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# Assessment of the fouling mechanisms of an ultrafiltration membrane bioreactor during synthesis of galacto-oligosaccharides: Effect of the operational variables

Andrés Córdova [a,b,*,1,2], Carolina Astudillo [b], Cecilia Guerrero [a], Carlos Vera [a], Andrés Illanes [a]

[a] School of Biochemical Engineering, Pontificia Universidad Católica de Valparaíso, Chile
[b] School of Food Engineering, Pontificia Universidad Católica de Valparaíso, Chile

## HIGHLIGHTS

- Four fouling mechanisms were assessed during enzymatic GOS synthesis in an UF-MBR.
- High lactose concentration (468 g/L) and different process conditions were tested.
- Strong statistical analyses avoided misinterpretation of the fitted model mechanism.
- Cake fouling and intermediate blocking were the predominant mechanisms.
- Boundary gel layer formation was due to the reaction products rather than the enzyme.

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## ABSTRACT

The flux decay of an ultrafiltration membrane bioreactor for the synthesis of galacto-oligosaccharides was modeled, by varying the processing conditions: temperature (40–60 °C), transmembrane pressure (2.5–4 bar) and cross-flow velocity (3.5–7 m/s) according to a $2^k$ design.

Fouling mechanisms varied according to the operational condition, showing that the predominant mechanism were the intermediate fouling, which was associated to the higher flux decay due to the partial adsorption of the enzyme on the membrane, and the cake fouling mechanism, which was associated to those runs where the flux declined by around 20% because of the high concentration of substrate used (40% w/w).

Strong statistical analysis allowed validation or rejection of initial adjustments given by a simple R-square statistical test, showing that misinterpretation of the fouling mechanism can be done under particular conditions, but also revealed that fouling equations have some limitations when drastic flux decay occurs or when this remains virtually unchanged.

The experimental design also showed that temperature was the variable having the main positive effect on flux stability by decreasing the solution viscosity; however, the interaction between cross-flow velocity and transmembrane pressure had the main effect on flux decay.



## 1. Introduction

Galacto-oligosaccharides (GOS) are powerful prebiotics which stand out for their ability to replicate the bifidogenic effect of human milk [12]. Their synthesis is conducted by the enzymatic bioconversion with β-galactosidases in a kinetically controlled reaction which can be tuned by increasing the substrate (lactose) concentration so depressing the hydrolytic potential of the enzyme [25,32,35]. This reaction has gained increasing interest, not only by the health-promoting properties of GOS, but also because it represents an opportunity for whey upgrading, which is a byproduct of cheese-making that may become a nuisance to the dairy industry because of its pollution potential [19].

Despite the impressive advances in biocatalysis, poor operational stability of enzymes is still a drawback for its widespread industrial application [21]. This has motivated research for the development of robust catalysts for the synthesis of GOS, using different immobilization strategies [15,17], as well as for the development of alternative processing such as membrane assisted systems, which allow reuse of the enzyme in the so-called membrane bioreactors (MBR) [34].

* Corresponding author at: School of Biochemical Engineering, Pontificia Universidad Católica de Valparaíso, Chile.
*E-mail address:* andres.cordova@ucv.cl (A. Córdova).
[1] Waddington 716, Playa Ancha, Valparaíso, Chile 2360100.
[2] Brasil 2085, Valparaíso, Chile 23628032.

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MBR enables the selective removal of products from the reaction site, resulting in an increase of the conversion, especially in thermodynamically disfavored or product-inhibited reactions [11] as occurs in the case of GOS synthesis. However, a critical issue in a membrane-based separation process is the decline in permeate flux during operation, a phenomenon attributed to membrane fouling [27]. This flux decline means that the hydrodynamic conditions at the membrane surface change with time during the process [24]. As a result, membrane fouling reduces the mass transfer rate, becoming a critical factor affecting the economic and technological viability of the processes, which essentially depends on the permeate fluxes obtained and their stability with operation time [37].

Because the synthesis of GOS is improved at high lactose concentrations, the processing of this kind of reacting-mixtures may lead to different interactions with the membrane walls, resulting in a reduction of the flux during filtration. In this sense, the identification of the predominant fouling mechanism is an important issue when there is a need to change operating variables in an ultrafiltration process [5] in order to find conditions fulfilling the needs of the process, taking into consideration the nature of the treated stream. This goal can be achieved by flux decline mathematical modeling [38].

