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Fouling evaluation in a MBR for dairy effluent treatment

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ABSTRACT

A submerged membrane bioreactor was used in the treatment of dairy wastewater, and three different sludge retention time (SRT) were evaluated. High removal efficiencies of organic matter, apparent color, and nutrients were observed for all the three conditions. However, the membrane fouling was considerably intense, and the concentration of soluble microbial products (SMP) and extracellular polymeric substances (EPS) and the critical flux of the system were analyzed for a better understanding of the reasons. Contrary to what other authors noticed, it was not possible to establish any relation between SMP concentration and fouling rate. In contrast, the EPS seem to have some influence on this phenomenon. The critical flux results justified the strong fouling observed, as almost all the measured values were below the established operational flux. The SRT of 60 d was selected as the best among the three evaluated because it resulted in lower EPS concentration and higher values of critical flux.

Keywords: Membrane bioreactor; Dairy industry effluent; Fouling; Sludge retention time; Soluble microbial products; Extracellular polymeric substances; Critical flux

1. Introduction

Dairy are considered to be the most polluting of the food industries because of its high water consumption. Water is used throughout all steps of the dairy industry, including cleaning, sanitization, heating, cooling, and floor washing [1]. As a result, great volumes of liquid effluents are generated, which constitute the main source of pollution of this industrial typology [2]. These wastewaters are characterized by the high organic matter and nutrients concentration, and are constituted mainly of carbohydrates, proteins and fat originating from the milk, milk products, and residual cleaning agents [3–5].

The highly variable nature of dairy wastewaters in terms of flow rates, pH, and composition makes it difficult to choose an effective wastewater treatment regime [5]. The conventional treatment systems for these effluents comprises the use of primary treatment for the removal of solids, oils, and fats; secondary biological treatment for the removal of organic matter and nutrients; and, in some cases, tertiary treatment for removal of specific substances as, for example, dyes. Nonetheless, several problems have been reported in these systems, such as the high production

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of scum, low sludge settleability, low resistance to shock loads, difficulties in the removal of nutrients (nitrogen and phosphorus), and problems in the degradation of fats, oils, and other specific types of pollutants, such as colors [6,7]. To comply with new discharge standards and overcome these difficulties, the membrane bioreactors (MBR) become a promising process for the treatment of dairy effluents.

The complete retention of biomass by the membrane is what distinguishes the MBRs from conventional treatment systems, such as activated sludge, so that the quality of the treated effluent does not depend on the characteristics of the settleability of the sludge [8]. Besides that, the MBRs can operate with higher concentrations of suspended solids and higher solids retention times (SRT). The advantages of these conditions are lower production of sludge, which reduces costs with treatment and final disposal of the sludge, and lower biological reactor volume, leading to smaller plant footprint [5]. Due to the membrane retention, compounds with high molecular weight and/or recalcitrant compounds can remain in the MBR for a longer time than the mean hydraulic retention time, stimulating the growth of micro-organisms that are better acclimatized to these compounds and that have a greater capacity to degrade them. That way, the MBRs also present greater efficiency in the removal of micropollutants, persistent organic pollutants, and slowly biodegradable compounds [9].

Despite the advantages in relation to the conventional active sludge, the membrane fouling remains as a restricting factor for the implementation of this wastewater recycling technology [10–12]. Membrane fouling has a direct effect upon the permeate flux and/or the system pressure differential, which comes to require higher power consumption, more frequent cleaning procedures, and therefore, reduce the membrane lifetime and raise the system operating overall cost [12–14].

Although researchers have been making a great effort to understand fouling and to develop techniques to reduce it, this phenomenon has not been completely elucidated yet [12]. Studies indicate that parameters related to the membrane characteristics (pore size, roughness, hydrophobicity, material, and superficial charge), of the feed (effluent nature, pollutant concentration, and toxicity) and of the sludge (mixed liquor volatile suspended solids (MLVSS) concentration, viscosity, temperature, floc size, and hydrophobicity), and related to the operational conditions (flux, transmembrane pressure, aeration, SRT) contribute, to some degree, to the membrane fouling in the MBRs [14–16]. Among these variables, several authors have presented results indicating positive and relevant relations between the presence of soluble microbial products (SMP) and extracellular polymeric substances (EPS) and membrane fouling rates [13,16–20].

The SMP are defined as compounds produced by micro-organisms found dispersedly in the mixed liquid after having been released during the metabolism and/or cellular lysis. The EPS are complex mixtures of organic aggregates that form a hydrated gel matrix responsible for the micro-organism aggregation in biofilms and flocs [21]. However, despite the numerous studies on the influence of SMP and EPS in fouling, no conclusive result has so far been obtained because of the complexity nature of membrane fouling and EPS in MBRs [12]. Contradictory results are frequently found; this can be attributed to the differences among the reactor's and membrane's configuration, membrane material, type of effluent, operational conditions, and analytical methods applied.

The critical flux has been used as one of the most useful practical tools for evaluating the fouling potential in a MBR system. According to Field [22], the critical flux corresponds to the flux below which no flux decrease takes place with time, and above which fouling is observed. Therefore, the critical flux is the maximum flux in which there is still a balance between the particle and colloid deposition rate on the membrane surface due to the convective flux of permeate and the back-diffusion rate of these particles to the bulk solution due to shear and diffusive forces. However, the existence of subcritical fouling in complex systems, such as the MBRs, has already been proven [10,15,23,24]. Below the critical flux, since no particle accumulation occurs on the region of the membrane, fouling is mainly caused by the organic macromolecules such SMP and EPS, termed as non-settable fraction of the sludge [11]. Despite the fact that fouling rates measured during experiments are higher than the ones obtained in long duration experiments [15], the critical flux tests are relevant in indicating the flux above which the fouling becomes really severe and in serving as a tool for the comparison of the fouling propensity of different systems.

Thus, this study aimed at evaluating the fouling in a bench scale MBR used in the treatment of dairy wastewater with pretreatment based on screening and flotation by compressed air. The system was operated with three distinct SRT, 80, 60, and 25 d, having as objective the comparison of performances under different operational conditions and the definition of the best one. The fouling was evaluated in terms of the pressure increase rate, and the investigation of its causes was based on analysis of the SMP and EPS concentrations and the critical flux.

2. Methodology

2.1. Dairy industry effluent

The effluent fed into the MBR was originated from a large dairy industry located in the state of Minas Gerais, Brazil, which produces UHT milk, yoghurt, cheese, cream cheese, and *fromage frais*. The milk processing capacity of the industry is 800 m/d.

