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Fabrication of Electrospun Nanofibers Membrane for Emulsified Oil Removal from Oily Wastewater

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Abstract:

The electrospun nanofibers membranes have gained considerable interest in water filtration applications. In this work, the fabrication and characterization of the electrospun polyacrylonitrile-based nonwoven nanofibers membrane are reported. Then, the membrane's performance and antifouling properties were evaluated in removing emulsified oil using a cross flow filtration system. The membranes were fabricated with different polyacrylonitrile (PAN) concentrations (8, 11, and 14 wt. %) in N, N-Dimethylformamide (DMF) solvent resulted in various average fiber sizes, porosity, contact angle, permeability, oil rejection, and antifouling properties. Analyses of surface morphology of the fabricated membranes before and after oil removal revealed increasing the fiber size, decreasing the fouling amount, and increasing the permeate flux. On the other hand, decreasing the fiber size resulting in increases the oil rejection. It was observed that 11 wt. % PAN based nonwoven nanofiber membrane was the optimum membrane for emulsified oil removal due to its good porosity, permeability with good oil rejection. In addition, fouled nonwoven nanofiber membrane cleaning was done by backwashing technique using warm distilled water which was effective in retaining the membrane permeability and oil rejection for 7 times. The obtained results confirmed an efficient performance of the fabricated nanofibers membrane for oil-water separation with oil rejection percentage of 92.5% and a permeate flux of 120 LMH.

Keywords: Backwash, Electrospinning, Emulsified Oil, Nonwoven Nanofibers, and Polyacrylonitrile

Introduction:

One of the major causes of water pollution is the oil spill [1]. Also, the generated oily wastewater from various industries (e.g., petrochemical, transport, food, clothing, pharmaceutical, etc.) is a significant contaminant source in the environment [2,3]. Discharging the oily wastewater to the natural environment causes a huge ecological issue in the world [4–6]. The traditional separation methods, including coagulation [7], air flocculation [8], skimming [9], flocculation [10], have been widely accepted as an effective, low-cost, primary treatment stage and flotation which are helpful for the separation of oil/water-free mixtures. However, they suffer from the limitations of low efficiency of emulsified oil droplet (the oil droplets size smaller than 20 µm) separation, energy costs, and secondary emissions [11]. In addition, removing emulsified oil requires a more complex separation process due to the small diameter of oil droplets.

Membrane technology is considered a green and strong technology for oily wastewater treatment. The membrane filtration technique has gained more interest than other water purification treatment technologies due to its integrity, low energy consumption, simple activity, and friendliness to the environment [12,13]. The major membranes for the separation of water and oil are microfiltration (MF) and ultrafiltration (UF) [14,15]. Earlier studies have shown that the fundamental parameters of oil droplet filtration are the membrane form (a higher flow of hydrophilic membrane), oil concentration, and flow velocity [16]. Maximum permeate flow and maximum oil rejection are the main criteria for optimizing the membrane processes [17].

Polymeric membranes are relatively inexpensive, but they have an asymmetrical structure that contributes to low surface porosity and low permeability [18]. However, the nonwoven nanofibers membrane is a polymeric membrane with unique characterizations such as high permeability and surface area. The nonwoven nanofibers can be fabricated via a flexible technique for creating nonwoven nanofibers of various diameters utilizing an electrostatic field called the electrospinning process [19,20]. For water filtration, the applications of electrospun membranes have been successfully demonstrated in ultrafiltration [21]. The electrospun Nanofiber membrane is commonly used for water treatment, including separation of oil/water emulsions due to high porosity, permeability, sizeable effective surface area, continuously interconnected pores, and stability. These attributes can directly improve the flux performance without sacrificing the contaminant rejection ratio [19,22,23]. Various polymers were used to prepare the electrospun Nanofiber membranes for oil-water separation including polyurethane (PU) [24], polytetrafluoroethylene (PTFE) [25], polysulfone (PSf) [26], cellulose acetate (CA) [27], and polyvinylidene fluoride (PVDF) [28]. These polymers had been modified by the addition of additional materials or by their coupling with various techniques to enhance the membranes efficiency.

Electrospun nanofibers membrane derived from Polyacrylonitrile (PAN) precursor has attracted great interest because of the good conductivity, thermal stability, high strength, high hydrophilicity, small fiber diameters, high surface area per volume ratio, and controllable pore size [29,30]. Effective oil-in-water emulsion separation typically requires a hydrophilic membrane to minimize oil fouling and increase water flow [31,32]. The hydrophilic surface can relieve membrane fouling caused by oil and increase the flow of water. The concentration of polymer solution has an important influence on the fiber size mechanical properties of electrospun mats [33]. In previous works, the PAN was used with other materials such as cellulose acetate (CA) [14] and polyaniline (PAN)[15] to fabricate efficient electrospun nanofibers membranes for removing the organic pollutant from industrial wastewater.

