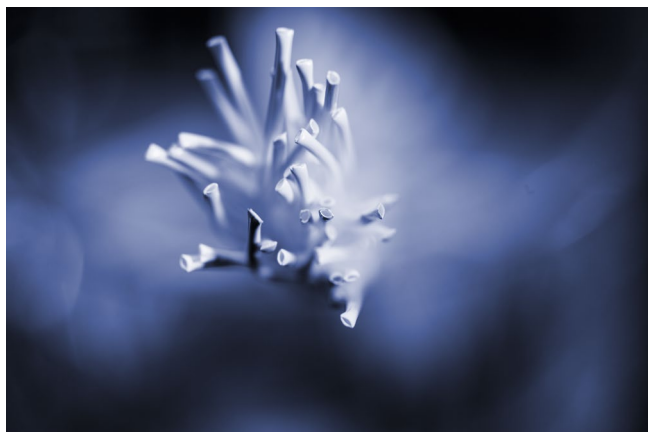


Monitoring of Membrane Fouling with Zeta Potential

Relevant for: water purification, desalination, membrane technology

Zeta potential measurements elucidate the fouling behavior of membranes and contribute to the optimization of membrane performance.



1 Introduction

Employment of polymer membranes for purification and separation processes experiences a steadily growing popularity. Besides their classical application in water purification, polymer membranes become increasingly attractive for the separation and up-concentration of products in the fields of food, biotechnology and pharmacy. Despite of these versatile application areas, there are restrictions for the optimum use of polymer membranes. The deposition of dissolved or dispersed matter from the feed on the membrane surface, known as membrane fouling, represents an often unresolved challenge especially for polymer membranes and pressure-driven filtration processes (such as nanofiltration and reverse osmosis). The conventional method for determining membrane fouling is monitoring transmembrane pressure (TMP) and flux is only sensitive, and thus applicable, at progressive fouling and does provide information about the characteristics of the deposited layer. Analytical methods for the characterization of the membrane surface and fouling layer, as well as of the efficiency of the related cleaning processes complement the measurement of TMP and flux. Among these methods, determination of the zeta potential at the interface between the membrane surface and the surrounding aqueous solution has been established in the past decades (1). The zeta potential represents the electric charge density at the membrane-water interface and

accounts for the electrostatic interaction between the membrane (solid surface) and dissolved compounds in water. This interaction is frequently the dominating force for the attraction or repulsion of ions, macromolecules, and suspended particles and, therefore, decisive for membrane fouling.

2 Experimental Setup

The zeta potential ζ at the membrane surface is determined from the measurement of the streaming potential. This so-called electrokinetic effect arises from the flow of liquid, in most cases an aqueous solution, through a capillary. The streaming potential is a DC voltage, which shows a linear dependence on a pressure gradient that is the driving force for liquid flow. A prerequisite for a successful analysis of the zeta potential is an appropriate assembly of the membrane sample, thereby generating a flow channel with a height of 100 μm . Figure 1 shows a flow channel with a rectangular cross-section that separates two sample pieces of a flat sheet membrane.

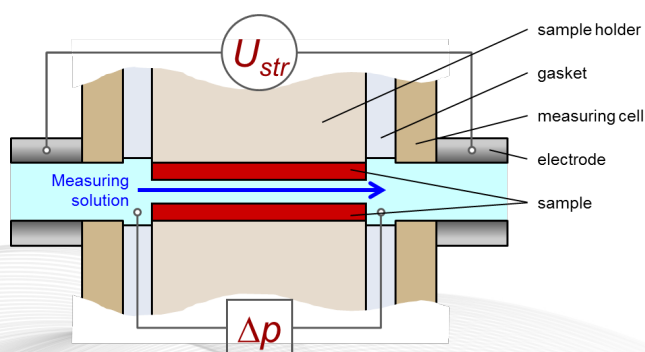


Figure 1: A schematic presentation of sample mounting for a flat sheet membrane in the Adjustable Gap Cell.

The zeta potential of membrane samples was determined with the SurPASS 3 instrument using the Adjustable Gap Cell. For the streaming potential measurement of flat sheet membranes, sample pieces are fixed on sample holders with a cross-section of 20 mm x 10 mm using double-sided adhesive tape.

