

Masar A. Akaood <sup>1</sup>  
Basma I. Waisi <sup>2</sup>  
Iftikhar M. Ali <sup>1</sup>

<sup>1</sup> Department of Physics,  
College of Science,  
University of Baghdad,  
Baghdad, IRAQ

<sup>2</sup> Department of Chemical Engineering,  
College of Engineering,  
University of Baghdad,  
Baghdad, IRAQ



# Fabrication of PAN:Cellulose Membrane for Oil/Water Separation

*In this study, we fabricated nanofiltration membranes using the electrospinning technique, employing pure PAN and a mixed matrix of PAN/HPMC. The PAN nanofibrous membranes with a concentration of 13wt% were prepared and blended with different concentrations of HPMC in the solvent N, N-Dimethylformamide (DMF). We conducted a comprehensive analysis of these membranes' surface morphology, chemical composition, wettability, and porosity and compared the results. The findings indicated that the inclusion of HPMC in the PAN membranes led to a reduction in surface porosity and fiber size. The contact angle decreased, indicating increased surface hydrophilicity, which can enhance flux and reduce fouling tendencies. Subsequently, we evaluated the efficiency of all prepared nanofiber membranes in separating emulsified oil from water using a cross-flow filtration system. It was observed that the 60:40wt% PAN/HPMC nanofiber membrane exhibited optimal performance in removing emulsion oil due to its favorable porosity and permeability, along with effective oil rejection.*

**Keywords:** Nanofibers; Electrospinning; Polyacrylonitrile; Emulsified oil

**Received:** 15 October 2023; **Revised:** 04 November; **Accepted:** 11 November 2023

## 1. Introduction

The Water crisis requires efficient, low-capitalized treatment technologies, including advanced nanomaterials in filtration, for economic growth and sustainable water treatment [1]. Nanomaterials are increasingly used in filtration technology for high water quality standards, offering high flux and low energy consumption [2]. Traditional water treatment methods fall short of the established standards and their ability to remove all impurities entirely [3]. Membrane technology has emerged as an appealing approach to addressing water quality in light of recent technological improvements and increased standards of water quality [4]. Polymeric membranes typically exhibit limited surface porosity and permeability. However, nonwoven nanofibers possess distinct properties such as high permeability and surface area. The electrospinning process can be utilized to manufacture membranes with these desirable characteristics [5]. The electrospun nanofiber membrane is usually employed in water-purification applications, especially for separating of oil and water emulsions. Emulsions pose specific challenges, including droplet deformability, coalescence phenomena in the bulk and on the membrane surface, wetting of the membrane by droplets and films, pore blockage, and oil infiltration [6]. The membrane filtering method has garnered more interest compared to other water purification treatment techniques. Oil filtration membranes' porous structure and wettability (the capacity to distinguish oil from water) are essential structural and surface properties [7]. PAN-derived electrospun nanofiber membranes offer

excellent conductivity, thermal stability, strength, hydrophilicity, and controllable pore size, surface roughness, nanofiber diameter, and surface energy [8]. Cellulose biopolymer-made nanofibers are widely used as water filtration adsorbents due to their high mechanical strength and strong structure [9]. Nanocellulose composites treat polluted water through the catalytic activity of organic contaminants in the hydroxyl and aldehyde groups [10]. Hydroxypropyl methylcellulose (HPMC) is frequently used as the basis for sustained-release hydrophilic matrix tablets, reducing surface tension and forming bundles or fiber [11]. Fiber morphology in electrospinning depends on polymeric solution concentration, overcoming surface tension and chain entanglement for continuous fiber preparation [12]. Hydrophilic membranes are essential for efficient oil-in-water emulsion separation [13,14]. Previous studies have explored the use of PAN in combination with other polymers like polysulfide (PSF) [15] and polyvinylidene fluoride (PVDF) [16] to create effective electrospun nanofiber membranes for the removal of organic pollutants from industrial wastewater. In this research, a series of electrospun PAN-based nanofiber membranes with varying concentrations of HPMC were fabricated to investigate their performance in the filtration procedure used to remove kerosene-emulsified oil from water. The study examined the influence of membrane fiber size, flow rate, contact angle, and porosity on the properties of the manufactured membranes.