This work deals with using PAN-based electrospun polymeric nanofibers (EPNF) membrane in the ultrafiltration process for emulsified oil (kerosene) removal from water. A series of (EPNF) membranes was fabricated based on different concentrations of PAN precursor solutions. The effect of membranes fiber size, feed flow rate, feed oil concentration, and pressure was investigated. Furthermore, cleaning the fouled membrane

Materials and Methods:

Materials

Polyacrylonitrile (PAN) (Mw =150,000 g/mole and density of 1.184 g/cm^3) was ordered from Sigma Aldrich. N, N-Dimethylformamide (DMF) (density of 0.948 g/cm^3) was supplied from Alfa Aesar and used as a solvent to dissolve PAN. Kerosene (from midland Iraqi refineries company) was used to prepare the emulsion solution using a distilled water.

Fabrication of Nonwoven Membranes

PAN-based nonwoven nanofibers membrane was prepared by electrospinning technique, a stretching motion of polymer droplets to resolve surface tension in a high voltage electrostatic field. First, the polymeric solutions were prepared by dissolving a certain amount of PAN in DMF to prepare 8, 11, 14 wt.% PAN/DMF solutions under continuous stirring for 4 hrs at 60 ºC until a homogeneous clear precursor solution was obtained. Then, the precursor solution was put in a plastic syringe and secured in a syringe pump. Next, a metal needle (inner diameter was 0.7 mm) was connected to the nozzle of the syringe. Then, the polymeric nanofiber was stretched through the tip of the metal needle with a flow rate of 1 ml/h and collected on the rotating drum (rotating speed of 70 rpm) by applying a high voltage (24, 22, and 19) kV for 8, 11 and 14 wt. % PAN-based EPNF membrane, respectively. More details about the electrospinning setup are shown in our previous work [34].

Emulsion Preparation

To prepare oil-water emulsion, 1g of kerosene (97%purity, Fluka) was added to 1,000 ml of distilled water and mixed in Hielscher ultrasonic processor (Hielscher UP400s, Teltow, Germany) at 10,000 rpm for 15 min. at room temperature to produce a stable emulsion. Three different oil concentrations were prepared: 100, 250, and 400 mg/L. The oil concentration in water was conducted by a UV/Vis spectrophotometer (Thermo Scientific Genesys 10S) at a wavelength of 196 nm.

Nonwoven Membrane Characterizations

The surface structure and morphology of the PAN-based nonwoven nanofiber membranes before and after oil removal were visualized by field emission scanning electron microscopy (FESEM, JEOL 6335F). The fiber size distributions and average fiber diameter were obtained from the SEM images by measuring the fiber sizes of twenty fiber diameter measurements of each membrane sample using Image J software (National Institutes of Health, USA).

To investigate the surface hydrophilicity of the fabricated EPNF membranes, the contact angle of water drops was measured using a contact angle analyzer (Theta Lite TL-101). The porosity (ε_m) of EPNF membranes was calculated by the gravimetric method, which is defined as the ratio of the volume of the pores by the total volume of the membrane and can be calculated using the following equation Eq. 1 [17,35]

$$\text{Porosity } (\varepsilon_m) = \frac{(w_1 - w_2)}{A * t * p} \qquad 1$$

W_1 is the weight of the wet membrane, W_2 is the weight of the dry membrane. A, t, and ρ are the membrane effective area, membrane thickness, and water density at room temperature, respectively. The wet membrane samples (2x2 cm) were dipped in distilled water (wetting agent) for 1 hr. Before weighting the membrane, they were left to dry at room temperature for half an hour.

Experimental Methods

Emulsified Oil Separation Experiments

The synthetic oily water treatment experiments were carried out using the shown filtration system in Fig.1. The system consisted of a homemade cross-flow filtration cell, feed pump, feed solution vessel, and pressure gauge. The fabricated PAN-based nonwoven nanofiber membrane's flux and oil rejection rate were investigated under different running conditions.

The fabricated EPNF membrane was cut into (2 x10 cm) and fixed in the membrane cell with an effective area of membrane 20 cm^2. First, the filtration system was operated with distilled water for the first 15 min. to stabilize the flux through the membrane. Then oil/water emulsion was instead to be filtered through the membrane for 1 hr. Baseline conditions were 1.5 psi transmembrane pressure, 25°C temperature, 250 mg/L inlet emulsified oil as a feed flow, and 60 ml/min as a cross feed flow rate.

The membrane flux (J) (LMH) and oil rejection percentage (R) (%) in operating running time of 1 hr. were calculated using Eqs. 2, 3, respectively [13].

$$J = \frac{V}{A * t} \qquad 2$$

$$R\% = [1 - \left(\frac{C_t}{C_0}\right)] * 100 \qquad 3$$

Where V (L) is the volume of permeate flow, A (m^2) is the effective area of the membrane, and t (hr.) is the filtration time. C_0 and C_t (mg/L) are the oil concentrations in the feed and at any time over the experiment, respectively. The effect of inlet emulsified oil concentration (100, 250, and 400) mg/L, the applied transmembrane pressures (1.5, 5, and 10) psi, and the inlet flow rate (30, 45, and 60) ml/min were studied to investigate the separation efficiency of the fabricated membranes. For each set of conditions, the experiments were repeated three times.

