [8–12]. TiO_2 nanoparticles are among those that have drawn the most attention because of their high chemical and thermal stability, accessibility, physicochemical properties, and antifouling properties [13–15]. For PVDF membranes a higher hydrophobicity was reported after grafting fluorocarbon groups onto nanomaterials and impregnated them to membranes [8,9].

The Polymeric Single Bore Hollow Fiber Membrane (PSBHFM) exhibits ease of installation and straightforward processing. On the other hand, the PSBHFM's main shortcomings are its poor mechanical properties, low strength, and high operating pressure. Thus, Multi Bore Hollow Fiber Membrane (MBHFM) is a promising membrane type because of its unique membrane configuration, which will enhance its mechanical properties and potentially combine the benefits of SBHF and flat sheet membranes. Cylindrical, straight, and uniform bores of MBHFM will increase the tortuosity of the membrane while little increasing hydraulic resistance [16, 17]. Triple orifices can be used to regulate the flow and dispersion of the polymer material during the extrusion process, resulting in a homogenous surface for hollow fibers. The hollow fiber's surface becomes more homogeneous and uniform due to the triple orifice's ability to precisely control the extruded material's shape and placement, which can enhance the hollow fiber's mechanical strength and separation performance [8]. Three distinct solutions can be simultaneously extruded using a triple spinneret, enabling the creation of a composite membrane with particular characteristics [18, 19].

The purpose of this study was to evaluate the PVDF/FTPs Composite tri-bore hollow fiber membrane for the treatment of phenolic wastewater using VMD separation. A triple orifice was used to create a hollow fiber membrane to achieve a more consistent and homogenous membrane surface. Different devices were used to study the characterization of the prepared membrane.

2 Materials and Methods

2.1 Materials

PVDF powder (Solef, PVDF), was obtained from Alfa Aeasr. N-methyl-2-pyrrolidone (NMP) (>99.5%), ortho-Phosphoric acid (H_3PO_4) (>85%), ethanol (>99.9%), acetone was obtained from Merck (Darm-stadt, Germany). TiO_2 nanoparticles (99.5% trace metal basis), were acquired from Sigma-Aldrich. Silane solution (heptadecafluoro-1,1,2,2-tetrahydrodecyl) triethoxysilane (FAS) was obtained from Sigma-Aldrich. Phenol detached crystals, extra pure 99.5%, purchased from Loba Chemie, INDIA)

2.2 Dope preparation for hollow fiber spinning

The predetermined amount of FTPs (prepared in accordance with the method described elsewhere [8]) was added to the organic solvent NMP to prepare the hollow fiber spinning dope. To prevent nanoparticle agglomeration, the solution was ultrasonicated for 30 minutes at 55°C. PVDF, acetone and phosphoric acid were added gradually into the prepared solution of NMP and FTPs. The mixed solution was mechanically stirred at 400 rpm for 6 h at 55°C until a clear homogeneous solution was formed. The prepared solution was stored in containers at room temperature and degassed for 12 h before being transferred to the spinning step. The compositions for the inner (IF) and external fluid (EF) are summarized in Table (1).

Table 1: Compositions of dopes and coagulants.

Inner dope composition (IF) (wt. %)					**External fluid composition (EF) (wt. %)**	**Bore fluid composition (wt. %)**	**External coagulant (v. %)**	
PVDF	NMP	acetone	H_3PO_4	FTPs	Water:20 NMP: 80	Water:80 NMP: 20	**First**	**second**
15	76.5	5	3	0.5			Water : 100	Water:97.8 IPA:2 Glycerol:0.2

2.3 TBHF Spinning process

A typical hollow fiber spinning process with liquid bore (NMP/water), a coagulation bath (water), and the treatment bath were illustrated in Figure 1. Hollow fibers were spun via the dry/wet spinning technique where, the two diluted polymer solutions are co-extruded

with an inert bore fluid at specified flow rates through the spinneret by three precise peristaltic pumps (BT100-2J). The bore fluid is extruded at room temperature through the three needles of the triple orifice spinneret. As the nascent membrane passes through a specific air gap, a small amount of its solvent is evaporated before entering the coagulating bath. After the fiber fall in the coagulating bath, the fiber undergoes rapid coagulation/cooling to solidify the polymer-rich region and forming the membrane. The operating spinning condition was selected based on the previous work [8] and the detailed optimum spinning conditions illustrated in Table 2.

