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Effect of hydrophilic modification with nano-titania and operation modes on the oil–water separation performance of microfiltration membrane

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ABSTRACT

The tubular Al_2O_3 microfiltration membranes modified with nano-TiO_2 coating were applied in the separation of waste oil-in-water emulsion. The separation performances of the MF membranes with and without nano-TiO_2 modification were studied under two different operation modes, i.e. the circulation mode and the concentration mode, respectively. The circulation mode in which the oil concentration in feed keeps constant simulates the condition of the great amount of feed to be treated, while the concentration mode in which the oil concentration in feed increases with the extraction of the filtrate simulates the condition of a small amount of feed to be treated. The results show that the operation mode has a less effect on the flux of the MF membranes, but has an important effect on the oil concentration of filtrate for the unmodified membrane. The oil concentration in filtrate under concentration mode is higher than that of circulation mode. For the modified membrane, the operation mode has a less effect on the flux and the oil concentration of filtrate, because the hydrophilic nano-TiO_2 coating prevents oil droplets from penetrating the membrane pores. Under both operation modes, the fluxes of the modified membranes are higher than those of the unmodified membranes.

Keywords: Microfiltration membrane; Membrane modification; Oil-in-water separation; Operation mode; Membrane fouling

1. Introduction

Oily wastewater emulsion was given an important attention because of its long-time and serious harmfulness to environments, which is given the maximum discharge limit of oil of ca. 10 mg/L [1]. Various conventional techniques were used to treat oily wastewaters, such as ultrasonic separation, coagulation/flocculation, air floatation, chemical de-emulsification followed by gravity settling, and so on [2–5]. Membrane separation technology—such as microfiltration (MF) membrane and ultrafiltration (UF) membrane—is more effective, cost-efficient, and environmental friendly

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because water and oil can be physically separated and re-used. However, membrane fouling is the major obstacle that weakens membrane performances, which is also one of the hot research topics. To reduce membrane fouling, the operational parameters and the membrane itself can be optimized. The optimization of operational parameters includes cross-flow velocity, transmembrane pressure [6], feed temperature [7], back-flushing [8], pre-treatment [9,10], or the other assistant treatment [11,12] according to the character of oil-in-water emulsions. The optimization of the membrane itself is indeed to choose the appropriate interface between emulsion/membranes, including the choice of the membranes with different materials [13–16] and the membrane modification [17–19]. The theoretical researches contribute to understand the separation process of oil-in-water emulsion, which was reported based on the experimental results [20–23]. In those researches, the oil concentration of the feed is usually set as a constant when the membrane fouling is studied. It is effective to a great amount of feed to be treated, because the change of the oil concentration in the feed can be neglected when the filtrate is extracted. In other words, the above-mentioned experimental results were valid only for the feed whose amount is so large that the oil concentration can be regarded as a constant during the separation process.

Membrane separation technology has the extra advantage in which the membrane module can be used in a large-scale industrial unit or used in a small-scale factory, laboratory, or family. In a special case of a small amount of oil-in-water emulsion to be treated, the filtrate is extracted in the practical application of membrane separation process. Here, the increase in the oil concentration in the feed must not be neglected. The continuous increase in the oil concentration in the feed has a negative effect on the membrane separation performance. Most of the researches focus on the oily emulsion with low oil concentration (≤1,000 ppm) [13,24–26]. Along with the increase in the oil concentration in feed, the other questions arise like: how much of the oil concentration in the feed can be treated by ceramic membrane and what is the performance of membranes to treat the emulsion with such high oil concentration is.

In the present work, the commercial ceramic MF membrane and the membrane modified by nano-TiO_2 coating [27–29] were used to treat a stable oil-in-water emulsion with oil concentration of 1–4 g/L. Two operation modes were applied: circulation mode and concentration mode. In the circulation mode, the filtrate comes back to the feed, so that the oil concentration in the feed keeps constant, which simulates the great amount of feed to be treated. In the concentration mode, the filtrate is discharged off. The oil concentration in the feed continuously increases, which simulates the little amount of feed to be treated. The flux and the oil concentrations of filtrate were studied to evaluate the separation performance of the MFs with and without modification under the two operation modes.