**2. Experimental Part**

Polyacrylonitrile (PAN) of average molecular weight (Mw) 150000 Da, Hydroxypropyl methylcellulose (HPMC), Dimethylformamide DMF (99%), Mw 73.10, and the emulsion solution were made using purified water and kerosene (from the midland Iraqi refineries firm).

This research prepared a PAN precursor solution by dissolving a predetermined preset quantity of PAN in DMF solvent to achieve a 13wt% PAN/DMF solution. The stirring process was carried out continuously for 2 hours at 50°C until a transparent and homogeneous solution was obtained. Furthermore, HPMC was added to the PAN/DMF solution in specific quantities (weight ratios of 60:40 and 50:50) and stirred using a magnetic stirrer for 4 hours at room temperature to ensure proper dissolution. The well-dissolved solutions exhibited a bright yellow tint and were clear. A regulated-diameter metallic needle is attached to the syringe's tip. Following that, these PAN and PAN/HPMC precursor solutions were put into a plastic syringe (5 mL) with a 21-gauge needle, and using an aluminum foil-wrapped collector, the electrospun nanofiber was collected 8 cm from the tip to the collection.

This investigation used an applied voltage range of 5 to 25 kV. Electromagnetic forces will draw the polymer solution from the needle to the collection. Generating charged solution jets, also called Taylor cones, will form at the needle's tip and on the collector's surface. The Taylor cone formation determines the stability of the method used to create nanofibers. The polymer droplet will be expelled as a jet to the grounded target that serves as a collector when the voltage rises because the electric force will break the droplet's surface tension. The polymer jet produces fragile fibers when electromagnetic force is present. A nanofiber polymer mat is created on the collector surface as a result of the solvent evaporating during this process. A depiction of an electrospinning procedure at a laboratory scale can be found in Fig. (1).

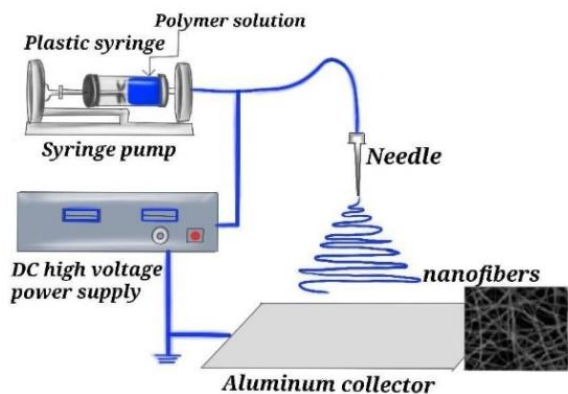


Fig. (1) Schematic illustration of electrospinning setup [12]

To prepare the emulsion solution by mixed 1g of kerosene (97% pure) with 1000 ml of purified water in an ultrasonic processor at 10000 rpm for 5 min at

room temperature, prepare was the emulsion solution of 250 mg/L of emulsified oil. UV/Vis spectrophotometer operating at a wavelength of 193 nm was used to measure the oil concentration in water. Tests of oily treatment of water were done with the filtering technology illustrated in Fig. (2).

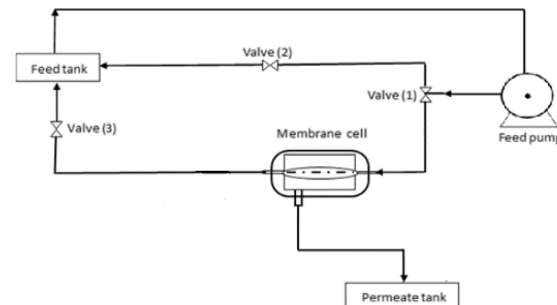


Fig. (2) Schematic diagram of the cross-flow filtration system in this work [23]