The effluent was collected at the effluent treatment plant of the industry after screening and flotation with compressed air. Six samples were collected throughout reactor operation. Approximately 150 L of the industrial effluent was collected each time and placed in 50 L gallons, which were stored in a cold chamber at 3℃ until the effluent was fed in the reactor.

2.2. Experimental apparatus

The bench membrane bioreactor and the membrane module used for performing the tests were built by the company *PAM Membranas Seletivas Ltda* (Rio de Janeiro, Brazil). The MBR had one submerged hollow fiber microfiltration membrane module (polyetherimide, average pore size of 0.5 μm, membrane area of 0.044 m, packing density of 500 m/m). The MBR consisted of three acrylic tanks (a 40 L feed storage tank, a 20 L total volume biological tank equipped with bottom air diffusers, and a 5 L storage tank for the permeate), a diaphragm pump used to promote both the microfiltration and the backwash, three-way solenoid valves, level sensors, needle valves for flow adjustment, rotameters to measure permeate, backwash, and air flows, pressure indicator and a skid with an electric panel for the automatic control of permeation and backwash operations (Fig. 1).

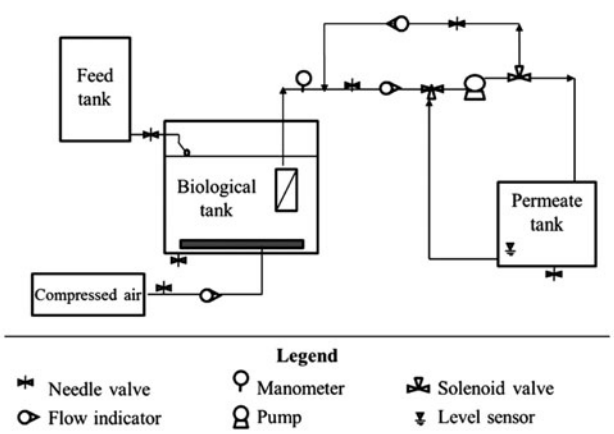

Fig. 1. Scheme of the MBR used.

The feed was stored in the feed tank and was transferred by gravity to the biological tank where the float valve controlled the level. This way, the feed flow was the same as the permeate one. The membrane module was positioned above the air diffusers in the biological tank, so that air bubbles could assist in fouling control.

2.3. Operational conditions

The MBR was initially inoculated with sludge from the activated sludge reactor of the industry providing the effluent. After an initial acclimatization stage of the micro-organisms to the conditions of the MBR and of the effluent, which lasted 29 d (similar to Farizoglu and Uzuner [5], who also studied MBR for dairy wastewater), the hydraulic retention time was established as 6 h (value defined having as basis the literature and previous tests) and SRT of 80, 60, and 25 d (obtained with different volumes of sludge wastage per day) were evaluated in order to determine the best operational condition. The mixed liquor volume in the MBRs was maintained at 4.45 L, so only a small part of the total biological tank was actually used. The operational flow was set in 0.80 L/h and the permeate flux was 18.2 L/h m^2. The membrane used had an average hydraulic permeability of 177 L/h m^2.bar. A 0.5 Nm/h air flow was used in the biological tank. The backwash was activated for 45 s at every 15 min of permeation, with a flow of 2.0 L/h. This frequency is similar to the one used by other authors [25,26].

The chemical cleanings of the membrane were performed when the operational pressure achieved the maximum value supplied by the pump (0.55–0.7 bar) or when tests of critical flux were going to be performed. The chemical cleanings were performed using a 200 ppm sodium hypochlorite solution for 20 min in an ultrasound bath. These procedure was similar to the one optimized by Amaral [27].

2.4. Process monitoring

During the MBR operation, the pressure was recorded daily. Also, feed and permeate COD concentrations were determined on a daily basis. Sludge aliquots were also collected for analysis of MLVSS three times a week. A greater volume of feed and permeate was collected weekly for analysis of apparent color (Spectrophotometer Hach DR2800), BOD, ammonia, and total phosphorus. All the analyses were performed in accordance with the recommendations of the Standard Methods for the Examination of Water and Wastewater [28].

2.5. SMP and EPS concentration

Although, theoretically, SMP refers only to soluble substances [10,12,29], in this study organic matter found both in soluble and colloidal form in mixed liquor was called SMP (or, as named elsewhere, free EPS). Moreover, substances aggregated to sludge suspended solids which could be removed by heating have been considered to be EPS (or bound EPS).

The extraction of SMP and EPS is shown in Fig. 2. First, the sludge was centrifuged at 4,500 rpm for 10 min and the supernatant liquid, mainly consisting of SMP, was collected. The solids resulting from the centrifugation were resuspended with 0.05% sodium chloride solution and heated at 80˚C for 10 min for EPS release [30]. This new suspension was centrifuged again and the supernatant liquid, constituting mainly of EPS, was collected.

A fraction of the supernatant SMP and EPS extractions was reserved (samples 1 and 3, respectively) and another fraction was filtered through standard AP40 filter (samples 2 and 4), so that the soluble and colloidal constituents could be characterized separately. The four samples were characterized in relation to carbohydrates [31], proteins [32], dissolved organic carbon (DOC) (TOC Analyzer Shimadzu TOC-V CPN), and transparent extracellular polymers (TEP) [33]. Soluble SMP concentrations corresponded to one obtained from sample 2; colloidal SMP, to concentrations obtained from sample 1 minus sample 2; soluble EPS, sample 4; and colloidal EPS, sample 3 minus sample 4.

The TEP are a class of organic substance present in fresh and salt waters that consists predominantly of large polysaccharide molecules [34]. Although the SMP and EPS are traditionally quantified only in terms of carbohydrates and proteins, in this study, TEP was also monitored because, according to De la Torre et al. [33], they may be an important component of the SMP and EPS, not quantified by the traditional Dubois method, which possibly presents good correlation with the fouling rate and can be the key to understanding this mechanism.

2.6. Critical flux measures

The critical flux was determined using the TMP-step method. Although the flux-step method is most commonly used [11], TPM-step can be applied efficiently [35]. The membrane module, previously chemically cleaned, as stated by Diez et al. [11], was submerged into the mixed liquor and the permeate flux was monitored at fixed values of pressure. For each value of pressure, the filtration time was 18 min, after which the pressure was increased by 0.05 bar. The critical pressure corresponded to the value in which there was a permeate flux reduction during the 18 min with constant pressure. The critical flux was the mean permeate flux observed for this critical pressure.

