Journal of Membrane Science xx (xxxx) xxxx–xxxx

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

The effect of permeate flux on membrane fouling during microfiltration of oily water

Zhengwang He, Daniel J. Miller[1], Sirirat Kasemset[2], Donald R. Paul, Benny D. Freeman*

Department of Chemical Engineering, Center for Energy and Environmental Resources, and Texas Materials Institute, The University of Texas at Austin, 10100 Burnet Road Building 133, Austin, TX 78758, USA

ARTICLE INFO

Keywords:
Critical flux
Threshold flux
Constant flux fouling
TMP profile
Critical pressure

ABSTRACT

Critical and threshold flux concepts were recently developed to distinguish no fouling, slow fouling and rapid fouling regimes. Membrane fouling behavior is expected to vary with respect to the imposed flux relative to the critical and threshold flux values. However, crossflow fouling tests are often performed independent of critical and threshold flux determinations. In this study, constant flux fouling experiments were performed in connection with critical and threshold flux determination. Fouling behavior was examined in the context of critical and threshold flux. A poly(vinylidene fluoride) microfiltration membrane was challenged with various oil-in-water emulsions. The critical and threshold flux values were estimated using the flux-stepping technique. Constant flux crossflow fouling tests were performed at selected fluxes below and above the critical and threshold fluxes. Below the critical flux, mass transfer resistance remained constant at the clean membrane value. Above the critical flux but below the threshold flux, mass transfer resistance approached a steady state resistance, R_B, which was determined from the linear regression of flux-stepping experiments. Above the threshold flux, a three-stage transmembrane pressure (TMP) was observed, consisting of: (1) an initial gradual increase, (2) a TMP jump stage, and (3) a pseudo-steady state. The pseudo-steady state TMP corresponded to the estimated critical pressure of the oil layer.

1. Introduction

The critical flux, J_c, was introduced by Field et al. in 1995 as follows "on start-up there exists a flux below which a decline of flux with time does not occur; above it fouling is observed" [1]. Realistic operations can rarely achieve the zero fouling scenario prescribed by the critical flux definition. In 2011, Field and Pearce introduced the threshold flux, J_t, defined based on the rate of fouling. Below the threshold flux, the rate of fouling is slow and nearly constant, where long-term, sustainable operation is possible. Many of the critical fluxes reported earlier than 2011 are, in fact, threshold fluxes [2]. Industrial membrane processes typically operate below the threshold flux to maintain sustainable operation. However, most reported laboratory fouling tests are performed without critical or threshold flux determination, which makes it difficult to gauge the effect of permeate flux on fouling behavior.

Ultrafiltration (UF) and microfiltration (MF) are pressure-driven separations. Membrane fouling tests can be performed either in constant transmembrane pressure (TMP) mode or in constant flux mode. Most laboratory fouling tests are conducted in constant TMP mode, while most industrial operations are in constant flux mode [3]. The two operations typically have different local hydrodynamic conditions at the membrane surface [4]. Fouling behavior and fouling mechanisms, which depend sensitively on hydrodynamic conditions, are likely to vary between the two operations [4–6]. However, direct comparisons of the two operational modes are very rare [4–6]. For example, Sim et al. compared fouling index and membrane resistance between constant TMP and constant flux ultrafiltration processes [5]. Vyas et al. observed that the two operational modes led to the same extent of fouling when the initial flux was below a certain flux [6]. Miller et al. observed similar fouling behavior below the threshold flux regardless of operational mode and dissimilar fouling behavior between constant TMP and constant flux operations above the threshold flux [4].

This study aims to provide a framework for constant flux fouling studies and to bridge constant TMP and constant flux operations using the threshold flux concept. A poly(vinylidene fluoride) (PVDF) MF membrane was challenged with various oil-in-water emulsions. Critical

* Corresponding author.
E-mail address: freeman@che.utexas.edu (B.D. Freeman).
[1] Current address: Joint Center for Artificial Photosynthesis, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720, USA.
[2] Current address: Evonik Corporation, 4201 Evonik Road, Theodore, AL 36582, USA.

http://dx.doi.org/10.1016/j.memsci.2016.10.002
Received 27 June 2016; Accepted 2 October 2016
Available online xxxx
0376-7388/

and threshold fluxes were estimated using the flux-stepping technique. Constant flux crossflow fouling tests were performed at selected fluxes to investigate the effect of permeate flux on fouling behavior. Below J_c, mass transfer resistance was constant and equal to the clean membrane resistance. Above J_c but below J_t, membrane resistance approached a steady state resistance predicted by flux-stepping experiments. Moreover, constant TMP and constant flux operations were comparable below J_t. Above J_t, fouling evolved in three stages in constant flux operations. The final pseudo-steady state TMP correlated with the critical pressure of the oil layer.

2. Background and theory

2.1. Critical and threshold flux concepts

The critical flux, J_c, concept was first proposed by Field in 1995 to describe a flux below which fouling is negligible [1]. Critical fluxes can take one of two forms, a strong form or a weak form, depending on whether or not adsorptive fouling affects mass transfer resistance. Adsorptive fouling is the spontaneous adsorption of foulants on a membrane surface, and it is not flux-driven. The critical flux is of the strong form if no adsorptive fouling occurs or if adsorptive fouling does not affect mass transfer resistance. The weak form critical flux accounts for adsorptive fouling. Threshold flux, J_t, separates the slow fouling regime from the rapid fouling regime, and lies at fluxes higher than the critical flux [2]. The mass transfer resistance, R, is defined as: [4]

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

where TMP is the transmembrane pressure, J is the permeate flux, and μ is the permeate viscosity. When membranes become fouled during filtration, R increases.

