Recycling of high temperature steam condensed water from petroleum refinery by thermostable PPESK ultrafiltration membrane

Shanshan Zhao, Peng Wang, Ce Wang, James L. Langer, Gulizhaer Abulikem, Xin Sun

State Key Laboratory of Urban Water Resource and Environment, School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150090, PR China
Serionix, Inc., 60 Hazelwood Dr., Champaign, IL 61820, United States

Highlights

- Excess oil and iron in high temperature condensed water are removed by UF membrane.
- Operation parameters affect permeate flux, removal efficiencies and membrane fouling.
- Membrane performance is recovered after NaOH in combination with ethanol washing.
- Reclaiming high temperature condensed water can prevent thermal emission pollution.
- Reclaiming it also reduces economic cost, saves energy and realizes water recycling.

Abstract

The purification and reclaiming of synthetic and industrial high temperature condensed water containing excess oil and iron is investigated in this study using thermostable poly(phthalazine ether sulfone ketone) (PPESK) ultrafiltration membranes. The results show operation parameters such as transmembrane pressure, temperature and pH of feed solution, initial oil and iron concentration each play important roles in the permeate flux and oil/iron removal efficiencies. Membrane performance is almost recovered after washing with a combination of NaOH and ethanol. High temperature condensed water from Daqing petroleum refinery can be consecutively purified using a PPESK ultrafiltration membrane. The turbidity of the solutions is almost removed. Oil and iron concentrations in the permeate solutions are below 1 mg/L and 50 μg/L, respectively, which satisfy the Quality Criterion of Water and Steam for Steam Power Equipment in China. UF process shows a promising alternative to existing technology in the Daqing petroleum refinery in terms of cost and environmental protection as well as energy recovery. For future possible combination of UF and NF process application, both economic cost and saving are evaluated, and the breakeven time is about 11 months.

1. Introduction

High temperature condensed water is produced from condensation of high pressure steam during the heat exchange process [1], and contains up to 20–30% of the heat quantity of the steam [2]. If the condensed water is discharged directly, heat energy is lost, large amounts of water are wasted, and sewage discharge fees are assessed, resulting in unnecessary expenses [3,4]. Moreover, direct discharge of condensed water into an aquatic environment causes thermal emission pollution—an increase in water temperature, which negatively influences both water quality and growth and distribution of aquatic organisms [5–8]. Reclaiming and utilizing high temperature condensed water is of great significance for conserving water and energy and for preventing thermal emission pollution.

Condensed water is typically used as boiler makeup water or, after treatment, hot water for residential use in winter. However, high temperature condensed water produced in petroleum refineries often contains excess oil and iron contaminants due to the leakage and corrosion of equipments [9]. This contaminated condensed water will damage or even destroy boilers if it is not properly purified before reuse. The two principle modes of damage are: (1) adherence of oil to boiler tubes resulting in overheating of the furnace due to reduced heat transfer [10,11]; (2) partial corrosion of boiler tubes resulting from iron contamination and leading to perforation of boiler tubes due to the deposition of iron scale on the metal surface [12].
Several technologies have been employed or explored to remove oil and iron, including activated carbon adsorption, mixed-bed ion exchange, powder resin filtration, functional fiber filtration and electrodeionization [9,13,14]. However, these conventional methods suffer from several problems, including operational instability, higher cost and potential secondary waste pollution from the replacement of adsorbent or other filter materials.

In contrast, membrane technologies are a promising alternative as they have the advantages of simple operation, small physical footprint, high separation efficiency, and low energy consumption [15,16]. Recently, a number of membrane separation processes, such as ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) have been applied efficiently for oil/water separation [17–19]. Yi et al. [20] introduced response surface methodology (RSM) to optimize operational parameters to mitigate membrane fouling during ultrafiltration of oil/water emulsions. Chakrabarty et al. [21,22] successfully applied several kinds of polysulfone membranes with different additives for treating oily wastewater from petroleum industries. Nearly all the membranes gave an oil rejection of over 90%, and the oil concentration in the permeate solution met discharge requirements. Although membrane technologies have been successfully applied for oily wastewater treatment, application in a high temperature condensed water purification process has only been reported—for example boiler feedwater treatment from GE Water & Process Technology. An UF system has been used for the removal of dissolved iron from boiler feedwater in a nuclear power plant in Colorado. Higher iron removal efficiency in this system has resulted in shortening the starting period of the nuclear power plant from a few days to just 8 h [23]. A RO system has also been successfully applied for reclamation of softened makeup water in an oil refinery in the Midwestern United States. Using these processes, it is estimated that over 250 billion BTUs of energy can be saved per year because of the lower blowdown rates [24].