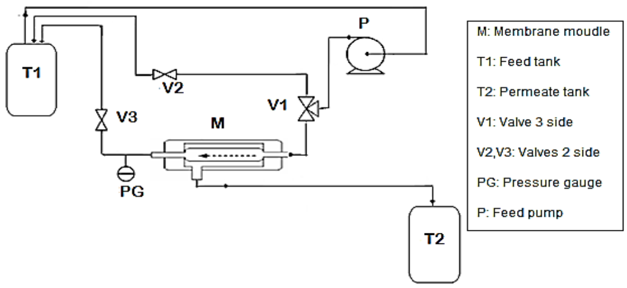

Figure 1. Schematic diagram of the cross-flow filtration system

Membrane Cleaning

The reduction in flux in membrane filtration results from the growth in membrane resistance due to membrane pores blocking and forming a cake layer on the surface of the membrane. Pore blocking increases membrane resistance while the development of cake produces an extra layer of permeate flow resistance. Therefore, blocking of pores and cake forming can be regarded as two fundamental membrane fouling mechanisms. For fouling cleaning, the backwashing method is widely used; it can be defined as a method for improving the performance in cross-flow ultrafiltration by reducing the concentration polarization and fouling effect on the membrane surface.

In this work, to clean the fouled EPNF membranes after the oil filtration experiment, the backwashing method was used with warm water (50 ^{o}C) for 20 min. and 1.5 psi using the same filtration system. It was found to be an effective method for cleaning the organic fouling from the EPNF membrane. The effectivity of backwashing to estimate the organic fouling resistant ability of the EPNF membranes before and after the backwashing was evaluated by estimating the fouling the flux recovery ratio (FRR) using Eq. 4 [14]:

$$FRR\% = \left(\frac{J_{Wt}}{J_{W0}}\right) * 100 \qquad 4$$

Where J_{w0} and J_{wt} are the permeate flux before and after oil filtration experiment, respectively. Higher FRR value meant less fouling existing on the membrane surface.

Results and Discussions:

Membrane Characterization

Figs.2 a, b, and c shows the surface morphology and the corresponding fiber size distribution of the prepared EPNF membrane as a function of PAN concentration (8, 11, and 14 wt. %). It has been observed that increasing PAN concentration from 8 to 14 wt. % increases the average fiber size from (150 to 400) nm, which is attributed to increasing the viscosity of the solution as the PAN concentration. Viscosity increasing results in more chain entanglements that impede the flow of the solution jet during its flight to the collector at defined process parameters resulting in an increased diameter [25]. The corresponding fiber size distribution showed that spinning a high precursor concentration (14 wt.% PAN/DMF) produced a wide range of fiber size (300-580) nm, while the fiber size range was narrow at the lower polymer concentrations. The viscosity of the precursor solution increases with increasing the concentration of the precursor solution, increasing its sensitivity to the electric field during the spinning process. The reduced drawdown force cannot overcome the viscous forces of the high concentration PAN solution [33]. Beside that, the polymer chains are more tangled in the high concentration precursor solution, resulting in a broader fiber diameter size [33,36].