In order to get the desired membrane structure and morphology, the solidified fiber was submerged in a second treatment bath for three to five days in order to eliminate any remaining solvent and non-solvent and to successfully control phase inversion. The treatment bath contains water/IPA/glycerol with compositions of 97.8, 2 and 0.2 v%, respectively. Finally, the fibers were cut into 15 cm long pieces and dried under ambient conditions.

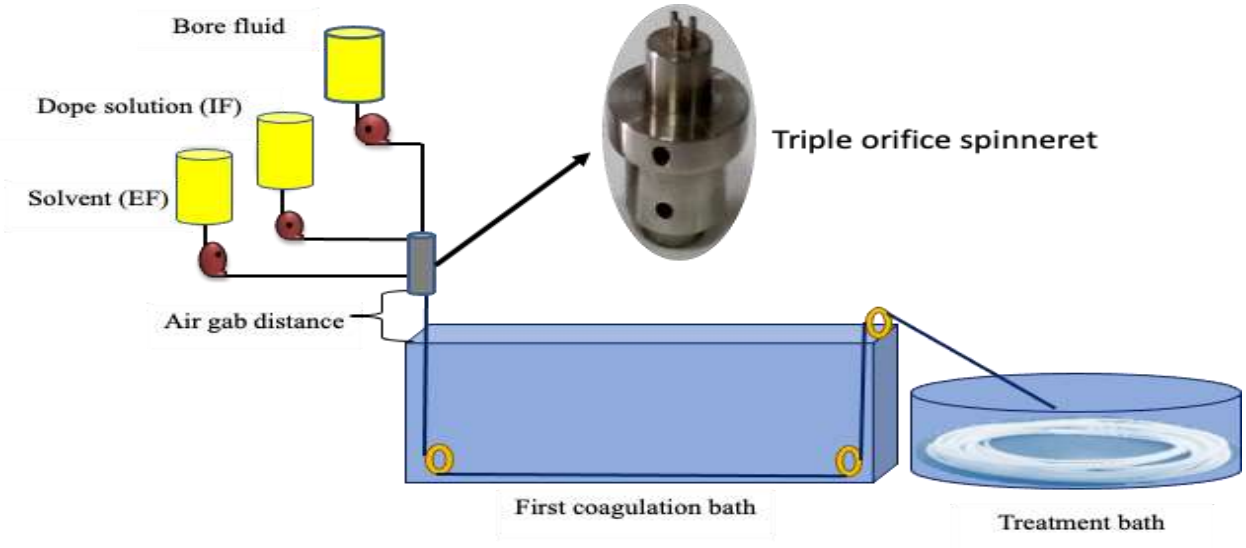

Fig. 1: Lab scale spinning system set-up.

Table 2: The operating spinning conditions

	TBHF
EF flow rate (ml/s)	1.6
IF flow rate (ml/s)	0.95
Bore fluid flow rate (ml/s)	0.29
Air gap (cm)	3
Take up rate (cm/min)	Free fall

2.4 Module fabrication

In the laboratory of the National Research Center, a membrane module was specifically designed and manufactured. Housing made of acrylic contained five hollow fibers arranged coaxially. Each end of the acrylic housing was welded to A five-holed cover. Every hollow fiber was inserted through the corresponding openings in the top and bottom covers, and its ends were sealed with epoxy resin. The purpose of the five-holed covers was to keep the hollow fibers parallel within the tubular module and to maintain a consistent distance between them and the tubing surface. The VMD tubular module had an effective length of 10 cm. The assembled module was covered on both sides with end caps that had ports to make connecting hoses easier [17].

2.5 TBHF membrane Characterization

2.5.1 Scanning electronic microscopy (SEM)

The surface topography and morphology of the as-prepared membrane were characterized by using scanning electronic microscopy (SEM) model JEOL 5410 SEM operating at 10 kV. The SEM was coupled with an energy-dispersive X-ray device (EDX) to identify the surface composition of the membrane. To provide electrical conductivity gold sputtering was applied to the dry samples.

