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Antifouling performance of polytetrafluoroethylene and polyvinylidene fluoride ultrafiltration membranes during alkali/surfactant/polymer flooding wastewater treatment: Distinctions and mechanisms

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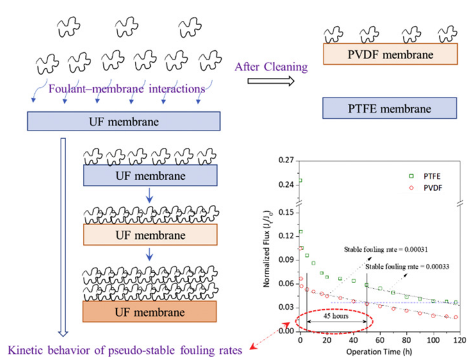
HIGHLIGHTS

- Foulant–membrane interactions control the kinetic behavior of stable fouling rates.
- Later achievement of the stable fouling rate corresponds to lower fouling resistance.
- APAM–PTFE interactions are significantly stronger than APAM–PVDF interactions.
- Great permeation fluxes and flux recoveries present superior antifouling performance.
- APAM co-occurred with metal ions in the fouling layers of PTFE and PVDF UF membranes.

GRAPHICAL ABSTRACT



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ABSTRACT

Alkali/surfactant/polymer (ASP) flooding wastewater is highly caustic, and membrane fouling is the main obstacle during ASP ultrafiltration (UF) treatment. To maintain favorable filtration performance, polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF) membranes were implemented here, and their antifouling properties and mechanisms were investigated based on the threshold flux theory. Compared with the PVDF membranes, the PTFE membranes exhibited superior antifouling properties with lower reductions in flux and smaller hydraulic resistance, and they presented a nearly identical pseudo-stable fouling rate at a later time point. In the fouling layers of the PTFE and PVDF membranes, anion polyacrylamide (APAM) was observed along with divalent/trivalent metal ions. The thermodynamic and molecular mechanisms of membrane fouling by APAM were elucidated using the Extended Derjaguin–Landau–Verwey–Overbeek (XDLVO) theory and atomic force microscopy (AFM), respectively. The calculated total interfacial free energy (mJ/m^2) of adhesion between the APAM and PTFE membranes was positive, and the value between the APAM and PVDF membranes was negative. Furthermore, the values and interaction distances of the measured intermolecular rupture and approaching forces were larger for APAM-PTFE than for APAM-PVDF. For the PTFE membranes, the positive free energies and smaller intermolecular interaction resulted in weaker APAM-PTFE adhesion and adsorption and therefore the lower levels of flux decline and the later achievement of the pseudo-stable fouling rate. Additionally, the total

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flux recoveries observed after physical cleaning reached 0.78–0.80 and 0.32–0.39 for the PTFE and PVDF membranes, respectively, which showed that the PTFE membranes can be cleaned easily. The PTFE membranes have considerable potential for extensive application in UF treatments for ASP wastewater. These results should promote understanding the essence of the threshold flux and the fouling control of UF membranes.

1. Introduction

Polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF) are fluoropolymers with repeated units of $(CF_4)_n$ and $(CH_2CF_2)_m$, respectively. Both materials exhibit high levels of thermostability, mechanical strength, chemical resistance and aging resistance, which are of paramount practical importance for the sustainable application of membrane technologies (B. Zhang et al., 2016; Zhang et al., 2013). PTFE membranes are widely used for membrane distillation (Bottino et al., 2015; Feng et al., 2016; Jafari and Moraveji, 2016; Zhang et al., 2017), high-temperature polymer electrolyte membrane fuel cell construction (Cao et al., 2012; Jeong et al., 2016; Mack et al., 2016; Rofaiel et al., 2012; Wei et al., 2013; Zhang et al., 2017), membrane gas absorption (Chen et al., 2011; Constantinou et al., 2014; Franco et al., 2012; Wang et al., 2015), gas sensor construction (Pirsa et al., 2016), gas filtration (Zhang et al., 2008) and regeneration procedures (Carbonell et al., 2014; Higuchi et al., 2016), and they have recently been used in water treatments (El-Abbassi et al., 2012; Lee et al., 2013; Xiong et al., 2016; Yonezu et al., 2014; Zhang et al., 2015; B. Zhang et al., 2016). PVDF membranes are among the most commonly used for water separation and purification (Robinson et al., 2016). Because of their considerable inertness, PVDF and PTFE membranes can maintain stable performance over long-term operations.