This paper focuses on the purification and recycling of the high temperature steam condensed water from petroleum refinery using thermostable UF membranes prepared using a phase-inversion method. The membrane material poly(p-hthalalene ether sulfone ketone) (PPESK) contains rigid phthalazine structure and aromatic rings, showing extraordinary mechanical strength, thermostability, and good chemical resistance [25]. Permeate flux and oil and iron removal efficiencies were measured as a function of changes in transmembrane pressure (TMP), temperature and pH value of feed solution, and initial oil and iron concentration. Various membrane cleaning methodologies were also considered. Lastly, purification efficiency and recycling of high temperature steam condensed water was studied using real samples acquired from the Daqing petroleum refinery. The economic feasibility was also evaluated.

2. Materials and methods

2.1. Materials

Commercial PEPESK powder (S:K = 1:1, Mw = 58000 g/mol) was purchased from Dalian Polymer New Materials Co. Ltd. (Liaoning, China). Diesel oil was provided by a local gas station. N-methyl-2-pyrrolidone (NMP) was purchased from Beijing Yili Fine Chemical Co., Ltd. (China). Polyethylene glycol (PEG, 4000 g/mol) was obtained from Aladdin Reagent (Shanghai, China). Sodium dodecyl sulfate (SDS) was chemically pure grade and provided by Tianjing Guangfu Fine Chemical Research Institute (Tianjin, China). FeSO4·7H2O and ferron agent (8-hydroxy-7-iodo-5-quinoline sulfonic acid) were purchased from Tianjing Bodi Chemical Co., Ltd. (China) and Beijing Hengye Zhongyuan Chemical Co., Ltd. (China). All reagents were analytical grade, except for SDS, and used without further purification. Deionized (DI) water from a Milli-Q system (Millipore, Bedford, USA) was used in all experiments.

2.2. Membrane preparation

The PESK membranes were prepared using a phase inversion method, the details of which can be found elsewhere [26]. The flow diagram of membrane preparation process is shown in Fig. S1 in Supplementary materials file. First, 6 wt.% PEG was dissolved in NMP with stirring at 60 °C. Next, 16 wt.% PESK power was added to the solution with continuous vigorous stirring at 60 °C for 6 h until it was completely dissolved. Afterwards, the solution was filtered to remove a small amount of insoluble impurity. Finally, a uniform and homogeneous solution was obtained and kept at 25 °C for 48 h to remove gas bubbles. Membranes were cast from the resulting solution using a glass plate with a 200-μm casting knife. After exposure to ambient air (temperature was 20 ± 2 °C and relative humidity was 30 ± 5%) for 10 s, the glass plate was immersed into a DI water coagulation bath maintained at 20 ± 1 °C. Membranes thus obtained were stored in DI water for 1–2 days to remove residual solvent, and then stored in 1% formaldehyde solution to avoid microbe growth. The molecular weight cut-off (MWCO) of the PESK membrane is about 60,000 Da, which was determined in our previous work [27]. Pore size distribution of PESK membrane was investigated using bubble point method by using a Capillary Flow Porometer (Porolux 1000, IB-FT GmbH, Germany) [28] and the profile is shown in Fig. S2. The PESK membrane exhibits a narrow pore size distribution, the bubble point pore size is 65 nm and the mean pore size is 36 nm.

2.3. Simulated high temperature condensed water preparation

A certain amount of diesel oil, SDS and FeSO4·7H2O (the mass ratio of diesel oil to SDS was 3:1) were added into 3 L DI water to give different oil and iron concentration solutions. SDS, as one common emulsifier, decreased the oil–water interface tension and coated the dispersed oil droplets, protecting them from coalescence and enhancing the emulsion solution stability. The solutions were mixed using high-shear emulsifying dispersion for 30 min (the mixing speed was 3000 rpm). After that, the solutions were sealed with preservative film and heated to 80 °C in a water bath. During each ultrafiltration test, the high temperature condensed water was kept at 80 °C using a water bath. Oil droplet size was in the range of 0.45–1.01 μm with a volume average particle diameter of 0.73 μm, as measured by a Malvern Mastersizer Particle size analyzer. Oil concentration was measured using an ultraviolet spectrophotometer at 224 nm (UV2550, Shimadzu, Japan) after extraction by hexane. Iron concentration was measured using Inductively Coupled Plasma-Atomic Emission Spectra (ICP-AES) (Optima 5300 DV, PerkinElmer, USA), the pH and turbidity were recorded using a pH meter (Corning pH/ion analyzer 455, Cole-Palmer, USA) and turbidity meter (Turb 550, WTW, Germany), respectively.