2.5.2 BET surface area

The nitrogen adsorption/desorption process known as Brunauer-Emmett-Teller (BET) was used to gain insight into the pore-level of the membrane. For a full day, the membrane sample was surface activated by degassing it at 60^{o}C

and 2–10 bar vacuum. Subsequently, the sample cell was moved to a Bel Sorp Max device manufactured in Japan to determine its nitrogen adsorption desorption isotherm at the temperature of liquid nitrogen.
Using the NLDFT method, the pore size distribution is calculated, and the specific surface area is estimated from the isotherm.

2.5.3 Mechanical properties

An Instron Tensiometer (Model 5542) from Instron Corp. was used to measure the mechanical properties of hollow fiber membranes at room temperature. The fiber, which had a 50 mm initial length, was clamped at both ends. All measurements were conducted at a fixed elongation rate of 50 mm/min. The average value derived from a minimum of three samples was reported for each spinning parameter.

2.6 VMD desalination experiments for TBHF module

Under optimized operating conditions, the VMD experiments were conducted to assess the phenol removal percentage (PhR%) and permeation flux of the three-bore hollow fiber membranes. The VMD experiments were conducted after making sure the membrane module was watertight. The lab-scale VMD unit with the prepared TBHF membrane module is shown in Figure 2. Approximately -1 bar of pressure, or zero absolute pressure, was applied to cause the feed phenolic solution to evaporate through the membrane. The temperature and flow rate of the solution were set at 60°C and 0.62 l/min, respectively. Using a peristaltic pump, the heated feed is introduced to the fibers on the lumen side. A vacuum pump is used to apply vacuum to the exterior (module shell) side. The vapor is directed toward the condenser after passing through the membrane. Each experiment took place for 30 minutes.
Measurements were taken of the absorbance and permeating volume. The equations listed elsewhere were used to obtain the phenol removal percent (PhR) and the water permeation flux (J) [8, 9].

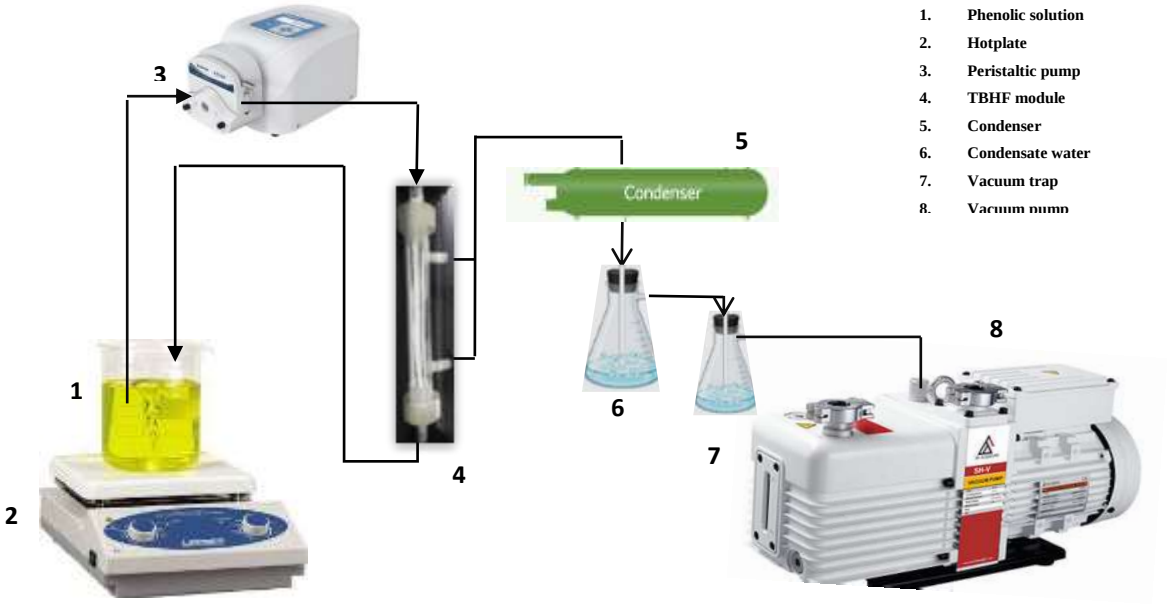

Fig.2: Process diagram of the lab scale VMD unit.