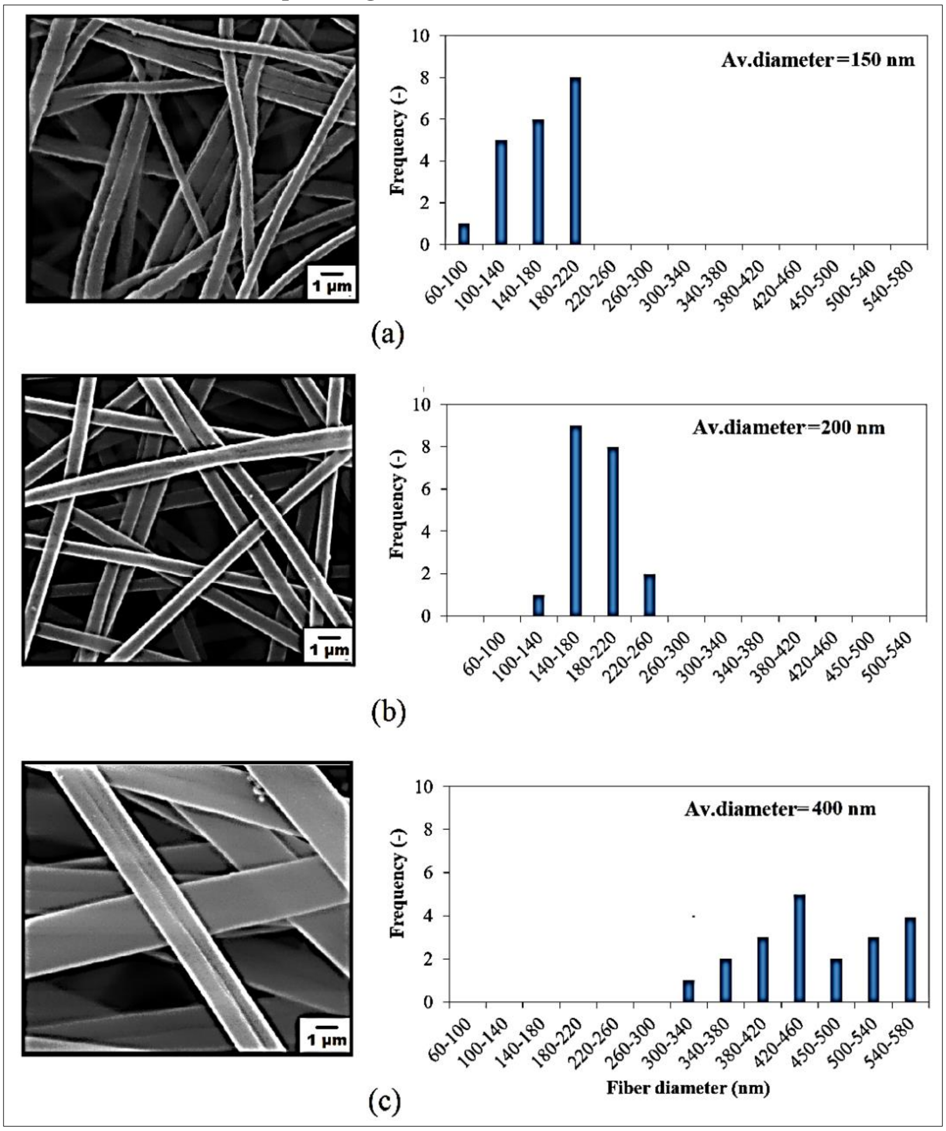

Figure 2. SEM images of PAN-based EPNF membranes (magnification is 10000 X) and the corresponded fiber size prepared from different PAN/DMF concentrations (a) 8%PAN/DMF, (b) 11%PAN/DMF, and (c) 14%PAN/DMF.

Table 1 shows the contact angle and porosity of the various fabricated EPNF membranes. The contact angle decreased with increasing the PAN concentration in the membrane, which can be due to settling the heavier fibers into a tighter mat during the fabrication process [37,38]. It can also be seen from Table 1 that the measured porosity of the fabricated EPNF increased from 91 % to 96 % with increasing

PAN concentration from 8 to 14 wt.%, which can be attributed as the average fiber diameter increases indicating increasing the hydrophilicity with increasing the PAN concentration. Therefore, fibers with larger diameters lead to smaller contact angles and more wettability [38,39].

Table 1. The porosity and contact angle measurements of the prepared EPNF membranes

wt.% PAN/DMF	Ava. fiber size (nm)	Contact angle (°)	Porosity (%)
8	150	55	91
11	200	33	94
14	400	20	96

Membrane Performance

Effect of Membrane Characterizations

The three types of prepared EPNF membranes have been investigated in emulsified oil separation from water using a cross filtration cell. Figs.3 a and b shows the results of the permeate flux and oil rejection percentage for the three different fabricated EPNF membranes under baseline conditions. All membranes showed a high oil rejection related to the large particle sizes of oil-water emulsions compared to the pore diameter of the fabricated membranes. However, the fabricated 8 % EPNF membrane showed the best size-sieving. These results can be attributed to its small fibers and pores resulted in the highest rejection of oil (99.9%) and resistance to permeate flux (90 LMH).

In all cases, the fabricated EPNF membranes have a good permeate flux due to their high permeability. However, 8 % EPNF membrane exhibited the quickest fouling after the oil emulsion was introduced into the membrane system; consequently, the permeate flux was the lowest. The SEM images in Fig.4 clarified the formed fouling layer on the three fabricated membranes after the oil filtration. The fouling was coalescences of oil droplets on the membrane surface during attempts at moving through the matrix. It can be noticed that the amount of fouling on the surface increased with decreasing the PAN concentration in the fabricated membrane because of decreasing the fiber sizes that enhanced excluding the oil droplets on the membrane surface. The optimum result was obtained using 11 % EPNF membrane, good permeability flux (120 LMH), and oil rejection (92.5 %), so it was selected to do the rest of the filtration experiments.

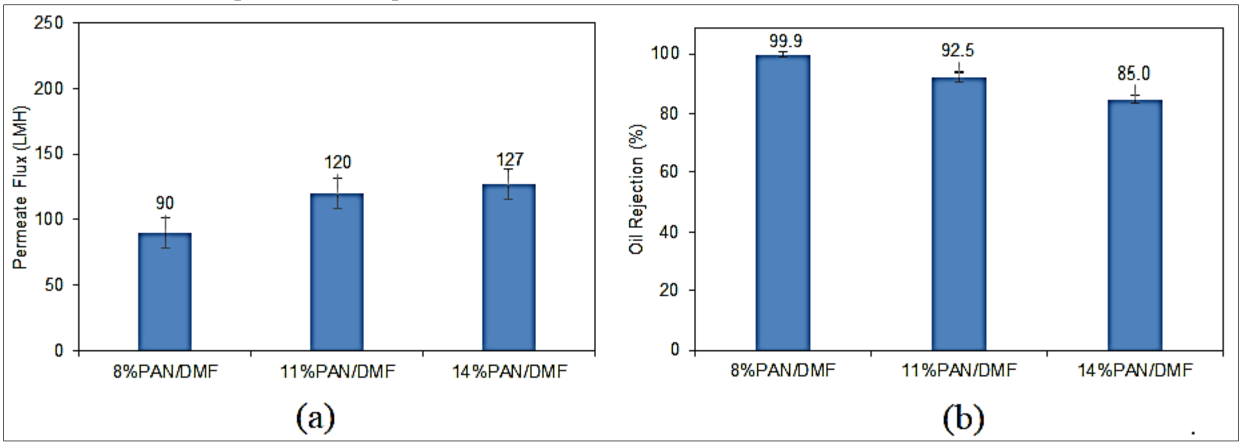

Figure 3. The separation efficiency of the different fabricated EPNF membranes used in oil filtration at baseline conditions (Feed flowrate= 60 ml/min, feed oil concentration = 250 mg/L, transmembrane pressure = 1.5 psi, and temperature= 25°C) (a) Permeate flux and (b) Oil rejection

