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A comprehensive description of the threshold flux during oil/water emulsion filtration to identify sustainable flux regimes for tannic acid (TA) dip-coated poly(vinylidene fluoride) (PVDF) membranes

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ABSTRACT

In the separation of oil/water emulsions using membrane separation methods, fouling remains a problem. To improve the fouling resistance effectively, a hydrophilic tannic acid (TA) coating was constructed on the poly (vinylidene fluoride) (PVDF) membrane via dip-coating method. Both the wettability and surface free energy were dramatically enhanced after the introduction of the TA coating. TA deposition with extended dip-coating time did not result in a corresponding increase in the pure water permeate quality, suggesting that there is a trade-off between the enhanced surface hydrophilicity and diminished pore size. Furthermore, the threshold fluxes were determined using the flux-stepping method, and explored to provide guidance on membrane fouling rates for oil/water emulsion filtration. The hydrophilic TA dip-coated PVDF membrane prepared at a dip-coating time of 9 h exhibited the highest threshold flux compared to the other membranes. The experimental evidences of the threshold fluxes can be used to predict the sustainable flux regimes for the TA dip-coated membranes. Constant flux verifiable experiments for oil/water emulsion were performed at fluxes near and below the threshold fluxes. By selecting a constant flux strategy below the threshold flux, membrane over-fouling can be avoided efficiently and the operating period can be prolonged favourably. More generally, operation below the threshold flux recognizes a modest fouling level, arising from the sufficient flux, which would result in the infrequent need for cleaning and is a compromise between capital expenditure and operating costs.

1. Introduction

Many industrial processes, such as petrochemical extracting, metal/steel smelting, food processing, and textile manufacturing, generate an enormous amount of oily wastewater [1,2]. These emulsified oil/water mixtures are required to handled appropriately before disposal to ensure that the presence of oily contaminants in freshwater meets quality criteria [3]. Compared with conventional wastewater treatments, membrane separation is one of the most advanced technologies, especially for suspended emulsified oil droplets, yielding discharge-quality water and having an acceptable capital investment with a small footprint [4,5]. However, filtration membranes are vulnerable to severe fouling, resulting in elevated transmembrane pressures and consequent operational expenses during the separation process. To maintain the overall flux at a sustainable level, various cleaning methods, such as backflushing, chemical cleaning, or air sparging, are carried out periodically. In recent years, numerous hydrophilization approaches have been used to modify the membrane surface to avert and alleviate oil fouling [6–8].

Membrane surface modification is an effective and stable approach in which hydrophilic ingredients are immobilised onto the membrane surface to confer fouling resistance. To date, most research has focused on the design of advanced functional membranes with the aim of enhancing permeability [9–11]. For example, Zhu et al. [12] fabricated a zwitterionic polyelectrolyte brush poly(3-(*N*−2-methacryloxyethyl-*N*,*N*-dimethyl) ammonatopropanesultone)-grafted poly(vinylidene fluoride) (PMAPS-*g*-PVDF) membrane via surface-initiated atom transfer radical polymerisation for oil/water emulsion separation. The modified PMAPS-*g*-PVDF membrane achieved ultrahigh separation efficiency and showed improved antifouling properties. Huang and co-

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workers [13] immobilised a poly(*N*-vinyl pyrrolidone) (PVP) layer on the alkali-treated PVDF membrane surface via hydrogen-bonded interactions for oily wastewater treatment. The modified PVDF/PVP membrane showed improved separation properties and exceeded the flux recovery of 90%. Kasemset et al. [14] modified a polyamide reverse osmosis membrane by direct dip-coating with a poly(dopamine) (PDA) coating, which exhibited a higher flux for oil/water emulsion filtration without additional modification. For these approaches, the vital issue to be addressed is the rapid decline in flux and separation efficiency because oil contaminants are highly susceptible to adsorption on the membrane surfaces. Achieving a sustainable flux operation at low fouling status is crucial for oil/water separation. However, less attention has been paid to obtaining an in-depth understanding the management of complex fouling phenomenon and how to manage it, both of which are often neglected but are extremely important. Therefore, it is vital to explore ways of controlling fouling during the oil/water separation process to ascertain the most appropriate compromise between permeability and prolonged operation.

Membrane-based oil/water emulsion separation with a zero-fouling rate is unrealistic. However, a pragmatic alternative, the “threshold flux” has been reported [15]. Below the threshold flux, a low and near constant rate of fouling occurs. Above it, the fouling rate increases markedly. In industrial membrane filtration, the threshold flux is considered to be the sufficient permeate flux that allows separation at an acceptable low rate of fouling so that the operating regime is affordable and does not require frequent membrane cleaning. The majority of threshold flux determinations are conducted using flux-stepping method, in which the imposed flux is a stepwise increased, and the response of transmembrane pressure (TMP) is monitored. The flux which results in a deviation from the linear TMP versus flux curve is explored as the nominally “threshold flux”. Using this method, He et al. [16] provided a framework to bridge constant pressure and constant flux operations during oil/water emulsion microfiltration. They observed that membrane fouling below the threshold flux was induced by the filtration process. In practical separation process, the fouling tendency of oil/water emulsion feeds is conspicuous, and in permeation flux should be selected with intention of avoiding rapid fouling and TMP rise. Kirschner et al. [17] investigated PDA-poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC)-modified membranes with oil/water emulsion at fluxes below and near the threshold flux. The PDA-PMPC modified membranes exhibited a low mass transfer resistance and sustainable operation below the corresponding threshold fluxes, while the membranes displayed rapid fouling above the corresponding threshold fluxes. Clearly economic factors have rightly played a vital role in this decision. It follows that the determined economically threshold in one set of circumstances will be adopted if energy prices increase and/or maintenance costs rise. Thus, the exploration of the threshold flux is a useful approach for achieving a sufficiently high flux that is a compromise between acceptable integrated peripherals (intensivism of capital expenditure) and moderate cleaning frequency (savings of operating costs).

