Accepted Manuscript

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PII: S1383-5866(16)30139-3

DOI: <http://dx.doi.org/10.1016/j.seppur.2016.03.034>

Reference: SEPPUR 12921

To appear in: *Separation and Purification Technology*

Received Date: 26 October 2015

Revised Date: 10 March 2016

Accepted Date: 17 March 2016

Please cite this article as: D. Lu, W. Cheng, T. Zhang, X. Lu, Q. Liu, J. Jiang, J. Ma, Hydrophilic Fe₂O₃ dynamic membrane mitigating fouling of support ceramic membrane in ultrafiltration of oil/water emulsion, *Separation and Purification Technology* (2016), doi: <http://dx.doi.org/10.1016/j.seppur.2016.03.034>

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Hydrophilic Fe₂O₃ dynamic membrane mitigating fouling of
support ceramic membrane in ultrafiltration of oil/water
emulsion

Submitted by

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ABSTRACT

Oil/water (O/W) emulsion is daily produced and difficult to be treated effectively. Ceramic membrane ultrafiltration is one of reliable processes for the treatment of O/W emulsion, yet still hindered by membrane fouling. In this study, two types of Fe_2O_3 dynamic membranes (i.e., pre-coated dynamic membrane and self-forming dynamic membrane) were prepared to mitigate the fouling of support ceramic membrane in O/W emulsion treatment. Pre-coated dynamic membrane (DM) significantly reduced the fouling of ceramic membrane (i.e., 10% increase of flux recovery rate), while self-forming dynamic membrane aggravated ceramic membrane fouling (i.e., 8.6% decrease of flux recovery rate) after four filtration cycles. A possible fouling mechanism was proposed to explain this phenomenon, which was then confirmed by optical images of fouled membranes and the analysis of COD rejection. In addition, the cleaning efficiency of composite membranes (i.e., Fe_2O_3 dynamic membrane and support ceramic membrane) was enhanced by substitution of alkaline water backwash for deionized water backwash. The possible reason for this enhancement was also explained. Our result suggests that pre-coated Fe_2O_3 dynamic membrane with alkaline water backwash can be a promising technology to reduce the fouling of ceramic membrane and enhance membrane cleaning efficiency in the treatment of oily wastewater.

Keywords:

Dynamic membrane; Oil/Water emulsion; Ceramic membrane fouling; Membrane cleaning;

Abbreviations

O/W emulsion	Oil in water emulsion
UF	Ultrafiltration
DM	Dynamic membrane
SDBS	Sodium dodecyl benzene sulfonate
PLD	Pulsed-Laser Deposition
SEM	Scanning electron microscopy
FEEM	Fluorescence excitation-emission matrices
LSCM	Laser scanning confocal microscopy
pH_{pzc}	Isoelectric points
J	Instantaneous permeate flux ($\text{L m}^{-2} \text{ h}^{-1}$)
J_n	Initial permeate flux after each back wash ($\text{L m}^{-2} \text{ h}^{-1}$)
J_0	Pure water permeate flux of ceramic membrane ($\text{L m}^{-2} \text{ h}^{-1}$)
FR_n	Flux recovery rate of each cycle (%)
V	Permeate volume (L)
A	Membrane area (m^2)
Δt	Filtration duration (h)
C_f	COD concentrations of the feed (mg/L)
C_p	COD concentrations of the permeate (mg/L)
R	COD rejection rate (%)

1. INTRODUCTION

Oil-in-water (O/W) emulsion is stable dispersion of microscopic oil droplets (size $< 10\ \mu\text{m}$) in an aqueous solution and daily produced by various industrial activities [1-3]. The ever-increasing O/W emulsion with high pollution loads has become a severe environmental issue. Ceramic ultrafiltration membrane is an effective technology for O/W emulsion separation. It has been widely applied in the treatment of O/W emulsion with its advantages of no addition of chemicals, relatively low operation cost and stable quality of purified water [4-6]. However, the performance of ceramic UF membrane is compromised by severe oil fouling during the treatment of O/W emulsion, which remains a major challenge for ceramic membrane to be successfully applied in O/W emulsion treatment [7-9].

