Total nitrogen removal in membrane sequencing batch bioreactor treating domestic wastewater

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ABSTRACT. This study aimed to evaluate the performance of a sequencing batch membrane bioreactor (SBMBR) in wastewater treatment for total nitrogen removal. The reactor, which was built on a pilot scale with a volume of 30 L, was operated for 154 days and fed with synthetic wastewater. The SBMBR was operated under a sequencing batch regime with a total cycle time of 4 hours, which was broken down into 5 min. at the feeding stage, 55 min. of an anoxic phase and 180 min. of aeration and filtration. The permeation flux used was 5.55 L m⁻² h⁻¹. The membrane bioreactor presented very efficient biological wastewater treatment, with COD, ammoniacal nitrogen and total nitrogen removal efficiency of 99, 98 and 96%, respectively. The high total nitrogen removal observed indicates that the SBMBR was able to promote effective nitrification and denitrification, with a concentration below 10 mg L⁻¹ of this parameter in the permeate.

Keywords: nitrification-denitrification, wastewater treatment, membrane bioreactor.

Remoção de nitrogênio total em biorreator à membrana em batelada sequencial tratando esgoto doméstico

RESUMO. Este estudo avaliou o desempenho de um biorreator à membrana operado na modalidade de batelada sequencial (SBMBR) na remoção de nitrogênio total de esgoto sanitário. O reator, em escala piloto e com volume de 30 L, foi operado por 154 dias e alimentado com esgoto sintético, simulando esgoto sanitário. O ciclo operacional do SBMBR era composto por três etapas: 5 min. enchimento; 55 min. de fase anóxica e 180 min de aeração e filtração, totalizando assim um ciclo de 4h. O fluxo de filtração utilizado foi de 5,55 L m⁻² h⁻¹. O biorreator a membrana apresentou elevadas eficiências de remoção, sendo observado para a DQO, nitrogênio amoniacal e nitrogênio total valores de 99%, 98% e 96%, respectivamente. A elevada remoção de nitrogênio total observada indica que o SBMBR foi capaz de promover efetiva nitrificação e desnitrificação do esgoto utilizado, gerando um efluente tratado com concentrações desse parâmetro sempre abaixo de 10 mg L⁻¹.

Palavras-chave: nitrificação-desnitrificação, tratamento de esgoto, biorreator à membrana.

Introduction

The advantages associated with the use of membrane bioreactors (MBR) in wastewater treatment are widely known (SANTOS et al., 2011). Harper et al. (2006) report that MBR operates similarly to the activated sludge process in which a membrane module replaces the secondary decanter. This membrane module, which is normally used for microfiltration or ultrafiltration, holds the biomass content inside the reactor regardless of its capacity to form floc and release sediment. This approach allows for the obtainment of a high concentration of organic biomass in the biological reactor, which, according to Judd (2006), intensifies the process of degradation of the carbonaceous matter and increases the efficiency of the treatment. The use of membranes instead of conventional sedimentation also enables a significant reduction of the area occupied by the treatment system and allows the generation of a pathogen-free effluent with low concentrations of suspended solids (MELIN et al., 2006).

Recently, MBR have been widely applied to the biological removal of wastewater nitrogen content (KIM et al., 2008). He et al. (2009) believe that this is due to the environmental impacts that are associated with the discharge of nitrogen compounds without proper treatment, such as: eutrophication, toxicity to aquatic organisms and
depletion of dissolved oxygen in receiving water bodies. Such adverse impacts have resulted in increasingly less permissive environmental legislation. The European Union (COMMISSION DIRECTIVE, 1998), for example, sets total nitrogen (ammonia, nitrite, nitrate and organic nitrogen) values between 10 and 15 mg L⁻¹ as the emission limit for sewage treatment plants, which requires the use of very efficient systems for the removal of these compounds.

Recent studies (DONG; JIANG, 2009; VARGAS et al., 2008; YANG et al., 2010) have demonstrated that the operation of sequencing batch membrane bioreactor (SBMBR) results in a large removal of nitrogenated compounds and generates an effluent capable of meeting restrictive emission standards. In SBMBR, nitrification and denitrification are enhanced, and as a result, high total nitrogen removal is achieved. This is due, according to Kim et al. (2007), to the control of aeration and non-aeration periods over time, which confers the system periods of aerobicis, where nitrification and oxidation of the carbon matter occurs, and periods of anoxia in which denitrification occurs. Therefore, the oxidation and subsequent reduction of nitrogen compounds are conducted by the alternation of the operational phases of the reactor. The presence of the membrane module in this system eliminates the need for the sedimentation phase, which is commonly observed in conventional batch reactors, and allows the removal of the treated effluent simultaneously to the aeration phase, thereby shortening the cycle time of the reactor (McADAM et al., 2005). Considering the advantages mentioned, this study aims to evaluate the performance of a sequencing batch membrane bioreactor in the treatment of domestic wastewater for total nitrogen removal.

