TREATMENT OF DAIRY WASTEWATER WITH A MEMBRANE BIOREACTOR

L. H. Andrade*, G. E. Motta and M. C. S. Amaral

Department of Sanitary and Environmental Engineering, Federal University of Minas Gerais,
Phone: + (55) (31) 34093669; Fax: + (55) (31) 34091879, Av. Antônio Carlos 6627,
Pampulha, Belo Horizonte - MG, Brazil.
E-mail: laurena@ymail.com

(Submitted: July 11, 2012 ; Revised: October 12, 2012 ; Accepted: October 22, 2012)

Abstract - Among the food industries, the dairy industry is considered to be the most polluting one because of the large volume of wastewater generated and its high organic load. In this study, an aerobic membrane bioreactor (MBR) was used for the treatment of wastewater from a large dairy industry and two hydraulic retention times (HRT), 6 and 8 hours, were evaluated. For both HRTs removal efficiencies of organic matter of 99% were obtained. Despite high permeate flux (27.5 L/h.m²), the system operated fairly stably. The molecular weight distribution of feed, permeate and mixed liquor showed that only the low molecular weight fraction is efficiently degraded by biomass and that the membrane has an essential role in producing a permeate of excellent quality.

Keywords: Membrane Bioreactor (MBR); Dairy wastewater; Molecular weight distribution; Hydraulic Retention Time (HRT); Dynamic membrane; Soluble Microbial Products (SMP); Extracellular Polymeric Substances (EPS).

INTRODUCTION

Among the food industries, the dairy industry is considered to be the most polluting one, because of its large water consumption and wastewater generation, which are the main source of pollution of this type of industry (Vourch et al., 2008). The effluents are produced in the process of washing and cleaning, loading and discharge and spillage and leakage (Machado et al., 2002). The process of washing and cleaning consists of rinsing milk cans, tanks and pipes for the purpose of removing milk residues and other impurities and of washing floors, and can generate 50 to 95% of the total effluent volume (Daufin, 2001).

The effluents of these industries are characterized by having high concentrations of organic matter and nutrients and are mainly composed of carbohydrates, proteins and fats originated from milk, and by residual cleaning agents (Perle et al., 1995). The conventional treatments of these effluents include the use of primary treatment to remove solids, oils and fats, secondary biological treatment to remove organic matter and nutrients and, in some cases, tertiary treatment as polishing. However, several problems have been reported, such as high production of scum, low sludge settleability, low resistance to shock loads, difficulties in removal of nutrients (nitrogen and phosphorus) and problems in the degradation of fats, oils and other specific types of pollutants, such as dyes (Machado et al., 2002).

Because of the reduction in water availability and the increase in water treatment costs, industries are searching for new technologies for wastewater treatment, aiming not only at the achievement of release standards but also at obtaining high quality treated effluent for reuse. Considering these, the membrane bioreactor (MBR) appears to be a promising process for the treatment of dairy industry wastewaters.

The main advantage of MBRs is the membrane’s capacity for completely retaining the biomass, with
the effect that the quality of the treated effluent does not depend on the sludge settling characteristics. In addition, MBRs can operate with a higher concentration of mixed liquor suspended solids and a higher solids retention time than conventional systems such as activated sludge. The advantages of these conditions are less sludge production, which causes a reduction in sludge treatment and disposal costs, and a reduction of the reactor volume. Due to the retention by the membrane, high molecular weight and/or recalcitrant compounds may remain in the MBR longer than the average hydraulic retention time, allowing the growth of microorganisms which are more acclimated to these compounds and have the ability to degrade them. Thus, MBRs also present better removal efficiency of micropollutants, persistent organic pollutants and slowly biodegradable pollutants (Bernhard et al., 2006).