Extensive efforts have been dedicated toward membrane modification through introducing hydrophilic material to reduce membrane fouling, e.g., the antifouling ability of PVDF membrane was significantly enhanced through post-fabrication tethering of surface-tailored superhydrophilic silica nanoparticles. [10-13]. However, the process of membrane modification is relatively complicated, and thus leading to an increase cost in practical industrial application. Dynamic membrane has advantages of simple preparation, ease of removal and regeneration [14]. It can be formed in situ by deposition of a suspension on a porous support, which was used as filtration membrane to enhance the rejection rate of protein or salt, etc. [15]. In the treatment of O/W emulsion, membrane fouling is mainly caused by direct contact and interaction between oil droplets and membrane surface [16]. Therefore, hydrophilic

dynamic membrane formed on the surface of support membrane can be used to mitigate fouling of support membrane through enhancing the hydrophilicity of membrane surface and reducing exposures of support membrane to oil foulants.

Dynamic membranes can be classified into two basic types: pre-coated membrane and self-forming membrane [17]. Pre-coated membrane is formed before the filtration of target solution by deposition of dynamic membrane material on the surface of a porous support. Self-forming membrane is formed during the filtration of target solution that contains dynamic membrane material. To our best knowledge, antifouling performance of these two types of dynamic membranes has never been compared, which will be helpful for the selection of appropriate dynamic membrane for O/W emulsion treatment. In addition, since membrane fouling is inevitable, an efficient membrane cleaning method for dynamic membrane under mild conditions is essential for its sustainable O/W emulsion treatment.

In this study, highly hydrophilic Fe_2O_3 dynamic membrane prepared by two methods was used as a protective membrane to reduce the fouling of support ceramic membrane in O/W emulsion treatment. The antifouling performance of Fe_2O_3 composite membranes (i.e., Fe_2O_3 dynamic membrane and ceramic membrane) was compared, and possible fouling mechanism was proposed. In addition, correspondingly cleaning method for Fe_2O_3 composite membranes was developed. This study provides a facile strategy to effectively reduce the fouling of ceramic membrane and enhance membrane cleaning efficiency in oily wastewater treatment.

2. Material and Methods

2.1 Preparation and characterization of O/W emulsion

Crude oil (Saudi Aramco) and sodium dodecyl benzene sulfonate (SDBS) (Sigma-Aldrich) were used as base oil and surfactant, respectively, to prepare oil/water (O/W) emulsion. Crude oil (100 mg L^{-1}) and SDBS (10 mg L^{-1}) were mixed in ultra-pure water (Milli-Q Academic, Millipore) and sonicated (Q700, Qsonica) for 50 min. The prepared O/W emulsion was at pH 6 (i.e., pH of the ultra-pure water) and stable in terms of average oil-droplet size and zeta potential for 5 days. All the experiments were conducted in the stabilization period of the emulsion.

The crude oil/water emulsion was characterized in terms of the size distribution of oil droplets and zeta potential. They were measured with a particle size and zeta potential analyzer (Nano ZS, Malvern). Microscopic configuration of oil droplets was characterized with laser scanning confocal microscopy (LSCM) (LSM710, Carl Zeiss) using Nile red (Sigma-Aldrich) as a stain [18].

2.2 Preparation and characterization of Fe_2O_3 composite membranes

Fe_2O_3 composite membranes consisted of Fe_2O_3 dynamic membrane (acted as protective and filtration membrane) and ceramic membrane (acted as support and filtration membrane) (Molecular weight cut off 50 kDa, TAMI Industries).

2.2.1 Preparation and characterization of Fe_2O_3 dynamic membrane

Fe_2O_3 particles with particle size larger than $0.45 \mu\text{m}$ were screened out for membrane preparation through filtration of Fe_2O_3 suspension (Sigma-Aldrich) by $0.45 \mu\text{m}$ membrane. The preparation process of dynamic membrane usually leads to

