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Treatment of refinery effluents by pilot membrane bioreactors: pollutants removal and fouling mechanism investigation

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ABSTRACT

The main purpose of this study is to evaluate the performance of a pilot-scale membrane bioreactor (MBR) in the treatment of effluent from a petroleum refinery plant focusing on the efficiency of organic matter and nutrient removal, and assessment and minimization of fouling. Two MBRs were assessed, one with flat sheet microfiltration membranes installed in the biological tank (8 m^3) (inside configuration) and another one with hollow fiber ultra-filtration membrane installed in the membrane tank (0.72 m^3) (outside configuration). Both MBRs share the same biological tank with HRT of 5.6 h and sludge age of 40 d. Performance of the MBRs was evaluated in terms of efficiency of organic matter (total organic carbon (TOC)) and nitrogen removal and membrane permeability. In order to assess fouling, resistance tests were performed, and soluble microbial products and extracellular polymeric substances concentrations were monitored, as was sludge filterability. As a fouling control strategy, MBR operation with operational flux lower than critical flux as assessed, and a permeability improver was used. Results showed that both MBRs had an average TOC and ammonia removal efficiency of 80 and 90%, respectively. The main contributor to fouling was the formation of cake on the surface of the membrane; the operation with operational flux lower than critical flux and the use of the permeability improver were shown to be good fouling control strategies.

Keywords: Membrane bioreactors; Refinery effluent; Fouling; SMP and EPS; Critical flux; Permeability improver

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1. Introduction

Petroleum refining processes require a high volume of water and thus generate a large amount of effluent. Usually, 246–340 L of water are required per crude oil barrel, generating an amount of effluent approximately 0.4–1.6 times the volume of oil processed [1]. In addition, to the thigh volume of effluent, a wide range of organic and inorganic compounds is also present. High costs of water collection and treatment and effluent discharge and, in some cases, even low water availability, along with increasingly restrictive environmental legislations and the pressure of the industry for sustainable development have prompted refineries to implement effluent reuse systems.

Treatment of such effluent usually requires a set of combinations of physical–chemical generally as pretreatment and biological processes [2]; those systems, however, do not allow the treated effluent to be reused, and therefore there is a demand for systems that generate water of higher quality. Membrane bioreactors (MBRs) have been widely used in the treatment of industrial effluent to remove organic matter and nutrients due to their better efficiency in removing pollutants when compared to conventional processes. Some advantages of MBR are: high efficiency in removing micropollutants, persistent organic pollutants, low sensibility to load variations, low sludge production, high sludge age, total removal of suspended solids, and others. However, membrane fouling still limits the use of such technology [3].

Membrane fouling is due to adsorption of solute molecules onto the membrane surface, obstruction of pores by suspended particles and deposit of suspended material onto the membrane surface, forming a cake [4]; it is influenced by several factors related to feed, membrane and operational conditions, and is determined by the propensity of the membrane to be incrusted with compounds of the liquid that deposit onto the membrane's internal and external structures. Fouling onto the membrane directly affects the permeate flux and/or the increase in differential pressure across the system, requiring more energy and demanding that the membrane is cleaned more often, and also decreasing the useful life of the membrane, and thus increasing operational costs. Therefore, monitoring and, especially, controlling fouling is critical for the technical and economic feasibility of MBRs for effluent treatment.

Some tests can be performed to characterize fouling, such as those for characterization and quantification of transport resistance of different types of fouling, and other tests to monitor fouling or propensity to fouling, such as measuring membrane permeability, sludge filterability, determining the concentration of compounds generated by bacteria, soluble microbial products (SMP), and extracellular polymeric substances (EPS), which some researchers consider the greatest responsible for membrane fouling in MBRs [5].

SMPs are compounds produced by micro-organisms found in the reaction liquid after being released during cellular metabolism and lysis. EPSs are complex mixtures of organic aggregates that form a hydrated gel matrix responsible for aggregating micro-organisms in flocs and biofilms [6]. Several authors have presented results indicating positive relations between the presence of SMPs and EPSs and membrane fouling rates [7]. However, despite the large number of studies on the influence of EPSs and SMPs on fouling, no conclusive results have been reached due to the complexity of the issues involved. Contradictory results are often found, which may be due to differences in reactor and membrane configurations, membrane material, type of effluent, operational conditions, and analytical methods used.

Filterability is an important parameter to evaluate sludge quality and potential for fouling [8]. This measurement, expressed in amount of permeate per unit of time, may directly impact fouling and plant productivity, although it is closely related to the sludge and not necessarily to the system, given that the tests are usually performed as a simple filtration. The geometry of the system tested is not always similar to that of the MBR, which may lead to apparently controversial conclusions. Several studies have shown the application of the filterability test to monitor fouling in MBRs [9].

Several strategies can be used to minimize membrane fouling in MBRs, such as sludge filterability control inside the MBR, use of coagulation agents or activated charcoal powder to improve sludge quality, improvement of MBR hydrodynamics to reduce the polarized layer near the membrane surface, and critical flux monitoring. The purpose of controlling such parameters is to improve operational conditions, making those MBRs technically and economically feasible to operate.

The critical flux is used as a quantitative parameter to determine the permeability of the membrane together with the activated sludge, combining effects of the characteristics of the membrane, the sludge, and the system's hydrodynamics [9], and may be used as a tool to control fouling, allowing the selection of the MBR's operational flux, considering that operating MBRs with a flux lower than the critical flux can lead to little or no fouling [10,11]. According to Field et al.

[12], the critical flux for microfiltration (MF) is that under which no decrease in flux is observed over time and above which there is fouling. The critical flux depends on the hydrodynamics of the process, membrane characteristics, operational conditions, and sludge properties [13]. Several techniques can be used to predict the critical flux, such as the inertial lift velocity, direct observation through the membrane, material balance of the components, and the flux-step method [10]. The occurrence of sub-critical fouling in complex systems, such MBRs, has been observed, and it is known that fouling rates measured during the experiments are always higher than those obtained in long-term experiments [10]; nevertheless, critical flux tests are an important indicator of the flux above which fouling becomes really severe, and it serve as tool for the comparison of propensity to fouling in several systems. Jiang et al. [14] determined the critical flux in a pilot-scale MBR and confirmed the validity of using critical flux to control fouling.

Some biopolymers have been developed to react with the biomass in MBRs, significantly reducing membrane fouling without modifying their surface. They usually have a cationic network that reacts with the biomass, and can be used as an operational tool to improve the sludge's microbiological conditions, ensure high and stable permeability, allow increased operational flow, reduce pressure differences across the membrane, reduce dispersion of fine particles in the medium, reduce cleaning frequency, and reduce SMP and EPS concentrations without damaging the biological treatment and oxygen transfer to the medium [15]. There is no data in literature about the use of flux improver in a single dosage as assessed and described in this study.

Wozniak [15] conducted a study in which a biopolymer (MPE30) was used at a concentration of 400 $\mathrm{mg\,L^{-1}}$ in a MBR to treat a leachate. Results showed an increased permeate flow and reduced pressure differences across the membrane after that dosage. The same authors assessed the use of biopolymer MPE50 in the effluent treatment plant of a food industry at a concentration of 600 $\mathrm{mg\,L^{-1}}$. MPE50 concentration was adjusted to the concentration of suspended solids, even ranging from 15,000 to 20,000 $\mathrm{mg\,L^{-1}}$, depending on sludge excess. In that study, the biopolymer was also shown to be an alternative for fouling control in MBRs.

Thus, the purpose of this study is to evaluate the performance of pilot-scale MBR in the treatment of effluent from a petroleum refinery plant focusing on efficiency of organic matter and nutrient removal and assessment and minimization of fouling. The importance of evaluating the fouling mechanism and control in a MBR-treating refinery wastewater is because the high fouling potential nature of this effluent due to high load variation and the presence of compounds that stimulate cell lysis of micro-organisms involved in biological processes.

