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# Advanced treatment of produced water from ASP (alkali/surfactant/polymer) flooding with polyethersulfone UF membrane for reinjection

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## ABSTRACT

Alkali/surfactant/polymer (ASP) flooding technology, as an important technology of tertiary oil extraction, has been successfully and widely applied in Daqing Oil Field (China). However, large amounts of produced water from ASP flooding (PWFAF) are always generated concomitantly. PWFAF is a more complex and stable emulsion system compared with the conventional produced water, and it is more difficult to reduce the oil content to meet the criteria of injection water by conventional water treatment systems, especially for low and ultra-low permeability reservoirs. In the present paper, advanced treatment of PWFAF with polyethersulfone (PES) ultrafiltration (UF) membranes in dead-end filtration was conducted, and the main purpose was to evaluate the effectiveness of the membrane on advanced treatment of PWFAF for reinjection. The effects of trans-membrane pressure (TMP), pH and total dissolved solids (TDS) on membrane flux decline were examined; the rejection rates of anionic polyacrylamide (APAM), sodium dodecyl benzene sulfonate (SDBS), especially oil as well as membrane cleaning methods were also investigated. The results demonstrated that TMP exhibited a more significant influence on membrane flux decline compared with pH and TDS, but the TMP, pH and TDS all exhibited little influence on the rejection rates of oil. The rejection rate of oil was more than 95%, and the oil content was always below 5 mg $L^{-1}$ in the permeate. A flux recovery rate of 95% could be obtained by a combined cleaning method of citric acid solution (0.5 wt. %) soak, sodium hydroxide solution (0.5 wt. %) soak and SDBS solution (0.5 wt. %) soak. Scanning electron microscopy (SEM) was employed for intuitive observation and comparison of the membrane morphology. It was concluded that the PES UF membrane had a potential feasibility and application for advanced treatment of the PWFAF.

*Keywords:* ASP flooding; Produced water; Polyethersulfone; Ultrafiltration; Membrane flux; Membrane cleaning

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## 1. Introduction

In recent years, many Chinese oil fields have been in their mid-stage or final stage of development, and technologies for tertiary oil extraction have been developed to improve oil recovery. Alkali/surfactant/polymer (ASP) flooding technology, as an important technology of tertiary oil extraction, has been successfully used full-scale in China [1–3]. Alone in Daqing Oil Field, oil production by ASP flooding technology had reached 3.5 × $10^6$ tons in 2015 (2015 Annual Report of China National Petroleum Corporation). However, large amounts of produced water from ASP flooding (PWFAF) are always generated along with ASP flooding oil extraction. According to recent statistics, the amount of PWFAF was beyond 2.8 × $10^7$ tons in Daqing Oil Field in 2015. Nevertheless, this problem is becoming more serious with the decreasing oil resource and the increasing application of ASP flooding technology. Due to the use of alkali, surfactant and polymer in the injected water by ASP flooding technology, the PWFAF contains not only large quantities of crude oil, salinity and suspended solids, but also large quantities of residual chemicals such as alkali, surfactant and polymer [4,5]. The surfactant could remarkably decrease oil-water interfacial tension and zeta potential on the surface of the oil droplets, making the PWFAF significantly emulsified. Thus the PWFAF is a more complex and stable emulsion system and more difficult to treat compared with produced water from water flooding, steam flooding and polymer flooding.

One of the important ways to the application of PWFAF is reinjected into stratum for reuse. A series of conventional technologies of treating produced water in oil fields have been developed [6–10], including gravity separation and skimming, dissolved air flotation, de-emulsification as well as coagulation and flocculation. However, for low and ultra-low permeability reservoirs, the local criteria requests the content of crude oil in the reinjection water should be lower than 5 mg $L^{-1}$ as specified in the Water Quality Standard and Practice for Analysis of Oilfield Injecting Waters in Clastic Reservoirs (SY/T 5329-2012) in China. Such stringent standard is difficult to meet by these conventional technologies. Therefore, with the increasing application of ASP flooding technology, as well as the progressive exploitation of the low and ultra-low permeability reservoirs, it is becoming more and more urgent and crucial to research for an effective process to treat the PWFAF for reinjection.

Membrane technology has gained significant popularity in water and wastewater treatment in recent years [11–13]. Distinct advantages of membrane technology for the treatment of produced water include reduced sludge, high quality of permeate and so on [14]. In many literatures, it has been reported that the membrane is an effective process alternative to treat produced water [15–18]. Although considerable researches have been devoted to produced water from water flooding, steam flooding and polymer flooding, rather less attention has been paid to PWFAF which is a relatively more complex and stable emulsion system and more difficult to treat.

In the present paper, a polyethersulfone (PES) ultrafiltration (UF) plate membrane in dead-end filtration mode was proposed for advanced treatment of PWFAF. The main aim of the paper is to evaluate the effectiveness of the membrane on advanced treatment of PWFAF for reinjection. The effects of important factors such as trans-membrane pressure (TMP), pH and total dissolved solids (TDS) on membrane flux decline were examined. Furthermore, the rejection rates of anionic polyacrylamide (APAM); sodium dodecyl benzene sulfonate (SDBS), especially oil; as well as membrane cleaning methods were also investigated.

