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Oily Wastewater Treatment by Forward Osmosis and Nanofiltration Membranes

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Keywords:
Forward osmosis; Membrane wettability; Nanofiltration mode; Oil removal; Reuse; Water flux.

Highlights:

- *Oily wastewater treatment rejection increased using forward osmosis (FO-HTI Cartridge and Pouch) flat sheet membrane rather than nanofiltration (NF-90 and thin film NF-DL).*
- *More water and reverse salt fluxes were found with HTI cartridges than with pouch membranes for oily wastewater treatment.*
- *Higher hydrophilicity of nanofiltration membrane was found than forward osmosis.*
- *Forward osmosis technology is high efficiency and reliable in oily wastewater treatment, especially when operated for a long time.*

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Abstract: Membrane technologies have been widely applied in water purification and wastewater treatment. This work describes and demonstrates two different membrane flat sheet modes, which are forward osmosis (FO-HTI Cartridge and Pouch) and nanofiltration (NF-90 and thin film NF-DL) for the treatment of oily wastewater (OWW). These membranes' performance efficiency and reliability for reuse were investigated, especially when operated for a period under initial load conditions. Experiments were conducted in FO and NF mode to determine the water flux, the reverse salt flux, membrane wettability, and oil rejection. It was found that about 100% oil rejection could be achieved for oily treatment by FO at a pH of 6.7 to 7.3. The water flux was found to change slightly at feed initial concentration up to 30 mg L^{-1}, indicating that the basic separation properties and the structure of the FO membrane have not been were unaffected. A less stable permeate flux was obtained for oil content ranging from 30 to 300 mg L^{-1}. The average water fluxes for the FO-HTI Cartridge and Pouch membrane were ~ 8.5 and ~ 5 $L.m^{-2}$ h^{-1}, respectively, using 0.5 M NaCl as a draw solution. It was observed that this flux decreased rapidly with increasing oil-content concentration of the feed solution due to concentration polarization. The hydrophilicity and wetting behavior of NF membrane with average contact angles of a range (49.6° to 52.7°) were slightly higher hydrophilic than that of FO membranes with a range of contact angles approximately (64.82° to 67.27°).

معالجة المياه العادمة الزيتية عن طريق التنافذ الأمامي وأغشية الترشيح النانوي

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الخلاصة

تم تطبيق تقنيات الأغشية على نطاق واسع في تنقية المياه ومعالجة مياه الصرف العادمة الزيتية. يصف هذا العمل ويوضح وضعين مختلفين للأغشية و هما التناضح الأمامي (FO-HTI Cartridge and Pouch) والترشيح النانوي (NF-90 والأغشية الرقيقة NF-DL) لمعالجة مياه الصرف الصحي الزيتية (OWW) ويبحث في كفاءتها وموثوقيتها في الأداء. إعادة الاستخدام، خاصة عندما تعمل لفترة من الوقت في ظل ظروف التحميل الأولية. أجريت تجارب في وضع FO لتحديد تدفق الماء، وتدفق الملح العكسي، ورفض الزيت oil. لقد وجد أنه يمكن تحقيق رفض للزيت بنسبة ١٠٠٪ تقريبًا للمعالجة الزيتية بواسطة FO عند درجة حموضة تتراوح بين ٦,٧ إلى ٧,٣. وجد أن تدفق الماء يتغير قليلاً عند التركيز الأولي للتغذية حتى ٣٠ ملجم/ لتر، مما يشير إلى أن خصائص الفصل الأساسية وبنية الغشاء FO لم تتأثر. تم الحصول على تدفق متخلل أقل استقرارًا لمحتوى الزيت الذي يتراوح من ٣٠ إلى ٣٠٠ ملجم/ لتر. نظرًا لزيادة محتوى الزيت إلى ٢٨٢٩ ملجم/ لتر، فقد لوحظ انخفاض كبير في تدفق الماء بسبب تلوث الأغشية. تم العثور على متوسط تدفقات المياه لغشاء FO-HTI Cartridge و FO-HTI Pouch لتكون ~ ٨,٥ و ~ ٥ لتر/ م٢. س، على التوالي. تم العثور على سلوك المحبة للماء والترطيب لغشاء NF مع متوسط زوايا التلامس التي تتراوح (٤٩,٦ درجة إلى ٥٢,٧ درجة) لتكون محبة للماء أعلى قليلاً من تلك الموجودة في أغشية FO مع مجموعة من زوايا التلامس تقريبًا (٦٤,٨٢ درجة إلى ٦٧,٢٧ درجة).

الكلمات الدالة: التنافذ الأمامي، رطوبة الأغشية، المرشح النانوي، أزالة الزيوت النفطية، أعادة الأستخدام ، تدفق الماء.

1.INTRODUCTION

Produced water (PW) and oily wastewater (OWW) represent the largest volume of liquid waste from fossil oil extraction operations and refinery processes, respectively. As a result of it being a complex mixture of pollutants (soluble and non-soluble organic, suspended, and dissolved solids and other chemicals) in high concentrations, it must be treated before being released into the environment or reused for industrial and agricultural purposes. A significant amount of research has been done to develop feasible technologies for treating oily wastewater from several refinery processes, especially from condensed stripping steam, cooling water, and tank draw-off processes. These technologies include biological treatment [1, 2], adsorption and electrochemical regeneration [3, 4], dissolved air flotation (DAF) [5, 6], induced gas flotation (IGF) [7], advanced oxidation [8], and membrane [9, 10]. Membrane technologies, such as reverse osmosis (RO), ultrafiltration (UF), nanofiltration (NF), and microfiltration (MF), are progressively being utilized to treat OWW [9, 11, 12]. Conversely, forward osmosis (FO) can be considered one of the most promising membrane techniques to eliminate organic pollutants from the aqueous phase of oily wastewater [10, 13]. Because of the considerably low hydraulic pressure required, FO has several advantages in comparison with other membrane processes, such as less energy input [14], less fouling tendency in pressure-controlled cycles, easier fouling removal [15, 16], less fouling tendency in pressure-controlled cycles (e.g., RO, NF, and UF), and higher water removal [17]. FO membranes have high rejection of dissolved matters as it has similar separation characteristics to RO membranes; however, they operate at low pressure driven by the natural osmosis process. Additionally, if the draw solution used in the FO process is promptly accessible, its energy consumption can be exceptionally low [10, 18, 19]. Contact angle and wettability are some of the most common membrane surface characterizations in terms of wettability in water treatment processes. A small contact angle value (less than 90°) corresponds to high wettability or hydrophilicity, i.e., demonstrates a tendency of the water to spread and adhere to the membrane surface, whereas a large contact angle value (more than 90°) corresponds to low wettability or hydrophobicity, i.e., show the membrane surface tendency to repel water [20]. Search Science Direct citations from the past ten years by keywords 'adsorption' and oily wastewater' yielded 4287 references, by keywords 'dissolved air flotation' and 'oily wastewater' yielded 803 references, while keywords 'forwards osmosis' and 'oily wastewater' yielded only 480 references. Therefore, in addition to the reasons mentioned earlier, forward osmosis flat sheet membrane was selected as a case study in this work for treating oily wastewater. The present study examined the ability of the FO and NF process to eliminate oil droplets from OWW and the environmental impacts of oily wastewater discharge.

