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Effect of polydopamine deposition conditions on polysulfone ultrafiltration membrane properties and threshold flux during oil/water emulsion filtration

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ABSTRACT

Surface modification of porous membranes for water filtration has been extensively reported in the literature to improve fouling resistance. However, surface modification can significantly change the membrane filtration properties, sometimes resulting in more severe fouling than with the original, unmodified membrane. This study focused on demonstrating surface modification strategies and membrane comparison strategies to better understand the complex, competing phenomena occurring when membranes are surface modified. Polysulfone ultrafiltration membranes were modified with polydopamine (PDA) at different initial dopamine concentrations and deposition times. Membrane properties, including surface hydrophilicity, roughness, and zeta potential, were characterized. PDA coatings significantly increased surface hydrophilicity, but they did not markedly change the surface roughness or zeta potential. The threshold flux during oil/water emulsion filtration was determined and used as a fouling parameter for membranes modified with PDA at various modification conditions. The threshold flux increased when PDA was deposited at low initial dopamine concentrations or short coating times. However, PDA deposition at high initial dopamine concentrations or long coating times decreased the threshold flux, suggesting that a tradeoff exists between increased hydrophilicity and reduced pore size due to surface modification. An increase in membrane surface hydrophilicity was observed at all PDA deposition conditions, which tends to reduce foulant adhesion and increase threshold flux. However, extensive PDA coating significantly decreased membrane pure water permeance, suggesting that some membrane pores may have been narrowed or blocked, increasing local permeate flux through the remaining pores in the PDA-modified membranes. This higher local flux would exacerbate fouling and decrease threshold flux. Comparing unmodified and PDA-modified membranes having similar pure water permeance values, the PDA-modified membranes had higher threshold fluxes than the unmodified membranes.

1. Introduction

Fouling remains a major challenge for water purification membranes. Fouling occurs when solutes or particles in a feed solution accumulate in the membrane pores or on the membrane surface, and in turn, reduces membrane permeance [1,2]. Membrane surface modification can reduce fouling by altering the surface properties to weaken membrane-foulant interactions [3,4]. Surface modification studies have been reviewed elsewhere [4,5]. Fouling mitigation in surface-modified membranes has been linked to increases in surface hydrophilicity, decreases in surface roughness, and decreases in surface charge [3,4,6]. However, application of coatings or grafting materials to membrane surfaces may

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introduce additional mass transfer resistance to the membrane, resulting in reduced pure water permeance [3,7,8]. For porous membranes, the permeance decrease is often due to membrane separation layer thickness increase and pore size reduction or pore blockage caused by surface modification [9,10]. During constant global (i.e., overall) permeate flux filtration, pore blockage or pore size decrease could increase local convective permeate flux through the pores, enhancing the forces responsible for bringing foulants to the membrane surface, thereby increasing fouling [6].

Polydopamine (PDA) is a highly hydrophilic material which non-specifically deposits onto many substrates from alkaline, aqueous buffered solution in an aerobic environment [8,11,12]. PDA is stable under mild acidic and basic conditions, so it is compatible with traditional membrane cleaning chemicals [13–15]. The hydrophilic PDA surface modification can reduce hydrophobic–hydrophobic interactions between the membrane and foulants, improving membrane fouling resistance [16–20]. Nevertheless, severe reductions in membrane pure water permeance due to application of the PDA coating on porous membranes should be minimized to avoid, at fixed global or overall flux, increases in local permeate flux due to pore narrowing or blocking as a result of PDA modification, which could exacerbate fouling [20]. Generally, the pure water permeance of these membranes can be controlled by varying PDA modification conditions such as coating solution concentration and coating time [8,9,17,20]. Since even a minimal application of PDA to the membrane surface can significantly improve surface hydrophilicity, and more substantial applications of PDA have little effect on hydrophilicity, PDA can be used to examine the effect of changing pore size in a hydrophilic membrane. This possibility makes PDA a useful tool for fundamental studies of fouling resistance in surface-modified porous membranes.

