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Influence of EPS and MLSS concentrations on mixed liquor physical parameters of two membrane bioreactors

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ABSTRACT

This work focuses on the comparison of two bench-scale membrane bioreactors (MBRs) using different flat sheet membranes (microfiltration [MF-MBR] and ultrafiltration [UF-MBR]) working for 170 days, without sludge extraction, with the aim of studying the influence of the concentration of extracellular polymeric substances (EPS) and mixed liquor suspended solids (MLSS) on settleability, viscosity, particle size and filterability. A statistical study was performed to identify the strength and direction of the correlation between MLSS, EPS and the sludge properties were studied. Sludge settleability behaved worse when the concentrations of MLSS and bound EPS increased. Nevertheless, this parameter improved with an increase in soluble EPS in the MF-MBR, and no influence was found with respect to soluble EPS in the UF-MBR. While viscosity increased when MLSS and bound EPS increased, being more evident in the MF-MBR, soluble EPS behaved in the opposite way. The mean particle size increased in the two MBRs until the concentration of MLSS reached approximately 6 g/L. Afterwards, the mean particle size remained steady for the MF-MBR and decreased for the UF-MBR. A suitable filterability was obtained for both MBRs and decreased as MLSS increased. No correlation between filterability and EPS was found.

Keywords: Extracellular polymeric substances; Membrane bioreactor; Microfiltration; Mixed liquor suspended solids; Ultrafiltration

1. Introduction

Membrane bioreactors (MBR) have become an alternative to conventional activated sludge (CAS) plants for municipal and industrial wastewater treatment. This is due to certain advantages, such as the high retention of total suspended solids which means better treated water quality, higher biomass concentration, small footprint, good stability and easier control/operation than CAS. MBR integrates membrane filtration modules into the biological reactor replacing the secondary clarification in the CAS and operating with mixed liquor suspended solids (MLSS) concentrations of up to 20 g/L [1].

However, membrane fouling is one of the major problems in terms of energy consumption, maintenance and operational costs in the widespread application of MBRs [2]. This problem is basically caused by the adsorption/deposition of extracellular polymeric substances (EPS), soluble or bound onto sludge flocs, or membrane pores, due to pore obstruction by colloids and/or by the deposition of a sludge film onto the membrane surface [3].

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Several studies have been carried out to study membrane fouling, taking into account membrane types, plant configuration, permeate quality, etc. [4], but few have been focused on the biological process applied in membrane separation processes. Several works have demonstrated the close relationship between the EPS found in mixed liquor and membrane fouling, concluding that during the filtration process, specific resistance increases when the EPS concentration increases [5]. Nevertheless, there is little research on the relationship between EPS and the parameters associated to mixed liquor, such as viscosity, settleability, etc.

Viscosity is one of the most widely studied parameters in biological sludges, and it has been said that it is closely related to MLSS of mixed liquor, with a considerable effect on membrane fouling [6]. It is well known that an increase in MLSS causes an increase in viscosity [7–9] and reduces oxygen transfer efficiency [10], generating severe membrane fouling. Nevertheless, the specific values of viscosity differ from one study to the next, because they depend (apart from MLSS concentrations) on different parameters and measurement conditions, such as temperature, floc size, the equipment used, the spindle speed and so on [11]. Viscosities of less than 5 mPa s have been found at MLSS concentrations of between 5 and 15 g/L [8] and viscosities of up to 400 mPa s at MLSS concentrations of between 15 and 25 [9].

With regard to settleability, it has been reported that by replacing the settling tank with a membrane filtration device, the MBR can provide a stable effluent and excellent performance independent of filamentous bulking or other phenomena affecting sludge-settling characteristics [12]. The performance of the MBR was not affected by filamentous bulking due to the efficient separation ability of the membrane, but a rapid increase in filamentous bacteria was observed during the operation of the MBR with complete biomass retention conditions aggravating the fouling [13]. It is thought that the sludge bulks when the sludge volumetric index (SVI) is higher than 150 mL/g MLSS [14]. However, values of SVI higher than 500 mL/g MLSS have been found in MBRs working at short sludge ages, which is not recommended for this kind of technology [15].

In MBR systems, the aggregates made up of microorganisms and the formations of high flocs are very important for the effective separation of suspended biomass and permeate by means of membranes. The distribution of floc size in biological sludges is very widespread, and large differences have been found not only in studies carried out for sludges obtained from MBRs and CAS, but also in many studies carried out on different MBRs [2]. In MBRs, flocs sizes tend to be smaller than in CAS due to the driving force caused by the suction in the filtration process and to aeration. This causes the fractionation of the flocs and the release of EPS, which contributes to membrane fouling [16]. Much research has been carried out with the aim of studying the influence of MLSS concentrations [17,18], aeration intensity [19], etc. on floc size distribution.

On one hand, an economical advantage of a MBR is the good filterability of the activated sludge. On the other hand, many studies have been carried out to find out what causes membrane fouling, as it is well known to be the main disadvantage of MBR technology. The following sludge properties influence the filtration process and dewatering properties: MLSS concentrations [20,21], viscosity [6,7], particle size distribution [17] and EPS [22,23]. As far as MLSS concentrations are concerned, when related to membrane fouling contradictions were apparent in that reportedly an increase in MLSS concentrations both diminishes [20] and increases [21] membrane fouling. With respect to viscosity, authors agree with the conclusion that an increase of MLSS concentrations causes an increase in viscosity and a decrease in filterability [6,7]. Floc size distribution has also been studied because it too influences membrane fouling [17]. According to the Carman–Kozeny equation, the specific resistance of sludge cake is inversely proportional to the particle diameter; in other words, membrane fouling increases as floc size decreases. As regards EPS, some authors have stated that filterability improves when the EPS increase, due to the fact that sludges with higher extractable EPS concentrations have a tendency to form larger flocs [22]. However, other authors have stated just the contrary, that is, better filterability was found at lower concentrations of EPS [23].

At the same time, it must be remembered that there is no optimal value of MLSS concentrations to operate at in MBR technology. It would therefore be interesting to evaluate the influence of MLSS concentrations on the behaviour of certain parameters associated to mixed liquor. Itonaga et al. [24] found that the critical SS concentration differs greatly between a hybrid and a conventional MBR with values of 17 and 10 g/L, respectively. Other authors recommended operating at between 10 and 12 g/L in order to minimise membrane fouling and to save energy [25]. Rosenberger et al. [26] carried out detailed research on the influence of MLSS concentrations on membrane fouling, finding that an increase in MLSS concentrations diminished membrane fouling working up to 6 g/L. At MLSS concentrations higher than 15 g/L membrane fouling was abrupt. They consequently concluded that the best interval of

MLSS concentration for operating the MBR was between 8 and 12 g/L.

