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Hybrid TiO_2/UV/PVDF ultrafiltration membrane for raw canola oil wastewater treatment

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ABSTRACT

Polymeric ultrafiltration (UF) membranes have been applied to treat raw canola oil wastewater (COW); however, membrane fouling was unavoidable. To solve this issue, this study examined sole UF, hybrid Fenton/UV/UF and TiO_2/UV/UF to investigate membrane fouling, which has the effect of decreasing membrane filtration performance. The experimental results showed that, of three methods, the hybrid TiO_2/UV-UF system significantly increased the permeation flux value, with chemical oxygen demand (COD) and oil removal efficiencies increased by 82 and 86%, respectively. This hybrid system was further explored under different transmembrane pressures (TMP) – 1, 2, and 3 bar – and cross flow velocities (CFV) – 400, 500, and 600 mL/min. Hermia's model was used to analyse the fouling mechanism; no model acted as the main mode, with nearly similar values of cake formation and other models regardless of the applied conditions. Membrane surface morphology and foulant composition were explored using scanning electron microscopy and energy dispersive spectrometry (SEM-EDS), demonstrating significantly different morphologies and chemical components between new and fouled membranes due to the trapped oil and other micro-pollutants on the membrane surface and pores. The effect of using different cleaning agents on membrane cleaning was also evaluated by measuring the flux recovery ratio (FRR). This study found that a combined chemical cleaning agent (0.1 M NaOH/0.1 M HNO_3) at elevated temperature and higher velocity resulted in a higher FRR value, by at least 97%. In conclusion, both the hybrid TiO_2/UV-UF method and combined chemical cleaning can be applied to treat raw COW to reduce fouling and lengthen membrane life.

Keywords: UF membrane; Hybrid; Fouling; Hermia's model; Membrane cleaning

1. Introduction

Discharging oily wastewater into the environment without proper treatment will lead to effects harmful to human health. For instance, the presence of various pollutants in industrial oily wastewaters, such as oil, organic and inorganic compounds, make a stream toxic, leading to carcinogenic diseases after long-term exposure or higher doses [1]. In order to mitigate the negative impacts of disposed oily wastewater, it is highly desirable to treat streams to prevent fatal environmental issues and allow water re-use. Various methods have been implemented to remove pollutants and improve the quality of oily wastewater before disposal in the environment [2].

Recently, advanced oxidation processes (AOPs) have been a preferred alternative treatment as they offer excellent capability of mineralising organic compounds [3]. The main power of this chemical treatment comes from producing hydroxyl radicals (•OH) which can destroy organic contaminants and mineralise them into CO_2 and H_2O. The

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AOPs can be classified into two types, homogeneous and heterogeneous processes. The most common homogeneous process, called Fenton and photo-Fenton, is the reaction between iron ions and H_2O_2 in the presence of light [4]. In heterogeneous processes, the photo catalytic degradation processes are supported by semiconductors, such as TiO_2, ZnO, ZnS, MgO_3, CeO_2, ZrO_2, SnO_2, WO_3, α-FeO_3, and CdS [5]. There remain some challenges when applying AOPs as a sole wastewater treatment, such as the high cost of chemicals, an upper limit of feed concentration and intermediate generations, that need to be addressed [6].

The use of membrane technology to treat oily wastewater has become more widespread due to superior permeate quality, simple equipment and its high rate of removal of organic and inorganic residues [2,7]. Nevertheless, the performance of membranes in treating oily wastewater can decrease due to membrane fouling which leads to permeate flux reduction, higher operation costs and a shorter membrane lifespan. These issues occur when pollutant particles deposit onto the membrane surface or into membrane pores. In general, membrane fouling can be divided into two types: reversible and irreversible fouling. Reversible fouling can be recovered by chemical cleaning or physical cleaning (e.g., water rinsing), while irreversible fouling can permanently damage the membrane surface and diminish its ability to filter [8].

In order to reduce membrane fouling, hybrid technologies can be applied. Wastewater should be pre-treated before it passes through the membrane system. Literature has shown that the application of hybrid treatment methods can lengthen membrane life in oily wastewater treatment by reducing fouling phenomena. Hybrid ultrafiltration (UF) – nanofiltration (NF) membrane technology used to treat oily restaurant wastewater achieved more than 90% chemical oxygen demand (COD) and turbidity removal [9]. Another study found that combined nanoporous membrane – powdered activated carbon (NPM-PAC) prolonged NPM usage and resulted in a significant reduction in both COD and total organic carbon (TOC) when compared to the sole NPM system [10]. A hybrid photo catalytic – polvvinylidenediflouride (PVDF) membrane implemented for synthetic oily wastewater degradation showed that TOC and oil removal were greater than if using a neat PVDF membrane [11]. Further studies applied a Fenton-like reaction, flocculation-sedimentation, and filtration as pre-treatment processes for oily wastewater prior to the NF membrane, reporting that these hybrid processes significantly reduced membrane fouling and enhanced the permeate flux [12].