Despite the high potential of the application of MBRs for the treatment of effluent from dairy industries, there are only few articles published in scientific journals dealing with this application. The papers that have been published usually refer to the treatment of small flows of wastewater generated intermittently in milk production farms (Castillo et al., 2007; Hirooka et al., 2009), cheese whey (Farizoglu et al., 2004), synthetic effluent (Bouhabila et al., 2001), and domestic sewage combined with effluent from small dairy farms (Bick et al., 2009), or, more recently, to the combination of coagulation and MBR for dairy wastewater treatment (Weiwei and Jinrong, 2012). We found no references to the treatment of real effluents from large dairy industries making use of a submerged aerobic MBR.

Therefore, the aim of this study was to evaluate the applicability of an aerobic MBR for the treatment of effluents from a large dairy industry. Tests were performed under two different hydraulic retention times and the focus was on the evaluation of pollutant removal mechanisms.

METHODOLOGY

Dairy Wastewater

The evaluated effluent was collected in a dairy industry located in the state of Minas Gerais, Brazil, which produces UHT milk, yoghurt, cheese, cottage cheese and processed cheese. The milk processing capacity of the industry is 800 m³/day.

The effluent was collected at the effluent treatment system of the industry after screening and flotation with compressed air. Six samples were collected throughout reactor operation. Approximately 150 liters of the industrial effluent were collected each time and placed in 50 liter gallons, which were stored in a cold chamber at 3 °C until the effluent was feed into the reactor.

Experimental Setup

The membrane bioreactor and the membrane module used were built by PAM Selective Membranes (Rio de Janeiro, Brazil). The submerged MBR had one microfiltration hollow fiber module (poly (etherimide), average pore size of 0.5 µm, membrane area of 0.02 m²). The permeate was collected at the upper end of the module. At the opposite end there were small holes for air introduction and promotion of aeration between the fibers. The MBR was composed of four acrylic tanks (a tank of 13.4 liters for feed storage, a biological tank with useful volume of 4.4 liters and two tanks for permeate storage of 4.0 L each, in one of which a vacuum was created to promote filtration), a vacuum pump used in microfiltration, a diaphragm pump used in backwash, solenoid valves, level sensors, control valves, flow indicators of permeate, backwash and air, a pressure indicator for the permeate and the backwash and a skid with an electrical panel (Figure 1).

![Figure 1: Scheme of the MBR used.](image-url)
was stored in the feed tank and discharged by gravity to the biological tank, where a float valve controlled the level. Thus, the feed flow was equal to the permeate flow. During filtration, the vacuum pump maintained the first permeate tank at negative pressure, providing the driving force for permeate suction. When the volume of permeate reached the top level in this permeate tank, it was discharged to the second permeate tank, which was open to the atmosphere and also served as the feed tank for backwash. Once the backwash was activated, the vacuum in the suction line was interrupted to allow the permeate to be pumped by the backwash pump into the membrane in the opposite direction from the filtration. The backwash flow rate was controlled by a bypass line and the backwash pressure was controlled by a needle valve.

**Operational Conditions**

The MBR was initially inoculated with sludge from the activated sludge reactor of the effluent’s supplier. After an initial phase of acclimatization of the microorganisms to the conditions of the MBR and the effluent, which lasted 28 days and in which the hydraulic retention time (HRT) was set to 10 hours, the solids retention time (SRT) was set to 60 days and HRTs of 8 and 6 hours were evaluated in order to determine the optimum operating condition. The choice of these HRTs were based on the literature, which states that the average HRT of activated sludge systems for dairy wastewater treatment is 7 hours (Braile and Cavalcanti, 1993), and on previous tests. For the definition of the applied SRT, the conclusions of the literature review presented by Meng et al. (2009) were taken into account, which states that the SRTs that cause less fouling are near 50 days, together with the principle that higher SRTs are usually desirable from a biokinetic standpoint because this produces more of the slower-growing microorganisms, as well as generating less sludge (Judd, 2006).

To maintain the HRTs of 8 and 6 hours, permeate flows and fluxes of 0.55 L/h and 27.5 L/h.m² and 0.75 L/h and 37.5 L/h.m², respectively, were employed. The membrane used had an average hydraulic permeability in water of 366 L/h.m².bar. The flows of air to the membrane module and to the biological tank were 3.5 Nm³/h and 0.5 Nm³/h, respectively. Backwash flow was adjusted to 2.0 L/h and it was triggered automatically for 15 seconds every 15 minutes of permeation. This frequency is similar to the one used by other authors (Bouhabila et al., 2001; Artiga et al., 2005; Matošića et al., 2008).

