Fabrication and Characterization of Nanofibers Membranes using Electrospinning Technology for Oil Removal

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Abstract:

Oily wastewater is one of the most challenging streams to deal with especially if the oil exists in emulsified form. In this study, electrospinning method was used to prepare nanofiberous polyvinylidene fluoride (PVDF) membranes and study their performance in oil removal. Graphene particles were embedded in the electrospun PVDF membrane to enhance the efficiency of the membranes. The prepared membranes were characterized using a scanning electron microscopy (SEM) to verify the graphene stabilization on the surface of the membrane homogeneously; while FTIR was used to detect the functional groups on the membrane surface. The membrane wettability was assessed by measuring the contact angle. The PVDF and PVDF / Graphene membranes efficiency was tested in separation of emulsified oil from aqueous solutions. The results showed that PVDF-Graphene nanofiber membrane exhibited better performance than the plain PVDF nanofiber membrane with average water flux of 210 and 180 $L.m^{-2}.h^{-1}$, respectively. Both membranes showed high oil rejection with more than 98%.

Keywords: Electrospinning, Fouling, Graphene, Oil removal, PVDF membrane.

Introduction:

Oil industry, refineries and power plants produced huge amount of oily wastewater every day (1). Oily wastewater is one of the most challenging streams to deal with especially if the oil exists in emulsified form. Different treatment methods have been studied for the separation of oil from water such as adsorption (2), advanced oxidation (3) and membrane process (4).

Polyvinylidene fluoride or polyvinylidene difluoride (PVDF) has been widely used in the manufacture of polymeric membranes. PVDF, a high performance plastic in several sectors, has many applications requiring the highest purity with low density of (1.78 g/cm^3). PVDF has gained considerable attention due to its outstanding properties of high chemical resistance to chemicals such as acids, bases, solvents and oxides shows the chemical structure of PVDF (5).

The membranes manufactured by this material are characterized by their high flexibility and permeability, as well as their hydrophobic nature (6). In general, fouling, the accumulation of organic and inorganic substances, is one of the most common problems in the membranes, which often lead to greatly reduced permeability and blockage of membrane pores, thus reducing the efficiency of separation processes. PVDF is considered as a standard binder material normally used in the production of composite materials. In recent years, a great deal of research has focused on the manufacturing of PVDF nanofibers for the different applications in membrane science (7). Electrospinning technique is typically used to produce nanofibers which have the benefits of high porosity and ease of preparation (8).

Electrospinning method was used in a very large extent to fabricate a selective PVDF

polymeric membrane, so by combining such membrane with a selective Nanomaterial (such as Graphene) wills possibly lead to improve the characteristics of the new fabricated membrane (9).

Graphene is derived from two words: graphite and the addition "ene", termed by Hanns-Peter Boehm and associates, who delivered and watched single-layer carbon thwarts (10). Boehm et al. presented the term Graphene in 1986 to depict single sheets of graphite. Graphene can be observed as an "unending alternant" (only six-part carbon ring) polycyclic sweet-smelling hydrocarbon. The word Graphene has to be used just when the responses, auxiliary relations or various aspects of distinct layers are talked about. Graphene is a crystalline allotrope of carbon with two dimensional properties. Carbon molecules of graphene are pressed thickly in a standard chicken wire at a nuclear scale. Graphene has a theoretical specific surface area of 2630 m^2/g, this value is a lot higher than that of activated carbon (ordinarily lower than 900 m^2/g) or of carbon nanotubes (about 1000 m^2/g) (11).

Electrospun nanofibers membranes have been used in many different applications (12,13). Recently nanofibers based membranes have been investigated in oil removal. Zaidouny et al. prepared poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) nanofibrous membranes and tested them for oil removal (14). Lou et al. incorporated graphene oxide and titanium dioxide nanoparticles into PVDF nanofibers membranes and used the obtained membranes in oil removal (15). Both researches showed promising results in terms of efficient oil removal and lower fouling propensity.

In this research, graphene was embedded in PVDF electrospun nanofibers membrane. The prepared membranes were characterized using SEM, FTIR and contact angle techniques. The performance of the obtained membranes was examined in treatment of oily wastewater using real wastewater from the southern Baghdad power station/2.