Although increasing research time has been devoted to membrane filtration for wastewater purification, membrane filtration as a treatment process has not been evaluated for all types of wastewaters and membranes; for instance, testing the treatment of raw canola oil wastewater (COW) using a polymeric UF membrane. Very few studies focused on the comparison and evaluation of hybrid homogeneous and heterogeneous AOPs -UF membranes as an efficient and effective method for raw oily wastewater treatment.

The current study was conducted to investigate the efficiency of sole UF, hybrid Fenton/UV-UF and TiO_2/UV-UF in treating raw COW with respect to permeation flux decline and permeate quality (COD and oil removal). The most effective technique was further explored for the effect of different TMP and CFV on permeation flux and the effect of cleaning agents on flux recovery. In addition, the membrane fouling mechanism, membrane morphology and foulant components were also specifically observed using Hermia's model, scanning electron microscopy and energy dispersive spectrometry (SEM-EDS) analysis, respectively.

2. Materials and methods

2.1. Membrane material

Tubular polymeric UF membrane type FP 100, produced by Xylem Water, UK, is made of PVDF [13]. This membrane was used in all experiments and has a molecular weight cut-off of 100 kDa and membrane surface area of 0.024 m^2.

2.2. Chemicals and analytical methods

A HACH DRB200 reactor, DR890 colorimeter and HACH COD reagent vials, HR 0–1500 mg/L, were purchased from Rowe scientific, Australia and used to measure COD concentration based on the procedure handbook provided (standard *method* 5220 D) [9]. TOC concentration (mg/L) was analysed using a Shimadzu TOC-V CPH analyser. Oil concentration analysis was performed using the Butchi Rotavapor R-210 series based on the gravimetric method [14]. Total dissolved solids (TDS) were measured using a TDS meter, Hanna, USA. Na_2SO_4 and n-Hexane for oil analysis and NaOH pellets and H_2SO_4 for pH adjustment, were purchased from Sigma–Aldrich, Australia. H_2O_2, an oxidising agent and $((NH_4)_2Fe(SO_4)_2\cdot 6H_2O)$, an iron standard solution, were purchased from Sigma Aldrich and Rowe Scientific, Australia. $FeSO_4\cdot 7H_2O$ was purchased from Ajax Finechem, Australia. Dry ice/dried carbon used for oil analysis was purchased from BOC, Australia. Ultrapure water from Ibis Technology, Australia, was used in all experiments.

2.3. Feed sample

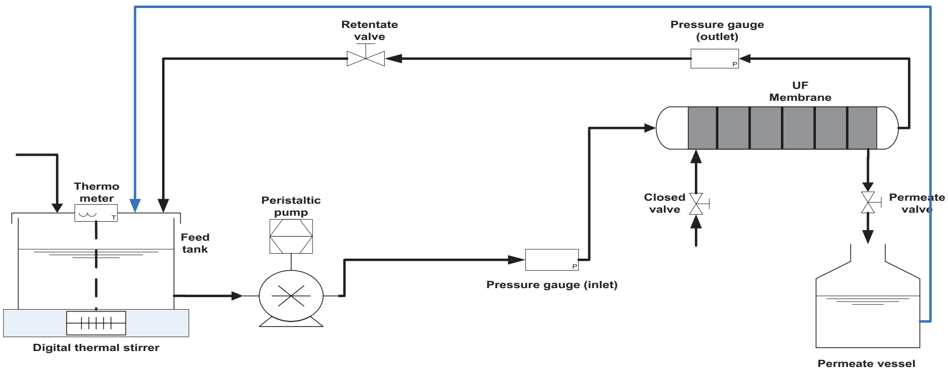
Raw COW, used as the feed sample, was collected from Australian Alba Edible Oil Pty, Ltd, located in Fremantle, Western Australia. This sample was filtered through a sieve to remove solid particles greater than a millimeter in size. The filtered sample was then analysed immediately for selected parameters, such as COD, TOC, TDS, pH and oil concentration (Table 1). The sample was placed in the laboratory fridge at a temperature of less than 4°C to minimise deterioration.

