Influence of unsteady membrane bioreactor operation on EPS formation and filtration resistance

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Abstract

Extracellular polymeric substances (EPS) are considered as the major cause of membrane fouling in membrane bioreactors. Recent studies have revealed a linear relationship between fouling rate (increase of filtration resistance over time) and polysaccharide (PS) concentration [1]. Several factors like the type of wastewater, sludge loading rate, sludge age, MLSS concentration, and mechanical stress are known to influence the concentration of dissolved EPS. Also, unsteady states like intermittent feeding or shifts in the oxygen supply have been identified as additional factors leading to an increase in EPS formation or to a change in its fouling propensity. However, no systematic investigation to quantify such influences has been undertaken so far. This study is aimed at determining the influence of discontinuous excess sludge withdrawal often applied in small decentralised plants and resulting unsteady loading rates on EPS formation and filtration resistance. The general trend of increased fouling rate at higher PS concentrations is confirmed but data show a larger scatter which could be due to a change in the PS structure and hence their fouling potential. The levels of dissolved oxygen and nitrate which also fluctuate more strongly in MBRs with irregular sludge wastage, appear to have a profound impact on EPS uptake rate and thereby on EPS concentration.

Keywords: Fouling rate, MBR, unsteady operation, EPS, polysaccharides

1. Introduction

The utilisation of membrane bioreactors (MBR) offers many advantages over the conventional activated sludge process [2]. Their widespread application, however, is restricted by membrane fouling which reduces permeate yield and increases investment and operating costs [3].

Despite the large number of technical publications on membrane fouling (around 30 % of all MBR relevant publications currently deal with fouling [4]), many questions remain unanswered to date. The phenomenon termed fouling is the decrease of flux over time. The extent of fouling – the fouling rate – can be quantified in terms of the derivative of the filtration resistance:

$$R = \frac{\Delta p}{\eta(T) \cdot J} \tag{1}$$

wherein J represents flux and Δp transmembrane pressure. The temperature dependence of the dynamic viscosity η can be compensated by:

$$\eta(T) = \eta_{20°C} \cdot e^{-0{,}0239 \cdot (T-20)} \qquad \text{with } T \text{ in °C [1] .} \tag{2}$$

In membrane filtration, permeability is influenced by membrane properties like pore size, porosity, hydrophobicity, and surface charge and by filtration conditions like transmembrane pressure, cross-flow velocity/aeration, and module geometry, as well as by sludge characteristics which depend on MBR operating conditions such as hydraulic and solids retention times (HRT and SRT), sludge age and loading rate [3, 5]. A number of attempts have been made to correlate flux with biomass concentration, floc size, and sludge rheology [3], but due to the complex nature of the biological system and the difference in experimental methods applied these are inconsistent and often contradictory [2, 3]. Recently, extracellular polymeric substances (EPS) have been identified as the major cause of fouling [6]. EPS consists of polysaccharides (PS), proteins, lipids, nucleic acids, etc. which can originate from cell-lysis, microbial metabolites or unmetabolised wastewater components. These constituents are either embedded in the floc matrix (bound EPS) or freely suspended/dissolved in the supernatant (soluble EPS, aka soluble microbial products - SMP) and can be present in varying amounts. EPS therefore have no fixed composition and two samples with equal net EPS concentration can exhibit largely different behaviour. Again, not least due to the large variety of (non-standardised) analytical tools [6], knowledge on EPS/membrane interactions and conditions leading to either uptake or formation of EPS are scarce.

Recent studies have revealed a linear relationship between fouling rate and polysaccharide concentration [1]. The authors showed that humic and low molecular weight substances pass the membrane and therefore are not responsible for fouling, while polysaccharides, proteins and organic colloids are retained almost completely. This is in agreement with Chu and Li [7] who observed that the sludge cake EPS contained more polysaccharides than the suspended sludge EPS, which contained a higher fraction of TOC and proteins. Rosenberger and Kraume [5] found that the specific concentration of soluble EPS increases with sludge loading rate (F/M ratio) and decreases with sludge age. For mineralisation of EPS, oxygen is required. From modelling SMP production and uptake, Lu et al. [8] concluded that a dissolved oxygen concentration below 1 mg L^{-1} leads to elevated EPS concentrations. Additionally, nitrate can be used for oxidation.

