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Comparative investigation on the impact of polymeric substances on membrane fouling during sub-critical and critical flux operation of a municipal membrane bioreactor

S. Lyko, T. Wintgens and T. Melin

ABSTRACT

Soluble organic macromolecules are ubiquitous in activated sludge supernatant. For the operation of membrane bioreactors (MBR) this group of substances is considered as the dominant factor causing severe membrane fouling due to the concentration polarisation phenomenon. The well established critical flux concept for the characterisation of membrane bioreactor's operation limits is based on filtration data only. As there is an cause-and-effect relation between the partial retention of organic compounds and the limited flux according the critical flux concept the aim of this study was to draw a comparison between different permeate fluxes on the retention of organic macromolecules. Thus, a municipal pilot-scale MBR with three capillary hollow fibre membrane modules was operated in sub critical, critical and supercritical flux mode, respectively and the retention of macromolecules was quantified by size exclusion chromatography. Three permeate extraction pumps allow a simultaneous operation with different operational conditions for each membrane module and proved the crucial impact of permeate flux on the fouling rate. The interchange of these conditions gave evidence of an optimised start-up procedure for MBRs characterised by higher permeate fluxes. An increased flux causes both a higher retention of soluble macromolecules and subsequent a higher fouling rate.

Key words | critical flux concept, fouling mechanisms, membrane bioreactors, polymeric substances

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INTRODUCTION

Recent studies identified soluble macromolecules (SMP)–also known as soluble extracellular polymeric substances (EPS)–occurring in activated sludge supernatant as the dominant factor causing severe fouling in municipal membrane bioreactors (MBRs) (Le-Clech *et al.* 2006; Jiang 2007). This fact is theoretically explained by the partial retention during activated sludge filtration and the resultant concentration polarisation phenomenon (Melin & Rautenbach 2004). The well established critical flux concept for the characterisation of membrane bioreactor's operation limits is based on filtration data only. As there is an cause-and-effect relation between the partial retention of organic compounds and the limited flux according the critical flux concept the aim of this study was to draw a comparison between different permeate fluxes on the retention of organic macromolecules. A significant retention of small sized compounds–even lower than the nominal molecular weight cut off of the membranes–was observed by Jiang (2007) and Lyko *et al.* (2007). As there is an influence of ionic strength and especially of calcium ion concentration on the retention of soluble EPS (proteins and carbohydrates) (Kim & Jang 2006; Savaria *et al.* 2006) variations in the observed

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retentions are very likely due to inevitable changes in the feed composition of municipal wastewater.

Whereas the introduction of the critical flux concept proved the negative impact of increased permeate fluxes on membrane fouling only limited information is available on the influence of permeate flux on the retention of soluble polymeric compounds. Especially comparative investigations on the influence of filtration parameters both on fouling and EPS retention by using one biological system simultaneously with several filtration units at different settings in order to minimise the impact of varying sludge conditions are hardly published up to now. Considering this, a pilot plant allowing the simultaneously investigation of different filtration modes with the same activated sludge was operated. Based on recent publications size exclusion chromatography (SEC) was chosen for the quantification of soluble macromolecules in supernatant and permeate (Le-Clech *et al.* 2006; Lyko *et al.* 2007, 2008) and compared with the associated fouling rates.

MATERIAL AND METHODS

MBR pilot plant

During this study the pilot plant was operated at the conventional municipal wastewater treatment plant in Aachen-Eilendorf, where the wastewater is 30% industrial and 70% domestic. The pilot plant has a biological reactor volume of 0.8 m^3. It consists of a 0.2 m^3 denitrification reactor followed by a 0.4 m^3 nitrification reactor. The pilot plant was configured to test three capillary hollow fibre modules in parallel. Each membrane bundle (PURON®, Koch Membrane Systems GmbH, Germany) provided a total membrane area of 1.7 m^2 and was characterised by a mean pore size of 0.05 μm. Frequent wastewater analysis of quality parameters such as COD (chemical oxygen demand) of feed and permeate as well as mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) of the activated sludge were carried out to monitor the performance (Figure 1).

