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The role of the operating parameters of SBR systems on the SMP production and on membrane fouling reduction

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Abstract

In this work, six identical laboratory SBRs treating simulated wastewater were operated in parallel studying the effect of three food-to-microorganisms ratio (F/M ratio; 0.20, 0.35 and 0.50 kg COD·kg MLSS^{-1}·d^{-1}), two hydraulic retention times (HRT; 24 and 16 h) and two values of number of cycles per day (3 and 6). Influence of these operational parameters on the SMPs production and reactor performance, were studied. Results indicated that the highest F/M ratio, HRT and cycles/day produced 72.7% more of SMP. In a second experimental series, biological process yielding the maximal and the minimal SMPs production were replicated and both mixed liquors (ML) and treated effluents were ultrafiltrated. The flux decay in the conditions of minimum and maximum SMPs production were 52% and 72%, when the SBRs effluents were ultrafiltrated while no significant differences in the ultrafiltration of ML were found. In terms of permeability recovery, this was lower for the case of the ML (73% and 49% of initial permeability recovered for effluent and ML ultrafiltration, respectively).

Keywords: SBR; operating conditions; SMP; ultrafiltration; membrane fouling

1. INTRODUCTION

The ultrafiltration (UF) membrane technology is used as a tertiary treatment in order to produce high effluent quality. This technique is used to treat the secondary effluents after biological treatment to reduce the total solids, biological or chemical oxygen demand (Acero et al., 2010; Norton-Brandão et al., 2013; Tchobanoglous et al., 1998) and other pollutants like pharmaceutical substances (Garcia-Ivars et al., 2017; Secondes et al., 2014). On the other side, UF is also used in membrane bioreactors (MBR) in order to separate the treated wastewater from the mixed liquor. These processes produce water that can be reuse in the agriculture or for other purposes like urban and industrial uses, aquifer recharge, etc. contributing to environmental sustainability.

However, one of the disadvantages of the UF that avoid a wider implementation in the wastewater treatment plants (WWTP) is membrane fouling. The main fouling mechanisms in the UF membranes are the pore blocking (due to small colloids deposition) and cake layer formation (due to build-up of particles on the membrane surface). Additionally, solutes adsorption onto the membrane increases the fouling process (Boerlage et al., 2002; Mousa and Al-Hitmi, 2007). On the other hand, in recent years it has been reported that the filtration resistance caused by chemical potential mechanism is the cause of the primary fouling of the membrane. This fouling mechanism, based on the Flory-Huggins theory, was proposed by Chen et al., 2016. It was also confirmed using alginate solution to mimic the polysaccharides of the extracellular polymeric substances in MBRs (Zhang et al., 2018). These authors also highlighted the important role of the calcium ions on the membrane fouling.

In the secondary effluent the main foulant substances are the soluble organic matter. Many researchers report that SMPs are the predominant components of the soluble organic matter (Gkotsis et al., 2015; Schiener et al., 1994). The main SMPs components are carbohydrates, proteins and humic substances (Barker and Stuckey, 1999). They are generated by three mechanisms: biomass growth, substrate metabolism and biomass decay and cell lysis (Laspidou and Rittmann, 2002). Thus, the mechanisms of microbial survival, under different substrates or operational conditions, influences on the SMPs amounts generated during the biological treatment (Wang and Zhang, 2010).

Concerning to the MBRs, there are more substances than in the UF process of secondary effluents that contribute to the membrane fouling like sludge fractions as suspended solids, colloids and dissolved solutes (Defrance et al., 2000; Fan et al., 2006) including the extracellular polymeric substances (EPS), which can be accumulated on the cellular walls of the microorganisms or dissolved in the reactor as SMPs (Hodgson et al., 1993; Jefferson et al., 2004).

The role of SMPs in membrane fouling is unclear. There are researchers that reported a positive correlation between SMPs productions and membrane fouling (Lee et al., 2004; Rosenberger et al., 2006), while others did not observe this relationship (Drews et al., 2008). On the other hand, there are not consensuses into researchers community about optimal operational conditions like F/M ratio (Ghangrekar et al., 2005; Prashanth et al., 2006).

In this work six SBRs worked under different operational conditions. Three different F/M ratio (0.20, 0.35 and 0.50 kg DQO·kg $SSLM^{-1}\cdot d^{-1}$), two HRT (24 h and 16 h) and two operational cycles per day (3 and 6 cycles/day) were tested. All of these values are typical in SBRs operation. The first objective was to study the relationship between these conditions and the biological reactors performance and their SMPs productions. This information allowed obtaining the operational conditions that minimized and maximized the SMPs productions. The second objective of this work was the study of the UF membrane fouling working under the extreme operational conditions obtained in the first experimental step. In this way, it was evaluated the membrane fouling due to SMPs and due to sludge flocs. For this purpose, it was assessed by filtrating both ML (operation similar a MBR system) and effluent SBR (simulating a tertiary treatment of secondary effluent).

2. MATERIALS AND METHODS

2.1. Biological reactors

2.1.1. First experimental step: relationship between operational conditions, SBRs performance and SMPs production

In this part, the objective was to assess the relationship between the SMPs concentrations produced during the municipal wastewater biological treatment and the operational conditions of the SBRs. For this purpose six identical SBRs were operated with synthetic wastewater (SWW), which simulates municipal wastewater, under operational conditions reported in Table 1. SBRs start-up was performed with sludge taken from a MWWTP located in Valencia (Spain).

The main components of each reactor consisted of a mechanical stirrer, two peristaltic pumps and a compressor that supplied air into the SBR through two air diffusers located on the reactor bottom. The system “On and Off” used in these equipments consisted of time programmers connected to the electrical network. Characteristics of each cycle are presented in Table 1.

Table 1. Operational SBRs conditions.

Reactor	Operating parameters			
	F/M ($kg\ COD \cdot kg\ MLSS^{-1} \cdot d^{-1}$)	HRT (h)	Cycles/day	$V_{feed/draw}$ (L)
SBR-1	0.20	24	3	2
SBR-2	0.35			
SBR-3	0.50			
SBR-4	0.20	24	6	1
SBR-5	0.20	16	6	1.5
SBR-6	0.20	16	3	3

Cycle characteristics		
	3 Cycles/day	**6 Cycles/day**
Filling + Aerobic reaction	6 h	3 h
Sedimentation	90 min	45 min
Draw	25 min	13 min
Idle	5 min	2 min

The SBRs (named SBR-n, where n values were between 1 and 6) were operated during 31 days. The reaction volumes of all SBRs were 6 L. As it can be shown in Table 1 different feed/draw volumes and COD concentrations of feed solution were used in order to achieve the required HRT and cycles/day in the SBRs operation. In all the SBRs a concentration of 2500 $mg \cdot L^{-1}$ of mixed liquor suspended solids (MLSS) was maintained. Periodically sludge withdrawals were carried out to maintain this value.