The system consisted of a homemade cross-flow filter cell, a feed pump, and a feed solution tank. The flux and oil rejection rates of the pure PAN and PAN: HPMC nanofiber membranes were evaluated under identical operating conditions. The manufactured EPNF membrane was cut into pieces measuring 2x10cm and attached to the membrane cell, resulting in an effective area of 20 cm<sup>2</sup>. Initially, the flux through the membrane was stabilized for the first 10 minutes by running the filtration system with pure water. Subsequently, the membrane was used to filter the oil-water emulsion for an hour. The baseline conditions included a temperature of 38°C, an inlet emulsified oil concentration of 250 mg/L, and a cross-feed flow rate of 60 ml/min. The gravimetric technique was used to compute the porosity of the ENMs sheets, which involves dividing the volume of the pores by the membrane volume. The following equation was used to determine the porosity[17]:

$$Porosity(\epsilon m) = \frac{(w1 - w2)}{A t \rho} \tag{1}$$

The weights w1 and w2 represent the weights of wet and dry membranes, respectively, (A, t and ρ) correspond to the membrane area (cm<sup>2</sup>), membrane thickness (cm), and water density (g/cm<sup>3</sup>) at room temperature, respectively. To measure the porosity of the ENMs membranes the specimen of every membrane was weighed and it was then submerged for five minutes in distilled water. The specimens' dry and wet weights were measured, representing the sample's weight before and after submerging in water, respectively. The oil rejection percentage (R) and membrane flow (J) during a one-hour operation were calculated using Equations 2 and 3, respectively:

$$J = \frac{V}{A t} \tag{2}$$

$$R\% = 1 - \frac{Ct}{C0} \times 100 \tag{3}$$

Here, V (L) represents the volume of permeate flow, A (m<sup>2</sup>) denotes the effective surface area of the membrane, and t (h) represents the duration of the

filtration process. The oil concentration in the feed is denoted as  $C_0$ , while  $C_t$  (mg/L) represents the oil concentration at any given point during the experiment.

### 3. Membrane Characterization

The surface morphology and structure of the PAN-only and PAN/HPMC nanofiber membranes were examined using field emission scanning electron microscopy (FESEM, JEOL 6335F) before and after oil removal. Image J software (Tescan, Czech Republic) was utilized to measure the diameters of 30 randomly selected fibers from each membrane sample. The fiber size distributions and average diameter were determined from the SEM images.

Fourier transform infrared (FT-IR) was used to examine the surface chemistry of the membrane samples made from PAN-pure and blend PAN: HPMC nanofibers. With 32 scans per specimen and a resolution of  $0.4\text{ cm}^{-1}$ , all spectra were collected for wave numbers ranging from  $400$  to  $4000\text{ cm}^{-1}$ .

The static water contact angle indicates a solid surface's hydrophobicity or hydrophilicity. The static water contact angle values are typically between  $89^\circ$  and  $180^\circ$ , and superhydrophobicity denotes how hydrophobic (fearful of water) the solid surface is. Surfaces are called hydrophilic when the contact angle is less than  $80^\circ$ . A Teta Lite optical tensiometer was used to measure the water contact angle (WCA) using the sessile drop technique at room temperature. Water droplets with diameters ranging from  $0.5$  to  $1.5\text{ L/s}$  were sprayed onto the membrane surface, and photos were captured automatically with the One Attention program.

### 4. Results and Discussion

The XRD pattern results shown in Fig. (3a) showed that the overall structure of the synthesized nanofiber is consistent with the conventional polyacrylonitrile (PAN) structure. As a result, a distinctive diffraction peak for the structure was observed at a  $2\theta$  value of  $17.1$  [18]. This peak is clear and strong and has a standard position at the phase (100). The PAN/HPMC electrospun membrane in figures (3b and c) showed two HPMC characteristic peaks at  $2\theta = 14.6^\circ$  and  $21.8^\circ$ , indicating that the lattice constant of the HPMC crystal has changed significantly, possibly due to drawing forces applied during the electrospinning process [10].