**Material and methods**

**Pilot–scale reactor**

A sequencing batch membrane bioreactor (SBMBR) was used in this study on a pilot scale with a volume of 30 L, as illustrated in Figure 1. The reactor is composed of an stirrer to maintain the biomass homogenous in the tank, two air diffusers for mixed liquor aeration and removal of solids on the surface of the membrane, and two peristaltic pumps, one for feeding and one for filtration (permeate production). The membrane module used in the system was a submerged hollow fiber membrane (Polymen Co. France) with an average pore size of 0.08 μm (microfiltration) and a filtration surface area of 0.09 m². The reading of the transmembrane pressure (TMP) was obtained by a digital pressure sensor that was installed at the permeate line.

**Synthetic feed and inoculum**

The pilot unit was fed with synthetic wastewater simulating domestic sewage. The feed solution ingredients and concentrations were: 1.63 g L⁻¹ of CH₃COONa (1,270 mg O₂ L⁻¹ as COD basis), 0.55 g L⁻¹ of NH₄Cl (150 mg L⁻¹ as NH₄⁺-N basis), 0.065 g L⁻¹ of KH₂PO₄ (15 mg L⁻¹ as PO₄³⁻-P basis), 0.014 g L⁻¹ of CaCl₂·2H₂O, 0.09 g L⁻¹ MgSO₄·7H₂O and 0.3 mL of the micronutrient solution per liter of wastewater produced. The micronutrient solution contained the following compounds (per liter): 1.5 g of FeCl₃·6H₂O; 0.15 g of H₃BO₃; 0.03 g of CuSO₄·5H₂O; 0.18 g of KI; 0.12 g of MnCl₂·4H₂O; 0.06 g of Na₂MoO₄·2H₂O; 0.12 g of ZnSO₄·7H₂O; 0.15 g of CoCl₂·6H₂O and 10 g of EDTA (TERADA et al., 2006).

The SBMBR was inoculated with sludge from the aeration tank of activated sludge of municipal wastewater treatment plant in Florianopolis, Santa Catarina State, Brazil. The mixed liquor suspended solids (MLSS) and mixes liquor volatile suspended solids (MLVSS) at the start SBMBR operation was 1,350 mg L⁻¹ and 1,040 mg L⁻¹, respectively.

**Analytical methods**

The samples were collected from the influent (synthetic wastewater) and the effluent (permeate) to perform the analysis of chemical oxygen demand (COD), NH₄⁺ -N, NO₂⁻ -N, NO₃⁻ -N by spectrophotometry. COD and NH₄⁺-N were measured according to manufacturer’s instructions using Hach Method 8000 and 10031, respectively. NO₂⁻-N and NO₃⁻-N were analysed by alfa-naftilamina methods and by brucine methods, respectively (APHA, 2005). The concentration of total nitrogen was based on the sum of the NH₄⁺ -N, NO₂⁻ -N, and NO₃⁻ -N values instead of the...
independent test. In addition, it was also performed cycle analysis, which consisted of a series of samplings and analyses during the anoxic and aerobic stages to follow the transformations of the nitrogenated matter along the operational cycle of the reactor. Transmembrane pressure, temperature, pH and dissolved oxygen readings were conducted on line.

Critical flux determination

Critical flux measurements were conducted using the ‘flux-step method’, which consists in monitoring of the transmembrane pressure (TMP) while the flux is gradually increased (BACCHIN et al., 2006). With each new increment in the flux, there was a rapid increase in TMP with a tendency to stability. The point at which this stability no longer observed after increase of flux was considered as the critical flux.

Reactor operation

The pilot unit was operated under a sequencing batch regime, and an electrical control panel controlled the duration of each stage of the cycle (Feeding, Anoxic and Aeration/Filtration phases). The total time of the cycle was 4 h, which included 5 min. of feeding, 55 min. of the anoxic phase and 180 min. of aeration and filtration, simultaneously.

The solid retention time (SRT) was the same operation time of reactor (i.e., 154 d) because no sludge was taken out of the pilot unit during the experimental period, except for sampling. The temperature in the reactor varied according to room temperature, which ranged from 12.1 to 32.2°C. The volumetric exchange ratio (VER) was kept constant at approximately 5%. In Table 1, other operational parameters are presented.