These configurations allowed studying the influence of F/M ratio comparing the performances and the SMPs concentrations of SBR-1, SBR-2 and SBR-3. Additionally, two different HRT and two operating cycles/day were evaluated, comparing SBR-1, SBR-4, SBR-5 and SBR-6. Finally, the operational conditions that minimized and maximized the SMPs productions were obtained.

2.1.2. Second experimental step: evaluation of UF membrane fouling.

In this part, the objective was to study the effect of SMPs concentration on the UF membrane fouling. For this purpose effluent and mixed liquor (ML) of two different SBRs were used as feeds for the UF membrane. These SBRs worked under the operational conditions obtained in the first experiment, which minimized and maximized the SMPs productions. When effluent and ML were UF the membrane operated like a tertiary treatment or a MBR system, respectively.

In this way, two additional SBRs were operated during 25 days according to mentioned objective. The UF experiments were carried out twice in each reactor (in the second and third week, named UF1 and UF2). In order to be valid the replication tests, it was previously proved that SMPs concentration was the same in both feeds. Each experiment was performed in two days: in the first one effluent was collected to perform the UF experiments and in the second day ML was tested. This ML was returned to SBR after the experiment to maintain the efficiency of the biological treatment until to perform the second test.

The UF module, which allowed locating a flat sheet membrane, was a Rayflow from Orelis (France). Filtration was done in cross-flow mode. UP150 P membrane from Microdyn Nadir (Germany) was used to carry out the experiments. The active layer material of the membrane was polyethersulfone with a molecular weight cut-off of 150 kDa. Its flow rate according to data supplier is ≥ 285 $L \cdot m^{-2} \cdot h^{-1}$ (with clean water, 2 bar, 20ºC and cross-flow operation). The effective area was 100 cm^2.

In all the experiments the cross-flow velocity was 2 $m \cdot s^{-1}$ (feed flow rate = 300 $L \cdot h^{-1}$) and temperature was 25ºC. The steps followed in each experiment were: membrane compaction at transmembrane pressure (TMP) of 3 bars during 2 h, initial membrane permeability (with deionised water and three TMP; 1, 2 and 3 bar), membrane fouling (with secondary effluent or ML and TMP = 1 bar), membrane rinsing (30 minutes with deionised water without applying TMP) and final permeability under the same conditions as the initial one. During the membrane fouling, the retentate and the permeate streams were recycled to the feed tank to work at constant concentration and membrane flux was measured periodically. All the fouling tests were performed until stationary permeate flux value was reached (around 105 min).

2.2. Synthetic wastewater

A synthetic wastewater (SWW) with peptone, meat extract and K_2HPO_4 (supplied by Panreac) diluted in tap water (mimicking municipal wastewater) was prepared for feeding the SBRs. Peptone and meat extract concentrations (in equal amount) were calculated to achieve the COD (Eq.(1)) to maintain the required F/M ratio .

Eq.(1)

where V_R = 6 L, MLSS = 2500 $mg{\cdot}L^{-1}$, F/M was the value in Table 1 specified for each reactor and $V_{feed|draw}$ was calculated according HRT and cycles/day also specified in Table 1.

K_2HPO_4 concentration was calculated in each case to have a relationship between COD and phosphorous (COD:P) of 100:1. Table 2 shows the four different compositions of synthetic wastewaters used.

Table 2. SWW preparation for the different operational conditions

Synthetic wastewater	F/M (kg COD·kg MLSS^{-1}·d^{-1})	HRT (h)	Peptone (mg·L^{-1})	Meat extract (mg·L^{-1})	K_2HPO_4 (mg·L^{-1})	COD (mg·L^{-1})
SWW1	0.20	24	225	225	28	500
SWW2	0.20	16	149	149	18	330
SWW3	0.35	24	390	390	49	875
SWW4	0.50	24	560	560	70	1250

2.3. Analysis

The parameters analysed in the effluent were: pH, conductivity, turbidity, COD, total nitrogen (N_T), ammonium nitrogen (NH_4^+–N) and total phosphorous (P_T). In the ML the suspended solids (MLSS) and volatile suspended solids (MLVSS) were measured. All of these analyses were performed twice a week.

Conductivity and pH were measured with an EC-Meter GLP 31+ and a pH-Meter GLP 21+ both from Crison. To measure COD, N_T, NH_4^+–N and P_T a Spectroquant NOVA 30 and reactive kits, both from Merck, were used. MLSS and MLVSS were obtained according to APHA, 2005.

Additionally, the sludge retention time (SRT) and the observed sludge yield (Y_{obs}) were calculated. According to the bibliography (Amanatidou et al., 2015; Klimiuk and Kulikowska, 2006), Y_{obs} allows to assess the biomass growth and it can be calculated by Eq.(2):

Eq.(2)

where t is the time interval between two days "i" and "j" (no sludge was withdrawn in between), X_e was the mean volatile suspended solids concentrations in the effluent (mg·L^{-1}) in this time span and COD_0 and COD_e were the initial influent COD and mean COD measured in the effluent at the time interval t, respectively.

The SMPs production was evaluated through the measurement of proteins and carbohydrates concentrations in the ML. Twice a week 25 mL of ML were collected from the SBRs and were centrifuged at 12000 x g. The clarified liquid was filtered at 0.45 µm. Analysis of proteins was performed by BCA method (Krieg et al., 2005; Zuriaga-Agustí et al., 2013) using the kits from Novagen, and carbohydrates were measured using the anthrone method (Frølund et al., 1996). For it, anthrone from Panreac was used. Both methods are colorimetric and the measurements of concentrations were performed with a Hach-Lange DR 5000 spectrophotometer. All measures were performed by triplicate.

2.4. Statistical analysis

An one-way ANOVA analysis (confidence level of 95 %) was carried out with Statgraphics Centurion XVII in order to study the statistical significance of operational conditions in the SMPs productions. The variance analyses of proteins, carbohydrates and SMPs (sum of proteins and carbohydrates) concentrations have been studied. Three levels of F/M ratio (0.20, 0.35 and 0.50 kg COD·kg MLVSS $^{-1}$·d^{-1}), two levels of HRT (24 and 16 h) and two levels of cycles/day (3 and 6 cycles/day) were evaluated.

3. RESULTS AND DISCUSSION

3.1. Relationship between operational conditions and SMPs production

In the first 10 days of the SBRs operation it was considered a period of biomass acclimation to both SWW and operational conditions.