3Results and discussion

3.1 TBHF morphology

Figure 3 displays the cross-section morphologies of the TBHF composite membranes. It was discovered that the membranes' typical asymmetric structure was created by an instantaneous demixing mechanism using the NIPS technique. Large voids and cavities of various sizes and shapes beneath the skin caused the cross-sectional area of TBHF membranes to exhibit different structures, as shown in Figure (3).

The TBHF membrane consisted of a layer resembling sponge, microvoids shaped like fingers, and a top skin layer. The non-solvent additive addition resulted in a looser and more porous sponge-like layer. It was also observed that the TBHF membrane appeared to have irregularly sized finger-like macro voids [20]. Based on its morphology, the TBHF composite membrane might guarantee a high permeate flux and less resistance to the transport of water vapor. Changes in the thermodynamic and kinetic properties of the dope system with various non-solvent additives can be linked to changes in the morphology of the membrane [21]. H_3PO_4 can significantly increase the viscosity of the PVDF/NMP dope solution, form spherical nodule aggregates in the polymer-rich phase area, change the sponge-like structures to be more porous, and improve the membrane porosity because it has strong interactions with both the solvent and the polymer. Due to the volatile nature of the non-solvent additive acetone, a dense top skin layer would form [22].

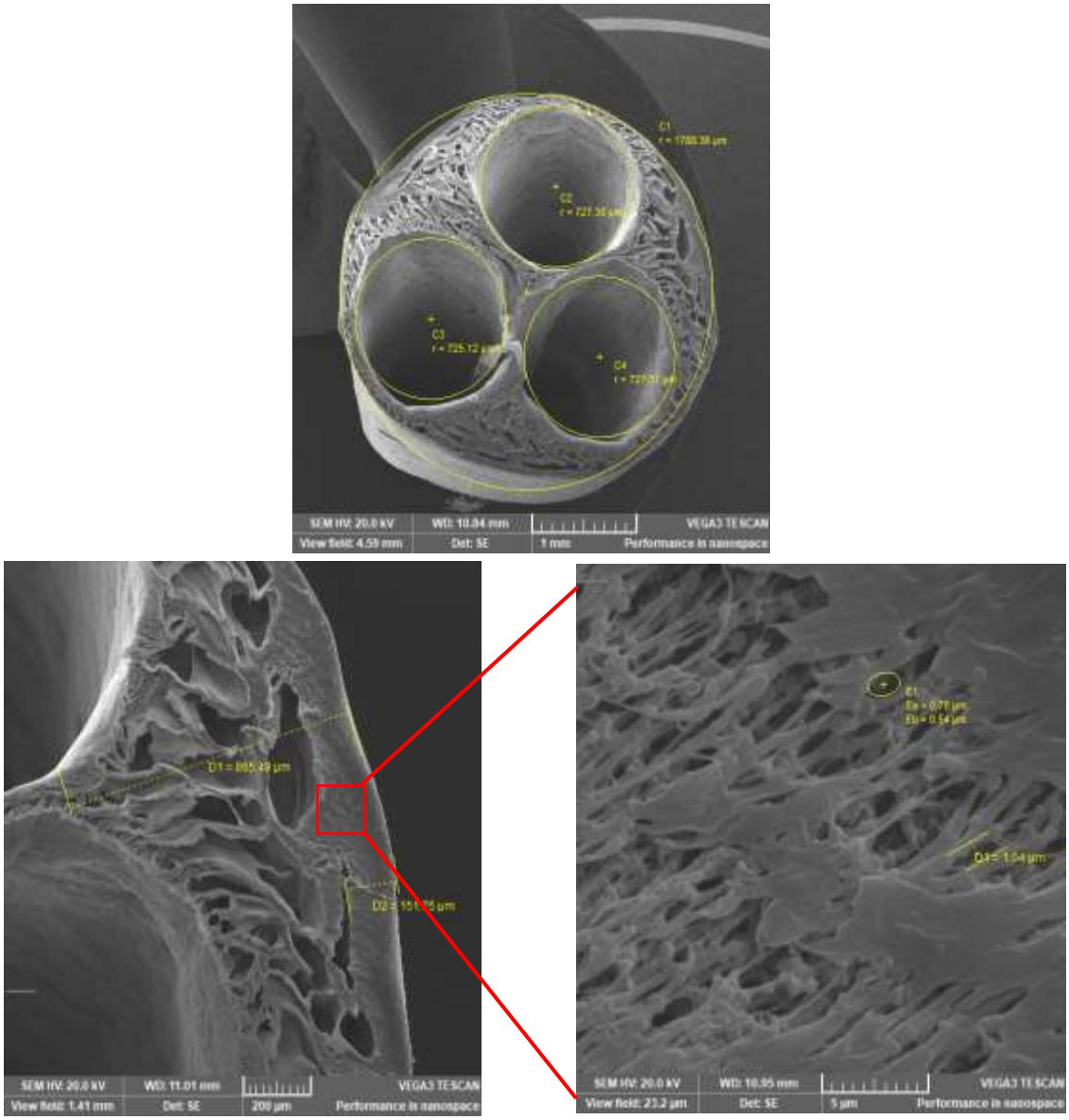

Fig.3: cross section morphologies for TBHF membrane.