the decline of membrane flux [15, 19]. The application of larger particles would minimize flux loss caused by pore blockage of small particles or the dense cover of small particles on membrane surface. **Scheme S1 (Supporting Information, SI)** shows two preparation methods of Fe_2O_3 dynamic membrane. Pre-coated Fe_2O_3 dynamic membrane was formed before the treatment of O/W emulsion as follows: Fe_2O_3 particles were first added into deionized water to prepare Fe_2O_3 suspension with Fe_2O_3 concentration of 1 g/L. The suspension was then filtered by support ceramic membrane at 1 bar. The permeate flux vs. time profile was recorded with an electronic balance connected to a desktop. The filtration of Fe_2O_3 suspension ceased at the permeate volume of 0.065 L, and the deposition dose of Fe_2O_3 on ceramic membrane surface was theoretically around 0.065 g. Self-forming dynamic membrane was formed during the treatment of O/W emulsion: Fe_2O_3 particles were directly added into the O/W emulsion at Fe_2O_3 concentration of 1g/L. Then, the O/W emulsion and Fe_2O_3 suspension were simultaneously filtered by support membrane. The filtration ceased at the permeate volume of 0.065 L, and the deposition dose of Fe_2O_3 on membrane surface was also approximately 0.065 g in theory.

Dynamic Fe_2O_3 membrane was characterized in terms of the average size of Fe_2O_3 particles, surface charge, hydrophilicity and microscopic configurations. The average size of Fe_2O_3 particles was measured with a zeta potential analyzer (Nano ZS, Malvern). The surface charge of metal oxides is developed through ionization of surface hydroxyl groups, which is pH dependent [20]. The isoelectric point of Fe_2O_3 particles was measured by cross-partition of two zeta potential-pH curves obtained at

different ionic strengths (adjusted with sodium chloride) with a zeta potential analyzer [21]. The hydrophilicity of Fe_2O_3 dynamic membrane was characterized with contact angle measurement (Attension, KSV). Since the infiltration of water droplet into large pores of dynamic membrane was too fast to measure contact angle, and high surface roughness of dynamic membrane also influences contact angle, [22, 23] Fe_2O_3 particles of dynamic membrane were deposited on a smooth silicon wafer (roughness < 0.5 nm) by Pulsed-Laser Deposition (PLD) (COMPexPro201, Coherent) for contact angle measurement. Contact angle of Fe_2O_3 deposited wafer was measured by 10 times using a water-droplet volume of 5 ± 0.2 μL . The mean value of contact angles was calculated with a standard deviation below 2° . The cross section morphologies of dynamic membranes were investigated with scanning electron microscopy (SEM) (Sirion, FEI) using gold vapor deposition for sample preparation.

2.2.2 Characterization of support ceramic membrane

Support ceramic membrane was characterized in terms of surface charge and hydrophilicity and microscopic configurations. The surface charge of ceramic membrane was measured by Electrokinetic Analyzer for Solid Surface Analysis (SurPASS, Anton Paar). The hydrophilicity was characterized with contact angle measurement following the same measurement procedure as that of dynamic membrane: filtration layer material of ceramic membrane (i.e., TiO_2 and ZrO_2 components) were deposited on a smooth silicon wafer and used for contact angle measurement. The cross section morphologies of ceramic membrane were investigated with SEM.

2.3 Fe_2O_3 composite membranes for O/W emulsion treatment

A dead-end filtration setup with back wash function was applied to investigate the fouling of Fe_2O_3 composite membranes in the treatment of O/W emulsion (**Fig. 1**). The filtration process of O/W emulsion was conducted for 4 cycles. Each cycle consists of dynamic membrane preparation, forward filtration of O/W emulsion and back wash as follows: 1) the initial permeate flux was obtained by measuring the pure water flux of ceramic membrane alone or the composite membranes at 1 bar for 30 min; 2) dynamic membrane was prepared; 3) the emulsion was filtered by ceramic membrane or the composite membranes at 1 bar until the permeate volume reached 0.065 L.; 4) back wash with pure water or alkalescent water was introduced at 2 bar for 4 min after the filtration of emulsion, and Fe_2O_3 particles and oil foulants removed by back wash were collected in disposal tank. It should be noticed that the preparation process of self-forming membrane was also the filtration process of O/W emulsion.

Fig. 1. Schematic diagram of dead-end filtration setup with back wash function.

