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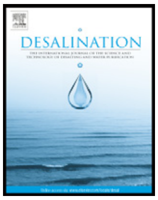

Influence of salts, anion polyacrylamide and crude oil on nanofiltration membrane fouling during desalination process of polymer flooding produced water

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HIGHLIGHTS

- Fouling mechanism when treating PFPW with NF membrane is proposed.
- Mutual influence between different foulants is revealed.
- Effect of various foulants on desalination performance is analyzed.
- Some research suggestions are given accordingly.

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ABSTRACT

The effective management of polymer flooding produced water (PFPW), co-produced in the process of polymer flooding oil extraction, will become a subject to solve urgently. To study membrane fouling properties, a commercial NF membrane (NF90) was adopted to treat model PFPW in this work, with different kinds of salt, anion polyacrylamide (APAM) and crude oil as target foulants. AFM, SEM-EDS, ATR-FTIR and contact angle were employed to analyze various membrane autopsies. The results showed that the membrane fouling was dominantly induced by APAM, as well as salts and crude oil. Various mutual influences between ions and APAM including charge screening, complexation, molecule coiling up and anti-scaling effect would aggravate or mitigate fouling in different combinations. The hydrophilic APAM could produce a “shielding effect” against crude oil because of its rapid adhesion on membrane surface under the strong hydrogen binding and complexation assisted by calcium. Membrane fouling induced by the three target foulants could improve salt rejection by strengthening size exclusion. In addition, the Donnan effect caused by APAM and nonpolar action caused by crude oil can also contribute in salt removal. Finally, fouling mechanism was proposed and some suggestions were put forward.

1. Introduction

Oil consumption is tremendously huge in modern civilization. Most of the current oil production comes from mature oilfields and many enhanced oil recovery (EOR) technologies have been presented to increase oil recovery from the aging resources [1]. Generally, the EOR technologies can be classified into thermal and non-thermal methods. Thermal methods (including hot water flooding, steam flooding, electrical heating technologies and so on) are primarily intended for heavy oils and tar sands, while non-thermal methods (including chemical flooding, gas flooding, microbial EOR technologies and so on) are normally used for light oils [2]. Despite their respective advantages, only a few of the EOR technologies have been commercially successful because of their high technical complexity and capital cost [2]. As one of the chemical flooding EOR techniques, polymer flooding has been successfully applied in full-industrial scale around the world particularly in China, due to its broad adaptability, easy operability and relative low capital cost [1,3,4]. Polymer flooding adds polymers especially anion polyacrylamide (APAM) into flooding water to increase the fluid viscosity and sweep efficiency [5,6]. By this way, the oil production could be increased by 5–30% [4]. Nevertheless, large amount of polymer flooding produced water (PFPW) is always generated along with polymer flooding oil extraction. Alone in *Daqing* oilfield of China, more than 75 million tons of PFPW is produced every year. This problem will be increasingly serious with the decrease of oil resource in the near future. Direct discharge of such gigantic volumes of PFPW without proper treatment will not only bring much harm to the environment, but also be a great waste of water resource, particularly in water-deficient areas. In addition, large amount of clean water is in demand when preparing APAM flooding solution. Therefore, it becomes quite reasonable

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to recycle PFPW for polymer flooding oil exploitation as an internal reuse pattern.

Compared with the conventional produced water, PFPW contains not only crude oil, minerals, and bacteria., but also residual APAM, which makes the wastewater more difficult to be treated with common methods. Even after a series of treatments, such as floatation, coagulation, sedimentation, sand filtration and ultrafiltration (UF), PFPW still contains relatively high salinity and some residual organic matters [7]. Cations, especially divalent cations, would cause the shielding of APAM's negative charge, thereby leading to the linear polymer chain's coiling up and then the decrease of solution viscosity, eventually making the recycled water not qualified for the preparation of APAM flooding solution [8]. Therefore, PFPW, even after the sequence of processes above, still has to be further treated in order to decrease salinity to an acceptable level.

Nanofiltration (NF) membranes with pores around 1 nm always acquire electric charges in aqueous solution, which makes the separation achieved by both size and charge exclusion [9,10]. NF is capable to effectively reject low molecule organics and multivalent ions, and partially remove monovalent ions, like sodium ions and chloride ions. Compared with reverse osmosis (RO), NF consumes less energy and discharges less concentrate. With all these features, NF is widely applied in water softening, brackish water and seawater desalination, food and medicine production [11–16]. Su et al. employed an integrated system of UF-NF to soften seawater and provided the permeate for offshore oilfield polymer flooding [17]. Their results demonstrated that this technology could effectively meet water standards for polymer flooding and ensure stable oil production. Many researchers [18–22] purified produced water with various NF and RO membranes aiming for water reuse, confirming the feasibility of this technical process. Based on the facts above, it is highly expected to adopt NF to realize PFPW reuse for polymer flooding extraction.