Figure 4 exhibits the uniform air -side and bore-side surface morphologies of TBHF composite membrane. The pore size on the surface of membrane was, evenly dispersed. In accordance with this observation, no obvious aggregation of TiO_2 nanoparticles was observed on the surface of membrane. It might be attributed to the non-solvent additive acetone's swelling action improved the dope solution's thermodynamic homogeneity and stability, resulting in the membrane exhibiting good uniformity on both the membrane surface and the sponge-like layer. Also, the final structure of the membrane was strongly influenced by the rate of phase inversion, which was controlled by the compositions of the non-solvents (NMP/DW wt% ratio = 20:80 and 80:20) used as the bore fluid and the external fluid [23,24].Furthermore, the fact that the silane may have provided rich coordination sites for the TiO_2 nanoparticles via hydrogen bonds together with steric hindrance effects, thereby promoting the dispersion of TiO_2 nanoparticles in the composite casting solution and their immobilization in the formed film explored [25].

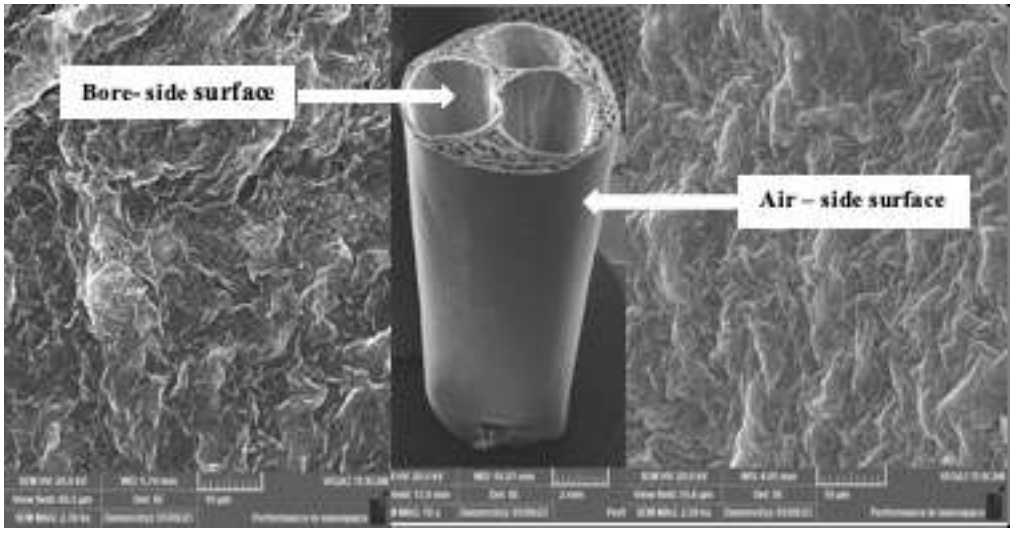

Fig.e 4: surfaces morphologies for TBHF membrane.

The TBHF was then selected for additional analysis through elemental mapping analysis and EDX. To find the elements in this membrane, line scanning was done on its cross-section as shown in Figure 5. These EDX images showed the elements titanium (Ti), silica (Si), carbon (C), oxygen (O), fluorine (F), and titanium (Ti). The detected elements depict PDVF polymer and hydrophobic modified nanosize TiO_2 with silane solution.

