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Evaluation of fouling resistances during the ultrafiltration of whey model solutions

María-José Corbatón-Báguena, Silvia Álvarez-Blanco, María-Cinta Vincent-Vela*

Department of Chemical and Nuclear Engineering, Universitat Politècnica de València, C/Camino de Vera S/n 46022 Valencia, Spain

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ABSTRACT

In the last decades, the ultrafiltration of whey has grown in importance as a "green" technique. However, since fouling is an important drawback, researchers focused on its prediction by mathematical models. In this work, three ultrafiltration membranes of different molecular weight cut-offs and materials were used to ultrafilter whey model solutions of different protein concentrations. As a novelty, a resistance-in-series model that accounts for the time evolution of the fouling resistances was considered. The results demonstrated that the higher the protein and salt concentrations in the feed solutions were, the greater the fouling degree was. The resistance-in-series model was accurately fitted to the experimental data for each membrane and feed solution used. The results showed that the resistance due to adsorption dominated the first minutes of operation, while the membrane characteristics (surface roughness and hydrophilicity/hydrophobicity) played an important role in the growth of the cake layer.

1. Introduction

During the manufacture of cheese and casein in the dairy industries, great volumes of a greenish-yellow liquid by-product named "whey" are obtained (Garrido et al., 2016; Carvalho et al., 2013). According to the literature, 8–9 kg of whey are produced per 1–2 kg of cheese, resulting in a worldwide production of about 180–190 millions ton/year (Baldasso et al., 2011). Traditionally, whey has been considered as a dairy wastewater. It has a high biological and chemical oxygen demand (of about 27–60 and 50–102 g O_2/L, respectively), thus it cannot be drained without a treatment. On the other hand, it can be reused as food supplement for livestock, organic fertiliser or as a biogas source (Carvalho et al., 2013; Chandrapala et al., 2016). Moreover, in the last decades, as a result of their outstanding properties, the recovery and fractionation of whey components is being performed (Acevedo-Correa, 2010). Among the different whey components, proteins can be remarked. Their biological, nutritional and functional properties make them attractive for being used in other industries, such as the food, pharmaceutical or cosmetics ones. These properties include their emulsification, gelling and foaming ability and their antioxidant and antimicrobial character (Ramchandran and Vasiljevic, 2013).

In the last years, membrane separation processes have grown in interest in the dairy industry, since they are considered as "green" technologies. Within these processes, ultrafiltration can be highlighted, as it shows a wide range of applications, such as the purification or fractionation of proteins (Wen-qiong et al., 2017; Zin et al., 2016), the production of whey protein concentrates and isolates with protein contents greater than 35 and 85%, respectively (Kazemimoghadam and Mohammadi, 2006) and the production of a lactose-enriched stream (permeate) (Metsämuuronen and Nyström, 2009). Among the numerous advantages of membrane separation processes, the following can be remarked (Zin et al., 2016; Daufin et al., 2001): they are modular processes, easy to scale up and adapt to different industrial requirements, no addition of chemicals is needed to perform the separation and the desired products are obtained with high quality since membrane processes are performed at mild operating conditions.

Nevertheless, the main drawback of ultrafiltration processes is membrane fouling, which gradually reduces the permeate flux and increases the hydraulic resistance and thus the overall process productivity diminishes (Cheryan and Álvarez, 1995). Regarding the dairy industry, proteins are the main compounds responsible for membrane fouling (Argüello et al., 2003). This phenomenon is due to the foulant-foulant and foulant-membrane interaction forces and depends on different factors such as the pH, the temperature and the composition of the feed solution, the characteristics of the membrane (pore size and material) and the

* Corresponding author.
E-mail address: mavinve@iqn.upv.es (M.-C. Vincent-Vela).

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operating conditions (transmembrane pressure and crossflow velocity) (Wang et al., 2012). Due to the great influence that the decline of permeate flux has on process productivity, research has been focused on the prediction of the time evolution of permeate flux by means of the development of mathematical models (Ho and Zydney, 2000; Choi et al., 2000; Bolton et al., 2006; Chen and Kim, 2006; Mondal and De, 2010). Among the different mathematical models available in the literature, semi-empirical models are the most appropriate to both achieve accurate predictions and determine the predominant membrane fouling mechanisms (Salahi et al., 2010; Vincent-Vela et al., 2009; Mah et al., 2012). These models are based on simplified equations of scientific laws that consider several fitting parameters with physical meaning. The resistance-in-series model is the most often used. For instance, Choi et al. (2000) characterized the permeate flux decline during the microfiltration of BSA adsorbed microspheres by means of a resistance-in-series model that considered two fouling resistances: the resistance due to the formation of a cake layer on the membrane surface and that due to the deposition of foulant molecules inside the membrane porous structure. Carrère et al. (2002) fitted a resistance-in-series model to the experimental data obtained during the microfiltration of lactic acid fermentation broths. As fouling resistances, they considered the concentration polarization resistance, the adsorption resistance and the cake formation one. As main results, they demonstrated that resistances due to concentration polarization and adsorption were the predominant ones. Carbonell-Alcaina et al. (2016) used a resistance-in-series model to determine the fouling mechanisms responsible for flux decline during the ultrafiltration of table olive storage wastewaters. These authors included as fouling resistances the one due to the adsorption of foulants on the membrane surface and that related to cake formation. They reported that pore blocking, adsorption and cake formation were the fouling resistances responsible for permeate flux decline.

