Journal of Membrane Science 362 (2010) 453–459

Contents lists available at ScienceDirect

Journal of Membrane Science

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

In situ quantification of membrane foulant accumulation by reflectometry

C.G.P.H. Schroën[a,*], A. Roosjen[a], K. Tang[a], W. Norde[b,c], R.M. Boom[a]

[a] Wageningen University, Department of Agrotechnology and Food Sciences, Food Process Engineering Group, Bomenweg 2, 6703 HD Wageningen, The Netherlands
[b] Wageningen University, Department of Agrotechnology and Food Sciences, Laboratory of Physical Chemistry and Colloid Science, Dreijenplein 6, 6703 HB Wageningen, The Netherlands
[c] University Medical Center Groningen and the University of Groningen, A. Deusinglaan 1, 9713 AV Groningen, The Netherlands

ARTICLE INFO

Article history:
Received 17 March 2010
Received in revised form 25 June 2010
Accepted 30 June 2010
Available online 7 July 2010

Keywords:
Reflectometry
Fouling
Fouling rate
Membrane
Surface
Polyethersulfon

ABSTRACT

In this paper, we present laser light reflectometry [1] (not to be mistaken with ultrasound reflectometry [2] that uses ultrasound waves) as a tool for quantitative investigation of (the initial stages of) fouling on membrane-like surfaces. Reflectometry allows in situ investigation of adsorption and accumulation of components near a surface. However, before the method can be applied, a membrane-resembling layer should be attached to a reflecting surface and this layer should have minimal roughness. This was investigated for the widely used membrane materials polyethersulfone (PES), polyvinylpyrrolidone (PVP), and a blend of both. The adsorption of typical foulants, such as BSA, dextrin, and tannin was followed in time. Both unmodified and modified surfaces, obtained through pre-adsorption of Tween components were investigated. The interactions responsible for adsorption of foulants could be charted, and surface modifications could be proposed that specifically target these interactions.

1. Introduction

Much effort is put into charting the fouling dynamics of membranes (e.g. [3]), and more importantly prevention thereof (in this paper, we will use the term fouling to indicate any effect that reduces the flux). Various approaches have been proposed, ranging from process and module design to obtain desirable hydrodynamic conditions, all the way to membrane modification to prevent component membrane interactions.

Regarding process and module design, the promotion of turbulence to enhance mass transfer near the membrane surface is widely spread, e.g. through specific turbulence promoters as suggested by Krstic et al. [4], rotating disks [5,6], gas sparging [7,8], or other fluid instabilities [9]. Alternatively, (sub-)critical flux concepts as presented by Field et al. [10], Howell [11] and recently reviewed by Pollice et al. [12] have been proposed to minimize deposition. Further, the uniform transmembrane pressure concept [13], which uses a uniform and low transmembrane pressure over the length of the membrane module, mostly by circulating the permeate, was shown to be an effective way to keep flux levels as constant as possible, through minimized deposition. Besides, different ways of back pulsing, back flushing (e.g. [14,15], or application of pulsated flow [16]) have been proposed to keep flux levels acceptable. All these methods remediate the flux decrease at least temporarily, but they do not target the origin of the flux decrease, which is the first layer of foulants that adhere to the surface. To remove (at least part of) the first and subsequent foulants layers mostly extensive cleaning and sanitation methods are applied, which leads to considerable down time of the production lines, and in the end reduces the life time of the membranes and the membrane modules [17].

Since membrane–foulant interactions are the first step in further fouling, membrane modification has been investigated already early on in the development of membranes in order to suppress these interactions as much as possible [18–20]. In biosensor applications, membrane modification is probably even of greater importance [21] given the number of possible foulants. The importance of the surface hydrophilicity for the prevention of adsorption has been stressed since e.g. protein adsorption is usually less on hydrophilic than on hydrophobic surfaces [22]. However, prevention of adsorption cannot be achieved by 'only' adjusting the membrane hydrophilicity. Not only are the interactions more complex, a typical feed will also contain a wide diversity of foulants. In order to develop effective membrane modification, the deposition process of foulants needs to be investigated in detail, along with the interactions that are involved.

Recently, a review by Le-Clech et al. [3] has become available, in which various methods were discussed to measure different aspects of fouling in membrane bioreactors. We noted that in general, the methods used to investigate fouling can be divided

* Corresponding author. Tel.: +31 317 482231; fax: +31 317 482237.
E-mail address: karin.schroen@wur.nl (C.G.P.H. Schroën).

0376-7388/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.memsci.2010.06.066

into four categories. The first category is based on flux measurements [23] or a related parameter such as the modified flux index [24]. In most cases, flux measurements are not sensitive enough to capture the first stages of fouling, but give a good impression of the later stages where fouling results in flux loss. The second category comprises methods that use autopsy of a membrane after fouling, leading to component and structural analysis through e.g. ATR–FTIR, EDX, CSLM, or SEM analysis [6,25–27]. Although these methods give information on deposited components at one specific time, they do not give much information on the dynamics, and the fact that the membrane has to be sacrificed for analysis is a drawback. Within the third category, surface characteristics are investigated for example by contact angle measurement [22] or streaming potential measurement [28], which gives a good impression on macroscopic properties of membranes, but still no information on the dynamics of the adsorption process. Finally, visual observation is used to investigate fouling [25,29], which is most effective in the later stages of fouling where the layer becomes visible, and which does yield information on the dynamics of fouling but specifically later in the process.