Most investigations have been carried out under steady state conditions. Nagaoka et al. [9] studied EPS formation under intermittent feeding conditions (continuous feed vs. alternating feed/no feed) and concluded that biomass associated EPS which is formed primarily under severe substrate limitation has a higher fouling potential than substrate utilization associated EPS. Therefore, in MBRs operated under unsteady conditions, e.g. with discontinuous or irregular excess sludge wastage typically employed in small decentralized plants, different EPS levels and compositions with different fouling behaviour can be expected.

2. Materials & Methods

2.1. Operated MBR Plant

A 140 L MBR was operated at a 13 L h^{-1} throughput of wastewater from a pumping station. The pumping station is located in a remote area on the outskirts of Berlin with separate sewer and therefore influent consists only of domestic wastewater devoid of industrial and storm water. This results in a highly concentrated influent with, e.g., COD concentrations of up to 4,000 mg L^{-1}. Enhanced biological phosphorus removal and post-denitrification without additional carbon dosing were installed. The MBR is cascaded into six zones: one anaerobic, two aerobic and anoxic zones each and one aerated membrane tank (Fig. 1) where a 1.4 m² PAN plate and frame module (GKSS, Germany, nominal pore size: 37 nm) is immersed. 14

minutes of permeate withdrawal are followed by a one minute filtration break, i.e., flux is set to 10 L m^{-2} h^{-1} to achieve 13 L h^{-1}.

Excess sludge is not withdrawn continuously but in general when 14 gTS L^{-1} are reached in the membrane chamber. 50 % of the sludge are then taken out and the plant is refilled with wastewater. At a flow rate of 13 L h^{-1} this takes 5.4 hours during which time no effluent is withdrawn. On average, a calculated virtual sludge age of 30 d was employed which in effect cannot be compared sludge ages under conditions of regular sludge wastage.

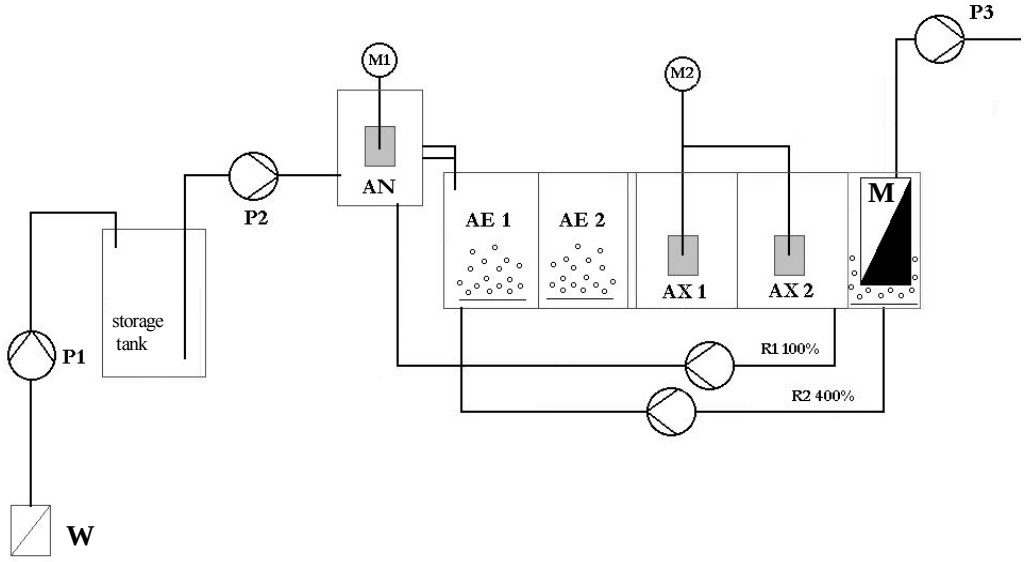

Fig. 1. Plant flow sheet, AN: anaerobic zone, AE: aerobic zone, AX: anoxic zone, M: membrane chamber.