3.1.1. F/M ratio

The influence of F/M ratio on the biological performance was studied comparing the SBR-1, SBR-2 and SBR-3. In Table 3, the mean values with their standard deviations for some parameters of effluent and ML measured between the 11st and 31st days, are presented. The SRT corresponds to the whole experimental period.

Table 3. Mean values of parameters measured for the SWW biological treatment with three different F/M ratios and the same HRT and cycles/day (24h and 3, respectively).

	SBR-1	SBR-2	SBR-3
	F/M = 0.20	F/M = 0.35	F/M = 0.50
Effluent			
pH	7.4 ± 0.4	7.4 ± 0.8	7.6 ± 0.3
Conductivity ($\mu S\cdot cm^{-1}$)	1226 ± 57	1528 ± 155	1943 ± 107
Turbidity (NTU)	0.4 ± 0.4	2.4 ± 1.3	7.0 ± 5.5
COD ($mg\cdot L^{-1}$)	34.0 ± 13.0	61.7 ± 15.4	90.3 ± 52.2
COD removal efficiency (%)	93.0 ± 2.7	92.5 ± 2.0	91.8 ± 4.9
ML			
MLVSS/MLSS	0.94 ± 0.02	0.93 ± 0.02	0.90 ± 0.02
Y_{obs} (kg MLVSS·kg COD^{-1})	0.28 ± 0.04	0.34 ± 0.04	0.37 ± 0.05
SRT (day)	37.5	14.4	7.3

It can be observed that effluent pH were similar in the three SBR, meanwhile conductivity increased as F/M ratio increased, since the concentration of all the components in the SWW had to be higher in order to increase of the F/M ratio. The mean turbidity values also increased with the F/M ratio, since high F/M ratio enhanced the sludge deflocculation (Liu et al., 2012; Xie et al., 2013). In this way, fine particles remained in the supernatant.

Additionally, for the three F/M ratio tested in this work, the COD removal efficiency remained constant (between 91.8% and 93.0%) in the SBRs. As expected, the effluent COD and the F/M ratio varied inversely proportional. On the other hand, observing the ML values, it can be seen that Y_{obs} increased according to F/M ratio. This phenomenon is due because an increase of F/M values improve the metabolic activity and the microbial growth (Lobos et al., 2008). This fact implied more frequent sludge withdrawals to maintain the MLSS around 2500 mg·L^{-1}. Consequently, SRT decreased when F/M ratio increased. These different SRTs affected slightly to the volatile suspended solids percentage, maintaining values between 90% and 95%.

The SMPs production was evaluated with the sum of proteins and carbohydrates concentrations, whose evolution for SBR-1, SBR-2 and SBR-3 are shown in Figure 1.

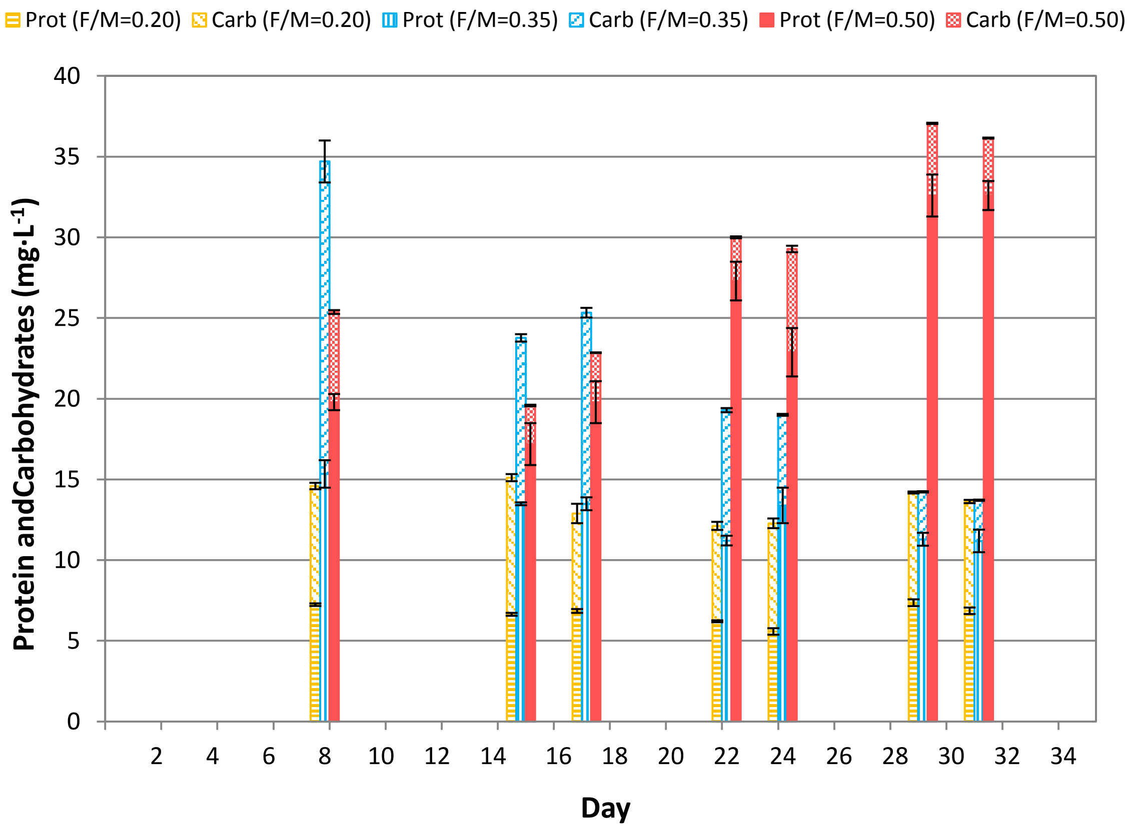


Figure 1. Evolution of SMP concentration (protein + carbohydrates): three different F/M ratio (0.20, 0.35 and 0.50 kg SSLM·kg DQO^{-1}·d^{-1}) and the same HRT and cycles/day (24 h and 3, respectively).

Overall, it can be observed that the proportion between proteins and carbohydrates was different depending on the F/M ratio. In this way, the mean proteins/SMP ratio during the experimental time was 48.7 ± 3.7% and 83.9 ± 7.1% for the SBRs with lowest and higher F/M ratio, respectively. For the SBR with intermediate value of F/M ratio this proportion changes from the 52.7% to 77.2% at the end of experimental procedure. This phenomenon can be due to the increase of cell debris in the SBRs with high F/M ratio. Since the dry weight of bacterial cells of activated sludge includes 50% of proteins (Shier and Purwono, 1994; Xiao et al., 2017), the SBRs with more cell debris due to higher FM ratio had higher proteins/SMP ratio.