2. Experimental

2.1. Preparation of the modified membrane

The used tubular Al_2O_3 MF membranes, purchased from Nanjing Jiusi High-Tech Co. Ltd, have a configuration of 19 channels. The main parameters are as follows: outer diameter of 31 mm, porosity of 40%, and nominal pore diameter of 0.2 μm. $TiO(SO_4)_2$ and urea (purchased from Sinopharm Chemical Reagent Co. Ltd, China) were used without further treatment.

$TiO(SO_4)_2$ and urea (mol ratio of $TiO(SO_4)_2$/urea is 1:2) were dissolved into distilled water, respectively, and then mixed directly at room temperature. The concentration of Ti^{4+} in the solution is 0.2 mol/L. The ceramic MF membranes were saturated with the mixed solution. The wet ceramic membranes were sealed with food wrapper, and then put into an oven at 85℃ for 3 h. The ceramic membrane was washed ultrasonically two times with distilled water, and then dried at 110℃ overnight. The above processes were repeated twice. The dried ceramic membrane was calcined at 950℃ at a heating rate of 3℃/min and annealed for 2 h. The cross-sectional microstructure of the modified Al_2O_3 membrane was observed by scanning electron microscope (JSM-6700F, JEOL).

2.2. Preparation of oil-in-water emulsion

The oil-in-water emulsion consisted of hydraulic oil 32 (kinematic viscosity is 32 mm^2/s at 40℃), Tween 80, Span 80, and distilled water. The mass ratio of hydraulic oil 32/Tween 80/Span 80 is 8/1/1. The oil concentration can be 1, 2, and 4 g/L. After weighted, oil and surfactants (Tween and Span) were added to the distilled water. The emulsion was generated using a blender (Fluko Equipment Shanghai Co., Ltd) by mixing for 2 min at medium speed. This method allowed the production of the stable emulsions of 1, 2, and 4 g/L, with the average oil droplet size of 3.31, 3.81, and 5.87 μm, respectively. All the emulsions have 90% of the oil droplets in the range of 0.2–20 μm, as measured using a particle size analyzer (Nano ZS, Malvern).

2.3. Operation modes

The membrane equipment and the operation method were reported in reference [18]. The operational parameters were: cross-flow velocity of 5 m/s, transmembrane pressure of 0.16 MPa, and feed temperature of 34℃. In the circulation mode, the 60 L feed was poured into the feed tank. The filtrate came back to the feed so that the feed was kept in the oil concentration. The separation process ran for 24 h. In the concentration mode, the 60 L oil-in-water emulsion with oil concentration of 1 g/L was poured into the feed tank. The filtrate was discharged off. When the volume of the feed was reduced to half, the 30 L emulsion with the oil concentration of 2 g/L was poured into the feed tank. When the volume of the feed was reduced to half again, the 30 L emulsion with the oil concentration of 4 g/L was poured into the feed tank. The separation process ran until the volume of the feed was reduced to half again.

The oil concentration of the filtrate was analyzed using an ultraviolet spectrophotometer (UV-1601).

3. Results and discussion

3.1. Hydrophilic modification of MF membrane

Fig. 1 shows SEM images of the cross-section of modified membranes by nano-TiO_2 coating. For comparison, SEM image of the unmodified membrane is also shown. As can be seen, nano-TiO_2 particle is distributed uniformly on the surface of alumina particles. The mean particle size of nano-TiO_2 particles is about 30 nm. It can be deduced that the nano-TiO_2 coating distributes on the surface of the membrane and membrane pore channels. The TiO_2 coating does not form a new separation layer, but changes the surface from feed/membrane to feed/nano-coating. Therefore, nano-TiO_2 coating changes the interaction between oil droplets with membrane surface, and thus has the effect on the membrane fouling. The contact angle of water on nano-TiO_2 coating changes from 33° to 8° before and after modification.