The contributions of convective flux, diffusion, surface interactions, and feed solution hydrodynamics to foulant accumulation were discussed by Bacchin et al. [21]. When the forces responsible for foulant removal from the membrane surface are balanced with or exceed the forces responsible for bringing foulants to the membrane surface, no accumulation of foulants occurs [22]. The permeate flux where these forces are balanced is the so-called critical flux (i.e., flux below which no flux-induced fouling occurs) [21,23–25]. Thus, below the critical flux, the fouling rate is zero [25–27], and the transmembrane pressure (TMP) increases linearly with flux (i.e., the membrane mass transfer resistance is constant and independent of flux) [21,26–30]. The rate of fouling can be estimated from the rate of TMP change with time (i.e., d(TMP)/dt) [21]. There are two forms of the critical flux: (i) the strong form (J_{cs}), below which the membrane resistance is the same as that during pure water filtration (i.e., the clean membrane resistance), and (ii) the weak form (J_{cw}), below which the membrane resistance is higher than that during pure water filtration as a result of foulant adsorption (but *not* due to flux-induced foulant accumulation) [21,28]. Another category of critical flux is the critical flux for irreversibility (J_{ci}), which is the flux below which fouling is reversible [21].

Membrane operation at zero fouling rate (i.e., below the critical flux) is rarely a realistic possibility [29,31,32]. However, a permeate flux below which the rate of fouling is stable and low, but not zero, is often observed. Recently, Field and Pearce defined this flux, which has been referred to as the critical flux in some earlier studies [25,29,31,33,34], as the "threshold flux" [28]. The threshold flux is the flux that separates the low-fouling, stable operating regime from the high-fouling, unstable operating regime [28]. Industrial membrane filtration is often operated near, but below, the highest permeate flux that results in low and acceptable fouling rates so that the operation is most economical [28]. For this reason, the threshold flux may be a more useful benchmark for practical membrane operation than critical flux. Similarities and differences between critical and threshold fluxes have been discussed in several publications [26,28,30]. A higher threshold flux allows a membrane to operate at higher capacity (i.e., higher permeate throughput) at a low fouling rate and may prolong the operational time between cleaning steps [28], potentially resulting in long-term capital and operating cost savings. Industrially, membranes are typically operated at constant permeate flux, so laboratory fouling tests at constant flux are more representative of industrial filtrations than tests at constant TMP [26]. Using bench-scale constant flux filtration, the threshold flux can be determined easily and can be used as an indicator of membrane fouling resistance.

This study examines the competing effects of surface hydrophilicity increase and permeance decrease resulting from PDA surface modification of ultrafiltration (UF) membranes *via* threshold flux measurement. In this work, PDA was chosen as the surface modification agent because it allows independent control of pore size of the modified membranes without substantially affecting hydrophilicity. Polysulfone UF membranes were modified with PDA at different initial dopamine concentrations and deposition times. The threshold flux was used to characterize membrane fouling propensity during oil/water emulsion filtration. A simple model foulant of soybean oil emulsion was used, as opposed to other more complex foulant mixtures. In addition, several membrane properties (i.e., surface hydrophilicity, surface roughness, and zeta potential) were investigated. Observed changes in threshold flux due to PDA modification were rationalized by a tradeoff between changes in membrane-foulant hydrophobic interactions and pure water permeance accompanying various modification conditions. The relation between changes in UF membrane pure water permeance and changes in pore size and pore size distribution due to PDA modification are reported separately [9].

2. Background

2.1. Threshold flux determination

Methods to measure critical and threshold fluxes are discussed in several publications [21,29,32]. A flux stepping method is commonly and conveniently used to determine threshold flux [32]. In the flux stepping method, the permeate flux is increased stepwise, and the TMP at each flux step is recorded [25,29,31]. The average TMP (TMP_{avg}) or the rate of fouling (d(TMP)/dt) at each flux step is then plotted as a function of flux.

The threshold flux is identified as the flux where the linearity of the TMP_{avg} vs. flux curve breaks [21,25,28]. Below the threshold flux, the TMP_{avg} increases linearly with flux, and total membrane resistance ($R_{total} = TMP/flux/\mu$) is constant, where μ is the permeate liquid viscosity. Above the threshold flux, the TMP_{avg} no longer increases linearly with flux, and R_{total} increases as flux increases (i.e., R_{total} becomes flux-dependent) [28,30]. However, the criterion of linearity of the TMP_{avg} vs. flux relationship below the threshold flux has not been standardized among most critical flux and threshold flux studies. In a few studies, values of the R^2 coefficient of linear regression higher than 0.99 [30] or 0.998 [35] were used to establish the best fit straight line through flux points below the threshold flux. However, in most cases, the linearity of the TMP_{avg} vs. flux relationship was established by visual observation, which could result in variations in the estimated threshold flux value.

The threshold flux can also be identified as the flux where d(TMP)/dt increases markedly relative to a regime of low, stable d(TMP)/dt values at lower fluxes [21,25,28,29,31]. This method directly monitors the increase in fouling rate at the threshold flux. Several studies chose an arbitrary d(TMP)/dt upper limit for the slow-fouling regime, beyond which the rate of fouling and,