2.2. EPS analyses

Samples were taken in the storage tank, the membrane chamber and in the permeate twice a week. In order to minimize the influence of daily and weekly fluctuations, samples were always taken periodically on the same days and hours. Sludge was separated from the liquid phase containing soluble and colloidal substances by paper filtration (black ribbon, Schleicher & Schuell). Polysaccharide (PS) concentration in the sludge and influent filtrate and in the plant permeate was measured according to the photometric method proposed by Dubois et al. [10] which yields results in glucose equivalents. Protein concentrations were measured according to Lowry et al. [11]. Both methods allow quick determination but yield only sums of either type of polymer.

Calibration for PS was carried out with glucose in the range of 2 - 80 mg L^{-1}. Nitrate in the sample impairs the photometric measurement and leads to elevated values. Therefore, nitrate is measured in each sample and the measured value is corrected by:

$$c_{PS} = c_{PS,meas} - 0{,}099 \cdot c_{NO_3-N} \tag{3}$$

Proteins were calibrated with BSA in the range of 5 – 200 mg L^{-1}. Since the method according to Lowry et al. [11] is not protein specific but also responds to humic substances, the modified method by Frolund et al. [12] is often used. In this study, the modified method could not be employed because precipitation occurred during analyses which lead to higher absorption. Hence, the presented protein data include humic substances.

3. Results and Discussion

Fig. 2 shows the evolution of biomass concentration, filtration resistance and PS concentration during the first 6 months of operation. For reasons of clarity, proteins are not plotted as they are thought to have a lesser impact on fouling than polysaccharides [6].

Sludge was withdrawn depending on loading, and hence resulting growth, and was therefore carried out at different intervals of 6 to 38 days. In addition, during the start up phase unplanned sludge losses occurred. The PS influent concentration was between 18 and 64 mg L^{-1}, ranging mostly from 20-30 mg L^{-1}. Protein influent concentration was between 90 and 200 mg L^{-1}. Spatial concentration profiles measured through the plant (data not shown) show that proteins reach a constant value already in the aerated chambers. For PS the situation was different. Lowest values were measured in the anaerobic tank, but also lowest TS concentrations occurred there. Due to the recirculation from the membrane to the first aerobic tank, PS concentration was higher at the start of the aerobic zone, but declined towards the end. It rose slightly in the anoxic zones. In the membrane tank, the PS concentration rose again due to the retention of PS by the membrane. There, PS concentrations between 4 and 49 mg L^{-1} were measured, mostly ranging from 10 to 35 mg L^{-1}.

