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Ultrafiltration hollow fiber membrane bioreactor (mbr) treating oil refinery wastewater C.G. Veronese¹, L.L. Beal*¹, V.M.J. Santiago², A.P. Torres², A.C. Cerqueira²

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INTRODUCTION

The membrane bioreactor is becoming a reliable technology for biological wastewater treatment and has a high potential for oil refinery wastewater treatment petroleum and oil pollution removal. However, there are limited investigations on the treatment and reuse of petrochemical wastewater using MBR technology (Qin et al., 2007). Recent experimental results showed that a submerged ultrafiltration process using modified PVDF membranes has a great potential for oil refinery wastewater treatment (Yuliwati et al., 2012).

In submerged MBRs, the membrane separation plays a significant role in maintaining high and stable COD removal. It serves as an addition purification phase to retain the remaining particulate COD and biomass, improving wastewater quality. The biological removal of COD occurs through three processes: COD utilization for biological denitrification, COD removal by aerobic oxidation and carbon converted to biomass (Sun et al., 2006; Dhamole et al., 2009).

The occurrence of a phenomenon known as *fouling* is extremely common in membrane filtration systems. This phenomenon is characterized by the adhesion of compounds to the membrane surface, causing the increase of the flow resistance. Therefore, the hydraulic performance of the membrane filtration is very important to make MBRs viable and economically attractive.

This paper evaluates the COD removal and nitrogen use efficiency through the use of biological process combined with submerged ultrafiltration membranes (SMBR) operating with anoxic and aerobic phase for the treatment of oil refinery wastewater, as well as evaluates the performance of the membranes through a period of approximately nine months of operation.

METHODOLOGY

The experiments were performed through a period of time of approximately six months in an experimental unit (Figure 1) comprising one anoxic reactor with a volume of 1.6 L, one aerobic reactor with a volume of 3.2 L and one membrane tank with an approximate volume of 3 L. The oil refinery wastewater flow rates ranged from 0.5 to 1.5 L/h on the two first months and from approximately 0.37 to 0.63 L/h on the last four months. The flow rates were changed according the purpose of the study. The two ultrafiltration membrane modules used in parallel, ZeeWeed ZW 1-3 (Figure 1-C), were made of PVDF (polyvenyldifluoride) with pore diameter of 0.04 µm. Aiming to produce turbulence on the membrane tank, to decrease reversible fouling, an air stone using compressed air was introduced into the bottom of the tank. Focusing on the reduction of the deposition of compounds on membrane surface, backwashes were performed for 30 seconds each 10 minutes.

The experimental unit is controlled by supervisory software. This software enables the acquisition of the following data: permeate flow rate, pressure in the membrane modules, DO concentration, pH, temperature and electrical conductivity on each reactor every 30 seconds.

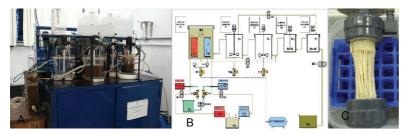


Figure 1 – Experimental unit (A), Software main screen (B) and ultrafiltration membrane modules (C)

Parameters such as chemical oxygen demand (COD) through closed reflux method, volatile suspended solids (VSS) and total suspended solids (TSS) were determined according to APHA (2005). Flocs size was weekly obtained using a particle size distribution analyzer HORIBA, LA-950V2 model.

During the unit operation the pH value was maintained at 7.0 on the anoxic reactor and at 7.5 on the aerobic reactor. This control was accomplished through the automatic dosage of 0.15 N sulfuric acid (H_2SO_4) and 0.15 N sodium hydroxide (NaOH). The aerobic reactor air flow rate was automatically controlled to allow a 2 mg/L DO concentration inside the reactor. The membrane module pressure control was also carried out assuming a maximum suction pressure of 450 mBar.

The wastewater characterization was weekly held. The supernatant of the reactors and the permeate parameters were determined twice a week. The membrane module flow resistance was evaluated over a period of approximately nine months. This membrane hydraulic resistance was obtained through five tests for membrane modules characterization, which were performed after chemical cleaning using sodium hypochlorite ranging from 100 to 250 mg/L. This tests were based on the permeate flux determination to pressures from 460 to 60 mBar applied.

RESULTS

The correlations made between floc size, volumetric organic loading rate, substrate utilization rate, food to microorganism ratio, volumetric nitrogen loading rate, nitrogen to microorganism ratio for the first two months of operation indicate that there is a really strong correlation between floc size and all these factors. Figure 1-A presents COD and total nitrogen for both oil refinery wastewater and permeate and Figure 1-B presents mean values of floc size distribution obtained.

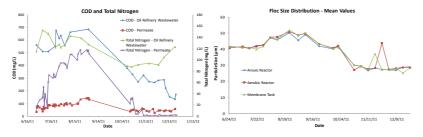
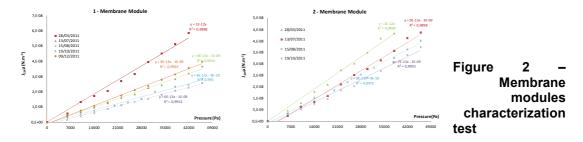


Figure 1 – COD and total nitrogen (A), mean values of floc size distribuition (B)

It was observed that for the typical COD values of the oil refinery wastewater with oil and grease segregation, the COD value of the permeate ranged from 45 to 100 mg/L most of the time. This is probably due to the presence of recalcitrant components that are not properly disposed with biological treatment. Also, it was verified a decrease in the permeate concentration of total nitrogen when the nitrogen to microorganism ratio of the system was purposely reduced.

Figure 2 presents the permeate flow rate at 20°C multiplied by the absolute viscosity versus the pressure applied to the membrane modules. The hydrodynamic resistance is represented by the linear adjustment coefficient obtained for each test.

It was found that the hydrodynamic resistance increased more than ten times after the first characterization test for both of the modules. This increase is probably due to the occurrence of irreversible *fouling* since the tests were performed after chemical cleaning. An increase on sodium hypochlorite concentration on the last characterization test, which went from 100 to 250 mg/L, caused a decrease of hydrodynamic resistance.



Keywords: membrane bioreactor, oil refinery wastewater, ultrafiltration