The experimental set-up of the current work has been used to carry out other experiments and the results were previously published [27]. The research was dealt with the comparison of the two MBRs, in order to study the influence of the influent organic load on membrane fouling, removal efficiency and biomass growth.

This work focuses on the comparison between the two bench-scale MBRs using different flat sheet membranes to study the influence of the EPS and MLSS concentrations on settleability, viscosity, particle size and filterability. Additionally, a statistical study has been carried out to identify the strength and direction of the correlation between MLSS, EPS and the studied sludge properties.

2. Materials and methods

2.1. Experimental set-up

Two 25 L bench-scale MBRs with microfiltration (MF-MBR) and ultrafiltration (UF-MBR) submerged membranes were constructed and fed with synthetic water. The scheme of the experimental set-up (the two MBRs are identical) is shown in Fig. 1. The average pore size of the MF membrane (Kubota) and the UF membrane (Toray) was 0.4 and 0.08 μm, respectively. The filtration area of both membrane modules was 0.116 m^2.

The nominal flow rate was 17 LMH and permeate was extracted using a pump (negative pressure), while the biomass rejected by the membranes remained in the reactor. A constant air flow was pumped into each reactor in order to diminish membrane fouling, maintain the biomass suspended and provide oxygen to micro-organisms.

The plant was automatically controlled by means of a programmable logic controller (PLC) as shown in Fig. 1, in order to constantly control and measure the principal variables of operation: transmembrane pressure (TMP), dissolved oxygen (DO), flux and temperature. These values were recorded every 30 s and shown online in the display. Both MBRs worked with an on/off cycle of 8/2 min.

Synthetic wastewater was used in order to control the influent into the MBRs with an average value of total chemical oxygen demand (COD) of around 650 mg/L. Peptone and meat extract were used as carbon sources; urea and K_2HPO_4 were used as nitrogen and phosphorous sources, respectively.

The systems were operated for 170 days without sludge extraction (with the exception of the sludge taken out for analysis). During the experimental period, the permeate flow rate was increased from 9 to 22 LMH and the hydraulic retention time decreased from 25 to 10 h.

Different chemical protocols for membrane cleaning were used in the experimentation: maintenance cleaning with sodium hypochlorite (500 mg/L) to remove organic fouling and intensive cleaning with sodium hypochlorite (5,000 g/L) and oxalic acid (1,000 mg/L) to remove inorganic fouling.

2.2. Analytical methods

According to standard methods, MLSS were analysed twice a week and settleability was determined using an Imhoff cone [28]. The sludge volumetric index (SVI) and diluted SVI (DSVI) are other parameters generally used to characterise the settleability capacity of mixed liquor. However, in the research at hand, neither SVI has been determined, due to its dependence on MLSS concentrations (SVI is defined as the ratio between settleability in mL/L and MLSS concentration in mg/L), nor has DSVI, because it is not a real parameter (MBR always work at high MLSS concentrations).

Viscosity was evaluated by means of a rotational viscosimeter SMART SERIES, Model L (Fungilab).

Particle size was measured with a laser diffraction particle size analyser COULTER (LS 230) using Franhoufer's optical method.

Filterability was determined by the volume of permeate obtained after filtering 50 mL of mixed liquor for 5 min (according to the *Manual of Operation of the KUBOTA MBR Pilot Plant* [29]).

The determination of COD was carried out once a week using Hach Lange kits (Germany).

According to Domínguez et al., soluble and bound EPS were extracted using a cationic exchange resin [30].

2.3. Statistical analysis

Statistical analysis was carried out to identify the correlation between SS, bound EPS and soluble EPS with the physical parameters associated to the mixed liquor. A bivariate linear correlation and the statistical package for the social science software, 17th version, were used. Pearson's product momentum correlation coefficient (r_p) was used for the direction and strength estimations between the two parameters. The Pearson coefficient is always between −1 and +1 (perfect correlation); 0 means absence of relationship. Correlations were considered statistically significant at a 95% confidence interval ($p < 0.05$).

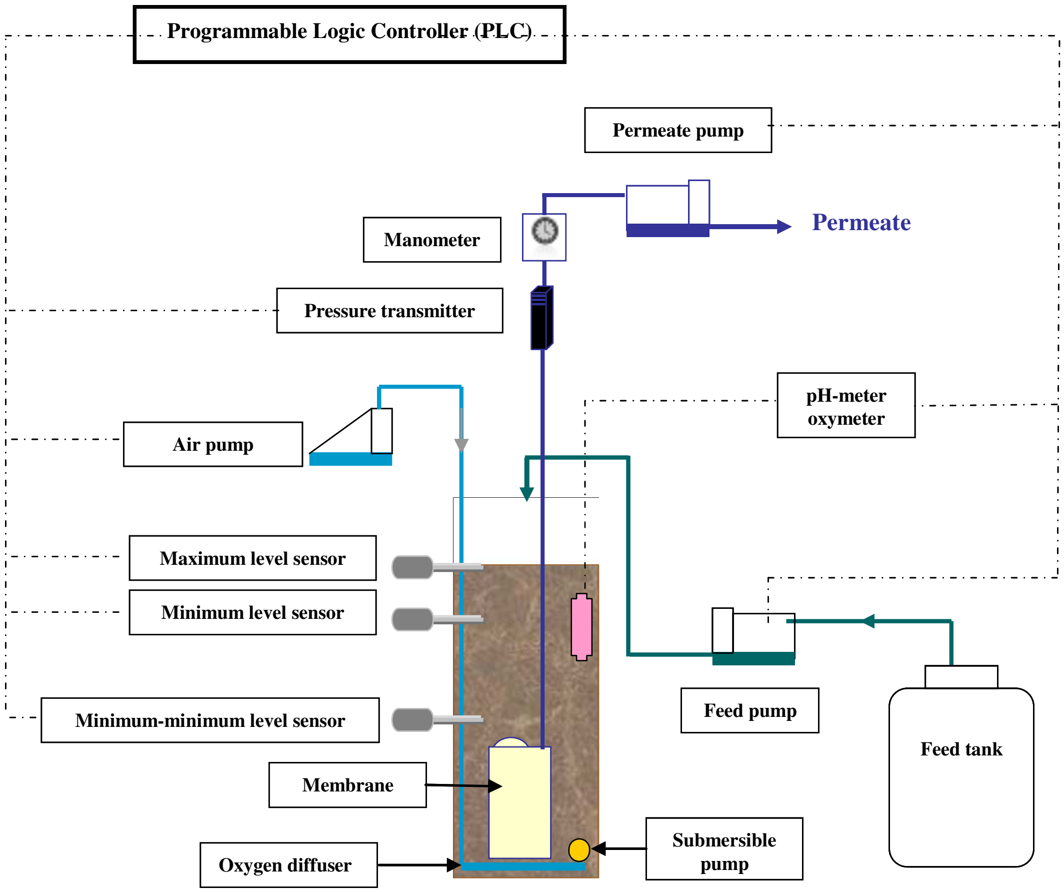

Fig. 1. Scheme of the membrane bioreactor.