Table 1
Characteristics of the raw COW that was used in all experiments

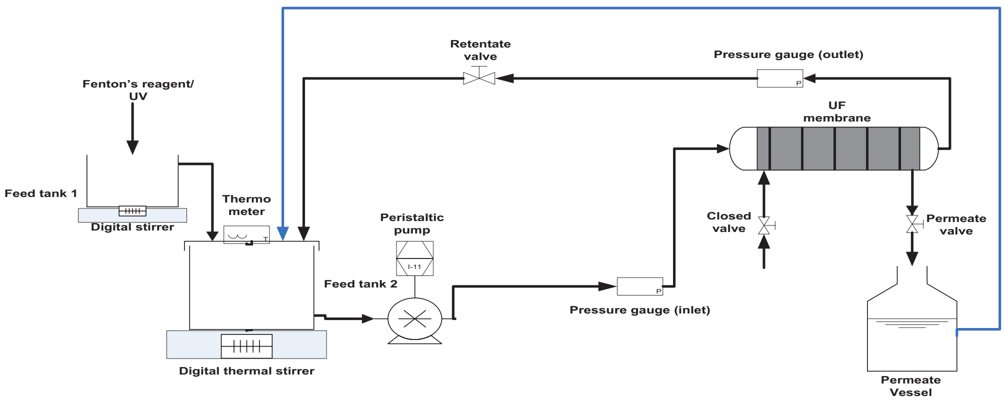
Parameter	Values
COD	450 mg/L
TOC	90 mg/L
TDS	250 mg/L
Oil	600 mg/L
pH	9

2.4. Experimental set up

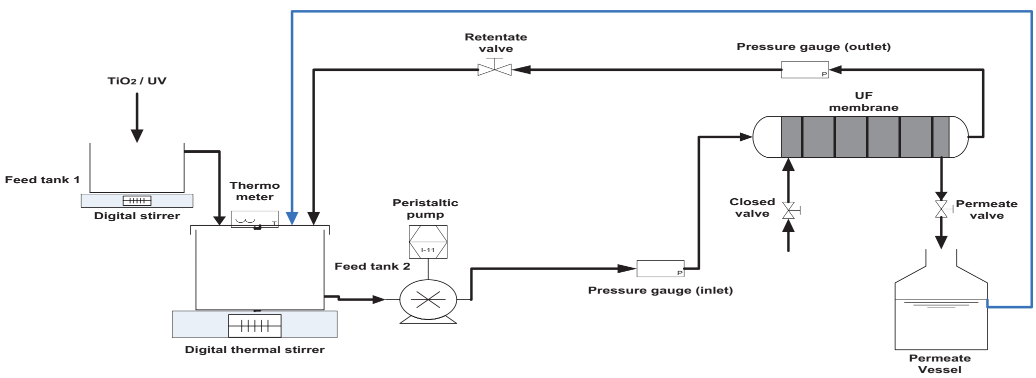
For the membrane system, the UF membrane was placed inside the membrane holder (Micro 240, made of 316 stainless steel). A 30 cm length of tubular UF membrane inside the holder was sealed using nitrile tube seals. For each experiment, two pieces of UF membrane were used. Previously, each piece of membrane was tested with ultrapure water. New membranes were used in each experiment to ensure homogenous starting conditions to compare membrane performance. The initial volume of raw COW in the feed tank was 10 L and the volume of the collected permeate was measured every 10 min. The experiments were run in a recycle system which the retentate stream was returned to the feed tank (Fig. 1). For the first mode (sole UF system), raw COW was fed directly to the membrane without any pre-treatment. In the second mode, raw COW in feed



(a) UF membrane system



(b) Hybrid Fenton/UV/UF membrane



(c) Hybrid TiO_2/UV/UF membrane

Fig. 1. Schematic diagrams for UF and hybrid UF membrane system.

tank 1 was pre-treated with Fenton/UV prior to starting the UF membrane filtration. Fenton's reagent concentrations of 0.5 mL/L H_2O_2 and 0.3 g/L $FeSO_4{\cdot}7H_2O$ were used in the pre-treatment process. For the last system, raw feed was pre-treated using 0.5 g/L TiO_2 /UV before being passed through the UF membrane system. During the experiment, the operating conditions of temperature, pressure and flow rate were fully controlled. The flow rate was adjusted using a programmable peristaltic pump and the pressure was controlled using valves.

