Separation of oil/water emulsion using nano-particle (TiO$_2$/Al$_2$O$_3$) modified PVDF ultrafiltration membranes and evaluation of fouling mechanism

X. S. Yi, S. L. Yu, W. X. Shi, S. Wang, L. M. Jin, N. Sun, C. Ma and L. P. Sun

**ABSTRACT**

In the present study, nano-sized TiO$_2$/Al$_2$O$_3$ modified polyvinylidene fluoride (PVDF) membranes (MM) were fabricated and then utilized for oil/water emulsion separation. The results showed that, compared with PVDF membrane (OM), the contact angle of MM decreased and hydrophilicity increased. The ultrafiltration (UF) of oil in water emulsions with transmembrane pressure (TMP) increasing results in a sharp fall in relative flux with time. The cake filtration models did not always predict the performance over the complete range of filtration times very well. In the initial 30 min, all the four cake models can simulate this UF process to a certain extent, and the suitability was: cake filtration > intermediate pore blocking > standard pore blocking > complete pore blocking models. However, they were no longer adapted well with UF time extent to 60 min, but only cake filtration ($R^2 = 0.9535$) maintained a high adaptability. Surface and cross-sectional morphology of the membrane was investigated by SEM to make an advanced certificate of this UF mechanism.

**Key words** | fouling mechanism, TiO$_2$/Al$_2$O$_3$ nano-particles, oil/water emulsion, PVDF ultrafiltration membranes

**INTRODUCTION**

Every year, a large volume of oily wastewater is produced by petrochemical, pharmaceutical, food industries, and especially by oil fields. Environmental regulations require that the maximum total oil and grease concentrations in discharge waters be 10–15 mg/L (Bevis 1992). However, the major pollutant in produced water generating from oil fields is oil which may range between 100 and 1,000 mg/L or higher depending on the efficiency of demulsification and the nature of the crude oil (Chakrabarty et al. 2008, 2010). In general, there are three categories of oil forms in industrial oily wastewater, which are free-floating oil, unstable oil/water emulsion and stable oil/water emulsion (Um et al. 2001). Free-floating oil or unstable oil/water emulsions can be easily removed by conventional separation processes, such as ultrasonic separation, coagulation/flocculation, electric field, and air flotation. But they are not efficient enough for removing stable oil/water (size ≤ 20 μm), especially when the oil droplets are finely dispersed (Chakrabarty et al. 2008, 2010). A lot of reports say that these conventional techniques can reduce oil concentration to barely 1% by volume of the total wastewater and cannot efficiently remove oil droplets below 10 μm size, resulting in terrible environmental pollution and resource utilization problems (Benito et al. 2002).

According to the literature reports (Freeman & Pinnau 2004), the use of membrane technology offers a potential solution to the problem of micron sized and submicron oily wastewater. This is because of its suitable pore sizes (Liu & Sun 2012a) and the capability to remove emulsified oil droplets without any de-emulsification processes. Moreover, the membrane process has other advantages, such as: lower capital cost, the non-requirement of any chemical addition and the capability of generating permeate of acceptable quality. Ultrafiltration (UF) is considered to be a versatile separation process which is widely used for separation, purification and concentration of water-soluble...
solute or water dispersible materials (Chen et al. 2009). Usually, UF membranes are classified into two kinds: polymeric membranes and inorganic membranes. The inorganic membranes such as ceramic and carbon membranes are quite suitable for processes involving high temperatures and harsh chemical environments and have been successfully applied to the oil wastewater treatment (Song et al. 2006; Benito et al. 2007). But it has a relatively high cost arising from the expensive raw materials, complicated fabrication procedure and low membrane surface area. Thus, polymeric membranes are still dominating the membrane separation field. It should be pointed out that serious membrane fouling is easily caused by emulsified oil droplets onto the membrane surfaces, thus, limiting their wide application in oily wastewater treatment.