The antifouling performance of Fe_2O_3 composite membranes was evaluated by flux recovery rate of each filtration cycle. The instantaneous permeate flux J ($\text{L m}^{-2} \text{ h}^{-1}$) was calculated with Eq. (1). Flux recovery rate of each cycle (FR_n) was calculated with Eq. (2), which represents the recovery extent of membrane permeability after back wash. Higher flux recovery rate indicates better antifouling performance and less fouling of support ceramic membrane.

$$J = V/A\Delta t \quad (1)$$

V (L) is the permeate volume, A (m^2) denotes the membrane area, and Δt (h) represents filtration duration.

$$\text{FR}_n = J_n/J_0 \times 100\% \quad (2)$$

J_n denotes the initial permeate flux after each back wash ($n = 1, \dots, 6$), and J_0 is pure water permeate flux of ceramic membrane.

In addition, COD rejection (R %) of the membranes was investigated with Eq. (3). The fluorescent organic contents in the feed and the permeates of O/W emulsion filtered by two composite membranes and ceramic membrane alone were also compared by three-dimensional fluorescence excitation-emission matrices (FEEM) (Aqualog CDOM Fluorometer, Horiba Scientific). The wavelength range of excitation and emission scans were 200-600 nm and 211.44-620.81 nm, respectively.

$$R = (1 - C_p/C_f) \times 100\% \quad (3)$$

R is the COD removal rate, and C_f and C_p are COD concentrations of the feed and permeate, respectively.

2.4 Enhanced backwash for Fe_2O_3 composite membranes

The pH of backwash fluid was changed from 6.0 to 8.0 by substitution of deionized

water (pH = 6.0) with alkalescent water (pH = 8.0) to enhance the cleaning efficiency of backwash for composite membranes. The alkalescent water was established at pH 8.0 with 10 mM phosphate buffer through addition of sodium dihydrogen phosphate and hydrochloric acid (Sigma-Aldrich).

3. Results and Discussion

3.1 Oil/water emulsion properties

Table 1 presents major characteristics of crude oil/water emulsion. O/W emulsion was negatively charged at pH 6.0 and pH 8.0. The zeta potential of oil droplets slightly increased from -45.5 ± 3.0 to -36.52 ± 3.0 mV with pH increase. The average size of oil droplets at pH 6.0 was almost the same as that at pH 8.0, which was independent to the pH. This phenomenon is consistent with that reported by Lobo et al [24]. The images of oil droplets show that the emulsion was composed of fine oil droplets which uniformly dispersed in the aqueous phase (**Fig. 2**). During the experiments, the emulsion was relatively stable in terms of droplet size distribution and zeta potential.

Table 1. Properties of crude oil/water emulsion *

pH	Zeta potential(mV)	Average droplet size (nm)
6.0	-45.5 ± 3.0	369.5 ± 12.8
8.0	-36.5 ± 3.0	362.2 ± 15.0

*Oil dosage = 100 mg L⁻¹; volume prepared = 12 L; sonication time = 50 min.

Fig. 2. Microscopic images of oil droplets in crude oil/water emulsion obtained with LSCM.

3.2 Properties of Fe_2O_3 composite membranes

Table 2 summarizes the properties of Fe_2O_3 dynamic membrane and support ceramic membrane. The average size of Fe_2O_3 particles was 784.4 nm that is much larger than the pore size of support membrane, indicating that Fe_2O_3 particles would deposit on membrane surface rather than penetrate into membrane pores. The isoelectric points (pH_{pzc}) of dynamic membrane and support membrane are 6.4 and 4.8, respectively (**Table 2** and **Fig. S1, SI**). The surface charge of Fe_2O_3 DM and support membrane would be positive and negative, respectively, during the process of membrane preparation, emulsion treatment and deionized water backwash ($\text{pH} = 6.0$). Therefore, electrostatic attraction would occur between Fe_2O_3 DM and support membrane which contributes to the stabilization of dynamic membrane on support membrane. While the surface charge of Fe_2O_3 DM would change to be negative in the period of alkaline water backwash ($\text{pH} = 8.0$), support membrane would remain negatively charged (**Table 2**). In this case, electrostatic repulsion would occur between Fe_2O_3 DM and support membrane. This would help for the detachment of

Fe₂O₃ DM from support membrane. The hydrophilicity of Fe₂O₃ DM was compared with that of ceramic membrane (**Table 2** and **Fig. S2, SI**). Fe₂O₃ dynamic membrane (contact angle = 26.6°) was more hydrophilic than ceramic membrane (contact angle = 39.9°). Since higher hydrophilicity indicates lower fouling potential, [25] Fe₂O₃ dynamic membrane covering on ceramic membrane surface would significantly improve the antifouling performance of ceramic membrane.

