Role of Surface Pores on Fouling of Polyvinylidene Fluoride Membranes in Submerged Membrane Bioreactors

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Abstract. In this study, the roles of surface pores on membrane fouling was investigated using three membranes in two lab-scale membrane bioreactors. Characterization of the pristine membranes revealed that increasing polymer concentration decreases pore sizes and porosity. Critical flux was found to decrease with decreasing pore sizes. The finding was consistent for both MBRs. The results of the long-term filtration were in agreement with the flux-stepping test. The fouling layer was easily removed and only a few small particles remained as were observed with scanning electron microscopy. Surface pore sizes and porosity declined for all cleaned membranes, indicating permanent pore blocking, and the effect was higher for membranes with larger pore size.

1. Introduction
Membrane bioreactors (MBRs) improve the conventional activated sludge process (CASP) by replacing the settling tank with a membrane separation. Implementation of MBRs offers advantages, such as reduced plant footprint, lower sludge production, increased process control and improved effluent quality leading to a higher economical value of the effluent. Applications of MBRs gains favorability due to a more stringent effluent standard and the need of effluent reuse. However, the attempts to further decrease operating costs are still being developed, mainly acting on reducing fouling and so increasing process efficiency [1,2].

Membrane fouling is the main drawback of MBR operation. It diminishes permeance reflected by an increase in the transmembrane pressure (TMP) when operating under constant flux or a decrease in fluxes when operating under constant TMP. To control fouling, three main approaches are generally followed: exploiting hydrodynamic conditions, improving favourable sludge properties and improving membrane properties. Fouling cannot be completely eliminated, so after a certain period of filtration (weeks, months) extensive cleaning of the membranes is still required and accumulation of permanent fouling will eventually lead to membrane replacement [3,4]. In this study, the effects surface pores of polyvinylidene fluoride (PVDF) membranes on the filtration performance and membrane fouling are investigated. The filterability was evaluated using critical flux methods and long-term filtration.
2. Experimental Method
The membrane was prepared using the phase inversion method. Polymer solutions were obtained by mixing 9, 12 and 15 %wt of PVDF in dimethylformamide as a solvent. The solution was cast on a non-woven polypropylene support. After casting, the casted solution was immediately immersed in a coagulation bath containing demineralised water, which act as a non-solvent. The flat-sheet membranes were assembled into modules to be usable in the MBR. From each membrane sheet, 2 modules were potted according to [5] for the two MBRs. The microstructure of the membranes were identified using scanning electron microscopy (SEM) The pore size and distribution of the membrane were extracted from the SM images using ImageJ.

Two lab-scale HT-MBR setups were employed: MBR-1 and MBR-2 were fed with synthetic and molasses wastewater, respectively. To allow parallel operation, a multichannel peristaltic pump (Watson Marlow) was used. The critical flux (CF) was determined using a flux step method [6]. For long-term filtration, a fixed sub-critical flux was selected to allow for stable filtration over an extended period of time.

3. Results and Discussion
3.1. Pristine membrane characteristics
SEM images of the virgin membranes are shown in Figure 1 and the results of image analysis are summarized in Table 1. The differences in pore sizes and porosity among the tested membranes are clear. The pores location were heterogeneously distributed over the membrane surface. The larger part of the membranes had homogenously distributed pores, only patches of low or absent porosity were observed over the three tested membranes. It is clear that porosity and pore sizes declines with increasing PVDF concentrations. A higher polymer concentration in the casting solution leads to an increased polymer volume fraction at the film interface, resulting in a lower porosity and smaller pore sizes. Membranes with a higher polymer concentration will therefore require a higher TMP for a given flux and also exhibit a higher filtration retention.