2.4. Ultrafiltration performance

The purification efficiency of high temperature condensed water was characterized using a cross-flow filtration cell (provided by Tianjin Polytechnic University, China) connected with a solution reservoir and an electric diaphragm pump. A schematic diagram of the experimental ultrafiltration set up is shown in Fig. 1. Effective membrane area was 17.71 cm² and cross-flow velocity was kept at 1.61 m/s. In order to keep the temperature of condensed water virtually constant, the entire experimental set up including the testing cell and all pipes – were wrapped up using cotton for
insulation. Since the initial pure water flux of each membrane varied slightly, membranes exhibiting similar initial flux were selected for each group experiment. Each membrane was firstly pre-compacted with 80 °C pure water at 0.2 MPa for 30 min to achieve steady-state permeate flow. Then, pure water flux was measured using 80 °C DI water at 0.1 MPa. Pure water flux of membranes ranged from 940 to 1050 L m$^{-2}$ h$^{-1}$. High temperature condensed water was filtered at a constant TMP of 0.1 MPa after membrane pre-compaction. Both permeate and retentate solutions were refilled into the feed solution to keep the concentration constant. The permeate flux ($J$, L m$^{-2}$ h$^{-1}$) was measured every minute until it levelled off after 30 min, which can be calculated using the following equation:

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

where $V$ is permeate volume (L), $A$ is membrane area (m$^2$), and $t$ is sample collection time (30 s).

The permeate samples were collected for measurement of the oil and iron concentrations and turbidity. The observed rejection can be calculated using the following equation:

$$R = \frac{C_0 - C_P}{C_F} \times 100\% \tag{2}$$

where $C_F$ and $C_P$ are the concentrations in feed and permeate solutions (mg/L), respectively.

The normalized flux ($J/J_0$) was applied to evaluate the membrane performance, where $J_0$ is the initial permeate flux (L/m$^2$ h). The flux decline rate ($FD$) was introduced to investigate the effects of several factors on the membrane fouling, which was determined using the following equation:

$$FD = \left(1 - \frac{J_P}{J_0}\right) \times 100\% \tag{3}$$

where $J_P$ is the permeate flux after 30 min filtration (L/m$^2$ h). Each experiment was repeated three times and the average value was reported.

2.5. Membrane cleaning methods

To investigate the effects of different cleaning methods, the pure water flux recovery rate ($FR$) was introduced, $FR = (J'_{F0}/J_0) \times 100\%$, where $J_{F0}$ and $J_0$ are the pure water flux of virgin membrane and cleaned membrane (L/m$^2$ h), respectively. Each membrane was filtered with high temperature condensed water for 60 min and $FD$ was around 50%.

The cleaning procedures are shown as below:

- **Method A**: after an UF experiment, the membrane was washed by 80 °C DI water for 5 min at 0.05 MPa.
- **Method B**: after an UF experiment, the test cell was washed by DI water in room temperature for 5 min at 0.05 MPa to remove residual contaminants in the cell and pipe and to cool down the cell. Then, the membrane was removed and gently cleaned by a sponge ball to remove any contaminants loosely bonded to the membrane surface. Finally, the membrane was washed thoroughly using DI water in room temperature.
- **Method C**: after an UF experiment, the membrane was washed using 0.1 M NaOH solution for 5 min followed by DI water washing for 5 min to remove residual detergent.
- **Method D**: after an UF experiment, the membrane was washed using 50% ethanol solution for 5 min followed by DI water washing for 5 min.
- **Method E**: after an UF experiment, the membrane was first washed using 0.1 M oxalic acid solution for 5 min followed by DI water washing for 5 min, and then the membrane was washed using 50% ethanol solution for 5 min followed by DI water washing for 5 min to remove residual detergent.
- **Method F**: the cleaning procedure was similar to method E, but the detergents were changed for 0.01 M NaOH solution and 0.1 M oxalic acid solution, respectively.
- **Method G**: the cleaning procedure was similar to method E, but the detergents were changed for 0.01 M NaOH solution and 0.1 M HCl solution, respectively.
- **Method H**: the cleaning procedure was similar to method E, but the detergents were changed for 0.01 M NaOH solution and 30% ethanol solution, respectively.

All of the detergents and DI water used in methods C–H were circulated in the testing cell at 0.05 MPa in room temperature.

2.6. Membrane surface morphology observation

The morphology of membrane surfaces was characterized using a scanning electron microscope (SEM) (S4800, Hitachi). All membrane specimens were dried at room temperature for at least 48 h and stored in a desiccator. The dry membranes were sputtered with a thin layer of gold under vacuum for 20 s (Emitech K575 Sputter Coater, Emitech Ltd., Ashford, Kent, UK) prior to imaging.

3. Results and discussion

3.1. Membrane surface morphology

The SEM images of surface morphology of virgin and fouled PPESK membranes are illustrated in Fig. 2. Membrane pores can be seen clearly on the virgin PPESK membrane surface, while an ordered and compacted cake layer is formed on the fouled membrane surface, due to the accumulation and deposition of oil emulsion and iron hydrolysates.