Chemical cleanings were performed when the operating pressure reached the maximum value of 0.6 bar or when other tests, like critical flux or a resistance test, were performed (results not shown in this work). The chemical cleanings were performed using a 0.5 g/L sodium percarbonate solution for 20 minutes in an ultrasonic bath.

**Process Monitoring**

During the operation of the MBR, the pressure was recorded daily, and samples of the permeate were collected and characterized in relation to the concentration of chemical oxygen demand (COD), dissolved organic carbon (DOC) (TOC Analyzer Shimadzu TOC-V CPN) and apparent color (Spectrophotometer Hach DR2800). Furthermore, aliquots of the sludge were collected for analysis of mixed liquor volatile suspended solids (MLVSS) three times a week. Weekly, a larger volume of permeate was collected for the analysis of total nitrogen (Analyzer Shimadzu TNM-1), ammoniacal nitrogen, total phosphorus and biological oxygen demand (BOD). All of these analyses were performed in accordance with the recommendations of Standard Methods for the Examination of Water and Wastewater (2005).

Every time a new 50 liter gallon began to be used for supplying the feed for the MBR, a sample of the effluent was also collected and analyzed in terms of all the physicochemical parameters, together with the permeate.

The results of permeate concentrations of COD, DOC and apparent color and the MBR’s removal efficiency for both HRTs evaluated were compared using the Mann-Whitney test for nonparametric samples, applying the software Statistica 6.1 at a significance level of 0.05.

**Molecular Weight Distribution**

The molecular weight distribution of feed, permeate and mixed liquor was determined periodically, using an ultrafiltration cell (Amicon, serie 8000, model 8200,) and commercial membranes with molecular cutoffs of 10 and 100 kDa (Millipore, Biomax Ultrafiltration Discs, polyethersulfone (PES)), according to the procedure described by Amaral et al. (2009). The different molecular weight fractions were characterized in terms of carbohydrates (Dubois et al., 1956) and proteins (Lowry et al., 1951).

The Lowry’s method quantifies protein, peptides and also amino acids (Peterson, 1979). Since most proteins are larger than 10 kDa, applying the Lowry’s
RESULTS AND DISCUSSION

Evaluation of the Hydraulic Retention Time

Figure 2 shows the biomass concentration, the feed to microorganism (F/M) ratio and the organic load received by the MBR during the operation with HRTs of 8 and 6 hours and an SRT of 60 days.

The average concentrations of biomass during operations with HRTs of 8 and 6 hours were 17,251 and 22,371 mgMLVSS/L, respectively. These values, which can be considered high, given that the average concentration of MLVSS in a submerged MBR ranges between 10,000 and 15,000 mg/L (Cornel and Krause, 2008), are justified by the fact that the effluent has a high concentration of biodegradable organic matter (Janczukowicz et al., 2008). Thus, there was enough substrate available for the microorganisms for both catabolism and the synthesis of new cells.

Figure 2: MLVSS concentrations, F/M ratio and organic load of the MBR during the operations with HRTs of 8 and 6 hours.

It was observed that the sludge concentration increased at the beginning of the operation with HRT of 8 hours. Although the concentration of solids had apparently stabilized during the acclimatization (data not shown), the reduction of the HRT to 8 hours, which had been maintained at 10 hours during the first period, caused a greater increase in MLVSS.

It can be seen that initially there was a reduction in the F/M ratio caused by an increase of the biomass in the reactor, and a subsequent stabilization at values close to 0.67 kgCOD/kgMLVSS.d. After the reduction of the HRT from 8 to 6 hours, there was again an increase in the F/M ratio due to an increase in wastewater flow and organic load received by the MBR. This increase resulted in biomass growth, which caused F/M to return to a level of 0.55 kgCOD/kgMLVSS.d and resulted in the stabilization of the MLVSS concentration. According to Judd (2006), the majority of real scale membrane bioreactors treating industrial effluents operate with F/M lower than 0.25 kgCOD/kgMLSS.d. Therefore, the values of 0.67 and 0.55 kgCOD/kgSSV.d can be considered high. Because the biomass concentration in the reactor was elevated, the high ratio of F/M could be justified by the high organic load, which presented an average value of 16.1 kgCOD/m³.d throughout the operation. It will be demonstrated that this fact did not cause any trouble in the reactor.

