Chemical Engineering Science 129 (2015) 58–68

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Flux kinetics, limit and critical fluxes for low pressure dead-end microfiltration. The case of BSA filtration through a positively charged membrane

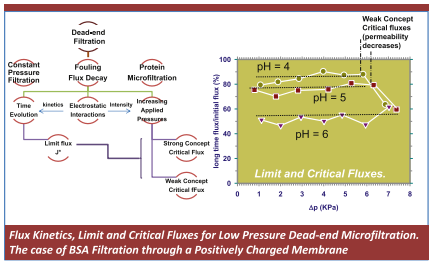
Carmen Velasco, JoséIgnacio Calvo, Laura Palacio, Javier Carmona, Pedro Prádanos, Antonio Hernández*

Group of Surfaces and Porous Materials UA UVA-CSIC, Dpto. de Física Aplicada, Paseo de Belén, Facultad de Ciencias Universidad de Valladolid, 47071 Valladolid, Spain

HIGHLIGHTS

- The relationship between limit and critical fluxes has been analysed in depth.
- Kinetic fouling equations, with non-zero limiting fluxes, have been proposed.
- Limit non-zero fluxes are possible for dead end low pressure microfiltration.
- BSA MF through a positive membrane has been studied vs. pH and Δp.
- Electrostatic protein–membrane interactions play a key role in fouling.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 7 November 2014
Received in revised form
2 February 2015
Accepted 5 February 2015
Available online 14 February 2015

Keywords:
Proteins
Dead-end microfiltration
Flux decay kinetics
Limit and critical fluxes
Adsorption

ABSTRACT

The influence of the applied pressure on the flux decay mechanism during Bovine Serum Albumin (BSA) dead-end microfiltration (MF) has been investigated for a polyethersulfone, positively charged, membrane (SB-6407®) from Pall®. BSA solutions, at pH values of 4, 5 (very close to the protein isoelectric point, IEP) and 6, were micro-filtered through the membrane at different low applied transmembrane pressures.

Although filtration was done in dead-end configuration, limit fluxes appeared for all pressures and pH values studied. The concepts of (long time) limit and critical fluxes and their correlation have been clarified and analysed too. The usual blocking filtration laws have been included in a common frame and both the cases with zero or non-zero limit fluxes have been incorporated. Within this frame, the standard model, that assumes an internal pore deposition, has been included as well; although, in our case, the acting mechanism seems to be mainly the so called complete blocking.

Protein adsorption has been analysed in terms of the protein–protein and protein–membrane electrostatic interactions. There is a faster flux-decay for the protein isoelectric point with a slightly slower decline in flux when there are both membrane-to-protein and protein–protein repulsion. The slowest kinetics appears for membrane-to-protein attraction with protein–protein repulsion. Moreover, adsorption is stronger, and the limit flux smaller, when the protein is attracted towards the membrane and there is protein–protein repulsion.

* Corresponding author. Tel.: +34 983423134; fax: +34 983423013.
E-mail address: tonhg@termo.uva.es (A. Hernández).

http://dx.doi.org/10.1016/j.ces.2015.02.003
0009-2509/

1. Introduction

Membrane microfiltration is a well-established procedure in biotechnological and biochemical industries, (Grandison and Lewis, 1996; El Rayess et al., 2011; Aspelund, 2010; Charcosset, 2012). Microfiltration membranes are especially adequate for the separation of fine particles with sizes in the range from 0.1 to 10.0 μm, especially in cell recovery from fermentation broths, polishing and sterilization of product solutions. It is also used to separate cell fragments caused by cell disruption for the recovery of intracellular enzymes.

Protein transmission and the rate of filtration during microfiltration of protein solutions has been extensively studied and reviewed, (Marshall et al., 1993; Opong and Zidney, 1991; Kelly et al., 1993; Bowen and Gan, 1991; de la Casa et al., 2007). In fact, the transmission of proteins through microfiltration membranes is usually high. Even so, the rate of filtration of apparently pure protein solutions decreases with time at a constant applied pressure. In some cases, this has been explained in terms of deposition of protein in the front face of the membrane, (Opong and Zidney, 1991). It has also been shown that in such cases the adsorption of protein (BSA) is associated with the deposition of trace quantities of aggregated and/or denaturated protein that act as initiators for the continued deposition of bulk protein, (Opong and Zidney, 1991; Kelly et al., 1993). However, a continuous decrease in filtration rate has also been reported in cases where there is neither deposition nor concentration polarization on the front face of the membrane, (Bowen and Gan 1991; Bowen and Gan, 1992, 1993; Franken et al., 1990).

Usually less attention than would be required has been devoted to the applied pressure used to measure the flux decrease linked to pore narrowing or clogging due to adsorption or deposition. A notable exception is the work of Grenier et al. (2008), where an extensive analysis of the pressure dependence of deposition parameters is performed in dead-end microfiltration of bentonite suspensions that do not show a non-zero limit flux. In any case, the convenience of a reduction of the operating pressure to decrease pore blocking was already recommended by Bowen et al., (Bowen et al., 1999).