A distance of 100 μm is then adjusted between membrane surfaces. The flow of the measuring solution is driven by a pressure gradient Δp applied between both ends of the flow channel and generates the streaming potential U_{str} . The ratio $dU_{\text{str}}/d\Delta p$ is then used for the calculation of the zeta potential.

Hollow-fiber membranes are mounted in a similar way to determine the zeta potential at the outer membrane surface. A series of chopped membrane pieces with a length of 10 mm are adhered onto the sample holders, and the measurement gap with an approximated rectangular cross-section is adjusted between the convex surfaces of the hollow-fiber membranes.

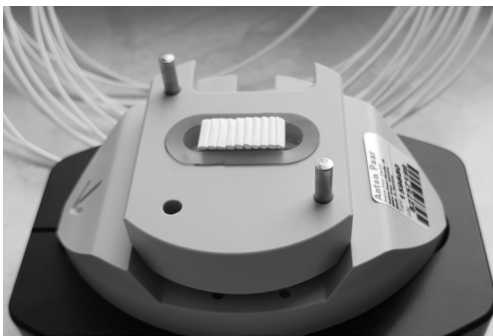


Figure 2: A series of chopped hollow-fiber membranes aligned on the sample holder of the Adjustable Gap Cell for the outer surface ζ analysis.

3 Results

3.1 Municipal Wastewater

Figure 3 shows the effect of a cross-flow filtration of Lake Ontario water (Toronto, Canada; 0.5 μm pre-filtration) for a period of 24 h on the zeta potential of a thin-film composite polyamide membrane for nanofiltration (NF270, Dow Chemical) (2). The zeta potential was determined in a wide pH range for the sake of a clear distinction between the pristine and used membranes and for a better conclusion on the properties of the deposited layer on the membrane surface. The pH dependence of the zeta potential also reveals the isoelectric point (IEP), i.e., the pH of the aqueous measuring solution where charge reversal occurs and the net charge density at the membrane-water interface diminishes. Due to the composition of the used feed water, which complies with the quality of potable water, an effect on TMP or flux was not observed during the 24 h cross-flow filtration process. However, the zeta potential of the membrane increases significantly in the range of $\text{pH} > 5$ and the IEP shifts from pH 2.8 for the pristine membrane to pH 2.3 after filtration. The shift of the IEP indicates a deposition of components with an acidic functionality from the feed water onto the membrane surface. The attached components introduce a hydrophilic character to the membrane surface, which is indicated

by the increase in the zeta potential at higher pH. Although a degradation of the membrane performance was not yet observed, the zeta potential shows a modification of the membrane surface and is, thus, applicable for the early detection of fouling processes.

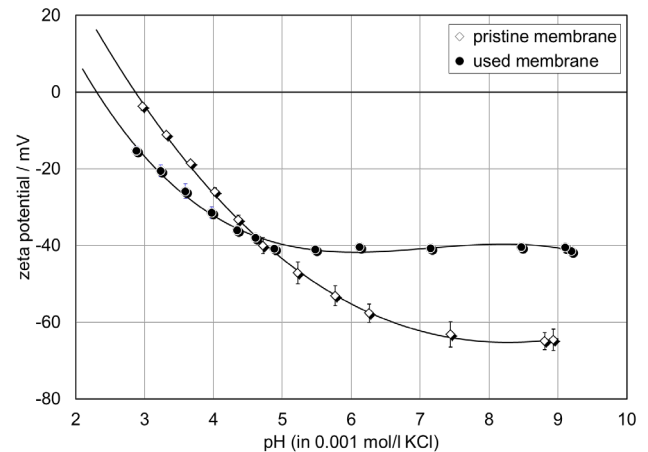


Figure 3: pH dependence of the zeta potential for a thin-film composite polymer membrane for nanofiltration before and after 24 h cross-flow filtration of Lake Ontario water.

3.2 Fermentation Broth

Figure 4 shows the effect of fouling by a fermentation both (*U. maydis*) of the outer surface of hollow-fiber membranes for ultrafiltration (poly(ether sulfone), pore size 0.05 μm , outer diameter 2.6 mm, inner diameter 1.2 mm; Puron, Koch Membrane Systems) (3). Due to the complex membrane geometry and arrangement in the measuring cell, Figure 4 shows the pH dependence of the streaming potential coupling coefficient $dU_{\text{str}}/d\Delta p$ instead of the calculated zeta potential. Despite of the complex geometry we observe good reproducibility for the pristine hollow-fiber membrane.

