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Estimation of membrane fouling parameters for concentrating lactose using nanofiltration

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Abstract

The paper deals with parameter estimation of permeate flux model with fouling for the nanofiltration process. We propose a new technique towards fouling estimation with fouling model being an explicit function of concentration. The objective is to experimentally concentrate lactose in a lactose-salt solution at constant temperature and pressure using cross-flow nanofiltration. The experimental results show a decrease in the permeate flux over time, as the concentration of lactose increases. The limiting flux model is used to model the experimental permeate flux data without fouling. This limiting flux model parameters and the fouling parameters are then estimated via least-squares method using the experimental flux data.

Keywords: Nanofiltration, Lactose, Parameter estimation, Limiting flux, Membrane fouling

1. Introduction

Nanofiltration is a liquid-phase separation process for removing dissolved solids, carried out by means of membranes. Nanofiltration covers a molecular cut-off range from 100 to 1,000 Daltons. The separation takes place mainly because of diffusion of the molecules of the solvent through the mass of the membrane material, driven mainly by a high trans-membrane pressure. Nanofiltration has found application in removal of chemicals, colorants and total organic carbon (TOC) of water and simultaneous removal of sodium chloride and concentration of organics in the food and pharmaceutical industries (Eriksson (1988)). Nanofiltration helps enhancing the edibility and nutritional value of whey products by partial demineralization resulting in concentrated lactose solution forming cheap beverages with pre-biotic properties, as studied in Verasztó et al. (2013).

As with any other membrane process, nanofiltration is susceptible to reduction in the permeate flux as the concentration of molecules increases. One of the simplest models defining this relation is the limiting flux model (Blatt et al., 1970; Cheryan, 1998; Balannec et al., 2005; Tang et al., 2007). The model defines the permeate flux as solely a function of the macro-solute concentration, i.e. the solute with the higher rejection coefficient. The model defines a limiting macro-solute concentration, c_{lim}, i.e. the maximum beyond which the membrane flux cannot be sustained. Aimar and Field (1992) analyzed the increase in concentration leading to limiting flux and deduced the values of the limiting flux parameters (k and c_{lim}).

The other reason for permeate flux decline, besides increasing concentration, is membrane fouling. Membrane fouling is defined as reversible or irreversible deposition of solutes on the surface of the membrane, or inside the pores of membrane. This deposition results in the loss of available membrane area for separation. The phenomenon of membrane fouling has been introduced and

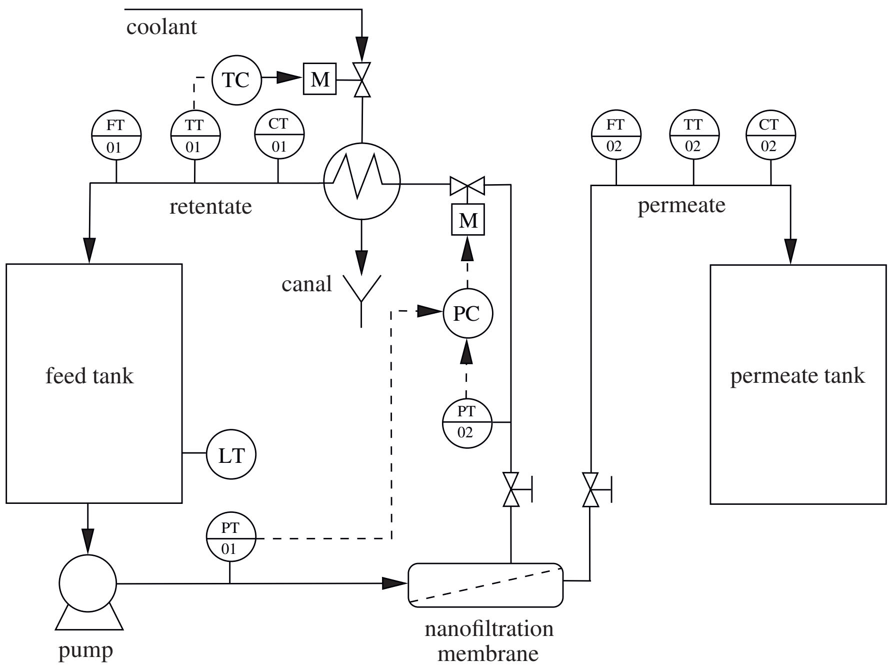

Figure 1: Nanofiltration process scheme.

modeled by Hermia (1982) who categorized the fouling behavior into four models depending on the form of deposition of solutes over a membrane. In Charfi et al. (2012) an estimation of the fouling parameters was conducted for micro and ultrafiltration using the experimental data reported in literature.