<table>
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<tr>
<th>Table 1. Operational parameters of SBMBR.</th>
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<tr>
<td>Permeate COD wastewater NH₄⁺-N wastewater Organic loading Nitrogen loading</td>
</tr>
<tr>
<td>flux (L m⁻² h⁻¹) wastewater wastewater rate rate</td>
</tr>
<tr>
<td>5.55 1.270 120 380 45</td>
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The cleaning of the membranes was performed when the TMP value reached the limit of 0.7 bar. During the cleaning process, the membrane module was removed from the reactor and conditioned in a separate container, where the module was subjected to a filtration of alkaline (sodium hydroxide, 4 g L⁻¹), acid (citric acid, 20 g L⁻¹) and disinfecting (sodium hypochlorite, 200 mg L⁻¹) solutions for one hour each. After cleaning, the membrane module was returned to the SBMBR.

Results and discussion

COD removal

Figure 2 shows the variations in COD concentrations of the influent and effluent and its corresponding removal efficiency on the operating days of the reactor. The SBMBR performed excellently in the removal of organic matter throughout the monitoring period, with a concentration of COD below 20 mg L⁻¹ in the permeate and an average removal efficiency of 99%.

![Figure 2. Influent and effluent concentrations and removal efficiency of total chemical oxygen demand (COD) during the operation time of the reactor.](image)

The high and consistent stable removal of COD can be partially attributed to the high concentration of biomass in the reactor and the efficient retention of suspended material by the membranes (DONG; JIANG, 2009). Sun et al. (2006) report that the mechanism of separation in membranes contributes significantly to the maintenance of high levels of COD removal compared to gravitational sedimentation practiced in activated sludge reactors.

According to these authors, the membranes act as a barrier against the passage of particles and macromolecular components in the treated effluent and guarantee low concentrations of organic matter in the permeate. This behavior can be confirmed by the analysis of Figure 3, which shows that the values of soluble COD in the mixed liquor after 3h of aeration are situated above that respective values of COD in the permeate. These results confirm that the membrane filtration retains a portion of the soluble organics in the reactor.
Nitrogen removal

Figure 4 shows the variations in the concentration of total nitrogen in the influent and effluent and their respective percentage of removal.

The MSBR achieved high efficiency in the removal of total nitrogen, with an average of 96% and a concentration in the effluent below of 10 mg L\(^{-1}\). This indicates that the reactor was able to successfully execute the nitrification-denitrification processes that are described as the main mechanisms for nitrogen removal from wastewaters (TAN; NG, 2008). The good performance of this process can be attributed to the high nitrifying activity observed in MBR. In these reactors, the membrane filtration process retains organisms with specialized functions, such as *Nitrosomonas* sp. and *Nitrospira* sp., increasing their density in the reactor and enabling the complete oxidation of ammonia into nitrates (LI et al., 2005).

The anoxic phase was also of great importance for the good performance of the SBMBR with regard to the removal of total nitrogen, as shown in Figure 5. Throughout the monitoring, there was a decrease on nitrate concentrations during the anoxic stage, indicating the existence of denitrifying activity. In an anoxic environment and with available organic substrates, denitrifying bacteria start using nitrate as an electron acceptor during cellular respiration, which consequently leads to the conversion of this nutrient into gaseous nitrogen and its subsequent escape into the atmosphere (ARTAN; ORHON, 2005).

Figure 6 shows the monitoring of one-cycle on day 150, chosen as representative of the system. Through this analysis is possible to observe the variations in the concentrations of NH\(_4^+\)-N, NO\(_2^-\)-N, NO\(_3^-\)-N and dissolved oxygen (DO) within the anoxic and aerobic phase. The low level of DO observed during the anoxic phase stimulates the activity of the denitrifying microorganisms, which results in decrease concentration of nitrate on mixed liquor at the end of the anoxic phase of this cycle. With the start of the aerobic phase, the dissolved oxygen content increases gradually in the biological suspension, and the decay of ammoniacal nitrogen by the nitrification process is verified, which leads to the formation of nitrite and nitrate ions in the mixed liquor. The saturation of dissolved oxygen reached after 150 minutes indicates that the biological degradation of ammonia is finalized (TERADA et al., 2006; SCHEUMANN; KRAUME, 2009), resulting in a near-zero concentration, or complete nitrification of NH\(_4^+\)-N.
Biomass evolution

Figure 7 shows the biomass evolution in the mixed liquor of SBMBR. The MLSS started at 1,350 mg L\(^{-1}\) at the first day and reached a final concentration of 5,500 mg L\(^{-1}\). The rates MLVSS/MLSS always around to 0.9 indicates non-occurrence of accumulation of inert inorganic substances in mixed liquor (SUN et al., 2006), although the reactor was operated without excess-sludge removal.