Regarding the SMPs values, the highest concentration was also achieved in SBR-3, which worked with the highest F/M ratio. This fact was confirmed by ANOVA analysis, which showed a statistically significance between both parameters as expected (F = 12.21; p-value = 0.0004). This behavior is due because the increase of F/M ratio values provides a high driving force for metabolic activity and microbial growth, so the SMPs productions increase (Liu et al., 2012), as it can be shown in the Tukey diagram (Figure 2). Another parameter that has an important influence on the SMPs concentration is the SRT. Some authors (Esparza-Soto et al., 2011; Yu et al., 2015) reported that the SRT increase results in a decrease of the generated SMP amounts, as happens in this experiment.

Summarizing, it can be stated that an increase of the F/M ratio resulted in a worse effluent quality with higher turbidity, COD and SMP concentration.

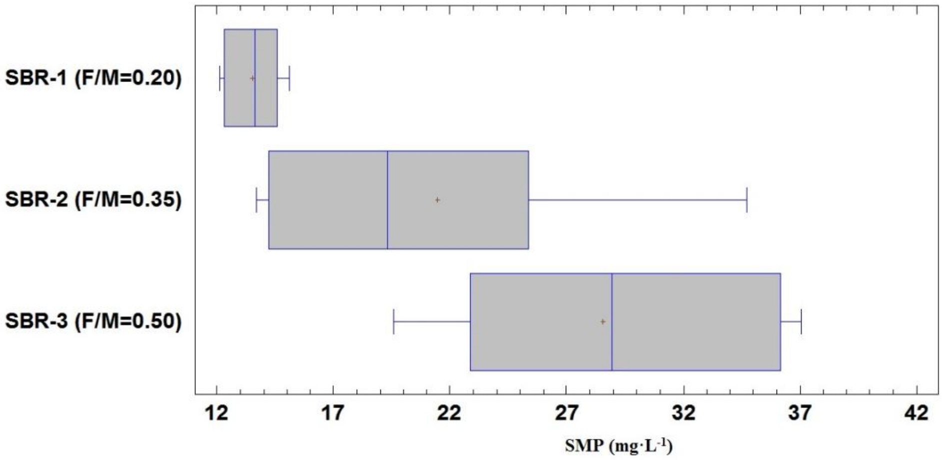


Figure 2. Tukey diagram for the SMP productions under three different F/M ratio (0.20, 0.35 and 0.50 kg SSLM·kg DQO^{-1}·d^{-1}) and the same HRT and cycles/day (24h and 3, respectively).

3.2.2. HRT and cycles/day

The four SBRs whose effluents and ML characteristics are shown in Table 4 were compared to evaluate the influence of HRT and cycles/day on the SBRs performance. Like Table 3, the mean values with their standard deviations between the 11st and 31st days, were presented.

Table 4. Mean values of parameters measured for the SWW biological treatment with two different HRT and cycles/day and the same F/M ratio (0.20 kg MLSS·kg COD^{-1}·d^{-1}).

	SBR-1 **HRT=24 h** **3 cycles/day**	**SBR-4** **HRT=24 h** **6 cycles/day**	**SBR-5** **HRT=16 h** **6 cycles/day**	**SBR-6** **HRT=16 h** **3 cycles/day**
Effluent				
pH	7.4 ± 0.4	7.2 ± 0.2	7.4 ± 0.4	7.4 ± 0.3
Conductivity (µS·cm^{-1})	1226 ± 57	1210 ± 47	1212 ± 52	1209 ± 63
Turbidity (NTU)	0.4 ± 0.4	0.3 ± 0.1	3.5 ± 6.6	0.2 ± 0.1
COD (mg·L^{-1})	34.0 ± 13.0	25.0 ± 7.2	33.3 ± 20.8	16.7 ± 2.5
COD removal efficiency (%)	93.0 ± 2.7	94.7 ± 1.9	87.5 ± 8.6	94.1 ± 1.1
ML				
MLVSS/MLSS	0.94 ± 0.02	0.94 ± 0.03	0.93 ± 0.02	0.93 ± 0.04
Y_{obs} (kg MLSS·kg COD^{-1})	0.28 ± 0.04	0.24 ± 0.07	0.34 ± 0.05	0.45 ± 0.09
SRT (day)	37.5	40.3	42.2	35.8

It can be observed that effluent pH, conductivity, turbidity and COD removal percentage were similar in the four reactors. Therefore, it could be said that the different HRT and cycles/day tested in this work, did not affect the biological treatment performance.

Furthermore, regarding the ML, the Y_{obs} was lower in the reactors with higher HRT because endogenous respiration increased as HRT did too, diminishing the apparent biomass growth (Huang et al., 2011; Luna et al., 2014). Nevertheless, the SRT was similar in the four reactors as the differences in the biomass growth did not affect this parameter. No relationship was observed for the two operational cycles/day values.

With respect to the SMPs production, the proteins and carbohydrates concentrations in the pairs SBR-1/SBR-6 and SBR-4/SBR-5 were compared to evaluate the influence of HRT on the SMP productions. In the same way, the pairs SBR-1/SBR-4 and SBR-5/SBR-6 were compared to evaluate the influence of cycles/day on the SMP production. The main conclusions were: proteins/SMP ratio was similar in all the reactors (around 50%) and SMPs concentration was higher in the reactors operating with 6 cycles/day (10.5 ± 4.5 and 16.0 ± 0.1 $mg \cdot L^{-1}$ for SBRs with 3 cycles and 6 cycles, respectively). In this way, the biological treatment should be operated at 3 cycles/day to minimize the SMPs production. Under this condition, it can be observed that the SMPs concentration was lower for the lowest HRT (Figure 3 and Figure 4).