Figure 3 exhibits the COD, DOC and color values of the feed and permeate of the MBR.

The MBR showed a high capacity for removing organic matter and color, which can be justified by the elevated biodegradability of the effluent (Janczukowicz et al., 2008) and the high concentration of biomass. The stability provided by the MBR can also be seen from the fact that, despite large variations in the concentration of organic matter and color of the feed, marked changes in the quality of the permeate did not appear at any moment. The reduction of the concentration of organic matter and color of the permeate and the increase in efficiency during the first days of operation may be related to the increase in sludge concentration and reduction of the F/M.

Table 1 shows the results of the nonparametric Mann-Whitney statistical test. The choice of a nonparametric test was due to the small sample sizes. Since a significance level of 5% was established, the results indicate that there is a statistically significant difference between the groups of samples evaluated when the p value is less than 0.05.

Despite small variations between the removals obtained in each operating condition, according to the statistical results of Mann-Whitney, the concentration of DOC and the color of the permeate and the removal efficiencies of COD and DOC obtained during the operations with both HRTs tested cannot be considered different at a significance level of 0.05. It was possible to reject the hypothesis that the
Figure 3: Concentrations of (a) COD, (b) DOC and (c) color of the feed and the permeate of the MBR during the operations with HRTs of 8 and 6 hours.

Table 1: Results from Mann-Whitney test for color and COD and DOC concentrations in the permeate and MBR removal efficiencies obtained for HRTs of 8 and 6 hours.

<table>
<thead>
<tr>
<th>Variable</th>
<th>n (HRT 8 hrs)</th>
<th>n (HRT 6 hrs)</th>
<th>p value</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD</td>
<td>8</td>
<td>11</td>
<td>0.0389</td>
</tr>
<tr>
<td>COD removal efficiency</td>
<td>8</td>
<td>11</td>
<td>0.5631</td>
</tr>
<tr>
<td>DOC</td>
<td>12</td>
<td>11</td>
<td>0.4984</td>
</tr>
<tr>
<td>DOC removal efficiency</td>
<td>12</td>
<td>11</td>
<td>0.8055</td>
</tr>
<tr>
<td>Color</td>
<td>13</td>
<td>14</td>
<td>0.2441</td>
</tr>
<tr>
<td>Color removal efficiency</td>
<td>13</td>
<td>14</td>
<td>0.0019</td>
</tr>
</tbody>
</table>

*a number of valid samples
samples did not show a significant difference only for the parameters permeate COD concentration (means of 50±10 mg/L and 43±10 mg/L for HRTs of 8 and 6 hours, respectively) and color removal efficiency (means of 97.8±1.4% and 98.7±1.0% for HRTs of 8 and 6 hours, respectively), and in this case the operation with an HRT of 6 hours was more efficient than the one with an HRT of 8 hours. In spite of the fact that higher HRTs may lead to bigger removal efficiencies because the substrate stays more time in the reactor, in this case, it seems that the higher concentrations of MLVSS observed with the HRT of 6 hours had a major effect on the system’s removal capacity.