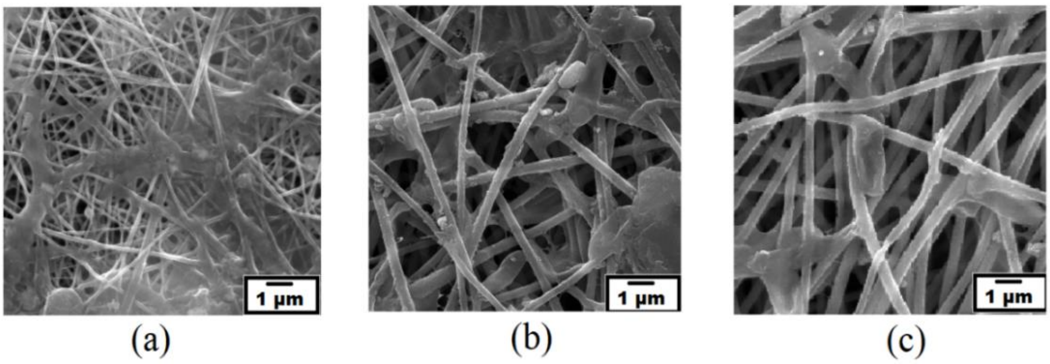

Figure 4. The SEM images of the different fabricated EPNF membranes (magnification is 10000 X) used in oil filtration at baseline conditions (a) 8% PAN/DMF, (b) 11 % PAN/DMF, and (c) 14 % PAN/DMF

Feed Flowrate

The feed flowrate effect on membrane separation efficiency is an important process parameters in oil/water emulsion separation. The smaller inlet flowrate resulted in more permeate flux and less oil rejection due to the slow accumulation of oil fouling on the membrane surface [40]. Fig.5 shows the effect of the inlet feed flowrate on the permeate flux and oil separation efficiency of the fabricated EPNF membrane (11 wt.% PAN/DMF). Increasing the flow (30 to 60 ml/min) resulted in decreasing the permeate flux (150 to 120 LMH) and increasing the rejection efficiency (90 to 92.5 %). This behavior can be attributed to the quick formation of the fouling layer on the membrane surface, increasing the inlet flow, consequently increasing the accumulated oil droplets on the membrane surface. Fig. 6 shows the SEM images of the membrane surface for the various inlet flowrate. At the highest feed flow rate, the total amount of inlet oil droplets is much more than at the lower feed flow rates for the same filtration time (1 hr.).

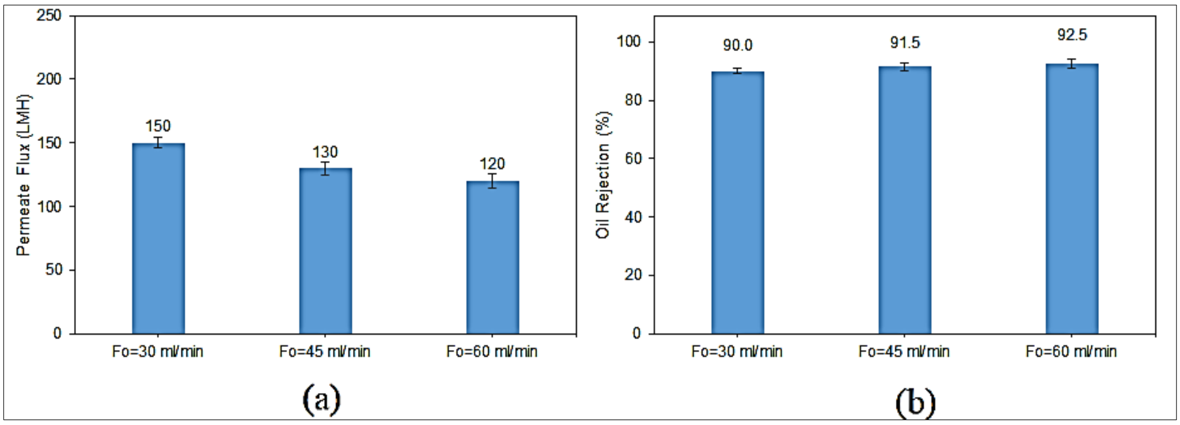

Figure 5. The separation efficiency of 11% PAN/DMF membrane under various initial feed flow rates (feed oil concentration = 250 mg/L, transmembrane pressure = 1.5 psi, and temperature= 25°C) (a) Permeate flux and (b) Oil rejection