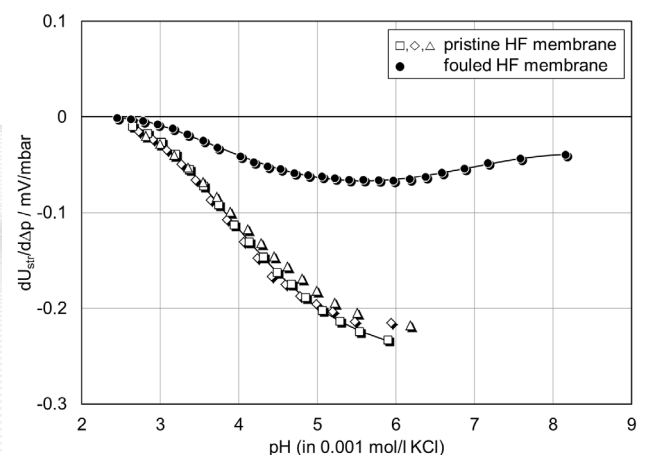


Figure 4: pH dependence of the streaming potential coupling coefficient for the outer surface of a hollow-fiber membrane before and after ultrafiltration of a fermentation broth.

The fouled membrane shows a significant shift in $dU_{str}/d\Delta p$ indicating a decrease in the negative interfacial charge, while the IEP at pH 2.5 remains almost unaffected. The deposition of components of the fermentation broth makes the outer surface of the hollow-fiber membrane more hydrophilic.

3.3 In-situ Analysis

The streaming potential method can also be used to observe the deposition of dissolved components on the membrane surface directly (*in-situ*). For this purpose the measuring solution is replaced either by dilute feed water or directly by the feed after pre-filtration to remove any suspended particles. For a better understanding of the interaction of dissolved compounds with the membrane surface and for the identification of those components of the feed, which are primarily responsible for membrane fouling, the analysis of the membrane zeta potential in the presence of individual components is preferred. Figure 5 shows the effect of humic acid (HA) on the zeta potential of another thin-film composite membrane for nanofiltration (NF90, Dow Chemical) (4). The results in Figure 5 suggest the adsorption of humic acid on the membrane surface, which causes the shift of the IEP towards a more acidic pH. The combination of humic acid and calcium ions (added as $CaCl_2$) leads to a synergistic effect. The divalent Ca^{2+} ions serve as a bridge between the negatively charged membrane surface and the anionic humic acid molecules.

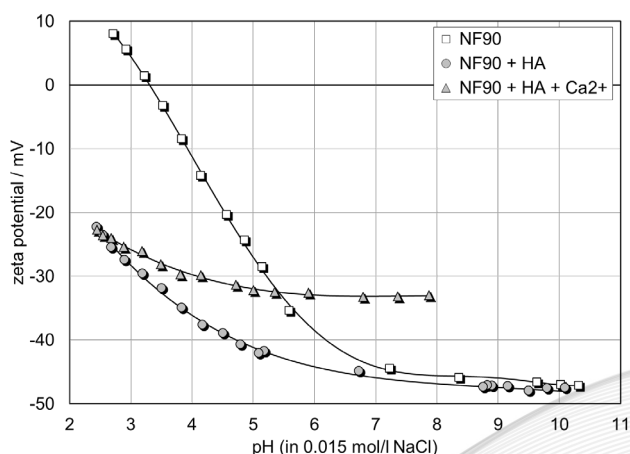


Figure 5: pH dependence of the zeta potential for a thin-film composite membrane for nanofiltration in the presence of humic acid (12.5 ppm) and Ca^{2+} ions (2.5 mmol/l).

3.4 Antifouling Coating

A remedy to prevent the effect of fouling, especially of polymer membranes, is to equip the membrane surface with functional groups or with a hydrogel layer, which turn the membrane surface hydrophilic.