3.2. Separation performance under the circulation mode

3.2.1. 1 g/L oil-in-water emulsion

Fig. 2 shows the fluxes of the modified membrane and the unmodified membrane to treat 1 g/L oil-in-water emulsion. As can be seen, the flux of the unmodified membrane declines from 368.3 L/m^2 h bar to 202.2 L/m^2 h bar. The flux of the modified membrane declines only from 529.6 L/m^2 h bar to 307.8 L/m^2 h bar. After separation has run for 24 h, the flux of the modified membrane is higher about 50% than that of the unmodified one. It can be explained by the existence of the hydrophilic nano-TiO_2 coating. The contact angle of the nano-TiO_2 coating is about 8°, which is far smaller than that of the dense alumina, indicating the TiO_2 coating is very hydrophilic [30]. This result is also applicable for the modified membrane, because the nano-TiO_2 coating distributes directly on the alumina particles of the membrane. The hydrophilic membrane surface repels oil droplets from adhering to the membrane surfaces, thus weakening the membrane fouling. At the same time, the pure water flux of the modified membrane increases from 30 to 40% than that of the unmodified one [31]. Therefore, the initial flux of the modified membrane is higher than that of the unmodified one.

Fig. 3 shows the oil concentration variations of the filtrates with time. For the unmodified membrane, the oil concentration of filtrate is about 20 mg/L. After 200 min, it decreases below 10 mg/L. However, for the modified membrane, the oil concentration of filtrate in the initial stage is very small (11.8 mg/L). The oil concentration is below 10 mg/L after 10 min and kept constant of about 6 mg/L after 40 min. This difference can be explained by the membrane fouling process. In the initial stage, the standard pore fouling is the major mechanism. Oil droplets can penetrate membrane pores by deformation, and then block them, which results in the sharp decline in the oil concentration of filtrate. Cake filtration becomes dominant

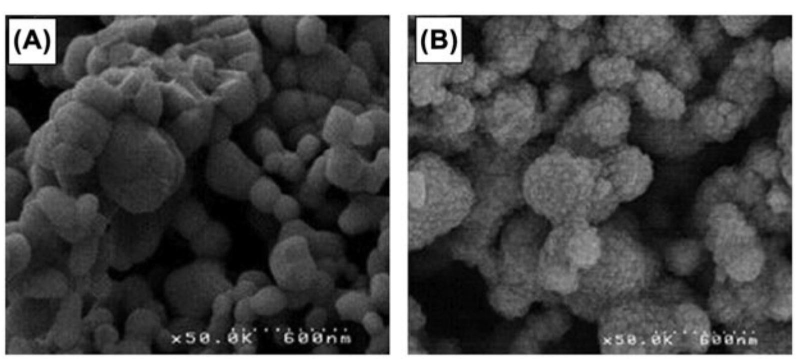

Fig. 1. SEM images of the cross-section of the membrane, (A) unmodified membrane and (B) modified membrane with nano-TiO_2 (0.2 mol/L $Ti(SO_4)_2$).

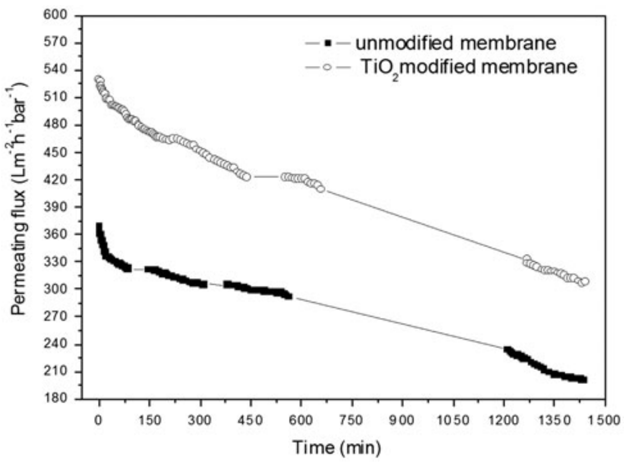

Fig. 2. Fluxes vs. time of the unmodified and the modified MF treating 1 g/L oil-in-water emulsion.