1.1.De-Oiling Technology

Oil and grease removal techniques and oil internal composition in end-use oily spills are shown in Table 1. This table shows performance and common treatment technologies for oil removal based on the molecule size of the eliminated oil. It can be noticed from Table 1 that membrane filter is effective with small size of oil droplets removal compared with other processes.

Table 1 The Dependence of the De-oiling Process Depend on the Size of Oil Droplets Removed [21].

De-oiling Process	Size of Molecules Removed (µm)
API Oil-Water Separator	150
Corrugated Sheet Separator	40
Coalescence Technique	5
Bed Filter	5
Spinning Oil-Water by Centrifuge Force	2
Membrane Technology	0.01
Flotation of Induced Gas (no Flocculant)	25
Flotation of induced Gas (with Flocculant)	3-5
Cyclone Separator	10-15

1.2.Forward Osmosis Applications

The forward osmosis (FO) technique is a membrane process that exploits the natural phenomenon of osmosis to transport pure water from the feed solution at low osmotic pressure to the draw solution that has a higher osmotic pressure across a semipermeable membrane [18]. The difference in the osmotic pressure drives pure water passes through the membrane from the lower osmotic pressure (low concentration) to the higher osmotic pressure (high concentration), while the specific property of the membrane retains the solutes in their particular solutions on both sides of the membrane (Fig. 1).

1.3.Membrane Fouling

Membrane fouling fundamentally affects the operation and the economics of the FO process. In water networks, the minimal fouling inclinations of FO membranes imply a decrease in their capital and operational expenses, increasing their appeal for treating water recycling and reusing applications. Normal organic foulants, such as algae, bovine serum albumin, and humic acid, are considered the most common fouling causes for FO membranes to be extensively examined [22]. Due to the low applied hydraulic pressure across the FO membrane, the process has a lower risk of irreversible fouling than pressure-driven processes, such as RO, NF, and UF [23]. The fouling tendency and the hydrophilicity of the FO membrane can be detected by measuring its contact angle [24]. This fouling could be washed off using sodium chloride with sodium dodecyl sulfate [25]. The present research specific objectives are to analyze the elements influencing the presentation of FO, e.g., reverse salt flux, water flux, rejection, contact angle, and pH influence, for oil droplets; investigate FO membrane fouling; and compare it to NF membrane. In this work, NaCl was selected as a draw solution for the FO experiment mainly due to its great solvency in water, its ability to produce a high osmotic pressure, which is pivotal for accomplishing high water flow, constancy, simplicity, ease of handing, and effectively accessible [18].

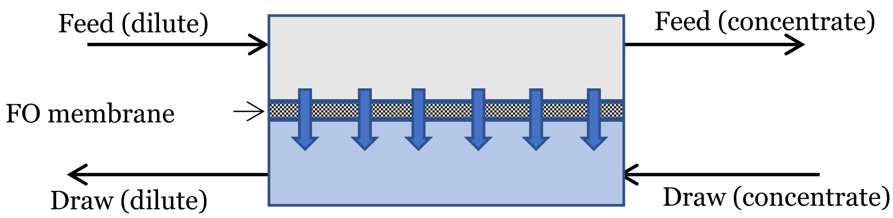


Fig. 1 Sketch a Diagram of Forward Osmosis Process.

2.MATERIALS AND METHODS

2.1.Materials

2.1.1.Membranes

Four types of flat sheet membranes were used in this study, two supplied by Hydration Technologies Inn. (HTI) and specifically used for FO applications [26]. They were labeled as HTI Pouch and Cartridge. Another two types were NF membranes supplied by Dow Filmtec and GE Osmonics (Sterlitech Corporation), namely NF-90 and Thin Film (TF) NF DL [27]. The HTI Cartridge (Fig. 2 (a)) was applied with a Hydro Well device. This membrane is an asymmetric cellulose triacetate layer with an implanted polyester screen mesh. It was supplied as flat sheet tests and was kept in vegetable-based glycerin to prevent it from drying out. Before any tests or investigations, the HTI Cartridge was soaked and flushed with distilled water for 30 minutes to eliminate any glycerin residual. The HTI Pouch membrane (Fig. 2 (b)) is a thin composite film with a slightly active layer of cellulose triacetate projected onto a nonwoven support comprising polyester fibers separately covered with polyethylene. This support layer can be welded by heat or radiofrequency, with the active layer using electromagnetic energy to bond materials and fabricate a membrane with a total thickness of 230 µm [28]. Pouch membrane was used in the Hydro Pack, Life Pack, X-Pack, and Sea Pack products available in the market from HTI. This membrane was also obtained as flat sheet tests and protected with vegetable-based glycerin. The NF90 (Fig. 3 (a)) and TF (Thin Film) NF DL (Fig. 3 (b)) membranes comprise a thin active skin layer produced using aromatic polyamide on a more porous polysulphone supporting layer.