## 2. Material and methods

### 2.1. Experimental setup

The schematic diagram of the experimental setup is shown in Fig. 1. This set-up contained a dead-end stirred filtration cell (MSC500, Mosu, CN) with a volume capacity of 300 mL with inner diameter of 68.5 mm, and the effective area of membrane is 36.85 $cm^2$. The PES UF plate membrane obtained from SePRO Corporation (USA) was used in this study, and some important characteristics of the membrane are shown in Table 1. The new membranes were soaked in Milli-Q water for 1 h prior to each run to remove the protective liquid such as formaldehyde. Each membrane was initially compacted for 1 h at 0.25 MPa using Milli-Q water prior to the determination of permeability for water. All the UF experiments were carried out under a certain TMP with extra nitrogen gas as pressed force, at room temperature of 25 ± 2°C and at magnetic stirring speed of 100 rpm. The stirring rate was maintained constant over all the experiments. The permeate flux, monitored automatically by a computer, was calculated from permeate weight and measured using an electronic balance (±0.01 g) with an accuracy of 0.5% by timed collection.

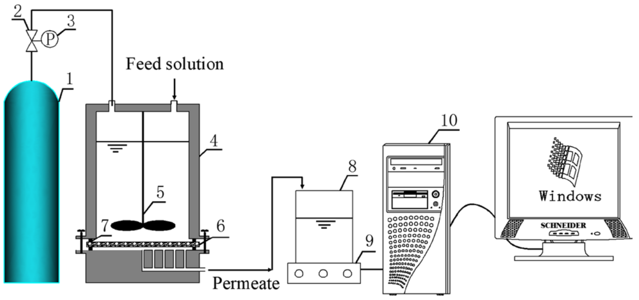

Fig. 1. Schematic diagram of the experimental setup.
Note: 1 = nitrogen gas, 2 = valve, 3 = pressure meter, 4 = ultrafiltration cell, 5 = magnet rotor, 6 = ultrafiltration membrane, 7 = sealing washer, 8 = flask, 9 = electronic balance, 10 = computer.

Table 1
Membrane characteristics

| Property | UF membrane |
|---|---|
| Type | Plate |
| Material | PES |
| MWCO (kDa) | 30 |
| Water flux at 25 ± 2°C and 0.25 MPa (L $m^{-2}$·$h^{-1}$) | 200~220 |
| Diameter (mm) | 68.5 |
| Effective area ($cm^2$) | 36.85 |
| Contact angle of water (°) | 74.5 |

### 2.2. Chemicals

Crude oil, APAM, SDBS and several kinds of inorganic salts were introduced to prepare the simulated PWFAF. The crude oil was provided by the 2nd Production Factory of Daqing Oil Field in China, with oil content of more than 99.5 wt. %, a density of 863 kg m$^{-3}$ (at 40°C) and a viscosity of 62.4 mPa s (at 40°C). Because the molecular weight (MW) of APAM in the PWFAF in Daqing Oil Field was normally in a range of (2~5) × 10$^3$ kDa, APAM with an average MW of 4 × 10$^3$ kDa and a hydrolysis degree of 23~27% manufactured by SNF Company (France) was used in this study. The SDBS of analytical grade was obtained from Shanghai Chemical Reagent Research Institute (Shanghai, CN). All other chemicals used in this study were of analytical grade unless otherwise specified.

### 2.3. Preparation of stock brine

The stock brine was prepared based on the in situ PWFAF after pretreatment with the traditional technology, that is, coagulation, gravity sedimentation, sand filtration and disinfection in Daqing Oil Field. Some important qualities of the PWFAF after pretreatment are shown in Table 2. According to the qualities, with particular attention to the ion composition, the stock brine was prepared. The salts contained in the brine were as follows (mg L$^{-1}$): [$NaHCO_3$] 26,000, [NaCl] 10,000, [$Na_2SO_4$] 3,000, [$MgCl_2 \cdot 6H_2O$] 855 and [$CaCl_2$] 600. Therefore, the TDS of the stock brine was 40,000 mg L$^{-1}$.

