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The effects of long-term feeding of high organic loading in a submerged membrane bioreactor treating oil refinery wastewater

Aline F. Viero[a,*], Thainá M. de Melo[a], Ana Paula R. Torres[b], Neemias R. Ferreira[b], Geraldo L. Sant'Anna Jr.[a], Cristiano P. Borges[a], Vania M.J. Santiago[b]

[a] *Programa de Engenharia Química, COPPE, Universidade Federal do Rio de Janeiro, P.O. Box 68502, 21941-972 Rio de Janeiro, RJ, Brazil*
[b] *Petrobrás-CENPES, Gerência de Biotecnologia e Tratamentos Ambientais, Av. Horácio de Macedo, 950 Cidade Universitária, Ilha do Fundão, 21941-915 Rio de Janeiro, RJ, Brazil*

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ABSTRACT

The treatment of a refinery wastewater (oily stream) was investigated using a submerged membrane bioreactor (SMBR) operating with constant permeate flux. During the operation, long-term high organic loading rates were applied in the SMBR by feeding blends of the oily stream with a high strength phenolic wastewater, also generated in petroleum refineries. The effects of high organic loadings were evaluated regarding the organic matter and phenols removal efficiencies. The influence of the loading rate on filtration was also assessed, including the effects on the production of soluble microbial products, namely polysaccharides and proteins, and retention of these compounds by the membrane. The membrane had a key role in the process, since it improved COD and TOC removal efficiencies by 17 and 20%, respectively. The results proved the ability of the SMBR to tackle with high strength feed during long-term exposition achieving high phenols removal efficiencies, even with such complex feed.

1. Introduction

Membrane bioreactors (MBRs) have been widely used for domestic and municipal wastewater treatment because of reduced HRT, low sludge production and permeate quality that can be suitable for reuse [1–6]. Industrial application of the MBR technology has gained attention because of these features and also because of the robustness of the process that allows the operation with shock loading rates and hydraulic fluctuations [1,7].

Little about treatment of oily refinery wastewater in MBR was reported, especially regarding high strength oily wastewaters with high concentrations of ammonia-nitrogen. The effects of high organic loading rates in such systems are still a challenge. Wastewater salinity is also a hindering factor regarding the degradation performance.

Oil refinery wastewaters are characterised by the presence of several aromatic hydrocarbons and also inorganic substances. Due to the refinery wastewaters diversity and complexity, phenols have been accepted as a suitable compound to give an indication on the performance of biodegradation. Nevertheless, the presence of phenols reduces the biodegradation of other compounds [8] and also nutrients removal, when phenols concentrations surpass 400 mg L^{-1} [9].

Aromatic compounds have a hindering effect in the bioflocculation process of activated sludge systems when the sludge receives a shock loading with mixture of phenols in a refinery wastewater treatment plant [10]. Once a reactor was shock loaded, the biosolids tend to deflocculate producing turbidity and reducing microorganisms activity [11]. Such condition might evolve until the complete failure of the treatment process, even regarding the filterability of the sludge.

Phenols biodegradation in both synthetic and real wastewaters had been intensively studied in other processes. The biodegradation of a phenolic wastewater, with phenols concentration around 1000 mg L^{-1}, by a pure immobilized cells culture was studied in a fluidized-bed bioreactor and reached removal efficiencies superior to 90%, although the hydraulic retention time (HRT) to achieve such results was 4 days [12].

Although Jou and Huang [13] reported 85–90% COD removal rates and nearly 100% degradation of phenol, while processing an oil refinery wastewater in a fixed-film bioreactor with HRT of 8 h, the concentration of phenols in the wastewater was relatively low, around 30 mg L^{-1}. It is generally accepted that the phenol molecule is rather preferred by the microorganisms than other compounds with more complex structure. In addition, the presence (or absence) of recalcitrant compounds was not reported.

* Corresponding author. Tel.: +55 21 2270 2189; fax: +55 21 2562 8300.
E-mail address: afviero@peq.coppe.ufrj.br (A.F. Viero).

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Hsien and Lin [14] studied the biodegradation of phenolic wastewater in a bench-scale fixed-biofilm reactor. The phenols concentration in the feed was 72 mg L^{-1}; the operation of the reactor with HRT of 12 h led to a phenols removal efficiency of 94%. The authors have not reported whether recalcitrant or toxic compounds were present in the phenolic wastewater. Such substances could impair the efficiency of the process or even reduce phenols concentration in feed due to reaction.