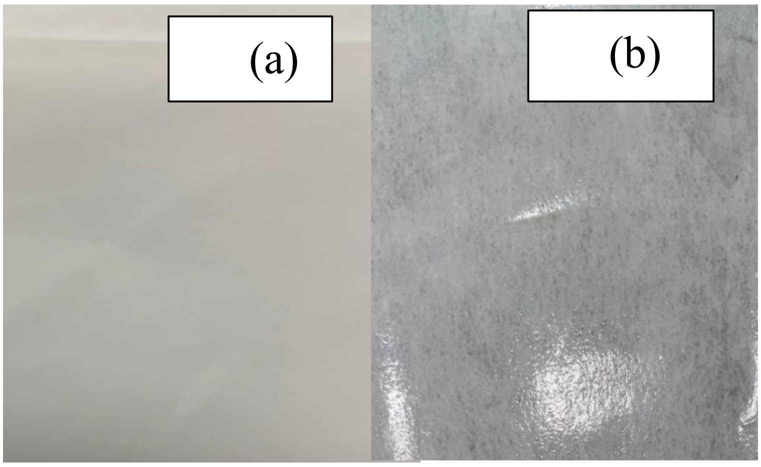


Fig. 2 Photograph Membrane for (a) HTI Cartridge and (b) HTI Pouch.

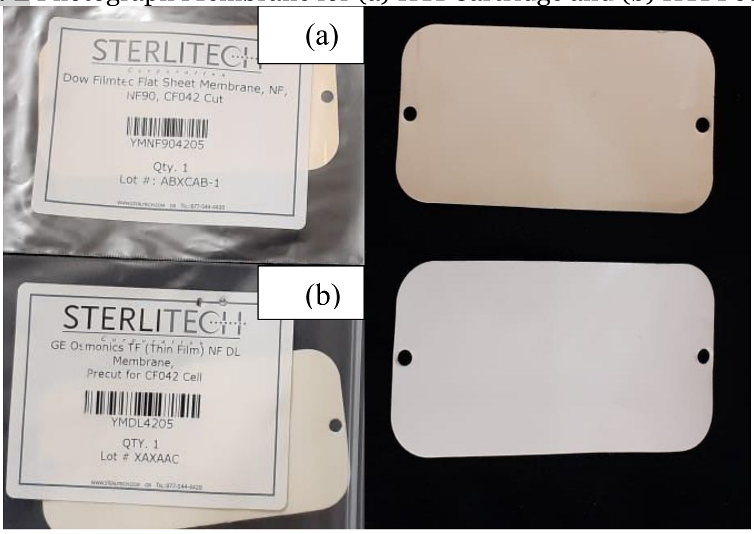


Fig. 3 Photograph Membrane for (a) NF90 and (b) TF, NF DL.

2.1.2.Membrane Cell

Laboratory-scale membrane cells for modified FO and cross-flow NF were supplied by Sterlitech Corporation CF042 membrane cells, USA. They were built to process the necessary volumes of water for the laboratory experimental investigations in a sensible time. These cells contain two identical half-cells made of acrylic plastic (Fig. 4). The membrane had a total active area of 42 cm² and a holdup volume of 17 mL.

2.2.Experimental Methodologies

In this research, several experiments were conducted to investigate the performance of FO and NF membranes at different operating conditions to treat synthetic and industrial OWW, as shown in Table 2.

For FO membranes mode using HTI Pouch and HTI Cartridge membrane, experiments were conducted at room temperature (27±2 °C), 0.5 M NaCl of draw solution, and a cross-flow velocity of 10-18 cm.s^{-1}. The same was done for RO membranes mode (HTI and NF-90 and Thin Film TF, NF DL).

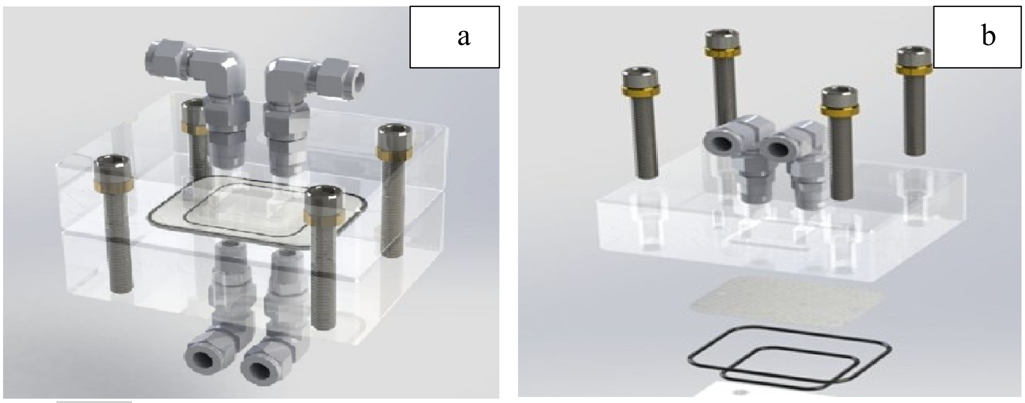


Fig. 4 A Membrane Cells for (a) Forward Osmosis CF042 (b) Nano filter [29].

Table 2 Experiments Conditions for FO and NF Mode to Treat Synthetic and Industrial Oily Wastewater.

Exp. No.	Process Mode	Solution Status	Feed Solution			Membrane Type
			NaCl (mg L^{-1})	Oil Content (mg L^{-1})	pH	
1	FO	Synthetic	30	0	7	HTI Cartridge and Pouch
2	FO	Synthetic	30	30	7 and 4	HTI Cartridge and Pouch
3	FO	Synthetic	30	300	7	HTI Cartridge
4	FO	Industrial*	470	2829	6.8-7.3	HTI Cartridge and Pouch
5	NF	Industrial*	470	2829	(6.8-7.3) and 4	(NF-90 & NF TF DL)