In the scientific literature, no article about the treatment of effluents from large dairy industries using an aerobic submerged MBR was found. However, Farizoglu et al. (2004) evaluated the use of an aerobic jet loop reactor coupled to membranes for the treatment of whey produced during cheese-making. The authors obtained COD removal efficiencies between 94 and 99%; however, the HRT and SRT applied, equal to 0.82 to 2.8 days and 1.1 to 2.8 days, respectively, were quite different from those used in this work. Another paper by Castillo and collaborators (2007) presents the results of tests using a bioreactor with a microfiltration membrane applied for the treatment of synthetic wastewater, simulating the white waters produced in the process of washing the equipments used in cheese manufacturing. The concentration of COD in the effluent varied between 800 and 1200 mg/L, and in the permeate it was about 75 mg/L, corresponding to removal efficiencies of 90-94%. Hirooka et al. (2009) worked with a similar effluent and obtained 88-99% of COD removal. It appears that the efficiencies obtained in this work are similar to those presented in other related studies, or even higher. This comparison should be drawn carefully however, because even though all effluents in question came from milk processing, they do not necessarily have the same characteristics.

Table 2 shows the average values of the main physicochemical parameters of feed and permeate of the MBR and their removal efficiencies.

In addition to the high organic matter removal discussed earlier, an efficient removal of nutrients may also be noted. The high SRTs usually applied in MBRs contribute to the occurrence of nitrification in these systems, since nitrifying bacteria, which are responsible for the conversion of ammonium into nitrate, are notoriously slow growing microorganisms (Judd, 2006). The tropical climate and high temperatures in the country also contribute to the systematic occurrence of nitrification in biological treatment systems implemented in Brazil (Von Sperling, 2005). Therefore, high removal efficiencies of ammoniacal nitrogen were predictable. Significant removals of total nitrogen, however, which indicate the occurrence of denitrification, were not expected once the reactor was fully aerated and had no anoxic zones. Nevertheless, this phenomenon may occur due to a reduced efficiency of oxygen transfer provided by a high concentration of biomass and high viscosity of the medium. In this manner, the inner regions of the biological flocs possibly did not receive oxygen and became anoxic zones, thereby providing favorable conditions for denitrification (Puznava et al., 2000). Moreover, since sludge growth was high, part of the total nitrogen removal may result from a higher nutrient uptake.

Table 2: Mean values of the main physicochemical parameters of feed and permeate and removal efficiencies of the MBR.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Feed</th>
<th>Perm.</th>
<th>Removal</th>
<th>Feed</th>
<th>Perm.</th>
<th>Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color (Hu)</td>
<td>1671.7</td>
<td>36.3</td>
<td>98%</td>
<td>3444.8</td>
<td>38.1</td>
<td>99%</td>
</tr>
<tr>
<td>DOC (mg/L)</td>
<td>863.6</td>
<td>8.0</td>
<td>99%</td>
<td>884.4</td>
<td>7.3</td>
<td>99%</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>4448</td>
<td>50</td>
<td>99%</td>
<td>4175</td>
<td>45</td>
<td>99%</td>
</tr>
<tr>
<td>BOD (mg/L)</td>
<td>2303</td>
<td>3</td>
<td>100%</td>
<td>2723</td>
<td>14</td>
<td>99%</td>
</tr>
<tr>
<td>TN* (mg/L)</td>
<td>74.7</td>
<td>3.5</td>
<td>98%</td>
<td>115.5</td>
<td>12.4</td>
<td>89%</td>
</tr>
<tr>
<td>N-NH₃ (mg/L)</td>
<td>4.6</td>
<td>0.2</td>
<td>96%</td>
<td>9.3</td>
<td>0.6</td>
<td>87%</td>
</tr>
<tr>
<td>Fosforous (mg/L)</td>
<td>27.5</td>
<td>12.5</td>
<td>53%</td>
<td>20.4</td>
<td>4.7</td>
<td>86%</td>
</tr>
<tr>
<td>TS* (mg/L)</td>
<td>5,227</td>
<td>1,734</td>
<td>65%</td>
<td>10,009</td>
<td>2,581</td>
<td>69%</td>
</tr>
<tr>
<td>TFS* (mg/L)</td>
<td>1,886</td>
<td>1,562</td>
<td>18%</td>
<td>3,117</td>
<td>2,146</td>
<td>29%</td>
</tr>
<tr>
<td>TVS* (mg/L)</td>
<td>3,341</td>
<td>172</td>
<td>94%</td>
<td>6,891</td>
<td>435</td>
<td>93%</td>
</tr>
</tbody>
</table>