3. Results and discussion

The evolution of settleability, viscosity, particle size and filterability was studied in the operation period for the two MBRs. Moreover, the influence of the concentrations of MLSS and EPS on these parameters was evaluated.

Aerobic sludge from a full-scale wastewater treatment plant in Alicante, with a MLSS concentration of 0.5 g/L was used in the two MBRs. Fig. 2 shows the biomass growth up to 15 and 8.5 g/L in the MF-MBR and the UF-MBR, respectively.

As can be seen, after each increase in flux, MLSS concentrations were stabilized reaching a steady state until the next flux increases. However, the evolution of the biomass in the MBRs was different, particularly at the end of the experimental period. Apart from the different membranes used in the two MBRs, the concentration of MLSS differed basically because the UF-MBR showed problems with the oxygen diffuser preventing a suitable supply of DO into the bulk. The lack of a constant supply of DO worsened the characteristics of the mixed liquor in the UF-MBR, and as a consequence, the biomass could not develop as fast as in the MF-MBR.

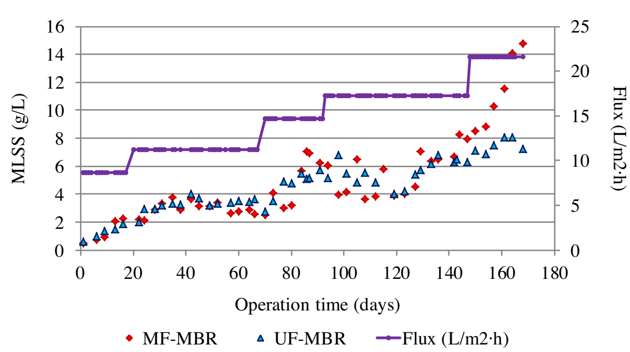

Fig. 2. Permeate flux and MLSS concentrations during the experimental period for the two MBRs.

Additionally, the inappropriate supply of oxygen caused a sudden increase in the TMP in this MBR, which clearly meant that membranes were severely fouled. Fig. 3 shows the filtration performance over almost 6 months of operation for MF-MBR and UF-MBR.

As can be seen, the permeate flux was increased gradually from 9 to 22 LMH in both reactors, to avoid severe membrane fouling. Nevertheless, the UF-MBR had to be cleaned more frequently than the MF-MBR in the same operation period, due to the previously mentioned aeration problems in the UF-MBR.

Physical cleaning by means of filtration/relaxation mode and maintenance of chemical cleaning were not enough to keep the membranes of UF-MBR working over long periods. As a result, two intensive chemical cleanings took place around the 70th and 125th days of operation. Additionally, a cleaning assay with NaOCl associated to sonication was carried out in the diffuser of this reactor, reaching the initial and necessary air flow rates for biomass growth and membrane cleaning. All of this corroborates how significant the aeration process in MBR technology is.

On the other hand, the operation of the MF-MBR was very stable showing only three filtration cycles (operation time between two chemical cleanings) during the whole period.

3.1. Influence of MLSS and EPS concentrations on settleability

Because of the lack of suitability of using conventional decantation processes at certain MLSS concentrations, the study of settleability was carried out in the two MBRs with a view to find out the concentration levels of MLSS from which membrane separation is more suitable. The settled volume of sludge obtained per litre of mixed liquor usually increased when MLSS concentrations increased, that is, settleability worsened. It is precisely for this reason that MLSS concentrations are limited in CAS systems, because an increase in MLSS concentrations implies a considerable increase in the dimensions of the secondary decantation system.

In the research at hand, as previously mentioned, an increase in MLSS concentrations worsened settleability (Fig. 4).

Settleability was suitable only at very low MLSS concentrations (less than 2 mg/L) in the two MBRs. This parameter worsened earlier in the UF-MBR than in the MF-MBR, the former reaching high volumes of

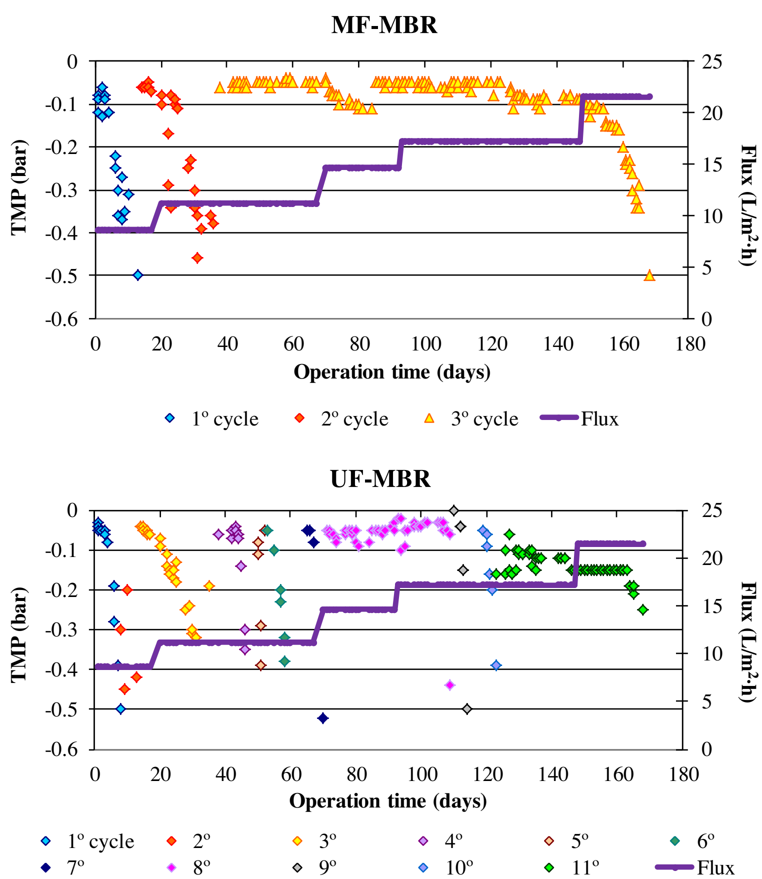

Fig. 3. TMP and flux variation in MF-MBR and UF-MBR during the experimental period.

settled sludge (over 800 mL) per litre of mixed liquor from 2 g/L of MLSS concentration.

The MF-MBR showed better settleability than the UF-MBR not only at low MLSS concentrations, but also at higher MLSS concentrations. This was probably caused by the worsening of the sludge quality in the UF-MBR due to the problems with the oxygen diffuser, as was previously mentioned. DO concentrations in the bulk solution around the flocs must be high enough to maintain an aerobic floc interior. Since, oxygen moves into the floc by diffusion, its bulk concentration needs to be high enough to reach the floc centres before becoming depleted.