The system is characterised by a direct relation between filtration flow rate and feed flow rate through level alarms, which control the feed into the plant. To ensure a stable

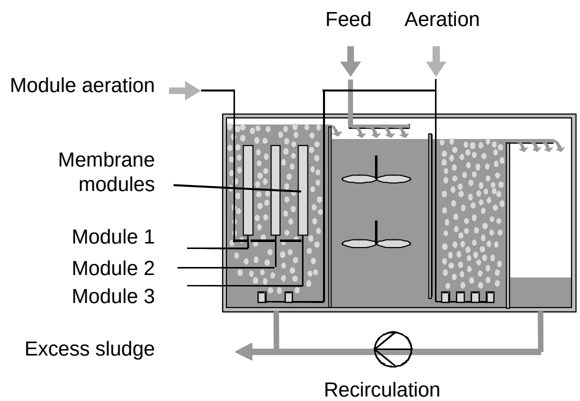

Figure 1 | Flow scheme of the pilot-scale submerged MBR.

sludge retention time (SRT) of approximately 25 d and a nearly constant F/M ratio of 0.04 kgBOD/kgMLSS/d even under varying filtration flow rates an adjustable permeate recirculation loop was applied.

To evaluate the fouling behaviour depending on the applied permeate flux the three modules ($i = 1, 2, 3$) of the pilot-scale MBR were operated with different permeate flow rates J_i at a ratio of 3:2:1. Figure 2 gives a scheme of the applied procedure. Two trials were conducted. Trial 1 was characterised by the duration of 530 h and was started directly after a recovery cleaning of the membranes. Due to the severely fouled condition of the membranes at the beginning of trial 2 the duration was significantly shorter (146 h). The operational parameters are given in Figure 2. The fluxes J_i of the modules 1 and 3 were interchanged after a time t (end of phase $j = 1$). At the end of phase $j = 2$ the total filtrated volume of each module $V_{F_{i,\text{total}}}$ is equal if the duration of the two phases is equal and if the ratio of the applied fluxes is 3:2:1. For the two trials a reference value

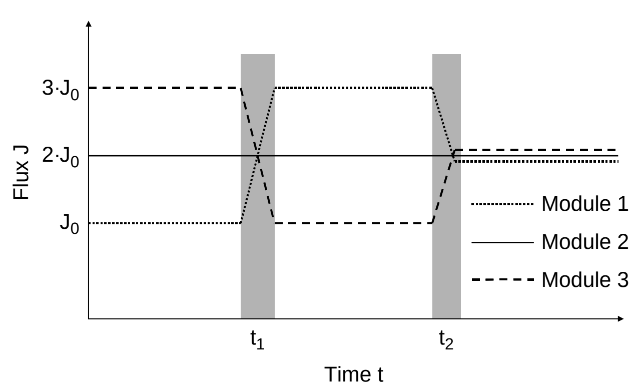

Figure 2 | Idealised flowchart of the pilot tests.

$J_0 = 15\,\text{L/m}^2/\text{h}$ was chosen.

$$V_{F_{i,\text{total}}} = \sum_j V_{F_{i,j}} \quad (1)$$

$$V_{F_{i,j}} = J_i \cdot t_j \quad (2)$$

$$J_i = i \cdot J_0 \quad (3)$$

Sampling and pre-treatment of samples

Activated sludge samples were taken from the membrane tank and permeate samples were taken from each membrane module. The samples were cooled during transport and storage ($T = 4°\text{C}$). The first separation step was a centrifugation of activated sludge for 30 min at 4,350 rpm (~4,400 g). Subsequently, a paper filtration was conducted with the collected supernatant (black ribbon). Permeate and supernatant were stored at 4°C for further analysis.

Photometric analysis of standard parameters

COD, TOC (total organic carbon), total phosphorous, nitrate and ammonia were determined photometrically with standard test kits (Dr. Lange, Düsseldorf, Germany).