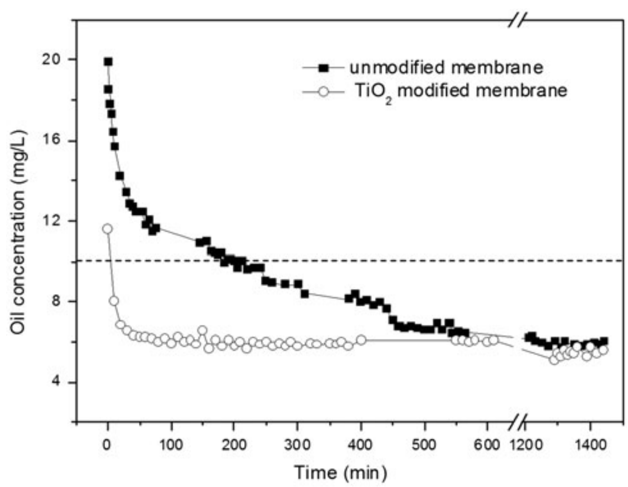

Fig. 3. Oil concentration variation of the filtrate via time.

after 100 min for the unmodified membrane. The cake layer acts as a "second separation layer" to reject oil droplets. The oil concentration of filtrate decreases with the increase in the cake thickness. For the modified membrane, oil droplets can only penetrate into and then block few large membrane pores because oil droplets beyond the active scope of the hydrophilic coating, which is similar to the unmodified membrane. This generates the oil concentration in the initial stage. For most of the modified membrane pores, the hydrophilic coating prevents oil droplets from penetrating membrane pores by deformation. The oil concentration of filtrate tends to be a constant for a short time. Even if the cake forms, the weak interaction between the cake and the hydrophilic coating results in the cake which is in the destroy-form dynamic balance by the flush of the feed. The oil concentration is nearly unchanged in the following time.

3.2.2. 2 g/L oil-in-water emulsion

Fig. 4 shows the fluxes of the unmodified and the modified membrane, treating 2 g/L oil-in-water emulsion. The variations of the fluxes are similar to those treating 1 g/L emulsion. However, it should be noted that the flux of the unmodified membrane declines sharply in the initial stage when the oil concentration of the emulsion increases from 1 to 2 g/L. Obviously, the concentration polar layer and the cake layer can be formed in a short time, due to the increase in the oil concentration of the feed. As can be seen, the flux of the modified membrane is still 35% higher than that of the unmodified membrane after 24 h, treating 2 g/L oil-in-water emulsion. The flux of the modified membrane declines from 439 L/m^2 h bar to 361 L/m^2 h bar. The flux of the unmodified membrane declines from 288 L/m^2 h bar to 214 L/m^2 h bar. Both of the fluxes are lower than those treating 1 g/L emulsion due to the relatively serious membrane fouling. The flux differences of the unmodified membrane and the modified membrane are 78 L/m^2 h bar and 74 L/m^2 h bar at the first point and the 1,440th point of the time. It indicates that the unmodified membrane has the similar membrane fouling after 24 h. In other words, the nano-coating on the membrane surface lost its repelling action once the continuous cake layer is formed. The interface changes from emulsion/nano-coating to emulsion/cake layer, which is similar to the unmodified membrane surface. The flux increment of the

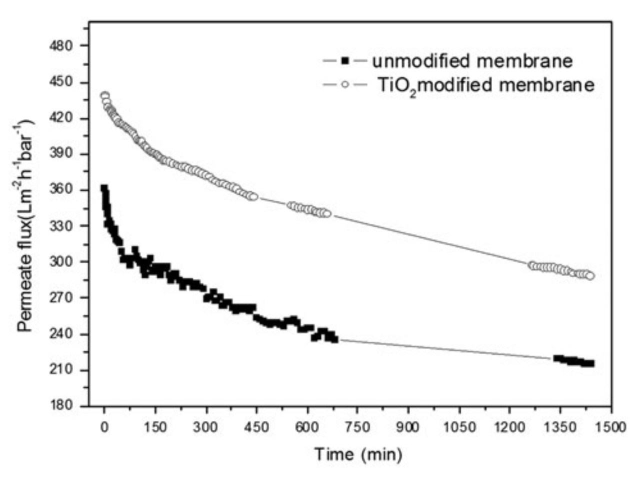

Fig. 4. Fluxes vs. time of the unmodified and the modified MF treating 2 g/L oil-in-water emulsion.

modified membrane than the unmodified membrane is derived from the nanoscale effect of the nano-TiO_2 coating in membrane pore channels accelerating water to penetrate [30,31].