Figure (4) depicts the FTIR analysis of both pure PAN and PAN/HPMC nanofiber membranes, which enables the identification of their respective functional groups. In the FTIR analysis of PAN-based nanofibers, a distinct and intense peak at  $1589\text{ cm}^{-1}$  is observed, which corresponds to the stretching vibration of the  $\text{C}=\text{C}$  group. The broadband ranging from  $950$  to  $520\text{ cm}^{-1}$  can be attributed to C-H bending. In the FTIR analysis of PAN/HPMC nanofibers, the most prominent peak is observed at  $1059\text{ cm}^{-1}$ , representing the stretching band of the C-O-C group

[19]. Additional peaks at  $2947.89$ ,  $1415.65$ ,  $1238.17$ , and  $1100\text{ cm}^{-1}$  are assigned to the stretching vibrations of  $\text{CH}_2$ ,  $\text{CH}$ ,  $\text{C-O}$ , and  $-\text{CH-O-CH}_2$ , respectively. The absorption of the  $-\text{OH}$  bond, resulting from absorbed water, is evident at the peak of  $3459\text{ cm}^{-1}$ . The presence of the  $(\text{C}\equiv\text{N})$  bond in the PAN/HPMC fiber structure leads to an increased absorption intensity, ultimately resulting in narrower fiber widths [14].

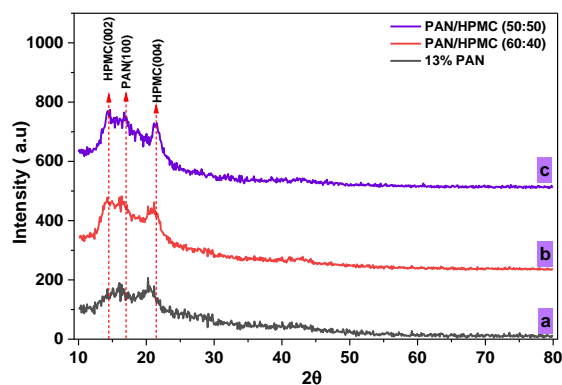


Fig. (3) XRD patterns of 13% PAN, PAN: HPMC (60:40), and PAN:HPMC (50:50) mixtures

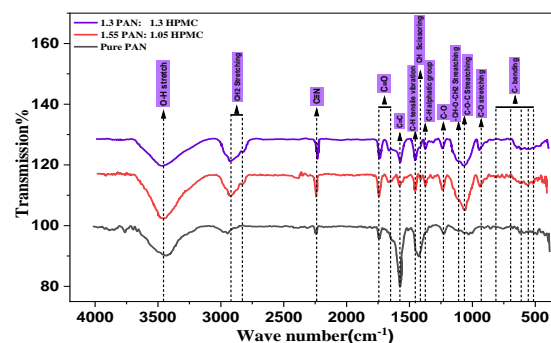


Fig. (4) FTIR spectra of pure PAN and PAN: HPMC-based nanofiber membranes

Figure (5) displays the surface characteristics of PAN and PAN: HPMC nanofibers at various concentrations (60:40 and 50:50), along with the corresponding distribution of fiber sizes in the prepared membrane. Adding HPMC reduces viscosity, causing increased chain tangles obstructing the solution jet's passage toward the collector under defined process parameters. As a result, the diameter of the nanofibers decreases. Detailed information regarding the average diameter (in nanometers) and porosity of the electrospun membranes can be found in table (1). The electrospun PAN membrane's porosity, which was determined to be  $70.4\%$ , is within the range of values mentioned in the literature [20]. We observe that the HPMC ratio added decreased the porosity value of PAN membranes by about  $17\%$ . This was anticipated because the addition of the HPMC layer decreased the membrane's surface porosity by reducing the gaps between fibers. The pure PAN membrane has the largest contact angle, measuring  $89^\circ$ , with the injection of a particular HPMC ratio into

the PAN membrane, the contact angle lowers and becomes super hydrophilic. The contact angle is affected by membrane pore sizes, with decreasing pore sizes causing a decrease [21]. A minimal connection angle in hydrophilic membranes lowers capillary pressure, improves flow rate, and rejects, at the same time, wettability significantly impacts membrane efficiency and helps get the surface wet, enhancing purification effectiveness.