Although all these methods are useful in their own right, it is not straightforward to translate these results to the initial stages of fouling, and the dynamics thereof, let alone to a membrane modification strategy. In principle, ultrasound reflectometry does have the potential to measure in situ [2], but it cannot be used to develop a modification strategy. Mostly, the methods do not allow in situ observation or are not sensitive enough to discern the important effects during the start-up of fouling. For these reasons, reflectometry [1,30] could be a great addition to the currently available techniques, since it allows direct measurement of small amounts of deposited material. The technique is developed for regular surface–component interactions, which means interactions with a very smooth silicon surface. In order to equip reflectometry for membrane applications, this surface should be adjusted in such a way that it allows measurement on a thin polymer layer which resembles a membrane. This allows us to isolate primary adsorption phenomena from related phenomena occurring in membranes, such as cake formation and concentration polarization.

The aim of the work reported in this paper was first to develop samples suitable for reflectometry with the surface characteristics of the 'membrane' materials PES, PVP, and their blends. Second, foulant–membrane surface interactions were studied by using typical foulants like BSA, dextrin, and tannin. Besides, anti-fouling properties of surfaces modified with Tween components were investigated. From all the results, the relevant interactions could be charted, which is useful for the development of anti-fouling strategies. The paper is concluded with a small outlook on the use of reflectometry in the development of membranes.

2. Materials and methods

Poly(ethersulfone) (PES) (Ultrason, E6020P), poly(vinylpyrrolidone) (PVP) (Luvitec, K90) were purchased from BASF (Ludwigshafen, Germany). Prime grade 150 mm silicon wafers type P/B with <1 −0 −0> orientation and thickness 660–690 μm were obtained from WaferNet Inc. (San Jose, CA, USA). KH_2PO_4, K_2HPO_4, dichloromethane (Suprasolv), ethanol (Pro-Analyse) were purchased from Merck (Darmstadt, Germany), bovine serum albumin (BSA, Lot# 05740737) and NN-dimethylformamide (>99.8%) from Sigma–Aldrich, tannic acid powder from Riedel-deHaën (Honeywell, Seelze), dextrin 5 (from maize starch), from Fluka (Neu-Ulm, Germany), and Tween 20, Tween 40 and Tween 60 from Sigma–Aldrich. The water used throughout the study is Milli-Q.

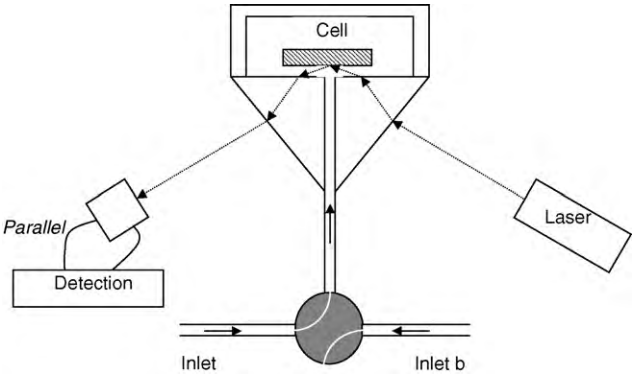

Fig. 1. Schematic diagram of the experimental set-up, dotted line is laser light path.

2.1. Reflectometry

2.1.1. Principle

This technique allows continuous and quantitative measurement of adsorbed amount per unit area on a macroscopic surface [1,30]. For this, a linearly polarized He/Ne laser beam enters the measurement cell through a 45° glass prism (see Fig. 1). The angle of incidence to the surface is equal to the Brewster angle. The laser beam is used to analyze the situation at a well-defined position (stagnation point) of the incoming fluid, which is formed at the spot where the impinging jet meets the flat surface, for which we use strips cut from a silicon wafer (see next section for preparation of surfaces). At the stagnation point, the adsorbent is homogenously distributed. The laser beam leaves the cell through a second 45° glass prism (4), and is split into its parallel and perpendicular components using a polarizing beam splitter, and the intensities of the normal (I_s) and parallel components (I_p) are measured continuously (Fig. 1). The laser, cell, target surface, and detector are lined up properly to ensure the laser is reflected correctly, and hits the detector. The entire set-up is placed in a dark cabinet to prevent any interference.

The output signal S, is defined in equation 1 as the ratio of the intensities parallel I_p and perpendicular to the plane of polarization I_s:

$$S = \frac{I_p}{I_s} \tag{1}$$

Upon adsorption, the ratio of these intensities changes, from which the adsorbed amount is obtained using the 5-layer matrix model proposed by Dijt et al. [1,30], in which the refractive index increment dn/dc is used. For BSA, dextrin and tannin a refractive index increment 0.155, 0.128, and 0.172 were found from refractive index measurements. All experiments were carried out at flow rates between 0.8 and 1.2 mL min^{-1}.

2.2. Preparation of model membranes

To prepare the membrane-resembling surfaces (from now called model membranes), which consist of reflective strips with a thin polymer layer, first clean reflective strips needed to be obtained. Silicon wafers were cut into strips of 1 cm × 4.5 cm, which were sonicated in ethanol for 15 min (sonicator 5210, Branson at 100% capacity), subsequently washed with water and ethanol, and dried with nitrogen. Next, the strips were plasma cleaned (pdc-32G, Harrick at RF-level high) for 15 min.

To obtain PES or PVP model membranes, a 0.25% (w/w) PES in dichloromethane or 1% PVP solution in ethanol was made, which was spin-coated on the cleaned silicon strips for 10 s at 2500 rpm. After this, the spin-coated strips were put 1 h at 300 °C for PES and 24 h at 150 °C for PVP model membranes. For the cross-linked