3. Results and discussion

3.1. System operation

Fig. 3 shows the MLVSS concentration, the feed to micro-organism rate (F/M) and the MBR organic load during the operations with SRT of 80, 60, and 25 d.

A decrease profile of the MLVSS concentration in the MBR can be observed throughout the operation. It is clear that, as expected, reducing the SRT results in biomass concentration reduction because it is related to the higher daily sludge disposal. The average MLVSS concentration obtained during the operations with SRT of 80, 60, and 25 d were of 8,278; 6,827 and 5,863 mg/L, respectively.

There was also a very large oscillation in the F/M rate. The F/M values oscillated between 0.36 and 2.57, and presented average values of 1.34, 0.99, and 1.64 for the operations with SRT of 80, 60, and 25 d,

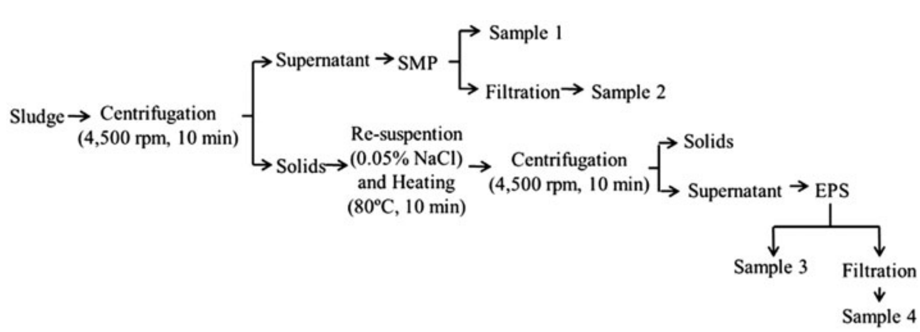

Fig. 2. Scheme of SMP and EPS extraction.

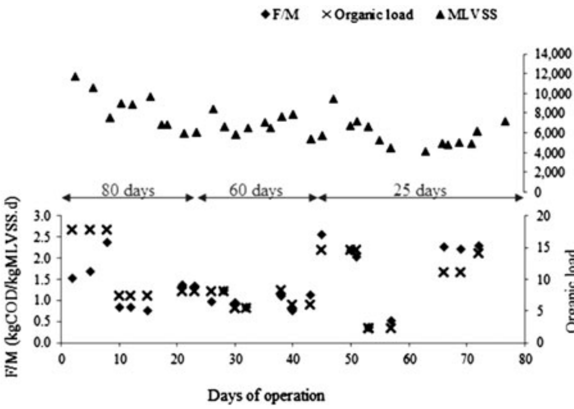

Fig. 3. MLVSS concentration, F/M rate and organic load in the MBR throughout the operation with SRT of 80, 60, and 25 d.

respectively. The oscillatory behavior happened due to variations in the MLVSS concentration and mainly due to alterations in organic matter concentration of the feed effluent. However, as will be shown next, this fluctuation was not harmful to the MBR operation, which kept its high efficiency during the entire period.

Fig. 4 presents MBR feed and permeate COD concentrations and the respective removal efficiencies.

The MBR presented high organic matter removal capacity, even when operating under unstable F/M conditions, which can be justified by the high biodegradability of the effluent [36].

A great stability provided by the MBR was also noticed since, even with great alterations in the feed quantity, justified by the fact that it was a real effluent from a dairy industry, the permeate COD

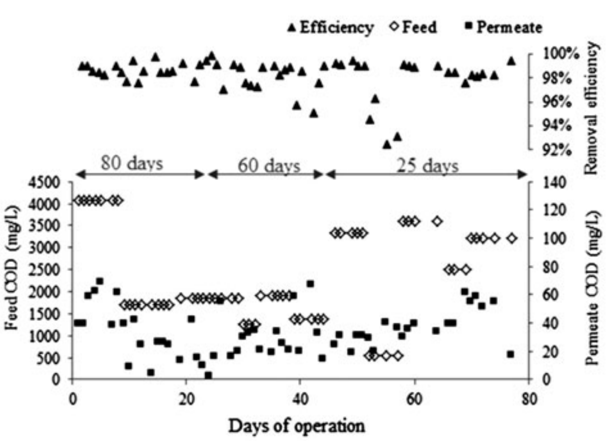

Fig. 4. MBR permeate and feed COD concentrations and removal efficiencies for the operations with SRT of 80, 60, and 25 d.

concentrations were kept low and approximately constant. It is important to notice that the decrease in COD removal efficiency observed between days 52 and 57 is related to an abrupt reduction in feed concentration, which reached 535 mg/L, and not to a decline in the permeate quality, since its concentrations were kept between 20 and 40 mg/L. This good result is related to the membrane retention contribution, which not only allows for the biomass retention, but also for retention of high molecular weight compounds that was not biodegraded [37].

Table 1 presents the average values of the main physicochemical parameters of MBR feed and permeate and the removal efficiencies. The average values were calculated based on the results obtained for three samples collected for each SRT.

In addition to high organic matter removal discussed earlier, an efficient removal of apparent color, ammonia, and phosphorus may also be noted. The ammonia removal was very high and similar for all three conditions evaluated. The high SRTs usually applied in MBRs contribute to the occurrence of nitrification in these systems, since nitrifying bacteria, which are responsible for the conversion of ammonium into nitrate, are notoriously slow growing micro-organisms [38]. The tropical climate and high temperatures in the country also contribute to the systematic occurrence of nitrification in biological treatment systems implemented in Brazil [39]. According to Cicek et al. [40], nitrification can be reduced when very low SRT, around 2 d, are used. However, for larger values, nitrification is not affected by SRT, which was observed here.

Average total phosphorus removals from 56 to 84% can also be noted. Traditionally, systems that are designed for phosphorus removal must contain aerobic and anaerobic chambers in series in order to select and provide the growth of phosphate accumulator's micro-organisms [39]. Farizoglu and collaborators [41] evaluated the nutrient removal in a jet loop reactor coupled with membrane treating whey and obtained phosphorus removal efficiencies between 65 and 85%, similar to those obtained in this study and higher than the ones expected for systems that have no specific configuration for advanced phosphorus removal (10–30%). According to the authors, these high values are due to a considerable uptake of phosphorus for cell synthesis since the biomass concentration in the reactor was high (between 6,000 and 14,500 mg/L), and to the precipitation of phosphate with the ions Ca^{2+} and Na^{+}, present in large amounts in the effluent concerned. Both reasons apply equally to this work.

