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

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**Highlights**

* Combination of QCM-D/MP-SPR enables fast screening of membrane antifouling properties.
* Fouling observed on QCM-D/MP-SPR sensors concurs with that in ultrafiltration tests.
* QCM-D and MP-SPR are powerful methods for predicting fouling in membrane separations.

**1. 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. Furthermore, conventional characterization techniques, such as contact angle measurements, are indirect and prone to lead to false conclusions about the anti-fouling strategy adopted.

This work presents an approach of overcoming the limitations of conventional methods by combining two 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 that they possess a high potential of significantly accelerating the screening of the efficiency of membrane modifications.

**2. 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 tested as these had been employed previously as the membrane material 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 cm2. 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.

**3. 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.



**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 in the polyamides (Figure 2, right). This corroborates that QCM-D/MP-SPR are excellent and fast screening tools for studying membrane antifouling properties.

Although the working principle of both techniques is entirely different, QCM-D and MP-SPR proved to be highly complementary: protein fouling layers were tendentially detected to be of higher mass by QCM-D than by MP-SPR. The underlying reason for this phenomenon is the amount of associated water which is detected by QCM-D, but not so by MP-SPR. Nevertheless, and most importantly, it was observed that the degree of fouling measured for different PA-PEG films in QCM-D and MP-SPR was in very good agreement with fouling data obtained during independent UF experiments using the very same membrane materials [2].

**4. Conclusions**

QCM-D and MP-SPR are powerful techniques to reliably monitor the build-up of the very first membrane fouling layers even at the nanoscale. 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 microliters of polymer solution and the microfluidic set-up saves sample volume, which in principle allows a high-throughput screening.

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**

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