3.2. The influences of important factors on the membrane performance for high temperature condensed water purification

3.2.1. Effects of transmembrane pressure

Variations in permeate flux and rejection of membranes during high temperature condensed water purification at different TMP are shown in Fig. 3. Fig. 3a shows that the normalized flux decreases with increasing time and finally levels off for each TMP, while the $FD$ values increase proportionally with increasing pressure. The lower the pressure, the faster the permeate flux equilibrates. For example, when the pressure is 0.05 MPa, the permeate flux is stable after 10 min filtration, while for the
pressure of 0.20 MPa, the permeate flux continues to decrease over the course of 30 min filtration. The permeate flux decline over time is mainly ascribed to concentration polarization and membrane fouling such as pore blocking and cake layer formation [29]. The concentration polarization phenomenon is inherent to all cross-flow processes and occurs immediately as soon as filtration starts. During the initial filtration period, as water passes through the membrane, oil and iron pollutants are retained and accumulated in the vicinity of the membrane surface and form a thin polarization boundary layer, which provides additional resistance to permeate flow [30]. The initial pore blocking caused by smaller oil droplets in the feed water also attributes to the sharp decline of flux [22]. Then, with the accumulation and deposition of oil emulsion and iron hydrolysates on the membrane surface, a cake layer grows progressively between the polarization layer and membrane surface, resulting in an increase of hydrodynamic resistance to permeate flow [31]. The initial pore blocking caused by smaller oil droplets in the feed water also attributes to the sharp decline of flux [22]. Then, with the accumulation and deposition of oil emulsion and iron hydrolysates on the membrane surface, a cake layer grows progressively between the polarization layer and membrane surface, resulting in an increase of hydrodynamic resistance to permeate flow [31]. The cake layer is gradually packed so as to attain minimum porosity [30]. Finally, the permeate flux levels off based on the cake layer filtration. Higher operation pressures present higher FD values ascribing to the build-up of concentration polarization boundary layer and pore blockage [32]. Higher pressure increases the collision between emulsion droplets causing the coalescence of oil droplets and formation of large droplets. Then, the layer containing large oil droplets above membrane surface may be compressed on surface and block the pores resulting in severe membrane fouling [21,33].

Fig. 3b shows the observed rejections of pollutants and their concentrations in permeate solutions (b) (initial oil and iron concentrations were around 50 mg/L and 1 mg/L, respectively).

Table 3. Effects of TMP on the permeate flux (a), pollutants rejections and their concentrations in permeate solutions (b) (initial oil and iron concentrations were around 50 mg/L and 1 mg/L, respectively).

3.2.2. Effects of feed solution temperature

Fig. 4a shows the variation of normalized permeate flux and FD at different feed solution temperatures. The higher the feed solution temperature, the less the permeate flux declines. This may be due to two causes: (1) the viscosity of solution decreases and the diffusion rate of water molecules increases at higher temperature; and, (2) membrane fouling is mitigated due to formation of polymeric ferric species at higher temperature. The ferric hydrolysates contain three kinds of species according to different extent of hydrolysis and polymerization [34], namely monomeric hydroxyl complex (Fe (a)), transitional oligomers (Fe (b)) and stable polymers (Fe (c)). The effect of temperature on the ferric species is investigated using Ferron-complexation timed spectrophotometric method and detailed information is shown in Supplementary materials. The result shows that at lower temperature (40 °C), the proportion of the monomeric species and oligomeric species represents more than 50% of all iron species. At increased...
temperatures, more transitional oligomeric species continue to be polymerized to form high polymeric species in the system. At 80 °C, the proportion of high polymeric species represents greater than 70% of all iron species (as shown in Fig. S4). The high polymeric species have a special three-dimensional stereoscopic porous like structure, which can sweep down the oil drops to form floccules [35]. These floccules are easily swept away by the hydraulic flush of cross flow instead of being adsorbed on the membrane surface. Consequently, the permeate flux decreases less at higher temperature as shown in red column inside Fig. 4a.

Fig. 4b shows the observed rejections of oil and iron are both very high with only small changes. The oil concentration in permeate solution increases with increasing temperature, while iron concentration shows the opposite variation trend. As mentioned above, more stable ferric polymeric species are formed in the system at higher temperatures. These volume-enlarged species improve the iron removal efficiency and lower iron concentration in permeate solution. Meanwhile, high temperature improves the oil solubility in water and accelerates the molecular diffusion. Thus, adsorbed oil drops on the membrane surface could easily pass through membrane along with the permeate flow under pressure, resulting in the increase of oil concentration.

3.2.3. Effects of initial oil concentration

The effects of initial oil concentration on the membrane performances are shown in Fig. 5. Fig. 5a reveals that the normalized permeate flux decreases sharply as initial oil concentration increases. The higher the oil concentration, the larger the flux decline value, which is attributed to the formation of a thicker cake layer on the membrane surface at higher oil concentration. With increasing initial oil concentration, more oil drops are prone to be deposited on membrane surface to form a cake layer, which aggravates the membrane contamination and increases the membrane filtration resistance [21].