2. Methodology

2.1. *Effluent from the petroleum refinery*

The effluent used in the study came from Refinery Gabriel Passos (REGAP Refinery) in Betim, Minas Gerais, Brazil. REGAP is a petroleum refinery owned by Petrobrás and produces paint thinner, asphalt, coke, sulfur, gasoline, LPG, diesel, and aviation kerosene. The effluent was sent to the pilot-scale units after a pretreatment in the oil–water separator, flotation, sand filter, and hydrogen peroxide dosage for sulfide concentration control. The effluent was characterized using the following physical–chemical parameters: COD, BOD, total organic carbon (TOC), alkalinity, ammonia, phosphor, sulfide, conductivity, and oils and greases. Analyses were performed in accordance with the recommendations from *Standard Methods for the Examination of Water and Wastewater* [16]. Samples used for effluent characterization were collected every week for a year.

2.2. *Experimental Apparatus and operational conditions*

Two submerged MBR configurations were assessed in this study. The first MBR has flat sheet MF membranes (Kubota) (MBR1), and the second MBR has hollow fiber ultrafiltration (UF) membranes (Zenon) (MBR2); both are installed at REGAP. Fig. 1 shows a scheme of the experimental apparatus.

MBR1 has a membrane module submerged in the biological tank, while MBR2 has a membrane module submerged in a membrane tank external to the biological tank that is MBR1's biological tank, which means both MBRs shared the same biological tank. In order to maintain similar solid concentrations or liquid

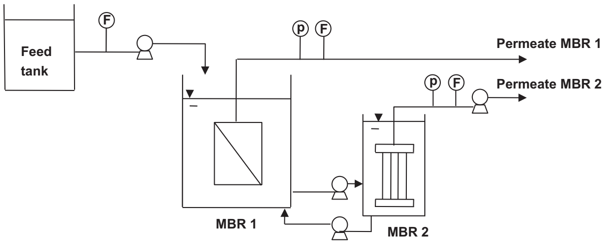

Fig. 1. Flat sheet (MBR1) and hollow fiber (MBR2) MBRs.

characteristics in both MBRs, the sludge from MBR1 was pumped into MBR2 at a flow rate of 2.5 times the permeation flow rate, and the sludge from MBR2 was pumped into MBR1, so the useful volume of MBR2 was kept constant.

The drive force for permeation in MBR1 was the hydrostatic pressure of the water column. The unit had an aeration system to ensure oxygen to the biological process requirements and to ensure fouling control by the shear caused by the ascending (tangential) flow of air bubbles. MBR2 was operating in low vacuum (10–50 kPa) induced by a centrifugal permeate pump. The unit also had an aeration system with two tubes with 3 and 10 mm holes in the lower extremity of the module.

Table 1 shows the characteristics of both MBRs, as well as the operational conditions of each one.

Since the MBRs were operated at a constant flow, the permeate flow was maintained by allowing 1 min of relaxation after every 9 min of permeation for MBR1, and by allowing 15 s of backwashing after every 15 min of operation for MBR2. Regarding membrane cleaning, MBR1 was initially planned to undergo a maintenance cleaning once a week with a 500-mg L^{-1} sodium percarbonate solution for 2 h and, at a second stage, it was submitted to a recovery cleaning with a 5,000-mg L^{-1} sodium hypochlorite solution when permeability reached 100 $L\,m^{-2}\,h^{-1}\,bar^{-1}$. MBR2 underwent weekly maintenance cleanings of the membranes with a 200-mg L^{-1} sodium hypochlorite solution for 20 min and recovery cleanings with a 1,000-mg L^{-1} sodium hypochlorite solution for 24 h and a citric acid solution with pH lower than 2 for 20 min when the pressure to keep a constant flow was higher than 0.4 bar.

MBRs performance was assessed by periodically monitoring the following process variables: permeate flow, applied pressure, temperature, pH, dissolved oxygen, and characteristics of the biomass and the permeate produced, such as sludge filterability, TOC concentration, ammonia, and total and suspended solids.

2.3. Fouling survey and control in MBR

In order to survey fouling in the MBRs, membrane permeability was monitored, resistance tests were performed, and sludge filterability and SMP and EPS concentrations were periodically monitored.

Sludge filterability was evaluated in accordance with the Kubota recommended method in which 50 mL of sludge are filtered in a filter paper (Whatman 42 filter paper 185 mm) folded with pleats with the aid of a simple funnel. The volume filtered during the initial 5 min was recorded as the sludge filterability ($mL\,5^{-1}\,min^{-1}$).

Resistance to filtration was assessed in accordance with the serial resistance model proposed by Choo and Lee [17]. With that model, total resistance of the fouling and the resistances of each fraction of the total resistance (membrane resistance (Rm), static adsorption (Ra), pore blockage (Rp), and cake (Rc)) are calculated. In order to do so, it was necessary to determine the J_i, J_a, J_f, and J_v flux. The J_i flux was determined for permeation of pure water in the clean membrane; this step was performed by determining membrane permeability to clean water. The J_a flux was determined for microfiltered water after static adsorption of the sludge onto the membrane for 2 h with no pressurization. The J_v flux was determined by the permeation of the sludge, and the J_f flux was determined by the permeation of microfiltered water after sludge permeation and washing of the module with running water to remove the cake. The flows were measured at a

Table 1
MBR characteristics and operational values

Parameters	Unit	MBR1	MBR2
Biological reactor volume	m^3	8	8
Membrane tank volume	m^3	–	0.72
Aeration flow	$Nm^3\,h^{-1}$	45	25
HRT	h	5.6	5.6
SRT	d	40	40
Organic load	$KgDQO\,d^{-1}$	13	13
F/M	d^{-1}	0.2	0.2
Permeate flow	$m^3\,h^{-1}$	0.5	1.2
Membrane área	m^2	70	60
Membrane material		PES	PVDF
Poro size	µm	0.4	0.04
Membrane configuration	–	MF/placa plana	UF/fibra oca

pressure of 0.2 bar. With the value of the J_i, J_a, J_f, and J_v flux, the Rm, Ra, Rp, and Rt resistances were calculated.

To evaluate SMP and EPS concentrations, a 50 mL sample of the sludge was collected and centrifuged at 4,500 rpm for 10 min, after which the overflow, comprised mainly of SMP, was collected. The solids from the centrifugation process were suspended in a 0.05% NaCl solution and heated to 80˚C for 10 min, in accordance with the EPS extraction method proposed by Morgan et al. [18]. That new suspension was centrifuged again, and the overflow, comprised mainly of EPS, was collected. The samples containing SMP and EPS were characterized in terms of carbohydrates [19] and proteins [20].

Two strategies were assessed as fouling control methods: keeping the operational flux lower than the critical flux and using a permeability improver.

The critical flux was determined by means of the flux-step method [21]. Initially, the membranes were chemically cleaned, and then the critical flux test was initiated, for which the applied pressure was monitored for constant flux levels. For each flow rate, the filtration time was 15 min, after which the flow rate was increased. The critical flux corresponded to the value at which the applied pressure increased during the 15 min of constant flux permeation.