Size exclusion chromatography

For determining the retention of certain organic fractions by the hollow fibre membranes size exclusion chromatography (SEC) was applied to supernatant and permeate samples. For that purpose a SEC was linked to an UV (254 nm) detection (Agilent, Germany). A single PSS Suprema (PSS, Mainz, Germany) column was used. Injection volume was 100 μL, mobile phase flow was 1 mL/min at room temperature. Molecular weight (MW) calibration was done by injecting dextran standards (supplied by PSS, Mainz, Germany) with MW from 180 Da to 277,000 Da, detected by the serial linked scattered light detector (Agilent, Germany). It has to be kept in mind that a molecular weight calibration using dextran standards is not exact and only a rough approximation for a mixture of various organic compounds like activated sludge supernatant. The use of the dextran solution is still regarded as appropriate as a determination of the concentrations of specific polymeric compounds in the activated sludge supernatant was not an objective of the SEC measurements. The SEC chromatograms of supernatant and permeate were compared in order to determine the molar mass-dependent retention of UV-active substances represented by characteristic peaks in the chromatograms. A detailed analysis and interpretation and definition of the SEC chromatograms are given elsewhere (Lyko *et al.* 2007).

Determination of sludge parameters

The parameters MLSS and MLVSS were analysed according to German DIN 38414 part 2 and 3 respectively.

To compare membrane filtration performance with the supernatant composition online data of the pilot-scale MBR were used. Permeate flux, transmembrane pressure difference TMP and effluent temperature were recorded. According to Rosenberger *et al.* (2006) the total filtration resistance R_t was calculated using a cake layer model with temperature correction to 20°C. Thus, temperature dependent permeate viscosity η was accounted for in the calculation of R_t:

$$R_t = \frac{\text{TMP}}{\eta J_\text{P} \text{e}^{-0.0239(T-20)}} \quad (4)$$

The viscosity of water at 20°C was assumed to be equal to the permeate viscosity η. The fouling rate was defined as the slope of the total filtration resistance over time.

According to Rabie *et al.* (2001) the parameter called "normalised fouling rate" NFR was calculated in order to assess and analyse the fouling behaviour and the effect of operation conditions during the pilot trials. Assuming that the total filtration resistance R_t is directly proportional to the specific volume filtered V_s, the volume collected per unit surface area per unit TMP at time t, a linear relation will be obtained between t/V_s and V_s

$$\frac{t}{V_\text{s}} = a + \text{NFR} \cdot V_\text{s} \quad (5)$$

where a is the intercept and NFR is the slope of the linear line. Hence, the higher the fouling rate the higher the calculated NFR. The method is sensitive to changes in operating conditions (Rabie *et al.* 2001).

RESULTS AND DISCUSSION

Impact of different permeate fluxes on the performance of the pilot plant

In total the pilot plant was operated approximately one year. During the start-up period (100 d) the biocenosis was adapted. Activated sludge of the conventional wastewater treatment plant was used as inoculum. The most important parameters of the raw wastewater are given in Table 1.

Figure 3 gives the trend of the sludge parameters F/M ratio and MLSS concentration during the operating time. Except for inevitable variations the defined criteria were achieved. An average SRT of 22.8 d was calculated for the total operating time.

During the operation an excellent permeate quality was achieved (COD, NH4—N, P_{total} removal > 90%). According to the stepwise procedure of Wu *et al.* (1999) the critical flux was determined prior to the test trials. With respect to the critical flux of 30 L/m^2/h the applied fluxes during the test trials can be defined as subcritical (15 L/m^2/h), critical (30 L/m^2/h) and supercritical (45 L/m^2/h), respectively. The default settings were characterised by a 250 s filtration cycle followed by a 30 s backflush cycle. For one module of the pilot plant the permeability (corrected to a temperature of 20°C) was continuously registered (Figure 4). Once the permeability reached approximately 100 L/m^2/h/bar the membrane modules were chemically cleaned using hypochlorite and citric acid.