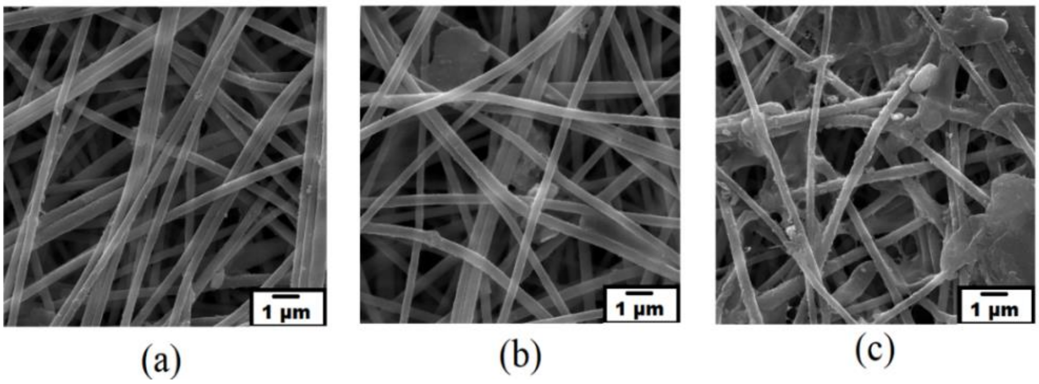

Figure 6. The SEM images of the 11 % PAN/DMF EPNF membranes (magnification is 10000 X) after emulsified oil removal under various initial feed flow rates (a) 30 ml/min, (b) 45 ml/min, and (c) 60 ml/min.

Feed Oil Concentration

The influent concentration is one of the parameters that have an important effect on the filtration process efficiency. Fig. 7 shows the permeation flux and separation efficiency of oil/water emulsion for 11 % PAN EPNF membranes at different feed oil concentrations (100, 250, and 400 mg/L). The results also indicated a strong effect of oil concentration on membrane permeate; higher oil concentration in the feed creates more fouling layer build-up on the membrane surface or inside the pores. A significant quantity of oil was accumulated on the membrane surface at a high oil concentration, creating an additional resistance to the permeate flow [41]. Increasing the oil content on the feed side (100 to 400 mg/L) resulted in decreasing the permeate flux (210 to 90 LMH) and increasing the oil rejection (88 to 97 %). This behavior is argued to the rapid fouling formation when the inlet oil concentration is high, as shown in Fig.8.

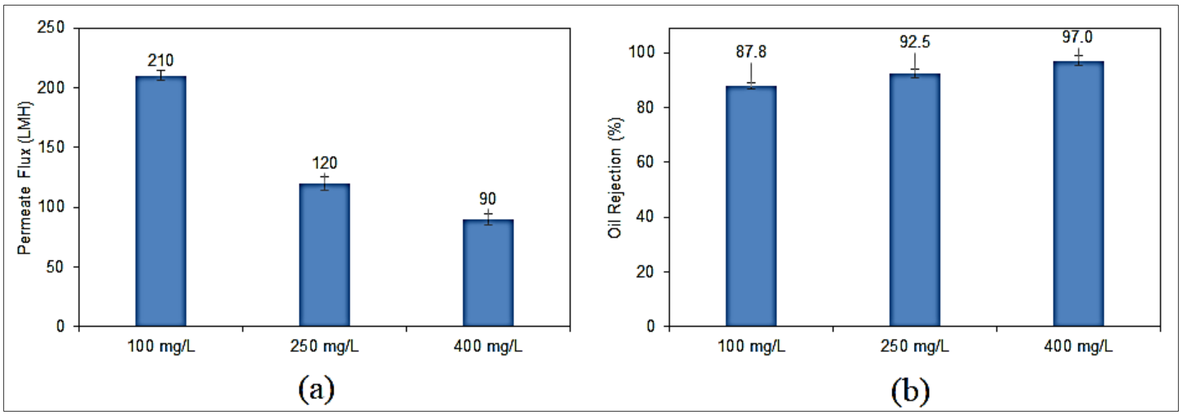

Figure 7. The separation efficiency of 11% PAN/DMF EPNF membrane under various feed oil concentrations (Feed flowrate= 60 ml/min, transmembrane pressure = 1.5 psi, and temperature= 25°C) (a) Permeate flux and (b) Oil rejection

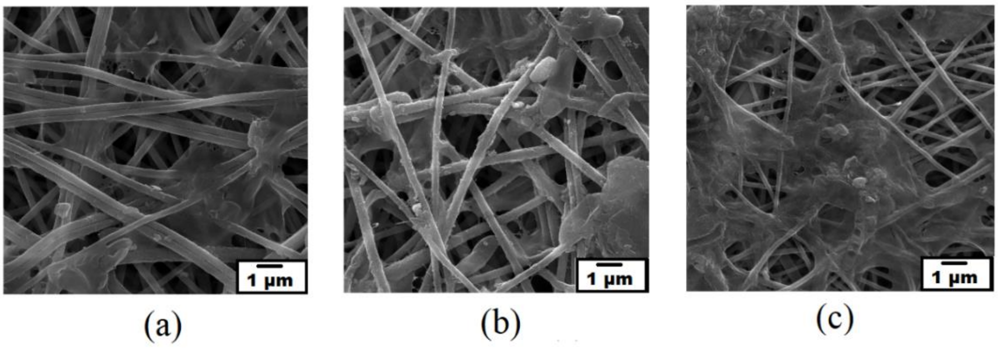

Figure 8. The SEM images of the 11% PAN/DM EPNF membranes (magnification is 10000 X) after emulsified oil removal under various feed oil concentrations (a) 100 mg/L, (b) 250 mg/L, and (c) 400 mg/L.