** COD=1036 mg L^{-1}, TSS=310 mg L^{-1}*

2.2.1.FO Experiment

The experimental setup of the FO process for removing oil from synthetic oily water and industrial oily wastewater is illustrated in Fig. 5. The active layer of the membrane was fixed inside the cell facing the feeding solution, while the support layer faced the draw solution. The synthetic oily water was prepared by mixing a certain amount of motor oil as a dispersed phase with a given volume of distilled water as a continuous phase. The mixture was taken in a conical flask and kept in a sonicator water bath (POWER SONIC410, Korea) for about 8 hours at a temperature of 27±2 °C. Industrial wastewater was provided by a power station south of Baghdad carbonated and tested under the FO process. Two variable speed liquid pumps (Diaphragm-pump, KNF Flodos AG, Wassermatte, Switzerland) were switched on to recirculate the draw and feed solutions at a flow rate ranging from 0.2 to 1.3 L min^{-1} with permissible pressure ranging from 1 to 6 bar. To determine the permeate flux, the draw solution reservoir (0.5 M NaCl) was placed on a digital scale (Mettler IUJIMNG, China). To keep a constant concentration of the draw solution during the experiment, a high salt concentration of 6 M NaCl was prepared and placed on a hot-plate magnetic stirrer (Fine TECH-SHPM-10, Korea) to compensate for any decrease in the amount of salt in the draw solution that transfers between the two reservoirs. Water flux through the FO membrane was calculated based on the change weight for the drain salt for each experiment run, as the permeate water transfer out of the semipermeable membrane from the feed side to the draw side. Consequently, the mass of the feed solution reduced while that of the draw solution expanded, so this flux (J_W) can be determined as follows [30]:

$$J_W = \frac{\Delta W}{A \times \Delta t} \quad (1)$$

where A is the surface area of the membrane (m^2), ΔW is the expansion in mass of the draw solution (kg), and Δt is the differentiation time (hr.). The conductivity of the draw and feed solutions was measured continuously with a conductivity meter (WTW, Cond. 7110, Germany). Different concentrations of sodium chloride were prepared at the same temperature and plotted against its conductivity, as shown in Fig. 6. A linear function for the conductivity meter of sodium chloride was discovered with its concentration. In view of this calibration data, the following relationship was obtained:

$$K = 0.0015\,C + 0.0766 \quad (2)$$

where K and C are the solution conductivity (mS cm^{-1}) and tracer concentration (mg L^{-1}), respectively. Hence, this concentration could be determined directly from the conductivity solution estimated. The reverse salt flux (J_S), which is the other way of water flux, is given by [30, 31]:

$$J_S = \frac{\Delta(C.V)}{A \times \Delta t} \quad (3)$$

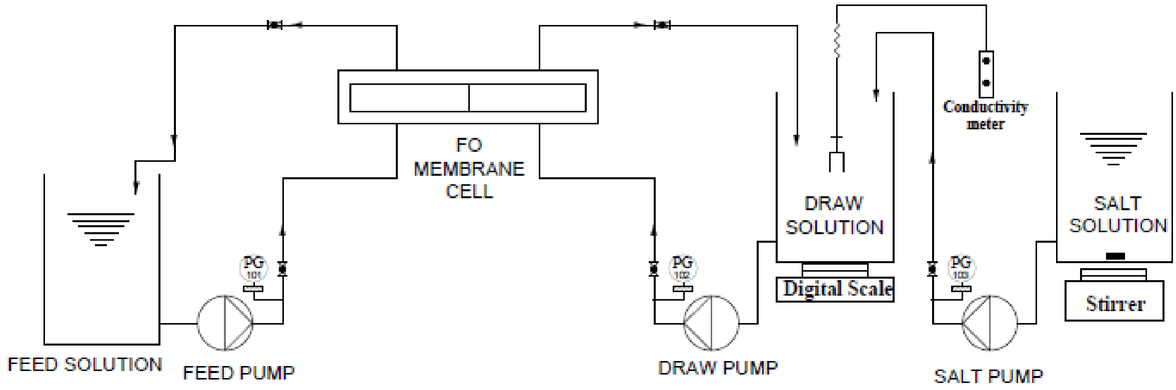
where ΔV is the change in volume (L), ΔC is the change in salt concentration of the feed solution over the time interval (g/L), A is the membrane surface area (m^2), and Δt is the differentiation time (hr.). Equations (4) and (5) can be applied to determine the salt rejection by the FO membrane. $C_{s(t)}$ is the real concentration of the objective solute, salt in this study, obtained by considering the dilution using a mass balance:

$$C_{s(t)} = \frac{C_{ds(t)}V_{ds(t)} - C_{ds(t-1)}V_{ds(t-1)}}{V_{w(t)}} \quad (4)$$

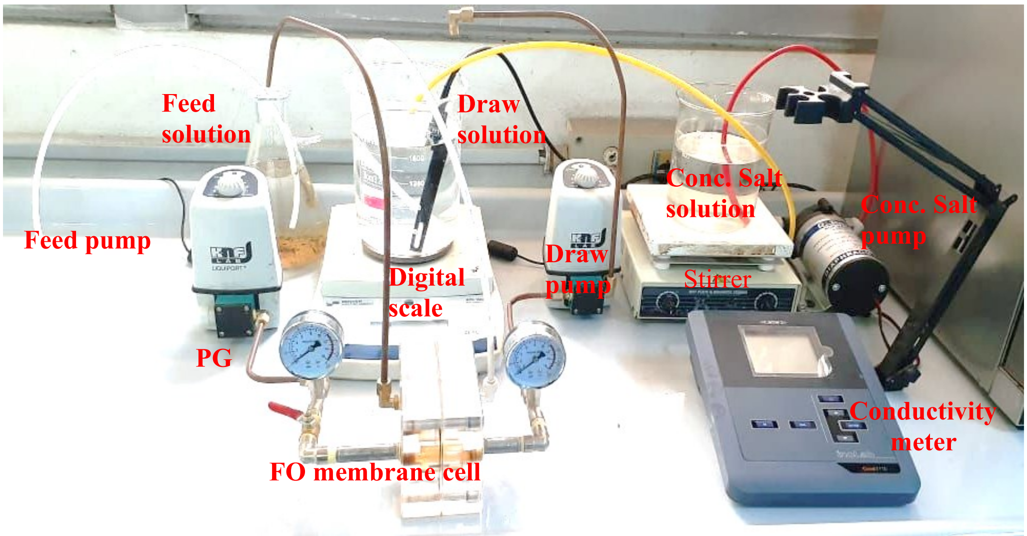
where $V_{ds(t)}$ and $V_{ds(t-1)}$ are the volume of the draw solution at times t and $(t-1)$, respectively. $V_{w(t)}$ is the permeate volume of water from the feed solution to the draw solution at time t. $C_{ds(t)}$ and $C_{ds(t-1)}$ are the measured concentration of the objective solute in the draw solution at times t and $(t-1)$, respectively. Consequently, the solute rejection by the FO membrane is determined using the real permeate concentration, yielding:

$$R_{FO} = \left[1 - \frac{C_{s(t)}}{C_{f(t)}}\right] \times 100\% \quad (5)$$

where $C_{f(t)}$ is the objective solute concentration in the feed solution at time t.