On the other hand, no further sedimentation took place from 3 to 6 g MLSS/L in the MF-MBR and the UF-MBR, respectively (Fig. 4). From these data, it can be inferred that for values of MLSS concentrations higher than 3 g/L, the use of a conventional decanter is not recommended for separating the supernatant from the sludge. On the other hand, when a physical separation by membranes is used (e.g. as occurs in MBR technology), MLSS concentrations are not a limiting factor. It is very well known that the operation at high MLSS concentrations in MBRs has many advantages with regard to the reduction of bioreactor volume and membrane fouling (MLSS between 8 and 12 g/L).

In order to evaluate the effect of the F/M ratio on sludge settleability, these two parameters were plotted as shown in Fig. 5. At high F/M ratios, from 0.4 kg COD/kg VSS·d, settleability improved when the F/M ratio increased for the two MBRs. Higher F/M ratios correspond to the first part of the experimentation, where the concentration of MLSS was still low (lower than 3–4 g/L). However, the F/M ratio had not any effect on settleability between 0.1 and 0.35 kg COD/kg VSS·d. In this case, the influence of MLSS concentrations was probably more significant than the F/M ratio. This phenomenon is specifically interesting for MBR technology, because it works at very low F/M ratios.

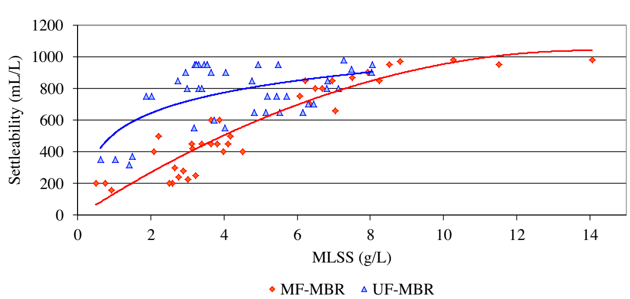

Fig. 4. Influence of MLSS concentrations on settleability in the two MBRs.

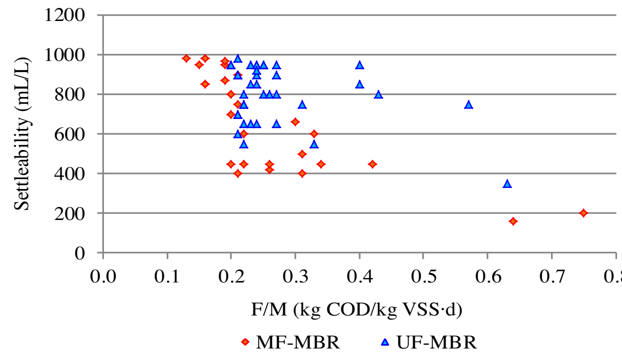

Fig. 5. Influence of F/M ratio on settleability in the two MBRs.

The behaviour of settleability of the studied sludges during the experimental period was associated to the presence of EPS, as they are considered to be bioflocculating agents of the aggregation on individual micro-organisms into biological flocs [31]. Fig. 6 shows the influence of bound EPS on settleability for the two MBRs.

The similarity of the trends observed for settleability as regards bound EPS (Fig. 6) and MLSS is evident (Fig. 4). Settleability behaved worse at higher concentrations of bound EPS, because it is well known that the increase in MLSS concentrations causes an increase in bound EPS. Larger floc sizes can be found when there is a high concentration of bound EPS, because they are the key components for the aggregation of micro-organisms, small particles, colloids, etc. as was previously stated. As a result, they provide highly hydrated gel matrix with low density, and this makes the settleability of the sludge difficult. In this case, at high MLSS concentrations, the density of the flocs probably had a greater influence on settleability than floc size, worsening the settleability process.

For soluble EPS (data not shown), no influence was found on settleability. Their concentration remained practically steady throughout the experimental period and was much lower than that obtained for bound EPS. Therefore, it can be inferred that sludge settleability is basically influenced by MLSS concentrations and indirectly by bound EPS, because they make up the flocs in mixed liquor.

3.2. Influence of MLSS and EPS concentrations on viscosity.

The analysis of viscosity is very complex because its measurement depends on many factors such as temperature, floc size, the equipment used, the spindle speed, etc. and the values obtained can only be

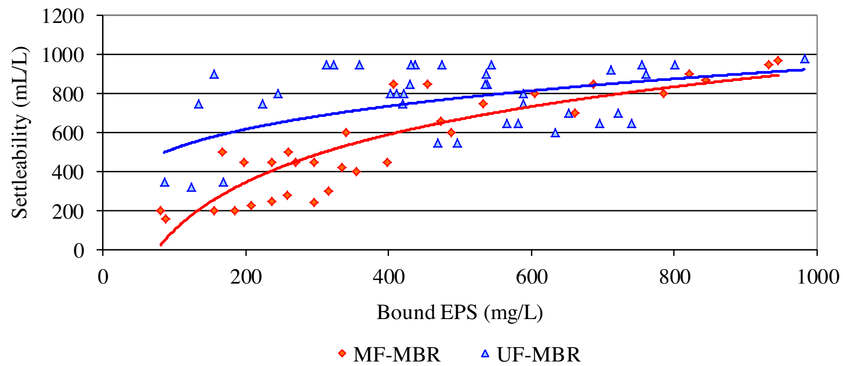

Fig. 6. Evolution of settleability with respect to bound EPS for the two MBRs.

compared with other studies if the measurement conditions are the same [11]. Consequently, its analysis has been divided into two parts, and the spindle speed had to be changed due to the increase in the concentration of MLSS.

Fig. 7 shows the behaviour of viscosity in relation to MLSS concentrations of up to 9 g/L at a spindle speed of 100 rpm.

As can be observed, viscosity rose when MLSS concentrations increased in the two MBRs, although in the MF-MBR it was more evident. This analysis showed an empirical exponential correlation between MLSS concentrations and viscosity, with correlation coefficients of 0.82 and 0.71 for the MF-MBR and the UF-MBR, respectively. Eqs. (1) and (2) represent these correlations for the MF-MBR and the UF-MBR, respectively.

$$\mu_{\text{MF-MBR}} = 1.11 \cdot \exp^{0.159 \cdot \text{MLSS}} \tag{1}$$

$$\mu_{\text{UF-MBR}} = 1.45 \cdot \exp^{0.102 \cdot \text{MLSS}} \tag{2}$$

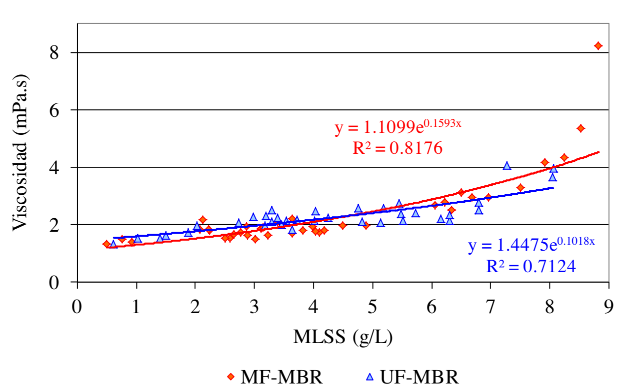

Fig. 7. Effect of MLSS concentration (up to 9 g/L) on viscosity for the two MBRs.