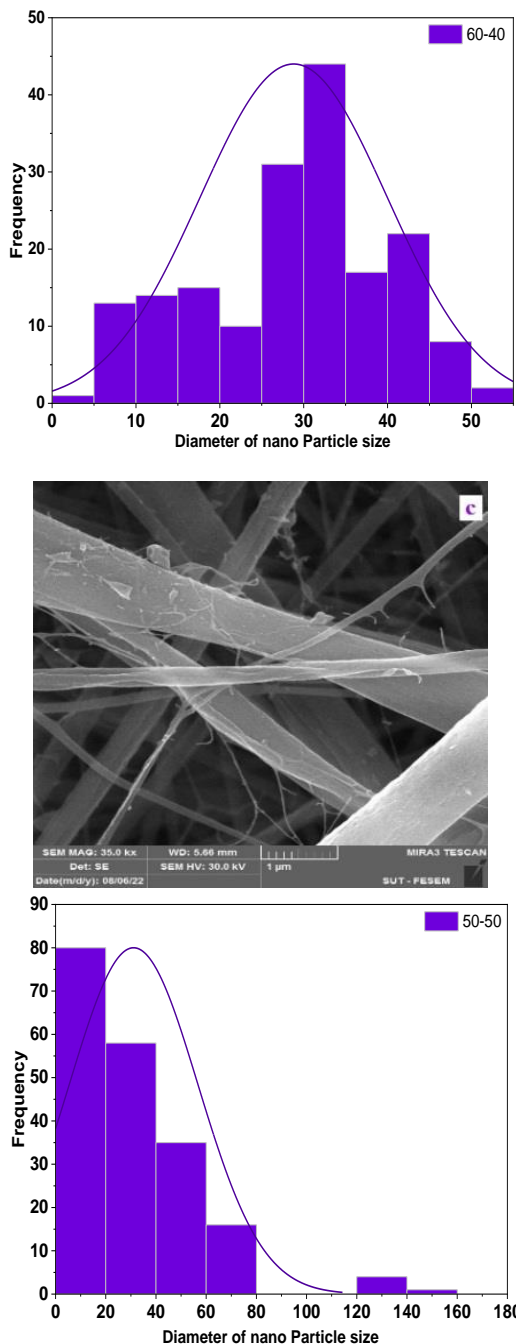
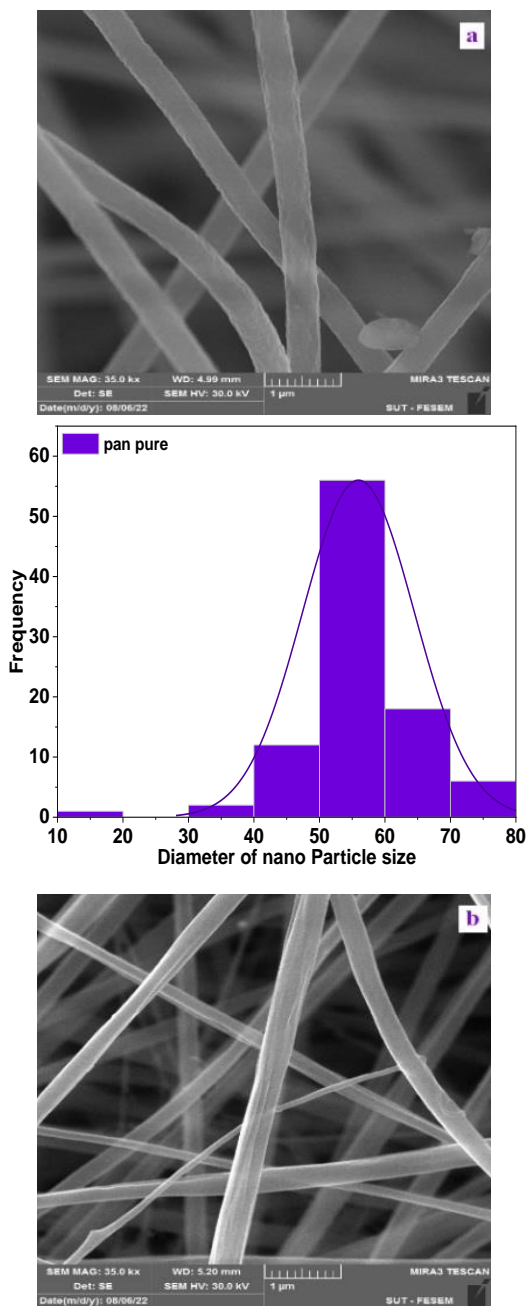