* Total nitrogen; ** Ammoniacal nitrogen; † Total solids; ‡ Total fixed solids; ‡ Total volatile solids
There were also phosphorus removals of 53 and 83% for the HRTs of 8 and 6 hours respectively. Traditionally, systems that are designed for phosphorus removal must contain aerobic and anaerobic chambers in series in order to select and provide the growth of phosphate accumulating microorganisms (Von Sperling, 2005). In the case of conventional biological treatment systems, partial removal of phosphorus happens through its assimilation by the biomass for cell synthesis. In this case, the disposal of excess sludge can result in a phosphorus removal ranging from 10 to 30% depending on the organic load of the effluent and the operating conditions (US Environmental Protection Agency, 1987). Farizoglu et al. (2007) evaluated the nutrient removal in a jet loop reactor coupled with membrane treating whey and obtained phosphorus removal efficiencies between 65 and 85%, similar to those obtained in this study and higher than the ones expected for systems that have no specific configuration for advanced phosphorus removal. According to the authors, these high values are due to a considerable uptake of phosphorus for cell synthesis since the biomass concentration in the reactor was high (between 6,000 and 14,500 mg/L), and to the precipitation of phosphate with the ions Ca²⁺ and Na⁺, present in large amounts in the effluent concerned. Both reasons apply equally well to this work.

With respect to solids, the higher removal was for the volatile solids, which consist of organic matter that can be biodegraded. The removal of fixed solids may be related to precipitation of salts and/or retention of inorganic particulate material by the membrane. It is important to note that MBRs achieve a complete retention of suspended solids.

Based on the results, 6 hours was set as the optimum HRT for the system. Since the removal efficiencies of pollutants by the MBR in both conditions evaluated were similar, the operation with an HRT of 6 hours can be chosen to be the most appropriate one as smaller hydraulic retention times allow the construction of a smaller reactor, which results in a smaller plant footprint.

Figure 4 shows flux, pressure and operational permeability of the MBR. Dotted lines mark the days when chemical cleaning of the membrane was carried out.

The MBR was operated with constant permeate flow and variable pressure. During operations with HRTs of 8 and 6 hours, the permeate fluxes were 27.5 and 37.5 L/h.m², respectively. Maximum fluxes for MBRs with submerged membrane modules for domestic sewage treatment are usually between 25 and 30 L/h.m²; however, for industrial effluents these values are substantially lower, often between 5 and 15 L/h.m² (Cornel and Krause, 2008). Although 27.5 L/h.m² could therefore be considered a very high value for permeate flux for a submerged MBR, in this phase the system operated stably without dramatic increases in operating pressure. This is due to the application of aeration among the membrane permeation fibers through small holes distributed evenly on the base of the module. In contrast to aeration performed with aerators placed under the membrane module, the aeration method adopted provides a better distribution of the air flux and a better contact of the air bubbles with the whole length of the membrane fiber. It can therefore be proven that this is an effective procedure to control fouling and achieve a more sustainable operation.

![Figure 4: Flux, pressure and permeability with sludge of the MBR.](image)

When the flux was increased to 37.5 L/h.m² on the other hand, operating pressure and the rate of increase in pressure rose substantially. It can also be observed that the increase of the permeate flux resulted in a decrease in permeability due to increased fouling on the membranes. The average and the standard deviation permeabilities in the operations with HRTs of 8 and 6 hours were 380 ± 100 and 187 ± 63 L/h.m².bar, respectively.

**Molecular Weight Distribution**

Figure 5 shows the results of the molecular weight distribution of feed, permeate and mixed liquor in terms of carbohydrates.
It can be verified that the highest concentration of carbohydrates in the feed is in the fraction smaller than 10 kDa. Because the mixed liquor is the biologically treated effluent and the concentration of carbohydrates smaller than 10 kDa was lower than in the feed, one can say that there was a good biological degradation of the compounds in this fraction.