Materials and Methods:
Materials
Polyvinylidene fluoride (PVDF, FR904) powder was purchased from Shanghai Fluorine Chemical Industry Co. Ltd, China. Graphene (GE), thickness < 5 nm, drop size= (0.1–5) µm was acquired from Shanxi establishment of coal science, Chinese institute of sciences. N,N-dimethyl formamide DMF (99.8 %), Acetone, and polyvinyl pyrrolidone (PVP, K-30) were ordered from Sigma-Aldrich. Deionized water was used for cleaning purposes.

Preparation
PVP and PVDF at a ratio of (1.5 and 15) wt. % respectively, were dissolved in a solvent mixture of DMF/Acetone with ratio of 60/40. Graphene was added to the previous solution at a ratio of 0.15 wt. %. The polymeric solution was mixed for 8 hr. at 60 ^{o}C and left overnight at ambient temperature for degassing. Before use in electrospinning, the polymeric solution was agitated at a sonic bath for 30 min at room temperature. The same procedure was used to prepare the PVDF pristine nanofiber membranes except there was no graphene added to the polymeric solution.

The electrospinning process was conducted using a custom-built system that consists of a high-voltage power supply, a syringe pump, and a rotating drum. More details about the electrospinning system are illustrated in our previous publication (7). The polymeric solution was spun at a flowrate of 2 mL/h and an applied voltage of 30 kV. The electro spinning process was carried out at ambient humidity and temperature.

Characterization
The structure of the prepared membranes was examined by scanning electron microscope (JOEL model. JSM-6460LV). The membrane samples were vacuum dried and, afterwards, appended on a sample holder by conductive copper tapes. The sample was then sputtered with a conductive metal (Gold >99.8%) coating under vacuum. SEM pictures were taken at randomly chosen areas at appropriate amplifications. Functional groups of the surface of graphene powder and PVDF/Graphene membrane were characterized by Fourier-transform infrared spectroscopy (Shimadzu IR-prestige-21). The contact angle measurements of the prepared pristine PVDF and PVDF/Graphene nanofibrous membranes was conducted using a contact angle analyzer (Theta Lite TL-101) to investigate the properties of membrane surface wettability before and after the addition of graphene to the membrane matrix. The measurements were carried out using distilled water and at room temperature. In order to minimize the experimental error, the values of the contact angle were obtained for the average of five readings.

Membrane performance test
In order to study the antifouling performance, the prepared membrane was tested using real oily wastewater from the southern Baghdad power station/2. This feed was analyzed at the Ministry of Science and Technology using (HORIBA, GOCOOINP).

A dead-end filtration cell from Sterlitech (HP4750) was used to test the prepared membranes

with an active membrane area of 14.6 cm^2 as shown in Fig. 1. To get a steady flux, the obtained membranes were pre-pressured at 1.5 bar, then the flux (J) was tested at 1 bar by monitoring the volume of permeate every one hour.

The water permeate flux J in LMH (L m^{-2} h^{-1}) of the membranes was calculated from the expression below (16)

$$J = \frac{V}{A.\Delta t} \qquad 1$$

where:

V: the permeate volume (L).

A: the membrane active area (m^2), and

Δt: the filtration duration (h).

Rejection of membranes was calculated from the change in oil concentration of the feed and the permeate from the below expression (12):

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100\% \qquad 2$$

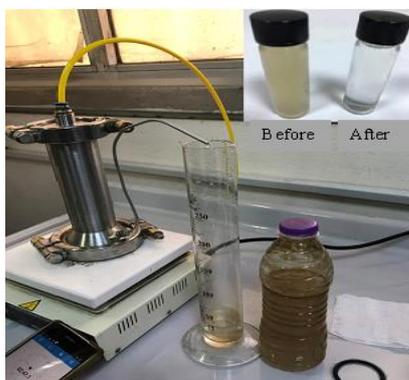where: C_p and C_f are permeate and feed concentrations (g/L) of oil, respectively.

Figure. 1. Photograph of the dead-end filtration cell.

Results and Discussions:
Morphology

Figure 2 shows the SEM images of the pristine Nano-fiber PVDF and PVDF/Graphene hybrid Nano-fiber membranes. The nanofibers are arbitrarily distributed on the aluminum sheet; the fibers' surface is very smooth.

