On-line monitoring of membrane fouling at the nanoscale combining advanced surface-sensitive techniques

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Introduction

Water membrane filtration processes are commonly affected by membrane fouling which until today is accepted to be to a certain degree inevitable. Therefore, attempts are being made to at least minimize the impact of fouling by either modifying the membrane surface chemically, or by adopting adequate operation strategies. Finding the right strategy, however, is often based on a time-consuming trial-and-error approach. Hence, on one hand, accurate, fast, and non-invasive techniques would be desirable in order to verify the efficiency of the membrane surface modification. On the other hand, real-time monitoring of the early-stage development of membrane fouling would enable adapting the optimal process operating conditions.

Unfortunately, current monitoring techniques neither reach such efficiency nor sensitivity. For example, it has so far been impossible to reliably detect the very first adsorbed layers of foulants, which occur at the nanoscale but play a crucial role on the subsequent development of the fouling phenomenon.

This work presents an approach of combining two powerful advanced surface-sensitive techniques for monitoring membrane fouling, namely quartz crystal microbalance with dissipation monitoring (QCM-D) and multi-parameter surface plasmon resonance (MP-SPR). It will be shown that these non-invasive techniques are both highly feasible for characterizing the build-up of the very first fouling layers at the nanoscale, and have a high potential of significantly accelerating membrane screening.

Material and Methods

As a model membrane polymer, polyamides (PA) modified with polyethylene glycol (PEG, n=12) at different degrees (0, 25, 50, and 75%, respectively) were employed. The same polyamides had been employed previously as membranes in an ultrafiltration (UF) process [1]. Ultra-thin films of these polymers were cast onto QCM-D and MP-SPR sensors by spin-coating. QCM-D and MP-SPR sensors had an area of less than 1 cm^2. Bovine serum albumin (BSA) was used as a model foulant in the UF process, as well as for the combined QCM-D/MP-SPR monitoring system.

Results and Discussion

Non-invasive and real-time monitoring of adsorption of BSA on the PA films revealed that QCM-D and MP-SPR enable a very fast detection with high temporal resolution. As an example, Figure 1 (left) illustrates how almost 90% of the steady-state signal was reached in an interval of only 40 seconds. This corroborates that the

QCM-D/MP-SPR is an excellent and fast screening tool for studying membrane antifouling properties.

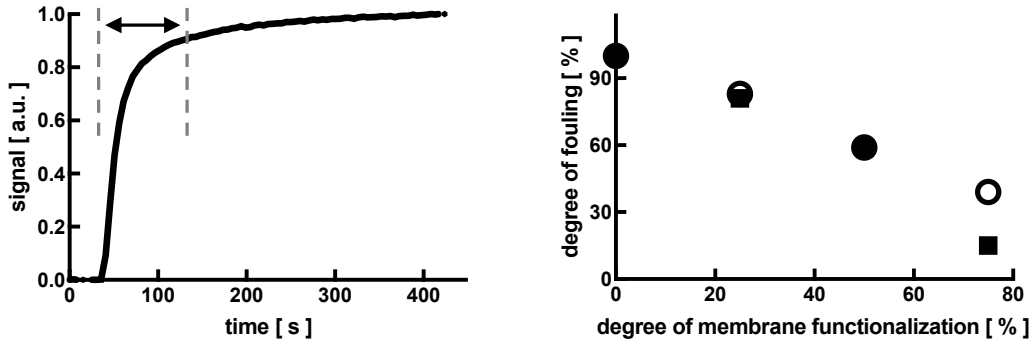


Figure 1. Left: Response of an ultra-thin PA film to the exposure to 100 mg·l^{-1} of BSA in water as measured by QCM-D. The arrow indicates the time interval needed to reach 90% of the signal. Right: Degree of fouling measured on polyamides with different degrees of functionalization by PEG and deposited as ultra-thin films on QCM-D (open circles) and MP-SPR (filled squares) sensors.

Both QCM-D and MP-SPR detected in very good agreement how the fouling tendency was reduced significantly with increasing content of PEG (Figure 2, right). Although the working principle of both techniques is entirely different, QCM-D and MP-SPR thus proved to be highly complementary. Most importantly, the degree of fouling measured for different PA-PEG films was in excellent agreement with fouling data observed from independent UF experiments using the very same membrane materials [2]. This demonstrates that QCM-D and MP-SPR are powerful techniques to reliably monitor the growth of the very first membrane fouling layers. A further advantage of this sensorial screening system is that it not only saves time, but also resources: the deposition of ultra-thin PA films on the sensors requires only a few microlitres of polymer solution and the microfluidic set-up saves sample volume.

A strategy for implementing QCM-D/MP-SPR as a water membrane filtration monitoring tool will be presented, and the operating window of this approach will be critically discussed.

References

[1] Molina S., et al., J. Mem. Sci. 454 (2014) 233-242.

[2] Rafaniello I., Schäfer T., patent submitted (2018).