According to Von Sperling [39], increase in SRT influences negatively in phosphorus removal. Since

Table 1
Average values of the main physicochemical parameters of feed and permeate and removal efficiencies of MBR

	Solids retention time								
	80 d			60 d			25 d		
Parameter	Feed	Perm.	Removal (%)	Feed	Perm.	Removal (%)	Feed	Perm.	Removal (%)
COD (mg/L)	2,607	34	98.7	1,650	30	98.1	2,648	36	97.9
BOD (mg/L)	1,513	6	99.6	819	2	99.7	1,471	3	99.8
Apparent color (Hu)	2,310	35	98.4	1,836	20	98.6	2,303	24	98.8
NH_3–N[a] (mg/L)	50	1	98.9	53	1	98.1	40	1	99.3
Phosphorus (mg/L)	33	14	60.4	45	7	84.4	24	11	56.3

[a]NH_3–N—ammonia nitrogen.

the main route for removing phosphorus from the system is through the disposal of sludge, elevate SRT leads to a reduction in the amount eliminated. However, Lesjean et al. [42] found no differences in the efficiency of phosphorus removal in MBRs operating with 15 and 26 d SRT. In this study, the effect of SRT in phosphorus removal could not be clearly noticed too.

3.2. Fouling investigation

Fig. 5 presents pressure and membrane operational permeability of the MBR. Permeability was calculated by dividing instant permeate flux by the measured pressure. The dotted lines mark the days when chemical cleaning of the membranes took place.

The fouling in the MBR was quite intense. The increase in pressure to maintain the permeate flow rate constant was quick and expressive, as a result highly frequent chemical cleaning was needed. In some instances, the cleaning frequency was of three times a week. The mean permeabilities and the standard deviations for SRT of 80, 60, and 25 d were 43 ± 30, 47 ± 33 and 44 ± 30 L/h m^2. bar, respectively. The standard deviations were quite elevated due to the high permeability decay rate and to the high chemical cleaning frequency necessary.

To investigate the cause of this intense fouling, the concentration of SMP and EPS and the critical flux were evaluated.

3.3. SMP and EPS production

Fig. 6 presents the concentration of soluble SMP, colloidal SMP, soluble EPS, and colloidal EPS in terms of carbohydrates for the three SRT evaluated.

The soluble and colloidal SMP remained reasonably stable during the operation with the three SRT, presenting average concentrations of 21 and 3 mg/L of carbohydrates, respectively. Because these concentrations can be considered relatively low, it is possible to say that the strong fouling observed cannot be

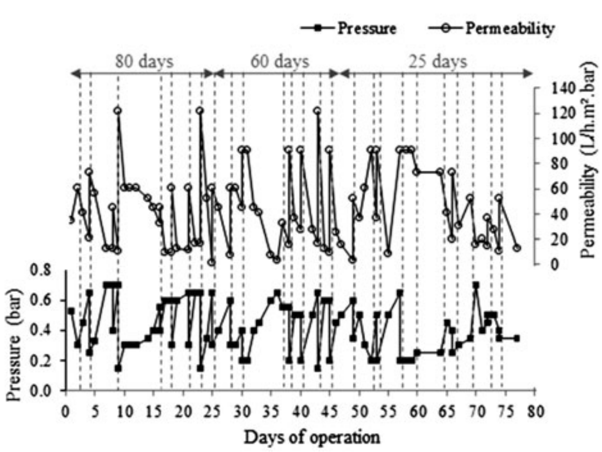

Fig. 5. The MBR permeability and pressure of operation.

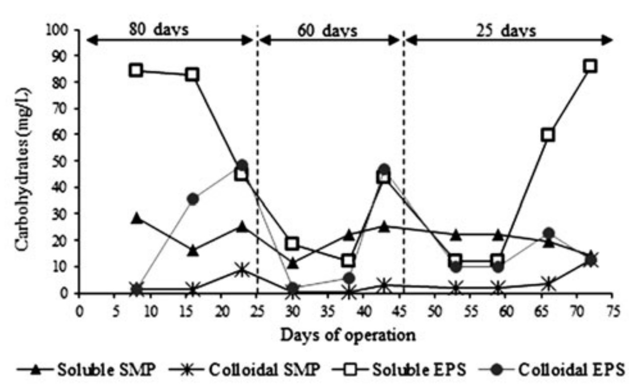

Fig. 6. Carbohydrate concentrations of soluble and colloidal SMP and EPS during the operations with SRT of 80, 60, and 25 d.

justified by the presence of the SMP. This conclusion contradicts results obtained by various authors [17,18,43], but corroborates the work of Kimura et al. [44], who were also not able to correlate fouling intensity and SMP when this class of substances was quantified in the traditional manner (through the concentration of carbohydrate and protein). Moreover, according to Li et al. [10], the SMP are crucial to the exponential resistance growth phase of subcritical filtration. In this study the MBR operated almost always above the critical flux (Fig. 11), and so SMP showed little influence on fouling.

Furthermore, during the operation with SRT of 80 d, the total EPS concentration remained approximately constant (average of 99 mg/L of carbohydrates), despite the soluble EPS having suffered a reduction and the colloidal, a rise. This behavior can be related to the increase in the cellular lysis, caused by the micro-organisms' long permanence in the reactor and their self-stabilization, resulting in a release of colloidal cells materials. On the other hand, the sludge seems to have developed the capacity to degrade the soluble EPS, which are more easily assimilated than the substances in the colloidal or suspense form.

The concentrations of both soluble and colloidal EPS decreased when the SRT was reduced to 60 d, although in the last sample under this condition both presented an increase. This increase may be related to a problem in the float valve that controls the level in the biological tank through effluent feed. On the 42nd day of operation, this valve had a blockage and the effluent entrance in the biological tank was interrupted for a while. As the permeation was continued, the volume of mixed liquor reduced. This situation of stress to the micro-organisms might have caused greater EPS production [12].

For SRT of 25 d, the colloidal EPS continued presenting low concentration, whereas the soluble EPS maintained their gradual raise. This is in accordance with results obtained by other authors, such as those of Ahmed et al. [45], who analyzed EPS only in the soluble form, and also observed an increase in $EPS_{carbohydrates}$ concentration with the reduction of the SRT from 60 to 20 d.