(a)



(b)

Fig. 5 (a) Schematic Diagram and (b) Annotated Photograph of Oily Synthetic Water and Industrial Wastewater Treatment by Forward Osmosis Membrane.

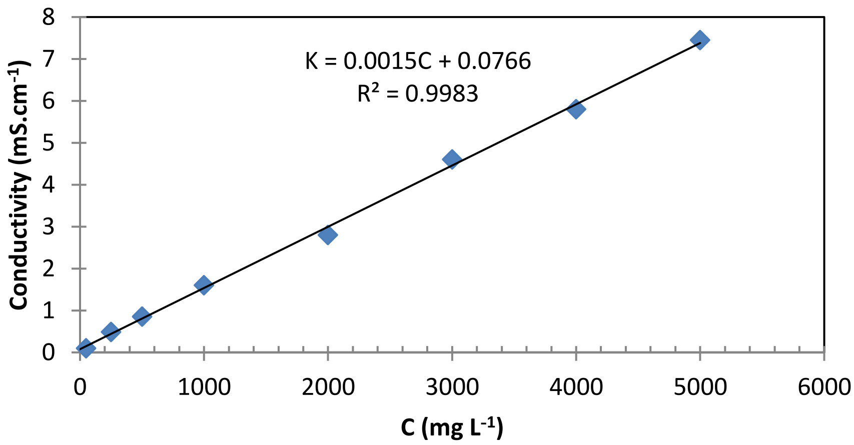


Fig. 6 Calibration Curve for Ionic Conductivity at a Range of NaCl Concentrations.

2.2.2.NF Experiment

The experimental setup used for the NF cross-flow process is shown in Fig. 7. To start, the NF membrane was compressed to about 6 bar using deionized water for an hour, and industrial wastewater (oil content about 2829 mg L^{-1}) was pretreatment using an MF (8 µm) at transmembrane pressure 12 – 30 kPa followed by UF (100 kD molecular weight cut-off) at 0.2 MPa. The permeate solution, obtained from UF, was diluted to 1000 mg L^{-1} and then fed to the NF membrane (above 200 Dalton) at 6-7 bar. The same permeate was also fed to the HTI-FO membrane at the same operating condition. Rejection by the NF membrane can be determined by the following equation [30].

$$R_{NF} = \left[1 - \frac{C_p}{C_F}\right] \times 100\% \qquad (6)$$

where R_{NF} is solute rejection percent, C_p is the permeate concentration of oil, and C_f is the feed concentration of oil.

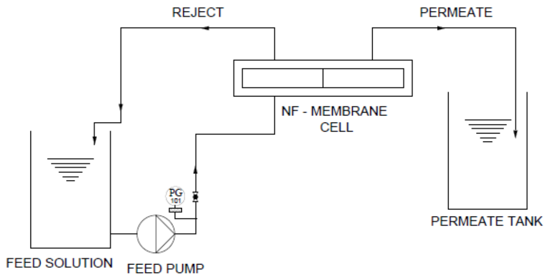


Fig. 7 Schematic Diagram of Industrial Power Station Wastewater Treatment by NF Cross-Flow Membrane.

The hydrophilicity of FO and NF membranes' active surfaces was evaluated by measuring the water contact angle using a contact angle analyzer (Theta Life, TL-101, Thailand). These measurements were achieved at three random positions for each membrane test, and the average values were reported in this examination.

3.RESULTS AND DISCUSSION

3.1.Contact Angles

The water contact angles for four types of virgin membranes were measured to examine their surface hydrophilicity, as shown in Fig. 8. The experimental error was considered by reporting the average contact angle values, as shown in Table 3. It can be observed from Table 3 that all tested membranes were hydrophilic due to their contact angles of less than 90°. The hydrophilicity of NF with average contact angles of a range (49.6° to 52.7°) were slightly higher than that of FO membranes with a range of contact angles approximately (64.82° to 67.27°). In terms of hydrophilicity, similar results were obtained to be higher for NF (32°) than FO (74.6°) by Tow et. al. [32].

3.2.Water Flux

HTI Cartridge and Pouch flat sheet membranes have been tested under the FO process (the active side of the membrane faces the feed solution whilst the support layer faces the draw solution). The flux flow of water was determined based on the amount of water that permeates through a semipermeable membrane from the feeding solution to the draw solution using Eq. (1). It can be noticed from Fig. 9 that the water flux flows for oil-free water was higher than oily synthetic solutions (30 mg L^{-1}) for the same membrane mode. Also, it can be seen from this figure that the average water flux for HTI Cartridge was (~ 8.5 L m^{-2} h^{-1}) higher than Pouch (~ 5 L m^{-2} h^{-1}) under the same operating conditions due to the difference in the internal structure and polymeric composition of the membranes, made from cellulose triacetate. This difference in membrane characterization caused differences in physio-chemical properties and membrane performance, which are also expected to lead to differences in their intrinsic separation properties [33]. In general, the flux flow for oily synthetic flow at 30 mg.L^{-1} initial oil concentration slightly decreased up to 25 hr. running, indicating that the essential separation properties and structure of FO membranes mode were unaffected. To study the influence of oil content on the performance of FO mode using HTI Cartridge membrane for oily synthetic water (300 mg L^{-1}) and industrial wastewater/ Baghdad power gas station (2829 mg L^{-1}) treatment, flux water flow was conducted at an inlet salt concentration of 30 mg L^{-1}, as shown in Fig. 10. The results showed that as the oil content increased from 300 to 2829 mg.L^{-1}, synthesis, and industrial local wastewater, respectively, the water flux decreased from 3.1 to 1.9 L m^{-2} h^{-1} after 40 hr. running. This decrease in the flux is due to the formed accumulated layer of oil droplets on the membrane surface and causes a high resistance for permeating oil-free water across the FO membrane. The fouling was significantly affected, and the membrane was severely fouled after 40 hr. running for industrial wastewater treatment. A solution of 1000 mg. L^{-1} sodium hydroxide and 300 mg.L^{-1} of sodium dodecyl sulfate could be used efficiently to wash off FO fouling. The same results have been observed for OWW treatment across FO membrane at different synthesis oil feed concentrations (100 and 1000 mg.L^{-1}) by Makki and Zghair [34] and (300 and 3000 mg.L^{-1}) by Abousnina [33].