However, during the application of NF in treating PFPW, the inevitable membrane fouling would decrease the water flux, change the effluent quality, as well as increase cleaning frequency and operating costs. Up to now, most studies on NF membrane fouling put their focus mainly on the foulants such as natural organic matters (NOMs), proteins, polysaccharides, and inorganic precipitations [23]. Systematic membrane fouling mechanism involving PFPW was scarcely identified. Although Alzahrani and Mondal [22,24] probed membrane fouling mechanism in NF treatment of produced water, the produced water in their experiments was actual wastewater from water flooding oilfield which did not contain APAM.

In this research, AFM, SEM-EDS, ATR-FTIR and contact angle goniometer were employed to analyze the autopsies of various fouled NF membranes obtained in the filtration experiments. Afterwards, different roles of salts, APAM and crude oil in membrane fouling as well as their mutual influence were revealed by comparing the flux attenuation characteristics during the treatment process of different model solutions. Furthermore, an effective treatment was demonstrated by NF of model PFPW, during which the changes of desalination performance with membrane fouling were primarily detected. Finally, the fouling mechanism during the desalination process of PFPW was proposed, and some suggestions were made accordingly. The present work can be a theoretical guidance for the membrane fouling control during desalination of PFPW by NF.

2. Materials and methods

2.1. Characterization of NF membrane

A thin-film composite NF membrane called NF90 (Dow FilmTec, Minneapolis, MN, USA) was used in this study. NF90 is a fully aromatic polyamide membrane made from 1, 3-benzenediamine and trimesoyl chloride via the process of interfacial polymerization [25]. Compared with other NF membranes, this membrane has a denser polyamide active skin layer, so its rejections of monovalent ions and low molecule organics are higher. Various properties of NF90 are summarized in Table 1.

2.2. Model foulants and chemicals

APAM is a hydrophilic linear polymer with high solubility in water. The molecule weight of the APAM used in this work is 500,000 g/mol, and its purity is higher than 99% (Daqing, China). The chemical structure can be found in [26]. As the APAM powder is easily to imbibe moisture in the air, it should be dried in oven at 100 °C (APAM would decomposes if temperature ≥ 150 °C) before use. The crude oil used in this study was provided by the 5th *Daqing* oil production factory. After electric dehydration, its moisture content is lower than 0.5%. No further purification was conducted before use. Other chemicals were all of analytical grade from Tianjin Benchmark Chemical Reagent Co. Ltd (Tianjin, China). Water used in this research was ultrapure water (Milli-Q water, Millipore Milli-Q reference ultrapure water purification system, USA).

2.3. Preparation of model solutions

All the feed solutions were model solutions prepared in laboratory. The ion composition and foulant concentration of the model solutions used in our experiments were similar to the real wastewater. As there were a mass of HCO_3^- in it, the buffering capacity of model PFPW was strong enough to keep its pH in 8.5–8.8. Therefore, the regulation of pH was not necessary in this work. The 14 kinds of model solutions used in filtration experiments are listed in Table 2. The ion composition of the saline water (SW) is shown in Table 3.

Crude oil stock solution was prepared as the following procedures: excessive crude oil which had been melted at 60 °C was added in flasks containing ultrapure water. Then ultrasonic dispersion and electric stirring were simultaneously lasted for 1 h. Afterwards, the oil slick in flasks was skimmed thoroughly and the oily solution was filtered by slow qualitative filter paper in order to remove dispersed oil. Eventually, stock solution containing crude oil was prepared. The accurate crude oil concentration of the stock solution should be measured with the method described in Section 2.5.

The SW was prepared by dissolving 1.5800 g NaCl, 0.1000 g K_2SO_4, 0.0200 g $CaCl_2$, 0.6408 g $MgCl_2 \cdot 6H_2O$, and 3.0000 g $NaHCO_3$ in every liter of ultrapure water; the FWCA10, FWCA30 and FWCA50 were

Table 1
Summary of the characteristics of membrane NF90.

Parameters	Values	Parameters	Values
MWCO (Da)[a]	100–200	Operating pH range [b]	3–10
Rejection of NaCl (%)[b]	85–95	Cleaning pH range [b]	1–12
Water permeability ($L/m^2 \cdot h \cdot bar$)[b]	5.2–8.1	Max operating pressure (bar)[b]	41
Contact angle (°)	61.5	Zeta potential (mv, pH = 6.3)[c]	−31.1
Max operating temperature (°C)[b]	45	Average pore diameter (nm)[d]	0.64 ± 0.01

[a] Data from [25] and [27].
[b] According to the manufactures.
[c] Data from [28].
[d] Data from [29].