# Does Fouling in MBR Depend on SMP?

A. Drews*, M. Vocks**, U. Bracklow***, V. Iversen* and M. Kraume*

* Dept. of Chem. Engineering, TU Berlin, Straße des 17. Juni 136, Sekr. MA 5-7, 10623 Berlin, Germany
(E-mail: *anja.drews@tu-berlin.de*)
** Berlin Centre of Competence for Water, Cicerostr. 24, 10709 Berlin, Germany
(E-mail: *martin.vocks@tu-berlin.de*)
*** Dept. of Urban Water Management, Gustav-Meyer-Allee 25, Sekr. TIB 13-16, 13353 Berlin, Germany
(E-mail: *ute.bracklow@tu-berlin.de*)

**Abstract**
Fouling still is one of the major issues of membrane bioreactor (MBR) research. Most attention is currently paid to extracellular polymeric substances (EPS) in either bound or soluble/colloidal (soluble microbial products, SMP) form. While several trends or correlations were reported, the comparability of results is still limited by the numerous differences in plant set-up and analytical methods. The aim of this study is to compare polysaccharide concentrations and their respective fouling potential in different MBR operated under different conditions using the same analytical and evaluation tools and considering all relevant differences. Results are also compared to literature findings in an attempt to come to more generally valid conclusions. Results indicate that SMP influence fouling only under certain conditions such as low sludge age and large pore size.

**Keywords**
fouling rate; MBR; soluble microbial compounds; polysaccharides; SRT; pore size

## INTRODUCTION

Fouling still is one of the major issues of membrane bioreactor (MBR) research. Extracellular polymeric substances (EPS) in either bound or soluble/colloidal (soluble microbial products, SMP) form are currently considered as the major cause of membrane fouling in MBR. Therefore, two aspects need to be considered: the occurrence and concentration of SMP on the one hand and their properties like molecular weight and fouling potential on the other. Regarding the former, several factors like the type of wastewater, sludge loading rate, sludge age, MLSS concentration, mechanical stress, and microbial growth phase are thought to influence the concentration of EPS and SMP in one way or another (Chang *et al.*, 2002; Rosenberger and Kraume, 2003; Trussell *et al.*, 2004; Chang and Lee, 1998). Also, unsteady states like intermittent feeding, irregular sludge wastage or shifts in the oxygen supply (Yun *et al.*, 2006; Yoon *et al.*, 2006; Drews *et al.*, 2006) have been identified as additional factors leading to an increase in SMP formation and – with regards to SMP properties – to a change in their fouling propensity. Despite the large number of investigations and publications, however, no universal explanation has been reported yet and findings are often contradictory. This can partly be attributed to the wide variety of plant configurations, operating conditions (both in terms of overall process, like SRT and F/M, and of membrane operation, like flux and backwash intervals), wastewaters and membrane materials used. The importance of considering the full set of information is only recently emerging, so frequently incomplete data are published. Another problem in evaluating and comparing results from different research groups is the difference in sample preparation and analytical methods as well as in the way fouling is characterised. The polysaccharide (PS) fraction of the SMP or soluble EPS are often considered as the major culprit components (e.g. Lesjean *et al.*, 2004; Judd, 2004; Rosenberger *et al.*, 2006). A linear correlation between PS concentration and fouling rate was reported (Lesjean *et al.*, 2004; Rosenberger *et al.*, 2006). The aim of this study is to compare PS concentrations and their respective fouling potential in MBR systems of different size and fed with different wastewaters using the same analytical and evaluation tools and considering all relevant differences. Results are compared to literature findings in an attempt to come to more generally valid conclusions.

## METHODS

### MBR plants

In this study, three MBR systems equipped with submerged flat sheet UF membrane modules were operated (see Table 1). For more details on the operation and performance of these plants see Bracklow *et al.*, 2007; Drews *et al.*, 2006; Vocks *et al.*, 2007). One was fed with synthetic, the others with real – because of a separate sewer basically domestic – wastewater. In all of them, enhanced biological phosphorus removal and post-denitrification without additional carbon dosing were implemented. The lab scale MBR was also initially operated in a pre-denitrification mode. In each plant and configuration, the development of SMP concentration in the influent and sludge filtrate (membrane tank) and in the permeate was followed over 2 - 6 months.