Transmembrane Pressure

Fig.9 shows the permeation flux and separation efficiency of oil/water emulsion for 11% PAN EPNF membrane at different transmembrane pressures. An increase in the filtration pressure (1.5 to 5 psi) led to a significant increase in the filtration flux (120 to 3450 LMH) and a decrease in the oil separation efficiency (93 to 48 %) which can explain the high driving force and forcing the small oil droplets to move through the nanofiber membranes. However, at higher transmembrane pressure (10 psi), the oil rejection increased to 65 % due to the formed thick oil fouling layer.

The highest transmembrane pressure resulted in the deposition of oil droplets through the membrane's pores and coalescing on the surface of the membrane forming a layer of oil and preventing the oil droplets from moving through the nanofibers membrane, as can be seen in Fig.10.

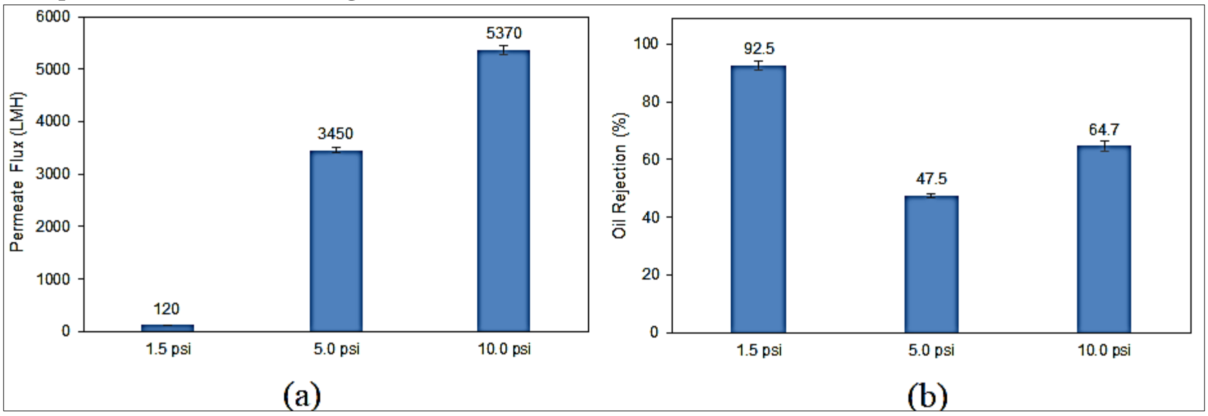

Figure 9. The separation efficiency of 11% PAN/DMF membrane under various transmembrane pressures (Feed flowrate= 60 ml/min, feed oil concentration = 250 mg/L, and temperature= 25°C) (a) Permeate flux and (b) Oil rejection

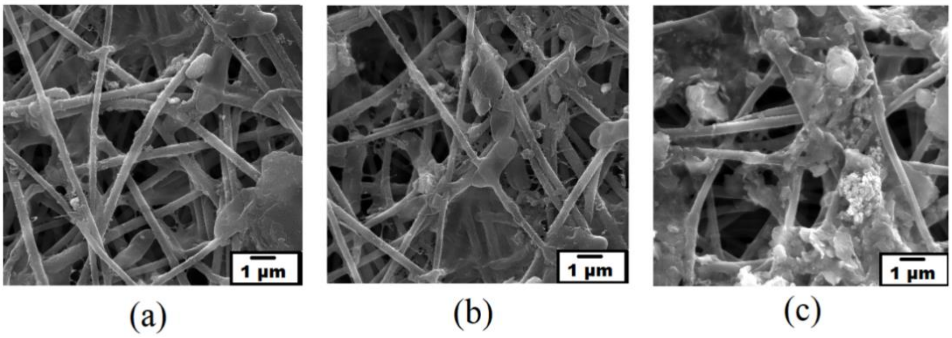

Figure 10. The SEM images of the 11% PAN/DM EPNF membranes (magnification is 10000 X) after emulsified oil removal under various transmembrane pressures (a) 1.5 psi, (b) 5 psi, and (c) 10 psi.

Fouled Membranes Cleaning

During membrane-based filtration of oily wastewater, membrane fouling is a commonly encountered problem resulting in many problems, including decreasing the permeate flux [42]. In addition, regeneration or cleaning the membranes is always an important issue [43]. In this study, to maximize flux recovery of fouled EPNF membrane, the backwashing method using warm distilled water was investigated as a cleaning strategy. The flux recovery ratio (FRR) was calculated to ensure the return from the backwash process. Fig.11 indicates a good flux recovery of the membrane after the oil separation experiments. The flux after 6 times reduced gradually to 79%. At the last backwash cycle however, the FRR increased to 92% which may indicate an increase in the distance between the fibers as a result of the many times of backwashing.

Fig.12 shows the SEM images of the fouled membrane before and after the backwashing. Although the backwashing with a warm water cleaning procedure was unable to remove all of the fouling, it was sufficient to remove most of the fouling layer from the surface of the membrane and clean the blocked pores on the nanofibers.

