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Fouling mechanisms of ultrafiltration membranes fouled with whey model solutions

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HIGHLIGHTS

- Three ultrafiltration membranes were fouled with whey model solutions.
- Several mathematical models were fitted to the experimental data.
- Model predictions were very accurate for all the membranes and feed solutions tested.
- Membrane characteristics were related to the fouling mechanisms and model parameters.

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ABSTRACT

In this work, three ultrafiltration (UF) membranes with different molecular weight cut-offs (MWCOs) and made of different materials were fouled with several whey model solutions that consisted of bovine serum albumin (BSA) (1% w/w), BSA (1% w/w) and $CaCl_2$ (0.06% w/w in calcium) and whey protein concentrate (WPC) with a total protein content of 45% w/w at three different concentrations (22.2, 33.3 and 44.4 $g \cdot L^{-1}$). The influence of MWCO and membrane material on the fouling mechanism dominating the UF process was investigated. Experiments were performed using two flat-sheet organic membranes and a ceramic monotubular membrane whose MWCOs were 5, 30 and 15 kDa, respectively. Hermia's models adapted to crossflow UF, a combined model based on complete blocking and cake formation equations and a resistance-in-series model were fitted to permeate flux decline curves. The results demonstrated that permeate flux decline was accurately predicted by all the models studied. However, the models that fitted the best to permeate flux decline experimental data were the combined model and the resistance-in-series model. Therefore, complete blocking and cake formation were the predominant mechanisms for all the membranes and feed solutions tested.

1. Introduction

Ultrafiltration (UF) membranes have been widely used in dairy industries for several applications such as preconcentration of milk, milk dehydration, fractionation of whey, purification of whey proteins, and enrichment of micellar casein for the manufacture of milk [1,2].

However, one of the major problems in the UF processes applied in dairy industry is membrane fouling. Among the different substances that are present in milk and whey, proteins are the main responsible for membrane fouling [3]. The most important consequence of fouling is the gradual permeate flux decline during filtration time. This effect depends on different parameters, such as operating conditions of the UF process (crossflow velocity, transmembrane pressure, feed concentration and temperature), interactions between foulants and the membrane surface or membrane characteristics (hydrophilicity, pore size and porosity) [1,4].

According to the literature, membrane fouling mechanisms can be divided in several types. When the solute molecules are smaller than or similar to the membrane pore size, these molecules can penetrate inside the membrane pores, reducing their effective radius gradually (adsorptive fouling) or causing the entire pore to be completely blocked (pore blocking mechanism) [5,6]. If solute molecules are much higher than membrane pores, they are deposited on membrane surface. In some cases, the deposited fouling layer may form a cake layer [7,8].

Because of the technical and economical importance of permeate flux decline, determining the optimum operating conditions to minimize fouling and obtaining a model to predict permeate flux decline with time are key steps in UF processes. Previous studies found in the literature have developed permeate flux decline models for UF processes [9–13]. Among them, empirical models are the most often used due to their high prediction accuracy because they describe experimental results by fitting a mathematical equation to the data obtained without

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considering any theoretical parameter (examples of these models are those provided by regression analysis) [14]. However, as the theoretical description of fouling phenomena and mechanisms is not reflected on the mathematical equation proposed by this type of models, the relationship between permeate flux decline and the fouling mechanism involved in the UF process cannot be explained with empirical models. On the other hand, theoretical models are able to explain the fouling phenomena during membrane filtration, although they are less accurate. For those reasons, semi-empirical models, which use simplified forms of scientific laws and include a certain number of parameters with physical meaning are more appropriate to provide accurate predictions of the permeate flux decline and also to describe the fouling mechanism at the same time [5,15,16].

Although several mathematical models can be found in the literature to explain the fouling mechanisms affecting UF membranes [9,13,17,18], Hermia's models [19] applied to dead-end filtration and their adaptations to crossflow UF are widely used to fit the experimental data of different UF processes. Previous studies found in the literature have demonstrated that Hermia's models can accurately predict permeate flux decline at different experimental conditions. Mohammadi and Esmaeelifar [20] analyzed the fouling mechanisms involved in the UF of wastewaters from a vegetable oil factory working at 3 bar and 0.5 m/s with a 30 kDa polysulfone membrane. Their results demonstrated that fouling was due to the cake layer formation mechanism, achieving a value of R^2 of 0.99. Vincent Vela et al. [15] investigated the fouling mechanisms involved in PEG UF using a ceramic membrane of 15 kDa. They obtained that intermediate blocking model was dominant for a transmembrane pressure of 3 bar and a crossflow velocity of 1 m/s and in the case of 4 bar and 2 m/s, with values of R^2 of 0.980 and 0.979, respectively. Salahi et al. [5] studied the UF of oily wastewaters using a polyacrylonitrile membrane of 20 kDa at different transmembrane pressures (1.5, 3 and 4.5 bar) and crossflow velocities (0.25, 0.75 and 1.25 m/s). For all the experimental conditions tested, the cake layer formation model followed by the intermediate blocking model were the models that fitted the best, with values of R^2 ranging from 0.9852 to 0.9999 in the case of the cake layer formation model and ranging from 0.8710 to 0.9321 for the intermediate blocking model. Kaya et al. [21] applied conventional Hermia's models to predict the fouling mechanism of two nanofiltration membranes (0.4 and 1 kDa) using a paper machine circulation wastewater as feed solution. The best fitting accuracy ($R^2 = 0.985$) was obtained for the cake layer filtration mechanism followed by the intermediate blocking mechanism ($R^2 = 0.982$) at a transmembrane pressure of 8 bar.