The fact that the permeate carbohydrate concentration smaller than 10 kDa was lower than that of the mixed liquor indicates that the membrane was able to retain some of these compounds which were not biodegraded. Since the membrane pores have an average size of 0.5 µm, molecules with a size below 10 kDa should not be retained. Therefore, the results indicate that a secondary or dynamic membrane composed of microorganisms and gel-like substances was formed on the surface of the polymeric membrane (Fan and Huang, 2002). Thus, it can be shown that, as previously noted by Kang and collaborators (2007), the formation of the dynamic membrane, despite causing an increase in filtration resistance, contributes to an increase in the efficiency of the system.

It should be noted, however, that there was not an accumulation of these compounds that were retained in the reactor, since no growth was observed in the concentration of the carbohydrates in the mixed liquor. What happens is that the retention time of these substances in the reactor exceeds the overall hydraulic retention time. Thus, slowly biodegradable or recalcitrant compounds may remain in the system until the microorganisms develop the capacity to degrade them (Farizoglu and Keskinler, 2006).

\[ \text{Figure 5: Concentrations of carbohydrates (a) smaller than 10 kDa, (b) between 10 and 100 kDa and (c) larger than 100 kDa.} \]
Analyzing the graph of carbohydrate concentrations larger than 100 kDa, we noted that the concentration in the mixed liquor was much higher than in the feed. This may be related to the hydrolysis of suspended solids from the feed and the release of carbohydrates to the soluble fraction or to the production of soluble microbial products (SMP) and extracellular polymeric substances (EPS). According to Jarusutthirak and Amy (2007) and Liang et al. (2007), SMP are the major constituents of the effluent treated by biological processes. However, these high molecular weight compounds were efficiently retained by the membrane, allowing the generation of a permeate with a low concentration of carbohydrates (average of the three combined fractions equal to 13 ± 10 mg/L, being 64% less than 10 kDa).

Figure 6 shows the results of the molecular weight distribution of feed, permeate and mixed liquor in terms of proteins.

Also for proteins, the fraction of highest concentration in the feed is smaller than 10 kDa. It was also noted that the profiles of concentration of protein smaller than 10 kDa in feed, permeate and mixed liquor of the MBR are similar to those of carbohydrates. Likewise, one can note that there was good biological removal of low molecular weight compounds and that the membrane had an essential role in producing a permeate of good quality with a mean total protein concentration (adding together the three fractions analyzed) of 20 ± 5 mg/L, of which 78% is in the fraction smaller than 10 kDa.

Although the total concentrations of proteins and carbohydrates in the mixed liquor are similar, the concentration of proteins with a molecular weight smaller than 100 kDa is higher, and the one with high molecular weight, greater than 100 kDa, typical of SMP and EPS (Dominguez et al., 2010), is lower than that of carbohydrates.

Figure 6: Concentrations of proteins (a) smaller than 10 kDa, (b) between 10 and 100 kDa and (c) larger than 100 kDa.
Because carbohydrates are synthesized extracellularly for a specific function and proteins often result in the excretion of intracellular polymers or cell lysis (Bura et al., 1998), the lower release of SMP and EPS regarding proteins indicates that the biomass was active and there was no situation of stress.

The importance of the membrane for the stability and efficiency of the process can be observed in the two previous figures, where it becomes clear that, regardless of fluctuations of the feed, changes in the biological removal efficiencies and the presence of SMP and EPS in the sludge, the permeate always had an excellent quality.

The mean efficiency of biological removal (%Biological), retention by the membrane (%Membrane) and the overall efficiency of the MBR (%MBR) for the three fractions of carbohydrates and proteins evaluated are presented in Figure 7. The efficiencies were calculated with the following equations:

\[
\% \text{Biological} = \frac{C_{\text{Effluent}} - C_{\text{MixedLiquor}}}{C_{\text{Effluent}}} \quad (1)
\]

\[
\% \text{Membrane} = \frac{C_{\text{MixedLiquor}} - C_{\text{Permeate}}}{C_{\text{MixedLiquor}}} \quad (2)
\]

\[
\% \text{MBR} = \frac{C_{\text{Effluent}} - C_{\text{Permeate}}}{C_{\text{Effluent}}} \quad (3)
\]

where \( C_{\text{Effluent}} \) is the average concentration in the raw wastewater, \( C_{\text{MixedLiquor}} \), the average concentration in the soluble fraction of sludge and \( C_{\text{Permeate}} \), the average concentration in MBR treated effluent.