Regarding the use of a membrane permeability improver, two strategies were evaluated: the first was the use of a single dosage of the permeability improver when a decrease in permeability was detected; and the second was using the improver continuously. The permeability improver of choice was a modified cationic polymer. The optimal dosage of flux improver was determined for both strategies. The optimal dosage was determined with a Jar test in which each vessel was filled with 2 L of sludge and dosed with MPE (50, 75, 100, 150, 200, and 500 mg L^{-1} for vessels 1–6, respectively). In order to determine, an optimal improver concentration, sludge filterability, and SMP and EPS concentrations were analyzed in terms of carbohydrates and proteins, as described earlier. When a single dosage of improver was used, a volume of improver permeability corresponding to the optimal dosage was added into the reactor when there was a sudden decrease in permeability; when continuous dosage was used, an initial dosage corresponding to the optimal dosage was added, and the MBR was daily refilled with an amount of improver equivalent to the amount that was discharged in the excess sludge and biodegradable fraction (1%). The effect of the addition of the permeability improver was assessed by monitoring membrane permeability and sludge filterability.

3. Results

3.1. Characterization of the refinery effluent

Petroleum refinery effluents are typically characterized by the presence of organic matter, oils and greases, ammonia, and sulfide (Table 2). Variation of the values thereof is due to variation of the effluent composition caused by eventual changes in the process, such as maintenance downtimes, equipment replacement, etc.

The organic matter content, in terms of COD, BOD, and TOC, in the pretreated effluent is within the range documented in literature for refinery effluent [22]. COD/BOD ratio values (average of 2.2) suggest that the effluent was suitable for biological treatment. Average sulfide concentration is lower than what is found in the literature: 887 mg L^{-1} [23], 22 mg L^{-1} [24], and 15–23 mg L^{-1} [25], which might be due to previous removal in the pretreatment. Sulfide concentration in the effluent depends on the characteristics of the petroleum being processed and on the refining process. Hydrogen peroxide is added in order to control sulfide concentration in the MBR feed, so that such concentration is kept lower than 10 mg L^{-1}. Results show average values lower than 10 mg L^{-1}, and values above that average were observed due to issues with sulfide removal during pretreatment, considering that average sulfide concentration in the effluent before the pretreatment stage is 16 mg L^{-1} (minimum of 3 mg $L^{-1}$and maximum of 80 mg L^{-1}). Oil and grease concentration is lower than the upper limit suggested for MBR feed 100 mg L^{-1} in Rule 217.157 of Texas Administrative Code that specify criteria for low-pressure, vacuum, and gravity UF or MF MBRs. This value was based on compiled surveys from vendors of membranes.

Table 2
Physical–chemical characterization of the refinery effluent

Parameter	Unit	Mean	Min	Max
COD	mg L^{-1}	610	213	977
BOD	mg L^{-1}	276	202	330
TOC	mg L^{-1}	205	101	849
pH	–	8.5	5.6	11.0
Alkalinity	mg L^{-1}	282.8	106.6	501.6
Ammonia	mg L^{-1}	30.4	11.2	82.8
Phosphorus	mg L^{-1}	0.31	0.07	1.5
Chlorides	mg L^{-1}	293	109	806
Sulfide	mg L^{-1}	6.2	1	25
Oils and greases	mg L^{-1}	14.4	5.2	48.2
Conductivity	mS cm^{-1}	1.7	0.6	5.6

3.2. Comparison of MF and UF in MBR system

As explained earlier, MBR1 is composed of MF membranes (average pore size is 0.4 μm), while MBR2 is composed of UF membranes (average pore size is 0.04 μm), which allows for performance comparisons relative to permeate production, permeate quality, and loss of MF and UF membrane permeability in MBRs.

MBR1's average organic matter removal efficiency was 80% in terms of TOC, while MBR2's was 79% (Fig. 2). Such results showed that there was no significant difference in organic matter removal efficiency between both MBRs, even though they had different membrane configurations and types (MBR1—flat sheet MF membranes and MBR 2—hollow fiber UF membranes). This is probably due to the fact that, during operation, a cake is formed because of the membrane fouling. Such cake is formed by microorganisms, cellular matter, proteins, etc., and works as a dynamic layer that favors an increase of filtration efficiency by reducing the effective pore size of the membranes [26]. This phenomenon is more intense in the MF membrane because it is not backwashed as is the UF membrane, and because it has larger pores, which can enable fouling by blocking the pores and adsorbing SMP [7,10]. According to Judd [4], flat MF membranes with a nominal pore size of 0.4 μm can have an effective pore size of 0.01 μm during operation and formation of cake, which is typical of UF membranes.

Both MBRs had an average nitrogen and suspended solids removal efficiency of 90 and 100%. Zhidong [27] evaluated the use of an MBR with an anaerobic and aerobic biological process to treat refinery effluent and observe a BOD, nitrogen, and suspended solids removal efficiency of 91, 91, and 98.2%, respectively. Ammonia removal in the assessed MBRs, exclusively aerobic, was relatively high in comparison to what was observed by Zhidong [27], which used a combination of anaerobic and aerobic processes for higher ammonia removal. The high sludge age applied to the MBRs assessed (40 d) may have contributed for nitrification to occur in the systems, given that nitrifying bacteria, which are responsible for converting ammonia into nitrate, are recognizably slow-growing organisms [4]. Furthermore, the tropical weather and high temperatures in the country also contribute to the systematic occurrence of nitrification in biological treatment systems implemented in Brazil. Therefore, high ammonia removal efficiencies were predictable.

Results show that solids concentration was constant throughout the operation (Fig. 3). Contrary to

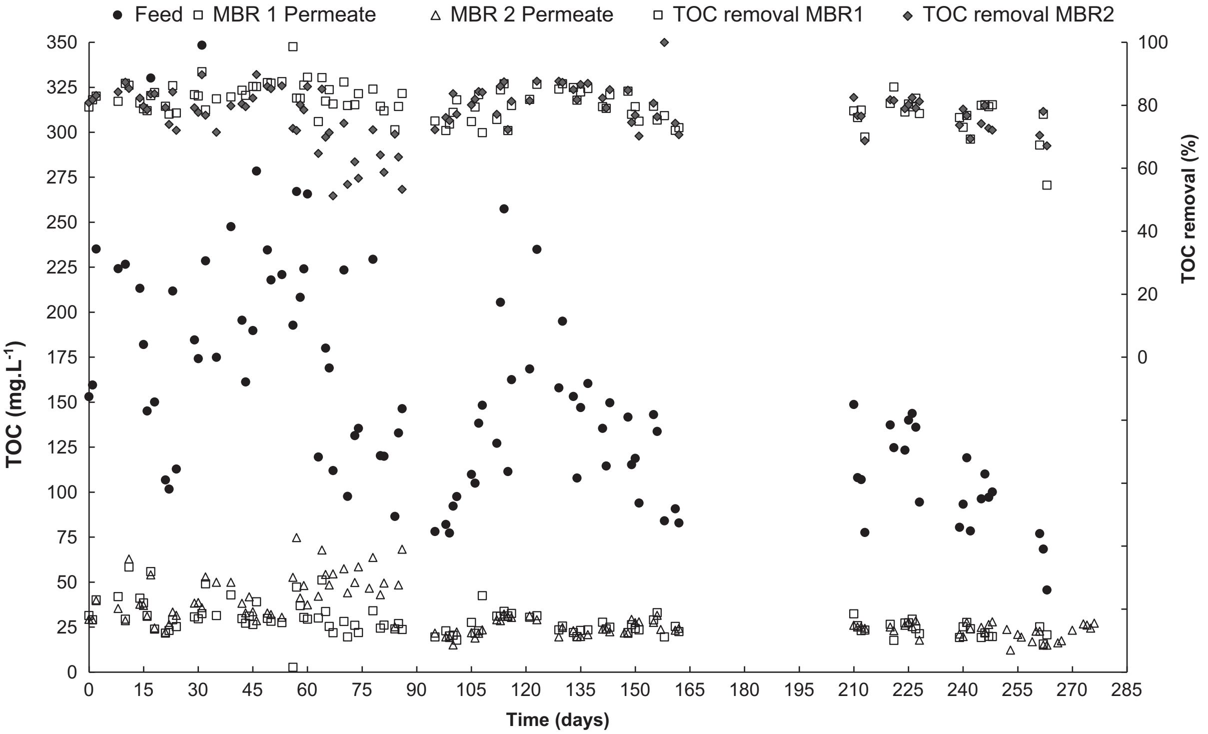

Fig. 2. TOC removal in the flat sheet membrane MBR (MBR1—Kubota) and hollow fiber membrane MBR (MBR2—Zenon).