Fig. (5) FE-SEM images of (a) 13%PAN and PAN:HPMC membranes with different concentrations (b) 60:40 and (c) 50:50)

The efficiency of the fabricated membranes in removing emulsified oil from water was evaluated based on permeate flux and oil rejection percentage, as shown in Fig. (6). The hydrophilic nanofiber membranes exhibited high permeability, allowing for interactions with water molecules and facilitating water flux [22]. Both pure PAN and the blend PAN: HPMC (60:40) nanofiber membranes exhibited favorable characteristics such as high permeate flux, low fouling, and hydrophilic-hydrophobic interactions, resulting in efficient water flow. On the other hand, the PAN:HPMC (50:50) nanofiber membrane showed lower permeate flux (60 LMH) and

higher oil rejection percentage (94%) due to oil droplet accumulation on the membrane surface, leading to clogged pores and reduced permeate flux passage. Based on the data in table (1), the most optimal performance was achieved using PAN: HPMC (60:40) with a high permeability flux of 300 LMH and good oil rejection of 89%. Consequently, this membrane was selected for further filtration experiments. Overall, all of the manufactured EPNF membranes showed good permeate flux, attributed which is due to their large permeability.

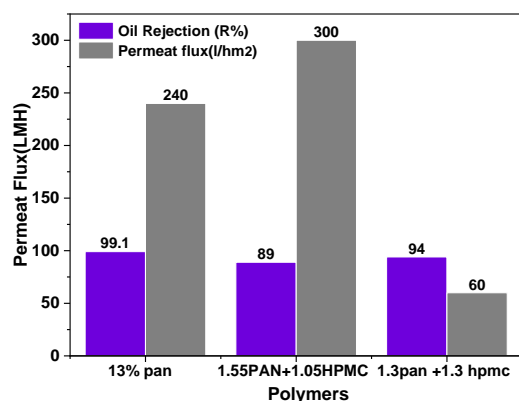


Fig. (6) Oil/Water filtration efficiency of various fabricated membranes at 250mg/L oil concentration and 28°C temperature

Table (1) Average diameter, porosity, Rejection (R%), and flux (l/hm<sup>2</sup>) data of the fabricated EPNF membranes

| Membrane         | Average Diameter (nm) | Porosity (%) | Rejection (R%) | Flux (l/hm <sup>2</sup> ) |
|------------------|-----------------------|--------------|----------------|---------------------------|
| 13% PAN          | 437                   | 70.4         | 99.1           | 240                       |
| PAN/HPMC (60:40) | 264                   | 61.3         | 89             | 300                       |
| PAN/HPMC (50:50) | 373                   | 53.8         | 94             | 60                        |

In Fig. (7a), the pure PAN membrane exhibited a fouling layer consisting of oil droplet aggregation on the membrane surface during the attempt to pass through the matrix. Conversely, in Fig. (7b), the emulsion flowed through the PAN: HPMC cross-section in the nanofibers' direction. This resulted in the complete exposure of the nanofiber surface to the oil-in-water emulsion. The PAN:HPMC nanofibers possessed adsorption sites along their surface, where a majority of the oil droplets were adsorbed. As the adsorption sites became occupied, the oil droplets coalesced, forming an oil layer on top of the nanofiber rather than solely within the nano-sized pores [23]. Consequently, there was an increase in the fiber size width after oil filtration, which can be attributed to the superhydrophilic surface characteristics of HPMC. This adsorption process significantly enhanced the rate of oil removal. It should be noted that an increase in cellulose concentration resulted in smaller pore sizes due to pore blockage, leading to a reduction in flow channel size. This, in turn, resulted in lower water flux and higher oil rejection, as depicted in Fig. (7c).