Table 3 Average Water Contact Angles of Virgin Membranes.

Process Mode	Membrane type	Average contact angle (°)
FO	HTI Cartridge	64.826
	HTI Pouch	67.272
NF	NF-90	52.737
	TF (Thin Film) NF DK	49.6

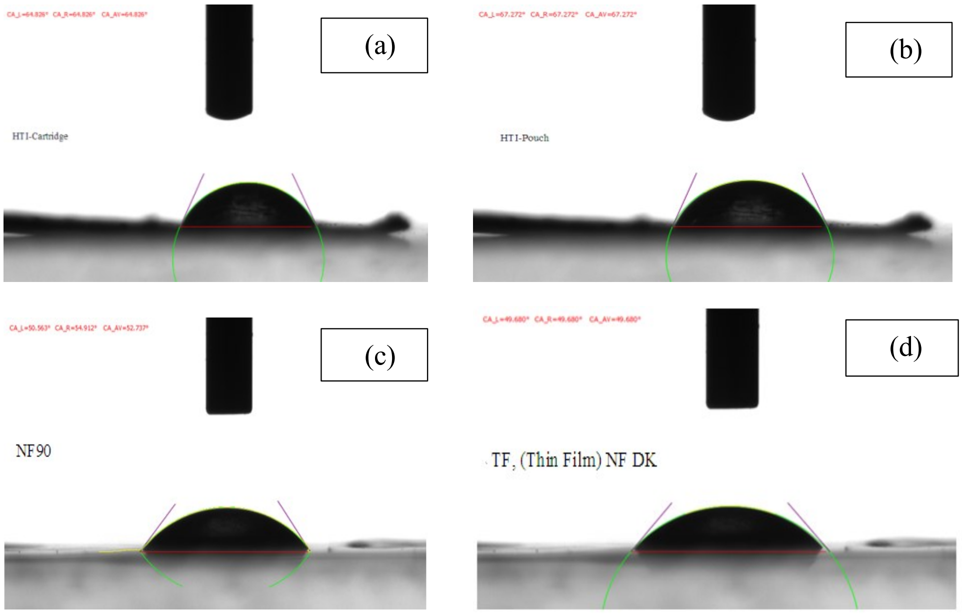


Fig. 8 Water Contact Angle Results on Different Virgin Membranes Surfaces (FO and NF mode): (a) and (b) for FO mode, and (c) and (d) for NF mode.

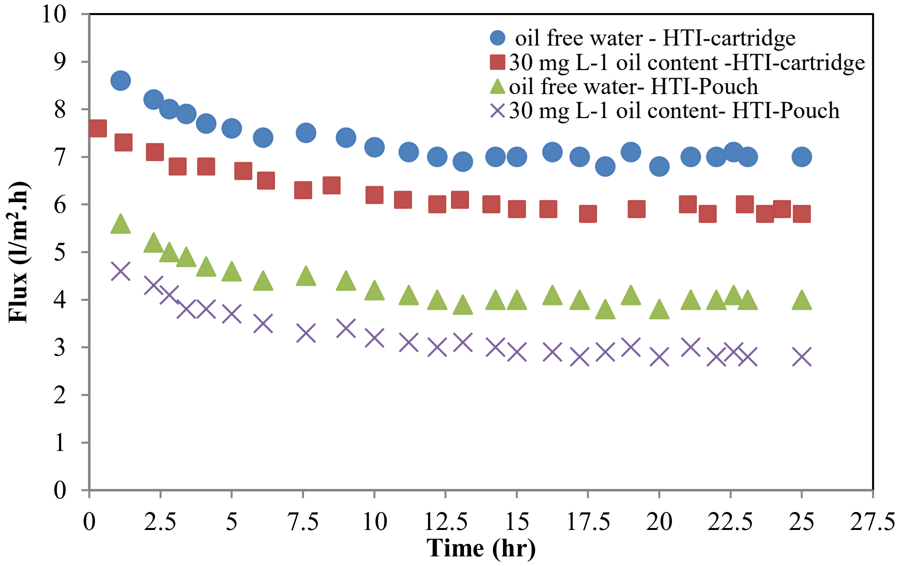


Fig. 9 Flux Flow for FO Mode Treatment using HTI Cartridge and Pouch Membrane for Oil Free Water and Oily Water at 30 mg L^{-1} Initial Concentration of Oil and 0.5 M NaCl in the Feed Solution.

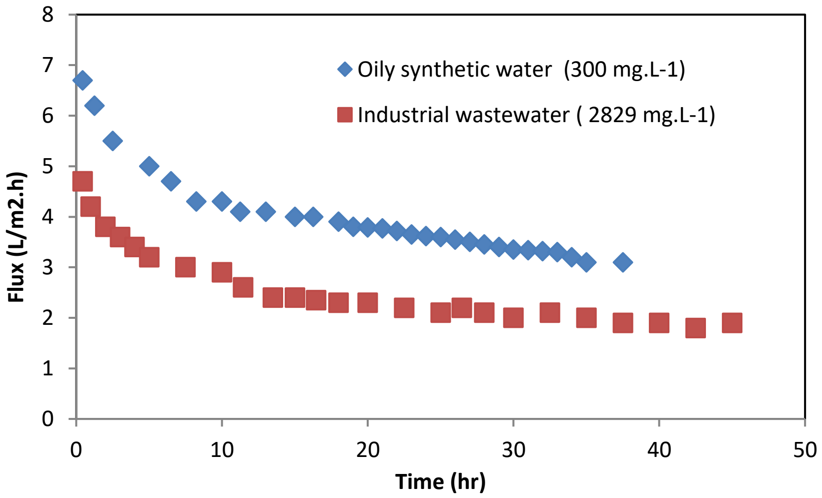


Fig. 10 Water Flux Flow for FO Mode Treatment using HTI Cartridge Membrane for 300 and 2829 mg L^{-1} Oil Content for Oily Synthetic Water and Industrial Wastewater, respectively at 30 mg L^{-1} an Inlet Concentration of 0.5 M NaCl in the Feed Solution.