Table 2. Properties of dynamic membrane and ceramic membrane*

Membrane	Average particle size (nm)	pH _{pzc}	Contact angle
Fe ₂ O ₃ dynamic membrane	784.4 ± 30.5	6.4	26.6 ± 1.6
Support ceramic membrane	-	4.8	39.9 ± 2.0

* pH_{pzc} and contact angle were obtained from Figure S1 and Figure S2 of Supporting Information.

The surface optical images and the cross-section SEM images of support ceramic membrane and two Fe₂O₃ composite membranes were shown in **Fig. 3** and **Fig. 4**, respectively. Compared with ceramic membrane (**Fig. 3A** and **Fig. 4A**), pre-coated composite membranes had a dynamic membrane evenly covered on support membrane surface (**Fig. 3B** and **Fig. 4B**). The permeate flux remained stable during the preparation process (**Fig. 5**), indicating that the pre-coated dynamic membrane had almost no influence on the flux of support membrane. For self-forming composite membranes (**Fig. 3C** and **Fig. 4C**), a more compact dynamic membrane was observed on support membrane which was confirmed by the decline of permeate flux (**Fig. 5**). This phenomenon may be ascribed to that Fe₂O₃ particles and oil droplets superimposed on each other during the preparation process, in which oil droplets

played an adsorption bridging effect between Fe_2O_3 particle-particle and particle-support membrane.

Fig. 3. Optical images of support ceramic membrane (A), Pre-coated composite membranes (B) and Self-forming composite membranes (C); below is the membranes after filtration process.

Fig. 4. Cross-section SEM of support ceramic membrane (A), Pre-coated composite membranes (B) and Self-forming composite membranes (C)

Fig. 5. Normalized permeate-flux curves for preparation of Fe_2O_3 dynamic membrane.

3.3 Fe_2O_3 composite membranes for O/W emulsion treatment

Two Fe_2O_3 composite membranes and ceramic membrane alone were, respectively, used for the treatment of O/W emulsion. Their antifouling performances were evaluated by flux recovery rate of each filtration cycle. **Fig. S3 (SI)** shows the normalized permeate flux decline of these membranes as a function of filtration time. All the membranes had flux decline during the filtration of O/W emulsion, which was caused by membrane fouling and cake layer [26].

Fig. 6 presents a comparison of flux recovery rate (FR_n , n represents the filtration cycles) of three membranes after each back wash. The FR_n of all membranes declined as the number of filtration/backwash sequence increased, indicating that their permeability decreased gradually. These membranes had significantly different flux recovery rates after four filtration cycles (**Fig. 6**). Pre-coated composite membranes, self-forming composite membranes and support membrane alone had 46.1%, 27.5% and 36.1% flux recovery rate, respectively. Pre-coated DM enhanced the flux recovery rate by 10% and significantly reduced the membrane fouling. In contrast,

self-forming DM decreased the flux recovery rate by 8.6% and aggravated the membrane fouling. However, self-forming DM has been reported to reduce membrane fouling in the cross-filtration of O/W emulsion through promotion of shear stress [27, 28]. This contrary trend in our study may be explained by that the antifouling performance of self-forming DM was investigated under dead-end filtration condition. The detailed analysis for this phenomenon was provided in the following proposed fouling mechanism. The filtration results demonstrate that pre-coated Fe_2O_3 dynamic membrane can be used as protective membrane to effectively reduce membrane fouling of ceramic membrane in O/W emulsion treatment.

Fig. 6. Decline of flux recovery rates for three membranes backwashed at pH = 6.0.

In addition, COD rejection rates ($R\%$) of three membranes were listed in **Table 3**. The COD rejection rates of ceramic membrane ($R\% = 95.7\%$) and pre-coated composite membranes ($R\% = 95.0\%$) were close to each other and less than that of self-forming composite membranes ($R\% = 97.8\%$). Higher COD rejection of self-forming composite membranes further confirmed that a more compact dynamic membrane was formed on the surface of support membrane.