Fig. 5 shows the oil concentration variations of the filtrate with time, treating 2 g/L oil-in-water emulsion. The oil concentration in filtrate of the unmodified membrane decreases sharply in a short time. After 90 min, the oil concentration is less than 10 mg/L, and then gradually reaches the constant of 7 mg/L. It can also be explained by membrane fouling processes. The cake layer acts as a "second separation layer" to reject oil droplets. For the unmodified membrane, the continuous cake layer penetrates the membrane pores by deformation. For the modified membrane, the nano-coating on the membrane surface cannot prevent the cake layer formation. However, the nano-coating on the surface of membrane pore channels still repels oil droplets from penetrating. The oil concentration in the filtrate of the modified membrane is still lower than that of the unmodified membrane.

3.2.3. 4 g/L oil-in-water emulsion

Fig. 6 shows the fluxes of the unmodified and the modified membrane, treating 4 g/L oil-in-water emulsion. The variations of the fluxes are also similar to those treating 1 and 2 g/L emulsions. Therefore, the membrane fouling processes are similar. The differences of the fluxes between the unmodified membrane and the modified membrane are 133 L/m^2 h bar and 75 L/m^2 h bar at the first point and the 1,440th point of the time. It implies that some of the membrane pores are blocked, resulting in the decline of water penetration in spite of the existence of nano-TiO_2 coating.

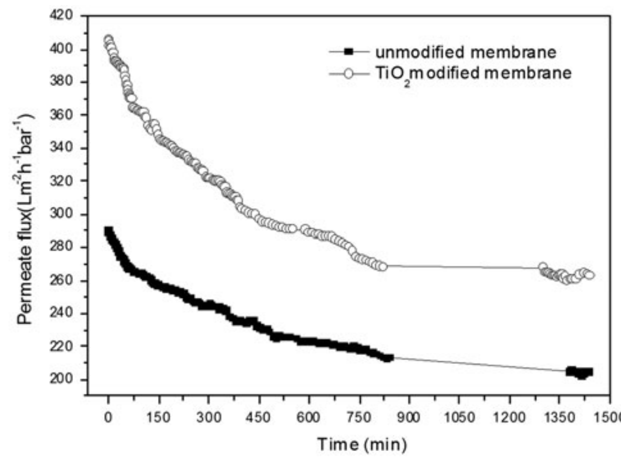

Fig. 6. Fluxes vs. time of the unmodified and the modified MF treating 4 g/L oil-in-water emulsion.

Fig. 7 shows the oil concentration variations of the filtrate with time, treating 4 g/L oil-in-water emulsion. The oil concentration of filtrate of the unmodified membrane decreases sharply in a short time. After 60 min, the oil concentration still keeps the value of 12–13 mg/L, indicating the filtrate cannot be discharged directly. The oil concentration of filtrate of the modified membrane quickly reaches the stable value of 8–9 mg/L. The oil concentration is higher than that treating 1 and 2 g/L emulsions. It can be induced that the cake layer becomes the continuous oil layer due to the high oil concentration of the feed. The oil droplets may penetrate the membrane through the larger pores by deformation. The hydrophilic capillary force generated by the nano-TiO_2 coating is so small that it is hard to repel the deformation of the oil droplets due to the larger pore size.

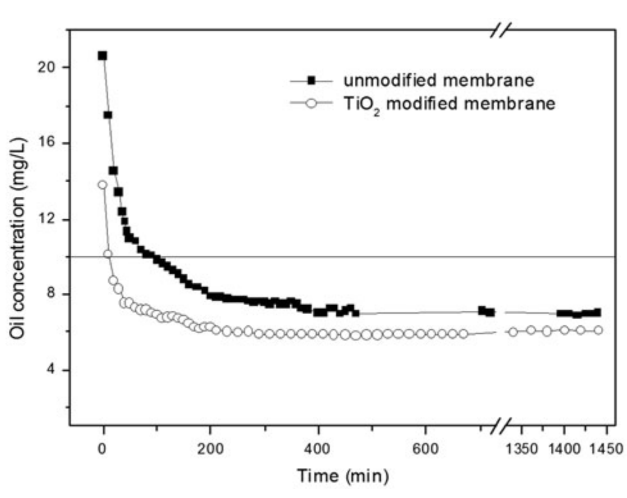

Fig. 5. Oil concentration variation of the filtrate via time.

