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Cleaning efficiency enhancement by ultrasounds for membranes used in dairy industries

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ABSTRACT

Membrane cleaning is a key point for the implementation of membrane technologies in the dairy industry for proteins concentration. In this study, four ultrafiltration (UF) membranes with different molecular weight cut-offs (MWCOs) (5, 15, 30 and 50 kDa) and materials (polyethersulfone and ceramics) were fouled with three different whey model solutions: bovine serum albumin (BSA), BSA plus $CaCl_2$ and whey protein concentrate solution (Renylat 45). The purpose of the study was to evaluate the effect of ultrasounds (US) on the membrane cleaning efficiency. The influence of ultrasonic frequency and the US application modes (submerging the membrane module inside the US bath or applying US to the cleaning solution) were also evaluated. The experiments were performed in a laboratory plant which included the US equipment and the possibility of using two membrane modules (flat sheet and tubular). The fouling solution that caused the highest fouling degree for all the membranes was Renylat 45. Results demonstrated that membrane cleaning with US was effective and this effectiveness increased at lower frequencies. Although no significant differences were observed between the two different US applications modes tested, slightly higher cleaning efficiencies values placing the membrane module at the bottom of the tank were achieved.

1. Introduction

Membrane technologies are widely applied for many industrial applications, such as, dairy and food technology, pharmaceutical industry, chemical industry or waste water treatment [1]. The main advantages of membrane processes are low-energy requirements and high versatility. In particular, ultrafiltration (UF) is a membrane separation technique widely used in the food and dairy industry for milk dehydration, whey (a byproduct of cheese making) concentration and protein purification or fractionation [2]. However, the major problem of their application is permeate flux reduction due to the fouling of the membranes during the production stage.

In dairy industry, membrane fouling is caused by both organic and inorganic compounds (mainly proteins and ions) of the dairy solutions [3]. These molecules are deposited on the membrane surface or into the pores involving cake layer formation and pore plugging [4,5]. In addition, membrane fouling can be classified as hydraulically reversible and irreversible. The first one can be removed in the water rinsing step and the second one, which is more problematic, requires a chemical cleaning step [6].

For all these reasons, the overall process efficiency could be improved by applying an optimum cleaning procedure. Typically, the choice of the cleaning method depends on the module configuration, the membrane material and the nature of the fouling involved in the membrane process [7]. These methods can be classified into physical and chemical. Even though chemical cleaning methods are the most commonly used, they can cause severe membrane damage, often membrane replacement, chemical costs and chemical waste disposal due to the large quantities of chemicals products consumed in the cleaning step [8].

Consequently, alternative cleaning methods are continually under development. Thus, the use of ultrasonic application for membrane cleaning is a promising technique as other authors have recently reported [8,9]. Particularly, Muthukumaran et al. [10] studied the effect of US application and sonication time on cleaning polysulfone (PS) flat sheet UF membranes. They reported that US were effective but cleaning efficiency was not affected by sonication time. Regarding ceramic membranes, Popović et al. [7] studied the effect of US on cleaning ceramic UF membranes fouled with proteins. They concluded that US were more effective combined with detergent solutions than with alkali solutions [7]. In addition, US were also effective to clean membranes fouled by other sub-

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stances and employed for other applications. For example, Alventosa-deLara et al. [1] studied the US application to clean ceramic UF membranes fouled with simulated textile waste water reporting that cleaning efficiency improves up to 25% with the use of US. On the other hand, Secondes et al. [11] combined US application with adsorption processes and UF. They demonstrated the capability of this hybrid system in removing emerging contaminants at high efficiencies. US irradiation enhanced the adsorption of the emerging contaminants onto activated carbon.

US mechanism consists of an agitation of the aqueous medium and creation of microbubbles by means of high-frequency sounds waves. When the collapse of the microbubbles occur, energy is released, which help to overcome the interactions between the foulant and the membrane, removing the foulant from the membrane surface or inside the pores [12,13]. Until now, ultrasounds have been tested submerging the membrane module inside the US bath [5,14–16]. In this study, as a novel aspect, US have been also tested applying them to the cleaning solution.

This work aims to study the effect of US application to clean organic and inorganic UF membranes fouled by model proteins solutions (BSA, BSA/$CaCl_2$ and commercial whey). In this work, two application modes were compared: US application in the membrane cleaning solution and in a bath where membrane module was submerged. Two chemical cleaning agents were tested in combination with US: NaOH and P3 Ultrasil 115 solution. The last one, is a specific surfactant specially recommended to remove organic foulants like proteins [17].