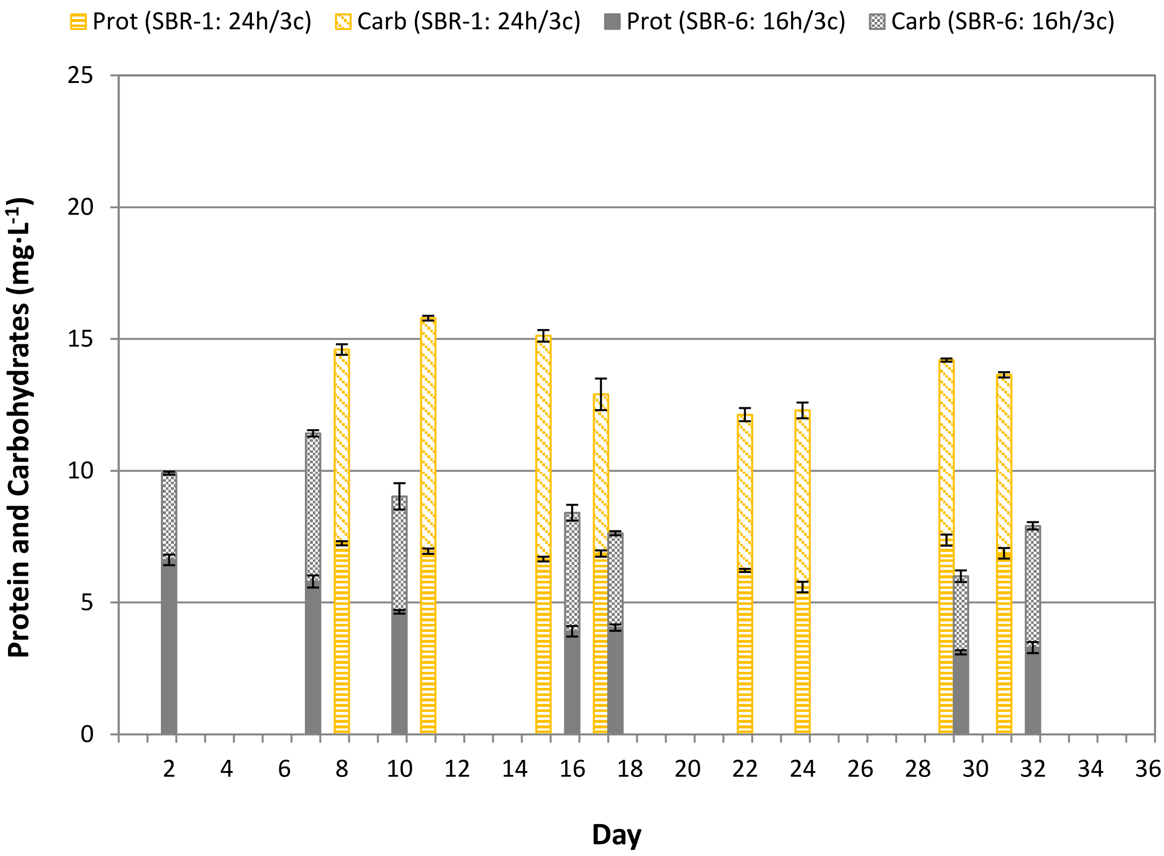


Figure 3. Evolution of SMP concentration (protein + carbohydrates): two different HRT (24 and 16 h) and the same F/M and cycles/day (0.20 kg MLSS·kg COD^{-1}·d^{-1} and 3, respectively).

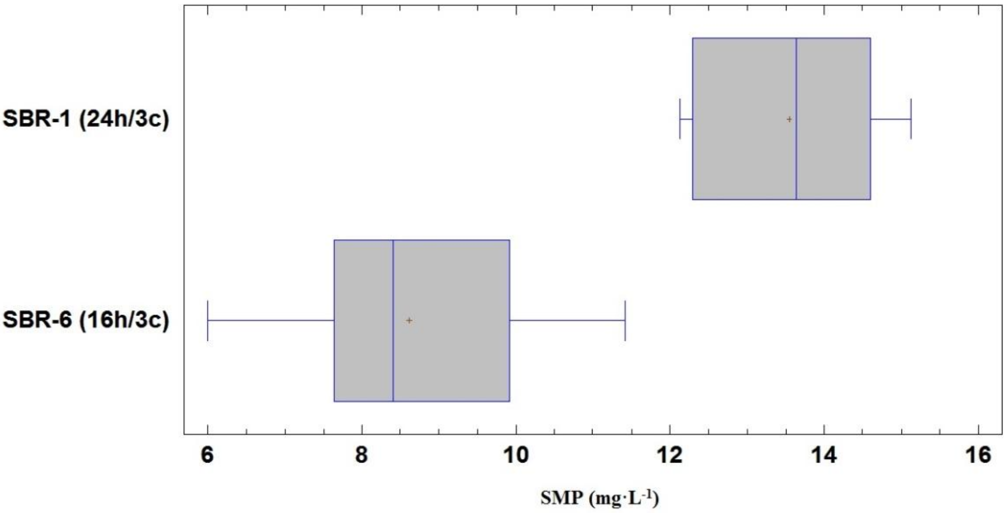


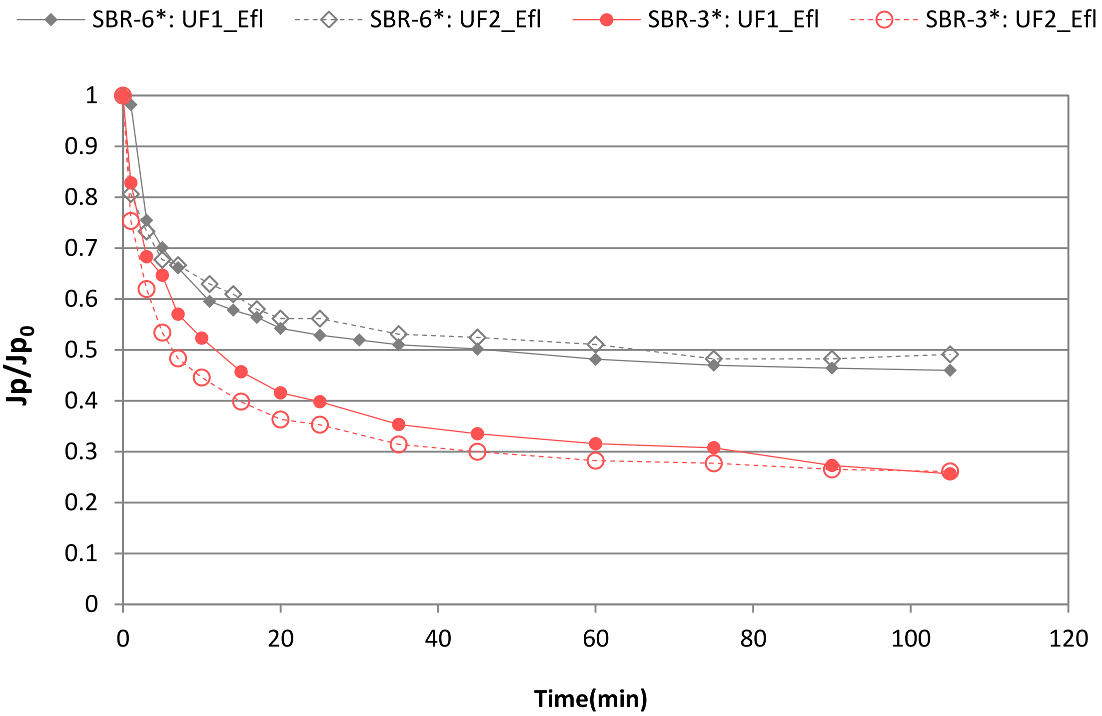
Figure 4. Tukey diagram for the SMP productions under two different HRT (24 and 16 h) and the same F/M and cycles/day (0.20 kg MLSS·kg COD^{-1-1}·d^{-1} and 3, respectively).