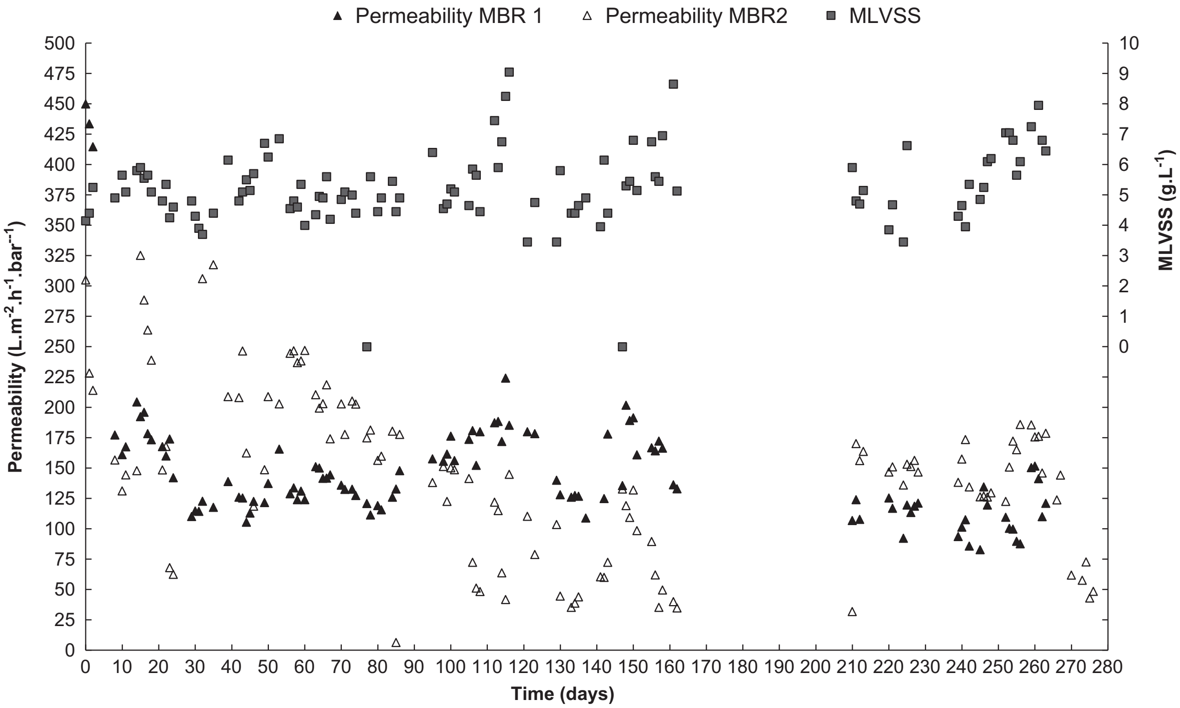

Fig. 3. MBR1 and MBR2 membrane permeability as a function of solids concentration (MLVSS).

what was expected, UF membrane permeability (MBR2) was similar to MF membrane permeability (MBR1), even though the former was operated at a permeate flow higher than the latter, which reinforces the hypothesis that, during operation of MBR with MF membranes, the dynamic layer reduces effective pore size to values that are typical of UF membranes. This result can also be associated with the contribution of backwashing, performed only in MBR2, and with the fact that the frequency of maintenance cleaning was under better control on MBR2 than on MBR1. However, MF membrane permeability is more stable compared to MBR2's UF membrane, which means the decrease in permeability over time is not as intense as in MBR2. Such behavior can be associated with the fact that MBR2, during this period, was operating at a higher permeate flow ($17\,L\,m^{-2}\,h^{-1}$) than that of MBR1 ($8\,L\,m^{-2}\,h^{-1}$), which increased solids concentration on the membrane surface, contributing to reduced permeability. Increased membrane permeability in MBR2 after the 210th day of operation is due to the chemical recovery cleaning.

Such results suggest that selection of the type of membrane, micro or UF, to be used in MBRs can be based on implementation and operational costs because there is no significant difference in the performance of MF and UF membranes regarding quality of the treated effluent.

3.3. Fouling survey in the MBRs

Membrane fouling in MBR2 was discretized by determining different types of fouling resistance (adsorption (Ra), pore blockage (Rbp), and formation of cake (Rc)), and the results are shown in Fig. 4.

It was observed that the major contributors to fouling onto the membranes were adsorption and the formation of cake. Both phenomena depend on sludge characteristics, such as solids concentration, type and characteristics of the sludge, and concentration of SMP and EPS. Pore blockage-related fouling was not identified/quantified. This is probably due to the small pore size of the membrane (0.04 μm), which is much smaller than the sludge flocs, micro-organisms, or even metabolic compounds produced during fouling, which also contribute to this kind of fouling. In many cases, formation of cake is the main contributor to fouling in MBR membranes. According to Lee et al. [28], resistance to fouling usually includes: membrane resistance (12%), formation of cake (80%), absorption and pore blockage (8%), which indicates that the formation of cake is the main cause of membrane fouling. Fig. 2 shows that, for some periods, membrane permeability increased with the increase in solids concentration and vice versa. Such behavior may indicate that the suspended fraction is not the main contributor to fouling onto the membrane.

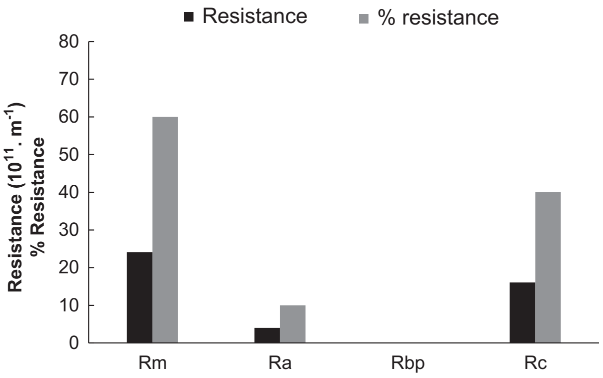

Fig. 4. Values of different types of fouling.

Regarding this behavior, laboratory tests were performed to asses resistance to fouling of the sludge, the suspended fraction, and the overflow (Fig. 5); the tests were performed with a module built with a membrane from the same supplier as that of MBR2. In order to get the suspended fraction, a sample of the sludge was left to sediment, and the overflow was later removed; a volume of distilled water equal to the volume of the overflow removed was added to the settled solid, thus producing the suspended fraction.

It was observed that fouling formed with the permeation of the overflow (soluble and colloidal) was more resistant than that formed with the solid fraction, thus confirming that the soluble and colloidal fraction is a stronger contributor to membrane fouling, be it by adsorption or cake formation. Several studies have assessed the degree and characteristics of fouling caused by each of the sludge fractions, and controversial results have been observed. Wisniewski and Grasmick [29] observed that the solid materials are the main contributors to fouling in MBRs. Defrance et al. [30] suggest that fouling is caused primarily by suspended materials (biological flocs). Bouhabila et al. [31] attributed fouling to colloidal materials. However, an analysis of those several studies enables one to extend the hypothesis that fouling, as a result of the contribution of the various sludge fractions, may be variable. This variation is a function of the characteristics of the membrane, hydrodynamic conditions, and physiological properties of the biomass.