3.3.Reverse Salt Flux

Mass transport of specific solutes in the FO interaction can be bidirectional, and reverse salt flux (RSF) occurs with a non-idealized membrane [35]. The calibration curve of the sodium chloride solution (Fig. 6) was used to determine this RSF by observing the conductivity increase in the feeding solution. It can be assumed that the significant part of dropping the osmotic difference between the feeding and drawing solutions was the flow of reverse salt by diffusion. In this work, the experiment was run at a feed containing 30 mg L^{-1} of each oily synthetic water and sodium chloride with 0.5 M NaCl of draw solution under different pH operating conditions. The diffused reverse salt flow (*Js*) was estimated and depended on the concentration and the volume of the feed solution at the initial and final condition of the FO experiments (Eq. (3)). Figure 11 shows the reverse sodium chloride flow achieved with the Cartridge and the Pouch membranes under different pH feed solutions, pH-X, where X corresponds to the quantitative measure of acidity with the kind of FO membrane, as shown in Table 4. This reverse was observed to be considerably higher with Cartridge than Pouch membrane at the same flow rate due to differences in membrane characterization, as previously discussed in the water flux flow section. It was also noticed from Fig. 11 that the pH effect of feed solution on RSF by both these membranes was insignificantly influenced [33].

Table 4 Quantitative Measure of Acidity for FO Membrane.

Initial Feed Solution pH	pH HTI Cartridge	pH HTI Pouch
pH=(6.8-7.3) (unadjusted)	pH-A	pH-C
pH= 4 (adjusted)	pH-B	pH-D

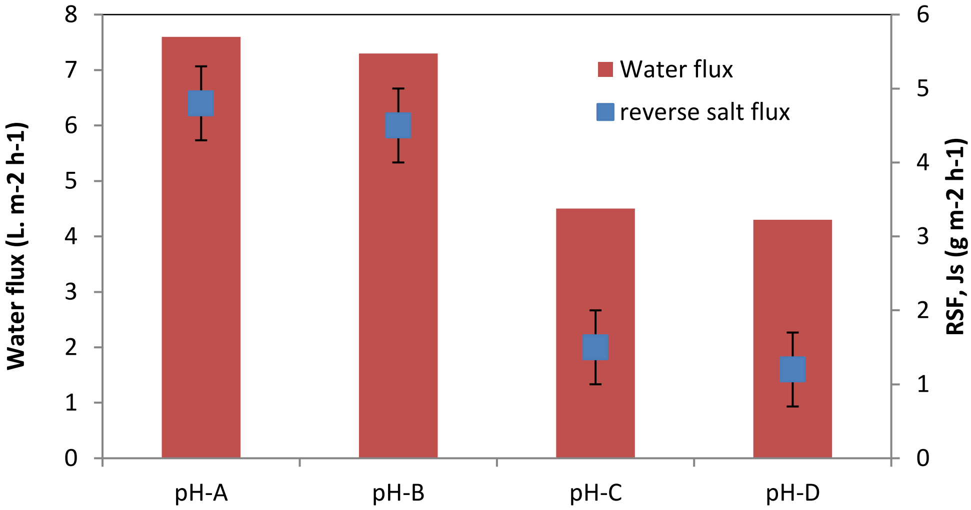


Fig. 11 Effect of pH Feed Solution on Water Flux and Reverse Salt Flux Flow of 0.5 M NaCl using HTI-Cartridge and Pouch Membranes for FO Process.

3.4.Membrane Rejection

The experiments of membrane oil rejection for FO (using Cartridge and Pouch membranes) and NF (using NF90, DL membranes) modes are plotted in Figs. 12 and 13, respectively. These experiments were conducted at 6-10 mg L^{-1} initial oil concentration in the feed solution (after pretreatment with micro-filter MF followed by ultra-filter UF as described above) and pH ranging from 6.8 to 7.3 using 0.5 M NaCl as a draw solution. The variable cross-low velocities were (10 -18) and 21.6 cm s^{-1} for FO and NF mode, respectively. Forward osmosis of the industrial oil rejection process was run for four periods, each 5 hours, as shown in Fig. 12. The results showed that a higher oil rejection was obtained for the Pouch than the Cartridge FO process. It is clearly observed that the oil rejection was above 90% under the pre-fouling process, indicating that this process had a lower fouling tendency. The performance of four types of membranes for industrial oil rejection was compared with the results of NF experiments operating at a pH of 4.0 and at un-adjusted pH, as shown in Fig. 13. It can be seen that much more significant improvement occurred in oil rejection by NF (NF-90 and TF, NF DL) membrane than the others. It is also evident from Fig. 13 that oil rejection slightly increased from 85% to 92% when pH increased from 4 to unadjusted for the HTI-Pouch membrane, as an example, due to the that the negative charge density of the membrane surface increased when pH increased, leading this membrane to an enhanced electrostatic interaction with charged solute and then to be more hydrophilic [33]. In general, the comparison of FO and NF for oil-water separation with those demonstrated by Li [25] is shown in Table 5. It can be shown that the FO membrane had only one significant impact on the performance of the oil separation process, called concentration polarization. This phenomenon occurs when selective transport across a membrane increases or decreases the concentration of a particular component at an interface near the membrane surface, leading to reduce the driving force for mass transfer across the FO membrane and following the efficiency decrease of the separation process. The lower water flux for FO was in this study than those studied by Li and Orecki, as shown in Table 5. However, if this flux normalized with oil-content concentration, it was found that the oil mass removal rate per unit area in this work was higher than that achieved by Li and Orecki [25, 36]. Also it can be observed that this mass removal rate for NF was higher in this study than achieved by Orecki and Al-Alawy [36, 37]. In terms of reverse salt flux, Table 5 shows that lower RSF was achieved in this work than those determined by Li [25], meaning a low membrane fouling occurred in this study.