### 2.4. Preparation of simulated PWFAF

Based on the qualities shown in Table 2, with particular attention to the diameter of oil droplets, the method for preparation of the simulated PWFAF in the lab was proposed, as follows: (1) A 20-L amount of Milli-Q water and 5 g of crude oil were added to a glass vessel, and the mixture was heated at 40°C in a water bath for 1 h. Then 1 L of the heated mixture was taken from the bottom of the vessel to a 1,000 mL beaker and emulsified for 15 min at 13,000 rpm with an emulsifier (AE500S-P 90G, Angni, CN); (2) the mixture in the beaker was transferred to a 1,000 mL separatory funnel and allowed to settle for 24 h. Then, about 800 mL of the lower mixture was drained from the separatory funnel into a beaker to obtain the oil-water mixture and its oil concentration was determined (different for each preparation), while the upper mixture (about 200 mL) was discarded; (3) a 1,000-mL stock solution with APAM concentration of 500 mg L$^{-1}$ was prepared by slowly adding 0.50-g APAM solid (dry weight) into a proper amount of Milli-Q water (900–950 mL) while the solution was being stirred. After calibration to 1,000 mL in a 1,000 mL volumetric flask with Milli-Q water, the stock solution was mixed overnight and should be used within 12 h; (4) a 400-mL amount of the stock APAM solution, 200 mg of SDBS, a proper amount of the stock brine, and a proper amount of the oil-water mixture were added to 2,000 mL volumetric flask to prepare several different simulated PWFAF. Hydrochloric acid solution (HCl, 2 wt. %) and sodium hydroxide solution (NaOH, 1 wt. %) were used for pH adjustment.

Table 2
Qualities of in situ PWFAF after pretreatment in Daqing Oil Field

| Property | Value | Property | Value |
|---|---|---|---|
| Median diameter of oil droplets (μm) | 0.2–2.5 | $Mg^{2+}$ (mg L$^{-1}$) | 5.76–12.04 |
| APAM (mg L$^{-1}$) | 50–110 | $Cl^-$ (mg L$^{-1}$) | 542–948 |
| Surfactant (mg L$^{-1}$) | 72–120 | $SO_4^{2-}$ (mg L$^{-1}$) | 126–284 |
| Oil (mg L$^{-1}$) | 52–130 | $HCO_3^-$ (mg L$^{-1}$) | 1,424–1,978 |
| $Na^+$ (mg L$^{-1}$) | 814–1326 | TDS (mg L$^{-1}$) | 3,200–5,100 |
| $Ca^{2+}$ (mg L$^{-1}$) | 12.68–22.52 | pH | 8.63–9.27 |

Simulated PWFAF with oil concentration of 100 mg L$^{-1}$; SDBS concentration of 100 mg L$^{-1}$; pH of 7; and TDS (provided by the stock brine, similarly hereinafter) of 0 mg L$^{-1}$, 2,000 mg L$^{-1}$, 4,000 mg L$^{-1}$, 6,000 mg L$^{-1}$ and 8,000 mg L$^{-1}$, and simulated PWFAF with oil concentration of 100 mg L$^{-1}$; SDBS concentration of 100 mg L$^{-1}$; TDS of 4,000 mg L$^{-1}$; and pH of 3, 5, 7, 9 and 11 were used in this study. The simulated PWFAF was freshly prepared before each experiment.

### 2.5. Analytical methods

The pH of solutions was measured using a precise digital pH meter (PHS-3C, Greenrise, CN). The size distributions and median diameters of oil droplets were determined by a laser diffraction particle size analyzer (LS13-320, Beckman, USA). The ultraviolet spectrophotometric method is employed to measure the concentrations of SDBS. The crude oil content in the feed and permeate was determined by a fourier transform infrared spectrometer (Spectrum One, Perkin-Elmer, USA). In this method, carbon tetrachloride was used to extract oil from the samples firstly; then absorbance was measured at infrared wavelengths of 3,030 cm$^{-1}$, 2,960 cm$^{-1}$ and 2,930 cm$^{-1}$; and finally the total oil content was obtained by a calibration curve made beforehand. The APAM content was measured by a starch-cadmium iodide method. Before APAM measurements, the samples were 20 times diluted by Milli-Q water to concentrations within the calibration range (0.5–10 mg L$^{-1}$). By this means, acylamino of the APAM was firstly oxidized with bromine, and the superfluous bromine was removed by sodium formate solution, and then solution mixed of starch and cadmium iodide was added, and the produced iodine could make the starch color. Finally, the APAM content was read with an ultraviolet spectrophotometer (UV-2550, Shimadzu, Japan) from a calibration curve, for which the absorbance had been measured at the ultraviolet wavelength of 580 nm. At the end of the study, scanning electron microscopy (SEM) was employed to observe the surface of the membrane before and after chemical cleaning. The experimental membrane sample was firstly fixed with 3.0 wt. % glutaraldehyde in 0.1 M phosphate buffer (pH 7.2) for 3–4 h, followed by the dehydration in a graded ethanol series as follows (v/v %, 15 min each): 50, 70, 80, 90, 100, 100 and 100. After that, the samples were gold-coated by a sputter and observed under a SEM (FEI, USA). The concentration of $HCO_3^-$ was determined by an acid-base titration method. Concentrations of metals and inorganic anions ($SO_4^{2-}$ and $Cl^-$) were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (Optima-5300DV, Perkin-Elmer, USA) and ion chromatography (IC) (ICS-3000, Dionex, USA), respectively.