Many investigations (Cui et al. 2008; Ju et al. 2008) have demonstrated that increasing membrane surface hydrophilicity could effectively decrease membrane fouling and display a relatively higher permeate flux. Chu et al. (2005) conducted the hydrophilic surface modification of ceramic-supported polyethersulfone (PES) membranes by synthesizing a poly(vinyl alcohol)/polyamide composite thin surface layer with an interfacial polymerization method. Chen et al. (2009) prepared Pluronic F127 modified PES UF membranes, which exhibited good fouling resistance and improved the efficiency of membrane washing. In our previous studies, nano-sized TiO$_2$ and Al$_2$O$_3$ were incorporated into polyvinylidene fluoride (PVDF) membranes to improve oil-adsorption-resistant ability. The hydrophilic nano-sized TiO$_2$ and Al$_2$O$_3$ were uniformly dispersed in the solvent, spontaneously dispersed on the membrane surfaces and firmly entrapped in the membrane bulk matrix, which could render the membrane with higher hydrophilicity, leading to lower protein fouling on the membrane surface and an increase in permeate flux compared with the control PVDF membrane.

In the present study, nano-sized TiO$_2$/Al$_2$O$_3$ modified PVDF membranes (MM) were fabricated. Water contact angle and scanning electron microscopy (SEM) were introduced to characterize the surface hydrophilicity and the morphology of these membranes, respectively. This modified membrane was then utilized for oil/water emulsion separation, and the permeation and oil fouling-resistant properties were extensively investigated. Finally, in order to make clear the fouling mechanisms to better understand the flux performance, a simple cake filtration analysis to predict the variation in flux rate with time during dead-end UF was carried out.

### MATERIALS AND METHODS

#### Apparatus

The schematic diagram of the experimental set-up (Figure 1) used in our study was similar to those described in previous papers (Ruiz-Beviá et al. 2008; Liu & Sun 2012b). This system contained a dead-end stirred filtration cell (XFUF 07601, Millipore Co., USA) with a volume capacity of 300 mL with inner diameter of 76 mm, and an effective area of the membrane of 40 cm$^2$. All the UF experiments were carried out under a certain TMP with extra nitrogen gas as pressured force, at room temperature of 25 ± 1°C and at stirring speed of 100 rpm. The distance from the membrane surface to the top of the solution was 60 ± 2 mm, so the volume of solution in the cell was large enough to guarantee that concentration change inside the cell would only take place near the membrane. Therefore, far from the membrane surface, the bulk concentration ($C_b$) remained unchanged during the process.

#### Characterization of PVDF membranes

The PVDF UF membrane used here (made in our laboratory) was prepared by the phase-inversion method. After fixing the membrane in the cell, the stirred cell and solution reservoir were filled with deionized water. Each membrane was initially compacted for 0.5 h at 0.2 MPa (Su et al. 2009). The surface and cross-sectional morphologies of MM observed using a HITACHI S-4800 scanning electronic microscope are shown in Figure 2. The membranes exhibited a typical asymmetric structure of UF membranes with a skin layer on top, a finger like intermediate layer and fully developed micro-pores at the bottom. The other important characteristics of the MM and its original membrane

![Figure 1 | Schematic diagram of experimental set-up for constant flux dead-end UF.](https://iwaponline.com/wst/article-pdf/67/3/477/441614/477.pdf)
(OM) are shown in Table 1. However, the structures of these two membranes were the same, the pure water flux of OM and MM are 170 and 260 L/m² h, respectively.

### Emulsion characteristics

The oil/water emulsion was prepared as follows: 200 mg crude oil from Daqing oil field as base oil and 400 mg anionic surfactant (sodium dodecylsulfate, 98%, Tianjin) were added to 500 mL of deionized water (Chen et al. 2009). The solution was mixed by high-shear emulsifying dispersion for 30 min, and then diluted in a 1,000 mL volumetric flask. The size of the oil droplets, which was measured using a Malvern Mastersizer Particle size analyzer, was in the range of 0.1–0.6 μm with a volume average particle diameter of 0.3 μm; even after 7 days, the oil droplets were still in the range of 0.2–0.8 μm, which indicated the oil emulsion was stable (as shown in Figure 3).

### Flux decline studies

To investigate the effect of the oil emulsion on pure water flux of these two kinds of membranes, flux was calculated every 2 min until the flux approached stability after 1 h (Jian et al. 2006). Pure water flux of this membrane was measured under the same conditions with the samples determined by collecting permeating flux weight for 2 min, and we called this initial flux J0. Flux (J) of both pure water and samples were calculated with the following equation:

$$J = \frac{m}{\rho_w A \Delta t}$$  \hspace{1cm} (1)

where $m$ was the permeate weight (kg), $\rho_w$ was the density of pure water (1.000 kg/L); $A$ was the effective membrane area (m²) and $\Delta t$ was the experimental time (h).