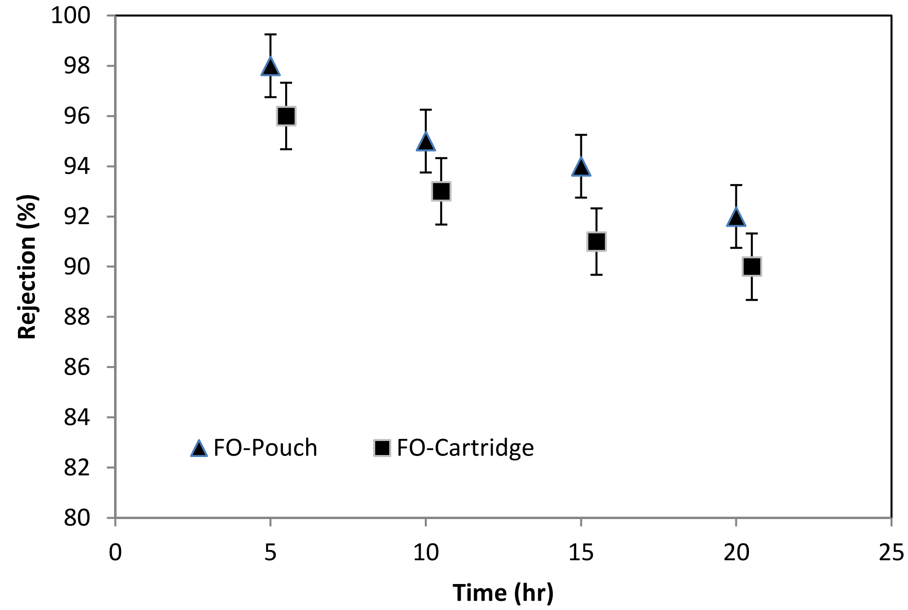


Fig. 12 Industrial Oil Rejections as Function of Time for FO Mode at Unadjusted pH of Feed Solution.

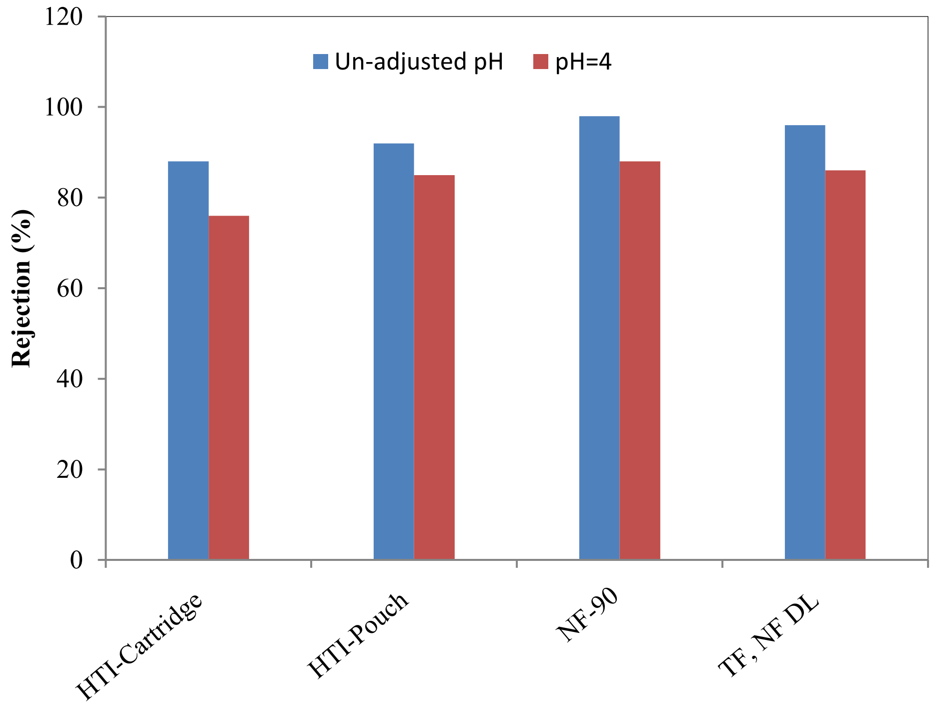


Fig.13 NF and FO Mode for Industrial Oil Rejection at pH 4 and Unadjusted of Feed Solution for Four Membrane Types.

Table 5 Comparison of Different Membrane Modes for Oily Wastewater Treatment.

Membrane mode	Feed solution concentration mg.L^{-1}	Water flux L.m^{-2}.h^{-1}	Reverse salt flux g m^{-2} h^{-1}	Oil mass removal rate per unit area (mg/m^2. h)	% Oil Rejection	Drawbacks	Ref.
FO (HTI Cartridge and Pouch) Flat sheet (as mentioned in Section 2.1.1)	2829 industrial OWW	5	4.5 HTI-Pouch 4.8 HTI-Cartridge at 0.5 M NaCl as a draw solution	14145	~ 100	Concentration polarization	This work
FO (TFC) Hollow fiber membranes synthesized on sulfonated polyphenylene sulfone	500 synthesis OWW	10.4	5.41±1.38 at 0.5 M NaCl as a draw solution	5200	80	Concentration polarization	[25]
NF (NF90 and NF DL) flat sheet(as mention in section 2.1.1)	2829 industrial OWW	8	-	22632	100	High energy consumption in comparison with FO.	This work
NF(NFAFC30) tubular module	112 synthesis OWW	10	-	1120	100	High energy consumption	[36]
NF (polyamide TFC)	10 synthesis OWW	29.5	-	295	89	High energy consumption	[37]

4.CONCLUSIONS

In the present work, two commercial flat sheet membranes, i.e., FO and NF, treatment processes could reject more than 90% of oil from a feed solution containing 300 and 2829 mg.L^{-1} of oily synthetic water and industrial wastewater, respectively. This rejection achieved using the FO process was slightly better than that achieved using the NF process under the same operating conditions.

The results are expressed in terms of reverse salt flux, water flux, oil rejection, contact angle, and pH effect. In terms of water flux, the experimental results of FO indicated that the Cartridge membrane performance was superior to that of the Pouch membrane. However, the rejection of oil by each membrane was slightly better for the Punch membrane than the Cartridge membrane. It also found that the water and reverse salt flux for un-adjusted pH were higher than those for pH of 4.0. It can be concluded that the treatment of OWW in two stages using a combination of MF and UF membranes in the first stage and NF membrane in the second phase showed better removal efficiency. In this case, the membrane fouling due to the presence of oil droplets did not occur. Fouling experiments were conducted, and it was noticed that with increasing oil-content feed concentration, water flux decreased rapidly. More oil mass removal rate per unit area and less fouling were found with FO and NF compared with those achieved by previous studied. However, the FO process remains preferable because it is economical and requires lower operational pressure than the NF process. Contact angle measurements found that all membranes were hydrophilic, and the hydrophilicity of the NF system was slightly higher than the FO system.

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