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Study of the contribution of the main pollutants in the oilfield polymer-flooding wastewater to the critical flux

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ABSTRACT

One of the major technical requirements of the crude oil exploitation industry is to minimize the concentration of hydrolyzed polyacrylamide (HPAM), crude oil and suspended solid (SS) in the oilfield polymer-flooding wastewater and realize the reuse of this wastewater. In this study, the membrane technology was used to achieve this goal in laboratory-scale dead-end test unit with flat polyvinylidene fluoride (PVDF) membrane (MW 100 kDa). We systematically inspected the membrane fouling mechanism, the variety of total membrane resistance, total fouling resistance, the dominant resistance, membrane fouling driving force and the filtration proceeds in the filtration process. The orthogonal method and multivariate linear regression method were applied to analyze the influencing degree of the main pollutant concentration on the critical flux. According to comparison of the average rates of change of the critical flux for the HPAM concentration, oil concentration and SS concentration in single solute solution, double solute solution and oilfield polymer-flooding wastewater, HPAM can decrease the average rate of change of the critical flux for other two solutes and has the crucial effect on the critical flux. The sequence of influence degree on the critical flux is the HPAM concentration (84.58%)>oil concentration (14.36%)>SS concentration (1.06%).

1. Introduction

Petroleum is an important chemical raw stuff and fossil fuel. After the water flooding process or secondary oil extraction, the tertiary oil extraction has been widely used in Chinese oilfield in recent years [1,2]. Industrial experiences show that polymer flooding can enhance oil recovery up to 12% and play a key role in the oil exploitation [3,4]. Although this technology can enhance the oil recovery up to 12% [3], it also produces more and more polymer-flooding wastewater as byproduct per year [4]. In addition, with the development of the mechanical processing industry, the output of the polymer-flooding wastewater becomes more and more [5]. The thin oil film existing on the water surface will cause the reduction of dissolved oxygen in the water body, leading to the death of aquatic life and make water resource toxic for irrigative or drinkable purpose [6–8]. Furthermore, the oil pollutant pollutes and poisons the atmospheric environment. Consequently, removing oil from the wastewater is an important aspect of pollution control in many industrial fields [9].

In crude oil exploitation, polyacrylamide (PAM) is one of the most widely used polymers. The hydrolyzed polyacrylamide (HPAM) is extracted together with crude oil from oil wells. The HPAM residue with anionic charge dissolved into water will increase the viscosity of oily wastewater, making the suspended solid and oil steady and difficult to remove [10]. Several methods, such as gravity settling [11], flotation [12,13], demulsification [14–16] and biotechnology [17,18] have been used for treating of oilfield polymer-flooding wastewater. Unfortunately, none of these traditional separation techniques can meet complex demands for purifying the polymer-flooding wastewater of tertiary oil extraction. How to treat the oilfield polymer-flooding wastewater efficiently still remains unsettled.

Currently, ultrafiltration technology plays a more prominent role in the treatment of oily wastewater [19,20]. However, the major problem arising from the membrane process is the decline in flux due to the concentration polarization and membrane fouling. The scientific practice suggests that the membrane fouling can be avoided [21] when the operating flux is lower than a certain flux (critical flux). In contrast, when the operating flux exceeds this flux, the colloids initially present in the polarized layer will transform from the liquid phase into an irreversible cake layer [22–24]. Since then, many studies have focused on the critical flux, including the effect of hydrodynamic factors such as cross-flow velocity (CFV) [25], sufficient shear stress [26], sludge concentration [27] and particle size [28,29] on the critical flux for colloidal suspension [22,30], mineral suspension [31], protein or yeast suspension [32] and activated sludge water [33]. As the study of the critical flux, the membrane resistance at sub-critical flux was investigated all along [34,35]. In addition, T.Y. Chiu et al. [36] reported that the gas could be used as a means of enhancing the critical flux in a non-circular multi-channeled (star-shaped) ceramic membrane module. T.H. Chong et al. [37] developed a sodium chloride tracer

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response technique to determine the critical flux of colloidal silica in reverse osmosis process.

However, the critical flux, as the function of main pollutant (HPAM, crude oil and suspended solid) concentration in synthetic oilfield polymer-flooding wastewater, is rarely reported in the present literature. So, this article aims to establish these relationships and quantitatively estimate the contribution of various pollutant concentrations to the critical flux. In this paper, main pollutants (HPAM, crude oil and suspended solid) and their fouling behaviors in treating synthetic oilfield polymer-flooding wastewater by UF membrane are also concerned.

