Oil refinery wastewater treatment in biofilm reactor followed by sand filtration aiming water reuse

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ABSTRACT

Oil refinery wastewater was sequentially treated in a moving-bed biofilm reactor (MBBR) and a slow-rate sand filter (SF) in order to obtain an effluent with adequate characteristics for downstream reverse osmosis (RO) operation. Experiments were conducted in bench scale units and the results showed that the MBBR was able to remove 90% chemical oxygen demand (COD), 75% NH_4^+, 95% phenols, operating with a hydraulic retention time (HRT) of 9 h. Additional removal of COD (15–40%) and ammonia (30–60%) was achieved in the slow-rate SF that was also effective for removing microorganisms. The silt density index (SDI) of the treated wastewater (4.5) was below the maximum limit recommended for RO operation. The quality of the effluent from the combined treatment system (MBBR+SF) was already adequate for cooling tower make-up. The RO produced an effluent with quality compatible with that required for use in boilers.

Key words | MBBR, refinery wastewater, sand filtration, water reuse

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INTRODUCTION

Water scarcity is a matter of concern in many countries, even in those that have significant water resources. Many industries located close to urban areas face the problem of water scarcity and have adopted practices of water economy and water reuse.

The oil industry, by its magnitude, is looking for more sustainable practices and, in particular, wastewater treatment at very efficient levels aimed at reuse is being implemented by several industries. However, the variety and complexity of wastewaters generated by the oil industry is enormous. Thus, several treatment techniques such as ozonation and sand filtration have been investigated to produce less polluted waters (Cha *et al.* 2010), distillation (Andrade *et al.* 2011), Fenton and photo-fenton oxidation (Coelho *et al.* 2006), biodegradation in moving bed bioreactor (Schneider *et al.* 2011), biodegradation in membrane bioreactor (Viero *et al.* 2008), advanced oxidation processes and carbon biological filtration (Souza *et al.* 2011).

Oil refineries utilize water in significant amounts, averaging 0.25–0.35 m^3 per barrel of oil processed. Most of these volumes are used in cooling and steam generation units. A survey of data from Brazilian refineries was made by Mariano (2001) and revealed the following water uses: steam generation (30%), cooling towers (30%), process water (28%), potable water (5%) and other uses (7%).

Removal of organic matter and salts is an essential requirement for water reuse in refinery boilers. Water quality requirements for cooling towers are not so strict, but removal of organic matter, solid particles and microorganisms is required.

Organic matter can be removed by several biological processes, activated sludge being one of the most used. Some biofilm processes are also effective in treating refinery wastewaters, such as rotating biological contactors (RBC). Another treatment system that has interesting features is the moving-bed biofilm reactor (MBBR). In such a reactor,

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the best characteristics of the activated sludge and biofilm reactors are combined (Rusten *et al.* 2006).

Salt removal can be reached by using reverse osmosis (RO), a process largely employed to produce water with a high purity degree and also to treat wastewater aimed at water reuse in some specific applications (Byrne 1995). Although very effective for salt removal, RO demands upstream treatments to remove suspended solids, organic compounds and microorganisms that cause membrane fouling. Some RO upstream processes are: activated carbon adsorption, microfiltration and ultrafiltration, sand filtration and others.

The aim of the present work was to investigate the utilization of a combined process, consisting of biological treatment in an MBBR and slow-rate sand filtration, to treat refinery wastewater in order to produce water for industrial uses. An additional objective was to investigate the performance of the MBBR to treat the industrial wastewater aimed at the replacement of the existing biological treatment (two aerated lagoons and two facultative lagoons with an overall hydraulic retention time (HRT) of 80 h) with a more compact system.

MATERIALS AND METHODS

Wastewater

Samples of wastewater were collected after the oil-water separation unit (flotation) of an oil refinery (Reduc, Petrobras, Brazil), transferred to the laboratory and kept under refrigeration (<4 °C) until use. The wastewater had a variable composition and its most prominent pollutants were hydrocarbons, phenols and ammonium nitrogen.