**Table 1**. MBR plant data

| | size | Type of membrane | Type of wastewater | Flux [L/(m²h)] | average TS [g/L] | SRT [d] | HRT [h] | F/M [gCOD/(gVSS d)] |
|---|---|---|---|---|---|---|---|---|
| Lab scale | 50 L | UF, PAN, 37nm | synthetic | 6 - 9 | 9 | 22-31 | 13 | 0.15 - 0.23 |
| Pilot scale | 170 L | UF, PAN, 37nm | real/domestic | 10 | 10 | 30 | 12 | 0.11 – 0.66 |
| Full scale | 10 m³ | UF, PES, 35 nm | real/domestic | ≠ const, <10 | 10 | 22 | 17 | 0.3 |

### Small-scale filterability trials

In order to investigate filterability under more defined conditions and at different fluxes, small-scale trials were carried out in addition to online permeability data evaluation from the plants. A single membrane plate (same material as in the lab and pilot scale plant) was immersed in the aerated chamber of the lab scale plant. Its individual permeate withdrawal enables permeability measurements at different fluxes without disturbing normal plant operation and normal HRT. As can be seen in Fig. 1, solid walls on both sides of the membrane plate simulate the wall effect in the real module and thereby yield similar air scour and flow regimes.

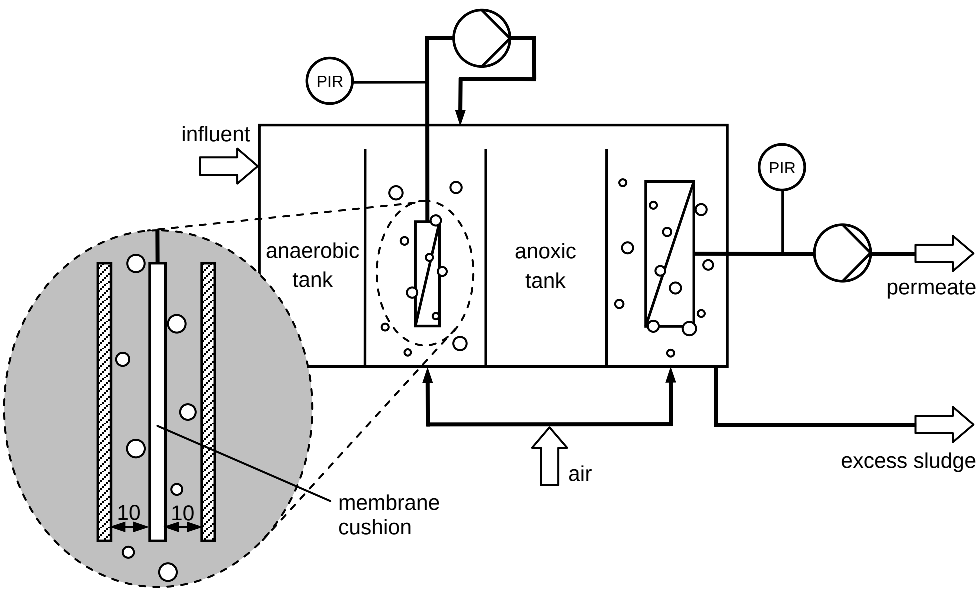


Fig. 1: Scheme of the small-scale filtration device

**Analyses and data evaluation**

Suspended solids were separated from the liquid phase containing soluble and colloidal substances by paper filtration (black ribbon, Schleicher & Schuell, cut-off approx. 25µm). PS concentrations in the sludge filtrate, influent filtrate and in the plant permeate were measured according to the widely used photometric method proposed by Dubois *et al.* (1956) which yields results in glucose equivalents. Protein concentrations were measured according to Lowry *et al.* (1951). Proteins were calibrated with BSA in the range of 5 - 200 mg $L^{-1}$. Calibration for PS was carried out with glucose in the range of 2 - 80 mg $L^{-1}$. Nitrate and nitrite in the sample were found to impair the photometric measurement and led to elevated PS values. Therefore, nitrate and nitrite were measured (ion chromatography) in each sample and the measured PS value was corrected using eq. (1):

$$c_{PS} = c_{PS,meas} - 0.099 \cdot c_{NO_3-N} - 1.9 \cdot c_{NO_2-N} \tag{1}$$

Relative deviations of duplicate measurements were ± 3 % on average for PS (maximum ± 9 %), with higher deviations found for small concentrations (2 - 10 mg $L^{-1}$), and ± 1.5 % on average for proteins (maximum ± 6 %).