This relation was confirmed by ANOVA analysis, observing a statistically significance relationship between HRT and SMPs production ($F = 39.26$; p-value < 0.0001). This fact can be explained because bacteria excrete organic materials (SMP) during starvation, which was longer when HRT increased. This is due by the bacteria to obtain energy for maintenance by endogenous respiration or by intracellular components metabolism (Boylen and Ensign, 1970; Burleigh and Dawes, 1967).

Finally, it can be concluded that working with F/M ratio of 0.20 kg MLVSS·kg $COD^{-1}\cdot d^{-1}$, HRT of 16 h and 3 cycles/day the SMPs production was minimized. Conversely, F/M ratio of 0.50 kg MLVSS·kg $COD^{-1}\cdot d^{-1}$, HRT of 24 h and 6 cycles/day maximized the SMPs production. These conditions were performed in SBR-6 and SBR-3 with average SMPs productions of 7.4 ± 1.2 and 28.6 ± 6.5 $mg\cdot L^{-1}$, respectively. Coefficients of variation (CVs) of these results were 0.17 and 0.23, respectively.

3.2. Relationship between UF membrane fouling and operational conditions.

As commented in methodology section, two additional reactors that minimized and maximized the SMPs productions were started-up. These reactors were named SBR-6* and SBR-3*, respectively. Figure 5 and Figure 6 show the UF membrane fouling experiments for these SBRs, for the effluent (Efl) and mixed liquor (ML), respectively. In these figures the normalized flux (Jp/Jp_0) was plot around the experimental time. Two replicates for each reactor, named UF1 and UF2, were performed. The average flow rate of the four membranes used in the test were 343 ± 19 $L\cdot m^{-2}\cdot h^{-1}$ (with clean water, 2 bar, 25ºC and cross-flow operation). This value is near to reported by supplier for similar conditions (≥ 285 $L\cdot m^{-2}\cdot h^{-1}$).



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297 **Figure 5. UF membrane fouling experiments for the effluent (Efl) of SBR-6* and SBR-3*. Two replicates**
298 **for each reactor: UF1 and UF2.**

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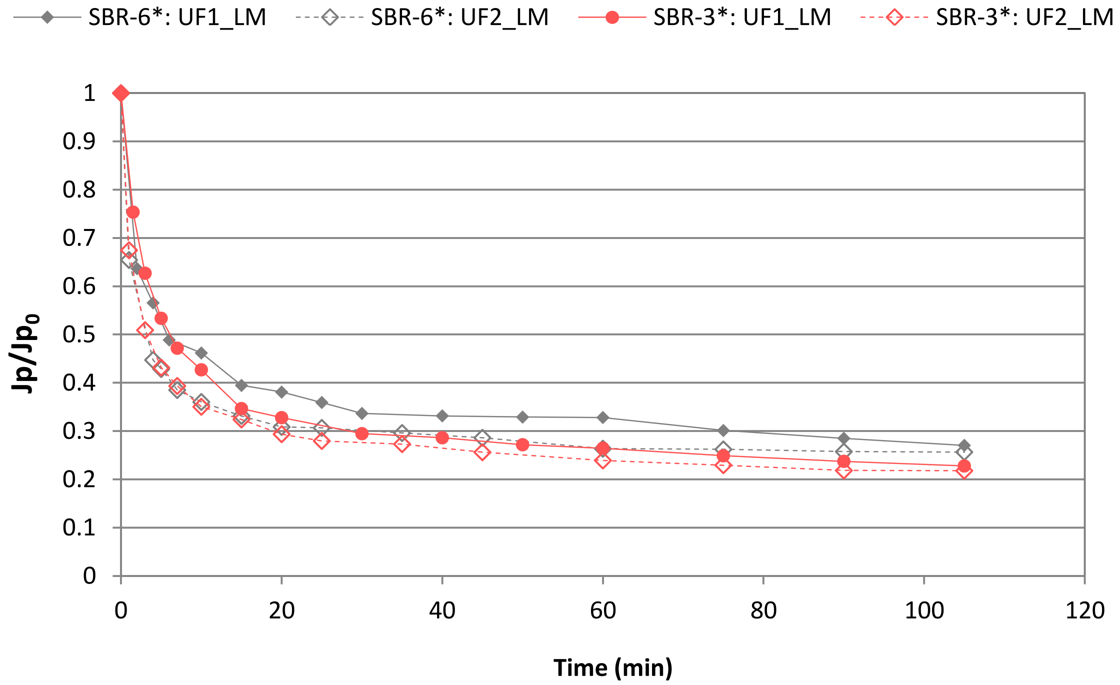

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301 **Figure 6. UF membrane fouling experiments for the mixed liquor (ML) of SBR-6* and SBR-3*. Two**
302 **replicates for each reactor: UF1 and UF2.**

The membrane fouling was significantly higher when the effluent from SBR-3* was ultrafiltrated, as observed in Figure 5. The fluxes decline between initial and stationary conditions (from 60 min) in both experimental days were around 72% for SBR-3* and 52% for SBR-6*. The average SMPs concentrations were 14.9 ± 3.1 and 21.5 ± 5.3 $mg \cdot L^{-1}$ in SBR-6* and SBR-3*, respectively. CVs of these results were 0.16 and 0.24, respectively. These values are very similar to those achieved in experiments with reactors SBR-6 and SBR-3, which confirmed that both experiments were comparable and measurements SMPs were performed with a reliable method. This is in concordance to the fact that SBR-3* was the highest SMPs producer due to the high F/M ratio (0.50 $kg\ MLVSS \cdot kg\ COD^{-1} \cdot d^{-1}$) and the low SRT (10 days) in this reactor. In other words, a significant difference in the SMPs concentration will affect to the UF performance significantly.