Figure 5 gives the evolution of the total filtration resistances for the first trial. During the first phase an increasing fouling rate with increased permeate flux was observable. Module 2 operated at a constant flux of

Table 1 | Raw wastewater composition

Parameter	No. of samples	Mean value	Minimum	Maximum
COD (mg/L)	60	401	83	714
P_{total} (mg/L)	55	9.4	1.9	25.5
NH_4-N (mg/L)	59	27.1	6.6	51.3
NO_3-N (mg/L)	59	0.9	0.2	5.2

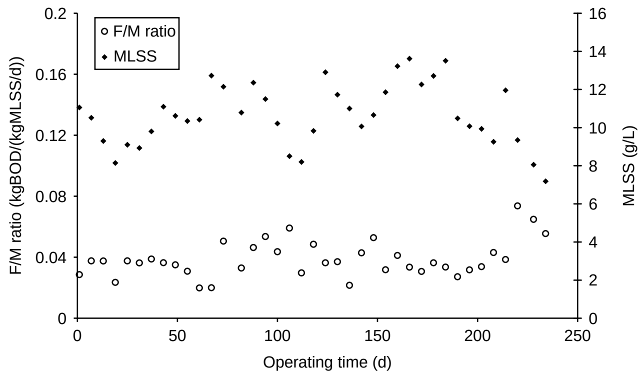

Figure 3 | F/M ratio and MLSS over time.

30 L/m^2/h acted as reference condition and showed a nearly constant fouling rate over time. The slight increase of the fouling rate for module 2 at the end of phase 2 is explained by a variation of the raw wastewater composition. Not surprisingly, the adverse impact of this variation was much more pronounced for the module operated at a higher flux (module 1) and resulted in a significant increase of the fouling rate. A more detailed analysis of the fouling behaviour was conducted on the basis of the normalised fouling rates (NFR).

For the quasi-stable operation the NFRs were calculated according to Rabie *et al.* (2001) (Table 2). The higher values at trial 2 are explained by a higher fouling potential of the raw wastewater. Because of nearly constant NFRs for the moderately (medium) operated module influences of varying activated sludge composition can be neglected. The change from a high flux to a low flux mode resulted in a significant decrease of the fouling rate. This decrease is explained by a reduced concentration polarisation and a

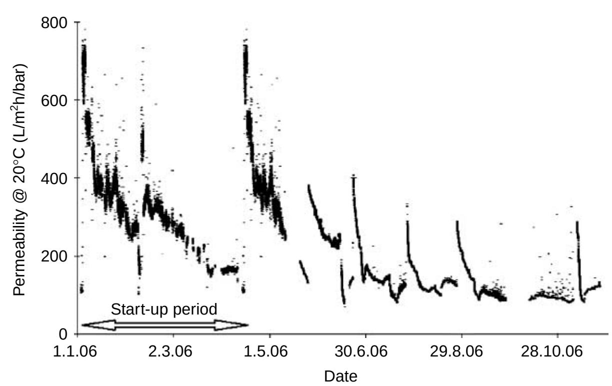

Figure 4 | Filtration performance of the pilot plant over time.

