Journal of Food Engineering 143 (2014) 69–73

Contents lists available at ScienceDirect

Journal of Food Engineering

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

Use of attenuated total reflectance infrared microspectroscopy combined with multivariate analysis to study membrane fouling

Tilahun K. Gelaw, Carme Güell, Montse Ferrando, Sílvia De Lamo-Castellví *

Departament d'Enginyeria Quimica, Universitat Rovira i Virgili, Avinguda Països Catalans, 26 campus Sescelades, 43007 Tarragona, Spain

ARTICLE INFO

Article history:
Received 17 September 2013
Received in revised form 19 April 2014
Accepted 25 June 2014
Available online 2 July 2014

Keywords:
Attenuated total reflectance infrared microspectroscopy
Membrane emulsification
Nitrocellulose mixed esters membrane
Multivariate analysis

ABSTRACT

Attenuated total reflectance infrared microspectroscopy (ATR-IRMS) combined with multivariate analysis was used to study the efficiency of different cleaning protocols applied to remove membrane fouling after membrane emulsification. An organic nitrocellulose mixed esters (MCE) membrane was used to prepare oil-in-water (O/W) emulsions. After the emulsification process, the membranes were cleaned with Tween 20 solutions at different concentrations (2%, 3% and 4%) in backwash mode with N_2 pressure (150, 500 or 700 kPa). The efficiency of the membrane cleaning process was also assessed by water flux recovery and membrane surface characterization by ATR-IRMS in the mid-infrared region (4000–800 cm^{-1}) The analysis of the raw spectra showed that the surface of fouled and cleaned membranes had mainly sunflower oil. Soft independent modeling of class analogy models (SIMCA) were created using the raw ATR-IRMS spectra to differentiate between new, fouled and cleaned membranes. Class projections of transformed ATR-IRMS spectra and interclass distances values showed clear differentiation between the clusters of different cleaning protocols tested, and using discriminating power IR bands sunflower oil was identified as the only foulant agent on the MCE membrane surface. This study shows the potential of applying ATR-IRMS combined with SIMCA models to study membrane fouling/cleaning of organic microfiltration membranes.

1. Introduction

Emulsification is a structure-forming process where two or more immiscible phases can be mixed to one another. Traditionally, colloid mills, rotor stator systems, high pressure homogenizers and ultrasonic homogenizers have been used to prepare emulsions. However, these techniques can cause loss of functional properties of the components which have heat and shear sensitivity, and it is also difficult to control the droplet size and their distribution (Karbstein and Schubert, 1995; Nazir et al., 2010). A relatively new technique to produce emulsions is membrane emulsification (ME). It is a process in which a to-be-dispersed phase is pressed through a membrane and the droplets formed are carried away with a continuous phase flowing across the membrane (van der Graaf et al., 2005; Piacentini et al., 2010; Silvestre de los Reyes and Charcosset, 2010; Trentin et al., 2010). In ME process, the accumulation of the different components of the emulsion on the membrane surface or within the membrane pores causes fouling that will inevitably result in a flux decline (Mallevialle et al., 1989; Scott, 1995; Chang et al., 2002; Charcosset, 2011; Trentin et al., 2011). Though membrane fouling is an inevitable phenomenon during membrane processes, it has been minimized by strategies such as appropriate membrane selection, choice of operating conditions and membrane cleaning. Among these strategies, the most feasible one to extend the life of membranes used in membrane emulsification is to perform physical or chemical/biochemical cleaning. The most straight forward methodology to test the efficiency of membrane cleaning is measuring the water flux of the new and cleaned membranes and calculating the water flux recovery. However, additional membrane characterization to determine which compounds have been left or removed from the membrane has been also widely applied. In the past decade, membrane surface has been characterized with different methods such as scanning electron microscope (SEM) (Güell and Davis, 1996; Väisänen et al., 2002), confocal scanning laser microscopy (CSLM) (Ferrando et al., 2005; Zator et al., 2007), spectroscopic techniques (Carlsson et al., 1998; Belfer et al., 2000) and atomic force microscopy (AFM) which has been used to study surface topography and pore size distribution (Hilal and Johnson, 2010). FT-IR spectroscopy has been used by several researchers to characterize membrane surface. Shon et al. (2006) used this technology to study fouled ultrafiltration membranes used in wastewater treatment. Rice et al. (2009) analyzed the fouling of lactose and calcium phosphate

* Corresponding author. Tel.: +34 977 559 673; fax: +34 977 559 621.
E-mail address: silvia.delamo@urv.cat (S. De Lamo-Castellví).

http://dx.doi.org/10.1016/j.jfoodeng.2014.06.032
0260-8774/

from skimmed milk on nanofiltration membranes by FT-IR-ATR. Wemsy Diagne et al. (2013) studied the cleaning efficiency of fouled polyethersulfone (PES) membranes by ultrafiltration of skimmed milk using the height ratio of two targeted IR bands, 1539 cm^{-1} related to amide II vibration of proteins and 1240 cm^{-1} characteristic of the PES membrane. In a previous research, we analyzed by ATR-IRMS combined with soft independent modeling of class analogy (SIMCA) nylon membranes before and after using them to obtain oil-in-water (O/W) emulsions stabilized with whey protein and also after performing cleaning cycles using combinations of 2–4% Tween 20 and 150–700 kPa of N_2 pressure. The sunflower oil was identified as the major component responsible for the fouling on this type of membrane (Kuzmenk et al., 2005; Trentin et al., 2011; Gelaw et al., 2011). However, the nylon membrane had an amide spectral band that was overlapping with the whey protein bands (emulsifier component) being impossible to conclude whether whey protein was causing the same extent of fouling as sunflower oil (Gelaw et al., 2011).