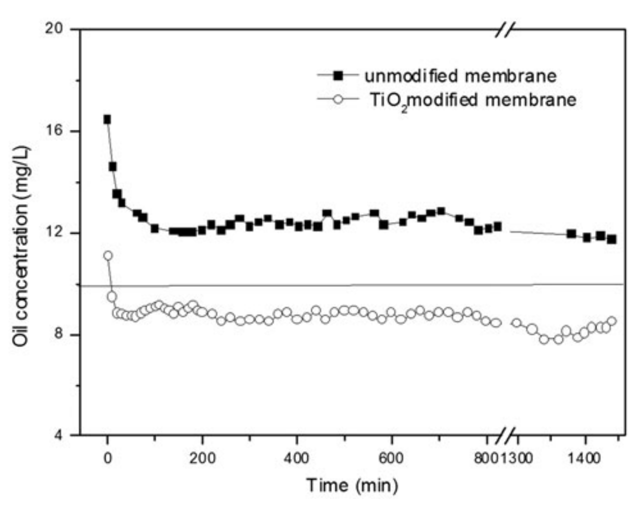

Fig. 7. Oil concentration variation of the filtrate via time.

Consequently, the operational parameters keep the constants under the circulation mode. The increase in the cake thickness results in the decrease of the flux and has the negative effect on the oil concentration of filtrate. However, the cake has the less effect on the filtrate oil concentration of the modified membrane, because the cake is in the destroy-form dynamic balance for the feed with low oil concentration. If the oil concentration of the feed is high enough, few oil droplets can penetrate through the larger membrane pores into the filtrate by deformation. On the whole, the continuous cake layer acts as a "second separation layer" which keeps the oil concentration in a stable state.

3.3. Separation performance under concentration mode

In an industrial membrane separation process, the removal of the filtrate has less effect on the oil concentration of the feed if the amount of the feed is abundant. The process could be regarded as circulation mode in laboratory. Otherwise, the oil concentration increases with the removal of the filtrate if the amount of the feed is limited. This process could be regarded as the concentration mode.

Fig. 8 shows the fluxes of the unmodified and the modified membrane under concentration mode. As can be seen, both the fluxes of the unmodified and the modified membrane decrease with the increase in the oil concentration of feed due to the removal of filtrate. The fluxes under concentration mode decline more dramatically than that under circulation mode at the same points of the permeating time. For the modified membrane, the fluxes obtained in the concentration mode are lower than that in circulation mode, when the oil concentrations are 1, 2, and 4 g/L, respectively. It indicates that the membrane fouling is seriously caused by the high oil concentration of the feed. To distinguish membrane fouling process, the membrane equipment is shut down without further operation, and thus the cross-flow velocity of feed is zero. In this case, the oil droplets come back to the feed body by diffusion. The concentration polar on membrane surface disappears. When the membrane equipment is open again, the concentration polar will be built step by step. Fig. 8 shows that the flux is obviously higher than that before the shutdown–open operation. And afterward, the flux declines sharply. Therefore, it can be concluded that the concentration polar is the main mechanism of membrane fouling for the modified membrane. However, once the continuous cake layer arises due to the high oil concentration, as discussed above, the cake layer becomes gradually the main membrane fouling. The cake layer also results in the decrease of the flux increment between the modified membrane and the unmodified one.