2.5. Cleaning process

The membrane cleaning process was performed for 30 min after the 2 h raw COW filtration process and conducted at higher velocity and temperature to elevate scouring behaviour and foulant solubility on the membrane surface [15]. In order to obtain comparable results on the efficiency of different cleaning solutions, the cleaning processes were conducted separately, side by side, using different membranes and separate raw COW with the same characteristics.

2.6. Theory

To determine the permeation flux of the membrane during the filtration process, the following equation was applied [16]:

$$J = \frac{V}{A\,t} \tag{1}$$

where J is the permeation flux (L/m² h), V is the collected permeate volume (L), A is the membrane area (m²), and t is the time taken to collect the permeate (h). The removal of a certain pollutant is expressed as follows:

$$\text{Removal efficiency},(\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \tag{2}$$

where C_p (mg/L) is the concentration of a certain pollutant in the permeate and C_f (mg/L) is its feed concentration.

For the analysis of membrane fouling phenomena, Hermia's model can be used to examine the permeation flux decline mechanism. The general equation for Hermia's model can be written as follows [17]:

$$\frac{d^2t}{dV^2} = K\left(\frac{dt}{dV}\right)^n \tag{3}$$

Using Eq. (1) for the derivation of permeation flux (J) with time (t), Hermia's model can be rewritten as follows:

$$\frac{dJ}{dt} = -K\left(J - J_{ss}\right)J^{2-n} \tag{4}$$

where K is a constant, J_{ss} is the steady state permeation flux, n = 0 for cake filtration, n = 1 for intermediate blocking, n = 1.5 for standard blocking, and n = 2 for complete blocking model. The cake formation model happens when pollutant particles are bigger than the average pore size, leading to accumulated build-up of the cake layer on the membrane surface. In intermediate blocking, particles block some membrane pores creating intermediate fouling due to the equivalent size of pollutant particles and membrane pores. In the standard model, a decrease in pore diameter caused by the non-uniformity of particle adsorption on the membrane pore leads to a decline in flux. The complete blocking model assumes that particles with a bigger size than membrane pores settle on the membrane surface causing a decline in flux [18,19]. The final forms of the equations fitted are shown in Table 2.

To investigate the efficiency of various cleaning agents on a fouled membrane, the flux recovery ratio was measured as follows [2]:

$$FRR = \left(\frac{J_{f,c}}{J_{f,i}}\right) \times 100 \tag{5}$$

where $J_{f,i}$ and $J_{f,c}$ are initial feed flux using a new membrane and feed flux using a cleaned membrane, respectively.

3. Results and discussion

3.1. Comparison of the hybrid and sole treatment methods

As shown in Fig. 2, flux decline occurred with time for both hybrid and sole treatment methods; however, applying pre-treatment as a hybrid process prior to using the UF membrane system can increase permeation flux and reduce fouling.

It can be seen that, after 240 min of the filtration process, the permeation flux of the sole UF membrane declined by more than 50% from its initial value (134 L/m²h), while for the hybrid TiO_2/UV-UF and Fenton/UV-UF, the flux decreases were 32 and 46%, respectively, compared to their initial values of 149 and 137 L/m²h.

Table 2
Hermia's model equations fitted in blocking mechanism

Blocking mechanism	n	Hermia's model
Cake layer formation	0	$\frac{1}{J^2} = \frac{1}{J_o^2} + K\,t$ (5)
Intermediate pore blocking	1	$\frac{1}{J} = \frac{1}{J_o} + K\,A\,t$ (6)
Standard pore blocking	1.5	$\frac{1}{J^{0.5}} = \frac{1}{J^{0.5}} + K\,t$ (7)
Complete pore blocking	2	$\ln(J) = \ln(J_o) - K\,t$ (8)

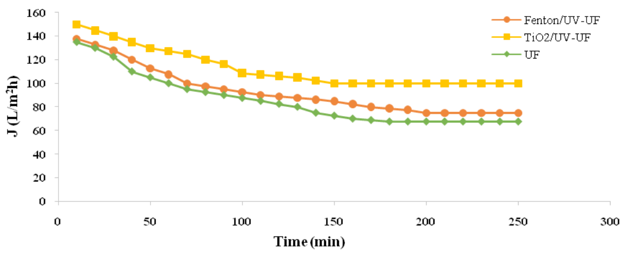


Fig. 2. Comparison of the efficiency of hybrid Fenton/UV-UF, TiO_2/UV-UF and UF on permeation flux.

The hybrid UF membrane method not only elevated permeation flux and reduced fouling, but it also increased the permeate quality with respect to COD and oil removal, as shown in Fig. 3.

