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Comparison of membrane fouling at constant flux and constant transmembrane pressure conditions

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ABSTRACT

Membrane fouling is often characterized in the laboratory by flux decline experiments, where an increase in transport resistance due to accumulation of foulants on and/or in a membrane is manifested as a decrease in permeate flux with filtration time at fixed transmembrane pressure. However, many industrial microfiltration and ultrafiltration applications operate at constant permeate flux, and there are few reports comparing these modes of operation. In this study, emulsified oil fouling of polysulfone ultrafiltration membranes was studied using both constant permeate flux and constant transmembrane pressure experiments. Mass transfer resistance changes during fouling were compared between constant flux experiments and constant transmembrane pressure experiments performed at an initial flux equal to the flux imposed during the constant flux experiment. At low fluxes, the transport resistance and its change with permeate volume per unit area agreed within experimental error regardless of operational mode. In contrast, at high fluxes, the change in membrane resistance with permeate volume per unit area was much higher in constant flux than in constant transmembrane pressure experiments. The threshold flux, defined recently as the flux at which the rate of fouling begins to increase rapidly, separates the regimes of good and poor agreement between the two types of experiments. The weak form of the critical flux, below which spontaneous adsorption is the only significant resistance imposed by foulant, was also observed.

1. Introduction

Emulsified oil is ubiquitous in wastewater streams from petroleum production and refining, metalworking, hydraulic fracturing, manufacturing, and other industrial operations [1]. Microfiltration and ultrafiltration systems utilizing polymeric membranes can produce high-quality permeate and provide a low-energy, small-footprint alternative to traditional separation techniques [1]. Unfortunately, fouling is a pervasive problem in water purification membranes [2–4]. Such membranes are frequently made of hydrophobic polymers via phase-inversion processes in which water is used as the nonsolvent [4], so hydrophobic wastewater components, such as oils, tend to aggressively foul membranes, necessitating: (1) increased energy expenditure or larger membrane area to maintain productivity, (2) frequent membrane cleaning, and (3) membrane replacement [5].

Laboratory-based membrane fouling studies are often accomplished by challenging the membrane with a model or realistic foulant solution at fixed transmembrane pressure (TMP) [6–10]. As the membrane fouls, permeate flux declines. This flux decline means that the hydrodynamic conditions at the membrane surface change with time during the experiment [11]. To address this point, some authors studied membrane fouling at constant permeate flux [12–18], where the flow of feed solution through the membrane is more constant than in fixed TMP studies [11]. Constant flux operation provides an operational mechanism by which fouling may be abated [14]. The severe fouling observed at the start of a constant TMP experiment, which occurs because of often very high initial flux (i.e., low initial membrane mass transfer resistance) of the clean membrane, is reduced by imposing a constant, and much lower, flux in constant flux operation [18]. Additionally, most industrial microfiltration and ultrafiltration applications operate at constant flux [19,20].

Although both constant flux and constant TMP studies have been reported, there are few direct comparisons of membrane fouling under both operational modes. In their work describing the critical flux concept, Field et al. provided qualitative observations of constant TMP and constant flux measurements [15]. They observed that the total mass transfer resistance of the membrane and foulant was generally low for constant flux experiments and high for constant TMP experiments, presumably due to the rapid fouling at the beginning of constant TMP experiments. Marshall,

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Munro, and Trägårdh developed a crossflow system capable of operating in constant flux or constant TMP modes [21]. They filtered skimmed milk with both ultrafiltration and microfiltration membranes. Although their study focused mainly on a comparison of ultrafiltration and microfiltration fouling, they also identified experimental conditions where ultrafiltration membrane resistances developed similarly in constant flux and constant TMP fouling studies. Decloux et al. considered the operation of ultrafiltration and microfiltration membranes under both control modes, finding that constant flux operation resulted in less severe fouling than constant TMP operation, resulting in reduced cleaning frequency [20]. A few publications, including two recent reports [22,23], have focused on methods for predicting the fouling propensity of certain solutions and have, to this end, evaluated fouling at both constant flux and constant TMP. Kanani and Ghosh developed a model to predict permeate flux decline in constant TMP operation by assuming that the flux decline is comprised of many sequential constant flux steps [24]. Model parameters were obtained from constant flux experiments, which offer an unchanging hydrodynamic environment at the membrane surface, facilitating the capture of data related to concentration polarization and fouling phenomena. Further investigation of fouling phenomena at constant flux and constant TMP is, however, warranted. As noted by Sioutopoulos and Karabelas, "uncertainty exists as to whether the more common constant-pressure UF and RO laboratory tests provide fouling resistances representative of conditions prevailing in the constant flux mode of commercial plant operation" [23].