Experimental set-up

Figure 1 shows the experimental set-up (MBBR+SF). The MBBR (5 L capacity) was made of Plexiglas®. Particles for biofilm adhesion were supplied by AnoxKaldenes (K1 biomedias). An amount of particles corresponding to a bed volume of 3 L (60% of the MBBR volume) was used in the experiments. A porous diffuser was placed close to the reactor bottom and air flow rate was adjusted to assure particle circulation and oxygen transfer. This aeration device assured dissolved oxygen concentration in the liquid phase above 2.5 mg/L during the reactor operation. The HRT was fixed at 9 h and the reactor was continuously operated during 300 days. The MBBR effluent was collected to perform filtration assays. The sand filter (SF) was a cylindrical glass column (height = 47 cm, diameter 3.7 cm), which contained 35 cm of sand bed. Sand particles size was between 0.43 and 1.2 mm. The slow-rate SF was operated at two different filtration rates: 3 and 6 m^3/m^2 d. In general, slow SFs operate at rates in the range of 2.4–12 m^3/m^2 d (Galvis & Duque 1985). Filtration was performed at constant flow-rate (variable head loss) and monitoring of pollutants and microorganisms in the filtrate started after filter maturation, a procedure necessary to stabilize sand-bed compaction and allow implantation of a bacterial community in the filter. Maturation was conducted, feeding the filter with the MBBR effluent for a given period of time at a fixed filtration rate and monitoring filtrate turbidity. Experiments with two filtration rates were independent and begun

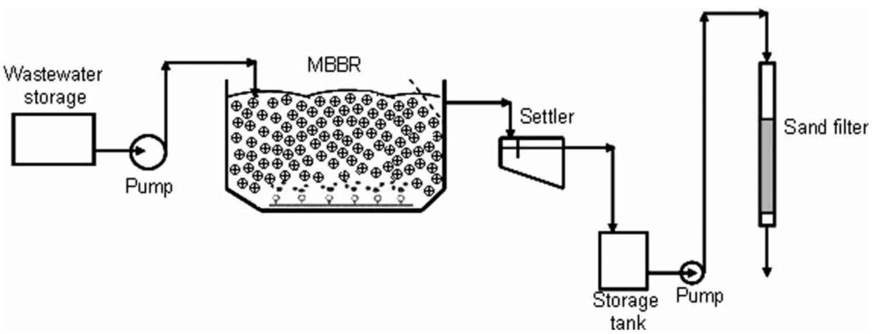

Figure 1 | Schematic view of the experimental set-up.

with the sand bed completely clean. Maturation was accomplished when filtrate turbidity remained constant. Filtration runs started, as soon as possible, after the filter maturation period.

Reverse osmosis assays

A bench-scale RO system supplied by (PAM Membranas, Brazil) was used to perform some long-term permeation experiments with the SF effluent (Figure 2). The sediment density index (SDI) of the SF effluent was determined using equipment designed by the Membrane Process Laboratory of our university. A view of this equipment is presented in Figure 2. SDI is a parameter that indicates membrane fouling tendency.

Analytical methods

Dissolved organic carbon (DOC) was determined in filtered samples (0.45 μm Millipore membrane), using a total organic carbon (TOC) analyzer (Shimadzu, model 5000 A). Chemical oxygen demand (COD), phenols, ammonia, total suspended solids (TSS) and volatile suspended solids (VSS) were determined according to Standard Methods (APHA 2005). Turbidity and conductivity were determined using a digital turbidimeter (Hach, model DR/2000) and a conductivity meter (Digimed, model DM-32). pH was measured using a digital pH meter (Oakton, model 110). SDI determination followed the recommendations of ASTM 4189-95. Microbial counts were made in samples of the SF effluent. This determination was performed according to classic techniques (Tortora *et al.* 2004) and the results were expressed as colony forming units (cfu/mL). Observations of microorganisms retained in the RO membrane were made by epifluorescent microscopy in a Zeiss equipment (model Axioplan 2) and also by scanning electron microscopy (SEM) in a FEI Company (model Quanta 200). The epifluorecence technique allows observation of biofilm attached to the membrane and microbial viability. SEM allows observation of biofilm structure and dispersion of microorganisms on the membrane surface.