As the fouling resistances due to adsorption and concentration polarization and cake formation phenomena are the predominant ones in the ultrafiltration of protein based solutions (Katsoufidou et al., 2005), the main objective of this work was to relate the model parameters of a resistance-in-series model to the different membranes and feed solutions tested. The solutions were composed of BSA and BSA + $CaCl_2$, respectively and a real whey protein concentrate (WPC) was considered as well. Three different membranes (in terms of molecular weight cut-off, MWCO, and material) were used, so that, as a novel aspect, the values of the fitting parameters could be related not only to the characteristics of the feed solutions, but also to these of the membranes (MWCO and hydrophilicity/hydrophobicity). As a novelty, the temporal evolution of the abovementioned model parameters was determined and the predominance of each fouling resistance as a function of time, feed solution and membrane tested was investigated.

2. Modelling

2.1. Resistance-in-series model

The resistance-in-series model considered in this work takes into account the contribution of four different hydraulic resistances on permeate flux evolution with time: the original membrane resistance, the resistance due to the adsorption of solute on the membrane surface and also on the pore walls, the resistance due to the concentration polarization and finally, the resistance due to the growth of the cake layer formed by the deposited solute molecules (Carrère et al., 2002; Carbonell-Alcaina et al., 2016). Thus the general equation for the resistance-in-series model is Eq. (1):

$$J_p = \frac{\Delta P}{\mu \cdot (R_m + R_{ads} + R_{cp} + R_{cl})} \quad (1)$$

where J_p is the permeate flux at each time, ΔP is the transmembrane pressure, μ is the viscosity of the feed solution, R_m is the resistance of the original membrane, R_{ads} is the resistance due to adsorption on membrane surface and on the pore walls, R_{cp} is the resistance due to concentration polarization and R_{cl} is the resistance due to the growth of the cake layer.

According to previous studies (Carrère et al., 2001, 2002; Juang et al., 2008), the resistances due to adsorption and concentration polarization have an exponential time dependence that makes these resistances grow at a rate constant b up to a steady-state value $R_{ads,\ ss} + R_{cp,\ ss}$. Therefore the general mathematical equation for these resistances is expressed as in Eq. (2):

$$R_{ads} + R_{cp} = (R_{ads,\ ss} + R_{cp,ss}) \cdot (1 - \exp(-b \cdot t)) \quad (2)$$

where $R_{ads,ss}$ is the resistance due to solute adsorption at the steady-state, $R_{cp,ss}$ is the resistance due to concentration polarization at the steady-state, b is the rate constant at which the resistances grow and t is the filtration time.

On the other hand, the same studies defined the resistance caused by the formation of a cake layer on the membrane surface by means of a pressure-dependent relationship as in Eq. (3):

$$R_{cl} = \left(\frac{m_{dep}}{A_m}\right) \cdot \alpha \quad (3)$$

where R_{cl} is the resistance due to cake formation, m_{dep} is the protein mass deposited on the membrane surface, A_m is the membrane area and α is the specific cake resistance.

The protein mass deposited on the membrane surface can be determined by means of a mass balance equation and considering that (i) the protein concentration at the membrane wall is greater than the protein concentration in the retentate stream and (ii) the temporal variation of the deposited mass is zero when the end of the tests is achieved, as follows (Juang et al., 2008):

$$\frac{dm_{dep}}{dt} = A_m \cdot C_r \cdot \left(J_p - J_{p,f}\right) \quad (4)$$

where C_r is the protein concentration in the retentate stream and $J_{p,f}$ is the permeate flux at the end of the tests.

By substituting Eqs. (2)–(4) in Eq. (1), the general equation for the resistance-in-series model is Eq. (5):

$$J_p = \frac{\Delta P}{\mu \cdot \left(R_m + (R_{ads,\ ss} + R_{cp,ss}) \cdot (1 - \exp(-b \cdot t)) + \left(\frac{m_{dep}}{A_m}\right) \cdot \alpha\right)} \quad (5)$$

3. Experimental

3.1. Experimental set-up

Experiments were carried out in a laboratory scale ultrafiltration plant (VF-S11 model, Orelis, France). This plant was equipped with a temperature control system, a 10 L stainless steel feed tank, a volumetric pump with speed regulation to select the crossflow velocity, a manometer at each side of the membrane module to maintain the transmembrane pressure constant and a scale (with