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The effect of permeation flux on the specific resistance of polysaccharide fouling layers developing during dead-end ultrafiltration

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ABSTRACT

Development of polysaccharide fouling layers during dead-end membrane ultrafiltration is an inherent problem in water treatment and similar separation processes. Despite its practical significance, ultrafiltration membrane fouling under *constant permeate flux J* has received inadequate attention. Therefore, constant-flux experiments, with typical alginate model-solutions covering the flux range of practical interest (i.e. 10–100 L/m^2 h), are employed to obtain new insights into fouling layer characteristics. The specific resistance α, as the most representative fouling-layer property, is used for data interpretation. The behavior of resistance α, with increasing permeate volume, confirms that these gel-type layers are strongly affected by flux J and generally compressible. Layer compressibility is evident beyond an initial phase of membrane coverage by alginates. The *initial resistance* α_i, corresponding to thin developing layers and relatively small pressure-drop across the layer/"cake" ΔP_c, is independent of ΔP_c, approximately linearly increasing with J. For all data-sets, variation of resistance α with ΔP_c is well correlated by a generalized expression involving (in addition to α_i) two parameters, n and P_a, considered to represent layer/cake compressibility index and reference pressure, respectively; these parameters also increase (and are fairly well correlated) with J. The usefulness of these data is demonstrated in elucidating issues such as "critical flux" for this filtration mode.

1. Introduction

Membrane ultrafiltration (UF) is commonly employed in a variety of water treatment processes, including municipal effluent upgrading for reuse, pre-treatment of feedwater to desalination plants and surface water purification for human consumption. In almost all these cases, membrane fouling by polysaccharides is a dominant operating problem [1], causing reduction of plant efficiency with negative economic and environmental consequences. For instance, in the rapidly expanding field of Membrane Bioreactors (MBR), the strong UF-membrane fouling propensity of polysaccharides (originating from the Extracellular Polymeric substances – EPS) is well documented even though other organic macro-molecules are also present in the treated mixed liquor [2–5]. For commonly used, relatively tight UF membranes (e.g. MWCO ~10 kDa to ~100 kDa) it has been established [6] that polysaccharides form rather coherent layers on the membrane surface and that the dominant fouling mechanism in dead-end filtration is that of so-called *"cake" formation*. Due to its significance, a large body of literature exists on fouling resistance due to polysaccharide layers. The majority of these works has been carried out in the (experimentally more convenient) constant-pressure filtration mode, even though in practice the constant-flux mode is usually employed [7–9]. In the relatively limited number of UF studies under constant flux, it is observed that the effect of flux J on fouling is significant. Ye et al. [10,11] using alginate solutions observed that the transmembrane pressure increased sharply at high flux levels. Similar results were reported by Bourgeous et al. [12] in UF membrane tests with treated waste-water effluents (after secondary treatment). Ghosh [13] using BSA solutions in a stirred dead-end cell reported a significant increase of fouling resistance with increasing flux. Sims et al. [14] using silica nanoparticles observed a systematic increase of MFI-UF (under constant flux) with applied flux. Useful insights were obtained by Wang and Waite [15,16] regarding the structure of alginate gel-layers developing during ultra-filtration under constant pressure and constant permeation rate. In particular, their data demonstrated the compressibility and high resistance of alginate gels, developing on the membrane surface, in the presence of calcium ions. The strong effect of permeation flux on TMP

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variation and resistance α is also exhibited by the data of Kovalsky et al. [17,18] obtained in microfiltration experiments with quite concentrated (10 g/L) dispersions of relatively large yeast particles (mean diameter 5 μm). These authors dealing with thick deposits (compared to those considered here) observed strong filter-cake compressibility effects and invoked cake consolidation to model the TMP variation with increasing permeate volume. However, such consolidation effects are inapplicable to alginate gels (where "instant consolidation" is considered to occur) as discussed by Wang and Waite [15].

The aforementioned preference in constant-pressure UF experiments, combined with the seemingly endless pursuit of a simplified membrane fouling "index" or of improving the SDI (also based on constant-pressure tests) (e.g. [19]) has caused, in the authors opinion, a significant set-back in this important research topic of understanding and quantifying UF fouling layer characteristics. Therefore, even in the simplest (from the fluid mechanical stand-point), yet practically important, case of dead-end filtration with no agitation, the situation is unclear on which control variable is the most appropriate for data presentation (among flux J, imposed trans-membrane pressure ΔP, or pressure drop across the cake ΔP_c) and which "cake" resistance parameter (among specific resistance α, fouling resistance R, several other) is the most representative. Consequently, despite several significant efforts (e.g. [10,13,15,16]), there is no generally acceptable quantitative relationship between key variables and a representative fouling-resistance parameter (i.e. between "cause" and "effect"), which would be helpful for optimizing UF units operating under constant flux. This uncertainty is compounded by the fact that in dead-end filtration systems of the type considered here a rather sharp increase of fouling resistance (of unclear origin) is observed beyond a certain level of flux J, which is referred to as "critical flux"; there is also no consensus (e.g. [2,4]) on the most appropriate method for experimental determination of this "critical flux". It will be recalled that the concept of "critical flux" was originally introduced (e.g. [20,21]) to explain the rather sharp increase of fouling resistance, beyond a certain flux, in the presence of significant lateral shear stresses at the membrane surface.