As the initial flux of every membrane was not quite the same, Relative Flux ($J/J_0$, %) was adopted to evaluate the flux decline. The calculating equation was:

$$\frac{J}{J_0} = \frac{m}{\rho_w A \Delta t} \frac{m_w/\rho_w}{m_w/\rho_w} = \frac{m}{m_w}$$  \hspace{1cm} (2)
where \( m_w \) was the permeate weight of pure water (kg); the concentration of anionic polyacrylamide (APAM) in permeate was nearly 0 mg/L, so \( \rho_w = \rho \) could be used.

**Cake filtration models**

In order to establish a predictive model for characterizing the flux variation, simple cake filtration models were chosen here. There are four kinds of forms widely used for depicting fouling mechanisms: cake filtration, intermediate law, standard pore blocking and complete pore blocking (Hermia 1982; Blankert et al. 2006). In the case of constant pressure filtration, membrane area, and membrane resistance \( (R_m) \) being constant, the filtration laws can be written as follows (Hu & Scott 2008):

a. Complete pore blocking:

\[
\ln (J^{-1}) = \ln (J_0^{-1}) + K_c t
\]

b. Gradual pore blocking (standard pore blocking):

\[
J^{-0.5} = J_0^{-0.5} + K_s t
\]

c. Intermediate filtration:

\[
J^{-1} = J_0^{-1} + K_i t
\]

d. Cake filtration:

\[
J^{-2} = J_0^{-2} + K_c t
\]

where \( J_0 \) depends on the transmembrane pressure (TMP) and the various \( K \) terms represent mass transfer coefficients for the associated filtration laws.

**RESULTS AND DISCUSSION**

**Effect of transmembrane pressure**

The permeate relative flux (RF) of MM membranes after 30 and 60 min during the separation of oil/water emulsion with different TMP is presented in **Figure 4**.

The effect of an increase in TMP on membrane relative flux performance is clearly seen to decrease, and shows a two stage linear downward trend: slight decline stage and sharp decline stage. The RF decline during UF can be associated with the fouling phenomenon which is caused by the accumulation and deposition of solutes on the membrane surface or within pores (Li et al. 2006). The degree of RF decline under different TMP with different times follows the order: 0.05 MPa < 0.075 MPa < 0.10 MPa < 0.15 MPa < 0.20 MPa. For example, it was observed that, there was a gentle decline of RF (from 0.35 to 0.33) with TMP increasing from 0.05 to 0.10 MPa, then followed by a drastic decline of RF (from 0.33 to 0.22) after TMP higher than 0.10 MPa at 30 min, and the same trend was also achieved at 60 min. That was because a layer containing large oil droplets formed above the membrane surface, and then may be compressed on the surface and blocked the membrane pores at higher pressure leading to membrane fouling at a higher rate (Ruiz-Beviá et al. 2008; Fernández-Sempere et al. 2009). In addition, the trend lines of 30 and 60 min are nearly parallel lines, indicating that the membrane fouling was also a function of time and increased with time. Considering the RF, the consistency of fouling lines, and the trends of permeating flux, 0.1 MPa has been considered as the most preferable TMP for achieving utmost membrane performance. Further analyses as well as investigations were carried out at this pressure only.

**Filtration models analysis**

**Figure 5** shows the correlation of the models for MM membrane at 0.1 MPa transmembrane pressure in the first 30 min of this UF process. In most cases, the models exhibit a reasonable agreement with the experimental data giving linear correlations.