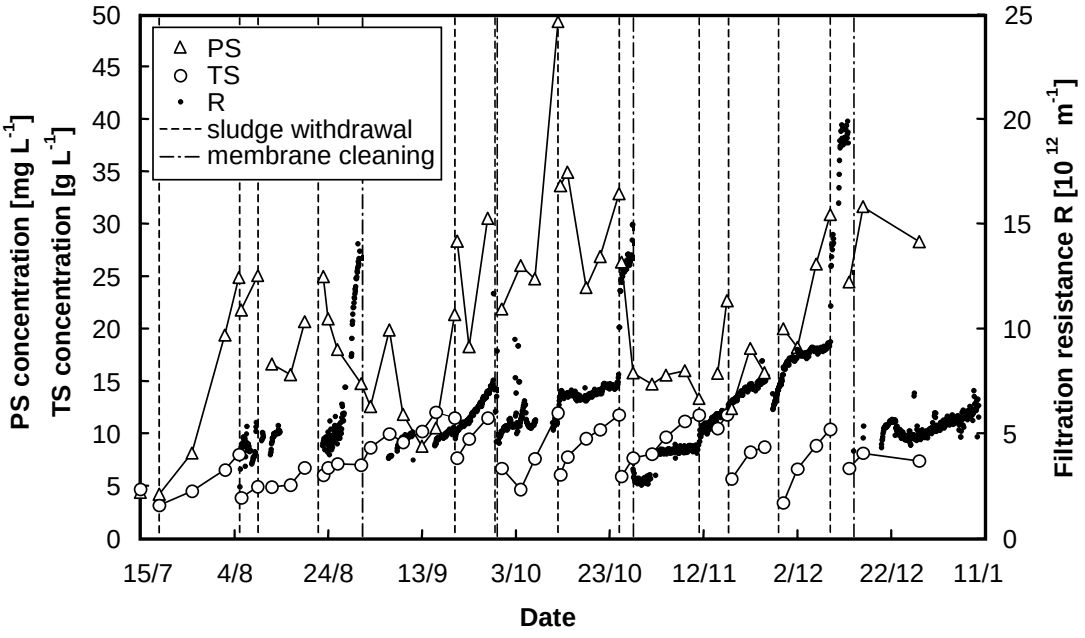

Fig. 2. Development of filtration resistance, biomass (TS) and PS concentration over time.

PS concentrations obviously varied strongly. In addition to the biological effects of PS uptake and release, and to that of PS retention by the membrane, PS content in the reactor is strongly influenced by the inlet PS concentration. Hence, this kind of illustration cannot lead to a final conclusion (compare Fig. 8). However, around sludge withdrawals generally a rise in PS concentration can be observed. An increase after a sludge wastage was anticipated due to the sudden stress on the microorganisms caused by sharply increased loading rates. The observed increases before sludge removals (6/9, 20/9, 27/9, 12/10, 21/10, 25/10, 17/11, 6/12) could be attributed to low oxygen concentrations of < 1 mg L^{-1} that occurred at high TS concentrations and were usually accompanied by low nitrate concentrations of < 5 mg L^{-1} in the membrane tank. Fig. 3 confirms this impression. PS concentration clearly decreases with increased nitrate concentration in the membrane tank.

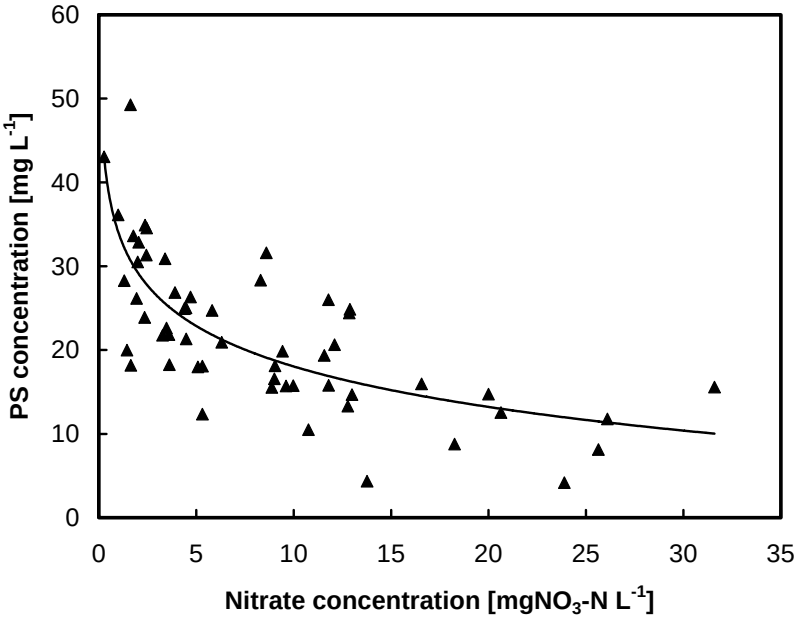

Fig. 3. PS concentration over nitrate concentration in the membrane tank.

The filtration resistance was between 3 and $20 \cdot 10^{12}$ m^{-1}. After each chemical membrane cleaning it dropped to approx. $4 \cdot 10^{12}$ m^{-1} but did not always show a constant increase during operation.