2. Materials and methods

2.1. Materials

Polyvinylidene fluoride (PVDF) flat membranes with a molecular weight cut-off (MWCO) of 100 kDa (Beijing Ande Membrane Separation Technology Engineering, China) were used as the filtration medium. Before conducting the experiment, the PVDF membranes were soaked in deionized water for 10–12 h to remove glycerin, which was used as a protective agent in membranes. The water content of crude oil (China Tianjin Dagang oilfield) was less than 0.5%. The polyacrylamide (PAM) with an average molecular weight cut-off of 2720 kDa was supplied by China Tianjin factory of leechdom.

2.2. Experimental system

A dead-end cell filtration system was designed to characterize the filtration performance of membranes which was described elsewhere in the literature [38–40].

The synthetic oilfield polymer-flooding wastewater was used as the test solution.

2.3. Preparation of feed solution

2.3.1. Preparation of synthetic oilfield polymer-flooding wastewater

Synthetic oilfield polymer-flooding wastewater was prepared in our laboratory as follows:First, according to Table 1, the initial water with a salinity of different types was prepared to gain the brine; then 180 g of this brine and 20 g of 1% surfactant ORS-41 were added to a 500 mL jar. The mixture was then heated to 45 °C. 200 g of crude oil at 45 °C was added consecutively. The mixture was finally emulsified for 5 min at 20,000 rpm to obtain the 50% oil–water mixture. A 99.6 mL stock solution with different concentrations of polyacrylamide was prepared in a 250 mL jar. Different weights of the 50% oil–water mixture and different weights of the suspended solid were then added to the polyacrylamide solution. Finally the produced water was transferred to a 100 mL beaker, and allowed to settle for 4 h at 45 °C in an oven [41].

2.3.2. Preparation of the single suspended solid, HPAM and oil solution

In order to achieve the desired concentration, a specific amount of the suspended solid, PAM and emulsified oil were dissolved into a specific amount of brine as shown in Table 1 with stirring for 20 min, and the suspensions were prepared daily and generally used within 24 h.

Table 1
Chemical components of prepared brine ($mg \cdot L^{-1}$).

Ion	Content
$K^+ + Na^+$	1195.4
Ca^{2+}	9.0
Mg^{2+}	1.8
Cl^-	806.7
SO_4^{2-}	2.4
HCO_3^-	1660.0
CO_3^{2-}	98.2
Total salinities	3773.5

2.4. Experimental procedure

In this study, firstly, the intrinsic resistance of the membrane was measured by the filtration experiment of deionized water. Secondly, the experiments of fouling mechanism were conducted under a transmembrane pressure (TMP) of 0.30 MPa at a temperature of 30 °C. Thirdly, the critical flux was studied in order to alleviate the membrane fouling, and the TMP-step technique [42] was used to determine it: the TMP was kept low firstly, and then increased at fixed intervals of 30 min. The data were noted at intervals of 30 s. If the TMP became non-linear with the permeate flux, it was indicative of a critical flux. The critical flux was the average value between the last time independent flux step and the first time dependent flux step as employed previously.

2.5. Microscopy

Scanning electron microscopy (SEM) images were obtained using an EVO40 Carl Zeiss microscope (Cambridge, London). Membrane samples were freeze-fractured and then coated by sputtering a thin gold layer. These samples were observed under high vacuum. The SEM images were used to analyze the pollution status of the membrane.

2.6. The total fouling resistanceR_f

According to Darcy's Law, the flux of the dead-end UF/MF membrane filtration can be expressed as follows [43]:

$$J = \frac{dV}{Adt} = \frac{TMP}{\mu\left(R_f + R_m\right)} \tag{1}$$

where J is the permeate flux with the unit in $m^3 \cdot m^{-2} \cdot s^{-1}$; TMP is the transmembrane pressure with the unit in Pa; $\mu$is the viscosity with the unit in Pa · s; R_m and R_f are the intrinsic membrane resistance and the total fouling resistance respectively with units in m^{-1}.

2.7. Fouling mechanism

The Blocking Law, first put forward by Herman et al. [44] in 1935, was used to study the fouling mechanism of filtration experiments [45]:

$$\frac{d^2t}{dV^2} = k\left[\frac{dt}{dV}\right]^n \tag{2}$$

where t is the filtration time with the unit in s; $V$is the total filtered volume with the unit in m^3; $k$is the proportional coefficient; $n$is the exponent, which characterizes the fouling mechanism.

Table 2
Range of concentration of various pollutants.

Factor	Range	Reference
HPAM concentration ($g \cdot L^{-1}$)	0.048–0.63	[41,48]
Oil concentration ($g \cdot L^{-1}$)	<2	[41]
SS concentration ($g \cdot L^{-1}$)	0.022–0.167	[48–50]