Filterability of the reaction liquid (biological sludge) can be used as an indicative parameter of its quality. The results (Fig. 6) showed that the higher the filterability, the higher the membrane permeability, which thus confirms that the quality of the reaction liquid directly influences fouling onto the membrane surface.

It is observed that the higher the filterability, the higher the critical flux (Fig. 7), which, again, confirms the influence of the quality of the reaction liquid on fouling onto the membrane.

SMP and EPS may significantly influence fouling onto the membrane surface. EPSs are secreted by cells or generated during cellular lysis and are composed of insoluble materials such as capsular polymers, gels, polymers, and organic matter. EPSs are important to define the physical–chemical properties of the biomass, such as structure, load, and hydrophobicity of the floc. SMPs are discharged by cells in response to an environmental or operational condition and/or during cellular lysis; they correspond to the majority of the effluent of biological processes.

No significant variations in EPS concentration in terms of carbohydrates and proteins are observed (Figs. 8 and 9) in the MBR2. SMP concentration in terms of proteins did not change significantly during that period either, suggesting that it does not contribute to fouling onto the membrane. An increase in SMP concentration in terms of polysaccharides was

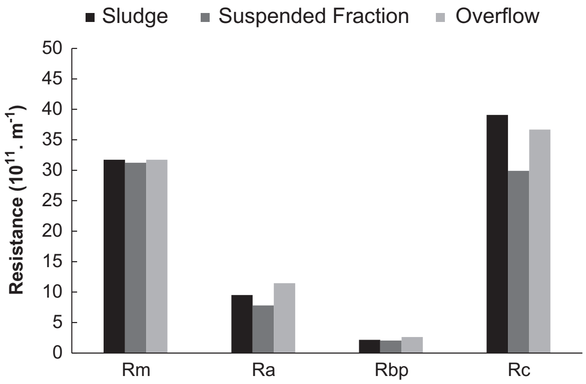

Fig. 5. Values of different types of fouling of the sludge, suspended fraction, and overflow.

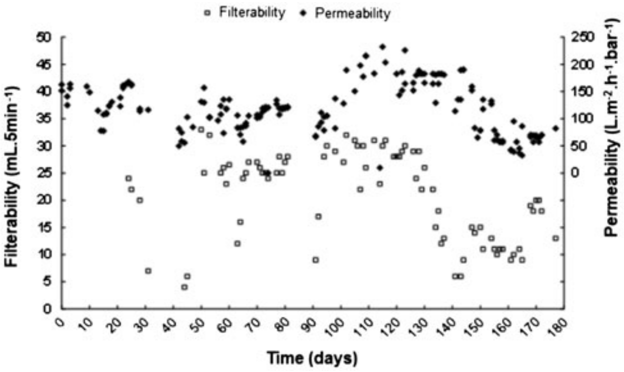

Fig. 6. Permeability and filterability profiles relative to operational time.

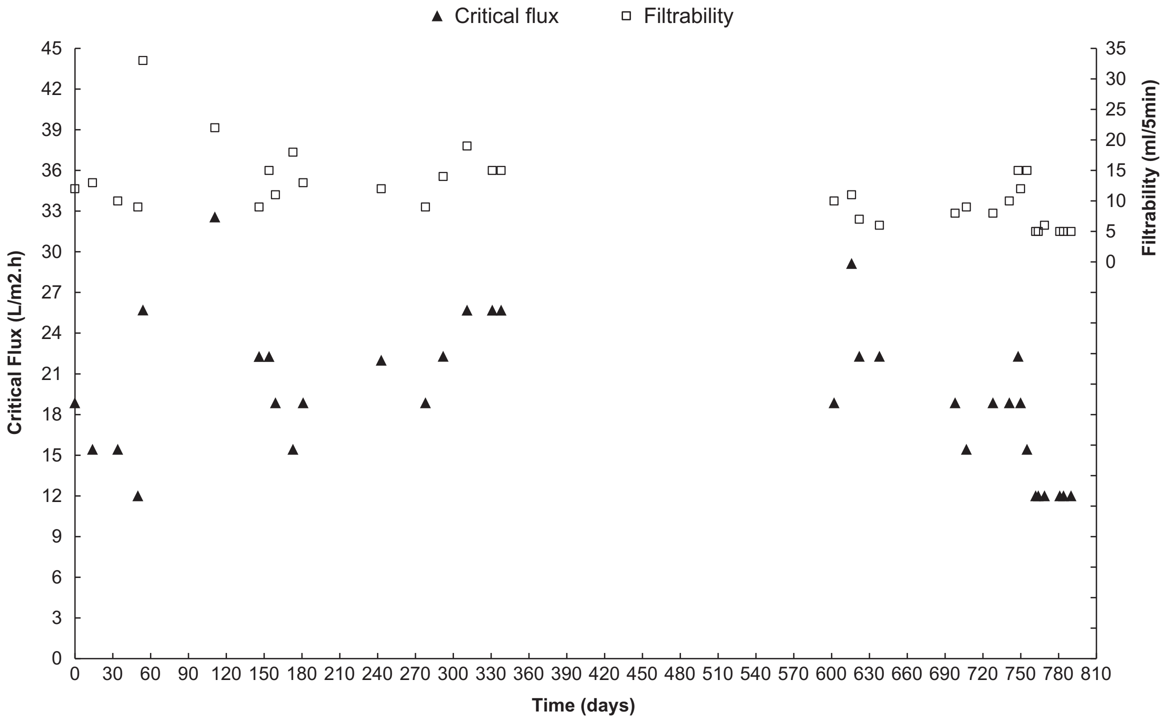

Fig. 7. Critical flux and filterability profiles.

observed over time; sludge filterability and membrane permeability are negatively influenced by such increase. This result suggests that SMP concentration in terms of polysaccharides may be contributing to fouling onto the membrane due to adsorption or formation of cake, which are major contributors to fouling, as shown in the fouling survey described above. Increased membrane permeability in MBR2 on the 210th day of operation is due to the chemical recovery cleaning of the membrane, which was required because of low membrane permeability on the previous days. These results endorse those obtained by Geng and Hall [32], who observed a higher contribution of SMP content than EPS content to fouling onto the membranes.

SMPs can gather on the membrane surface or penetrate into its pores, increasing resistance to filtration. The influence of SMP and EPS concentration in MBRs have been thoroughly investigated by several researchers [31]. According to Meng et al. [33], SMPs are more easily gathered in MBRs due to rejection by the membranes, which results in poor sludge filterability. Furthermore, several researchers have pointed out that polysaccharide-like substances in the SMP fraction contribute more to fouling than protein-like substances [34]. According to the literature, polysaccharides contribute to cell cohesion, thus having an important role in maintaining the structural integrity of biofilms [35]. Other studies also have related polysaccharide concentration to fouling rate in MBRs [34]. However, results that contradict those can also be found in the literature. According to Lee et al. [36], proteins provide more hydrophobicity to the sludge than carbohydrates do, resulting in higher adsorption onto the membrane surface, and thus more fouling onto the membrane. Massé et al. [37] clearly showed that the fouling rate increases with the amount of proteins or polysaccharides in the overflow, and, that, for different differential pressures across the membrane, the specific resistance of the cake formed indicated that the cake may be compressible, and that its compressibility is related mainly to the concentration of proteins in the overflow.

Fig. 10 shows the relation between critical flux, operational flux, and pressure for the MBR1 and MBR2.