According to Sweity et al. [46], lower EPS concentration in the reactor reduces fouling rates at longer sludge ages. In addition, increasing SRT could enhance the development of slow growing micro-organisms that are able to consume polysaccharides and proteins as substrates and produce less biopolymers [47]. However, there appears to be an upper SRT limit above which EPS is again increased. Meng et al. [16] suggest that in SRT between 20 and 50 d the EPS production is lower, depending on the characteristics of the system. In this work, the total EPS concentration reduces when the SRT was lowered from 80 to 60 d, and later increase when it reached 25 d (average total EPS concentrations for the SRT of 80, 60, and 25 d were of 99, 43, and 52 $mg_{carbohydrates}/L$, respectively). Thus, the SRT which resulted in the lowest EPS concentration is close to the higher limit mentioned by Meng et al.

Fig. 7 presents the SMP and EPS results in terms of protein. The graphic in the top right-hand corner of the figure shows the same points of the samples referring to the soluble SMP, colloidal SMP, and colloidal EPS, but with the y axis scale reduced to allow for a better observation of the variations in low concentrations.

The colloidal SMP, as can be observed, was low and stable during the entire period with an average concentration of 5 $mg_{protein}/L$, independently of the applied SRT. The soluble SMP profile presented some decrease with the SRT reduction, with the average protein concentrations for the operations with SRT of 80, 60, and 25 d being of 23, 14, and 7 mg/L, respectively. This may indicate that the sludge could have acclimatized itself to these substances and developed the capacity to degrade them. Apparently, this acclimatization happens in a slow manner, demanding time superior to that necessary for the initial acclimatization of the micro-organisms to the effluent organic matter. Once again, no relation between SMP and fouling rate could be directly observed.

The colloidal EPS concentration variation profile in terms of proteins was similar to that observed for this fraction in terms of carbohydrate, so the same considerations can be made. The total EPS concentration variation between the three SRT evaluated was more

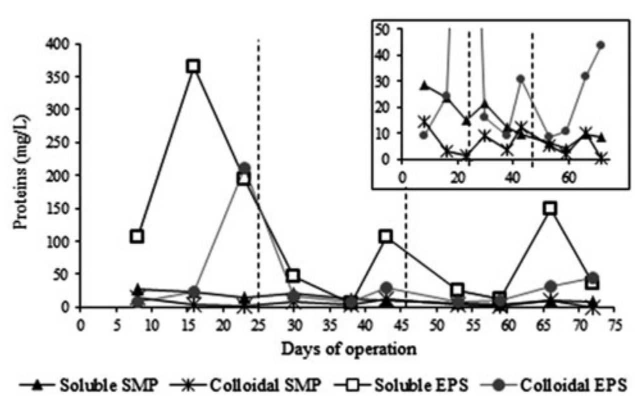

Fig. 7. Protein concentrations of soluble and colloidal SMP and EPS during the operations with SRT of 80, 60, and 25 d.

intense for proteins than for carbohydrates, which contradicts the results by Brookes et al. [48] and Malamis and Andreadakis [49], for whom the SRT effect is more expressive for the EPS in terms of carbohydrate.

Table 2 shows the average relationship between carbohydrate and protein (C/P) for SMP and EPS. It may be noted that there is more carbohydrates than proteins in SMP and more protein than carbohydrates in EPS. Since carbohydrates are products of microbial decay [13], one may note that SMP found in this study were mostly biomass-associated products (BAP) rather than substrate-utilization associated products (UAP). According to Lin et al. [12], polysaccharides are generally more biodegradable than proteins. As a result, proteins would attach on sludge flocs more readily to become part of EPS, which explains the lower C/P found in EPS.

Fig. 8 presents the concentrations of soluble and colloidal EPS and SMP in terms of TEP (transparent exopolymer particles).

The profile of EPS and SMP concentration in terms of TEP was completely different of the observed for the EPS and SMP in terms of carbohydrate and proteins, which might mean that this type of substances does not participate in the microbial metabolism in the same manner as carbohydrate and proteins [50].

The colloidal and soluble SMP and EPS in relation to DOC concentrations are shown in Fig. 9.

There was an increase in colloidal and soluble DOC EPS during operations with SRT of 80 d, which might be related to the cellular lysis stemming from the auto-stabilization of the sludge caused by the elevated time of permanence of the biomass in the MBR. However, after a reduction in the SRT to 60 d, the EPS concentration reduced and remained approximately stable. Only on day 43, correspondent to the last sample during the operation with SRT of 60 d, there was an elevation in the soluble EPS. This was also observed for carbohydrates and proteins.

As observed for proteins, the DOC concentration related to the soluble SMP continually decreased with the reduction in SRT, probably because the acclimatization effect discussed. The mean SMP_{DOC}

Table 2
Carbohydrate and protein ratio (C/P) for SMP and EPS during the operations with SRT of 80, 60, and 25 d

	SRT		
C/P	80 d	60 d	25 d
SMP	1.15	1.06	2.77
EPS	0.43	0.72	0.73

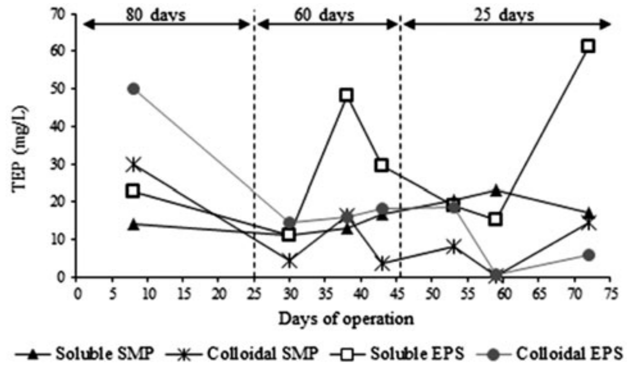

Fig. 8. TEP concentrations of the colloidal and soluble SMP and EPS during the operations with SRT of 80, 60, and 25 d.

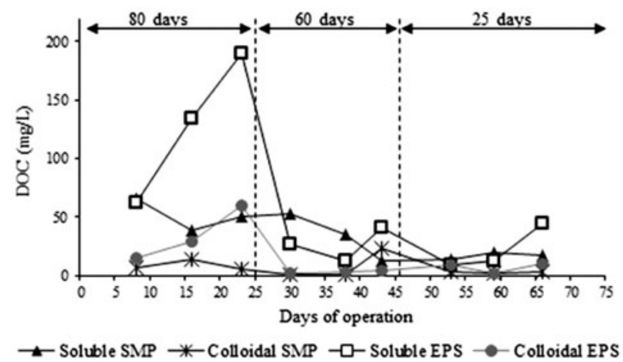

Fig. 9. The colloidal and soluble SMP and EPS DOC concentrations during the operations with SRT of 80, 60, and 25 d.

were 51, 33, and 17 mg/L for the operation with SRT of 80, 60, and 25 d, respectively.