The SEM image for the pristine Nano-fiber PVDF demonstrated that permeable microstructure of consistently stuffed microspheres at a distance across of 4-5 micron. Also, the surface of the PVDF/Graphene hybrid Nano-fiber membranes contains small microspheres that connect with each other as also reported by other researchers (13-18). Moreover, the hierarchic micro/nanoscale structures contribute to the hydrophobicity nature of the prepared membranes. In addition, the modified membrane surface contains developing microstructures estimated to be around 100 nm which improves the particular filtration performance and surface area.
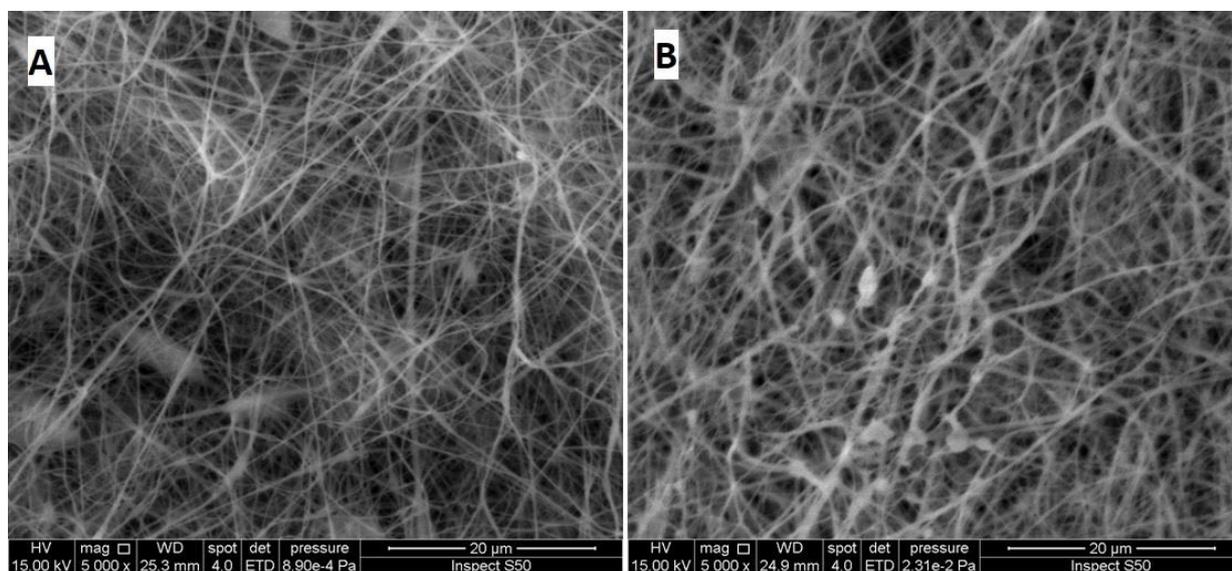

Figure. 2. SEM images of the prepared membrane (A) Pristine PVDF membrane, (B) PVDF-Graphene Nano-hybrid membrane

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FTIR Analysis of GE Powder and Nanohybrid Membrane