A variation in critical flux is observed during the time of observation, which may be associated with the variation of feed characteristics and, thus, of the quality of the biological sludge, as discussed earlier, which is confirmed by studies described in the literature [10]. Operation of the unit at an operational flux higher than the critical flux results in a high fouling rate, as expected. However, it is observed that, even operating the MBR at an operational flow lower than the critical flux, there is still fouling onto the membranes,

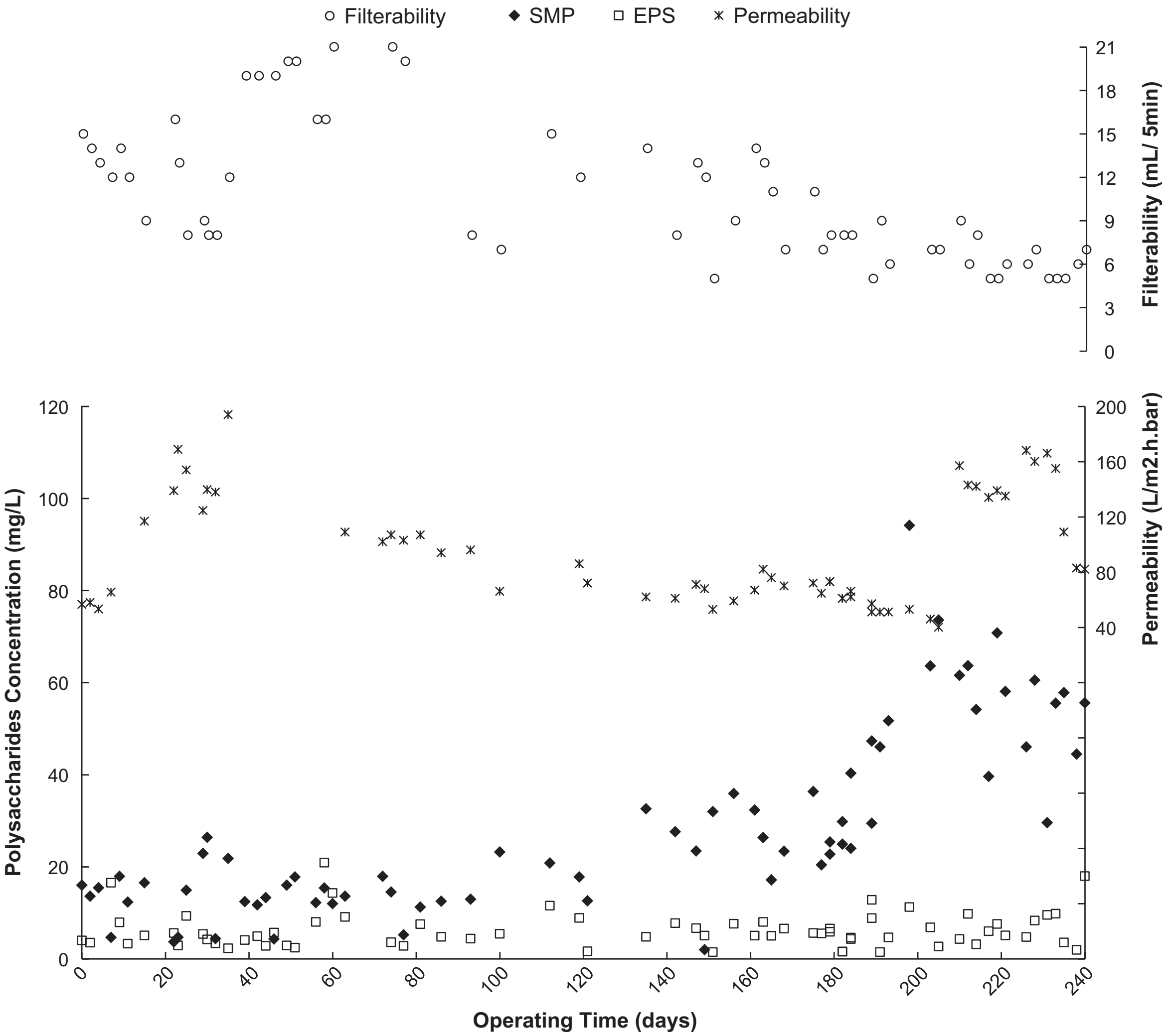

Fig. 8. SMP and EPS concentrations in terms of polysaccharides, filterability, and membrane permeability.

although the larger the difference between critical flux and permeate flow, the lower the fouling rates, which is consistent with the results obtained by Le-Clech et al. [10], who observed the occurrence of sub-critical fouling in complex systems, such as MBRs. It is important to note that the critical flux measurements were performed punctually once a week and after cleaning the membrane; since the critical flux depends on sludge characteristics, which change constantly, and membrane characteristics, operation under the critical flux level cannot be ensured during the entire time of evaluation. Nonetheless, the critical flux test has the importance of being an indicative of the flux above which fouling becomes really severe and of serving as a tool to compare propensity to fouling in several systems, thus helping the selection of the MBR's operational flux, considering that operating MBRs, at a flow lower than the critical flux, can lead to little or no fouling; [10,11] observed that operational pressure increases when the system is operated above the critical flux, thus reducing the system's productivity, which requires more often cleaning downtimes.

Therefore, the importance of controlling the operational flux to keep it lower than the critical flux becomes clear. However, in most applications, the operational flux must be kept constant because it is necessary to treat all the effluents generated. Thus, the best way to keep the operational flux lower than the critical flux is to increase the critical flux, and not to reduce the operational flux. One way to increase the critical flux is to improve the quality of the sludge. An alternative to do so is to use permeability improvers.

Fouling in MBRs can also be reduced using permeability improvers, which have been developed to help control fouling in MBRs. The operation of such products is based on coagulation/flocculation of the