Temporal fluctuation of DOC concentration was quite similar to those of carbohydrates and proteins. Concentrations of carbohydrates and proteins from SMP and EPS were transformed into DOC using the theoretical ratios of 0.4 $g_{DOC}/g_{carbohydrate}$ and 0.545 $g_{DOC}/g_{protein}$ suggested by Juang et al. [13]. It was observed that approximately 100% of EPS_{DOC} consists of carbohydrates and proteins. Moreover, on average, only 40% of SMP_{DOC} is carbohydrate and protein, which shows significant presence of other substances such as humic acids, aromatic substances, nucleic acids, lipids, and uronic acids [12,13].

Fig. 10 shows the concentrations of total EPS (soluble + colloidal) measured in terms of carbohydrates, proteins, TEP, and DOC together with the sludge permeability. The SMP are not shown in this figure because, as had been discussed before, their

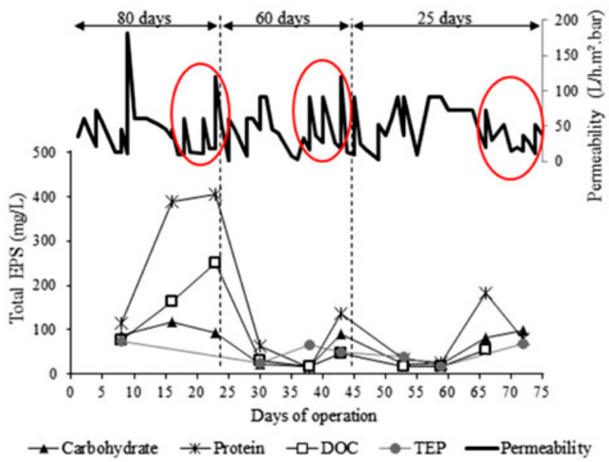

Fig. 10. Total EPS concentrations and MBR permeability during the operations with SRT of 80, 60, and 25 d.

concentrations were low and did not have enough variations, so it could not be related to the intense membrane fouling observed.

As can be noticed, between days 19 and 25, 37 and 45, and 66 and 74 (marked periods in Fig. 10) there was a more accentuated decrease in permeability and need for chemical cleanings. These same days coincide with periods in which there was an increase in carbohydrates, proteins, and DOC EPS concentrations, thus indicating the relationship between these substances and the membrane fouling. However, this is not the only relevant factor for fouling, since other points of rapid permeability loss were observed and could not be related to higher EPS production.

Probably, the high fouling rate observed is not only to the presence of EPS but also to cake layer formation, since the membrane aeration was not optimized in this study. The use of aeration helps reducing the fouling layer formation by improving the hydrodynamic conditions nearby the membrane, which increases shearing and decreases the accumulation of pollutants over the membrane surface. Using a 5 g/L yeast suspension, Chang and Fane [51] found that the permeate accumulated volume was increased by 30% when aeration was used compared to single flow filtration. Other authors [11,52] showed reduction in the fouling rate as superficial gas velocity increased.

In this study, no similarity between the profiles of fouling and TEP concentration was observed and the conclusions of De La Torre et al. [33] could not be confirmed.

3.4. Critical flux

Fig. 11 presents the operational flux and the critical flux measurements performed throughout the MBR operation.

The critical flux results oscillated between 21.5 and 9.6 L/h m^2. The critical flux presented a certain tendency to contrary alterations in relation to those observed for the EPS concentration: when the EPS concentration increased, the critical flux reduced, and vice-versa. However, this relationship is not linear and could not be confirmed in all the sampling points. The critical flux, as can be noticed, was reduced throughout the operation with the SRT of 80 d, which might be related to the increase in the colloidal EPS concentration observed during this period. With the decrease in the SRT to 60 d and consequent reduction in EPS concentration, there was an increase in the critical flux value, which reached an average value of 15.3 L/h m^2. Nevertheless, with the even greater reduction in SRT to 25 d and new increase in EPS, especially in the colloidal form, the critical flux fell again, averaging 12.1 L/h m^2 in the period.

According to the literature, the critical flux is one of the parameters that most influences the fouling [53]. The established flux value of operation was of 18.2 L/h m^2, above almost all the critical fluxes measured. The bioflocs deposited on membrane surface above the critical flux can act as a secondary membrane that, despite causing an increase in cake filtration resistance, has a beneficial effect by screening out material that would otherwise cause pore blockage and have a high fouling impact. As colloidal materials are more difficult to remove, some authors suggest operating above the critical flux, so that some particles act as filter-aid making easier to remove the colloidal

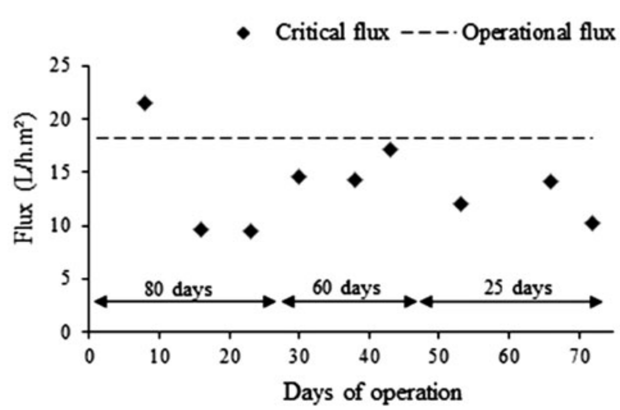

Fig. 11. Operational flux and critical flux during the operations with SRT of 80, 60, and 25 d.

matter [11]. However, in this study, operation above the critical flux caused great permeate flux decay. Observing Fig. 5, one can see that the period of lowest fouling (days 9–15) also corresponds to the only instance that the operational flux was below the critical flux.

This way, having as basis the EPS and SMP quantification results and the critical flux measurements, the 60-d SRT is chosen as the most adequate for the system. It was observed that the critical flux reached its highest average value under such condition. Besides that, maintaining the biomass for long periods of time in the reactor caused an increase in the EPS concentration. This also took place with the SRT of 25 d.

4. Conclusions

Based on this study, the MBR was shown to be a system which can be applied to the treatment of dairy industry effluent considering the high efficiency in COD, apparent color and nutrients removal. The stability in the organic matter removal provided by this type of system was also verified because the permeate always presented excellent quality, despite the great variations in the pollutant concentration of the feed and in the organic load received by the MBR. However, the fast increase in the operational pressure and the decrease in the observed permeability indicated intense fouling.