Table 3. COD rejection rate of three membranes*

Membrane	R%
Ceramic membrane	95.7
Pre-coated composite membranes	95.0
Self-forming composite membranes	97.8

* COD of feed emulsion is 327 mg/L

The fluorescent organic contents of O/W emulsion before and after filtration by three membranes were also compared using FEEM (**Fig. 7**). Two major peaks adjacent to each other (centered at Ex/Em of 215/297 and 225/337 nm) presented in feed (**Fig. 7a**), which can be ascribed to aromatic-like compounds (benzene derivatives) [29][30]. Another peak area centered at Ex/Em of 250/450 nm with relatively intense signals can be assigned to fulvic acid-like compounds [30]. In contrast to the feed, most of the fluorescent constituents were removed to great extent by three membranes (**Fig. 7b, c, d**). The emulsion filtered by self-forming composite membranes had the lowest fluorescent organic contents indicating their high oil rejection (**Fig. 7d**), which is consistent with the COD rejection. Taken together, those results indicate that Fe_2O_3 composite membranes are highly efficient to remove oil from O/W emulsion.

Fig. 7. FEEM spectra of the feed and the permeates of emulsion treated by three membranes.

3.4 Possible membrane fouling mechanism

Membrane fouling mechanism of three membranes in O/W emulsion treatment was hypothesized and schematically shown in **Scheme 1**. The following two reasons may account for the better antifouling performance (i.e., high flux recovery rate) of pre-coated Fe_2O_3 composite membranes (**Scheme 1b**): 1) high hydrophilicity of Fe_2O_3 DM enhanced the removal of oil foulants from its surface by backwash; and 2) the Fe_2O_3 dynamic membrane on surface of support membrane reduced the exposure of support membrane to oil foulants, and Fe_2O_3 particles of surface layer directly interacted with oil foulants were easily washed out by backwash.

Scheme 1. Proposed membrane fouling mechanism for three membranes

In contrast, self-forming Fe_2O_3 composite membranes had a higher fouling propensity (i.e., low flux recovery rate). This phenomenon can be explained by two reasons in **Scheme 1c**. The first reason was that some oil droplets absorbed on Fe_2O_3 particles in the suspension before the preparation of dynamic membrane, and some oil droplets and Fe_2O_3 particles were simultaneously deposited on support membrane surface during the preparation process. These oil droplets were stuck in the gaps of Fe_2O_3 particles (i.e., the pores of dynamic membrane) and cannot be easily removed by backwash, thus leading low flux recovery and high rejection of oil droplets. This

hypothesis was supported by the results of COD rejection and FEEM for self-forming composite membranes (**Table 3** and **Fig. 7**). The other reason was that Fe_2O_3 particles on the surface of self-forming composite membranes were not readily washed out, because they were “glued” on each other due to the adsorption bridging effect of oil foulants between the gaps. The photographs of three fouled membranes after backwash confirmed this assumption (**Fig. 3**). Compared with ceramic membrane and pre-coated composite membranes (**Fig. 3a and 3b**), self-forming composite membranes had more oil foulants and Fe_2O_3 particles adhered to their surface (**Fig. 3c**).

3.5 Enhanced backwash for pre-coated Fe_2O_3 composite membranes

The fouling of ceramic membrane can be increased or reduced through electrostatic interactions between membrane surface and solutes, which was largely influenced by membrane surface charge [24, 31]. The surface charge of metal oxides is developed through protonation/deprotonation of surface hydroxyl groups at pH below or above pH_{pzc} of the metal oxide [20]. In this study, electrostatic attraction between positively charged Fe_2O_3 DM (**Table 2**) and negatively charged oil droplets (**Table 1**) may compromise the cleaning efficiency by water backwash (pH 6.0). In order to improve the cleaning efficiency of pre-coated Fe_2O_3 composite membranes, alkalescent water was used as backwash fluid to replace deionized water (i.e., pH changing from 6.0 to 8.0). In this case, the surface charge of Fe_2O_3 DM changes from positive to negative according to its pH_{pzc} (**Table 2**).