However, when the MLs were ultrafiltrated, similar flux declines were observed in both reactors (around 72% and 76% in SBR-3* and SBR-6*, respectively). That can be explained considering that the main substances that caused the membrane fouling in this case were the sludge flocs, forming a cake layer that decreases at the same extent Jp in both cases. This fact is contrary to the results reported by Fan et al., (2006), which concluded that MLSS had little impact on the critical flux in a MBR operated with municipal wastewater. However, other authors concluded that cake layer is the main mechanism in MBR treating municipal wastewater (Wang et al., 2007; Zuthi et al., 2017). It has to be underlined that the flux declines in both effluent and ML ultrafiltration from SBR-3* were very similar. It may be probably due to the fact that in the secondary effluent the SMPs are transported more easily into the membrane pores (what implies a severe flux decline), meanwhile the aforementioned cake layer formed by the suspended solids of the ML hinder their transport to the membrane pores.

After the rinsing step, irreversible membrane fouling was higher for the ML experiments. The percentages of the initial permeability recovered were around 73% in the experiments performed with effluents for both reactors. In the same way, this percentage decreased to 49% when membranes worked with ML.

4. CONCLUSIONS

The results of this work reveal that F/M ratio had a positive correlation with the SMPs production based on the rise of the protein concentration. Additionally, the same positive correlation was observed for both HRT and cycles/day parameters. In this way, the maximal (28.6 ± 6.5 $mg \cdot L^{-1}$) and the minimal (7.4 ± 1.2 $mg \cdot L^{-1}$) SMPs production occurred for the highest and lowest values of F/M ratio, HRT and cycles per day, respectively.

In the UF experiments, the flux decay was 27.8% higher when effluent from the SBR with the highest SMPs concentration was UF. No significant differences were found when mixed liquors were treated. On the other hand, permeability recovery after rinsing was lower in the ML test (73% and 49% of initial permeability recovered for effluent and ML experiments, respectively). This behavior indicates that irreversible fouling was higher when ML was ultrafiltrated.

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References

Acero, J.L., Benitez, F.J., Leal, A.I., Real, F.J., Teva, F., 2010. Membrane filtration technologies applied to municipal secondary effluents for potential reuse. J. Hazard. Mater. 177, 390–398. doi:10.1016/j.jhazmat.2009.12.045

Amanatidou, E., Samiotis, G., Bellos, D., Pekridis, G., Trikoilidou, E., 2015. Net biomass production under complete solids retention in high organic load activated sludge process. Bioresour. Technol. 182, 193–199. doi:10.1016/j.biortech.2015.01.119

APHA, 2005. Standard Methods for the Examination of Water and Wastewater, 21st. ed. American Public Health Association, Washington, DC.

Barker, D.J., Stuckey, D.C., 1999. A review of soluble microbial products (SMP) in wastewater treatment systems. Water Res. 33, 3063–3082.

Boerlage, S.F.E., Kennedy, M.D., Dickson, M.R., El-Hodali, D.E.Y., Schippers, J.C., 2002. The modified fouling index using ultrafiltration membranes (MFI-UF): Characterisation, filtration mechanisms and proposed reference membrane. J. Memb. Sci. 197, 1–21. doi:10.1016/S0376-7388(01)00618-4

Boylen, C.W., Ensign, J.C., 1970. Intracellular substrates for endogenous metabolism during long-term starvation of rod and spherical cells of Arthrobacter crystallopoietes. J. Bacteriol. 103, 578–587.

Burleigh, I.G., Dawes, E.A., 1967. Studies on the endogenous metabolism and senescence of starved Sarcina lutea. Biochem. J. 102, 236–50.

Chen, J., Zhang, M., Li, F., Qian, L., Lin, H., Yang, L., Wu, X., Zhou, X., He, Y., Liao, B.Q., 2016. Membrane fouling in a membrane bioreactor: High filtration resistance of gel layer and its underlying mechanism. Water Res. 102, 82–89. doi:10.1016/j.watres.2016.06.028

Defrance, L., Jaffrin, M.Y., Gupta, B., Paullier, P., Geaugey, V., 2000. Contribution of various constituents of activated sludge to membrane bioreactor fouling. Bioresour. Technol. 73, 105–112. doi:10.1016/S0960-8524(99)00163-7

Drews, A., Vocks, M., Bracklow, U., Iversen, V., Kraume, M., 2008. Does fouling in MBRs depend on SMP? Desalination 231, 141–149. doi:10.1016/j.desal.2007.11.042

Esparza-Soto, M., Núñez-Hernández, S., Fall, C., 2011. Spectrometric characterization of effluent organic matter of a sequencing batch reactor operated at three sludge retention times. Water Res. 45, 6555–6563. doi:10.1016/j.watres.2011.09.057

Fan, F., Zhou, H., Husain, H., 2006. Identification of wastewater sludge characteristics to predict critical flux for membrane bioreactor processes. Water Res. 40, 205–212. doi:10.1016/j.watres.2005.10.037

Frølund, B., Palmgren, R., Keiding, K., Nielsen, P.H., 1996. Extraction of extracellular polymers from activated sludge using a cation exchange resin. Water Res. 30, 1749–1758. doi:10.1016/0043-1354(95)00323-1

Garcia-Ivars, J., Durá-María, J., Moscardó-Carreño, C., Carbonell-Alcaina, C., Alcaina-Miranda, M.I., Iborra-Clar, M.I., 2017. Rejection of trace pharmaceutically active compounds present in municipal wastewaters using ceramic fine ultrafiltration membranes: Effect of feed solution pH and fouling phenomena. Sep. Purif. Technol. 175, 58–71. doi:10.1016/j.seppur.2016.11.027

Ghangrekar, M.M., Asolekar, S.R., Joshi, S.G., 2005. Characteristics of sludge developed under different loading conditions during UASB reactor start-up and granulation. Water

Res. 39, 1123–1133. doi:10.1016/j.watres.2004.12.018

Gkotsis, P.K., Batsari, E.L., Peleka, E.N., Tolkou, A.K., Zouboulis, A.I., 2015. Fouling control in a lab-scale MBR system: Comparison of several commercially applied coagulants. J. Environ. Manage. 203, 838–846. doi:10.1016/j.jenvman.2016.03.003

Hodgson, P.H., Leslie, G.L., Fane, A.G., Schneider, R.P., Fell, C.J.D., Marshall, K.C., 1993. Cake resistance and solute rejection in bacterial microfiltration: The role of the extracellular matrix. J. Memb. Sci. 79, 35–53. doi:10.1016/0376-7388(93)85016-P

Huang, Z., Ong, S.L., Ng, H.Y., 2011. Submerged anaerobic membrane bioreactor for low-strength wastewater treatment: Effect of HRT and SRT on treatment performance and membrane fouling. Water Res. 45, 705–713. doi:10.1016/j.watres.2010.08.035

Jefferson, B., Brookes, A., Le Clech, P., Judd, S.J., 2004. Methods for understanding organic fouling in MBRs. Water Sci. Technol. 49, 237–244.