RESULTS AND DISCUSSION

Wastewater characteristics

Samples collected over 10 months were characterized in terms of several parameters, their average values and range of variation are shown in Table 1. As already mentioned, wastewater presented high variability as a consequence of changes on the oil processed quality and

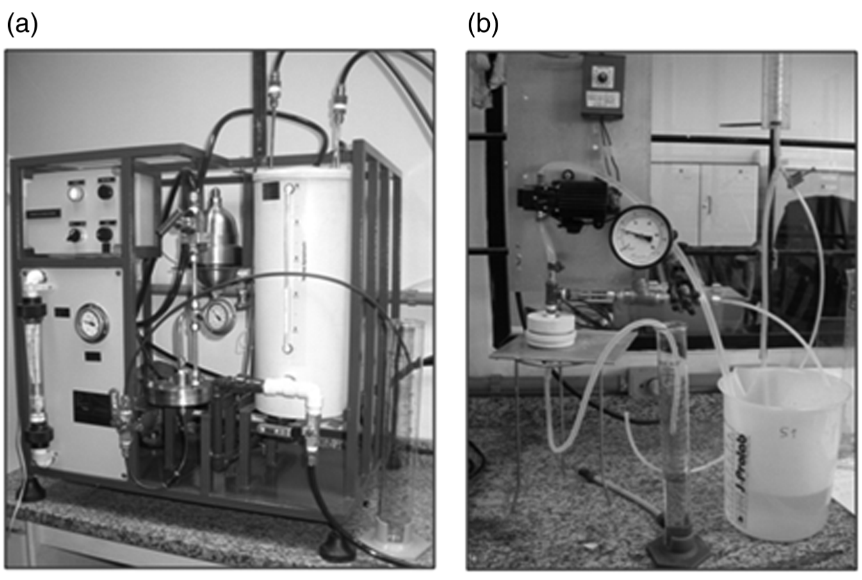

Figure 2 | Systems used for reverse osmosis experiments (a) and SDI determination (b).

Table 1 | Oil refinery wastewater characteristics

Parameter	Range of variation
Temperature	25–27
pH	6.5–8.5
Conductivity (μS/cm)	800–1,500
COD (mg/L)	200–5,500
DOC (mg/L)	20–200
Ammonia (mg/L)	10–30
Phenols (mg/L)	5–10
TSS (mg/L)	100–730
VSS (mg/L)	95–600

Table 2 | Characteristics of the MBBR effluent

MBBR effluent	Range of variation
DOC (mg/L)	9–40
COD (mg/L)	20–80
COD filtered (mg/L)	15–80
Ammonia (mg/L)	1–5
Phenols (mg/L)	0.02–0.2
Conductivity (μS/cm)	800–1,500
TSS (mg/L)	4.5–15
VSS (mg/L)	4–15
pH	6.3–9.1
Temperature (°C)	23–31

the refining conditions. The ranges of variation of COD and DOC were particularly large. This could pose some problems to the biological treatment that was submitted to variable organic loads. An unexpected high ratio of COD/TOC was observed, ranging from 10 to 27, indicating that the wastewater contains compounds in reduced forms, such as sulfides and mercaptans.

MBBR performance

The MBBR was very effective at treating the industrial wastewater. It assimilated large fluctuations on organic load and produced an effluent with COD and DOC lower than 80 and 40 mg/L, respectively. Figure 3 shows the time course variation of influent and effluent COD in the MBBR. Table 2 shows the range of variation of some relevant parameters of the MBBR effluent. The stable and good performance of the MBBR for removing organic matter seems to be an interesting attribute of this type of reactor, already highlighted by Ødegaard *et al.* (2004). Treating a similar wastewater, Schneider *et al.* (2011) reached COD removals in the range of 69–89%, operating a bench-scale MBBR with a HRT of 6 hours.

Besides organic matter removal, the MBBR removed ammonium nitrogen and phenols in percentages of 75 and 95%, respectively (Table 2). High ammonia removals (>90%) were also attained in an MBBR treating saline wastewater pretreated by activated carbon adsorption to remove inhibitory compounds, as reported by Bassin *et al.* (2011).