### *2.6. Cleaning procedure*

Membrane cleaning was done after each UF experimental run. Seven membrane cleaning methods were employed to clean the fouled membranes, as follows: (1) water washing, (2) mechanic scraping, (3) soaking with Milli-Q water, (4) soaking with citric acid solution (0.5 wt. %), (5) soaking with NaOH solution (0.5 wt. %), (6) soaking with SDBS solution (0.5 wt. %) and (7) a combined cleaning method of soaking with citric acid solution (0.5 wt. %), soaking with NaOH solution (0.5 wt. %) and soaking with SDBS solution (0.5 wt. %). Each soaking time was 15 min, and water washing of 5 min was conducted between two soaks in the combined cleaning method.

## 3. Results and discussion

### *3.1. Size distribution and median diameter of oil droplets*

Fig. 2 shows the size distribution and median diameter of oil droplets in the simulated PWFAF and the in situ PWFAF before and after pretreatment. It can be seen from Fig. 2 that the size distribution and median diameter of oil droplets were very similar between the simulated PWFAF and the in situ PWFAF after pretreatment. The size distribution of oil droplets of the former was from about 0.5 to 3 μm, and that of the latter was from approximately 0.3 to 3 μm. Both the median diameters were about 1.5 μm. In addition, for comparison and reference, the size distribution and median diameter of oil droplets of the in situ PWFAF before pretreatment were also provided. As shown in Fig. 2, both the size distribution range and median diameter declined obviously after pretreatment with the traditional technology. This suggests that the pretreatment had a good effect on the removal of oil droplets and might play a good protective effect on the following PES UF membrane if necessary.

### *3.2. Effect of pH on membrane performance*

To study the effect of pH on the membrane performance, experiments were performed using various initial solution pH values, changing from 3 to 11. The permeate relative flux (RF), which is the ratio of permeate flux (J) to the water flux (initial flux $J_0$) [19], was employed to evaluate the decline of flux. The RF of the membrane during the separation of the simulated PWFAF with different pH is presented in Fig. 3. Contrary to expectations, the RF did not change regularly with the increase of pH. As shown in Fig. 3, the minimum RF was at pH 3; however, the maximum RF was at pH 5 instead of pH 11. At present, the reasons for this still remains unclear for us, and more attention would be paid to in our future research. Nevertheless, it could be easily observed that the RF decreased with the increase of time and sharp decline of RF at the beginning of permeation was followed by a mild decline for each pH. The first sharp decline of RF might be due to concentration polarization and the formation of gel layer (cake layer) which occurred immediately as soon as the filtration starts, while the second mild drop of the flux was mainly due to the slow consolidation and compaction of the gel layer. Concentration polarization, an important factor determining the performance of ultrafiltration membranes, can cause membrane fouling due to deposition or adsorption of foulants on the membrane surface, as described in many papers in detail [20,21]. Gel layer is mainly caused by the retained foulants on the membrane surface and could form a secondary barrier to flow through the membrane and decrease the membrane permeability. In addition to deposition, the oil, APAM, SDBS and some inorganic substances in the simulated PWFAF could be adsorbed onto the membrane surface and into the pores of the membrane through interactions taking place between the foulants and the membrane material such as hydrophobic/hydrophilic interactions, hydrogen bonding, Van der Waals interaction and electrostatic effects [22]. For instance, the amino groups of the APAM could form hydrogen bonds with the membrane, the crude oil and itselves; the divalent cations like $Ca^{2+}$ and $Mg^{2+}$ could bridge the negatively charged groups of the foulants such as carboxyl groups of the APAM. With the operation of the membrane,

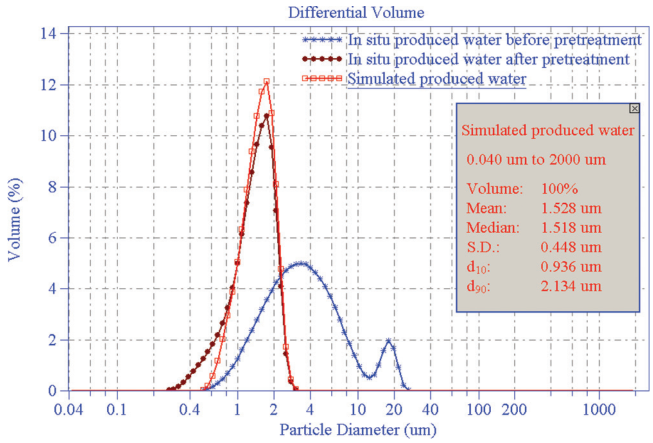

Fig. 2. Size distribution and median diameter of oil droplets in the simulated PWFAF (oil: 100 mg L$^{-1}$, SDBS: 100 mg L$^{-1}$, TDS: 4,000 mg L$^{-1}$, pH: 9) and the in situ PWFAF after pretreatment.