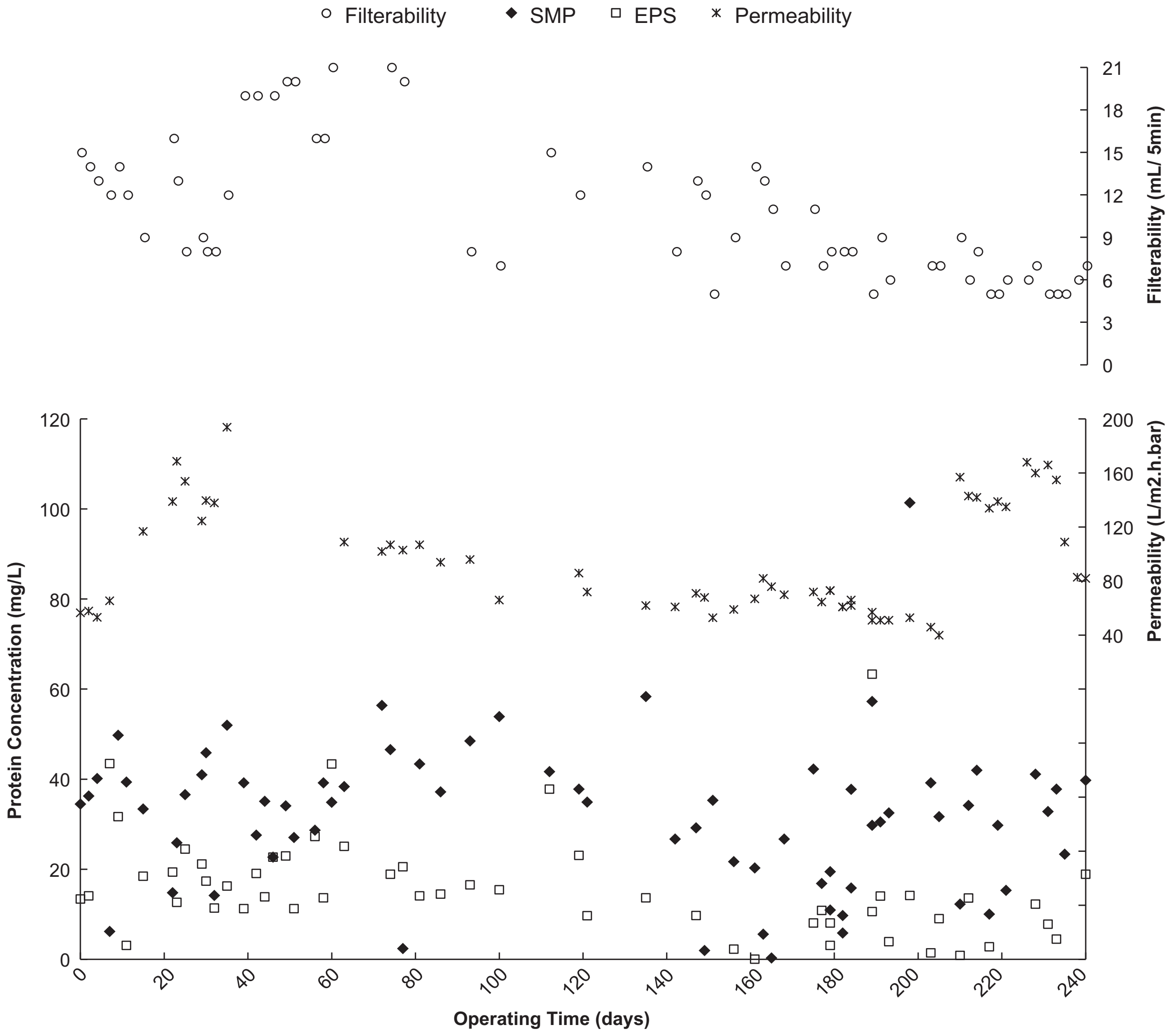

Fig. 9. SMP and EPS concentrations in terms of proteins, filterability, and membrane permeability.

sludge, increasing the size of the flocs and retaining SMPs and EPSs in them, thus reducing their concentration in the medium and increasing membrane filterability.

The use of permeability improvers was assessed by dosing such compounds in pilot-scale units. The MBR1 and MBR2 received a certain dosage of a modified cationic polymer (commercial permeability improver) during a period of 18 months. During that time, two strategies of using commercial permeability improvers were evaluated; the first one was to add the improver only to recover sludge quality; the second one was to add an initial shock dosage, followed by continuous dosage to recover what was lost when sludge was disposed off to control sludge age and degradation inside the reactor.

The optimal dosage was determined by tests with variable concentrations of the commercial flux improver, in a methodology similar to that described by Koseoglu et al. [38]. The optimal polymer concentration was the one that resulted in better sludge filterability and higher SMP and EPS removal from the medium.

The results of the preliminary dosage tests with the commercial permeability improver for recovering sludge filterability shown in Table 3 indicate that, for improver concentrations higher than a certain value (150 $\mathrm{mg\,L^{-1}}$), no significant increase in biological sludge filterability was observed, which indicates that this concentration is enough for the recovery. However, analysis of the data presented in Table 3 shows that concentration higher than 200 $\mathrm{mg\,L^{-1}}$ results in higher SMP and EPS removal, both in terms of carbohydrates and proteins. Association of the results from this optimal dosage test, i.e. the concentration for sludge filterability recovery together with SMP and

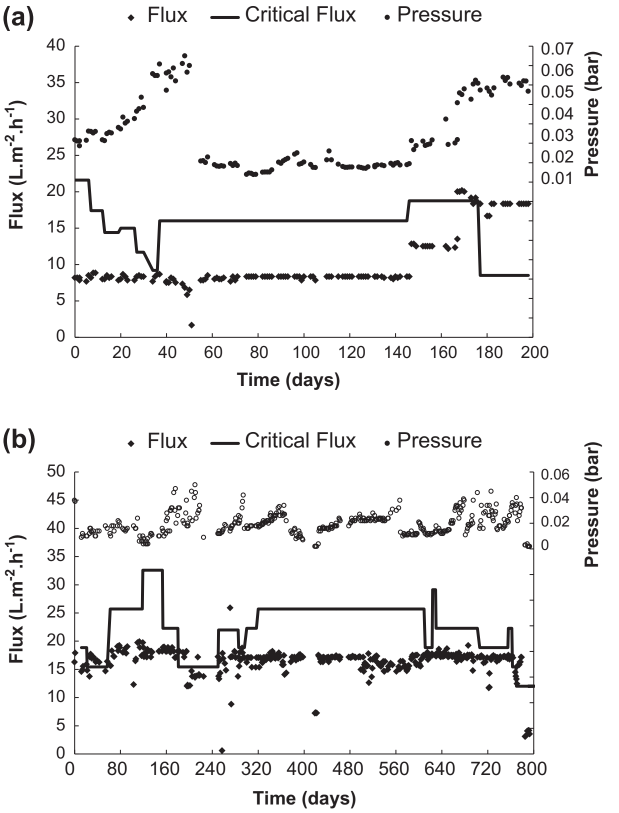

Fig. 10. Values of flux, operational pressure, and critical flux for (a) MBR1 and (b) MBR2.

EPS removal in terms of carbohydrates and proteins, respectively, led to the determination of a permeability improver concentration of 200 mg L^{-1} for the long-term tests. The value predetermined in this study is consistent with permeability improver dosages established in the literature [15,38]. After the optimal concentration was determined, the use of permeability improver was evaluated as a single dosage and as continuous dosage.

The single dosage of improver was assessed with the purpose of recovering membrane permeability in the event it decreases due to loss of sludge quality, for example, when composition or concentration of the feed varies. Fig. 11 shows the monitoring of the sludge filterability recovery and the behavior of membrane permeability with the improver dosed in an interval of approximately 80 d.

The permeability improver dosage is indicated by the dotted line in the figure. It was observed that, on the 30th day of operation of the MBR, the sludge filterability decreased from 20 to 5 mL 5^{-1} min^{-1} due to an alteration in the feed composition that stressed the biomass and resulted in reduced membrane permeability. There was such an intense decrease in permeability that no permeate was produced. On the 40th day of operation, a chemical cleaning was performed on the membrane with the purpose to recover permeability; however, no significant increase in permeability was observed. After the flux improver was added, which is indicated by the dotted line in the graph, an increase in filterability and recovery of membrane permeability were observed. After the dosage, both filterability and membrane permeability were stable, although no stressful situation affecting the biomass was detected in the period. The system was monitored over a period of 30 days due to the fact that part of the sludge was accidentally lost. However, during that period, the permeability improver proved to be an efficient way to control emergency situations of filterability loss caused by stress to the biomass.

In the second stage, the continuous use of the permeability improver was evaluated with the purpose to prevent fluctuations in sludge characteristics that might result in loss of permeability (Fig. 12). In this assessment, an initial dosage was added so that the concentration in the reactor was 200 mg L^{-1}; a continuous dosage was then added to recover what was lost in the sludge that was disposed off to control sludge age and degradation inside the reactor (1%). Again,

Table 3
Effect of different dosages of flux improver on sludge filterability and SMP and EPS removal

Flux improver concentration (mg L^{-1})	Filterability (mL 5^{-1} Min^{-1})	SMP		EPS	
		Protein	Carbohydrate	Protein	Carbohydrate
0	7	0	0	0	0
50	20	68	4	16	4
75	21	61	16	22	14
100	23	57	22	43	29
150	33	68	30	50	23
200	32	73	39	72	68
500	33.5	77	47	99	88