The observed rejections of oil and iron and their concentrations in permeate solutions are illustrated in Fig. 5b. As the initial oil concentration increases, the rejections of both oil and iron increase, whereas their concentrations in permeate solutions show a reversed trend with each other. With increasing oil concentration, more oil drops are accumulated on the membrane surface building up a thicker cake layer, which enhances the rejection of oil and iron. However, the increase of oil concentration in the cake layer causes more oil molecules to be pressed through the membrane along with permeate flow under pressure, resulting in the increase of oil concentration in permeate solution.

3.2.4. Effects of initial iron concentration

The effects of iron concentration in feed solution on the permeate flux and removal efficiencies of oil and iron are illustrated in Fig. 6. Fig. 6a indicates that as the initial iron concentration increases, the normalized permeate flux drops and FD values increase correspondingly. The accumulation of more corrosion contaminants on the membrane surface aggravates membrane fouling, resulting in the decrease of permeate flux.

As shown in Fig. 6b, at higher initial iron concentration the oil rejection stays fairly consistent while the oil concentration in permeate solution decreases. The iron rejection decreases while its concentration in permeate solution shows the reversed trend. With the increase of iron concentration, more high polymeric species of ferric hydrolysates are formed in the system, which in turn sweep down of the oil drops and improve the oil removal efficiency. Meanwhile, the amount of Fe (a) is also increased with increasing initial iron concentration, which can easily pass through the
membrane due to the smaller size, resulting in the increase of iron concentration in permeate solution.

### 3.2.5. Effects of feed solution pH value

According to measurement results, the pH values of industrial high temperature condensed water from four process units in the Daqing oil refinery (China) vary between 7 and 9.5 [11], and pH values of condensed water from residue oil and wax oil units are around 5. In addition, PPESK membrane can tolerate extreme pH [36]. Then, the variation range of feed solution pH values is chosen at 3–9, and the effect of feed solution pH on the permeate flux and removal efficiencies of oil and iron is investigated. Fig. 7a shows the normalized permeate flux and $FD$ values are not obviously affected at pH 5–7. However, a severe permeate flux decline and a higher $FD$ value are presented at lower pH. At lower pH, the ferric hydrolyzing process is restricted and more small oil droplets block the membrane pore under pressure, aggravating membrane fouling and flux decline. When pH further increases, the permeate flux also drops quickly in the initial few minutes of filtration and the $FD$ values increase with increasing pH. The permeate flux highly depends on the deposition of emulsion droplets, which is affected by the interaction between emulsion droplets and membrane materials (i.e., hydrogen bonding, hydrophobic/hydrophilic action and electrostatic effects) [21]. As the pH value increases, the functional group of emulsion droplets may be changed resulting in a higher affinity between emulsion droplets and membrane surface [33], resulting in membrane fouling aggravation and permeate flux decline. At the same time, higher pH may accelerate the ferric hydrolysis and precipitation process [37]. The deposition of hydrolysates and precipitates on the membrane surface also causes severe membrane fouling.

![Fig. 6](image_url)

**Fig. 6.** Effects of initial iron concentration on the permeate flux (a), pollutants rejections and their concentrations in permeate solutions (b) [TMP was 0.1 MPa, temperature was 80 °C and initial oil concentration was around 50 mg/L].

![Fig. 7](image_url)

**Fig. 7.** Effects of pH of feed solution on the permeate flux (a), pollutants rejections and their concentrations in permeate solutions (b) [TMP was 0.1 MPa, temperature was 80 °C, initial oil and iron concentrations were around 50 mg/L and 1 mg/L, respectively].

Fig. 7b indicates that when pH is higher than five, the oil and iron removal efficiencies change little, and the oil and iron concentrations in permeate solution decrease with increasing pH. The iron ion totally passes through the membrane at pH 3. At higher pH value, more iron can be rejected due to the enlarged volume of ferric precipitate.

As above discussion, five operation parameters each play important roles in the permeate flux and oil/iron removal efficiencies. The temperature and pH of feed solution influence ferric hydrolyzing species. In acidic solution, iron ion hydrolyzing process is restricted and there is no rejection of iron ion. Higher pH accelerates ferric hydrolyzing and precipitation process. At higher temperature, more ferric polymeric species with a special three-dimensional stereoscopic porous like structure are formed. Oil droplets can be swept down by the polymeric species to form flocs which are easily swept away by the hydraulic flush, thereby membrane fouling can be mitigated. Higher operation pressure increases the collision and coalescence of oil droplets, leading to formation of large droplets layer above membrane surface. Then, the large oil droplets layer may be compressed on surface and block the pores resulting in severe membrane fouling. As initial oil and iron concentration increase, more pollutants are deposited on the membrane surface, aggravating membrane fouling.