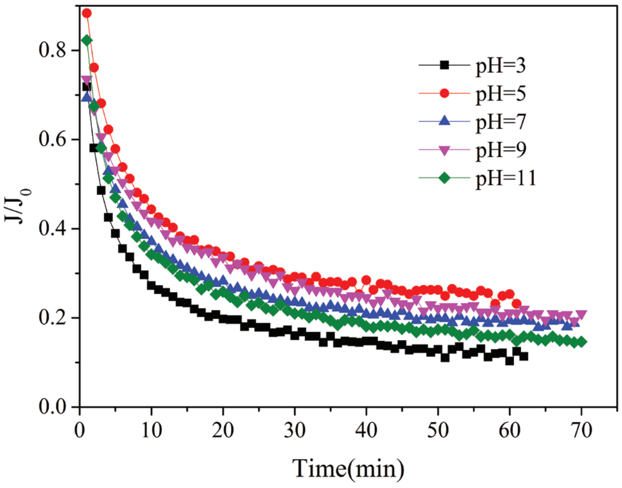

Fig. 3. Effect of pH on RF. (TMP: 0.15 MPa, TDS: 4,000 mg L$^{-1}$).

more and more foulants might deposit or be adsorbed onto the membrane surface and into the pores of the membrane and aggravate the membrane fouling [23]. Therefore, the RF declined continuously with time during the operation.

Effect of pH on rejection rate of oil, APAM and SDBS was investigated, as shown in Fig. 4. High rejection rates of oil and APAM, which were, respectively, more than 95% and 90%, could be seen from Fig. 4, and the oil content in the permeate was always below 5 mg $L^{-1}$. It demonstrated that the PES UF membrane showed a good removal efficiency of oil for the PWFAF, although the emulsifiability and stability of the oil in the PWFAF could be greatly improved in presence of the surfactant SDBS compared with the produced water from water flooding, steam flooding and polymer flooding. Contrastively, the rejection rate of SDBS was relatively low with variation from 70% to 80%, although the SDBS had a strong ability to combine with the oil droplets as a surfactant. The most important reason for this might be that the MW of SDBS was relatively low and it was more difficult to be effectively rejected by the membrane. The second important reason for this might be that the SDBS combined with a small portion of oil droplets could promote the emulsification of these oil droplets and penetrate through the membrane with them. The third most important reason might be that the concentration of SDBS in the feed solution was lower than its critical micelle concentration. It also could be observed from Fig. 4 that the oil rejection rate first decreased mildly between pH 3 and 7 and then increased between pH 7 and 11, while the rejection rates of APAM and SDBS decreased continuously with the increase of pH. The main reason for the former might be that the oil droplets in the unneutral solutions were more inclined to aggregate into bigger droplets and could be rejected more easily by the membrane. The main reason for the latter might be that more APAM could be hydrolyzed into small molecules with the increase of pH, so that it became difficult to be rejected by the membrane, while the SDBS, which might be mainly removed through adsorption instead of screening, became difficult to be adsorbed by the membrane with the increase of pH. Based on the comprehensive consideration of the RF and rejection rate of oil, pH 9, which was very close to the original pH (8.63–9.27) of the in situ PWFAF, was considered as a preferable pH for the membrane performance. Further analyses as well as investigations were carried out at this pH only.

### 3.3. Effect of TMP on membrane performance

The RF of the membrane during the separation of the simulated PWFAF with different TMP is given in Fig. 5. As shown in Fig. 5, curves similar to that in section 3.2 could be observed. That was, the RF also declined sharply at the beginning of permeation and then declined relatively mildly for a prolonged time for each TMP. The main reason for this was referred to section 3.2 as discussed above. The RF declined continuously with time during the operation could be associated to membrane fouling which was caused by the accumulation and deposition of foulants on membrane surface or within pores. Moreover, it can be seen from Fig. 5 that the RF first increased and then decreased with the increase of TMP. When the TMP increased from 0.05 to 0.15 MPa, the RF increased; however, when the TMP continued to increase from 0.15 to 0.25 MPa, the RF decreased. That might be mainly because there was a critical pressure for the membrane treating the simulated PWFAF. When the TMP was below the critical pressure, the effect of concentration polarization was small, and the gel layer was thin or not yet formed on the membrane surface, so the membrane flux was mainly controlled by the TMP according to Darcy's permeability law [24,25], and the RF increased with the increase of TMP (0.05 to 0.15 MPa). However, the increasing RF could lead to the increase of concentration polarization and concentrations of retained oil, APAM, SDBS and some inorganic substances on the membrane surface or within pores. When the TMP increased beyond the critical pressure, the concentration polarization and gel layer forming above the membrane surface became notable enough. Therefore, further increase of TMP only increased the thickness and compactness of the gel layer but not the flux, and even led to membrane fouling at a higher rate, so the RF tended to be constant (from 0.10 to 0.15 MPa) or even declined (from 0.15 to 0.20 MPa). Similar results had also been observed by other researchers [26]. After TMP was higher than 0.20 MPa, a balance between the incremental TMP and the incremental membrane fouling had reached,