During the overall operational period, a 0.061 mgMLVSS mgCOD\(^{-1}\) sludge yields were obtained. The low biomass production is similar to the value of 0.06 mg MLVSS mg COD\(^{-1}\) sludge yields obtained by Khongnakorn and Wisniewski (2007), who also operates the MBR under complete sludge retention. According to these authors, in condition of complete sludge retention, the system maintains a high degree of organic removal and low sludge yield. This minimization of the sludge production may be associated with low Food/Microorganisms ratios (F/M) that occur in high SRT-systems. At low F/M ratios, the substrate is essentially consumed in order to ensure the cell maintenance requirements instead of growth functions (LOW; CHASE, 1999). In this study, due to the biomass growth, the F/M ratios decreased over time, ranging from 0.36 to 0.08 mg COD mg SSV day\(^{-1}\), as show in Figure 8.

Many previous studies on membrane bioreactor have been performed at a F/M ratio around 0.1 mg COD mg MLSSV day\(^{-1}\) (ROSEMBERGER; KRAUME, 2002; LOBOS et al., 2008) in which the endogenous respiration is dominant, leading to a low biomass growth. Brown et al. (2011) report that the low F/M ratios of the MBR allow it to operate more efficiently and to handle higher COD loads than a conventional system.

Membrane performance

The Figure 9 shows the results of critical flux determination for the membrane module used in this research.

After the increase flux of 8.4 L m\(^{-2}\) h\(^{-1}\) to 11.1 L m\(^{-2}\) h\(^{-1}\) the TMP provides a non-linear relation with the applied flux. According to Cho and Fane (2002), this deviation from linearity between flux and TMP occurs under conditions of critical flux filtration, in which the fouling is more intense. Thus, was considered that the critical flux of the membrane module used was 11.1 L m\(^{-2}\) h\(^{-1}\) because it is from this limit that the PTM becomes non-linear. Therefore, it was decided to adopt the value of 5.55 L m\(^{-2}\) h\(^{-1}\) for the operation of the SBMBR, which is located below the critical value of 11.1 L m\(^{-2}\) h\(^{-1}\).

Figure 10 shows the evolution of the transmembrane pressure (TMP) and the mixed liquor suspended solids during reactor operation. In the first 30 days, the TMP behaved unstably, reaching the critical value of 0.7 bar, which was adopted as the limit for the chemical cleaning of membranes. Due to the high TMP registered, the system was stopped and the membrane module was subjected to a cleaning process with chemical agents. After cleaning, a more stable TMP behavior was observed, reaching a value of 0.24 bar on the 154th day of operation. These results demonstrate that on this occasion the TMP was in a lower range than the one found before stopping the reactor to clean the membrane module, even in a period of operation five times greater.

The rapid increase of TMP recorded during the first 30 days of operation was due to...
inadequate positioning of the membrane module in relation to the air diffuser, which allowed the high deposition of solids on the membrane surface, resulting in rapid fouling of the membranes observed during this short period.

It can be seen in Figure 10 that the increase of MLSS did not have a significant influence on the TMP. Chang and Kim (2005) report that the increase of MLSS may result in an increase in the resistance filtration process because a higher content of this parameter may result in higher fouling formation on the surface of the membrane. In spite of that, there is disagreement in the literature about the effect of MLSS on the filterability of membrane bioreactors (LOUSADA-FERREIRA et al., 2010), including studies that demonstrate the existence of a direct relation between MLSS and the TMP (KATAYON et al., 2004; MENG et al., 2006) and other studies in which no major evidence of such parameters were found (ROSEMBERGER; KRAUME, 2002; LOBOS et al., 2008).

Conclusion

The sequencing batch membrane bioreactor was able to promote effective total nitrogen removal. During the overall operational period, the total nitrogen concentration at permeate remained always below of 10 mg L⁻¹, value that falls within the limits imposed by the European community (15 mg L⁻¹) (COMMISSION DIRECTIVE, 1998) and by the Brazilian legislation (20 mg L⁻¹ - CONAMA 430/2011) established in the form of ammonia nitrogen (BRASIL, 2011). Additionally, the SBMBR was very efficient in removing COD because the concentration in the permeate was always below 20 mg L⁻¹.

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References


DONG, B.; JIANG, S. Characteristics and behaviors of soluble microbial products in sequencing batch membrane

Figure 10. TMP evolution and MLSS concentration during the operation time of the reactor.

Kim et al. (2008) attribute these differences to the different operating conditions adopted in each work, such as different F/M, wastewater characteristics, aeration rate and hydraulic retention time, which can alter the characteristics of the mixed liquor and influence the resistance during the filtration process.

Thus, it is clear that apart from the biomass content in the reactor, other factors must also be considered. In the specific case of membrane bioreactors that employ low-flow filtration, as in this study, the increase in MLSS content does not seem to bring much damage to the permeability of the membranes. It is believed that the small TMP oscillations observed after cleaning are due to temperature variations, which are lower (during winter), eventually interfering with the viscosity of the mixed liquor and thus impacting negatively on transmembrane pressure.


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