



Contents lists available at ScienceDirect

Journal of Membrane Science

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

Real-time fouling monitoring with Raman spectroscopy

Tiina Virtanen^{a,*}, Satu-Pia Reinikainen^a, Martin Kögler^{b,c}, Mika Mänttari^a, Tapani Viitala^b, Mari Kallioinen^a^a LUT School of Engineering Science, Lappeenranta University of Technology, P.O.Box 20, 53851 Lappeenranta, Finland^b Division of Pharmaceutical Biosciences, University of Helsinki, P.O. Box 56, 00014 Helsinki, Finland^c Institute of Biotechnology, Technische Universität Berlin, Ackerstr. 71-76, D-13355 Berlin, Germany

ARTICLE INFO

Keywords:

Online
Organic fouling
Vanillin
Raman
Principal component analysis

ABSTRACT

The possibility to detect and identify early stage membrane fouling in real-time is a key to understand fouling phenomena. In this study normal Raman spectroscopy was explored as a novel online tool for monitoring membrane fouling. Raman spectra were measured during cross-flow experiments in which vanillin was used with different concentrations as a model compound for organic foulants. The measured Raman spectra were analyzed and interpreted by using principal component analysis and external calibration in order to determine the adsorbed amount of vanillin during the fouling process. Fouling induced changes in pure water permeabilities and off-line measured FTIR spectra were also analyzed in order to confirm the results of the real-time monitoring system. It was found that an increase in the solution concentration increased the degree of vanillin adsorption and led to better water permeabilities. The procedure used is able to provide results that describe well the accumulation of foulants in a straightforward and semi-quantitative way. The results demonstrate that the introduced monitoring tool has potential for gaining new knowledge about fouling layer formation.

1. Introduction

Membrane-based systems have globally gained interest as one of the most efficient technologies for filtration and purification for a broad range of applications [1]. The major challenge in the use of membrane technology is membrane fouling, which causes a decrease in filtration capacity and increases filtration time. Fouling might also affect the selectivity of the used membrane and the contents of the fractions produced in the filtration. Therefore, it influences the efficiency and cost-effectiveness of a filtration process. [2–4] Understanding the mechanisms behind fouling is a key point to give insights how to control and minimize fouling [5,6,2]. Most of the previous fouling studies have been performed off-line and a fouling layer formed during experiments has been studied as a one complete layer because there are only limited possibilities to obtain information on the fouling process in real-time.

Raman spectroscopy (RS) is a minimally invasive spectroscopic technique that has widely been used for off-line characterization of membrane structures and fouling [2,7–15]. Qualification of functional groups, hydrogen bonding, conformations, orientation of polymeric chains and morphology-membrane transport relationship are all

examples of molecular level objects which can be studied by RS [16]. Raman spectroscopy has also been used in a wide range of applications for process and synthesis monitoring [17–21]. The utilisation of normal RS in real-time fouling monitoring has gained growing interest but until recently there have been some technical challenges limiting its use. To our knowledge, this is the first reported study that used normal Raman spectroscopy to examine fouling in real-time.

Previous Raman based real-time fouling monitoring studies have been conducted by applying surface-enhanced Raman spectroscopy (SERS) because it allows higher detection sensitivity when compared to normal Raman spectroscopy [22]. Raman signal is enhanced through the use of metal nanostructures (gold, silver etc.), which enables even single molecule level detection. Cui et al. used SERS to study the nature of reversible and irreversible fouling caused by naturally occurring protein foulants [2]. Lamsal et al. applied SERS to examine fouling caused by naturally occurring organics on a polymeric nanofiltration membrane, which is used for the treatment of drinking water [8]. Development of both single and dual-species biofilms on membrane surface [23] and layer-by-layer chemical variation during biofouling and cleaning processes [24] have also been studied using the SERS based techniques. Kögler et al. recently demonstrated the use of an

* Corresponding author.

E-mail addresses: tiina.virtanen@lut.fi (T. Virtanen), satu-pia.reinikainen@lut.fi (S.-P. Reinikainen), martin.kogler@helsinki.fi (M. Kögler), mika.manttari@lut.fi (M. Mänttari), tapani.viitala@helsinki.fi (T. Viitala), mari.kallioinen@lut.fi (M. Kallioinen).<http://dx.doi.org/10.1016/j.memsci.2016.12.005>Received 20 September 2016; Received in revised form 29 November 2016; Accepted 1 December 2016
0376-7388/ © 2016 Elsevier B.V. All rights reserved.

online sensing approach for detection of biofouling in drinking water membrane filtration [25].

Because SERS phenomenon is bound to the surface of the nanoparticles, the target analyte has to be on or in very close proximity to the metal surface in order to experience an enhancement. Therefore the magnitude of the SERS enhancement is distance dependent. [8] The SERS performance is depended both on nanoparticle concentration and their three dimensional distribution profile on the studied substrate [26], and it is difficult to immobilize the nanoparticles reliably on the membrane surface [25]. Furthermore, addition of nanoparticles can have a significant influence on the permeability, pore size and morphology of the membranes in comparison with virgin membranes [27]. It is highly possible that this kind of membrane modification also changes fouling mechanisms.