The SRT that presented lower EPS concentration among the evaluated ones was that of 60 d, having been selected as the most adequate as a consequence. Higher SRT may result in micro-organisms' death and lysis, resulting in intracellular polymeric material release. On the other hand, the SMP presented a decreasing profile during the operations with SRT of 80, 60, and 25 d, which can be related to the micro-organisms' acclimatization to these substances and to the development of the capacity to degrade them. The results show that this sludge acclimatization to the SMP requires a longer period than that of the initial acclimatization of the micro-organisms to the MBR and effluent conditions.

Because of no relation between colloidal or soluble SMP and fouling could be observed, it was also concluded that, for the system in question, the presence of these is not a preponderant factor for the membrane fouling. Only the EPS were shown to influence fouling to some degree. However, other variables might also influence fouling.

The fact that the operational flux was above the critical flux for most of the time justifies the intense fouling observed. On the other hand, the critical flux results seem to inversely mirror the EPS ones, that is, when the EPS concentration increases, the critical flux reduces.

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References

[1] B. Sarkar, P. Chakrabarti, A. Vijaykumar, V. Kale, Wastewater treatment in dairy industries—Possibility of reuse, Desalination 195 (2006) 141–152.

[2] M. Vourch, B. Balannec, B. Chaufer, G. Dorange, Nanofiltration and reverse osmosis of model process waters fromthe dairy industry to produce water for reuse, Desalination 172 (2005) 245–256.

[3] M. Perle, S. Kimchie, G. Shelef, Some biochemical aspects of the anaerobic degradation of dairy wastewater, Water Res. 29 (1995) 1549–1554.

[4] L.H. Andrade, F.D.S. Mendes, N. Cerqueira, J.C.A. Espíndola, M.C.S. Amaral, Molecular weight distribution in a membrane bioreactor for dairy effluent treatment, Eng. Sanit. Ambient. 19 (2014) 325–334.

[5] B. Farizoglu, S. Uzuner, The investigation of dairy industry wastewater treatment in a biological high performance membrane system, Biochem. Eng. J. 57 (2011) 46–54.

[6] F. Carta-Escobar, J. Pereda-Marín, P. Álvarez-Mateos, F. Romero-Guzmán, M. Durán-Barrantes, F. Barriga-Mateos, Aerobic purification of dairy wastewater in continuous regime, Biochem. Eng. J. 21 (2004) 183–191.

[7] M. Cammarota, D. Freire, A review on hydrolytic enzymes in the treatment of wastewater with high oil and grease content, Bioresour. Technol. 97 (2006) 2195–2210.

[8] T.-H. Bae, T.-M. Tak, Interpretation of fouling characteristics of ultrafiltration membranes during the filtration of membrane bioreactor mixed liquor, J. Membr. Sci. 264 (2005) 151–160.

[9] M. Bernhard, J. Müller, T.P. Knepper, Biodegradation of persistent polar pollutants in wastewater: Comparison of an optimised lab-scale membrane bioreactor and activated sludge treatment, Water Res. 40 (2006) 3419–3428.

[10] J. Li, X. Zhang, F. Cheng, Y. Liu, New insights into membrane fouling in submerged MBR under subcritical flux condition, Bioresour. Technol. 137 (2013) 404–408.

[11] V. Diez, D. Ezquerra, J. Cabezas, A. García, C. Ramos, A modified method for evaluation of critical flux, fouling rate and *in situ* determination of resistance and compressibility in MBR under different fouling conditions, J. Membr. Sci. 453 (2014) 1–11.

[12] H. Lin, M. Zhang, F. Wang, F. Meng, B.-Q. Liao, H. Hong, J. Chen, W. Gao, A critical review of extracellular polymeric substances (EPSs) in membrane bioreactors: Characteristics, roles in membrane fouling and control strategies, J. Membr. Sci. 460 (2014) 110–125.

[13] L.-C. Juang, D.-H. Tseng, Y.-M. Chen, G.U. Semblante, S.-J. You, The effect soluble microbial products (SMP) on the quality and fouling potential of MBR effluent, Desalination 326 (2013) 96–102.

[14] F. Meng, S.-R. Chae, A. Drews, M. Kraume, H.-S. Shin, F. Yang, Recent advances in membrane bioreactors (MBRs): Membrane fouling and membrane material, Water Res. 43 (2009) 1489–1512.

[15] P. Le-Clech, V. Chen, T.A. Fane, Fouling in membrane bioreactors used in wastewater treatment, J. Membr. Sci. 284 (2006) 17–53.

[16] F. Meng, H. Zhang, F. Yang, Y. Li, J. Xiao, X. Zhang, Effect of filamentous bacteria on membrane fouling in submerged membrane bioreactor, J. Membr. Sci. 272 (2006) 161–168.

[17] A. Drews, M. Vocks, U. Bracklow, V. Iversen, M. Kraume, Does fouling in MBRs depend on SMP? Desalination 231 (2008) 141–149.

[18] Z. Wang, Z. Wu, S. Tang, Extracellular polymeric substances (EPS) properties and their effects on membrane fouling in a submerged membrane bioreactor, Water Res. 43 (2009) 2504–2512.

[19] H. Luna, B. Baêta, S. Aquino, M.R. Susa, EPS and SMP dynamics at different heights of a submerged anaerobic membrane bioreactor (SAMBR), Process Biochem. 49 (2014) 2241–2248.

[20] A. Santos, W. Ma, S.J. Judd, Membrane bioreactors: Two decades of research and implementation, Desalination 273 (2011) 148–154.

[21] N. Janga, X. Ren, G. Kim, C. Ahn, J. Cho, I.S. Kim, Characteristics of soluble microbial products and extracellular polymeric substances in the membrane bioreactor for water reuse, Desalination 202 (2007) 90–98.

[22] R. Field, D. Wu, J. Howell, B. Gupta, Critical flux concept for microfiltration fouling, J. Membr. Sci. 100 (1995) 259–272.

[23] G. Guglielmi, D.P. Saroj, D. Chiarani, G. Andreottola, Sub-critical fouling in a membrane bioreactor for municipal wastewater treatment: Experimental investigation and mathematical modelling, Water Res. 41 (2007) 3903–3914.

[24] A. Pollice, A. Brookes, B. Jefferson, S. Judd, Sub-critical flux fouling in membrane bioreactors—A review of recent literature, Desalination 174 (2005) 221–230.

[25] P. Artiga, E. Ficara, F. Malpei, J. Garrido, R. Méndez, Treatment of two industrial wastewaters in a submerged membrane bioreactor, Desalination 179 (2005) 161–169.