The extent of fouling can be determined from the simple cake layer model with $R_t$ being the total filtration resistance:

$$R_t = \frac{\Delta p}{\mu(T) \cdot J} \tag{2}$$

Herein, $J$ represents flux and $\Delta p$ transmembrane pressure difference. The temperature dependence of the dynamic viscosity $\mu$ can be compensated by:

$$\mu(T) = \mu_{20°C} \cdot e^{-0.0239 \cdot (T-20)} \quad \text{with } T \text{ in °C (Rosenberger } et\ al.\text{, 2006)}. \tag{3}$$

In order to quantify fouling as a progressing phenomenon, the long-term fouling rate can be quantified either in terms of the resistance increase (Rosenberger *et al.*, 2006) or the permeability drop (Trussell *et al.*, 2006) over time. Here, the former, i.e. $dR_t/dt$ was applied. "Sensible" intervals d*t* were used, i.e. times when the slope of the resistance curve was constant. Since SMP concentrations which were to be correlated to fouling rate were measured at least twice a week, d*t* was mainly approx. 1 d. This value is short, e.g., in comparison with the 10 - 14 d used by Trussell *et al.* (2006) but long in comparison with fluctuations which even occur during otherwise stable operation such as temperature differences between day and night.

## RESULTS AND DISCUSSION

**SMP profiles**

Fig. 2 shows the development of PS concentrations in the influent filtrate, sludge filtrate and permeate for all plants and configurations. Proteins basically showed a parallel behaviour and are therefore not shown.

Sludge filtrate concentrations were typically lower than the respective influent concentration or at least in a similar range. Only in the pilot plant (Fig. 2 c)), sludge concentrations exceeded the influent values for prolonged periods. During these, special operational problems like low nitrification (March), high temperature gradients and influx of firefighting water (May), and massive growth of the sludge worm *Tubifex tubifex* (July) occurred. In all three periods, rejection was elevated while normally rejection was lower (and permeate concentration higher) than in the other plants. Higher rejection indicates a change in PS properties like molecular weight. Along with the elevated sludge values this could mean that during these disturbances, PS elimination

diminished and larger influent PS accumulated in the tank unchanged. Elevated nitrification activity was already found to decrease SMP rejection in lab scale trials (Drews *et al.*, 2007). In all other plants, PS permeate concentration was more stable and generally < 3 mg $L^{-1}$.
Despite using synthetic wastewater with relatively constant COD concentration representative of municipal wastewater (Bracklow *et al.*, 2007), the PS concentration in the lab scale (Fig. 2 a) and Fig. 2 b)) influent varied a lot and was generally higher than in the other plants. This could be due to use of starch which forms small lumps or clusters. Accumulations of these in the inlet pipe sometimes get flushed away thus yielding fluctuating PS values. PS concentrations in the sludge filtrate, however, were found to be in the range of the plants fed with real wastewater. The configuration (pre- or post-denitrification) does not seem to influence the sludge PS concentration much. Disturbances as described for the pilot plant and wastewater characteristics or concentrations appear to have a stronger effect. For example, a reduction of the sludge age from approx. 50 d to the targeted 25 d at the end of April 2006 led to a steep drop in sludge PS concentration to < 10 mg $L^{-1}$ (see Fig. 2 b)). At the end of June 2006, the synthetic wastewater recipe was changed slightly, i.e., no acid for stabilisation was added which apparently led to less hydrolysis and therefore higher PS concentrations. Apart from this, PS concentrations in the post-denitrification lab scale configuration were very stable as were the ones observed in the full scale plant (Fig. 2 d)). The values are also closer to those generally reported for plants during stable process operation.