### 3.3. Cleaning of fouled membrane

To recover the permeability of fouled membrane, different physical and chemical cleaning methods are applied. The pure water flux recoveries (FR) of membranes after cleaning are shown in Fig. 8. It can be seen that the single alkali cleaning method (C) and alkali in combination with ethanol cleaning method (H) are
efficient for contaminants removal. The FR values are above 95% and the membrane surface pores reappear after cleaning as shown in Fig. 9. High temperature DI water washing only removes the reversible pollution of membrane as well as the residual pollutants in the testing cell and pipe, and thus the FR value is only 55.6%. Sponge ball cleaning is used for the removal of soft scale which is loosely bonded to membrane surface, and the FR value is 69.5%. Table 1 shows water contact angles of the membranes before and after chemical cleaning. From Table 1, it can be seen that the virgin PPESK membrane has an average water contact angle of 59.9 ± 2.5°. After fouling by high temperature condensed water, it is increased to 86.2 ± 1.4° due to the deposition of hydrophobic organic pollutants on the membrane surface. Chemical cleaning is efficient for removing the pollutants and restoring water contact angles of membranes to around 70°. It has previously been shown that NaOH can desorb a large amount of organic matter from fouled membrane [38]. It is efficient for oil removal in our experiment. Ethanol is often used as membrane wetting reagent, and can remove otherwise-irreversible fouling of membrane [39]. After cleaning by method D and E, the FR values approach 80%. Although acid is a common detergent for inorganic matters removal, the cleaning efficiencies of method F and G are not as high as other ones. It may be because that compared with ferric scale, the membrane pore blockage and cake layer formation by the deposition of oil droplets on membrane surface is responsible for the severe fouling, and it is difficult to remove the cake layer using a lower concentration NaOH solution. NaOH in combination with ethanol cleaning method is effective because both NaOH and ethanol are able to remove foulants from the membrane surface and in the membrane pores. Considering that high alkali concentration damages membrane materials during long duration runs, method H would be the best choice for high temperature condensed water treatment.

### Table 1

<table>
<thead>
<tr>
<th>Membranes</th>
<th>Water contact angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin membrane</td>
<td>59.9 ± 2.5</td>
</tr>
<tr>
<td>Fouled membrane</td>
<td>86.2 ± 1.4</td>
</tr>
<tr>
<td>Cleaned by method C</td>
<td>67.5 ± 3.8</td>
</tr>
<tr>
<td>Cleaned by method D</td>
<td>71.9 ± 6.9</td>
</tr>
<tr>
<td>Cleaned by method E</td>
<td>72.3 ± 6.6</td>
</tr>
<tr>
<td>Cleaned by method F</td>
<td>71.5 ± 3.8</td>
</tr>
<tr>
<td>Cleaned by method G</td>
<td>71.5 ± 5.1</td>
</tr>
<tr>
<td>Cleaned by method H</td>
<td>69.4 ± 4.3</td>
</tr>
</tbody>
</table>

3.4. Purification of high temperature steam condensed water from the Daqing petroleum refinery

3.4.1. Permeate flux and purification efficiency

During oil refinery process, high temperature steam with about 1.0 MPa pressure is used for heating various oil products. After heat exchange, the steam is condensed to form high temperature condensed water (80–120°C). As mentioned previously, the condensed water often contains excess oil and iron due to the leakage of heater and corrosion of pipeline. Two kinds of high temperature steam condensed water in our experiment were provided by the Daqing Petroleum Refinery. One is from a residual oil storage tank pipeline, and another is from a wax oil storage tank pipeline.

The lab-scale experiments were conducted using a cross-flow module using the total recycle mode. The variation of permeate flux with time is shown in Fig. S5. The water quality of high temperature condensed waters before and after UF treatment and quality criterion for boiler water are listed in Tables 2 and 3, respectively. The result shows that the thermostable PPESK UF membrane is efficient for removal of oil, iron, and turbidity. The turbidity of solutions are almost completely removed after treatment and the permeate solutions have become clear and...
transparent. The oil and iron concentrations in the permeate solutions are below 1 mg/L and 50 μg/L, respectively, which satisfy the Quality Criterion of Water and Steam for Steam Power Equipment (GB/T 12145-2008, China) listed in Table 2. The hydrolysis and precipitation of iron at high temperature enlarges its volume and thus the iron can be efficiently retained by membrane. However, the UF membrane pore size is not small enough to retain other ions, such as Mg2+, Ca2+ and Na+. Further softening technique or NF membrane separation processes are needed to remove hardness and other dissolved ions. For large scale application, the volume of UF retentate stream will be very small and the heating value would not be reclaimed. However, the concentrated retentate solution may still be collected to recover oil as fuel using an oil/water separator [23]. Since the iron in the high temperature condensed water is only produced from the corrosion of pipeline, the iron concentration is very low. Iron precipitation in the retentate solution would be treated as sewage sludge.