The MF-MBR equation provided good fits for the experimental data at lower concentrations of MLSS, as can be seen in Fig. 7. If the concentration of MLSS is zero, the viscosity obtained corresponds to the viscosity of the permeate. In this case, the calculated viscosities are 1.11 and 1.45 mPa s for the MF-MBR and the UF-MBR, respectively. This result is in good agreement with the experimentally obtained values (1.27–1.30 mPa s) in both cases.

Liu et al. [32] determined a similar correlation between the viscosity of mixed liquor (2–7 mPa s) and its MLSS concentration (1–20 g/L), likewise giving the following exponential equation:

$$\mu = 1.61 \cdot \exp^{0.07 \cdot \text{MLSS}} \tag{3}$$

The analysis of viscosity for MLSS concentrations higher than 10 g/L was carried out only for the MF-MBR, because the spindle speed had to be changed to 1 rpm due to the high viscosities of the mixed liquor.

In this case, viscosity increased from approximately 200 to 500 mPa s when MLSS concentrations increased from 10 to 14 g/L. This trend was also adjusted to an exponential equation, but it will not be taken into account due to the few experimental results obtained.

In experiments, the abrupt change of viscosity could be visually verified; at 8 g/L of MLSS concentration the sample was totally liquid and at 10 g/L it acquired a consistent aspect.

The results obtained in the experiments carried out agree with those obtained previously by other authors and referred to in the literature [8,9]. In this way, Khongnakorn et al. [8] measured viscosities of between 2 and 5 mPa s approximately at MLSS concentrations of between 5 and 15 g/L. Trussell et al. [9] operated a MBR at high MLSS concentrations (between 10 and 28 g/L), and found viscosities of between 50 and 400 mPa s.

On the other hand, there is a MLSS critical concentration that is defined as the MLSS concentration from which the viscosity of mixed liquor increases exponentially, and below which the viscosity shows low values, increasing slightly with the increase of MLSS concentrations [24]. In the study at hand, it has been considered that the MLSS critical concentration in the MF-MBR is around 9 g/L. In the UF-MBR, it could not be determined because there was no sudden change in viscosity at the MLSS concentrations during operation.

With respect to EPS, viscosity increased when bound EPS increased. In the MF-MBR, this was more evident as occurs with the correlation of viscosity and MLSS concentrations. The viscosity of many substances such as proteins and carbohydrates is responsible for the high viscosity found in the mixed liquor; therefore, the increase in the concentration of EPS (mainly made up of these compounds) causes the increase in viscosity in the mixed liquor [33].

The concentration of soluble EPS diminished when MLSS concentrations increased (the opposite trend to bound EPS). In the MF-MBR, viscosity decreased when soluble EPS increased and in the UF-MBR, viscosity remained steady for the analysed concentrations of soluble EPS. Therefore, it can be supposed that the viscosity of the supernatant decreased with the increase of MLSS concentrations because supernatant is associated to soluble EPS. However, the measurement of viscosity was carried out in the mixed liquor; therefore, the increase in viscosity with MLSS concentrations is attributed to the increase in bound EPS and not to the decrease in soluble EPS. Additionally, it is important to highlight that the concentrations of bound EPS were always much higher than those obtained for soluble EPS.

In conclusion, bound EPS were responsible for the increase in viscosity showing the same trend of viscosity with respect to MLSS concentrations as observed by Meng et al. [34]. These authors correlated diverse variables with membrane fouling in a MBR and demonstrated that total EPS (basically associated to bound EPS) had the greatest influence on the viscosity of the mixed liquor.

3.3. Influence of MLSS and EPS concentrations on particle size.

Particle size was measured throughout the experimental period with the aim of studying its evolution in relation to MLSS and EPS concentrations. Fig. 8 shows particle size distribution for different MLSS concentrations in the MF-MBR. The range of particle size measured was between 0.375 and 2000 μm.

It can be seen that the curves go from left to right with the medium particle size increasing as MLSS concentrations increasing from 3.3 to 7 g/L. In MF-MBR, particle sizes of 31.5 and 45.8 μm were found (highest probability of 6%) at MLSS concentrations of 3.3 and 5.5 g/L. From 7 g/L, the curves are superimposed indicating that the most likely particle size to be found is 73 μm (5.3–5.8% probability). The mean particle size for MLSS concentrations between 7 and 14 g/L was between 56 and 63 μm; for 9 and 10 g/L of MLSS concentration the figure showed a bimodal particle size distribution with particles higher than 400 μm, which is why the highest mean particle sizes were found at these MLSS concentrations.

Fig. 9 shows the evolution of particle size with respect to MLSS concentrations in the two MBRs for the whole experimental period.

As can be seen, there are three well-defined regions for each MBR:

- *Region I*: mean particle size remains constant for MLSS concentrations of between 2–4 and 2–5 g/L approximately in the MF-MBR and the UF-MBR, respectively.
- *Region II*: mean particle size increases for MLSS concentrations of between 4–7 and 5–7 g/L approximately in the MF-MBR and the UF-MBR, respectively.
- *Region III*: mean particle size remains steady in the MF-MBR and decreases in the UF-MBR up to the final concentrations (15 and 8 g/L, respectively).

The main difference in the evolution of the mean particle size with respect to MLSS is observed after 7 g/L, showing a decrease in UF-MBR and remaining constant in MF-MBR. Massé et al. [18] studied the influence of MLSS concentrations on certain operational variables, and determined that particle size decreased while MLSS concentrations increased, as occurred in the third region of the UF-MBR. The decrease in floc size as sludge age increases (sludge age is directly related to MLSS concentrations), is associated to a reduction in the concentration of bound EPS per gram of MLSS. At high sludge ages, there is friction among the particles due to an increase in cellular density with floc break occurring, which reduced their size. Moreover, the decrease in floc size has been attributed to an increase in aeration intensity [19].