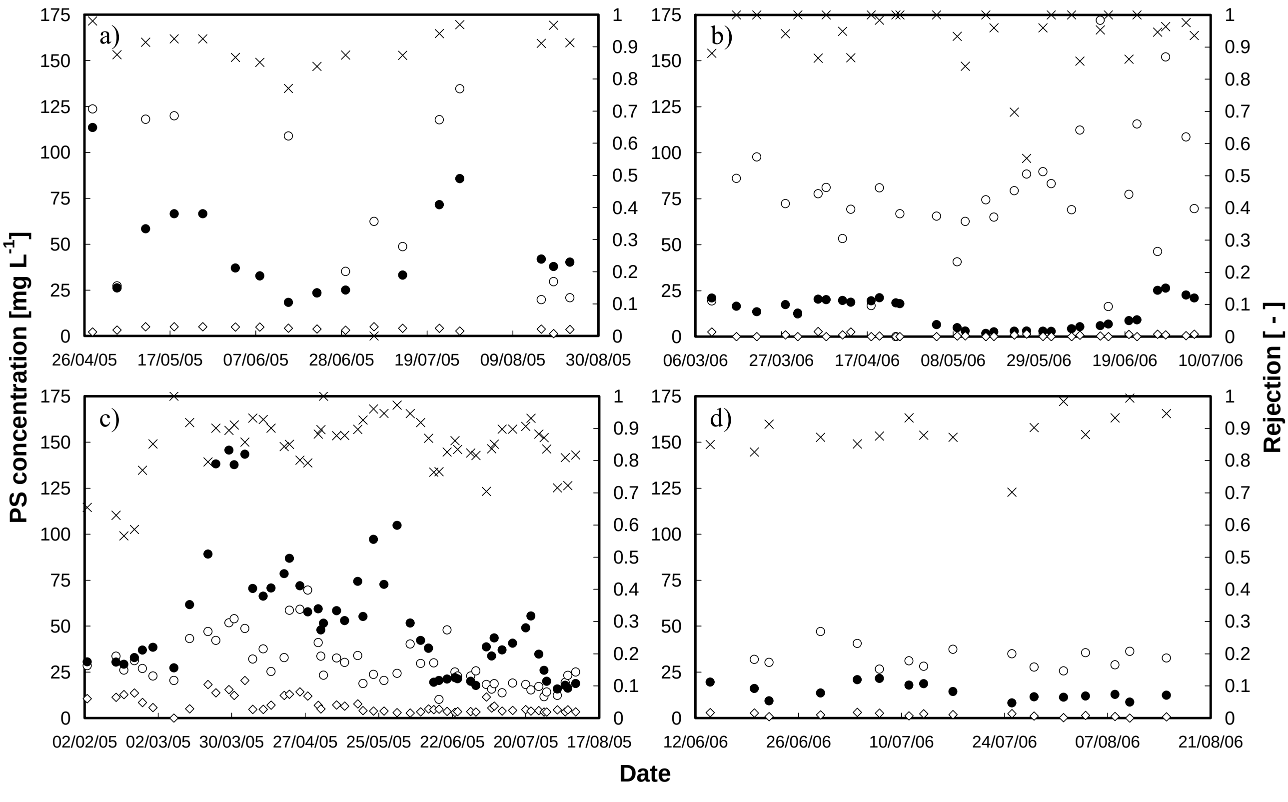


Fig. 2: Development of PS concentrations in the ○ influent filtrate, ● sludge filtrate and ◇ permeate, and × PS rejection, a) lab scale (pre-denitrification), b) lab scale (post-denitrification), c) pilot scale and d) full scale plant.

## Fouling rates

Fig. 3 shows a summary of fouling rates over respective SMP concentrations for the lab scale plant during post-denitrification and for the pilot plant. In addition, data from the latter during a period of irregular sludge wastage are plotted (Drews *et al.*, 2006). As can be seen, the linear correlation as observed for SRT = 8 d (Lesjean *et al.*, 2004; Rosenberger *et al.*, 2006) cannot be confirmed here for either of the plants and operational strategies. Despite at times very high PS concentrations, fouling rates were mostly below $5 \cdot 10^{10}$ $m^{-1}$ $d^{-1}$ in both plants (and even < $2 \cdot 10^{10}$ $m^{-1}$ $d^{-1}$ in the full scale MBR) whereas this was the lowest rate in the reference study. Only during a period of strong fluctuations through discontinuous sludge removal (Drews *et al.*, 2006) higher fouling rates were observed which, however, also do not follow the linear correlation.