With the gradual increase in crude oil demand, alkali, surfactants and polymers are extensively being used to enhance oil recovery from oilfields during the middle and later development periods. Consequently, large volumes of alkali/surfactant/polymer (ASP) flooding wastewater is produced during oil extraction (e.g., 3×10^8 m^3/d from the Daqing oilfield in China (G. Liu et al., 2018; B. Zhang et al., 2016)), and this wastewater is generally characterized by a pH of 10.0–11.0, a high concentration of polymers (e.g., 460–840 mg/L anion polyacrylamide (APAM)), and a high concentration of total dissolved solids (e.g., 10,000–12,000 mg/L). Because of the potential risks to the environment, ASP flooding wastewater must be treated prior to its reuse or discharge. Membrane separation processes, especially ultrafiltration (UF) processes, are considered superior technologies for ASP flooding wastewater treatment. In addition, the permeation water can be reused as oilfield injections and feed water for electrodialysis, thus providing economic and environmental benefits. However, membrane fouling is generally inevitable (Shi et al., 2016), even under optimized operational conditions.

Based on the aforementioned advantages of fluoropolymers, PVDF and PTFE membranes could be used to treat ASP flooding wastewater, which is highly caustic. In addition, PTFE has the lowest friction coefficient and surface tension levels among similar construction materials, thus leading to favorable levels of lubricity and inadhesion and maybe satisfactory antifouling performance. The concept of threshold flux, which depends on fouling rates, is used to distinguish the low and high fouling regions (Field and Pearce, 2011). With the flux at or below the threshold flux, the fouling rate was low and pseudo-stable; whereas, when operating above the threshold flux, the fouling rate was high and kept increasing (Field and Pearce, 2011; W.X. Zhang et al., 2016). Based on concepts associated with the threshold flux, few studies have investigated the distinctions in the antifouling performance between PTFE and PVDF membranes. Moreover, the fouling mechanisms of PTFE and PVDF UF membranes used for ASP flooding wastewater treatment must be subjected to a quantitative analysis.

The extended Derjaguin–Landau–Verwey–Overbeek (XDLVO) theory is used to quantitatively evaluate the non-covalent interfacial interactions, and atomic force microscopy (AFM) is available to quantitatively measure intermolecular forces. Both of them have been highlighted in investigation of the mechanisms of membrane fouling in aqueous systems (Brant and Childress, 2002; Gao et al., 2017; Liu et al., 2016; Mi and Elimelech, 2010). XDLVO theory is based on three interfacial interactions of Lewis acid-base (AB), Lifshitz–van der Waals (LW) and electrostatic double layer (EL) interactions. AB interactions have been reported to play a prominent role in membrane colloid fouling (Kim and Hoek, 2007) and bacterial and organic material deposition onto membranes (Li et al., 2014; Subhi et al., 2012; Subramani et al., 2009). Moreover, the weakening of energy barriers between natural organic materials and aged membranes promote fouling tendencies (Gao et al., 2017). AFM in conjunction with a foulant-modified probe has been utilized to quantify the foulant-membrane and foulant-foulant adhesion forces. In particular, membrane—foulant adhesions correspond to the antifouling property of membranes (Tiraferri et al., 2012; Wang et al., 2013). Accordingly, both the XDLVO theory and AFM technology should be applied to quantify the fouling mechanisms of PTFE and PVDF membranes in the UF treatment of ASP wastewater.

In this study, PVDF and PTFE membranes were applied for the UF treatment of ASP wastewater (obtained from Daqing oilfield in China) in a semiautomatic facility. Based on the threshold flux theory, the fouling behaviors between the PVDF and PTFE membranes were compared. Then, the major foulants were identified and the calculated interfacial free energies and measured intermolecular forces among the foulants and membranes were analyzed. The relationships between the fouling behaviors and foulant-membrane interactions were discussed here to reveal interfacial thermodynamic and molecular mechanisms underlying the distinct antifouling performance between the PVDF and PTFE membranes. These results are expected to promote understanding the essence of the threshold flux and the fouling control of UF membranes. In addition, the flux recoveries measured after physical and chemical cleaning were investigated to further understand the differences in antifouling performance.

2. Materials and methods

2.1. Semiautomatic UF setup

A semiautomatic UF device (see Fig. 1, fouling/cleaning cycles were applied) was established to treat ASP flooding wastewater from the Daqing oilfield in China. The plan primarily involved the use of a membrane module, a constant flow pump, a pressure transducer, a raw water tank and an automatic control device equipped with a data acquisition system (B. Zhang et al., 2016). The fouling/cleaning cycles were performed using this semiautomatic setup, and the cleaning procedures were conducted in situ. Flat-sheet PTFE and PVDF membranes were used for the UF setup, and the quality index for the ASP flooding wastewater is presented in Supporting information (SI), Table S1. The permeation quality of the UF tests under optimized conditions were as follows: concentrations of crude oil and suspended solids (SS) were 1.5–4.0 mg/L and 1.0–2.0 mg/L, respectively, and the median diameters were not detected. All of these values were lower than the higher limits of 5.0 mg/L, 3.0 mg/L and 1.0 μm according to the SY/T5329-94 regulation prescribed by the People's Republic of China.