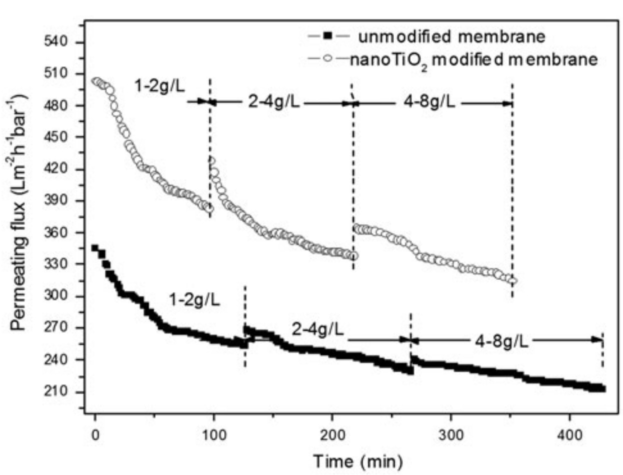

Fig. 8. Fluxes of the unmodified and the modified membrane under concentration mode.

It is not obvious that the above-mentioned phenomenon occurred in the flux of the unmodified membrane, indicating that the cake layer is always the main membrane fouling. Factually, the cake layer has a very important effect on the oil concentration of filtrate, because the cake layer acts as a "second separation layer" for the unmodified membrane. Fig. 9 shows the oil concentration variations of filtrate of the unmodified membrane and the modified membrane under concentration mode. As can be seen, the oil concentration of the unmodified membrane is higher than that of circulation mode, assuming the oil concentrations of the feed are same. Moreover, the shutdown–open operation has a significant effect on the oil concentration, because the oil droplets can easily penetrate the membrane pores by deformation without the obstacle of concentration polar layer. It indicates that the cake layer formed in concentration mode is not so denser than that formed in circulation mode. Therefore, under concentration mode, the oil concentration of filtrate of the unmodified membrane is easily affected by the factors which have the effect on the cake layer.

For the modified membrane, the concentration of the feed has less effect on the oil concentration of filtrate. The oil concentration under concentration mode is similar to that under circulation mode, assuming the same oil concentration of the feed. The reason is that the hydrophilic nano-TiO_2 coating prevents oil droplets from deforming. The oil droplets in the cake layer cannot penetrate the membrane pores by deformation. The verification of the oil concentration of the

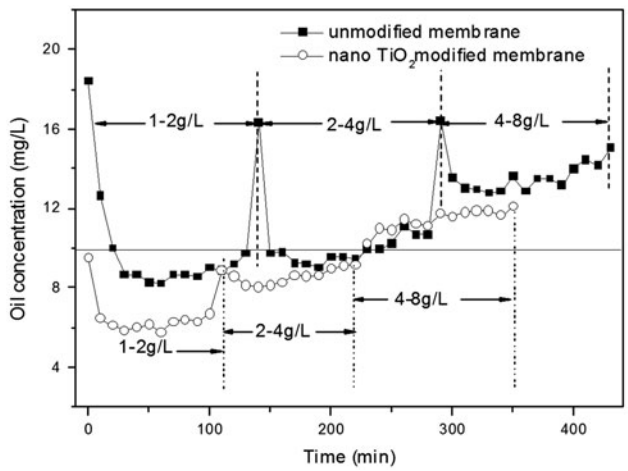

Fig. 9. Oil concentration variation of the filtrate via time under concentration mode.

feed has the effect on the cake layer on membrane surface, but has no effect on the hydrophilic nano-TiO_2 coating on the surface of the membrane pore channels. The concentration mode has less effect on the modified membrane.

4. Conclusion

In this study, the effect of the operation modes and the modification on the separation performances of the commercial MF membrane with and without modification of nano-TiO_2 coating, treating the stable oil-in-water emulsion. For the unmodified membrane, the operation mode has a less effect on the flux of the MF membrane, but has an important effect on the oil concentration of filtrate. The oil concentration in filtration under the concentration mode is higher than that under the circulation mode. For the modified membrane, the operation mode has a less effect on the flux and the oil concentration of filtrate, because the hydrophilic nano-TiO_2 coating prevents oil droplets from penetrating the membrane pores. Under both the operation modes, the fluxes of the modified membranes are higher than those of the unmodified membranes. The repelling action of the nano-TiO_2 coating on membrane surface is weakened, if the oil cake layer is formed from the feed with a high oil concentration.

Acknowledgments

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