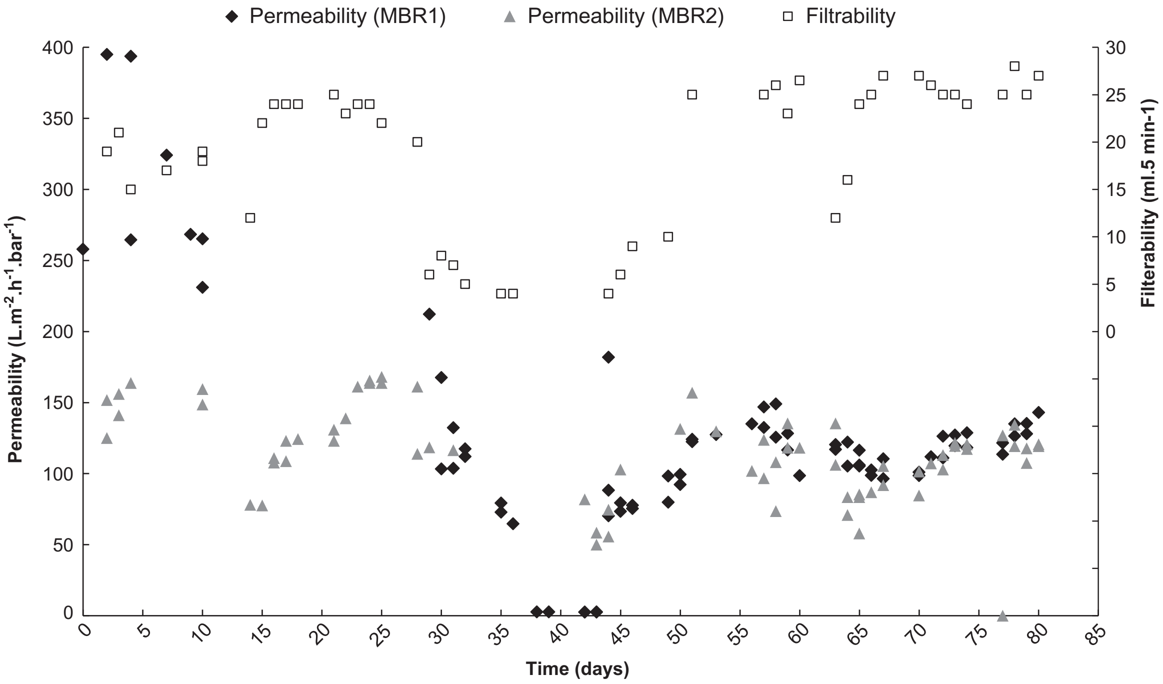

Fig. 11. Effect of a single dosage of flux improver on permeability recovery.

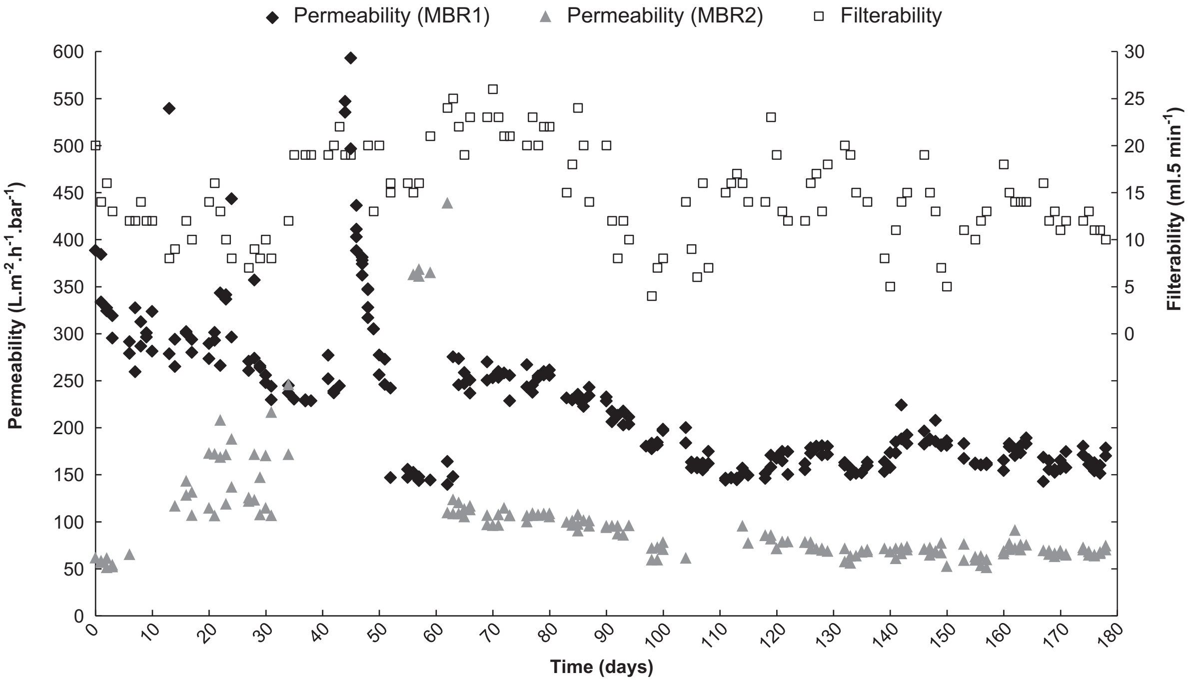

Fig. 12. Effect of the continuous dosage of flux improver on the recovery of sludge filterability.

the initial dosage or shock dosage is indicated by the dotted line.

On the 38th day of monitoring, the initial MPE dosage was added so that the permeability improver concentration in the reactor was 250 mg L^{-1}, the optimal value determined in the test for optimal dosage in the sludge. After the initial dosage of permeability improver, there was an increase in filterability, but its effect on permeability was only significant after the membrane was cleaned on the 42nd day, which shows that the permeability improver only affects the quality recovery of the suspended sludge, and not of the cake formed; this illustrates the importance of conjugating cleaning with the use of the flow improver. The improver affected the permeability recovery in the MBR1 only, which may be related to the fact that, during the period in which the shock dosage was added, the MBR2 membrane had regular permeability values, and also to the fact that, right after the improver was added, the membrane had a maintenance downtime of 22 d, even though there was no reduction in sludge filterability during that time; also, the MBR2 undergoes a weekly maintenance cleaning, which does not happen with the MBR1.

From the 87th day forward, there was a reduction of filterability to values that were considered awfully low. In that period (87–100th day), only the necessary amount of permeability improver to replace the exceeding, biodegraded amount that was lost in the disposed sludge was added. On the 100th day of monitoring, a sample of the sludge was collected and the necessary amount of permeability improver was determined, i.e., the optimal dosage for filterability recovery. The optimal dosage was added to the bioreactor, recovering sludge filterability. However, 40 d later, a filterability loss was observed again and a shock dosage was added. After successive shock dosages, it was observed that it was no longer possible to sustain sludge filterability for a significant period. This behavior might be related to the excessive dosage of permeability improver, which may act as a deflocculant of the sludge inside the MBR, reducing the size of the flocs, as observed by Koseoglu et al. [38]. These results suggest that a good alternative for sludge recovery after a stressful situation is cause-effect, i.e. determining an optimal concentration of the improver and adding a single dosage, so that this is the concentration inside the reactor when loss of sludge quality is detected.

4. Conclusion

The MBRs were thus shown to be potentially effective in the treatment of effluents from petroleum refining processes, ensuring the quality of the treated effluent even with variations in effluent characteristics, typical of industrial environments. The MBRs had an average efficiency of organic matter removal of 80% in terms of TOC and 90% in terms of ammonia. The selection of the type of membrane, micro or UF, to be used in MBRs can be based on implementation and operational costs because there is no significant difference in the performance of MF and UF membranes regarding quality of the treated effluent. Fouling in the MBRs is caused mainly by adsorption and formation of cake. This kind of fouling is influenced mainly by sludge characteristics, which are extremely important to ensure that the operational flux is kept lower than the critical flux, so that fouling occur at a low rate. One way to increase the critical flux is to improve the quality of the sludge. The use of commercial permeability improver in single dosage, when permeability decreased was detected, is an alternative to improve the sludge quality.

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