The present authors have recently presented [7] a successful correlation of specific cake resistance α obtained with UF membranes under constant flux and constant pressure (all other conditions being the same, including the deposited foulant mass density) by employing the pressure drop across the cake ΔP_c as a correlating parameter. The data employed were obtained with relatively small alginate concentration (10 mg/L) and corresponded to the initial stage of membrane fouling (and initial specific resistance α). However, as discussed at fair length [7], the key parameter in such membrane-filtration processes is the permeate flux J which appeared to affect the resistance α rather strongly, although no specific J-dependence was provided [7]. In other similar studies (e.g.[22]), ΔP_c has also been used to interpret fouling resistance α data. Of particular interest are the resistance α data recently obtained by Iritani et al. [23,24] using bentonite and protein dispersions. These data, plotted versus the ΔP_c variation during a filtration test, reveal strong fouling cake compressibility effects, and they are fitted with an expression involving three adjustable parameters. The functional form of that expression [23] appears to be appropriate for correlating resistance α data of the type reported in this study, as subsequently discussed.

In the context of interpreting fouling resistance data for the similar case of RO membrane desalination, the present authors have recently argued [25] that the specific resistance α is the most representative fouling layer property characterizing its permeability and that the development of generalized (constitutive type) expressions of α as a function of the main process parameter J should be systematically pursued. Therefore, along the same lines, the main objectives of this work are as follows:

- To perform well-controlled UF tests, with model polysaccharide solutions under constant flux J, in order to characterize the evolution of fouling-layer resistance α.
- To clarify the conditions leading to manifestation of significant compressibility effects and related increased resistance α values, thus getting new insights into the cause of high fouling rates frequently encountered in practice.
- To pursue the development of a correlation of α with J, thus enhancing the value of the new measurements, and facilitating future comparisons with similar data as well as the development of comprehensive process models.

2. Theoretical background

2.1. Specific cake resistance determination under constant permeate flux

Membrane filtration under either constant pressure or constant permeate flux J is described by a generalized form of the Darcy equation

$$J=\frac{1}{A}\frac{dV}{dt}=\frac{[\Delta P]}{\mu[R_m+R_c]} \tag{1}$$

For the purpose of this discussion, one can recognize an initial trans-membrane pressure (TMP) $[\Delta P]_0=\mu R_m J$ which is effective at time $t=0$, i.e. when the fluid with foulants is first brought in contact with the membrane. R_m and R_c are the clean membrane and fouling resistance, respectively. Considering that gel-layer formation is the dominant fouling mechanism and assuming that R_m remains constant, the measured increase of TMP due to fouling, ΔP_c, is given as

$$[\Delta P]-[\Delta P]_o\equiv\Delta P_c \tag{2}$$

This quantity is related to fouling parameters as follows:

$$[\Delta P]=\mu J R_m+\mu J R_c=[\Delta P]_0+\mu J R_c \tag{3}$$

Starting with a clean membrane, the resistance R_c is related to specific fouling resistance α, i.e.,

$$R_c=\alpha m=\frac{\alpha C V}{A} \tag{4}$$

Since in most cases in practice the effective foulant concentration C (for fouling layer formation) is unknown, it is common to employ the quantity $I=(\alpha C)$ which is called fouling index. For the case of ultra-filtration of polysaccharide solutions, the rejection of organic species is known to be high [6] but not 100%. Therefore, an effective concentration C, used in Eq. (4), is obtained by multiplying the known bulk concentration with an experimentally determined rejection factor.

To determine α, the realistic and convenient approach is to deal with the *initial phase* of membrane fouling, starting from a membrane characterized by a "clean-membrane" resistance R_m. The fouling resistance can be determined by combining Eqs. (1)–(4),

$$\frac{\Delta P_c}{[\Delta P]_0}=\frac{\alpha C}{R_m}\cdot\frac{V}{A}=\frac{\alpha C}{R_m}Jt=\frac{IJ}{R_m}t \tag{5}$$

This simple expression is very useful for the study of membrane fouling; e.g. [7]. In the initial phase of membrane filtration under constant flux J and for constant R_m, by recording ΔP_c as a function of time, one can directly compute the temporal variation of I and (knowing the concentration C) to determine the temporal evolution of resistance α. Moreover, it is argued elsewhere [25], that for the common case of constant flux filtration, Eq. (5) offers valuable insights in efforts to develop reliable tools for fouling predictions. It is evident that Eq. (5) is applicable to the case of dead-end ultra-filtration (of interest in this paper) if fluid properties and flux