Since no information exists about membrane fouling by GOS solutions, the aim of this work was to mathematically model the flux decline during the synthesis of GOS in an ultrafiltration membrane bioreactor (UF-MBR), in order to identify the predominant fouling mechanism, as well as evaluating the effect of the operational variables on the flux reached at the end of the process, as an indicator of the system performance.

## 2. Theoretical background

Classical fouling models (filtration laws) can describe the reduction of flux during constant pressure filtration based on the blocking laws and cake filtration theory proposed by Hermia [16]. This theory was then modified by Field et al. [10] for cross-flow filtrations. Hence, flux variation is, according to Eq. (1):

$$\frac{-dJ}{dt} = K(J-J^*)J^{2-n} \tag{1}$$

where the type of fouling considered depends on the value of the parameter $n$, $J^*$, which can be taken to be the "steady state flux" achieved at long time and $K$ is a constant depending on the fouling phenomena. The four most common different fouling mechanisms can be described by solving Eq. (1) [9], as follows:

### 2.1. Complete pore blocking model ($n=2$)

it is assumed that each solute molecule arriving at the membrane surface participates in blocking by means of pore sealing [20]. Moreover, a molecule never settles over another molecule that has been previously deposited on the membrane surface. Thus, the fractional reduction in permeate flux is equal to the fractional reduction of the membrane surface area corresponding to unblocked pores, but not inside the membrane pores [18]. This mechanism implies that for the resolution of Eq. (1), $n$ must take a value equal to 2. Thus, complete pore blocking is described by Eq. (2):

$$J = (J_0-J^*)\exp(-k_c t) + J^* \tag{2}$$

where J is the flux ($m^3/m^2/s$) at any time (t), $J_0$ is the initial flux ($m^3/m^2/s$), and $k_c$ is the plugging constant for complete blocking law ($s^{-1}$).

### 2.2. Standard blocking model ($n=1.5$)

This model considers that molecules enter the membrane pores and deposit over the pore walls due to the irregularity of pore passages, reducing the membrane pore volume. As a result, the volume of membrane pores decreases proportionally to the filtered permeate volume [37]. The decrease in the volume of membrane pores with time is equal to the decrease in their cross section. In this case, flux decline can be expressed by Eq. (3):

$$J = \left(J_0{}^{-0.5} + k_s t\right)^{-2} \tag{3}$$

where $k_s$ is the plugging constant of standard blocking law $(m\ s)^{-0.5}$.

### 2.3. Intermediate fouling ($n=1$)

In comparison to the complete pore blocking model, the intermediate fouling or intermediate blocking model considers the probability that some molecules may settle over others [20]. The non-blocked membrane surface diminishes with time, thus the probability of a molecule blocking a membrane pore reduces continuously with time:

$$J = \frac{J^*}{\left[1-\left(\frac{J_0-J^*}{J_0}\right)\exp(-J^* k_i t)\right]} \tag{4}$$

In this case $k_i$ may be interpreted as the membrane surface blocked per unit of total volume permeated through the membrane and unit of initial membrane surface porosity ($m^{-1}$).

### 2.4. Cake fouling ($n=0$)

This model considers that solute molecules do not enter the membrane pores, but they form a gel layer over the membrane surface. Flux decline is then represented by Eq. (5):

$$k_g t = \frac{1}{J^{*2}}\left[\ln\left(\frac{J}{J_0} * \frac{J_0-J^*}{J-J^*}\right) - J^*\left(\frac{1}{J}-\frac{1}{J_0}\right)\right] \tag{5}$$

where $k_g$ may be interpreted as a ratio between the characteristics of the gel layer and those of the non-fouled membrane ($m\cdot s^{-1}$).

A schematic representation of the different fouling mechanisms according to Iritani [20] is shown in Fig. 1.

The classical fouling models developed for cross-flow filtration are useful in providing non-ambiguous interpretation of complex phenomena that limit the filtration rates of feeds which are complex solutions of molecules with a wide size distribution [40]. Furthermore, this approach has been successfully used in different systems, showing a good relationship between the experimental and predicted values, displaying a consistent behavior [37,33]).

## 3. Materials and methods

### 3.1. Materials

All reagents were analytical grade and purchased from Sigma or Merck. For the quantification of the reaction mixture, standards of D(+) lactose monohydrate, D(+) galactose, D(+) glucose and 4β-galactobiose were supplied by Sigma. The enzyme β-galactosidase from *Aspergillus oryzae* (Enzeco® Fungal Lactase) was kindly donated by Enzyme Development Corporation, EDC (New York, USA). The enzyme had a pH optimum between 4.5 and 5.0 and optimum temperature of 55 °C with respect to its

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