Recently, Jelemenský et al. (2015) developed a method of optimal control of a diafiltration process under fouling conditions. The diafiltration process is used for fractionation of the species in the solution, where the membrane filtration is employed. The developed optimizing control law is strongly dependent on the parameters of flux and fouling models. Thus, the parameters must be known in order to run the diafiltration process optimally, which motivates our present study.

The aim of this paper is to investigate limiting flux and fouling behaviour with nanofiltration membranes for solutions containing lactose and salts. We assume that the flux model is composed of two parts. The lower-level one defines unfouled membrane properties and we will estimate it using the limiting flux model. The upper-level part uses the model from the lower level and enhances the model with a fouling mechanism. Separation of the model into these two parts makes the model more flexible and suitable for further analysis and optimal operation.

2. Process Description

In general, a membrane process consists of a feed tank and a membrane unit. The solution, consisting of a solvent and solutes, is brought from the feed tank to the membrane unit by means of mechanical energy (pump) as depicted in Figure 1. The membrane is designed to retain the macro-solute and to allow the passage of the micro-solute. Part of the filtered solution rejected by the membrane (retentate) returns back to the feed tank. Permeate stream leaves the system at a flowrate $q = AJ$, where A is the membrane area and J is the flux subjected to unit membrane area.

The nanofiltration experiments were conducted in cross-flow mode and controlled at constant transmembrane pressure (TMP) defined as

$$\mathrm{TMP} = \frac{P_{\mathrm{feed}} + P_{\mathrm{retentate}}}{2} - P_{\mathrm{permeate}} = 25\,\mathrm{bar}, \tag{1}$$

and the control was attained using a proportional feedback controller (PC) by manipulating the retentate valve (permeate pressure is atmospheric pressure, and is constant). Nanofiltration is generally operated at the pressure range 10 – 40 bar, and hence the nominal value of 25 bar was chosen for these experiments. The temperature of the solution was maintained at a constant value of 25 °C using a heat exchanger and an on-off controller (TC) for cooling water circulation. Besides these, the plant is equipped with conductivity sensors (CT) on both permeate and retentate sides. The volume of the solution in the feed tank at any time can be recorded by a level sensor (LT).

2.1. Materials

Lactose monohydrate (M = 360.31 g/mol) and sodium chloride (M = 58.44 g/mol) manufactured by Centralchem (Slovakia) were used as solutes, and reverse osmosis water was used as a solvent to prepare the experimental solution. The plant holds an NFW-1812F nanofilter membrane manufactured by Synder Filtration, U.S.A, with a cut off range from 300 – 500 Da, and membrane area of $A = 0.465\,\mathrm{m}^2$. Lactose was concentrated from $40\,\mathrm{g/L}$ to a concentration factor of 6.25 where the volume of the initial solution was 30 L.

2.2. Process model

The mathematical model of the process is given by material balances of solutes and the overall material balance as:

$$\frac{\mathrm{d}c_i}{\mathrm{d}t} = \frac{c_i}{V} A J R_i, \qquad c_i(0) = c_{i,0}, \quad i = 1,2, \tag{2a}$$

$$\frac{\mathrm{d}V}{\mathrm{d}t} = -AJ, \qquad V(0) = V_0, \tag{2b}$$

where J is the permeate flux, c_i represents the concentration of the ith solute, V is the volume of the processed solution. R_i represents the rejection coefficient for the ith solute defined as $R_i = 1 - c_i/c_{\mathrm{p},i}$, where $c_{\mathrm{p},i}$ is the concentration of ith component in permeate.

In our case, the solution to be separated consisted of lactose as the macro-solute (of concentration c_1) and sodium chloride as the micro-solute (of concentration c_2). Complete rejection was considered for lactose, i.e. $R_1 = 1$ (according to the membrane manufacturers it is $R_1 = 0.97$), and complete passage for sodium chloride, i.e. $R_2 = 0$. The experiments were entirely run in concentration mode meaning no inflow of feed or diluant. As the rejection of lactose is complete, it does not leave the system, thus at any time

$$c_1(t)V(t) = c_{1,0}V_0. \tag{3}$$

Several experiments with different concentrations of lactose and salt revealed that the flux does not depend on the amount of the salt. Therefore, the flux J_0 of the unfouled membrane is formulated as a function of macro-solute concentration c_1 using the limiting flux model

$$J_0(c_1) = k \ln \frac{c_{\mathrm{lim}}}{c_1}, \tag{4}$$

where k is the mass transfer coefficient and c_{lim} is the limiting concentration of macro-solute.