### Table 2
High temperature condensed water quality before and after UF purification.

<table>
<thead>
<tr>
<th>Items</th>
<th>Residue oil condensed water</th>
<th>Wax oil condensed water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil concentration (mg/L)</td>
<td>Influent</td>
<td>10.8</td>
</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>0.86</td>
</tr>
<tr>
<td>Iron concentration (mg/L)</td>
<td>Influent</td>
<td>0.136</td>
</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>0.0386</td>
</tr>
<tr>
<td>Calcium concentration (mg/L)</td>
<td>Influent</td>
<td>1.09</td>
</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>0.515</td>
</tr>
<tr>
<td>Magnesium concentration (mg/L)</td>
<td>Influent</td>
<td>0.231</td>
</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>0.179</td>
</tr>
<tr>
<td>Sodium concentration (mg/L)</td>
<td>Influent</td>
<td>0.919</td>
</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>0.809</td>
</tr>
<tr>
<td>Conductivity (μs/cm)</td>
<td>Influent</td>
<td>9.55</td>
</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>7.22</td>
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<tr>
<td>Turbidity (NTU)</td>
<td>Influent</td>
<td>25.9</td>
</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>0.12</td>
</tr>
<tr>
<td>Hardness(1/2Ca2++1/2Mg2+) (μmol/L)</td>
<td>Influent</td>
<td>18.3</td>
</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>10.1</td>
</tr>
</tbody>
</table>

### Table 3
Quality criterion for boiler water [40].

<table>
<thead>
<tr>
<th>Furnace type</th>
<th>Boiler pressure (MPa)</th>
<th>Oil concentration (mg/L)</th>
<th>Hardness (μmol/L)</th>
<th>Iron concentration (μg/L)</th>
<th>Conductivity (μs/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam drum boiler</td>
<td>3.8–5.8</td>
<td>≤1</td>
<td>≤5</td>
<td>≤50</td>
<td>≤10</td>
</tr>
</tbody>
</table>

3.4.4. Recovery property of PPESK membrane

The excellent reusability of the membrane will provide stable performance without a significant decline of separation efficiency. Fig. 10 presents the recycling property of PPESK membrane during wax oil condensed water treatment. After four runs of wax oil condensed water ultrafiltration, the flux recovery rate is above 90%. The PPESK membrane shows good flux recovery and high temperature condensed water can be treated consecutively with a certain membrane cleaning period.

![Figure 10](image1.png)

**Fig. 10.** Permeate flux decline over time of PPESK membrane during four runs of wax oil condensed water ultrafiltration (the filtration parameters: TMP was 0.1 MPa and temperature was 80 °C).

3.4.3. Economic evaluation of future combined UF and NF processes for condensed water recycling

Suppose the handling capacity of the system is 50 t/h, and the water recovery rates of UF and NF units are 95% and 90%, respectively. The annual operation time is 8400 h. GE Duratherm Excel series UF and NF membrane modules are applied. The economic evaluation includes economic cost and economic saving.

1. Economic cost evaluation
   - Membrane investments: Fifty UF membrane modules and seventy NF membrane modules are needed based on the estimated permeate flows of UF and NF at 1 m³/h and 0.7 m³/h, respectively. One UF membrane module costs about $2500 and one NF module costs about $2800. The lifetimes of UF and NF membranes are 3 years and 5 years, respectively. Then, membrane investment is estimated at $321,000.
   - Mechanical engineering investments: costs for pump, piping, valve system and automatic control system are around $256,800 (80% of membrane investments). Depreciation period is 15 years.
   - Operating costs:
     - Energy costs: In UF unit, the energy power for one pump (rated flow: 50 m³/h, lift: 30 m) is 7.5 kW/h. In NF unit, the energy power for three pumps (rated flow: 100 m³/h, lift: 117 m) are 135 kW/h (The data is provided by Nanfang pump industry Co., Ltd., China). The power consumption coefficient is 0.7 and the average commercial power cost in China is approximately $0.12 [41]. Then, the annual energy cost is approximate $100,548.
     - Chemicals costs: the annual cost of chemicals is about $15,000.
   - Maintenance costs: $5,136 (2% of total mechanical engineering investments).
   - Labor costs: annual cost of two maintenance workers is about $7,620.

Then, the total economic cost for the UF and NF processes is estimated at $706,104.

2. Economic saving evaluation
   - Desalination water saving

The effluent flow of NF is calculated as 42.75 t/h based on the above mentioned assumption. Then, the total reclaimed amount...
of desalination water per year (M) is 359,100 t. The desalination water saving is calculated $574,560 (per ton cost of desalination water is $1.6).

- **Energy saving**

In addition to desalination water saving, the residual heat of high temperature condensed water can also be saved.

The energy that a material absorbs or releases can be calculated using the following equation:

\[
Q = CM\Delta T \quad (4)
\]

where \( Q \) is the absorbed or released energy (J), \( C \) is the specific heat of the material (J kg\(^{-1}\) K\(^{-1}\)) (the specific heat of water is 4.182 \times 10\(^3\) J kg\(^{-1}\) K\(^{-1}\)), \( M \) is material mass (kg) and \( \Delta T \) is temperature difference (K).