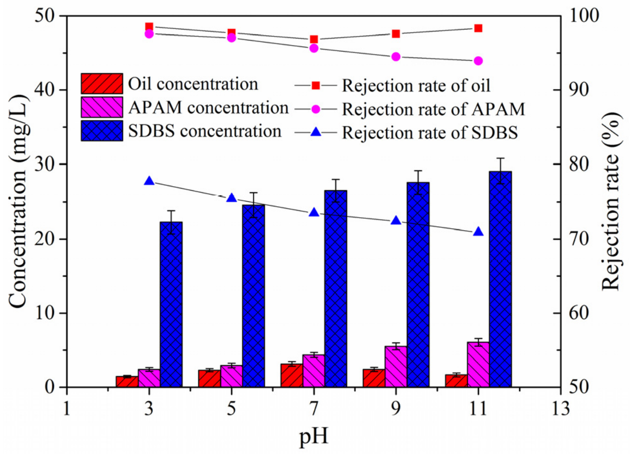

Fig. 4. Effect of pH on rejection rate of oil, APAM and SDBS (TMP: 0.15 MPa, TDS: 4,000 mg $L^{-1}$).

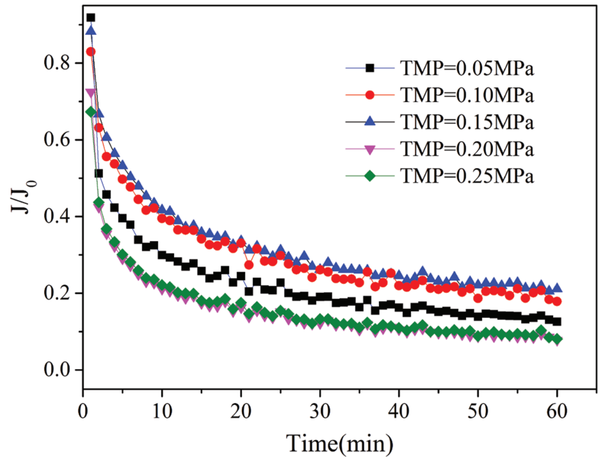

Fig. 5. Effect of TMP on RF (pH 9, TDS: 4000 mg $L^{-1}$).

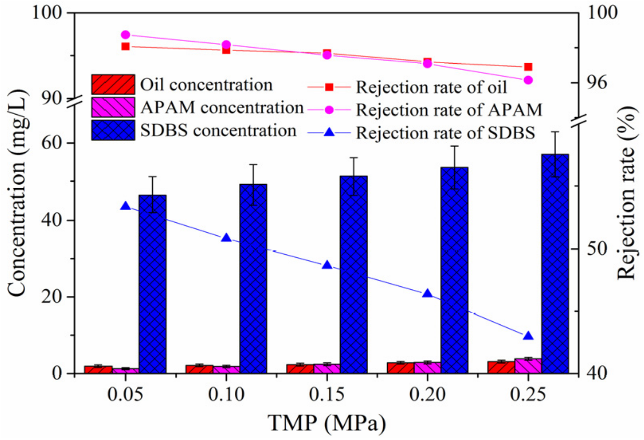

Fig. 6. Effect of TMP on rejection rate of oil, APAM and SDBS (pH 9, TDS: 4,000 mg $L^{-1}$).

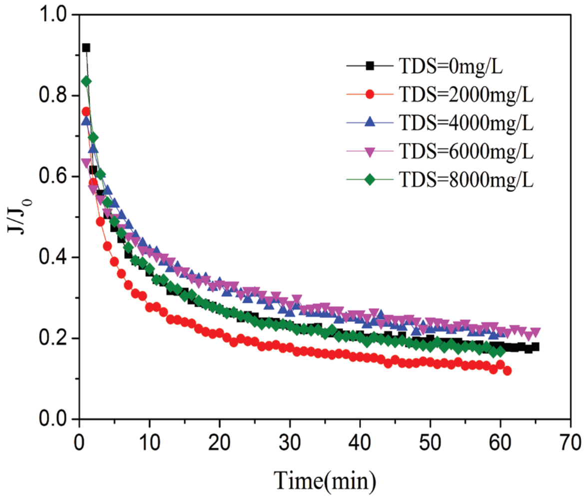

Fig. 7. Effect of TDS on RF (pH 9, TMP: 0.15 MPa).

and the RF decreased unobviously with the increase of TMP (0.20 MPa to 0.25 MPa).