The membrane flux under fouling conditions can be, according to Hermia (1982), categorized into four divisions. This division is on the basis of how solutes deposit in, or over the membrane, i.e. cake filtration model ($n = 0$), intermediate blocking model ($n = 1$), internal/standard blocking model ($n = 1.5$) and complete pore blocking model ($n = 2$). The first three flux models can be described by the following equation:

$$J = J_0 \left(1 + K(2-n)(AJ_0)^{2-n} t\right)^{\left(1/(n-2)\right)}, \tag{5}$$

while the complete pore blocking model can be expressed as:

$$J = J_0\, \mathrm{e}^{-Kt}. \tag{6}$$

3. Parameter Estimation

In this section, the parameters of limiting flux model and the parameters of the four fouling models described above are estimated. Several experiments were performed and one of the experimentally obtained permeate flow rate data w.r.t. increasing concentration of lactose and time as depicted in Figure 2 is used here to perform the estimation. The minimization of the sum of squared differences between experimental flux data (J_{exp}), and estimated flux model (J_{est}) can be formulated as:

$$\min_{K,k,c_{\text{lim}}} \sum_{j=1}^{m} (J_{j,\text{exp}} - J_{j,\text{est}})^2 \tag{7a}$$

$$\text{s.t.} \tag{7b}$$

$$\frac{\mathrm{d}c_1}{\mathrm{d}t} = \frac{c_1^2}{c_{1,0}V_0} A J, \qquad c_1(0) = 40\,[\text{g/L}], \tag{7c}$$

$$J_0 = k \ln \frac{c_{\text{lim}}}{c_1}, \qquad J = J(J_0, K, n, t), \qquad J_{j,\text{est}} = J(J_0, K, n, t_j), \tag{7d}$$

where m is the number of data points, and J is the permeate flux defined either by (5) or by (6). The Eq. (7c) is derived from (2a), by replacing $V(t)$ from (3). The volume of the processed solution in the beginning of the operation is $0.03\,\text{m}^3$. Based on technological considerations, the three estimated parameters (K, k and c_{lim}) are expected to lie within the intervals $K \in [0, 1000]$ units, $k \in [0, 10]$ m/h, $c_{\text{lim}} \in [0, 1500]$ g/L. The experimental measurements show that the flow rate of permeate decreases with time, because of the gel-polarization layer formed on the membrane surface, and due to the fouling of membrane.

Non-linear least-squares estimation was performed to identify the values of the parameters k, c_{lim} of the limiting flux model (4) and the fouling rate constant K for all the four fouling models. The linear least-squares method (Foley, 2013) was also used to estimate the limiting flux model parameters k and c_{lim} assuming no fouling. A non-linear estimation of the parameters (k, c_{lim}) of limiting flux model without fouling was also done for comparison, and they were estimated to be: $k = 0.0066\,\text{m/h}$ and $c_{\text{lim}} = 880.97\,\text{g/L}$. These values as seen in Table 1 are analogous to the linearly estimated limiting flux model. All the optimization problems were solved in MATLAB using the SQP solver implemented in the function *fmincon*. MATLAB function *ode45* was used for numerical solution of the initial value problem (7c) – (7d).

Figure 2 shows the comparison between experimental data, limiting flux model, and the four fouling models. It can be observed that the performance of the limiting flux model is the worst as it does not account for fouling. On the other hand, all four fouling models fit the data reasonably well. The cake filtration model with $n = 0$ is estimated to be linear w.r.t. time as seen from the figure, and hence does not fit the experimental data with high precision. The other three fouling models are of non-linear nature and all fit the experimental data with satisfactory precision. This similarity of the models suggests that the fouling behavior could occur due to nanofiltration being