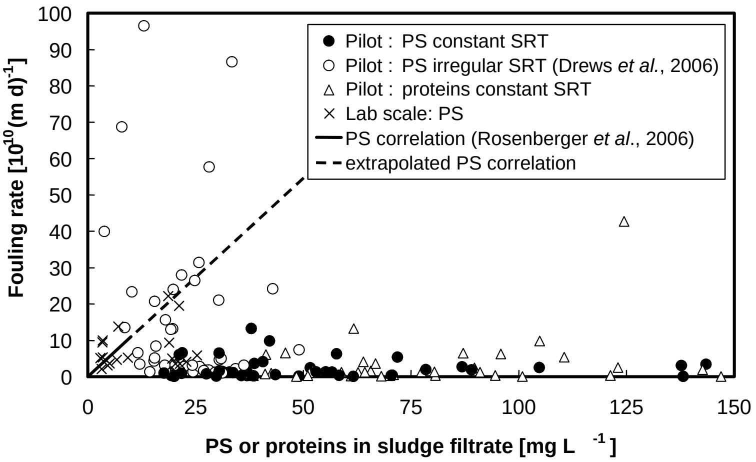


Fig. 3: Fouling rate over SMP concentration: comparison of literature correlation with own data.

Due to the differences in set-up and operational parameters, there are numerous possible reasons for this deviation. As can be seen from Fig. 3, plant size and type of wastewater do not seem to play a major role. Table 2 lists relevant conditions and fouling results from several literature studies along with the current study data. The given maximum resistances are the ones when filtration was stopped before membrane cleanings were carried out. As can be seen, a correlation between PS and fouling rate was mainly found for hollow fibre modules with larger pores. At a given particle size distribution of PS, microfiltration membranes are more susceptible to internal fouling since a higher PS fraction can enter their larger pores and adhere to their insides. In contrast to flat membranes, hollow fibres are typically backwashed, thus removing a cake more thoroughly than relaxation of plate and frame modules does. Hence, internal fouling caused by PS could be the dominant mechanism in microfiltration hollow fibres whereas external fouling could dominate in ultrafiltration plate and frame modules. Since Ahmed *et al.* (2007) found a correlation between bound EPS and specific cake resistance for flat sheet MF membranes, pore size might play a bigger role than the backwashing or relaxation procedure.

One important factor for the relevance of PS for fouling seems to be SRT. Even Rosenberger *et al.* (2006) found the linear correlation only for 8 d and not for the also investigated 15 d. Grelier *et al.* (2006) observed that both fouling rate and the colloids' contribution to the total resistance decreased with higher SRT. Trussell *et al.* (2006), who give fouling rates as the drop in permeability over 10 - 14 d of stable operation (converted into resistance increase for Table 2) confirm this trend for fouling rates. Ahmed *et al.* (2007) showed that the specific cake resistance decreases with SRT. Apart from the UF membranes, the rather high SRT in this study could therefore be another reason for a) low fouling rates and b) the non-existent correlation with PS concentration.

Another potentially relevant difference is that the plants in this study were operated at sub-critical flux conditions. While Grelier *et al.* (2006) could correlate fouling rate with SRT, they did not find a relation between PS concentration and resistance or fouling rate in the plant. Besides, they carried out separate small scale (stirred cell) experiments where a drop in filterability with increased PS concentration was found. Since these were performed at a constant pressure of 0.5 bar, initial fluxes in this dead end cell are likely to have been well above the critical flux which could have accelerated colloids fouling. Geilvoet *et al.* (2006) determined the filterability of sludge from a hollow fibre MBR in an 8 mm tubular membrane at a crossflow velocity of 1 m $s^{-1}$ and a flux of 60 L $(m^2\ h)^{-1}$. Despite the high flux, they also found no clear correlation with SMP concentrations. However, since both these test cell experiments were carried out without air scour of the membrane, fouling mechanisms might not be completely comparable to plant conditions (Schaller *et al.*, 2007).