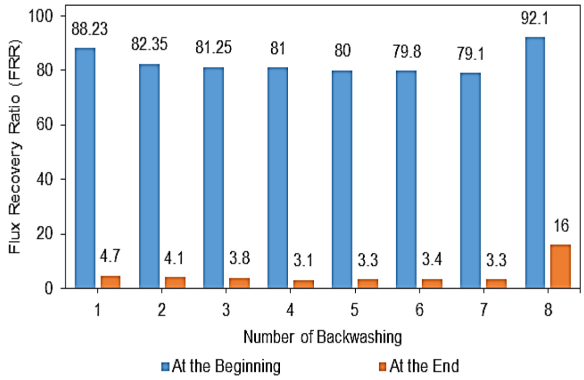

Figure 11. The backwashing cycles of 11 wt.% PAN/DMF membrane (Feed flowrate= 60 ml/min, feed oil concentration = 250 mg/L, transmembrane pressure = 1.5 psi, and temperature= 25°C)

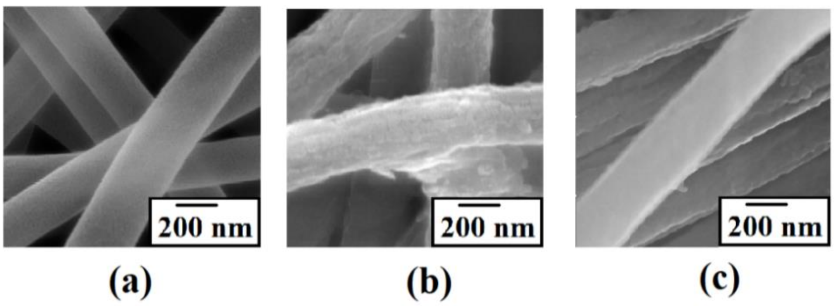

Figure 12. High resolution SEM images of the surface of 11 wt. % PAN/DMF membrane (magnification is 160000 X) (a) Clean membrane (b) Fouled membrane, and (c) Backwashed membrane

Conclusion:

This work presents the separation of emulsified oil from water using PAN-based electrospun nonwoven nanofiber membranes in a cross-flow filtration system. The used membranes have been prepared via electrospinning technique. Spinning a low concentration of PAN resulted a membrane of smaller fiber size and porosity. The membrane of the smaller fiber sizes has lower permeate flux and higher oil rejection due to its small permeability. It was found that decreasing the feed flow rate resulted in increasing the permeate flux due to the slow formation of the fouling layer on the membrane surface. At higher inlet oil concentration, the permeate flux was the smallest due to the high accumulated oil droplets on the membrane surface that clogging the pores of the membrane. Also, increasing the transmembrane pressure increases the permeate flux due to the increase in driving force across the membrane. However, oil rejection decreased because the applied pressure forced the small-sized oil droplets to pass through the pores of the membrane. The membrane could be reused using the backwashing strategy with a reasonable flux recovery rate for 6 times without damaging the membrane.

Authors' declaration:

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are mine ours. Besides, the Figures and images, which are not mine ours, have been given the permission for re-publication attached with the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee in University of Baghdad.

Authors' contributions statement:

S. M. A.: Drafting the MS, acquisition of data, and analysis. B. I. W.: Supervision, revision, and proof reading

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تصنيع اغشية الياف نانوية مغزولة كهربائيا لازالة النفط المستحلب من المياه الملوثة بالنفط

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الخلاصة:

اكتسبت أغشية الألياف النانوية المصنعة بطريقة الغزل الكهربائي اهتمامًا كبيرًا بتطبيقات ترشيح المياه. في هذا العمل، تم تصنيع وتوصيف غشاء ألياف نانوية غير منسوج بطريقة الغزل الكهربائي. بعد ذلك، تم تقييم أداء الغشاء وخصائصه المضادة للترسبات في إزالة النفط المستحلب باستخدام نظام الترشيح القطعي. تم تصنيع الأغشية باستخدام محاليل بوليميرية ذات تراكيز مختلفة من البولي أكريلونيتريل (PAN) (8,11,14%) المذاب في (DMF) N-N-Dimethylformamide ونتج عنه معدل أحجام مختلفة من الألياف ، والمسامية ، وزاوية التلامس ، والنفاذية ، وفصل النفط ، و خصائص مضادة للترسبات. أظهرت تحليلات التشكل السطحي للأغشية المصنعة قبل وبعد إزالة النفط كبر حجم الألياف وتقليل كمية الترسبات وزيادة تدفق النفاذية. من ناحية أخرى، يؤدي تقليل حجم الألياف إلى زيادة فصل النفط. لوحظ أن غشاء الألياف النانوية غير المنسوج المصنع من PAN/DMF 11% هو الغشاء الأمثل لإزالة النفط المستحلب بسبب مساميته الجيدة ونفاذه مع قابلية فصل جيد للنفط. بالإضافة إلى ذلك، تم تنظيف أغشية الألياف غير المنسوجة المستخدمة للترشيح مسبقا بواسطة تقنية الغسيل العكسي باستخدام الماء المقطر الدافئ والتي كانت فعالة في الحفاظ على نفاذية الغشاء وقابلية فضل الزيت لمدة 7 مرات. النتائج تثبت الكفاءة الجيدة لغشاء الالياف النانوية المصنعة لإزالة النفط من الماء بنسبة ازالة نفط تصل الى 92.5% ومعدل جريان 120 LMH

الكلمات المفتاحية: غسل عكسي، الغزل الكهربائي، نفط مستحلب، الياف نانوية غير منسوجة، وبولي اكريلونايتريل