The flux decline was also observed on support membrane alone and pre-coated

Fe_2O_3 composite membranes in O/W emulsion treatment using alkaline water backwash (i.e., pH = 8.0) (**Fig. S4, SI**). These two membranes backwashed by deionized water and alkaline water were compared in terms of flux recovery rates (**Fig. 8**). The flux recovery rate of Fe_2O_3 composite membranes after alkaline water backwash ($\text{FR}_3 = 53.7\%$) increased by 7.6% compared with that after deionized water backwash ($\text{FR}_3 = 46.1\%$). The enhancement of flux recovery rate by alkaline water backwash can be attributed to the reversal of Fe_2O_3 surface charge (i.e., from positive to negative) and subsequently the change of electrostatic interaction.

Fig. 8. Decline of flux recovery rates for pre-coated composite membranes and ceramic membrane backwashed at pH = 6.0 and pH = 8.0, respectively.

Scheme 2 shows the possible fouling mechanism. As described above, Fe_2O_3 dynamic membrane was negatively charged when alkaline water was used as backwash fluid (pH = 8.0). Electrostatic repulsion would occur between Fe_2O_3 DM and similarly charged oil droplets, which contributes to the desorption of oil droplets on dynamic membrane thus causing high recovery rate. Furthermore, electrostatic repulsion would also occur between Fe_2O_3 particles and the support membrane

surface with the same charge. This would facilitate the detachment of some Fe_2O_3 particles from support membrane, which carried off some oil foulants also causing higher recovery rate. It should be noticed that oil saponification by alkaline water had almost no influence on flux recovery, which can be verified by the similar flux recovery rates of ceramic membrane backwashed by deionized water ($\text{FR}_3 = 36.1\%$) and that by alkaline water ($\text{FR}_3 = 37.4\%$) (**Fig. 8**). The FR values of pre-coated Fe_2O_3 composite membranes backwashed by deionized water and alkaline water were both higher than that of ceramic membrane in **Fig. 8**. This again demonstrates the pre-coated Fe_2O_3 DM can effectively reduce membrane fouling in O/W emulsion treatment.

Scheme 2. Proposed interaction between Fe_2O_3 DM and oil droplets, Fe_2O_3 DM and support membrane during backwash at two pH values

The fouled Fe_2O_3 particles washed out by alkaline water can be treated through ozone technology and reused for the preparation of dynamic membrane. Under this

alkalescent condition, ozone oxidation would be more efficient for oil removal from Fe_2O_3 particles that can act as a oxidation catalyst [32, 33]. In addition, alkalescent water backwash ($\text{pH} = 8.0$ and room temperature $25\text{ }^\circ\text{C}$) has distinct advantage of less corrosion to membrane filtration system and lower cost than alkaline backwash ($\text{pH} > 10$ and high temperature demand 80°C) [34, 35]. Therefore, it could be significantly valuable for the application of alkalescent water backwash for Fe_2O_3 composite membranes in O/W emulsion treatment to enhance cleaning efficiency and prolong the life of membrane filtration system.

4. Conclusion

1. Pre-coated Fe_2O_3 dynamic membrane had better performance for O/W emulsion treatment than self-forming dynamic membrane in terms of reducing ceramic membrane fouling. It is a simple and efficient strategy to reduce the fouling of support membrane in oily wastewater treatment.
2. Fouling mechanism for two types of Fe_2O_3 dynamic membranes was proposed and confirmed, which helps to select appropriate dynamic membrane for oily wastewater treatment.
3. High cleaning efficiency for Fe_2O_3 composite membranes under mild conditions was obtained through using alkalescent water as backwash fluid, which is essential for sustainable O/W emulsion treatment.

ASSOCIATED CONTENT

Supporting Information.

One table, one scheme and four figures are included in the supporting information.

This information is available free of charge via the Internet at

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ACKNOWLEDGEMENTS

This work was supported by National Key Technology Support Program of China (2012BAC05B02). The authors want to thank Daqing Oilfield Company of China for providing the crude oil for the experiment.

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Graphical abstract

HIGHLIGHTS

1. A facile strategy was provided to reduce membrane fouling in O/W emulsion treatment.
2. Antifouling performances of pre-coated and self-forming Fe_2O_3 dynamic membranes were compared.
3. Fouling mechanism for two types of dynamic membranes was proposed.
4. An eco-friendly efficient cleaning method for Fe_2O_3 composite membranes was developed.