Suppose the effluent temperature of NF is 75 \(^\circ\)C, then the residual energy (Q) of reclaimed high temperature condensed water per year (M) can be calculated using Eq. (4) (room temperature water is 25 \(^\circ\)C).

\[
Q = CM\Delta T = (4.182 \times 10^3) \times (3.591 \times 10^8) \times (75 - 25) = 7.51 \times 10^{13} \text{J}
\]

To obtain the energy shown above, the amount of standard coal (m) is calculated using Eq. (5). Where \( m \) is the amount of standard coal (kg), \( Q \) is released energy that complete combustion of the coal (kJ), \( q \) is the calorific value of standard coal, namely, 29,274 kJ/kg.

\[
m = Q/q = 7.51 \times 10^{10} / 29,274 = 2.565 \times 10^7 \text{kg}\]

If the standard coal price is $79.4 per ton, and then the saved fuel cost is estimated about $203,661.

- **CO\(_2\) emission reduction saving**

Three tons of \( \text{CO}_2 \) will be released by combustion of per ton of standard coal. If the entire saved \( \text{CO}_2 \) emission reduction amount is sold according to Clean Development Mechanism (CDM) ($4.8 per ton), $12,312 can be saved.

- **Sewage discharge fee saving**

Suppose the sewage treatment fee is $0.12 per ton, the saved sewage discharge cost is $43,092.

In summary, approximate $833,625 is saved annually by reclaiming the condensed water. Therefore, the breakeven time of the process is about 11 months.

### Table 4

<table>
<thead>
<tr>
<th>Items</th>
<th>‘Blocking and intercept’ process</th>
<th>Items</th>
<th>UF process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron removal equipment investment</td>
<td>79,400</td>
<td>Membrane modules investment</td>
<td>125,000</td>
</tr>
<tr>
<td>Oil removal equipment investment</td>
<td>317,500</td>
<td>Mechanical engineering investment</td>
<td>100,000</td>
</tr>
<tr>
<td>Annual operating cost</td>
<td>42,000</td>
<td>Annual energy cost</td>
<td>5292</td>
</tr>
<tr>
<td>Annual materials replacement cost</td>
<td>33300</td>
<td>Annual chemicals cost</td>
<td>3200</td>
</tr>
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<td>Annual maintenance cost</td>
<td>3969</td>
<td>Annual maintenance cost</td>
<td>2000</td>
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<tr>
<td>Annual labor cost</td>
<td>7620</td>
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</tr>
<tr>
<td>Per ton cost</td>
<td>0.27</td>
<td>Per ton cost</td>
<td>0.16</td>
</tr>
</tbody>
</table>

#### 3.4.4. Economic comparison of UF process and existing process for oil and iron removal

Now, a ‘blocking and intercept’ oil removal process using fiber coated with strong polarity functional groups is operating in the Daqing petroleum refinery for oil removal of high temperature condensed water. The maximum long term influent oil concentration is 150 mg/L, operating temperature is 50–80 \(^\circ\)C and pH < 7.5. Raw oil and pitch are forbidden in the system. The investment of oil removal equipment is estimated at $4,760–6350 per ton per hour, operating cost is about $0.10 per ton. Fiber lifetime is one year, and cost for fiber replacement is about $33,300–39,700 every year [3]. Another filter tank is required for suspended matter and iron removal prior to oil removal.

Investment and cost comparison of this process and UF process for oil and iron removal is listed in Table 4. The result shows that for depreciation period of 15 years, per ton cost of this process and UF process are approximate $0.27 and $0.16, respectively. UF is a promising and cost-effective process for oil and iron removal.

### 4. Conclusions

In the present study, the purification and recycling of synthetic and industrial high temperature condensed water from petroleum refinery with thermostable PPESK UF membrane has been investigated. The effects of several important factors on the permeate flux and oil/iron removal efficiencies have been investigated in detail. The suitable membrane cleaning method was also considered. The economic cost and saving of UF and NF processes was evaluated as well. The findings of this study may be summarized as follows:

1. In consideration of the permeate flux, removal efficiency and operation cost, 0.1 MPa is selected as the optimal TMP. Higher feed solution temperature is beneficial to mitigate membrane fouling and increase the permeate flux. As initial oil and iron concentrations increase, the permeate flux decreases due to the aggravated membrane fouling. Between pH 5 and 7, permeate flux changes slightly.
2. NaOH in combination with ethanol cleaning method is effective and the FR value is above 95%.
3. High temperature condensed water from the Daqing petroleum refinery can be purified and reclaimed efficiently using PPESK UF membrane. The turbidity of solution is almost completely removed. The oil and iron concentrations in permeate solutions satisfy the Quality Criterion of Water and Steam for Steam Power Equipment (GB/T 12145-2008, China).
4. Compared with an existing process, UF, with per ton cost of $0.16, is a promising and cost-effective process for oil and iron removal. For future possible UF and NF processes application, an estimated $833,625 is saved annually by reclaiming the condensed water, and breakeven time is about 11 months.

### Acknowledgments

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Appendix A. Supplementary material


References