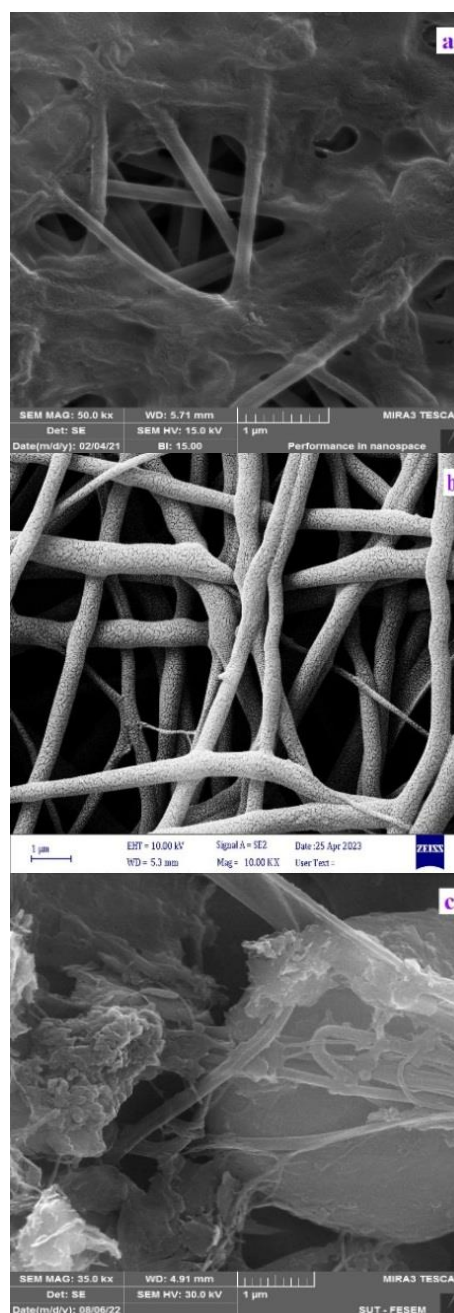


Fig. (7) FE-SEM images of (a) 13%PAN and PAN:HPMC membranes with different concentrations (b) 60:40 and (c) 50:50 after oil filtration

### 5. Conclusion

Using a cross-flow filtration system, this study evaluated PAN-based and PAN:HPMC electrospun nanofiber membranes for separating emulsified oil from water. Results showed that the blend PAN: HPMC (60:40) nanofiber membranes with a high permeability flux of 300 LMH and good oil rejection of 89%. Consequently, this membrane was selected for further filtration experiments. Overall, all of the manufactured EPNF membranes showed good permeate flux, attributed which is due to their large permeability.