Another interesting result refers to suspended solids. Even considering that a small sedimentation tank was

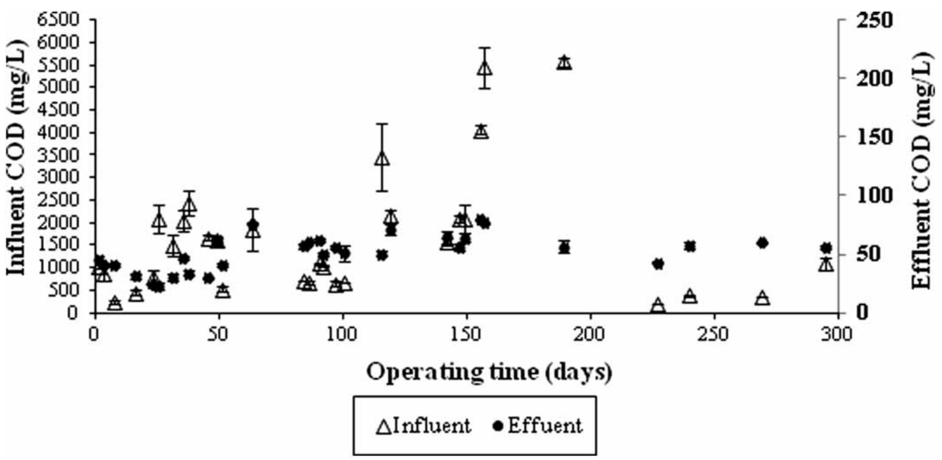

Figure 3 | Variation of influent (Δ) and effluent (•) COD in the MBBR.

installed downstream from the MBBR, average values of TSS and VSS were consistently low (≤15 mg/L). These values contrast with the high TSS and VSS contents of the MBBR influent. Thus, the MBBR followed by a sedimentation unit was able to produce an effluent presenting low levels of suspended solids.

Sand filtration results

As mentioned, filtration experiments were conducted after a period of filter maturation that lasted approximately 3 and 2 days for filtration rates of 3 and 6 m^3/m^2 d, respectively. The so-called filtration run correspond to a period of time in which the filter is operated continuously at a fixed rate (3 or 6 m^3/m^2 d). The filtration runs lasted 160 and 63 days for the filtration rates of 3 and 6 m^3/m^2 d, respectively. Results obtained during the filtration runs are shown in Table 3. Average values and standard deviations were supplied for turbidity, pH, conductivity and colony forming units, for the other parameters ranges of variation were given. In general, the two tested filtration rates led to similar results.

The SF promoted an additional removal of organic matter, since effluent COD and TOC values were 35±5 and 11±2 mg/L, respectively. Ammonia concentration in the SF effluent was low (0.7±0.2 mg/L) and turbidity dropped to 4–5 FTU. The number of colony forming units (cfu/mL) dropped slightly but remained in the level of 10^4 or 10^5 cfu/mL in the SF effluent. It would appear that a more pronounced drop of cfu/mL was observed in the filter operated at 3 m^3/m^2 d. A better filter maturation was probably achieved at that filtration rate. Some reports state that lower filtration rates and higher filter bed maturity are factors that contribute to improve microorganism retention (Bellamy *et al.* 1985).

The characteristics of the filtered water shown in Table 3 reveal that it can be used in cooling towers. Although no specific standards exist for water used in oil refinery cooling towers, some recommendations can be found in the literature (JIS 2006; Oenning & Pawlowsky 2007). Some upper limits for turbidity (<50 NTU), conductivity (<12,000 μS/cm), pH (6.9–9.0), ammonia (<20 mg/L) and COD (<75 mg/L) were recommended by these authors. The filtered water presented values of these parameters far below the limits suggested by these authors and can be considered for some applications in the oil refinery, including cooling tower make-up.