Effect of TMP on rejection rate of oil, APAM and SDBS is shown in Fig. 6. It could be seen that the variation of rejection rates of foulants with TMP were inconsistent with the variation of RF with the TMP. All the rejection rates of oil, APAM and SDBS in the permeate decreased mildly with the increase of TMP. That might be mainly because more oil droplets, APAM and SDBS, which had a strong ability to combine with the oil droplets as a surfactant, were extruded through the membrane under high TMP and led to the mild decrease of rejection rate. However, both the rejection rates of oil and APAM were still over 95%, while that of SDBS was relatively low with variation from 70% to 80%, and the oil content was always below 5 mg $L^{-1}$ in the permeate. The reason was the same as that discussed in section 3.2. High TMP leads to high energy consumption and high cost. Taking into account the membrane flux and energy saving simultaneously, 0.15 MPa was considered as a preferable TMP for the membrane and further analyses, as well as investigations were conducted at this TMP only.

### *3.4. Effect of TDS on membrane performance*

In this study, ions might affect the solution or membrane performance in eight ways: (1) to cause an increase in the degree of dissociation of the APAM by facilitating the protonation [27], and the more the cation the more dissociation of APAM; (2) to shield the electrostatic potential generated by functional groups of the membrane surface; (3) to bridge the negatively charged groups between the foulants (oil, APAM, SDBS) and the membrane and the foulants themselves by some divalent cations like $Ca^{2+}$ and $Mg^{2+}$; (4) to neutralize the charge associated with functional groups of APAM and thus reduce the radius of gyration; (5) to reduce the repulsive force between the membrane and the negatively charged foulants and lead to more membrane fouling; (6) to bridge the negatively charged groups between the APAM itselves and thus reduce the radius of gyration by some divalent cations; (7) to neutralize the negative charge of the foulants and create an electrostatic attraction force between them; and (8) to lead some inorganic substances to the membrane. Based on these, the effect of TDS on RF was investigated and is presented in Fig. 7.

As revealed by Fig. 7, although there was some variation in RF as the TDS varies from 0 to 8,000 mg $L^{-1}$, the effect of TDS on RF was not changed significantly as expected. That was, the membrane fouling facilitated by ions was not significant, which was in agreement with the result obtained by Nghiem [28]. It was possible that the membrane fouling contributed by hydrophobic/hydrophilic interactions, hydrogen bonding and Van der Waals interaction was more than that contributed by electrostatic effects, and dominated the variation of the RF. As discussed above, hydrophobic/hydrophilic interactions, hydrogen bonding and Van der Waals interaction could take place between the foulants (oil, APAM, SDBS) and the membrane and the foulants themselves. For instance, the amino groups of the APAM could form hydrogen bonds with the membrane, the crude oil and itselves. All these could contribute the dominant fouling to the membrane, even though in the presence of some divalent cations like $Ca^{2+}$ and $Mg^{2+}$ which could bridge the negatively charged groups of the foulants and aggravate the membrane fouling.

Variations of rejection rates of oil, APAM and SDBS with TDS were investigated, as shown in Fig. 8. It could be seen that the TDS had a significant effect on the rejection rate of SDBS, and the SDBS concentration in the permeate decreased with the increasing TDS. This might be due to that the combination of SBDS and oil was strengthened with the increase of the TDS, and more SBDS could be rejected with oil. In addition, the solubility of SDBS would also decrease with the increase of the TDS, leading more SDBS to be rejected by the membrane. However, the effects of TDS on the rejection rates of oil and APAM, both of which were more than 95%, were unobvious as that of SDBS, and the content of APAM was lower than 10 mg $L^{-1}$ and that of oil was below 5 mg $L^{-1}$ in the permeate. This might be because that the sizes of both the oil and the APAM, no matter what the structure and morphology might be, were smaller than the membrane pore size. Therefore, both of them could be rejected efficiently by the membrane.

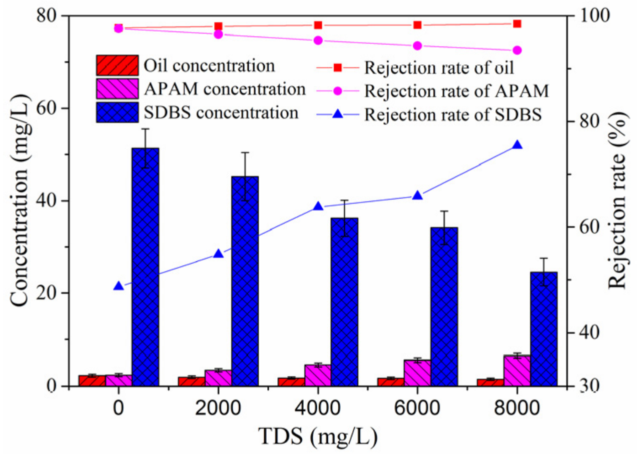

Fig. 8. Effect of TDS on rejection rate of oil, APAM and SDBS (pH 9, TMP: 0.15 MPa).