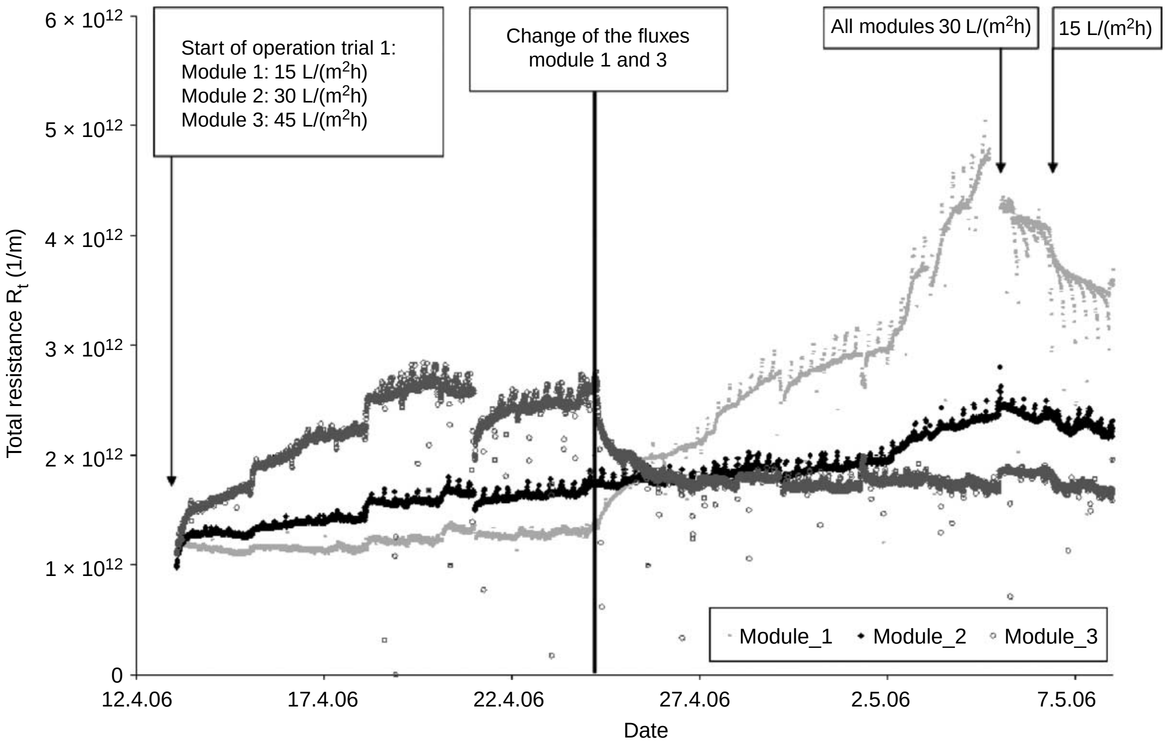

Figure 5 | Permeability depending on the applied permeate fluxes for trial 1.

decompression of the cake layer. The reduction and decompression of the cake layer as reason for the decreased filtration resistance was proven by the investigation of the continuously registered backflush permeability. The change to lower fluxes did not affect the backflush permeability which remained nearly constant (negligible increase from 230 to 238 L/m^2/h/bar).

A more serious fouling was observable when starting with lower fluxes and changing to higher flux values. These results support the hypothesis of the positive influence of the top layer acting as a secondary membrane (Melin & Rautenbach 2004).

Table 2 | Normalised fouling rates for trial 1 and trial 2

	NFR (10^{-2} bar^2 h/m^2)			
	Trial 1		Trial 2	
Fluxes (L/m^2/h)	(Phase 1)	(Phase 2)	(Phase 1)	(Phase 2)
Medium (30)	1.18	0.94	1.07	1.17
High (45) → Low (15)	4.9	−0.58	9.6	−10.5
Low (15) → High (45)	0.37	7.63	(−5.54)	21.6

Comparison of fouling rates in the pilot plant in contrast to operation conditions and soluble EPS removal

A less porous top layer could result in an increase of the retention of soluble compounds. Thus the effect of applied permeate flux on retention of soluble EPS was investigated by sampling permeate and supernatant during the described pilot tests. This sampling campaign was repeated for each phase of the trials. By SEC measurements the molar masses and the intensity of the signal were correlated to operating conditions. Figure 6 shows the typical retention behaviour for a municipal MBR. The molar mass distribution of supernatant and permeate is characterised by four typical peaks. The low molecular peak 1 occurring in permeate only is considered as artefact by the analysing method. A partial retention was observed for soluble macromolecules within the range between 700 and 3,000 Da.