Short-term RO experiments

Initially, SDI determination was performed using the effluent from the SF. The time interval used in the assay was 15 min, so SDI_{15} was determined given an average value of 5. A recommended range for SDI is 3–5 (Amjad 1992). Following this determination, the RO set-up was operated and the permeate quality was accessed. COD and conductivity

Table 3 | Sand-filter influent and effluent characteristics

Parameter	Filtration rate (3 m^3/m^2 d) Influent	Effluent	Filtration rate (6 m^3/m^2 d) Influent	Effluent
COD (mg/L)	60±3	35±5	45±9	35±5
DOC (mg/L)	18±2	n.d.	14±2	n.d.
TOC (mg/L)[a]	n.d.	11±2	n.d.	11±2
Ammonia (mg/L)	2.0±0.7	0.7±0.2	1.3±0.2	0.7±0.2
Conductivity (μS/cm)	870–1,300	860–1,200	960–1,200	950–1,200
Microbial counts (cfu/mL)	$(1.4–7.8) \times 10^5$	$(6–46) \times 10^4$	$(5.3–7.9) \times 10^5$	$(5–14) \times 10^4$
Turbidity (FTU)	11–14	4–5	11–14	4–5
pH	6–8	6–8	6–8	6–8
Temperature (°C)	23±0.5	23±0.5	26±1	26±1

[a]For the sand-filter effluent, TOC and not DOC was determined.

Table 4 | Reverse osmosis permeate and concentrate COD and conductivity values and recommended values for steam boilers

Parameter	Permeate	Concentrate	LPSB[a] (<10 bar)	MPSB[b] (10–50 bar)	HPSB[c] (>50 bar)
COD (mg/L)	1.8	55	5[d]	5[d]	1[d]
Conductivity (μS/cm)	13.7	1,240	4,000[e]	600–1,000[e]	60[e]

[a]Low pressure steam boiler, [b]Medium pressure steam boiler, [c]High pressure steam boiler, [d]Oenning & Pawlowsky (2007); [e]JIS (2006).

of RO permeate and concentrate are shown in Table 4. As expected, the permeate presented adequate characteristics for low and medium pressure steam boilers, whose requirements concerning these two parameters are shown in Table 4 (JIS 2006; Oenning & Pawlowsky 2007). In addition, the organic matter content of the concentrate is below that imposed by the local regulations and this stream can be discharged in local receiving bodies.

An experiment was performed to monitor the permeate flux drop along operation time. The same experiment was also carried out with the MBBR effluent. Figure 4 shows the flux profiles for the two experiments. For the MBBR effluent sharp flux decay was observed after 1 day of operation, whereas for the SF effluent, permeate flux decreased smoothly. Comparing the RO permeate flux of these two feeding streams, we observe that feeding the RO with the

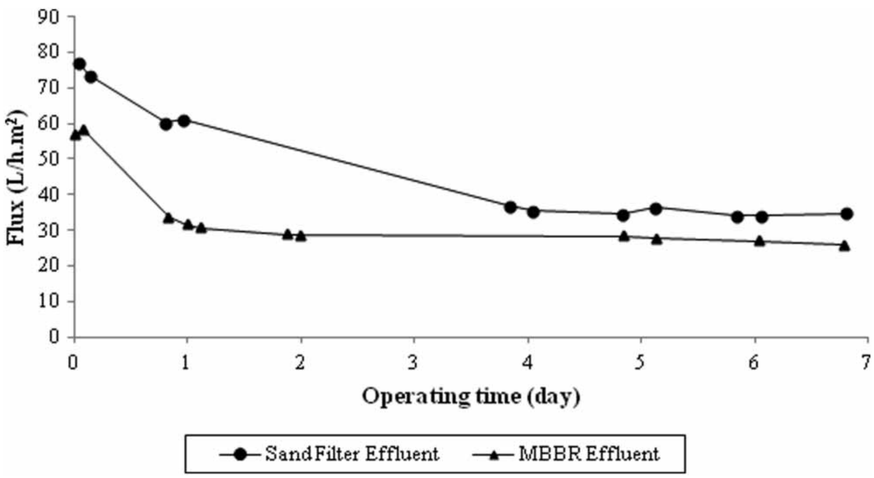

Figure 4 | Permeate flux variation: (▲) MBBR effluent (HRT = 9 h), (•) sand-filter effluent (3 m^3/m^2 d).