**Table 2**. Comparison of relevant conditions and fouling results (HF = hollow fibre, P = plate and frame/flat sheet)

| | Module type | Nom. pore size [µm] | Flux [L (m² h)$^{-1}$] | TS [g L$^{-1}$] | SRT [d] | HRT [h] | Total resistance [$10^{12}$ m$^{-1}$] | Fouling rate [$10^{10}$ (m d)$^{-1}$] | Influence of increasing SRT | Correlation with PS concentration |
|---|---|---|---|---|---|---|---|---|---|---|
| Trussell *et al.*, 2006 | HF | 0.035 | 30.6 | 6.9 - 8.6 | 2 - 10 | 1.1 - 3.6 | 0.12 - 2.8 | 0.9 - 19 | fouling rate ↓ | - |
| Geilvoet *et al.*, 2006 * | tubular | 0.03 | 60 | - | - | - | < 2.9 | - | - | no |
| Grelier *et al.*, 2006 | HF | 0.1 | 17.5 - 20 | 3.2 - 8 | 8 - 40 | 4.5 - 12 | 1.4 - 7.7 | 4 - 40 | fouling rate ↓, colloids contribution to $R_t$ ↓ | no/yes * |
| Rosenberger *et al.*, 2006 | HF | 0.1 | 19 - 21 | 7.1 - 14.1 | 8 - 14.8 | 11 | 2.3 - 6 | 3 - 17 | PS concentration ↓ | yes |
| Bouhabila *et al.*, 2001 | HF | 0.1 | 13 | 7 - 27 | 10 - 30 | 3.3 | 1.3 | - | - | yes (with colloids) |
| Nagaoka *et al.*, 1996 | HF | 0.1 | 0.8 - 5 | 5 - 26 | - | 18 - 110 | < 500 | - | - | yes |
| Ahmed *et al.*, 2007 | P | 0.25 | 12.5 | 4.6 - 10 | 20 - 100 | 8 | - | - | less bound EPS, spec. cake resistance ↓ | yes (with bound EPS) |
| this study, lab scale | P | 0.037 | 6 - 9 | 9 | 22 - 31 | 12 - 14 | 2.8 (average) | 2 - 22 | - | no |
| this study, pilot scale | P | 0.037 | 10 | 10 | 28- 35 | 11 | 2.2 - 10 | 0 - 14 | - | no |

* data from investigations in a non-aerated test cell instead of in the plant

In order to determine if the applied flux (sub- or super-critical) is responsible, trials were carried out with the single membrane cushion (see Fig. 1) immersed in the aerated tank of the lab-scale plant. Fouling rates are generally much higher than those obtained from normal module operation. This was attributed to the non-optimised fluid dynamics in the small scale module but also to the fact that in the aerobic tank still some undegraded COD (including PS fractions) was present which can cause high fouling. Operation at supercritical flux showed higher fouling rates than sub-critical flux (Fig. 4), but again they did not follow the linear correlation. It is concluded that higher flux accelerates fouling in general but not PS fouling in particular.

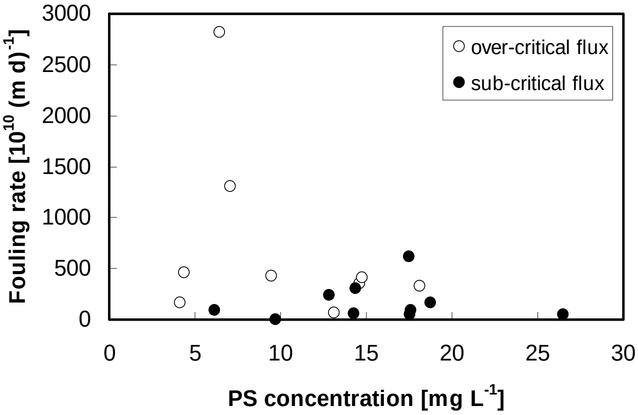


Fig. 4: Fouling rate over PS concentration at sub- and supercritical flux (small-scale filtration device)

## CONCLUSIONS

SMP concentrations and fouling rates were determined over several months of operation in three MBR plants of different size equipped with flat sheet ultrafiltration modules and operated under different conditions. In contrast to several literature studies, no correlation between PS concentration and membrane fouling was observed. This was attributed mainly to the fact that literature correlations were found for microfiltration membranes where pores are more susceptible to penetration by PS. Results in the current study which were obtained at rather high SRT (20 - 30 d) also confirm recent literature indications that as SRT increases, the relevance of SMP for filtration resistance and fouling decreases.

Results indicate that SMP influence fouling only under certain conditions such as larger pore size and low sludge age.

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