The effect of dissolved oxygen (DO) concentration on the EPS uptake or formation/release rate was investigated in separate lab trials using sludge from this MBR (see Fig. 4).

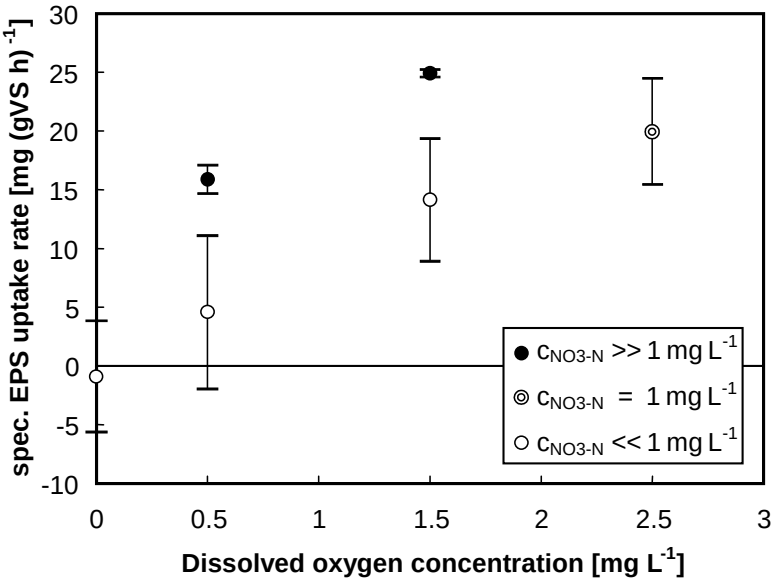

Fig. 4. Specific EPS uptake rate as a function of dissolved oxygen and nitrate concentration (bars represent the measured ranges of uptake rates which result from changing EPS concentration over approx. 24h of operation at each DO concentration).

While results show some scattering, an increase of EPS uptake rate with rising DO concentrations can clearly be seen. At DO concentrations of less than approx. 0.5 mg L^{-1}, EPS is even released rather than taken up. This is in agreement with Lu et al. [8]. Also, a strong influence of nitrate concentration can be observed. Especially at lower oxygen concentrations, a nitrate concentration approaching zero leads to far smaller specific uptake rates.

In Fig. 5, the polysaccharides and proteins retention by the membrane

$$R_i = 1 - \frac{c_{i,Permeate}}{c_{i,Reactor}} \tag{4}$$

is illustrated. Both retentions varied during the operating period, while at up to 90 % PS retention was generally higher than protein retention which reached only 70 %. In this context it has to be born in mind, however, that the fraction analysed as proteins also contains humic substances, which normally can pass the membrane.