![Figure 1. SEM images of (a) PVDF-9, (b) PVDF-12 and (c) PVDF-15 at 5000x](image)

**Table 1.** Membrane characteristics obtained by image analysis of SEM images.

| Sample            | Pore Size ($\mu$m$^2$) | Area Fraction (%) |
|-------------------|------------------------|-------------------|
| Pristine          |                        |                   |
| PVDF-9            | 0.062                  | 21.4              |
| PVDF-12           | 0.037                  | 16.7              |
| PVDF-15           | 0.016                  | 10.8              |
| Cleaned membrane (after fouling) | | |
| PVDF-9            | 0.036                  | 12.9              |
| PVDF-12           | 0.031                  | 12.2              |
3.2. Filterability performances

Figure 2 shows flux-stepping plots. The CF values for PVDF-9, -12 and 15 in MBR-1 are 8.56, 8.56 and 0.91 lm⁻²h⁻¹; and for PVDF-9, -12 and 15 in MBR-2 are 15.22, 13.32 and 8.56 lm⁻²h⁻¹, respectively. After plotting the TMP vs time, the critical flux was not as obvious as found by others [7]. This is probably due to the poor accuracy of the analogue pressure gauges. The difference between the three membranes and the two reactors is nevertheless clear.

CF increases with increasing membrane pore size and porosity. For the corresponding membranes, CFs in MBR-1 in general are lower CF than MBR-2. PVDF-9 and PVDF-12 showed a similar TMP profile in MBR-1, but after CF was reached, a sharper TMP increase was observed for the latter. The low CFs for PVDF-15 can be explained by the low porosity and small pore sizes of the membrane. Low porosity leads to high local fluxes to and through the pores, even when global flux is still low. These results are in agreement with the ones obtained by van der Marel et al. (2010) [7]. When testing membranes of different polymers on 0.02 to 3 µm in pore size, they also observed higher CFs for increased pore sizes. Since operating parameters are identical, the difference between the two MBRs can only be attributed to the different feed compositions. The results obtained in this experiment are a first indication to the effect of pore size and porosity on membrane filtration of activated sludge and requiring confirmation from a long-term filterability test.

![Flux stepping results and Long-term filtration graphs](image)

**Figure 2.** Filterability tests

For the long-term operation test, a flux of 7 lm⁻²h⁻¹ was applied, based on the results obtained in the CF test. With this flux, all membrane modules but PVDF-15 in MBR-1 would operate below their CF, what should result in sub-critical flux condition. This experiment is therefore more representative to commercial MBR operations. Applying a flux lower than the CF for PVDF-15 in MBR-1 would lead to very low fouling rates for the other modules and be of little relevance to full-scale MBR operations.

Results from this experiment clearly shows the importance of working under the CF values. Compared to the flux stepping experiment, a stable filtration was obtained for over 300 h in MBR-2. Fouling in MBR-1 was more severe, particularly for PVDF-15 which was operated above its CF and reached a TMP of 25kPa merely within 6 days after which it reached a maximum allowed TMP on the set-up. PVDF-9 and PVDF-12 have a very similar TMP profile in MBR-1, ascribed from their CF values. Based on this profile, fouling rates are still significant. It still took however about 10 days until a TMP of 20kPa was reached. Since the initial TMP for each module in MBR-1 was higher compared
to those in MBR-2, it is assumed that MBR-1 has a higher sludge filterability resistance, although MLSS is lower.

### 3.3. Image analysis

After removal of the cake and gel layer (cleaned membranes), membrane porosity is not completely restored, especially for PNDF-9 (data not shown). This is caused by internal pore blocking or external pore blocking by strongly attached particles. PVDF-9 has a large decrease in mean pore size indicating that the large pores are partially or completely blocked. The decrease in porosity and mean pore size for PVDF-12 is much lower, which results in similar surface characteristics for both membranes. While PVDF-9 still has some larger pores, it can be assumed that with successive filtration, these pores will also gradually get blocked, decreasing the difference in filtration performance. This effect is probably related with the pore size distribution and supports the hypothesis that smaller pore size membranes suffer less irreversible pore fouling which is beneficial for long-term operation.

### 4. Conclusions

Characterization of the virgin membranes revealed decreasing pore sizes and porosity with increased polymer concentration. Overall results demonstrate that CF declines with decreased pore sizes and porosity and is also influenced by mixed liquor characteristics and operating parameters. The result obtained from CF test was in agreement with the long-term test. Nevertheless, membrane with high pore size is prone from pore blocking and would most likely suffer in long-term operation that involve multiple chemical cleanings.

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