Figures 3 and 4 show the analysis of Graphene (GE) and hybrid Nano-fibrous membranes PVDF / Graphene using an infrared spectrometer (FT-IR), It has been observed that the peak appeared clearly visible at 1627-1630 cm^{-1}, for the stretching vibration of remaining sp2 character absorb of the C-C bond. The peak at a higher frequency in the range of 3400-3500 cm^{-1} is attributed to the -OH stretching vibration. Aldehydes have two C-H signals around 2800 and 2900 cm^{-1}. Some additional peaks appearing around 1404 and 1072 cm^{-1} are the vibrational absorption peak for the C-O-C group (19). This shows that under our test conditions, a high hydrophilic exhibition by PVDF/Graphene membrane after the process of adding graphene to the polymeric membrane matrix was obtained. Functional groups including -OH, C-C, C-O-C and -OH extension in the carboxylic group (-COOH) (20).
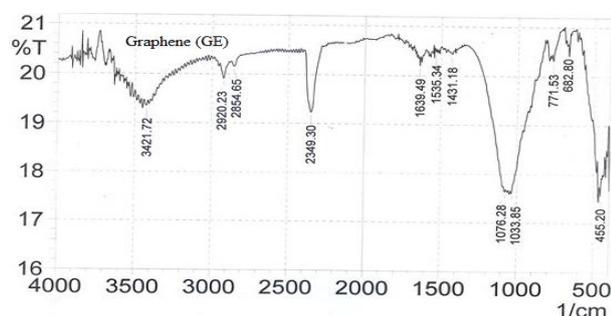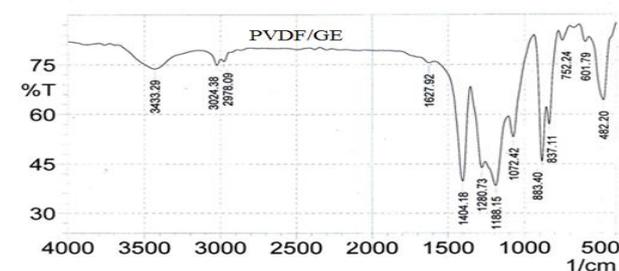
Figure. 3. FTIR spectra of Graphene (GE)

Figure 4. FTIR spectra of compsite membranes PVDF /Graphene

Contact Angle Evaluation of PVDF/Graphene Nanohybrid Membranes

Figures 5A and 5B show that the contact angles of the membrane before and after the addition of Graphene were approximately 109° and 88° respectively. The increase in hydrophilicity recommends that the addition of graphene altogether influences the surface properties and the morphology of the prepared membranes. This increase in hydrophilicity is attributed to the

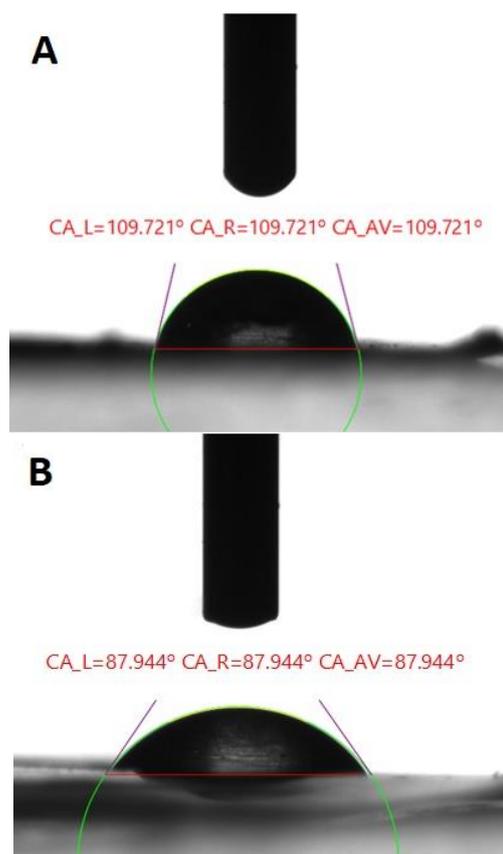carbonyl and hydroxyl functional groups as also confirmed by the findings of Wang et al. 2018 (21).

Figure 5. Contact angle results of prepared Nano-fiber membranes (A): pristine PVDF membrane, (B): PVDF-Graphene membrane