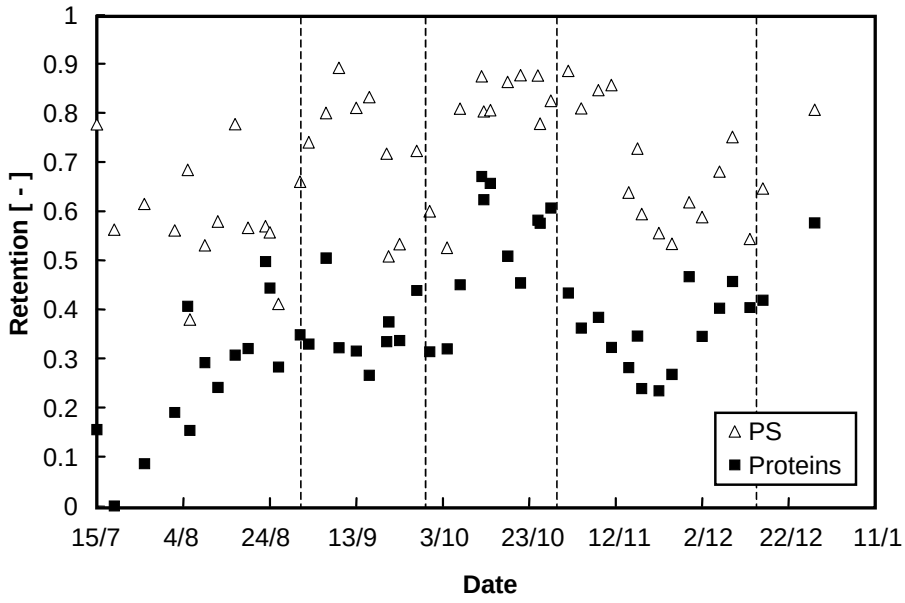

Fig. 5. Retention of PS and proteins over operation time (--- membrane cleanings).

During the start up phase, the protein retention was under 20 % and rose constantly afterwards. Obviously, some time was needed to build up an additional separation layer which was not removed by chemical membrane cleanings. The variations of the retentions (both PS and proteins) might be explained by a change in the structure and in the size of the polymers, but could not be linked explicitly to special events. Likewise, high filtration resistances which lead to membrane cleanings could not be correlated with high retentions. Protein retention generally rose with increasing protein concentrations in the reactor (data not shown), a tendency which could not be observed for PS.

In Fig.6, the specific soluble EPS concentration (c_{EPS} / c_{TS}) is shown as a function of F/M ratio:

$$F / M_{TS,COD} = \frac{\dot{V} \cdot c_{COD,in}}{V_R \cdot c_{TS}} \tag{5}$$

EPS concentration is the sum of measured PS and protein concentration. For comparison, data from four different MBR plants for domestic and municipal wastewater treatment as given by Rosenberger [13] are included. Those had been operated at sludge ages above 100 d, hence the F/M ratio was smaller.

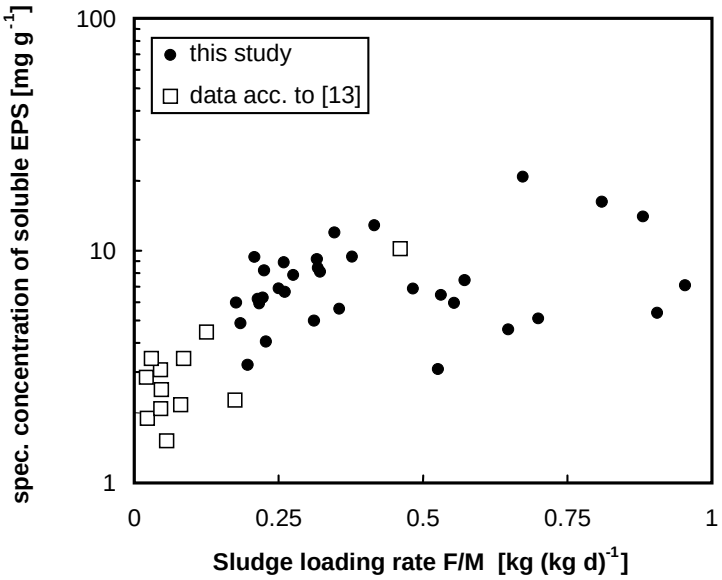

Fig. 6. Specific concentration of soluble EPS as a function of sludge loading rate.

Due to the discontinuous sludge withdrawal and the resulting changes in biomass concentration employed here, sludge loading varied strongly between 0.15 and 1 kg (kg d)$^{-1}$. Very high COD influent concentrations between 1,500 mg L^{-1} and 4,000 mg L^{-1} resulted from high organic solids concentration in the influent, yielding loading rates of up to 2 kg (kg d)$^{-1}$. In the range of 0.2 to 0.4 kg (kg d)$^{-1}$, the measured specific EPS concentrations fit in well with the previously observed tendency. For higher F/M ratios, fluctuations become larger and the curve flattens. This may be due to the higher organic solids concentration in the influent.