### 3.5. Membrane cleaning

Membrane cleaning was done after each UF experimental run. Seven different clean methods had been employed to clean the fouled membrane in this study, as shown in Fig. 9. It could be seen that the membrane could not be recovered satisfactorily with a single cleaning method. The recovery rates of water washing, mechanic scraping and soaking with Milli-Q water were all below 40%. It demonstrated that both the reversible and irreversible fouling of the membranes occurred during the separation of the simulated PWFAF. Moreover, irreversible fouling accounted for about 60% of the whole membrane fouling and was more likely to exist in the membrane pores. The recovery rates were all increased to more than 65% for soaking with citric acid solution (0.5 wt. %), soaking with NaOH solution (0.5 wt. %) and soaking with SDBS solution (0.5 wt. %). This indicated the complexity of membrane fouling and foulants, which were composed of not only organic substances (oil, APAM, SDBS) but also inorganic substances (mineral salts). A high recovery rate of 95% could be obtained by the combined cleaning method of soaking with citric acid solution (0.5 wt. %), soaking with NaOH solution (0.5 wt. %) and soaking with SDBS solution (0.5 wt. %). It demonstrated that the foulants could be removed efficiently by the combined cleaning method, and there was a good possibility that the gel layer became loosened after the citric acid solution soaking, and then organic substances could be removed by the following NaOH solution and SDBS solution soaking. This was consistent with the complexity of membrane fouling and foulants discussed above.

For intuitive observation, the surface SEM images of the original membrane, fouled membrane and cleaned membrane are given, as shown in Fig. 10. It could be seen from Fig. 10(a) that the surface of the original membrane was smooth and there were no foulants on the surface. Contrastively, a layer of foulants could be observed obviously on the surface of the fouled membrane, as shown in Fig. 10(b). After cleaning with the combined method, the surface of the membrane became smooth again in spite of some residual foulants, as given in Fig 10 (c).

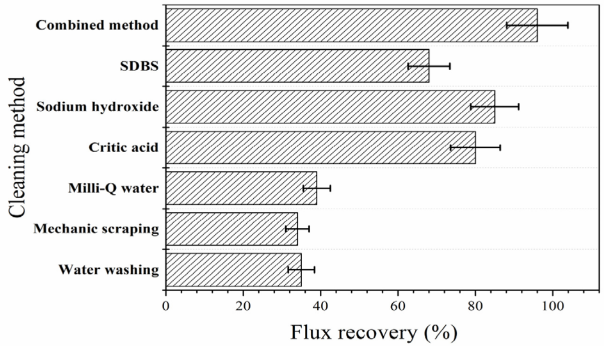

Fig. 9. Flux recovery with different cleaning methods.

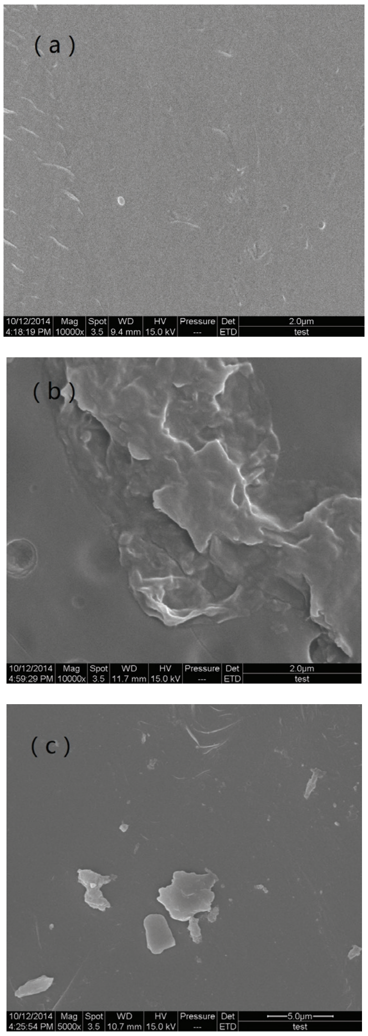

Fig. 10. SEM images of membrane surface: (a) original membrane; (b) fouled membrane and (c) cleaned membrane.

## 4. Conclusions

Advanced treatment of PWFAF with a PES UF membrane in dead-end filtration has been conducted. The effects of important factors such as TMP, pH and TDS on membrane flux decline were examined, and the rejection rates of APAM, SDBS, especially oil as well as membrane cleaning methods were investigated. The obtained results are concluded as follows: (1) Compared with pH and TDS, the TMP had a more significant influence on the membrane flux decline; however, three of them all exhibited little influence on the rejection rates of oil; (2) pH of 5 and TMP of 0.15 MPa were feasible or preferable operating conditions for the membrane; (3) both the reversible and irreversible fouling of the membranes occurred during the separation, and a high recovery rate of 95% could be obtained by the combined cleaning method; (4) the membrane exhibited a high removal efficiency of oil from the PWFAF despite the presence of the surfactant SDBS, and the oil content was always below 5 mg $L^{-1}$ in the permeate and that could meet the highest reinjection standard specified in the Water Quality Standard and Practice for Analysis of Oilfield Injecting Waters in Clastic Reservoirs (SY/T 5329-2012) in China. All these suggested a potential feasibility and application of the PES UF membrane for advanced treatment of the PWFAF.

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