The success of silane grafting on TiO_2 particles was confirmed by low concentration of silica (Si) element [26]. The high concentration of each element is highlighted as bright dots, which were distributed homogeneously. The elemental compositions, in the modified membranes, were measured. It was noted that elemental peaks with 49.2 wt. %, 22.65wt%, 22.65 wt. %, 3.4 wt. % and 0.51 wt. % were observed corresponding to the titanium element, carbon, fluorine, oxygen and silica. It implies that FTPs were well dispersed throughout the PVDF membranes. It is noted that the C and F elements account for the highest proportion of elements on the sample surface after Ti, because the body polymer PVDF is made of hydrocarbon compounds [27, 28].

3.1 Pore size distribution

Figure 6 displays the constructed TBHF membrane's pore size distribution. It is evident that the distribution of pore sizes narrowed around the mean pore diameters (4.34 nm). The combined action of the mixed non-solvent additive and FTPs, as previously described for membrane morphology, may be responsible for the TBHF membrane's small pore size and narrow pore size distribution [29].

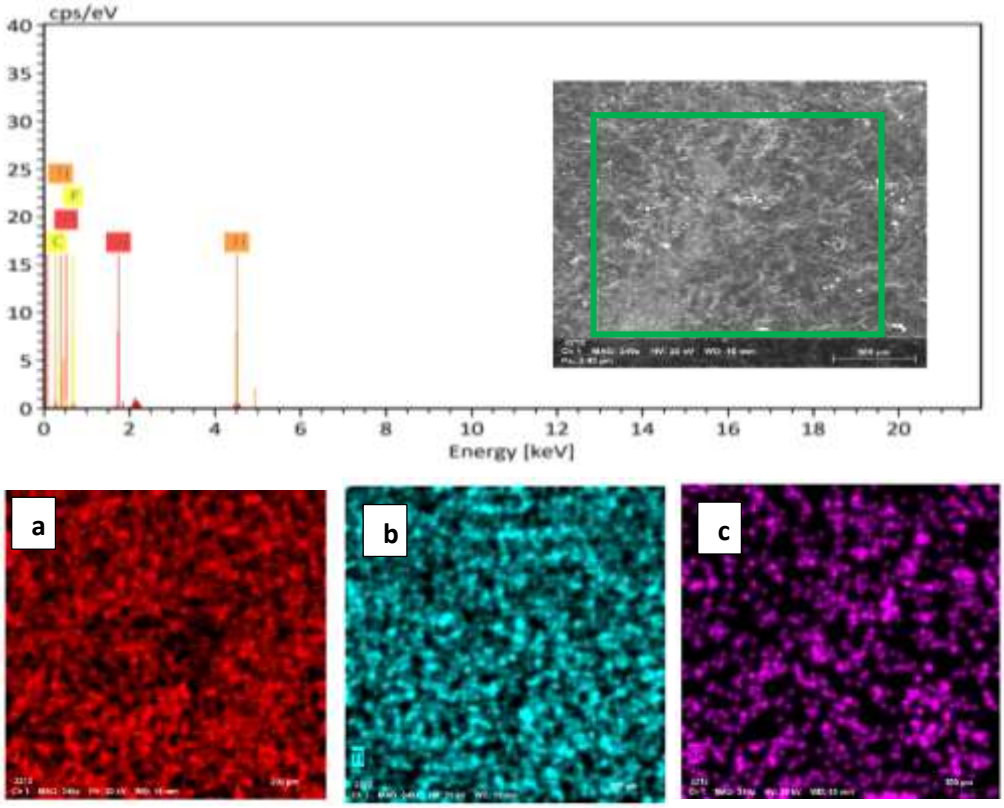

Fig.5: EDX mapping and element analysis on TBHF surface : (a) SEM image and EDX spectrum of selected area; (b) F element distribution; (c) Ti element distribution; (d) Si element distribution.