The model correlations for each case are given in **Figure 5(b)**. The estimation of the flux at \( t = 0 \) \( (J_0) \), from
the intercept, gives the following values, 143.31, 136.18, 149.29 and 133.54 L/m² h for the intermediate pore blocking, standard pore blocking, cake filtration, and complete pore blocking models respectively. These values are less than the initial experimental flux, which was 157.09 L/m² h, indicating that each of the four models lacks accurate prediction at the initial time period of filtration. However, after using the model correlations for each case considered, a comparison is made with the experimental data of the estimation of the flux, with filtration time 30 min; the $R^2$ values were as follows: 0.98779, 0.95958, 0.93675 and 0.90804 for the cake filtration, intermediate pore blocking, standard pore blocking, and complete pore blocking models, respectively. Obviously, the cake formation model had the best agreement with the experimental data, which tends to agree with the fouling behavior observed in the traditional sand filter (Hu & Scott 2008). Moreover, the intermediate pore blocking model could also be considered as an appropriate predictive model for this case. However, the regression values of the standard pore blocking and complete pore blocking model are lower, and each of them has a big curve in their regression lines. This outcome suggested that during the initial 30 min, pore blocking and gel layer fouling played a determining role.

Compared with Figure 5, it can be seen from Figure 6 that the flux curve changed greatly with filtration time. Figure 6(a) shows us the ability of the resulting model correlations to predict filtration flux with a longer filtration time range of 1 h, where reasonable correlations are achieved (shown in Figure 6(b)). However, the regression values are very poor in all cases except perhaps for the cake formation law. Overall, it appears that the cake formation model gives the best predictions of flux with the $R^2 = 0.9535$. Thus, no models gave a good correlation over the complete range of filtration times of 60 min and roughly two regions of filtration appeared to occur. Moreover, all the models at the initial stage of filtration underestimate the filtration rates. This may be attributed to the membrane itself which exhibits a high resistance due to its higher hydrophilic properties, when the oil emulsion contacts the membrane surface (Hu & Scott 2008). This situation would correspond to the behavior of the emulsion filtration with the hydrophilic membrane where the emulsion passed through the membrane due to the relatively high pressure used. At this time, the $R^2$ values order of the four models were: cake filtration (0.9535) > intermediate pore blocking (0.8953) > standard pore blocking (0.8557) > complete pore blocking models (0.8096), which had a consistency with that of 30 min. Consequently, it was safe to say that the cake filtration model was suitable and a good prediction model in this oil emulsion UF process.

Fouling analysis of the membrane surface

SEM was used to estimate the effect of oil emulsion filtration on the surface of the membrane. Figure 7 shows us the surface and cross-sectional morphology of the membrane with UF time.

Compared with Figure 2, it was observed from Figure 7 that the amount of pollutants deposited on the surface increased with filtration time. The bulge and sag on the membrane surface were covered by a layer of solid bulk substances which must be the aggregation of oil particles.
Moreover, it seems that the status of the oil layer on the surface of 60 min was more compact compared with that of 30 min, apparently. The SEM of the membrane surfaces generally shows that the extent of fouling of the membrane is much greater with longer UF time, where there is more coverage of the surface by pollutants.
However, although the pores of the membrane were blocked by contaminants to some extent, it was not particularly serious congestion from 30 to 60 min. As the UF time progressed, more and more serious gel polarization occurred, which played a determining role in the membrane fouling between 30 and 60 min, leading to the three kinds of pore blocking models becoming increasingly unsuited. Thus, cake filtration can be well used to predict the characteristics of this oil emulsion UF by modified PVDF membrane to some extent.

CONCLUSIONS

The UF of oil in water emulsions with TMP increasing results in a fall in relative flux with time. This can be attributed to the increase in TMP, a significant increase in the mass transfer rate and compressed oil droplets on the surface, and blocked membrane pores.

In the case of oil emulsion UF by modified PVDF membrane, the cake filtration models do not always predict the performance over the complete range of filtration times very well. In the initial 30 min, all the four cake models can simulate this UF process to a certain extent, and the suitability was: cake filtration > intermediate pore blocking > standard pore blocking > complete pore blocking models. However, the four models were no longer adapted well with UF time extent to 60 min, and only cake filtration ($R^2 = 0.9535$) maintained a high adaptability.

Surface and cross-sectional morphology of the membrane was investigated by SEM to make an advanced certificate of this UF mechanism. The bulge and sag on the membrane surface were covered by a layer of solid bulk substances at 30 min, which was more compact at 60 min, however, the cross-sectional morphology had no obvious change. Thus, pore blocking models were no longer suitable with UF time, but cake filtration can be well used to predict the characteristics of this oil emulsion UF by modified PVDF membrane to some extent.

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