With regard to the behaviour of particle size in MF-MBR, it can be seen that it remained constant at around 60 μm. It has been determined that the decrease in or the maintenance of floc size in some kinds of sludges is associated to floc compacting. Khongnakorn et al. [8] worked with a MBR at high

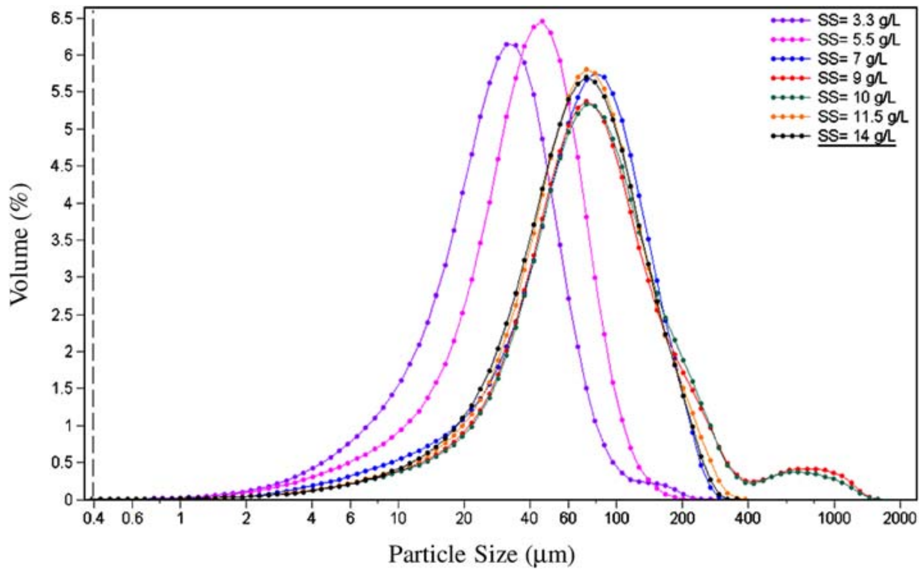

Fig. 8. Particle size distribution at different MLSS concentrations in the MF-MBR.

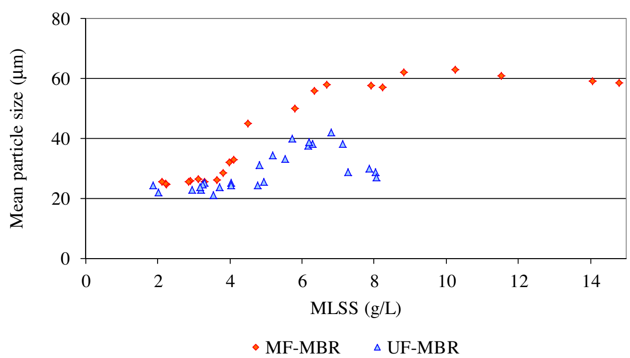

Fig. 9. Effect of MLSS concentrations on mean particle size in the two MBRs.

sludge ages, and they determined that in the final 100 days (MLSS concentrations of between 10 and 16 g/L), the mean particle size remained steady at around 70 µm.

On the other hand, particle size between both reactors was compared, showing that in the MF-MBR it was always higher than in the UF-MBR, for MLSS concentrations higher than 4 g/L: between 25 and 63 µm for the MF-MBR and between 21 and 42 µm for the UF-MBR. Floc size basically depends on the aeration intensity and the linear velocity in the recirculation process. These phenomena cause shear stress and larger flocs could break up. In the current study, the aeration intensity was similar, but there were problems with the aeration diffusor in the UF-MBR as it was previously described. Therefore, the differences of particle size between both MBRs at the same MLSS concentration could be attributed to the characteristics of mixed liquor that were influenced by the operational conditions. Several authors have studied the evolution of floc sizes under different membranes and operational conditions; in general, the mean floc size found in MBRs working with MF membranes are generally bigger than those obtained in UF MBRs. Bae and Tak [17] carried out a floc characterisation operating a MBR with UF membranes, and found floc sizes between 10 and 40 µm and a mean particle size of 25 µm. However, MBR systems working with MF membranes have showed floc sizes in an interval of 40–160 µm [18] and 40–140 µm [35] at different MLSS concentrations.

The influence of EPS on size particle was also studied (Fig. 10).

In the case of bound EPS, it was observed that they followed the same trend as that obtained for particle size in relation to MLSS concentration (Fig. 9).

This can be explained by the fact that one function of EPS is to bond bacteria in the flocs or biofilms, allowing for the formation of a protection barrier and the retention of water inside the flocs [31].

As can be seen, there are two well-defined regions for the MF-MBR: from 170 to 600 mg/L of bound EPS, where mean particle sizes are below 40 µm and at EPS concentrations higher than 600 mg/L, where particle sizes are around 60 µm.

For the UF-MBR, mean particle sizes below 24 µm were found at a bound EPS concentration of below 330 mg/L. However, at higher bound EPS concentrations, the mean particle size was between 20 and 40 µm.

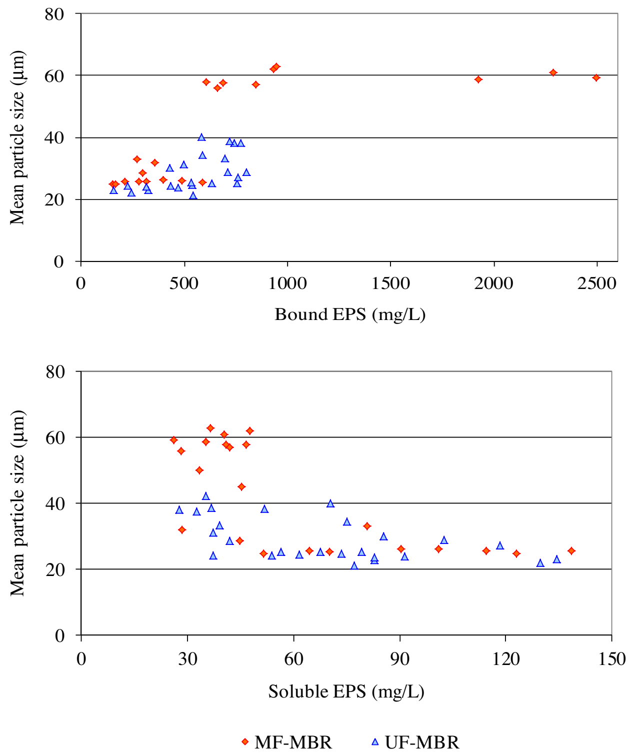

Fig. 10. Effect of bound and soluble EPS concentrations on mean particle size in both MBRs.

A decreasing trend of mean particle size with an increase in the concentration of soluble EPS for the MF-MBR was observed. Mean particle size had approximately the same value (between 20 and 30 µm) for 50 mg/L of soluble EPS, as occurs in this MBR at low concentrations of bound EPS. The highest particle size (around 60 µm) was found when the concentration of soluble EPS was low.

In the UF-MBR, there is a slight decrease in mean particle size while the concentration of soluble EPS increased. However, this was negligible with respect to the MF-MBR.