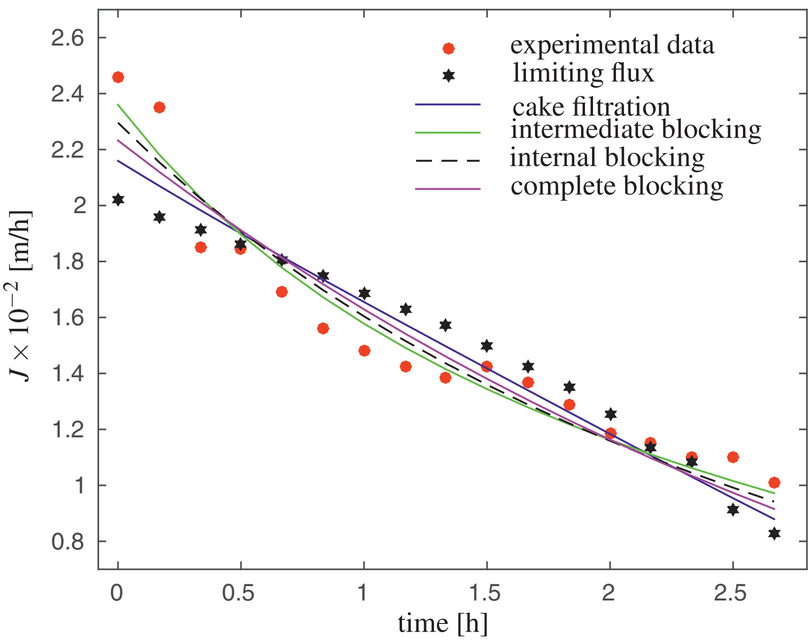

Figure 2: Comparison of estimated four fouling models, limiting flux model (with no fouling), and experimental data.

Table 1: Comparison of estimated values of K, k and c_{lim} for different fouling models, and limiting flux model, along with the value of least squares criterion, $f = \sum_{j=1}^{m}(J_{j,\text{exp}} - J_{j,\text{est}})^2$.

model (n)	K	$k \times 10^{-2}$ [m/h]	c_{lim} [g/L]	$f \times 10^{-5}$ [m/h]
cake filtration (0)	494.14 [s/m^2]	1.30	210.43	3.43
intermediate blocking (1)	33.47 [1/m]	0.76	880.89	1.36
internal blocking (1.5)	2.59 [$1/\sqrt{\text{s}}$]	0.74	880.98	1.91
complete blocking (2)	0.19 [1/s]	0.72	880.97	2.55
limiting flux (–)	–	0.66	880.97	5.98

a higher pressure based separation process. It is a well-known phenomenon that the fouling in the form of pore blocking increases with increasing pressure for membrane processes operated in cross-flow mode, and higher pressures tend to foul the membrane internally rather than externally on the surface due to higher sweep-off in-flow rate. The cake filtration fouling model, on the other hand, states fouling on the surface of the membrane by forming a layer of solutes, which is quite prominent in dead-end membrane separation rather than in cross-flow filtration. The other three fouling models account for blocking of membrane pores by solutes too, and hence fit the experimental data more precisely.

Table 1 provides estimated values of all parameters. The value of the objective function qualifies the intermediate fouling model (Figure 2) as the best fit for the experimental case studied here. The study done on nanofiltration of water in Chang et al. (2011) suggested the same model defining the behavior of fouling. Note also the comparison of different values for the parameters k, and c_{lim} of the limiting flux equation with the cake filtration fouling model, to other three models. This also points to appropriateness of the cake filtration model. On the other hand, the limiting flux parameters estimated for other three fouling models are in a very close proximity of linearly and non-linearly estimated limiting flux model without fouling.

4. Conclusions

We studied the parameter estimation of membrane flux models with fouling, by using the experimentally obtained data of permeate flux for concentrating lactose using nanofiltration. This estimation was conducted by non-linear least squares method. The results of parameter estimation of limiting flux model showed that the mass transfer coefficient (k) and limiting concentration (c_{lim}) for this experiment were quite high, and lactose could be concentrated with even higher factor. The estimation of fouling parameters resulted in internal/standard blocking model ($n = 1.5$), intermediate blocking model ($n = 1$) and complete blocking model ($n = 2$) as the better fits, while intermediate blocking model fits the best.

The obtained model will be used in the future for experimental evaluation of optimal control theory for membrane processes developed in Jelemenský et al. (2015). An interesting direction of further studies would consider the design of an experiment that would achieve a better possibility of discriminating among the different fouling models.

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