Performance Testing

The performance of the prepared membranes was tested using dead end filtration cell. PVDF electrospun nanofiber membrane exhibited an average water flux of 180 LMH as shown in Fig. 6. However, it can be seen that the PVDF-Graphene nanofiber membrane showed better efficiency in filtration of oily wastewater with average water flux of about 210 LMH. Rejection data in Fig. 7 revealed that no significant difference was noticed between both PVDF and PVDF-Graphene membranes. These results come in agreement with a previous research (22). Also, the improvement in oil antifouling properties of the PVDF-Graphene nanofiber membranes was confirmed by Ahmedi et al. 2017 (23).
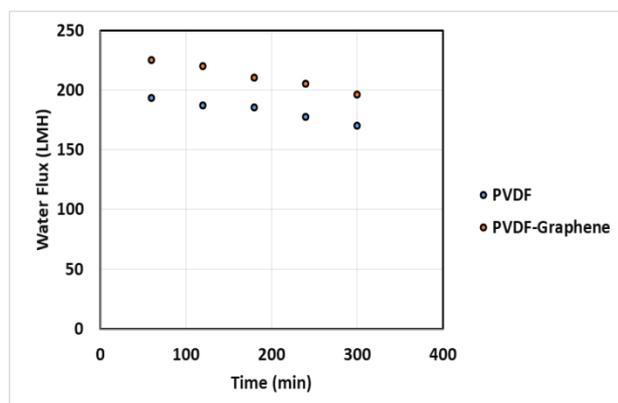
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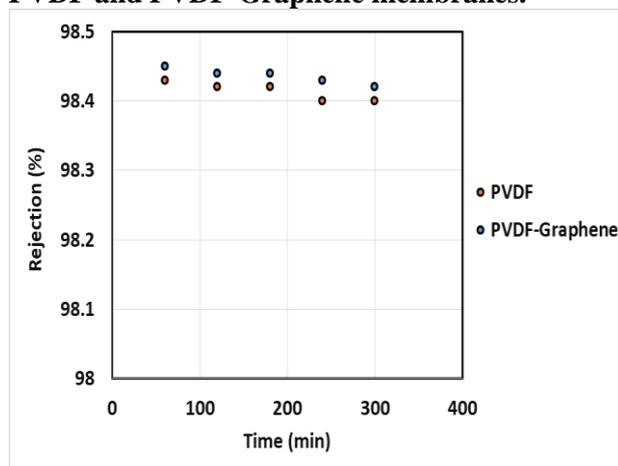**Figure 6. Water flux with time of experiment for PVDF and PVDF-Graphene membranes.**

Figure 7. Oil rejection with time of experiment for PVDF and PVDF-Graphene membranes.

Conclusions:

PVDF and PVDF-Graphene nanofiber membranes are prepared by electrospinning method. The basic structure properties and oil-water separation performance of nanofiber membranes have been examined. The results show that the composite has a lower contact angle and a higher flux for separation oil-in-water emulsion is achieved. The oil content in water of the integrated membrane is reduced from 300 mg/l to less than 5 mg/l, with a separation efficiency of more than 98 %. The results indicate that the combination of graphene (GE) with PVDF nanofiber membrane make a good candidate for oil-water emulsion separation and remarkable antifouling execution of the membrane, that is considered a significant factor for useful applications.

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 Ministry of Science and Technology.

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تحضير و تشخيص أغشية الالياف النانوية باستخدام تقنية الغزل الكهربائي لازالة الزيت

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الخلاصة:

تعتبر المياه العادمة الزيتية أحدى أكثر التدفقات التي يصعب التعامل معها خاصة إذا وجد الزيت على شكل طور مستحلب. في هذه الدراسة، تم استخدام طريقة الغزل الكهربائي لتحضير أغشية الياف نانوية رقيقة من البولي فينيل فلورايد ودراسة أدائها في إزالة الزيت. تم تضمين جسيمات الجرافين في غشاء البولي فينيل فلورايد المغزول كهربائيا لتعزيز كفاءة الأغشية. تم توصيف الأغشية المحضرة باستخدام الفحص المجهري الإلكتروني الماسح للتحقق من استقرار الجرافين على سطح الغشاء بشكل متجانس، بينما تم استخدام التحليل الطيفي بالأشعة تحت الحمراء للكشف عن المجموعات الوظيفية على سطح الغشاء. تم تقييم قابلية الغشاء و مدى كونه محب للماء عن طريق قياس زاوية التلامس. تم اختبار كفاءة غشاء البولي فينيل فلورايد / جرافين في فصل الزيت المستحلب عن المحاليل المائية مقارنة مع غشاء البولي فينيل فلورايد المصنعة بنفس الطريقة ولكن بدون اي اضافات. أظهرت النتائج أن غشاء ألياف النانو البولي فينيل فلورايد / جرافين أظهر أداء أفضل من غشاء ألياف النانو بدون إضافات بمتوسط تدفق مياه 210 و 180 لتر /م[2] ساعة على التوالي. أظهر كلا الغشاءين رفضًا عاليًا للزيت بنسبة تزيد عن 98٪.

الكلمات المفتاحية: الترسبات، الغزل الكهربائي، الكرافين، غشاء PVDF

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