2. Materials and methods

2.1. Fouling and cleaning chemicals

To simulate feed streams from dairy industry, three model solutions were used to carry out the fouling step: BSA (66 kDa of molecular weight) supplied by Sigma Aldrich (Germany), BSA plus $CaCl_2$ (Panreac, Spain) and whey protein concentrate solution (Renylat 45) from Reny Picot (Spain). The first solution tested was BSA with a concentration of 1% w/w. The second one was a mixture between BSA and $CaCl_2$ with a concentration of 1% w/w and 0.6% w/w in calcium, respectively. The last one was a Renylat 45 solution with a concentration of 2.22% w/w. Renylat 45 composition was described in a previous work [18]. Fouling chemicals were dissolved in deionized water and solutions were stored at 4 °C to maintain them in optimal conditions.

Particle size distribution of Renylat 45 was measured with Zetasizer Nano ZS from Malvern.

The cleaning agents used were a surfactant P3 Ultrasil 115 and NaOH solution (Panreac, Spain). The first one is a specific surfactant to clean membranes used in the dairy industry. It was provided obtained from Ecolab (Spain) and the second one was supplied by Panreac (Spain).

2.2. Membranes

Four membranes of different cut-off, configuration and material were selected to carry out the experiments. In this way, two flat sheet polymeric membranes from Microdyn Nadir (Germany) and two monotubular ceramic membranes Inside Céram from Tami Industries (France) were tested. The criterion to select these membranes was to compare the influence of the membrane material and molecular weight cut-off (MWCO) in terms of protein rejection, membrane fouling and cleaning. Membrane MWCO were chosen with pore size between 1 and 100 nm to achieve high retention of proteins [2]. Table 1 summarizes the characteristics of these membranes.

Table 1
Membrane characteristics.

Characteristic	Inside Céram 50 kDa	UH030	Inside Céram 15 kDa	UP005
Active layer	ZrO_2/TiO_2	PESH[a]	ZrO_2/TiO_2	PES[a]
Type	Tubular	Flat sheet	Tubular	Flat sheet
MWCO (kDa)	50 kDa	30 kDa	15 kDa	5 kDa
Water flux at 25°C (l/m^2 h bar)	>210	>180	>80	>71
Maximum operating temperature (°C)	300	95	300	95
pH range	0–14	0–14	0–14	0–14
Effective area (cm^2)	35.81	100	35.81	100

[a] Polietersulphone hydrophilic (PESH) and polietersulphone (PES).

2.3. UF plant

A UF laboratory plant from Orelis (France) was used to carry out the fouling and cleaning experiments. The main elements of the laboratory plant were: a feed tank solution with a capacity of 15 L, a volumetric pump, two manometers placed on the inlet and outlet of the membrane module, a system to regulate the temperature and a precision balance to measure gravimetrically the permeate flux. Depending on the US application mode, two different UF plant configurations were arranged (Fig. 1). The US equipment consists of an US generator and US bath supplied by TSD Machinery (USA). Two different membrane modules were employed. The first one was a Rayflow flat sheet module from Orelis (France) whit capacity for two membranes of 100 cm^2 each one. The second one was a Carbosep tubular module from TAMI Industries (France) used for testing tubular inorganic membranes.

2.4. Experimental procedure

Experimental methodology includes the following stages: an initial deionized water flux measurement, a fouling step with the protein model solutions, a cleaning step and finally, measurement of water flux.

2.4.1. Water flux measurements and fouling step

The initial and final water flux measurements were performed to determine the membrane permeability before and after each experiment. Both water flux measurements and fouling experiments were carried out at a temperature of 25 °C. Membranes were fouled with three different fouling solutions: BSA (1% w/w), BSA/$CaCl_2$ (1% w/w and 0.6% w/w in calcium) and Renylat 45 (2.22% w/w). Table 2 summarizes the experimental conditions applied for the experiments. All fouling tests were carried out at the same experimental conditions to evaluate and compare the different cleaning procedures studied, excepting cross flow velocity, which was different for organic and ceramic membranes since its value depended of the limitations of each membrane module.

Initial and final membrane filtration resistances (R_m and R_c, respectively) were calculated at the beginning or at the end of each test, as appropriate, by means of Darcy's law Equation (Eq. (1)).

$$J = \frac{\Delta P}{\mu \cdot R_m} \quad (1)$$

where J is the initial or final membrane permeate flux, ΔP is the transmembrane pressure and μ is the water viscosity. In the same way, the membrane resistance at the end of the fouling step (R_t) was determined using Eq. (1), replacing J by the membrane flux after the fouling step.