[26] M. Matošić, M. Vuković, M. Čurlin, I. Mijatović, Fouling of a hollow fibre submerged membrane during longterm filtration of activated sludge, Desalination 219 (2008) 57–65.

[27] M.C.S. Amaral, *Tratamento de efluente do branqueamento de pasta celulósica empregando sistema de microfiltração conjugado com biorreator a membrana* (Treatment of Pulp Bleaching Effluent Employing Microfiltration Coupled with Membrane Bioreactor), PhD thesis, Federal University of Minas Gerais, Belo Horizonte, 2009.

[28] APPA, WEF, Standard Methods for the Examination of Water and Wastewater, twenty-first ed., American Public Health Association, Washington, DC, 2005.

[29] Y. Tian, L. Chen, S. Zhang, S. Zhang, A systematic study of soluble microbial products and their fouling impacts in membrane bioreactors, Chem. Eng. J. 168 (2011) 1093–1102.

[30] J. Morgan, C. Forster, L. Evison, A comparative study of the nature of biopolymers extracted from anaerobic and activated sludges, Water Res. 24 (1990) 743–750.

[31] M. Dubois, K.A. Gilles, J.K. Hamilton, P. Rebers, F. Smith, Colorimetric method for determination of sugars and related substances, Anal. Chem. 28 (1956) 350–356.

[32] O.H. Lowry, N.J. Rosebrough, A.L. Farr, R.J. Randall, Protein measurement with the Folin phenol reagent, J. Biol. Chem. 193 (1951) 265–275.

[33] T. De la Torre, B. Lesjean, A. Drews, M. Kraume, Monitoring of transparent exopolymer particles (TEP) in a membrane bioreactor (MBR) and correlation with other fouling indicators, Water Sci. Technol. 58 (2008) 1903–1909.

[34] S.H. Arruda Fatibello, A.A. Henriques Vieira, O. Fatibello-Filho, A rapid spectrophotometric method for the determination of transparent exopolymer particles (TEP) in freshwater, Talanta 62 (2004) 81–85.

[35] S. Liang, T. Zhao, J. Zhang, F. Sun, C. Liu, L. Song, Determination of fouling-related critical flux in self-forming dynamic membrane bioreactors: Interference of membrane compressibility, J. Membr. Sci. 390-391 (2012) 113–120.

[36] W. Janczukowicz, M. Zieliński, M. Dębowski, Biodegradability evaluation of dairy effluents originated in selected sections of dairy production, Bioresour. Technol. 99 (2008) 4199–4205.

[37] L. Andrade, G. Motta, M. Amaral, Treatment of dairy wastewater with a membrane bioreactor, Braz. J. Chem. Eng. 30 (2013) 759–770.

[38] S. Judd, The MBR Book. Principles and Applications of Membrane Bioreactors in Water and Wastewater Treatment, Elsevier, Oxford, 2006.

[39] M. Von Sperling, Lodos Ativados (Activated sludge). Princípios do Tratamento Biológico de Águas Residuárias (Principles of Biological Wastewater Treatment), Segrac, Belo Horizonte, 2005.

[40] N. Cicek, J. Macomber, J. Davel, M. Suidan, J. Audic, P. Genestet, Effect of solids retention time on the performance and biological characteristics of a membrane bioreactor, Water Sci. Technol. 43 (2001) 43–50.

[41] B. Farizoglu, B. Keskinler, E. Yildiz, A. Nuhoglu, Simultaneous removal of C, N, P from cheese whey by jet loop membrane bioreactor (JLMBR), J. Hazard. Mater. 146 (2007) 399–407.

[42] B. Lesjean, R. Gnirss, C. Adam, Process configurations adapted to membrane bioreactors for enhanced biological phosphorous and nitrogen removal, Desalination 149 (2002) 217–224.

[43] N. Fallah, B. Bonakdarpour, B. Nasernejad, M. Alavi Moghadam, Long-term operation of submerged membrane bioreactor (MBR) for the treatment of synthetic wastewater containing styrene as volatile organic compound (VOC): Effect of hydraulic retention time (HRT), J. Hazard. Mater. 178 (2010) 718–724.

[44] K. Kimura, T. Naruse, Y. Watanabe, Changes in characteristics of soluble microbial products in membrane bioreactors associated with different solid retention times: Relation to membrane fouling, Water Res. 43 (2009) 1033–1039.

[45] Z. Ahmed, J. Cho, B.-R. Lim, K.-G. Song, K.-H. Ahn, Effects of sludge retention time on membrane fouling and microbial community structure in a membrane bioreactor, J. Membr. Sci. 287 (2007) 211–218.

[46] A. Sweity, W. Ying, M.S. Ali-Shtayeh, F. Yang, A. Bick, G. Oron, M. Herzberg, Relation between EPS adherence, viscoelastic properties, and MBR operation: Biofouling study with QCM-D, Water Res. 45 (2011) 6430–6440.

[47] A. Massé, M. Spérandio, C. Cabassud, Comparison of sludge characteristics and performance of a submerged membrane bioreactor and an activated sludge process at high solids retention time, Water Res. 40 (2006) 2405–2415.

[48] S.A.J. Brookes, E. Reid, E. Germain, S. Smith, H. Alvarez, P. Le Clech, T. Stephenson, E. Turra, B. Jefferson, Characterization and impact of biomass foulants in membrane bioreactors, in: Proceedings of Fifth International Membrane Science and Technology Conference, Sydney, 2003.

[49] S. Malamis, A. Andreadakis, Fractionation of proteins and carbohydrates of extracellular polymeric substances in a membrane bioreactor system, Bioresour. Technol. 100 (2009) 3350–3357.

[50] L.H. Andrade, F.D.S. Mendes, J.C. Espindola, M.C.S. Amaral, Internal versus external submerged membrane bioreactor configurations for dairy wastewater treatment, Desalin. Wat. Treat. 52 (2014) 2920–2932.

[51] S. Chang, A. Fane, The effect of fibre diameter on filtration and flux distribution—Relevance to submerged hollow fibre modules, J. Membr. Sci. 184 (2001) 221–231.

[52] I. Martin-Garcia, V. Monsalvo, M. Pidou, P. Le-Clech, S. Judd, E. McAdam, B. Jefferson, Impact of membrane configuration on fouling in anaerobic membrane bioreactors, J. Membr. Sci. 382 (2011) 41–49.

[53] P. Bacchin, P. Aimar, R.W. Field, Critical and sustainable fluxes: Theory, experiments and applications, J. Membr. Sci. 281 (2006) 42–69.