Klimiuk, E., Kulikowska, D., 2006. Organics removal from landfill leachate and activated sludge production in SBR reactors. Waste Manag. 26, 1140–1147. doi:10.1016/j.wasman.2005.09.011

Krieg, R.C., Dong, Y., Schwamborn, K., Knuechel, R., 2005. Protein quantification and its tolerance for different interfering reagents using the BCA-method with regard to 2D SDS PAGE. J. Biochem. Biophys. Methods 65, 13–19. doi:10.1016/j.jbbm.2005.08.005

Laspidou, C., Rittmann, B.E., 2002. A unified theory for extracellular polymeric substances, soluble microbial products, and active and inert biomass. Water Res. 36, 2711–2720. doi:10.1016/S0043-1354(01)00413-4

Lee, N., Amy, G., Croué, J.P., Buisson, H., 2004. Identification and understanding of fouling in low-pressure membrane (MF/UF) filtration by natural organic matter (NOM). Water Res. 38, 4511–4523. doi:10.1016/j.watres.2004.08.013

Liu, Y., Liu, H., Cui, L., Zhang, K., 2012. The ratio of food-to-microorganism (F/M) on membrane fouling of anaerobic membrane bioreactors treating low-strength wastewater. Desalination 297, 97–103. doi:10.1016/j.desal.2012.04.026

Lobos, J., Wisniewski, C., Heran, M., Grasmick, A., 2008. Sequencing versus continuous membrane bioreactors: Effect of substrate to biomass ratio (F/M) on process performance. J. Memb. Sci. 317, 71–77. doi:10.1016/j.memsci.2007.08.041

Luna, H.J., Baêta, B.E.L., Aquino, S.F., Rodríguez Susa, M.S., 2014. EPS and SMP dynamics at different heights of a submerged anaerobic membrane bioreactor (SAMBR). Process Biochem. 49, 2241–2248. doi:10.1016/j.procbio.2014.09.013

Mousa, H.A., Al-Hitmi, S.A., 2007. Treatability of wastewater and membrane fouling. Desalination 217, 65–73. doi:10.1016/j.desal.2007.09.004

Norton-Brandão, D., Scherrenberg, S.M., van Lier, J.B., 2013. Reclamation of used urban waters for irrigation purposes - A review of treatment technologies. J. Environ. Manage. 122, 85–98. doi:10.1016/j.jenvman.2013.03.012

Prashanth, S., Kumar, P., Mehrotra, I., 2006. Anaerobic degradability: dffect of particulate COD. J. Environ. Eng. 132, 488–496. doi:10.1061/(ASCE)0733-9372(2006)132:4(488)

Rosenberger, S., Laabs, C., Lesjean, B., Gnirss, R., Amy, G., Jekel, M., Schrotter, J.C., 2006. Impact of colloidal and soluble organic material on membrane performance in membrane bioreactors for municipal wastewater treatment. Water Res. 40, 710–720. doi:10.1016/j.watres.2005.11.028

Schiener, P., Nachaiyasit, S., Stuckey, D.C., 1994. Production of soluble microbial products (SMP) in an anaerobic baffled reactor: composition, biodegradability and the effect of process parameters. Environ. Technol. 19, 391–400.

Secondes, M.F.N., Naddeo, V., Belgiorno, V., Ballesteros, F., 2014. Removal of emerging contaminants by simultaneous application of membrane ultrafiltration, activated carbon adsorption, and ultrasound irradiation. J. Hazard. Mater. 264, 342–349. doi:10.1016/j.jhazmat.2013.11.039

Shier, W.T., Purwono, S.K., 1994. Extraction of single-cell protein from activated sewage sludge: thermal solubilization of protein. Bioresour. Technol. 49, 157–162. doi:10.1016/0960-8524(94)90079-5

Tchobanoglous, G., Darby, J., Bourgeous, K., McArdle, J., Genest, P., Tylla, M., 1998. Ultrafiltration as an advanced tertiary treatment process for municipal wastewater. Desalination 119, 315–322. doi:10.1016/S0011-9164(98)00175-1

Wang, X.M., Li, X.Y., Huang, X., 2007. Membrane fouling in a submerged membrane bioreactor (SMBR): Characterisation of the sludge cake and its high filtration resistance. Sep. Purif. Technol. 52, 439–445. doi:10.1016/j.seppur.2006.05.025

Wang, Z.P., Zhang, T., 2010. Characterization of soluble microbial products (SMP) under stressful conditions. Water Res. 44, 5499–5509. doi:10.1016/j.watres.2010.06.067

Xiao, K., Chen, Y., Jiang, X., Seow, W.Y., He, C., Yin, Y., Zhou, Y., 2017. Comparison of different treatment methods for protein solubilisation from waste activated sludge. Water Res. 122, 492–502. doi:10.1016/j.watres.2017.06.024

Xie, W.M., Ni, B.J., Seviour, T., Yu, H.Q., 2013. Evaluating the impact of operational parameters on the formation of soluble microbial products (SMP) by activated sludge.

Water Res. 47, 1073–1079. doi:10.1016/j.watres.2012.11.022

Yu, H., Qu, F., Sun, L., Liang, H., Han, Z., Chang, H., Shao, S., Li, G., 2015. Relationship between soluble microbial products (SMP) and effluent organic matter (EfOM): Characterized by fluorescence excitation emission matrix coupled with parallel factor analysis. Chemosphere 121, 101–109. doi:10.1016/j.chemosphere.2014.11.037

Zhang, M., Hong, H., Lin, H., Shen, L., Yu, H., Ma, G., Chen, J., Liao, B.Q., 2018. Mechanistic insights into alginate fouling caused by calcium ions based on terahertz time-domain spectra analyses and DFT calculations. Water Res. 129, 337–346. doi:10.1016/j.watres.2017.11.034

Zuriaga-Agustí, E., Bes-Piá, A., Mendoza-Roca, J.A., Alonso-Molina, J.L., 2013. Influence of extraction methods on proteins and carbohydrates analysis from MBR activated sludge flocs in view of improving EPS determination. Sep. Purif. Technol. 112, 1–10. doi:10.1016/j.seppur.2013.03.048

Zuthi, M.F.R., Guo, W., Ngo, H.H., Nghiem, D.L., Hai, F.I., Xia, S., Li, J., Li, J., Liu, Y., 2017. New and practical mathematical model of membrane fouling in an aerobic submerged membrane bioreactor. Bioresour. Technol. 238, 86–94. doi:10.1016/j.biortech.2017.04.006