In laboratory studies, critical and threshold fluxes are typically estimated using a flux-stepping technique [7]. TMP is monitored while the permeate flux is increased in a stepwise fashion. Critical and threshold flux values can be estimated via linear regression of the average TMP of each flux step, TMP_{avg}, with respect to the imposed flux, as illustrated in Fig. 1. The dashed blue line is the TMP-flux relationship corresponding to no fouling (i.e., pure water filtration). Line A is the linear regression of TMP_{avg} below J_c. For a strong form critical flux, such as that illustrated in Fig. 1, Line A coincides with the pure water line, and its mass transfer resistance is equal to that of the clean membrane. For the weak form critical flux, Line A should still intercept the axes at the origin, while its slope is the sum of the clean membrane resistance and the resistance due to adsorption [4]. In cases of severe fouling, the critical flux may be too low to be measured or may not exist. Line B is the linear regression of TMP_{avg} between J_c and J_t. Often overlooked in the literature is that the linearity of Line B indicates a constant resistance at these fluxes. The slope of Line B represents a constant resistance value labeled as "R_B", which will be discussed in detail in following sections. Line C is the linear regression of the first two data points beyond J_t, and corresponds, generally, to a region of rapid fouling.

2.2. Constant TMP and constant flux modes

Although most industrial ultrafiltration and microfiltration processes are operated at or near the constant flux, many literature studies are conducted at constant TMP [3]. At constant TMP, J decreases as R increases, so fouling is often characterized in the form of declining permeate flux over time. At constant permeate flux, TMP increases as R increases, so fouling is characterized by an increasing TMP over time. To compare data between these two operations, mass transfer resistance should be compared as a function of cumulative permeate volume per unit membrane area [4]. This allows comparing the extent of fouling when membranes have been challenged with the same amount of feed and have produced the same amount of permeate.

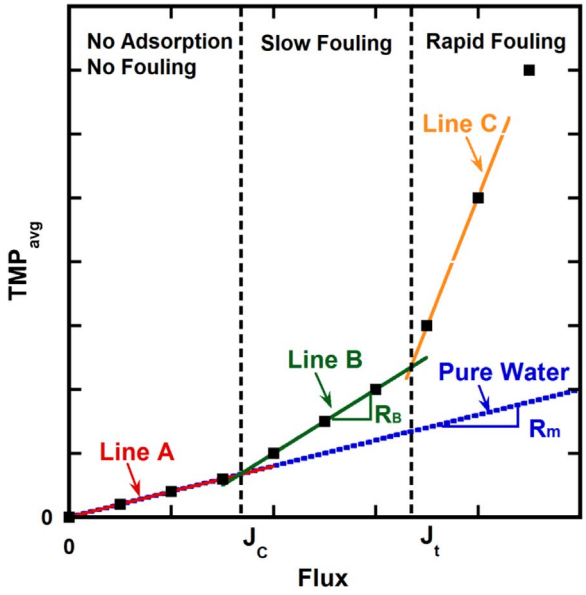

Fig. 1. An illustration of critical and threshold flux determination. The dashed blue line is the TMP-flux relationship for a clean membrane (i.e., pure water filtration). Line A is the linear regression below J_c, and corresponds to the strong form of the critical flux. The slope of Line A corresponds to clean membrane resistance, R_m. Line B is the linear regression between J_c and J_t. The slope of Line B corresponds to a constant resistance of R_B. Line C is the linear regression of the first two data points beyond J_t. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this article.)

At constant TMP, the initial flux is always the maximum flux, because the mass transfer resistance is lowest at the beginning of such an experiment. At the membrane surface, the local hydrodynamic conditions vary as permeate flow rate decreases with time. On the other hand, at constant flux, the overall permeate flow rate is kept constant, so the local hydrodynamics are likely more consistent throughout an experiment. Differences in fouling behavior between the two operations are expected as a result of the differences in local hydrodynamic conditions, making it difficult to directly compare results from constant TMP and constant flux experiments. For the results reported in this study, such comparisons are only made of the constant TMP and constant flux experiments beginning at similar initial fluxes.

2.3. Critical pressure

Typically, ultrafiltration and microfiltration are considered size sieving processes [8]. The selectivity (i.e., sieving coefficient or rejection) depends, among other things, on the relative size of solutes to membrane pores [8]. Solutes (e.g., particulates, proteins, macromolecules) that are larger than membrane pores are rejected. However, emulsified oil droplets differ from rigid particulates in that they are deformable. Oil droplets can coalesce and breakup into smaller droplets, such that they can enter and penetrate pores that are apparently smaller than the average droplet size [9–12]. The deformation of oil droplets at a membrane pore entrance has been investigated [9–12]. For example, Nazzal and Wiesner calculated the critical pressure, ΔP_c, which prevents an oil droplet from entering a membrane pore: [10]

$$\Delta P_c = \frac{4\gamma_{O/W}}{d_p}\left[1 - \frac{2 + 3\cos\theta - \cos^3\theta}{4\left(\frac{d_d}{d_p}\right)^3 \cos^3\theta - (2 - 3\sin\theta + \sin^3\theta)}\right]^{1/3} \tag{2}$$

where $\gamma_{O/W}$ is the interfacial tension between the oil phase and the