In this report, we compare constant flux and constant TMP fouling of ultrafiltration membranes being used to filter an emulsified oil solution. The resistance to permeation, which increases due to foulant accumulation on the membrane [21], is calculated as a function of the permeate volume per unit membrane area. Experiments were performed such that the initial flux in a constant TMP test was equal to the flux imposed in the corresponding constant flux test (and, consequently, the initial TMP in the constant flux experiment was equal to the TMP imposed throughout the constant TMP experiment). Agreement between the experimental protocols was good at low fluxes but not at high fluxes. The threshold flux, as recently defined by Field and Pearce [25], was found to separate the flux regime of good agreement from that of poor agreement.

2. Background

The permeate flux through a porous membrane is often described as the applied transmembrane pressure driving force, TMP, divided by the resistance to mass transfer, R, and the permeate viscosity, μ [15,25]:

$$J = \frac{\mathrm{TMP}}{\mu R} \tag{1}$$

For pure water filtration, R will represent the resistance to mass transfer associated with the clean membrane. During a fouling experiment, the resistance to permeation increases due to various mechanisms, such as pore plugging, cake layer formation, concentration polarization, osmotic pressure, etc. [26]. The total resistance to mass transfer is often described by a resistance-in-series model. In this way, the total resistance is described by individual resistances, such as the resistance of the membrane itself, the resistance due to adsorption fouling, and the resistances due to reversible and irreversible fouling. For clarity, "adsorption fouling" refers to the spontaneous adsorption of foulant to the membrane surface that occurs even under zero flux conditions. "Reversible fouling" and "irreversible fouling" refer to the accumulation of foulant that is brought to the membrane during operation; that is, when the permeate flux is greater than zero. Therefore, in reversible and irreversible fouling, as defined here, foulant is brought to the membrane primarily by convection associated with the permeate flux [11,14,18]. In constant TMP operation, the increase in R causes permeate flux to decline; in constant flux operation, TMP increases as R increases. Therefore, the change in resistance during fouling provides a convenient benchmark for comparing constant flux and constant TMP experimental results.

If the flux is sufficiently low, mechanisms such as Brownian diffusion, shear-induced diffusion, axial transport along the surface, and inertial lift can act to remove foulant particles as they reach the membrane surface due to permeate flow [18,27]. Under these conditions, the total resistance remains constant, and the permeate flux scales linearly with TMP. At somewhat higher fluxes, the aforementioned foulant removal mechanisms cannot overcome the inexorable flow of foulant towards the membrane surface, so foulant accumulates on, and perhaps in, the membrane during filtration, and the resistance increases with time. The flux no longer scales linearly with TMP and, eventually, a limiting flux is reached where further increases in TMP do not produce increases in flux [4].

Field et al. introduced the concept of critical flux—the maximum flux that can be achieved with slight or negligible fouling—to distinguish the regime of invariant resistance from that where resistance changes with flux [15]. The exact value of the critical flux depends upon foulant properties (e.g., concentration and particle size), membrane properties (e.g., pore size and material), and crossflow velocity [28]. Two forms of the critical flux are further defined: the strong form and the weak form [28]. At fluxes below the strong form of the critical flux, the only contribution to R is that of the clean, unfouled membrane itself; i.e., fouling does not contribute to the resistance to permeation [25]:

$$J = \frac{\mathrm{TMP}}{\mu R_m} \quad \text{for } J < J_{cs} \tag{2}$$

where J is the flux, TMP is the transmembrane pressure, R_m is the membrane resistance, and J_{cs} is the flux associated with the strong form of the critical flux. For the weak form of the critical flux, the resistance to permeation is given by the sum of the membrane resistance and resistance from adsorption of foulant to the membrane surface [25]:

$$J = \frac{\mathrm{TMP}}{\mu(R_m + R_{ads})} \quad \text{for } J < J_{cw} \tag{3}$$

where R_{ads} is the resistance due to adsorption, and J_{cw} is the weak form of the critical flux. The resistance due to adsorption reflects foulant whose adsorption to the membrane occurs spontaneously and independently of flux [25]. Therefore, whether a particular membrane/foulant system exhibits the strong form of the critical flux or the weak form of the critical flux is dictated by whether or not foulant adsorption to the membrane is a significant contributor to resistance. Because such adsorption occurs spontaneously and independently of flux (and even in the absence of flux) [25], a membrane/foulant system will show either the strong form or the weak form of the critical flux, but not both.

At fluxes above the two forms of the critical flux, the resistance to permeation is increased due to reversible and irreversible fouling [25]:

$$J = \frac{\mathrm{TMP}}{\mu(R_m + R_{rev} + R_{irrev})} \quad \text{for } J > J_{cs} \tag{4}$$

$$J = \frac{\mathrm{TMP}}{\mu(R_m + R_{ads} + R_{rev} + R_{irrev})} \quad \text{for } J > J_{cw} \tag{5}$$

where R_{rev} is the resistance due to reversible fouling, and R_{irrev} is the resistance due to irreversible fouling. As noted previously, R_{rev} and R_{irrev} refer to resistances due to permeation-driven fouling of the membrane.