## References

- [1] M. Anjum et al., "Remediation of wastewater using various nano-materials", *Arab J. Chem.*, 12(8) (2019) 4897-4919.
- [2] I.M. Alarifi et al., "Water treatment using electrospun PVC/PVP nanofibers as filter medium", *Int. J. Mater. Sci. Res.*, 1(2) (2018) 43-49.
- [3] X. Qu et al., "Nanotechnology for a safe and sustainable water supply: enabling integrated water treatment and reuse", *Acc. Chem. Res.*, 46(3) (2013) 834-843.
- [4] A. Mark, "Science and technology for water purification in the coming decades", *Nature*, 452 (2008) 20.
- [5] P.M. Huck, "Drinking Water Treatment and Supply in Developed Countries in 2045—Where Will We Be?", in **"Conflict Resolution in Water Resources and Environmental Management"**, K.W. Hipel et al. (eds.), Springer Cham (2015) 145-158.
- [6] M.M.A. Shirazi, S. Bazgir and F. Meshkani, "Electrospun nanofibrous membranes for water treatment", *Adv. Membr. Technol.*, 57(3) (2020) 467-504.
- [7] M. Mulder, **"Basic principles of membrane technology"**, Springer Science & Business Media (1996).
- [8] M. Al-Furaiji et al., "Preparation of thin-film composite membranes supported with electrospun nanofibers for desalination by forward osmosis", *Drink. Water Eng. Sci.*, 13(2) (2020) 51-57.
- [9] A. Lanna et al., "Performance of novel engineered materials from epoxy resin with modified epoxidized natural rubber and nanocellulose or nanosilica", *Adv. Polym. Technol.*, (2020) Article ID 2123836.
- [10] H. Wei et al., "Environmental science and engineering applications of nanocellulose-based nanocomposites", *Enviro. Sci. Nano*, 1(4) (2014) 302-316.
- [11] J.L. Ford, "Thermal analysis of hydroxypropylmethylcellulose and methylcellulose: powders, gels and matrix tablets", *Int. J. Pharm.*, 179(2) (1999) 209-228.
- [12] H.M. Hawy and I.M. Ali, "Enhancement the photosensitivity of PVA NFs/Si prepared by electrospinning technique", *Optik*, 267 (2022) 169659.
- [13] C.-L. Xu and Y.-Z. Wang, "Novel dual superlyophobic materials in water--oil systems: under oil magneto-fluid transportation and oil--water separation", *J. Mater. Chem. A*, 6(7) (2018) 2935-2941.
- [14] S. Alkarbouly and B. Waisi, "Dual-layer Antifouling Membrane of Electrospun PAN: PMMA Nonwoven Nanofibers for Oily Wastewater Treatment", in *Proc. of 2<sup>nd</sup> Int. Multi-Discip. Conf. Theme: Integ. Sci. Technol., IMDC-IST 2021*, 7-9 September 2021, Sakarya, Turkey.
- [15] B.I. Waisi et al., "Activated carbon nanofiber nonwovens: improving strength and surface area by tuning fabrication procedure", *Ind. Eng. Chem. Res.*, 58(10) (2019) 4084-4089.
- [16] Q. Zhao et al., "Effect of hydroxypropyl methylcellulose on the textural and whipping properties of whipped cream", *Food Hydrocoll.*, 23(8) (2009) 2168-2173.
- [17] M. Al-Furaiji et al., "Triple-layer nanofiber membranes for treating high salinity brines using direct contact membrane distillation", *Membranes (Basel)*, 9(5) (2019) 60.
- [18] B.L. Abbood, K.A. Sukkar and J.A. Al-Najar, "Characterization and Aerodynamics of Synthesized Polymeric Nanofibers via Electrospinning Process to Capture PM10 and PM2.5 from Air", *J. Appl. Sci. Nanotech.*, 1(4) (2021) 91-104.
- [19] L. Wannatong, A. Sirivat and P. Supaphol, "Effects of solvents on electrospun polymeric fibers: preliminary study on polystyrene", *Polym. Int.*, 53(11) (2004) 1851-1859.
- [20] L. Huang, S.S. Manickam and J. R. McCutcheon, "Increasing strength of electrospun nanofiber membranes for water filtration using solvent vapor", *J. Memb. Sci.*, 436 (2013) 213-220.
- [21] A. Hamta et al., "Manipulating of polyacrylonitrile membrane porosity via SiO<sub>2</sub> and TiO<sub>2</sub> nanoparticles: Thermodynamic and experimental point of view", *Polym. Adv. Technol.*, 32(2) (2021) 872-885.
- [22] O. Habimana, A.J.C. Semião, and E. Casey, "The role of cell-surface interactions in bacterial initial adhesion and consequent biofilm formation on nanofiltration/reverse osmosis membranes", *J. Memb. Sci.*, 454 (2014) 82-96.
- [23] S.M. Alkarbouly and B.I. Waisi, "Fabrication of Electrospun Nanofibers Membrane for Emulsified Oil Removal from Oily Wastewater", *Baghdad Sci. J.*, 19(6) (2022) 1238-1248.