To summarise, it can be said that in the MF-MBR, mean particle sizes were much higher than in the UF-MBR at higher MLSS concentrations. Moreover, larger particle sizes were found at the highest concentrations of bound EPS and at the smallest concentrations of soluble EPS in both MBRs (more evident in the MF-MBR). As occurred with the previous parameters studied, the trend of bound EPS is always very different from that found for soluble EPS. It is logical that the influence of bound EPS is much stronger in all cases on the parameters studied (settleability, viscosity and particle size), because they appear at higher concentrations and form flocs which are closely associated to the phenomenon discussed.

3.4. Influence of MLSS and EPS concentrations on filterability.

Filterability is the capacity of activated sludge to be filtered through a membrane and is closely related to cake resistance and MLSS concentrations. Fig. 11 shows that the permeate volume decreased with an increase in the concentration of MLSS, hence decreasing filterability. This is due to the fast formation and deposition of the sludge layer onto the membrane at high MLSS concentrations, while at low MLSS concentrations, the pore blockage by colloids and small particles takes place more progressively [16].

Differences on filterability of the two MBRs are negligible. These minimal dissimilarities could be explained by the difference of the membranes, as it was previously discussed, because the two reactors are isolated systems. Moreover, a decreasing trend was found for the two systems, as can be seen in Fig. 11.

In the control of filterability, the maximum and minimum volumes of permeate obtained in the MF-MBR for 5 min were 32 and 11 mL, respectively; in the UF-MBR, they were 39 and 15 mL, respectively. According to the *Manual of Operation of the KUBOTA MBR Pilot Plant* [29], if the filtrated volume is higher than 10 mL, filterability is considered to be good. If it is less than 5 mL, it is considered to be bad. In the case at hand, filterability was good in the two MBRs, although it is not appropriate to operate at such high MLSS concentrations as those reached by the MF-MBR.

In conclusion, an increase in MLSS concentrations causes a decrease in filterability. As a result, according to this, analysis operating at MLSS concentrations lower than 12 g/L is recommended, as filterability decreased only 50% of its maximum value. As previously stated, the critical SS concentration in the MF-MBR was 9 g/L. Therefore, if operating with the MF-

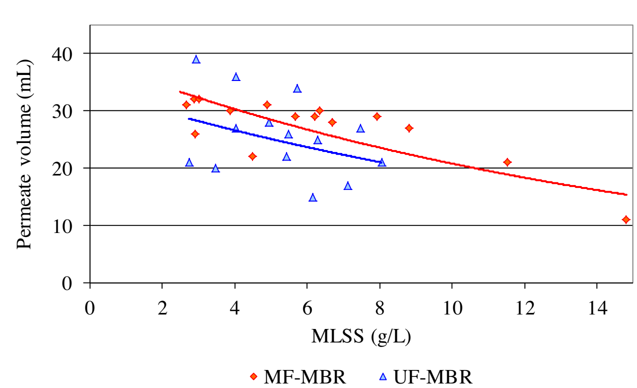

Fig. 11. Effect of MLSS concentrations on filterability for the two MBRs.

MBR, 9 g/L is the recommended concentration. In the UF-MBR, it is possible to work without an abrupt increase in viscosity or a sudden decrease in filterability when working at SS concentrations of up to 8 g/L.

The influence of MLSS concentrations on filterability associated to membrane fouling has been widely studied, and the conclusions have proven contradictory [20,21]. Le-Clech et al. [20] reported that an increase in MLSS concentrations lowered membrane fouling. However, Chang and Kim [21] found that an increase in MLSS concentrations increased membrane fouling. The results at hand agree with those of Le-Clech et al. [20]. Rosenberger et al. [26] recommend working at MLSS concentrations of between 8 and 12 g/L, as there was no increase in membrane fouling. This study also recommends operating at below 12 g/L and from this point, filterability decreased 50% of its maximum value.

Moreover, filterability is not only influenced by MLSS concentrations, but also by other parameters such as viscosity, particle size distribution, EPS and so on. In this study, viscosity increased and filterability decreased with an increase in MLSS concentrations. Therefore, this behaviour could be related to viscosity. Yeom et al. [6] concluded that an increase in viscosity increases membrane fouling, that is, a decrease in filterability was found. They reported that at a MLSS concentration higher than 15 mg/L, viscosity suddenly increased causing a decrease in filterability.

With regard to floc size distribution, although according to the Carman–Kozeny equation membrane fouling increases while floc size decreases, in the present study the interval of floc size measured did not contribute to any great extent to the decrease in filterability. It has been demonstrated that a particle with a diameter of less than 2 μm causes more membrane fouling than large particles, as smaller particles enter the membrane and the phenomenon of clogging and adsorption takes place [16]. Larger flocs only deposit onto membrane surfaces, which are removed by the aeration process. In the present study, large floc size was found in both MBRs (between 21 and 63 μm), which is recommended in this type of technology so as to prevent severe membrane fouling.

EPS was in some way related to filterability, but no clear relationship was found. It has been said in the literature that filterability improves with an increase in EPS, because sludges with higher extractable EPS concentrations have a tendency to form larger flocs [22]. However, other authors have stated the contrary, that is, at lower concentration of EPS, better filterability was found [23].

3.5. Correlation between MLSS, bound EPS and soluble EPS and the physical parameters associated to mixed liquor

In order to identify the strength and direction of the correlation between the two parameters, Pearson's coefficients (r_p) were calculated. Table 1 shows the correlation between MLSS concentrations and the studied parameters of mixed liquor.

As can be seen, settleability had a significant correlation at level 0.01 for the two MBRs, although in the MF-MBR, the correlation was stronger between MLSS and this parameter ($r_p = 0.896$). This high positive number indicates that an increase in MLSS concentrations causes an increase in the settled volume of sludge, that is, settleability worsens.

Viscosity was the parameter with the strongest correlation with MLSS in both MBRs, supported by the high values of r_p obtained (0.822 and 0.809 for the MF-MBR and the UF-MBR, respectively). It is well known that an increase in MLSS causes an increase in viscosity [7]. In MBR technology, it is not recommended to operate when the suspension has high viscosity because the permeate flow rate and the oxygen

Table 1
Correlation between MLSS concentrations and other parameters associated to the mixed liquor using Pearson's correlation coefficients

Parameters	MLSS (g/L)			
	MF-MBR		UF-MBR	
	r_p	p	r_p	p
Settleability (mL/L)	0.896**	0.000	0.455**	0.002
Viscosity (mPa s)	0.822**	0.000	0.809**	0.000
Particle size (μm)	0.839**	0.000	0.357	0.053
Filterability (mL)	−0.695**	0.006	−0.420	0.119

**Correlation is significant at level 0.01 (two-tailed).

transfer to micro-organisms decrease. Additionally, high viscosity causes less turbulence in the proximities of the membranes, thus increasing the possibility of the deposition of a larger quantity of particles with more fouling taking place [6].