Fig. 3 illustrates that hybrid TiO_2/UV/UF exhibits the best performance compared to other methods, reaching approximately 82 and 86% of COD and oil removal, respectively; it is followed by Fenton/UV/UF, showing approximately 77 and 80% of COD and oil removal, respectively. In general, the UF membrane has significantly better ability to reduce oil content (more than 80%) compared to Fenton/UV and TiO_2/UV which showed oil removal of only 13 and 43%, respectively. These AOPs and UF membranes still have competitive efficiency in COD removal. Furthermore, the outstanding performance of hybrid TiO_2/UV/UF in reducing membrane fouling and increasing permeate quality may be clarified by the greater oil molecule adsorption on TiO_2 particles [20]. Viewing Table 3, it is noticeable that the pre-treatment process has a profound effect, increasing membrane performance by reducing certain parameters, including COD, TOC and oil concentration. With the assistance of UV light, this oil and other adsorbed organic molecules will be further mineralised into harmless components. A separate study has reported that hydrophilic TiO_2 contributed to the fouling resistance mechanism by forming a hydration layer to prevent oil from contacting the membrane surface [21].

3.2. Effect of TMP

Fig. 4 illustrates the evolution of permeate flux with different TMP values (1, 2, 3, and 4 bar) conducted with the UF membrane. Fig. 5 depicts the permeation flux profile for different applied TMP values (1, 2, and 3 bar) at a temperature of 25°C, CFV of 600 mL/min and pH of 9.

Fig. 4 shows the curve of permeate flux as a function of TMP with a fixed solution concentration. As can be seen in the figure, TMP has a significant effect on permeation flux which increases when a greater TMP is applied. The logical reason for this flux enhancement is that it is due to increasing driving forces enabling the solution to pass through membrane pores more rapidly [1,22]. Fig. 4 also shows that, at lower applied TMP values (1–2 bar), the permeate flux value achieved the best percentage increase. In this region of values, the flux is governed by the rate at which solution passes through the porous membrane material; however, at higher TMPs, the percentage increase is slower, even, in some extreme cases, showing a negative response to pressure [23]. According to Darcy's law, this occurrence is influenced by concentration polarisation, viscosity of the solution, membrane resistance and fouling resistance [24,25]. Based on Fig. 4, it can also be deduced that the optimum operating conditions occur at a TMP value of 3 bar.

Fig. 5 illustrates permeation fluxes as a function of filtration time, with a higher TMP causing a sharper flux decline. Meanwhile, at the lowest TMP value (1 bar), a steady flux could be achieved faster (100 min). This result is due to the tendency of oil droplets or solute particles to accumulate more at lower pressures, causing concentration polarisation, both on the membrane surface and in the membrane pores, so the membrane fouls more easily [16,26].

3.3. Effect of CFV

Fig. 6 represents the effect of different CFV values (400, 500, 600 mL/min) plotted with time for the permeation flux profile evaluation.

It can be observed, that increasing CFV levels increase permeation flux and decrease the steep flux decline. This phenomena is caused by decreasing concentration polarisa-

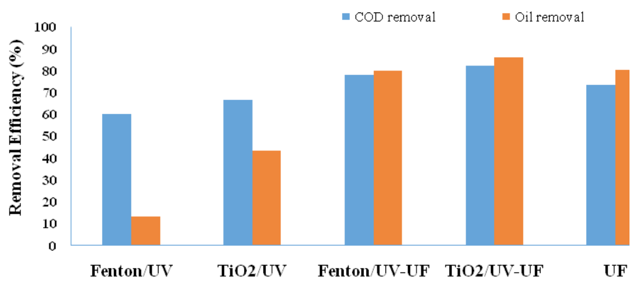


Fig. 3. Comparison of COD and oil removal efficiency for different treatment methods.

Table 3
Characteristics of the raw and treated COW (pre-treatment step)

Parameters	Values		
	Raw	Fenton/UV	TiO_2/UV
COD (mg/L)	450	180	150
TOC (mg/L)	90	40	38
Oil (mg/L)	600	520	340
pH	9	8.5	8.5

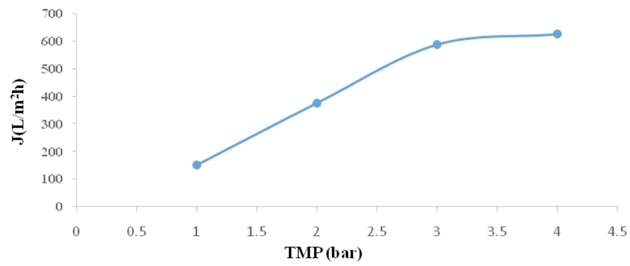


Fig. 4. The influence of different TMP on permeation flux for UF membrane (T 25°C, CFV 600 mL/min).