The aim of this study was to assess whether fouling could be monitored by normal Raman spectroscopy without any disturbance on the membrane surface. We placed an immersion probe inside a cross-flow filtration cell and followed the adsorption of a model foulant, i.e. vanillin, as a function of time. To the best of our knowledge, this kind of online monitoring system has never been reported before. The setup used produces multivariate spectral data that can be utilized for analysis after simple preprocessing. The development of the concentration profile for the adsorbed amount of vanillin during the fouling process was determined by principal component analysis, while an external calibration method was used for the scaling of the results. FTIR spectroscopy and pure water permeability measurements were employed as complementary analyses to evaluate fouling.

2. Materials and methods

A summary of the procedure used in this study is shown in Fig. 1. The first test set was compiled in order to see how vanillin adsorption affects membranes' performance. Pure water permeabilities were measured and compared before and after fouling in order to determine fouling induced changes in permeabilities. The second test set was compiled for spectrum analysis. The measured Raman spectra were processed and analyzed to find out how adsorbed vanillin accumulates on the membrane. Extraction results were used for calibration of the

results.

2.1. Organic model compound

Vanillin (152.15 g/mol) was purchased from Acros Organics with a purity of 99%. Vanillin is a slightly water soluble (7.303 g/L at 25 °C [28]) phenolic compound that is widely used as a natural food flavoring agent. Vanillin is also a promising, sustainable candidate for controlling biofouling of water treatment membranes. [29–32] Vanillin can easily be synthesized from various raw materials, but the majority of synthetic vanillin is made either from guaiacol or lignin [33]. Due to its chemical structure, vanillin has been commonly used as a simple monomeric lignin model compound [34–36]. The aromatic ring of vanillin has an intense Raman response because the delocalized electrons are easily polarizable [37].

2.2. The ultrafiltration membrane

Hydrophilic polyethersulphone membrane UH004P supplied by Microdyn-Nadir GmbH was used in this study. The membrane has a molecular weight cut-off of 4 kDa and a contact angle of 64° [38].

2.3. Fouling experiments

The experiments were carried out by using a cross-flow flat-sheet module. A schematic diagram of the filtration system is shown in Fig. 2. The effective membrane surface area was 45 cm². Both the concentrate and the permeate were recirculated into the feed tank. During pure water permeability measurements the permeate was collected into a beaker and weighted with an electronic balance. Temperature was kept at 25 ± 5 °C by using a heat exchanger. The cross-flow velocity was measured by a rotameter and transmembrane pressure was adjusted by using a needle valve. Cross-flow velocity was adjusted to 1.5 m/s during flushing, pressurizing and pure water permeability measurements. The fouling step was carried out by using a lower cross-flow velocity (1.1 m/s).

Before all tests fresh membranes were treated by filtering pure water under 3 bar for 30 min to remove preservatives. The aim was also

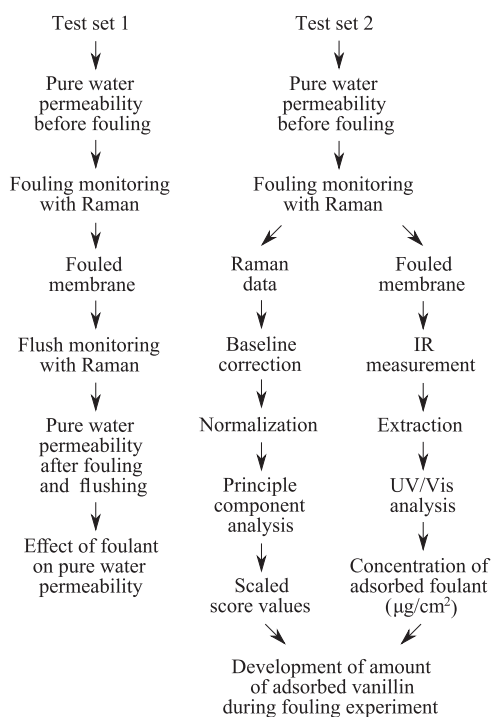


Fig. 1. Summary of the procedures used in this study.

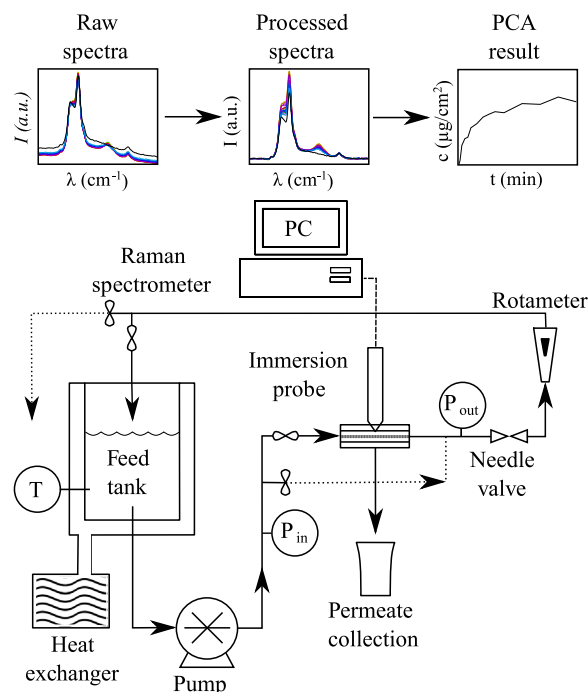


Fig. 2. Schematic of the cross-flow filtration system combined with the Raman sampling setup.

Download English Version:

<https://daneshyari.com/en/article/4989417>

Download Persian Version:

<https://daneshyari.com/article/4989417>

[Daneshyari.com](https://daneshyari.com)