Figure 6 shows the effect of coating of a thin-film composite membrane for reverse osmosis (AG, GE Water) with a derivative of poly(ethylene glycol) (5). The diacrylate functionality in PEGDA shifts the IEP of the membrane from pH 3.8 to pH 3.3. This IEP coincides with the IEP of a stand-alone PEGDA film, which shows a dramatically higher zeta potential as compared with the PEGDA-coated membrane. This difference in the zeta potential is explained by the swelling propensity of PEGDA and the significantly larger thickness of the stand-alone film. The process of swelling shifts the solid-water interface towards the bulk aqueous solution, which reduces the magnitude of the zeta potential (6). While swelling is restricted to the thin-film PEGDA coating of the surface of the RO membrane, we may assume bulk swelling of the stand-alone film.

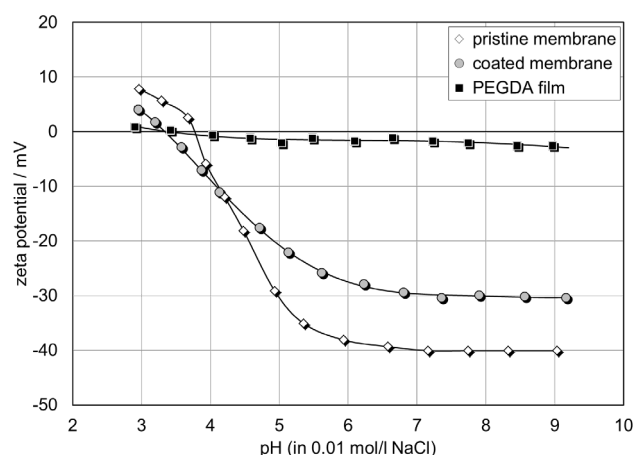


Figure 6: pH dependence of zeta potential for a thin film composite RO membrane coated with poly(ethylene glycol) diacrylate (PEGDA).

3.5 Membrane Cleaning

In any case it is necessary to apply an appropriate cleaning strategy to re-establish the filtration performance of the initially employed pristine membrane. Especially in huge filtration plants, it is desirable to reduce the frequency of cleaning cycles. For ecological and economical reasons the consumption of chemicals for cleaning of fouled membranes shall be minimized. Furthermore, oxidative cleaning agents may affect the durability of polymer membranes (7).

Zeta potential may be used to assess the efficiency of cleaning cycles. Figure 7 shows the effect of adsorption (*in-situ*) of the protein fibrinogen (FGN) on different microfiltration membranes (MF) and of the subsequent cleaning step by rinsing with deionized water. According to these results, fibrinogen adsorbs both on the MF membrane made of hydrophilized PVDF (MF-1) and on the MF membrane made of cellulose acetate (MF-2). After rinsing with deionized

water, fibrinogen gets completely removed from membrane MF-1, while for membrane MF-2 only partial removal of FGN is observed.

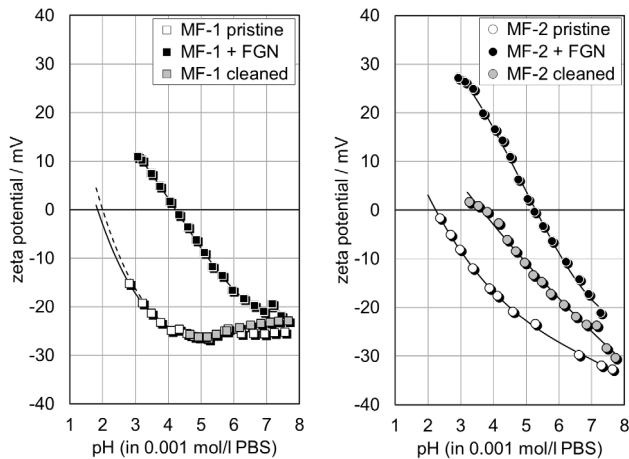


Figure 7: pH dependence of zeta potential for microfiltration membranes made of hydrophilized PVDF (MF-1, left) and cellulose acetate (MF-2, right) before and after adsorption of fibrinogen (FGN, 300 ppm) and cleaning with deionized water.

4 Summary

The zeta potential at the interface between a membrane surface and an aqueous solution informs about the charging behavior at this interface, and on the functional groups and the isoelectric point of the membrane surface. The high sensitivity of the zeta potential to recognize changes in the membrane surface by a deliberate modification or by the adsorption of dissolved compounds from the feed enables early detection of fouling processes. The direct analysis of the interaction between the membrane surface and dissolved compounds is as easy as the determination of the efficiency of cleaning cycles.

5 References

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