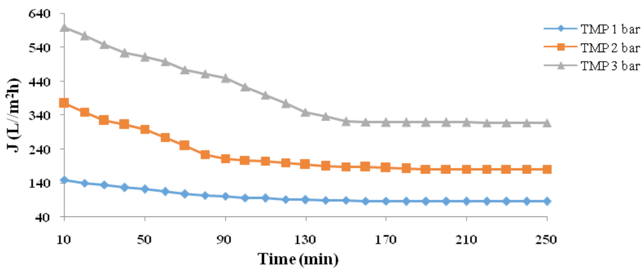


Fig. 5. The effect of TMP on permeation flux in the hybrid TiO_2/UV-UF membrane system (pH 9, T 25°C, CFV 600 mL/min).

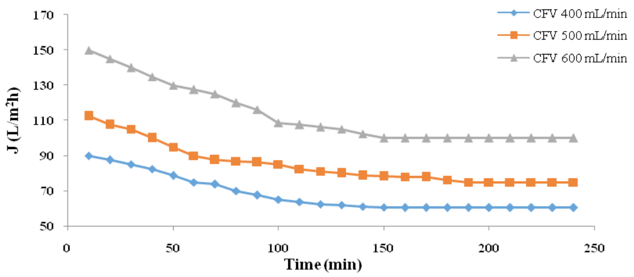


Fig. 6. The effect of CFV on permeate of hybrid TiO_2/UV-UF (pH 9, T 25°C, TMP 1 bar).

tion and increasing the shear stress on the membrane surface and pores due to the velocity increase.

Higher velocity can reduce the thickness of the oil and dissolved solid accumulation on a membrane surface [27]. The steep flux declines occurring in the first 100 min were a 28, 25, and 20% reduction from their initial values for CFVs of 400, 500 and 600 mL/min, respectively. Additionally, the initial flux doubled when the CFV increased from 400 to 600 mL/min. It can be surmised that increasing the velocity level elevates the restriction force to the occurrence of cake layers on the membrane surface. This result also reflects the higher turbulence and improved mass transfer of rejected solutes back to the bulk solution; however, based on Fig. 6, it should also be noticed that steady state flux can be achieved faster at a lower CFV level as cake layer formation is easier and behaves as an additional barrier on the membrane surface and pores, leading to increased oil rejection [1,28].

3.4. Fouling analysis

3.4.1. Hermia's model

The analysis of the membrane fouling mechanism was evaluated using Hermia's model for the entire duration of the raw COW filtration process. Data fitting of the experimental results conducted under various conditions of TMP (1, 2, 3 bar) and CFV (400, 500, 600 mL/min) in Hermia's model are depicted in Table 4.

Hermia's model provides a useful concept for understanding the phenomena of flux decline. As summarised in Table 4, correlation coefficient values (R^2) appear to be similar, leading to an assumption that there is not a single model acting as a main mechanism. Regardless of TMP and CFV values, the correlation coefficient values of the cake filtration model give only a slightly better fit with the obtained experimental data than intermediate pore blocking, complete and standard models. Cake filtration illustrates that, during filtration, particles and oil droplets larger than the average pore size accumulate on the membrane surface forming a cake layer and thickening with time [29]. Meanwhile, the intermediate model explains that each particle or oil droplet of equivalent size to the membrane pore can block the pore or settle on other particles which previously blocked membrane pores. In addition, a lower correlation coefficient value in the complete pore blocking model could be assumed as the impact of hydrophobicity characteristic of oil molecules in wastewater due to the greater interaction of oil droplets on the membrane surface which assists deeper oil molecule penetration [30]. The report of other

Table 4
Estimated correlation coefficient (R^2) of permeation flux predicted by Hermia's model

Condition		R^2 values			
TMP (bar)	CFV (mL/min)	Complete	Standard	Inter-mediate	Cake
1	600	0.817	0.834	0.850	0.877
2	600	0.794	0.816	0.836	0.870
3	600	0.887	0.894	0.898	0.901
1	500	0.815	0.836	0.856	0.890
1	400	0.842	0.847	0.851	0.857

study also indicated flux decline for the polymeric UF membrane for oily wastewater treatment was better fitted to the cake filtration model [18].