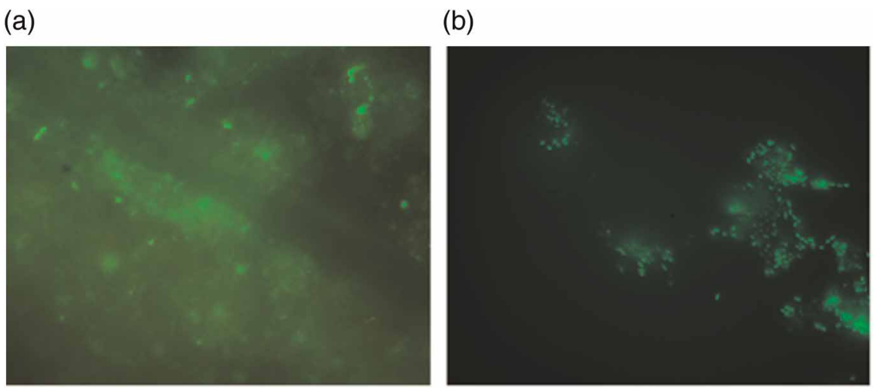

Figure 5 | Images obtained by epifluorescence microscopy of RO membranes: (a) feeding with MBBR effluent and (b) feeding with sand-filter effluent.

(a) (b)

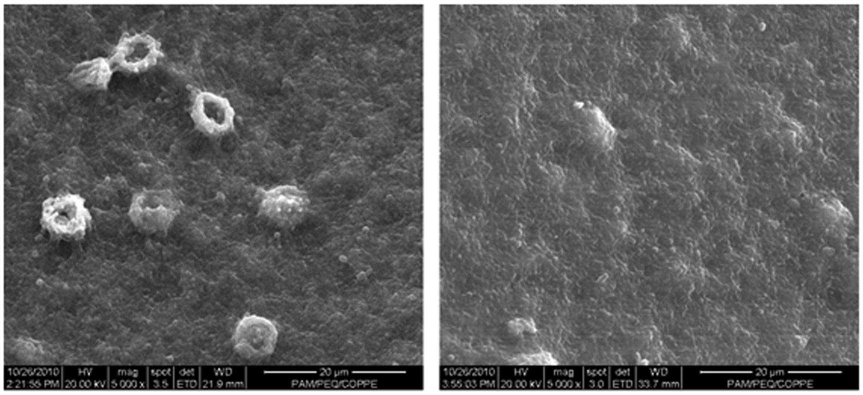

Figure 6 | SEM micrographs of RO membranes. Feeding streams: (a) MBBR effluent, (b) sand-filter effluent.

SF effluent led to higher flux values during the entire period of operation.

Results obtained by epifluorecence microscopy also reveal that a higher number of viable microbial cells (green) were observed on the membrane surface when the RO system was fed with the MBBR effluent (Figure 5). Also, electron scanning microscope images show that there were a larger number of microorganisms on the membrane surface of the RO system fed with the MBBR effluent (Figure 6). Thus, the microscopy results also render it evident that sand filtration is an adequate operation to perform upstream RO.

CONCLUSIONS

Biological treatment of the oil refinery wastewater in an MBBR led to high removal efficiencies of organic matter, ammonia and phenols. The MBBR was able to operate efficiently even when submitted to variable organic loads. The MBBR can replace the existing biological treatment system (lagoons) leading to a more compact installation (HRT of 9 h against 80 h in the lagoons).

The SF operated at two different filtration rates (3 and 6 m^3/m^2 d) produced effluents with similar characteristics but improved quality. Significant removals of COD and ammonia were achieved in the SF and the filter effluent can be used for some industrial applications such as cooling tower make-up. The SF effluent presented an SDI_{15} of 5 and permeation assays performed with two streams (SF and MBBR effluents) revealed that filtration contributed to reduce organic matter content and microorganisms, resulting in high permeate flux and less biofouling of the RO membranes.

The permeate produced by RO has a low content of organic matter (1.8 mg/L COD) and low conductivity (13.7 µS/cm). When presenting with these characteristics, the RO effluent can be considered for feeding low and medium pressure steam boilers.

The combination of MBBR and SF proved to be a promising treatment sequence to be implanted upstream of the RO system.

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