With respect to particle size, the behaviour of the two MBRs differed in the last period as shown in Fig. 9. In the MF-MBR, particle size increased while MLSS increased, although at the end of the experiment MLSS remained steady. For this reason, a high positive value of r_p was found ($r_p = 0.839$). Nevertheless, due to the increase and the decrease in particle size during experiments no strong correlation was found between these parameters in the UF-MBR ($r_p = 0.357$). In spite of this, the correlation seems to show an increasing trend. Many studies, which have analysed the influence of certain variables on the behaviour of particle size, have obtained contradictory results. This means that the behaviour not only depends on MLSS concentrations [18], but also on other factors, such as sludge age.

Filterability decreased in both MBRs, while MLSS concentrations increased as shown in Fig. 11. For this reason, r_p values for both MBRs are negative. A stronger correlation between filterability and MLSS was found for the MF-MBR than for the UF-MBR. Filterability and MLSS concentrations are associated to membrane fouling [16]. It is obvious that an increase in membrane fouling causes a decrease in filterability. Therefore, in the research at hand, an increase in MLSS concentrations caused membrane fouling, although it is more evident in the MF-MBR, probably due to the higher concentrations of MLSS during operation.

In general, MLSS concentrations had a strong correlation with all sludge properties analysed in the MF-MBR (less with filterability). In the UF-MBR, the strongest correlation was found between MLSS concentrations and viscosity.

Table 2 shows Pearson's coefficients (r_p) obtained from the correlation between bound EPS, soluble EPS and the four parameters analysed.

First of all, it can be observed that the correlation is always stronger in the MF-MBR than in the UF-MBR (higher values) for bound and soluble EPS. In addition, all parameters showed an opposite trend when comparing the correlation between bound and soluble EPS. For example, the settled volume increased in both MBRs with an increase in EPS, but it increased as the soluble EPS decreased. Pearson's coefficients corroborate this behaviour showing the plus and minus signs for bound and soluble EPS, respectively. One of the functions of bound EPS is to join groups of bacteria generating larger flocs [31], which makes settleability difficult. Therefore, it is coherent to find similar behaviour in the correlation observed between MLSS and settleability ($r_p = 0.896$ and 0.455 for the MF-MBR and the UF-MBR, respectively), and bound EPS and settleability ($r_p = 0.740$ and 0.425 for MF-MBR and UF-MBR, respectively).

As regards viscosity, the coefficients showed high values in the correlation with bound EPS for both MBRs, as found in the correlation between viscosity and MLSS. Soluble EPS showed a weak correlation with viscosity. Dynamic viscosity is associated to different polymers, such as proteins, carbohydrates, etc. (EPS are mainly made up of these compounds). Therefore, an increase in the concentration of EPS causes an increase in viscosity [33]. As in the present study, much research has demonstrated that the accumulation of EPS in the MBR causes an increase in dynamic viscosity leading to a severe decline in membrane permeate flux [16].

Particle size was another factor influenced by EPS in the MF-MBR, increasing as bound EPS increased ($r_p = 0.692$) and soluble EPS decreased ($r_p = -0.712$). Nonetheless, the correlation between MLSS and particle size was stronger ($r_p = 0.839$) than that obtained

Table 2
Correlation between EPS and other parameters associated to the mixed liquor using Pearson's correlation coefficients

Parameters	Bound EPS (mg/L)				Soluble EPS (mg/L)			
	MF-MBR		UF-MBR		MF-MBR		UF-MBR	
	r_p	p	r_p	p	r_p	p	r_p	p
Settleability (mL/L)	0.74**	0.000	0.425**	0.009	−0.446**	0.008	−0.309	0.080
Viscosity (mPa.s)	0.807**	0.000	0.706**	0.000	−0.381*	0.026	−0.330	0.093
Particle size (μm)	0.692**	0.000	0.155	0.431	−0.712**	0.000	−0.248	0.232
Filterability (mL/L)	−0.478	0.080	−0.495	0.072	0.455	0.102	0.017	0.953

*Correlation is significant at level 0.05 (two-tailed).

**Correlation is significant at level 0.01 (two-tailed).

with EPS. It seems to be clear that there is a direct relationship between particle size and MLSS concentrations, and an indirect relationship with EPS. As previously explained, one of the functions of EPS (bound EPS in this case) is the formation of aggregation of bacterial cells in flocs, increasing their size [31].

On the other hand, soluble EPS decreased as particle size increased, but there is no direct relationship. This could be verified by means of the correlation between bound and soluble EPS. In the study at hand, bound EPS increased and soluble EPS decreased while MLSS concentrations increased (data not shown). Soluble EPS are basically defined as the polymers found in the supernatant, that is, those that are not bound to flocs. When MLSS concentrations increase, soluble EPS make up an increasing part of the flocs, diminishing their concentration in the supernatant and becoming bound EPS.

Filterability and EPS showed a weak correlation. However, it is interesting to highlight that filterability decreased (increased membrane fouling) as bound EPS increased. In this case, the impression is that bound EPS are responsible for membrane fouling in both MBRs. Much research has been carried out to study the influence of EPS on membrane fouling, but contradictory results have been obtained [5,36]. Geng and Hall [36] concluded that the accumulation of soluble EPS causes a decline in filterability. Li and Yang [37] demonstrated that soluble EPS are more related to flocculation and sedimentation, and not to membrane fouling. In any case, the characteristics and behaviour of EPS depend on many factors associated to the MBR system, such as influent characteristics [20], sludge age [38] and others.

To sum up, all parameters in the MF-MBR (except filterability) had a strong correlation with bound EPS. In the UF-MBR, the strongest correlation for bound EPS was found firstly with viscosity and secondly with settleability. In the case of soluble EPS, only the particle size showed a strong correlation in the MF-MBR. In the UF-MBR, no correlation was found between soluble EPS and all the sludge properties were analysed.

4. Conclusions

Settleability in both MBRs worsened as MLSS and bound EPS concentrations increased. Viscosity increased in both MBRs when MLSS and bound EPS increased, although this was more evident in the MF-MBR. The mean particle size increased in both MBRs up to MLSS concentrations of approximately 6 g/L. For higher concentrations, mean particle size remained steady for the MF-MBR and decreased for the UF-MBR. The highest mean floc sizes were found in both MBRs at higher bound EPS concentrations. Bound EPS showed a stronger influence on the physical parameters studied than soluble EPS. Suitable filterabilities were obtained in both MBRs and no correlation was found between filterability and EPS.

The main conclusions obtained from the statistical analysis carried out were that MLSS concentrations and bound EPS had a strong correlation with all sludge properties analysed in the MF-MBR (except filterability) and only with viscosity in the UF-MBR. All parameters showed the opposite trend when comparing the correlation between bound and soluble EPS.

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