3.4.2. Membrane surface morphology

In order to further verify membrane fouling phenomena caused by trapped foulants, SEM and EDS analyses were applied to examine the membrane surface morphology and its chemical components, as illustrated in Fig. 7.

Fig. 7 shows the images obtained by SEM and EDS analysis before and after the filtration process of raw COW. These figures indicated a great difference in surface morphology and chemical components between new and fouled membranes. As illustrated in Fig. 7a, the new membrane has a nano-network surface which is free of any contaminant; its structure shows the potential ability to filter oil and other organic and inorganic particles and allow water to pass through its pores. Figs. 7c and e demonstrate that the same fouled membrane contain trapped foulants in a dense cake layer formation. This fouled membrane surface is much denser than that of a new membrane and has irregularly distributed oil droplets and micro particles on its surface and pores [31]. Additionally, in some parts, fouled membrane surfaces show a thicker cake layer due to the cross-flow suspension type. This effect may be caused by previously trapped particles being pressed by other particles, resulting in a prominent flux decrease.

Furthermore, based on the EDS analysis shown in Figs. 7b, d and f, there are different chemical components in new and fouled membranes, as compiled in Table 5. A new membrane shows that F and C are the main PVDF membrane materials. Meanwhile, a fouled membrane contains more elements than that of a new surface. The detected elements or chemical components of fouled membranes were C, O, F, Fe, Na, Mg, P, K, Si, S, Ti and Ca. This result demonstrates that some contaminants remain in the membrane surface during the filtration process, including the presence of metal elements that could inhibit the performance of membranes leading to flux decline [32].

3.4.2. Membrane flux recovery

Fig. 8 shows membrane flux recovery after the application of membrane cleaning using different cleaning agents: water, acidic solution (0.1 M HNO_3), alkaline solution (0.1

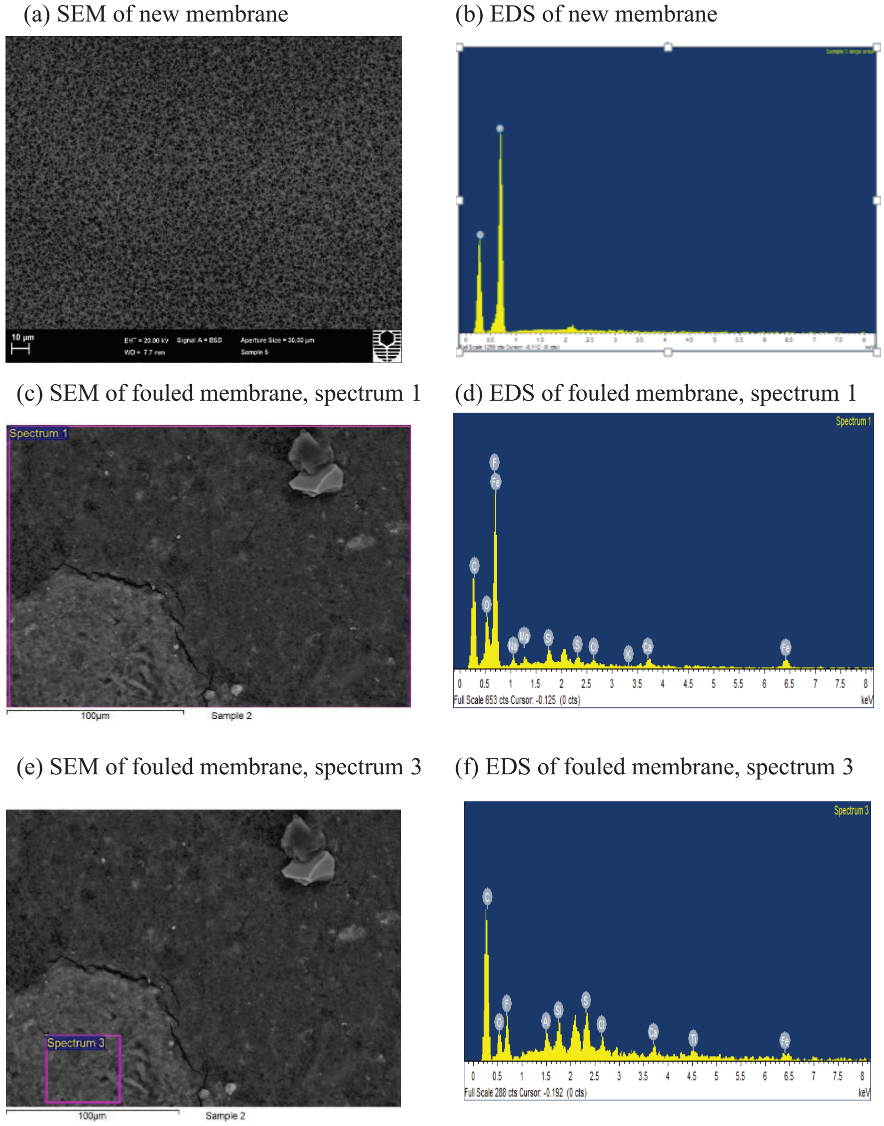


Fig. 7. SEM-EDS photographs of membrane surfaces.