For this research, a nitrocellulose mixed esters (MCE) membrane was selected instead of nylon one to produce O/W emulsions stabilized by whey protein. Membrane fouling and the efficiency of different cleaning protocols applied were characterized by ATR-IRMS combined with multivariate analysis (SIMCA).

2. Materials and methods

2.1. Materials and membrane

Oil-in-water (O/W) emulsions were prepared using commercial sunflower oil as a disperse phase, MiliQ water (18.2 MΩ cm) as a continuous phase and whey protein (WPC, Lactalbumin® 75 L, from Milei-Sttuttgart, Germany) as emulsifier. Nitrocellulose mixed esters membrane (0.8 μm pore size, Sterlitech Corporation, Kent, WA 98032-1911 USA) was used for premix membrane emulsification. The effective membrane diameter was 47 mm, giving an effective filtration area of 1.73×10^{-3} m^2 for the membrane module employed in this research.

2.2. Premix emulsification procedure

Premix membrane emulsification is a two-step process. The first step consists of preparing a coarse O/W emulsion by mixing the disperse phase and the continuous phase containing the emulsifier by means of a rotor-stator (Ultra-Turrax®, model T18, IKA) at 15,500 rpm for 2 min. In the second step of the process the coarse emulsion is forced to pass through a MCE membrane by using nitrogen pressure (500 or 900 kPa) resulting in a reduction of the droplet size. This second step was repeated five times (cycles) to obtain the final emulsion droplet size. More detail in the experimental procedure and equipment can be found in Trentin et al. (2010). Each experimental condition tested in the present study was repeated three times and a new membrane was loaded into the membrane module at the beginning (1st cycle) of each experiment. Membrane cleaning was performed after emulsification using Tween 20 (polyoxyethylene sorbitan monolaurate; CAS no. 9005-64-5 Sigma–Aldrich, Spain) dissolved in milliQ water at three different concentrations selected according to previous experience (Gelaw et al., 2011; Trentin et al., 2012). The procedure for membrane cleaning consisted of forcing 700 mL of the cleaning agent (divided in four batches) at room temperature (22 ± 2 °C) through the membrane in a backwash mode at different pressures. The cleaning solutions and the cleaning pressures employed are as follows: 2% Tween 20 and 150 kPa N_2 pressure (TW2P1.5), 3% Tween 20 and 700 kPa N_2 pressure (TW3P7) and 4% Tween 20 and 500 kPa N_2 pressure (TW4P5) (Gelaw et al., 2011; Trentin et al., 2011).

2.3. Water flux recovery

To calculate the efficiency of the cleaning method, water flux recovery (WFR) was calculated according to Eq. (1):

$$\mathrm{WFR} = \left(\frac{J_c}{J_0}\right) * 100 \quad (1)$$

where J_0 is the water flux of the new membrane and J_c is the water flux of the cleaned membrane. J_0 and J_c were obtained by pushing 170 mL of water at 150 kPa through the new and cleaned MCE membrane, respectively.

2.4. Sample preparation for ATR-IRMS analysis

MCE membranes were used as a support for the analysis of sunflower oil and whey protein spectra by ATR-IRMS. An aliquot (5 μL) of 10% whey protein solution or sunflower oil was placed onto half MCE membrane and dried for 2 h. Each dry membrane and half of the fouled and cleaned MCE membranes were mounted on a microscope slide before being analyzed by ATR-IRMS. Six spectra per each sample and day of experiment were collected in the attenuated total reflectance (ATR) mode in the mid-infrared region (4000–800 cm^{-1}).

2.5. Spectra acquisition by ATR-IRMS

The different MCE membrane samples were characterized by ATR-IRMS using FT-IR microscope (Illuminate IR, Smiths detection) interfaced with mercury–cadmium–telluride (MCT) photoconductive detector and equipped with a microscope with a motorized *x–y* stage, 5× and 50× objectives, and slide-on attenuated total reflection (ATR) diamond objective (Smiths detection). The microscope was software-controlled using Wire 3.2 version software (Renishaw plc,). Spectra were collected from 4000 to 800 cm^{-1} with a resolution of 4 cm^{-1}. Each spectrum was an average of 128 scans being the acquisition time around 40 s. The spectrometer was completely software controlled by synchronize IR basic version 1.1 software (SensIR Technologies, Smiths detection).

2.6. Cleaning efficiency

The cleaning efficiency was calculated using Eq. (2) (Trentin et al., 2011).

$$\mathrm{Efficiency} = \left(\frac{A - Bn}{A}\right) * 100 \quad (2)$$

where A is the average area (Grams/AI version 8.0 software, Thermo Fisher Scientific Inc., Smiths Detection) of IR band at 1743 cm^{-1} for the fouled membrane and Bn is the average area of the same band for each cleaned membrane.

2.7. Multivariate analysis

Spectra were exported to the Pirouette® multivariate analysis software (version 4.0, InfoMetrix, Inc., Woodville, WA). The spectral data were mean-centered, transformed to their second derivative using a 15-point Savitzky–Golay polynomial filter, and vector-length normalized. Sample residuals and Mahalanobis distance were used to determine outliers (Dunn and Wold, 1995; Kansiz et al., 1999; Hruschka, 2001). Soft independent modeling of class analogy (SIMCA) was used to build a predictive model based on the construction of separate principal component