It can be observed that the biological system presents higher degradation efficiency for the fraction of carbohydrates and proteins smaller than 10 kDa, which, according to the literature, is the most readily biodegradable fraction (Sonnenberg et al., 1995). Biological degradation of the other two fractions, between 10 and 100 kDa and greater than 100 kDa, is significantly lower. Moreover, it can be seen that, for carbohydrates greater than 100 kDa, there is even a negative removal, i.e., the concentration in the biologically treated effluent is greater than that of raw wastewater. A reason for this, other than the fractions being less biodegradable, is the production of SMP and EPS by the biomass and the hydrolysis of suspended solids in the reactor.

The membrane on the other hand was effective in retaining compounds of all sizes, especially the ones with a molecular weight greater than 100 kDa. As discussed above, the retention of soluble compounds by a microfiltration membrane is justified by the formation of a dynamic membrane on the surface of the polymeric membrane. This dynamic membrane is denser and more susceptible to adsorption than its support medium. Therefore, it is responsible for retaining many of the low molecular weight compounds that would pass through the pores of the polymeric membrane.

This study highlights the importance of the membrane for the greater efficiency of MBRs than that of conventional biological systems. Apart from allowing the complete retention of biomass and the operation with larger SRT and MLSS concentration, the membrane in MBRs can also contribute to the retention of compounds that were not biodegraded. It is noteworthy that the quality of treated effluents from conventional biological processes is lower than,
or at maximum equal to, the quality of mixed liquor, because the secondary sedimentation tank, when present, only removes the suspended biomass and not soluble compounds.

CONCLUSION

The use of the MBR for the treatment of dairy industry wastewater was shown to be feasible. The permeate of the MBR showed excellent quality with low concentrations of organic matter and nutrients. The efficiencies of the MBR operating at HRTs of 6 and 8 hours were similar, so the HRT of 6 hours was chosen as the optimum, since its adoption would allow the use of smaller reactors. It was possible to maintain the system pressure stable even with permeate fluxes as high as 27.5 L/h.m², because of the effective aeration applied among the fibers. However, there was an increase in fouling when the flux was raised to 37.5 L/h.m².

The molecular weight distribution has proved to be an important tool for a better understanding of the mechanisms of pollutant removal. It was shown that only low molecular weight compounds are efficiently degraded by the biomass. Compounds of the feed that were not biologically degraded and SMP and EPS produced by microorganisms have largely been retained by the membrane. It was shown that, although the formation of a dynamic membrane on the polymeric membrane increases the resistance to filtration, it is essential for the stability and efficiency of the MBR.

ACKNOWLEDGMENTS

The authors are grateful to PAM Membranas Seletivas for providing the membrane bioreactor and the membrane modules, to CNPq (National Council of Scientific and Technological Development of Brazil) for the scholarship and to FAPEMIG (Foundation for Research Support of the State of Minas Gerais) for the financial resources.

NOMENCLATURE

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOD</td>
<td>Biological Oxygen Demand</td>
</tr>
<tr>
<td>COD</td>
<td>Chemical Oxygen Demand</td>
</tr>
<tr>
<td>DOC</td>
<td>Dissolved Organic Matter</td>
</tr>
<tr>
<td>EPS</td>
<td>Extracellular Polymeric Substances</td>
</tr>
<tr>
<td>HRT</td>
<td>Hydraulic Retention Time</td>
</tr>
<tr>
<td>MBR</td>
<td>Membrane Bioreactor</td>
</tr>
<tr>
<td>SMP</td>
<td>Soluble Microbial Products</td>
</tr>
<tr>
<td>SRT</td>
<td>Solids Retention Time</td>
</tr>
</tbody>
</table>

REFERENCES


Domínguez, L., Rodriguez, M. and Prats, D., Effect of different extraction methods on bound EPS