The origin of limit fluxes – those reached in stationary conditions after long enough times—is not well understood. It is worth noting that in some texts, the more or less pressure independent fluxes reached after applying high enough pressures have been also called limit fluxes, (Bacchin, 2004). Here, we will only use “limit fluxes” to refer to the long time stationary flux reached at each constant pressure. The cause of critical fluxes, those appearing for relatively high pressures with a decrease in permeability, is neither well identified nor understood. It is clear, that when there is a high pressure flux plateau with a very low permeability, this critical flux can be attributed to an extreme blockage of pores. We will further discuss the conceptual differences and the correlation of limit and critical fluxes below. Nevertheless, we will not refer here to other conceptually different critical fluxes as, for example, those corresponding to the maximum flux before arriving to an irreversible fouling, (Bacchin et al., 2002, 2006; Bacchin and Aimar, 2005; Espinasse et al., 2008).

Limit fluxes were originally attributed to factors like cake erosion or deposit removal or back flux, (Field et al., 1995). Actually the introduction or quantification of these limit fluxes has been, from the very beginning, substantially phenomenological, (Agbangla et al., 2012; van der Sman and Vollebregt, 2013; Li et al., 2013). Though the limit fluxes were originally introduced for cross-flow microfiltration, they can also appear in dead end microfiltration, (Lim and Mohammad, 2010; Kim and DiGiano, 2009). Although, of course, the sweeping action of tangential flow would cause the partial loss of the deposit, other causes, as for example the equilibrium between pressure and the attraction or repulsion between the membrane and the solute or the solute–solute interaction, can play a similar role, by limiting the extension and compactness of the deposit. It seems clear that these subtle balances would be more plausible for low pressures because high pressures would always overcome any other interaction. An extensive review of the different theoretical and experimental methodologies applied to cross-flow and dead-end limit and critical fluxes was presented by Bacchin, Aimar and Field, (Bacchin et al., 2006).

In any case, as pointed out by Franken, (Franken, 2009), present day micro- and ultrafiltration (as well) equipment is designed and operated with a strong accent on avoiding the rise of membrane resistance. Nearly all membrane installations in water treatment are using a very low transmembrane pressure. Whatever way the phenomenon is described (critical flux, limit flux, low pressure), it all comes down to keep the overall resistance as low as possible. In practice this, however, can lead to very low fluxes and/or to the requirement of huge membrane surfaces, this is why the question on what pressures can be applied to avoid an inconvenient increase of the membrane resistances while keeping the needed membrane within reasonable limits is relevant.

Our aim here is to study how the applied pressure intensity can affect both the intensity and kinetics of flux decay or fouling due to deposition. This for a charged membrane should depend on the solution pH and on the details of the membrane charge. The influence of pH in dead end microfiltration of proteins has been previously addressed by us using BSA and Lysozyme and positive, SB-6407®, and negative membranes, ICE-450®, (Ouammou et al., 2007), for a relatively high pressure. The influence of pressure for BSA microfiltration was also analyzed, (Velasco et al., 2003), with the negatively charged membrane, ICE-450®. In all these cases, the fouling kinetics was clearly faster for high pressures although limit fluxes were always very small and could be considered zero without affecting substantially retention that remained insignificant. Here we will use the positive SB-6407® membrane to microfilter BSA at low pressures and different pH values. We will find non-zero limit fluxes for all pressures and pH and we will analyze the intensity and kinetics of flux decay in terms of both membrane–solute and solute–solute electrostatic interactions.

2. Theory

2.1. Flux decay mechanisms

Usually, the kinetics of flux decline is analysed in terms of different blocking laws which are customarily four, namely: standard blocking, intermediate blocking, cake filtration and complete blocking models, (Calvo et al., 1993; Bowen et al., 1995; Herrero et al., 1997; Hermia, 1982). In the first of these models, the standard model, it is assumed that the solute molecules or particles are adsorbed onto the walls of the pores decreasing their effective radii. The other three models assume that deposition happens externally. In the complete blocking model each molecule or aggregate (or particle) is assumed to obstruct a pore. In the intermediate model some of the pores clog up while some molecules attach to external non-porous surfaces or on other pre-existent deposits. Finally, in the cake filtration model, a cake can form on the membrane.

For all of these mechanisms, it has been shown, (Calvo et al., 1993; Bowen et al., 1995; Herrero et al., 1997; Hermia, 1982), that there is a common simple characteristic equation:

$$\frac{d^2t}{dV^2} = \alpha\left(\frac{dt}{dV}\right)^{\beta} \tag{1}$$

The physical meanings of the parameters of the four usual models, constants α and β, are well known, (Calvo et al., 1993; Bowen et al.,