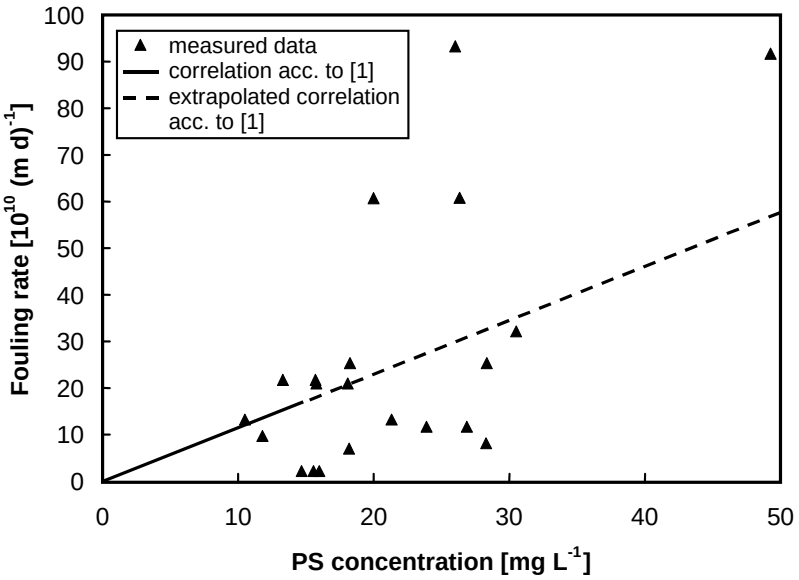

Fig. 7. Fouling rate as a function of polysaccharide concentration.

The correlation between PS concentration and fouling rate is plotted in Fig. 7. Sudden increases of the filtration resistance, i.e. fouling rates of more than $200 \cdot 10^{10}$ (m d)$^{-1}$ (see Fig. 2) were not considered because they resulted from operational problems. It is apparent that the fouling rate tends to increase with increasing PS concentrations, but data show a larger scatter around the linear correlation reported in [1] which was established between 2 and 15 mg L^{-1}. The dashed line represents the extrapolation to higher concentrations. Data from this study are in the same order of magnitude but sometimes differ by more than 100 %. It is not unlikely

that the highly unsteady nature of plant operation can cause varying polysaccharides compositions. Possibly, certain fractions of the polysaccharides cause faster fouling than other fractions.

From a mass balance for the component *i* (i: PS or proteins)

$$\frac{dc_i}{dt} = \frac{\dot{V}}{V_R} \cdot \left(c_{i,in} - c_{i,Permeate}\right) - \dot{r}_i \,, \tag{6}$$

the specific uptake rate for PS and proteins for a discrete interval Δt can be expressed by:

$$\frac{\dot{r}_i}{\bar{c}_{TS}} = \frac{\frac{\dot{V}}{V_R} \cdot \left(\bar{c}_{i,in} - \bar{c}_{i,Permeate}\right) - \frac{\Delta c_i}{\Delta t}}{\bar{c}_{TS}} = F / M_{TS,i} - \frac{\dot{V} \cdot \bar{c}_{i,Permeate}}{V_R \cdot \bar{c}_{TS}} - \frac{\Delta c_i}{\Delta t \cdot \bar{c}_{TS}} \,. \tag{7}$$