Table 5
EDS analysis

Chemical components	
New UF membrane	Fouled UF membrane
C, F	C, F, O, Fe, Na, Mg, P, K, Si, S, Ti, Ca

M NaOH) and combined alkaline/acidic solution (0.1 M NaOH/0.1 M HNO_3),which were separately employed under certain conditions (TMP of 1 bar, CVF of 600 mL/min and a temperature of 45°C).

According to the experimental results obtained, using combined 0.1 M NaOH/0.1 M HNO_3 as a cleaning agent gives better membrane flux recovery by yielding the highest flux recovery ratio (97%), followed by alkaline, acidic and water which were about 95, 93 and 82%, respectively.

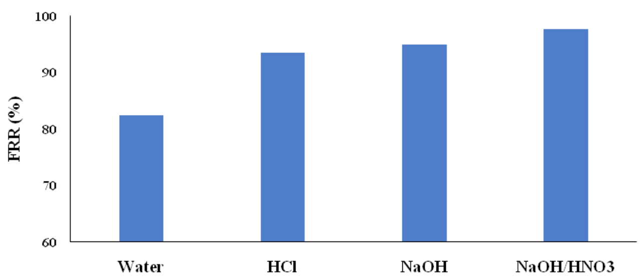


Fig. 8. Comparison of different cleaning agents on membrane flux recovery ratio (TMP 1 bar, CFV 600 mL/min, T 45°C).

This result indicate that rinsing with water alone is less effective than chemical cleaning agents for retrieving the original feed flux. The excellent results from combined chemical cleaning of a fouled membrane can be explained by the fact that different chemical solutions can target different types of foulants. Alkaline solutions act better to remove and wash away organic foulants on membrane surfaces via hydrolysis and solubilisation reactions, while acidic solution can remove metal oxides and other inorganic compounds. In addition, applying a suitable chemical cleaning agent is beneficial by increasing permeation flux recovery and lengthening membrane life as the chemical solution can work more aggressively to prevent irreversible fouling, reduce cake thickness and dissociate pollutant or foulant agglomeration on the membrane surface [2,33].

4. Conclusions

Hybrid TiO_2/UV/UF, Fenton/UV/UF and sole UF membrane filtration systems were designed and investigated for both mineralisation of raw COW and the evaluation of methods to decrease fouling. According to the laboratory-scale experimental results, a hybrid TiO_2/UV-UF showed the best performance by achieving approximately 82 and 86% of COD and oil removal, respectively, and reducing the permeate flux decline with only a 32% decline from its initial value, compared to 46 and 50% decline from initial values for hybrid Fenton/UV-UF and sole UF membrane, respectively.

This study finds that increasing TMP from 1 to 2 bar and increasing velocity from 400 to 600 mL/min doubles the permeation flux value. Furthermore, based on Hermia's model, even though the cake filtration model is better fitted to the experimental data, it cannot be assumed that cake filtration is the main model working in the blocking mechanism as the values of the coefficient correlation (R^2) are very similar to other models. SEM and EDS analyses indicate significant differences in surface morphology and chemical components between new and fouled membranes, with trapped foulants consisting of hydrocarbon, organic and inorganic compounds. Membrane cleaning applied to recover membrane permeation flux showed that a combined chemical cleaning agent (0.1 M NaOH/0.1 M HNO_3) resulted in a better flux recovery ratio (at least 97%), followed by alkaline, acidic and water rinsing. In addition, it is considered that the results obtained in a recirculation test cannot always be extrapolated to real operations immediately, especially for fouling evaluation; therefore, further research is needed before its industrial-scale application.

Symbols

A — Membrane area (m^2)
C_f — Concentration of a certain pollutant in feed
C_p — Concentration of a certain pollutant in permeate
J — Permeation flux ($L/m^2 h$)
t — Permeate collection time (h)
V — Collected permeate volume (L)

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