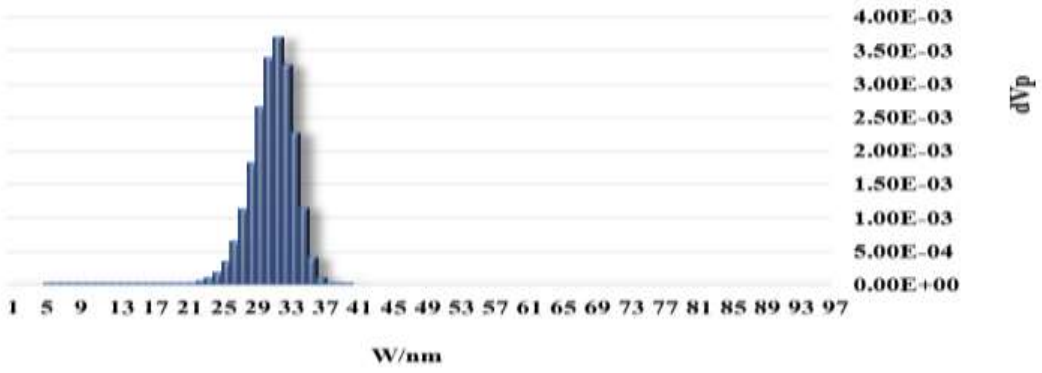

Fig.6: Pore size distribution histograms on the surfaces of PVDF/FTPs TBHF composite membranes.

3.2 Mechanical properties

The characteristics that can elucidate the mechanical properties of the membrane are its tensile strength and elongation. Figure 7 depicts tensile tests on TBHF- PVDF membrane @ TiO_2 with composition (0.5wt %). It takes three tests to determine the average tensile strength value. This indicates a tensile strain of 38.46% and a tensile strength of 1.32 MPa for TBHF-PVDF @ TiO_2 with composition (0.5wt %). The use of TBHF membrane consequently greatly boosts the membrane's mechanical strength, which also affects membrane life [30].

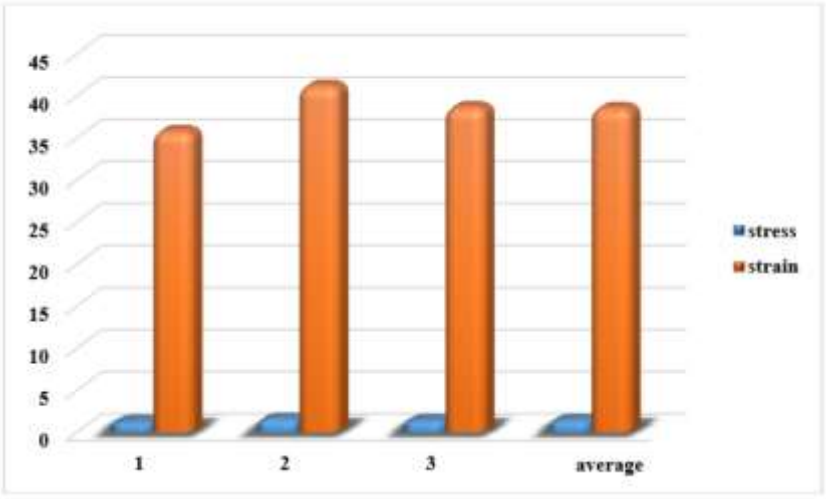

Fig.7: mechanical properties for PVDF/FTPs TBHF composite membrane.

3.3 TBHF module performance for phenolic solution in MD unit

For thirty minutes, the prepared TBHF membrane is conducted in VMD desalination. The feed solution's temperature at the inlet is 60°C. Compared to flat sheet membrane, the penetration flux and phenol removal exhibit a discernible rise when employing TBHF. The permeation was 23l/m^2h. A high phenol rejection was also provided by the TBHF membrane, which prevented 91.8% of the phenol from passing through. The performance of the membrane separation process for phenol improved when the working temperature was raised to 80°C; it reached approximately 93.9% and a flux of 27 l/m^2h.

4 Conclusion

The prepared hollow fiber membranes possess improved porosity due to the presence of, macrovoids or finger-like cavities underneath the top skins and the sponge-like layer. Also, the top-skin of the membrane became thinner, and the pore size of its surface was smaller compared to other membranes. All of these features can reduce the resistance of the mass transfer, so a higher permeate flux was achieved. During the VMD process at hot feed temperature 80°C, the maximum permeate flux was found to be 27l/m^2.h. Also, the TBHF membrane was, able to retain 93.2% of the phenolic content in feed at 80°C. As demonstrated by high rejection values, only water vapor was permitted to pass through the superhydrophobic and microporous membrane.

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