For both trials less intensive peak maxima were found at high permeate flow rates (>42 L/m^2/h). This phenomenon was more pronounced for macromolecules larger than 1,000 kDa (Peak 3 and 4). In order to minimise variations

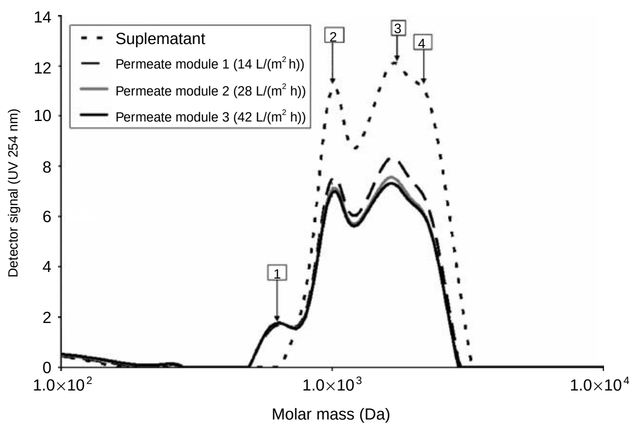

Figure 6 | Molar mass distribution in supernatant and permeate.

of the absolute peak maxima values due to variations in supernatant composition the absolute values were related to the results of the lowest flux. The peak maxima of the module operated at a flux of $15\,\mathrm{L/m^2/h}$ were defined to 100%. By analysing the detector signals (DS) and according to

$$rel.DS_{J_i,k} = \frac{abs.DS_{J_i,k}}{abs.DS_{J_0,k}} \cdot 100\%$$

relative peak intensities $rel.DS_{J_i}$ were determined for each peak k ($k = 2, 3, 4$). Especially for the larger macromolecules (>1200 Da) a clear relation between permeate flux and concentration of soluble organic compounds was observable (Figure 7). Thus soluble macromolecules (1,000–2,000 Da) are considered as the most significant fraction of soluble compounds causing fouling in municipal MBRs. Therewith an increased flux causes both a higher retention of soluble macromolecules and subsequent an higher fouling rate

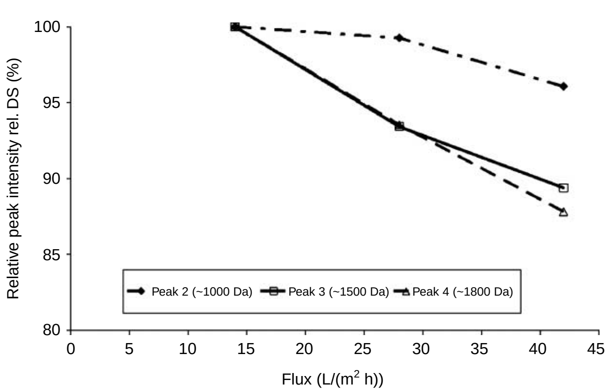

Figure 7 | Soluble organic compounds in permeate dependent on the applied flux.

(Table 2). Because of the molecular weight of these compounds–an order of magnitude below the cut off of the microfiltration membranes–adsorption or bindings in the top layer and in the membrane material is considered as retention mechanism (Rosenberger *et al.* 2006; Liang *et al.* 2007).

CONCLUSION

Within this study the impact of different permeate fluxes on the retention of organic macromolecules and on membrane fouling were investigated at a municipal pilot-scale submerged MBR. Sub critical, critical and supercritical flux conditions were defined according the stepwise procedure of the critical flux concept. Three hollow fibre membrane modules were operated in parallel at the defined flux modes and proved the crucial impact of permeate flux on the fouling rate. The interchange of these conditions gave evidence of an optimised start-up procedure for MBRs after an intensive chemical cleaning. A start-up with higher–even critical–fluxes and subsequent lowering of it resulted in higher permeability levels compared to a start-up with moderate subcritical flux conditions. The retention of macromolecules was quantified by SEC and a clear relation between permeate flux and concentration of larger macromolecules in permeate was observed. An increased flux causes both a higher retention of soluble macromolecules and subsequent a higher fouling rate and proves the theoretical explanation by concentration polarisation of rejected organic compounds.

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