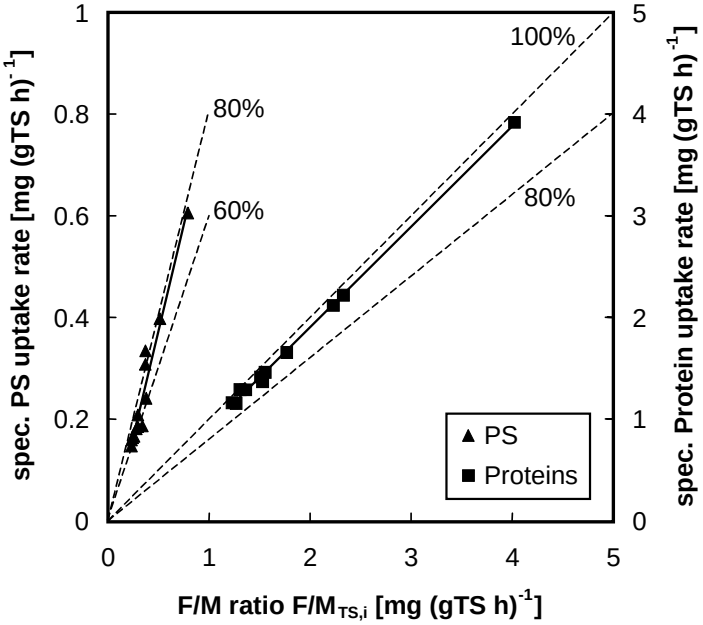

Fig. 8. Specific uptake rates of PS and proteins as a function of respective sludge loading rate.

These specific uptake rates are plotted in Fig. 8 as a function of the respective loading rate $F/M_{TS,i}$. Both uptake rates show a linear relation. This means that each cell proportionally takes up more the more is fed. Inaccuracies resulting from the fact that sampling was done every 3 to 4 days can be neglected since the value of the difference quotient $\Delta c_i / \Delta t$ is well below the influent mass flow. In contrast, the mass flow in the permeate cannot be neglected (see Fig. 5). Additionally, lines of constant degrees of uptake are plotted. It becomes apparent that the elimination of each EPS fraction did not depend on the respective loading rate. For PS the degradation was just under 80% while it was around 95% for proteins. The faster degradation of proteins was also observed during the refill after a sludge wastage. The proteins were supplied in high concentrations but reached a lower constant level very quickly, while no significant degradation of PS could be observed during the refill time of 5.4 h. It should be noted that the uptake rates are calculated from summary readings, i.e., a possibly higher uptake of influent EPS followed by excretion of different fractions cannot be excluded.

4. Conclusions

Six months operation of an MBR with irregular excess sludge wastage show that the relationship between polysaccharide concentrations and fouling rates is in same order of magnitude as the known correlation for steadily operated plants but data scatter in a clearly bigger range. This might be due to the unsteady operation and resulting stress situations for the biomass, which possibly leads to the emission of structurally different fractions of PS with different inherent fouling potential. This could not be determined with the used summary analyses. In order to gain a deeper insight and more universal correlations, the different EPS and PS fractions have to be identified in more detail.

Net degradation of proteins was constantly above 90%, while net PS degradation was between 60 and 80%. If this value was purely caused by degradation or by the excretion of a changed fraction after an even higher uptake could not be resolved by the used summary analyses. While overall EPS formation is not significantly affected by the unsteady operation, the nature or structure and hence the fouling propensity of the polysaccharides seems to vary.

The levels of dissolved oxygen and nitrate which also fluctuate more strongly in MBRs with irregular sludge wastage appear to have a profound impact on EPS uptake rate and thereby on EPS concentration. In addition to more detailed and preferably standardised analytical methods, an integrated approach taking account of all and possibly interdependent parameters is required in order to obtain universally valid correlations for prediction of EPS levels and their fouling propensity.

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Symbols

c	[g L^{-1}]	concentration
F/M_{TS}	[kg (kg d)$^{-1}$]	sludge loading rate (F/M ratio)
J	[L m^{-2} h^{-1}]	flux
$\dot{r}$	[mg (L h)$^{-1}$]	uptake rate
R	[m^{-1}]	filtration resistance
R	[-]	retention
Δp	[bar]	transmembrane pressure
t	[h]	time
T	[°C]	temperature
V	[L]	volume
$\dot{V}$	[L h^{-1}]	volumetric flow rate
η	[mPa s]	dynamic viscosity

Subscripts

F	feed
i	component
in	inlet

meas measured
R reactor
TS total solids

Abbreviations
BSA bovine serum albumin
COD chemical oxygen demand
DO dissolved oxygen
EPS extracellular polymeric substances
MBR membrane bioreactor
PS polysaccharides
TS total solids
VS volatile solids

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