De la Casa et al. [22] combined two fouling mechanisms of Hermia's models. They proposed two different combinations: the first one considers that only a fraction of membrane surface pores (α) is completely blocked (complete blocking model equation) while part of the foulant molecules may pass through the membrane and be adsorbed on the pore walls that were previously unblocked (1-α) (standard blocking model equation). The second combination takes into account that a cake layer of foulant molecules (cake layer formation model equation) can be formed on the previously deposited molecules that have previously completely blocked the pores (complete blocking model equation). The combined models were fitted to the experimental data obtained during the microfiltration of 0.25 $g \cdot L^{-1}$ BSA solutions at a transmembrane pressure of 1 bar and a crossflow velocity of 3.28 $m \cdot s^{-1}$.

On the other hand, the resistance-in-series model is one of the most widely used empirical models due to its high accuracy. Choi et al. [23] applied a resistance-in-series model to batch microfiltration of BSA. They considered that total resistance was the sum of the membrane resistance, the cake layer resistance and the fouling resistance. This last one represented the foulant deposits inside the membrane pores. Flux decline predicted by the model was in a good agreement with the experimental data obtained. Carrère et al. [24] used a resistance-in-series model to predict permeate flux decline of lactic acid fermentation broths crossflow filtration at a transmembrane pressure of 2 bar and a crossflow velocity of 4 $m \cdot s^{-1}$. Their model considered four different resistances (the membrane resistance, the resistance of the adsorbed molecules on the membrane surface, the resistance due to concentration polarization and the cake layer resistance). They obtained a good agreement between predicted and experimental data.

The aim of this work was to investigate the fouling mechanisms that affect different UF membranes (two polymeric membranes of 5 and 30 kDa and a ceramic monotubular membrane of 15 kDa) using several whey model solutions (BSA (1% w/w), BSA (1% w/w) and $CaCl_2$ (0.06% w/w in calcium) and whey protein concentrate (WPC) with a protein content of 45% at three different concentrations (22.2, 33.3 and 44.4 $g \cdot L^{-1}$)) as feed solutions during the fouling step. For this purpose, several models were fitted to the experimental data obtained during the UF of whey model solutions: Hermia's models adapted to crossflow UF, a resistance-in-series model and a combined model based on the complete blocking and cake layer formation fouling mechanisms. As a novelty, the last model was developed for this work based on the Hermia's equations adapted to crossflow for the two fouling mechanisms considered. The influence of both membrane MWCO and material on the dominating fouling mechanism was investigated. The values of model parameters were estimated for the models with the highest fitting accuracy. Different equations that relate model parameters with operating conditions such as the membrane roughness and the particle size and the protein concentration of the feed solutions were developed.

2. Modelling

2.1. Hermia's models

The models developed by Hermia [19] are based on classical constant pressure dead-end filtration equations. They consider four main types of membrane fouling: complete blocking, intermediate blocking, standard blocking and cake layer formation. These models can be adapted to consider a crossflow configuration [15,25,26]. Adapted models to crossflow ultrafiltration incorporate the flux associated with the back-transport mass transfer, which is evaluated at the steady-state [27]. The general equation for Hermia's models adapted to crossflow ultrafiltration is shown in Eq. (1):

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

where J is the permeate flux, K is a model constant and J_{ss} is the permeate flux when the steady-state is achieved.

According to the value of the parameter n, four different models can be distinguished, based on four different fouling mechanisms: complete blocking ($n = 2$), intermediate blocking ($n = 1$), standard blocking ($n = 1.5$) and cake layer formation ($n = 0$).

In the complete blocking model, a solute molecule that settles on the membrane surface blocks a pore entrance completely, but it cannot penetrate inside the pores. This model assumes that a monomolecular layer is formed on the membrane surface.

The intermediate blocking model is similar to the complete blocking one because it considers that fouling takes place on the membrane surface and not inside the pores. However, intermediate blocking model allows solute molecules to deposit on previously settled ones.

The standard blocking model takes into account that all the membrane pores have the same length and diameter and the solute molecules are smaller than the membrane pore size. Therefore, these molecules can penetrate inside the pores.

When the solute molecules are larger than the membrane pores, they may accumulate on the membrane surface forming a permeable cake layer. This is the basis of the cake layer formation model.