Tannic acid (TA), a low-cost and environmental friendly polyphenol, can be extracted from plants including tea leaves, oak wood, nettle, and Chinese galls [18]. The presence of abundant catechol or galloyl groups in TA provides an inspiration for the nature-derived coating in a similar way to the adhesive mechanism of PDA polymerisation [19]. Compared with dopamine, TA has already garnered interest as a hydrophilic surface modification agent for a variety of membrane processes because it is nontoxic, colourless, easily accessible, and cost-effective [20–22]. Zhang et al. [20] fabricated a co-deposited coating with TA and diethylenetriamine on three types of microfiltration membrane surfaces and found that the surface wettability and pure water permeation were dramatically improved. Fan et al. [21] reported a TA-Fe(III) composite coating on the poly(ether sulfone) (PES) nanofiltration membrane surface and observed that the permeation and separation properties of the membrane were enhanced. Wu et al. [22] employed a TA/PVP coating on the polyamide reverse osmosis membrane surface and revealed that the surface hydrophilicity and fouling resistance of the membrane were obviously enhanced. For oil/water emulsion separation processes, comprehensive investigation of the antifouling property and threshold flux of ultrafiltration membranes using TA as a hydrophilic coating has never been reported. Herein, we report the development of a TA coating that can be applied via the simple dip-coating of a PVDF ultrafiltration membrane. The effect of adjusting different deposition times on the chemical composition, surface morphology, and wettability was analysed. The results for pure water permeability were rationalised as a result of a trade-off between the variation in the mean pore size and hydrophilicity accompanying various dip-coating times. Moreover, the threshold flux of the membranes during oil/water emulsion filtration was obtained quantitatively using flux-stepping experiments. The deposition characteristics of TA provide the possibility of controlled fouling by exploring the threshold flux. Constant flux verifiable experiments were conducted at fluxes above, near, and below the threshold flux, and we used the predicted fluxes to understand the fouling behaviour in long-term fouling experiments. Clarifying the methodology for the threshold flux could provide an economic viewpoint for achieving a sufficiently high permeability over prolonged operating periods.

2. Experimental

2.1. Materials

PVDF powders (Solef 1010, M_w = 352,000 g/mol, M_w/M_n = 2.3) were purchased from the Solvay Company, Belgium. Polyethylene glycol (PEG, M_w = 6000 g/mol, density = 1.08 g/cm^3) was bought from Kemiou Fine Chemical Research Institute (Tianjin, China). Before use, PVDF and PEG were dried for several hours under vacuum to remove residual water until a constant weight was achieved. Tris(hydroxymethyl) aminomethane (Tris) was purchased from Sigma-Aldrich, and the pH value of the prepared Tris buffer was adjusted to 8.5. Tannic acid was obtained from Aladdin Chemistry Co., Ltd. (Shanghai, China) and used without further purification. Sodium chloride (NaCl) was purchased from Fengchuan Fine Chemical Research Institute (Tianjin, China). *N*,*N*-dimethylformamide (DMF) was used as the solvent and obtained from Guangfu Technology Development Co. Ltd (Tianjin, China). Rice oil (Golden Dragon Fish) was purchased from a local supermarket. Other reagents were all analytical grade and used without further purification.

2.2. Preparation of the PVDF membrane

PVDF membranes were prepared by the immersed phase inversion process. A proportion of PVDF and PEG was added into a DMF solution and stirred for 6 h at 60 °C. For the casting solution, the mass ratio of PVDF, PEG, and DMF was 13:7:80. After the components had been dissolved, the mixture was left for 24 h at 60 °C to remove bubbles. The casting solution was cast on the glass plate using a 300 μm casting knife and dipped into a coagulation bath of deionised water at 25 °C. After repeated washing, the as-prepared membranes were immersed in deionised water for at least 24 h to remove any residual solvent. Partial samples were taken out and dried naturally; the others were stored in deionised water.

2.3. Preparation of TA-modified PVDF membrane

The pre-treated PVDF membranes (8 × 8 cm^2) were submerged in Tris buffer containing 0.6 M NaCl and 2.0 M TA, and the pH value of the buffer was adjusted to 8.5. The TA coatings were produced by immersing the membranes in the dip-coating solution with mild shaking for designated periods at 25 °C, and the shaking velocity was constant at 60 tilts per minute. The modified membranes ($M_{\text{TA-PVDF}}$) were repeatedly