The conventional activated sludge step of a process treating oilfield produced water was found to achieve phenols removal efficiency around 61% [15] of the original concentration (0.62 mg L^{-1}). However, Vázquez et al. [16] observed that the increase in the pH up to 8 improved the biodegradation of phenols allowing 96% removal efficiency.

Barrios-Martinez et al. [8] reported phenols removal efficiency of 100% during the treatment of a synthetic wastewater containing high phenols concentrations (~1000 mg L^{-1}) in an external membrane bioreactor using adapted biomass.

In this work, an oil refinery wastewater was treated in a submerged membrane bioreactor (SMBR) in order to evaluate the feasibility of the process for substitution of the conventional activated sludge process currently used in the refineries. The final goal is the introduction of a combined process, where the SMBR permeate percolates a granulated activated carbon filter (GAC), for recalcitrant organics removal. The effluent of the GAC feeds an electrodialysis unit, for dissolved salts removal, producing a final effluent suitable for reuse in cooling tower systems.

After an acclimatisation step, in which the SMBR operated with oily stream, high strength phenolic wastewater was added to the feed, to assess the performance of the reactor regarding the fouling of the membranes and the removal efficiencies of chemical oxygen demand (COD), total organic carbon (TOC), and phenols. During the operation, the role of the polyetherimide membrane in the process was studied. The effects of the combination of the wastewaters on biomass growth and production of soluble microbial products (SMP), which are mainly constituted by polysaccharides (PS) and proteins (PT), were also addressed.

2. Experimental

2.1. Activated sludge and oil refinery wastewaters

The wastewater treated was an oily stream (OS) from oil desalting process mixed with acid wastewater from FCC units, and oily water drained from crude oil storage tanks. A phenolic wastewater (PW) drained from the bottom of cracked gasoline tanks was added to increase the recalcitrant compounds content in the feed. Both wastewaters, PW and OS have high NH_4^+-N content and some salinity (<3.0 g L^{-1} chloride). Currently, the OS is treated by conventional activated sludge process after mixing with other streams generated in the refining process. The PW is even more difficult for biodegradation, because of its characteristics, and generally causes severe impairment to the activated sludge.

The activated sludge was sampled in a Petrobras oil refinery in Brazil, and sedimented to reach total suspended solids concentration around 10 g L^{-1}. After that, the sludge was acclimatised during 33 days, in the SMBR, processing the oily wastewater with characteristics shown in Table 1.

Table 1
Characterisation of the oily wastewater (OS)

	CN^{-1} (mg L^{-1})	Cl^{-1} (mg L^{-1})	NH_4^+-N (mg L^{-1})	S^{-2} (mg L^{-1})
Average	0.34	1084	110	2.23
Range	0.12–0.86	79–2526	15–331	0.02–12.51

Table 2
Characterisation of the stock phenolic wastewater (PW)

	COD (mg L^{-1})	Phenols (mg L^{-1})	NH_4^+-N (mg L^{-1})
Average	55,754	628	562.5
Range	2,278–145,455	523–875	500–750

The oily wastewater was previously filtered in a sand filter to reduce oil and grease content from 400 mg L^{-1} to around 50 mg L^{-1} before feed into the reactor. Sodium tripolyphosphate was added to the feed in the ratio 100 COD:2 P to enhance the activity of microorganisms, because the wastewaters do not contain phosphorus. After the addition of sodium tripolyphosphate, the pH in the reactor was around 8. In the 34th day of operation, the OS was combined with the phenolic wastewater, which characterisation is shown in Table 2, to give high phenols concentration. Both OS and PW were generated in the same oil refinery where the activated sludge sample was taken.

The reactor was operated with three different operation conditions regarding the wastewater, as shown in Table 3. The first one refers to the adaptation of the sludge to the operational conditions and wastewater, while the second is related to high organic loading operation and the third to the operation with the regular wastewaters flowrates as used in the refinery.

2.2. Experimental set-up

A schematic drawing of the SMBR used in this study is shown in Fig. 1 [17]. The reactor consisted of a cylindrical acrylic tank

Table 3
Wastewaters used during the experiments

Phase	Days	Wastewater	PW:OS	COD (mg L^{-1})	Phenols (mg L^{-1})	NH_4^+-N (mg L^{-1})
1	1–33	OS	–	616 ± 231	14 ± 21	109 ± 28
2	34–63	OS + PW	1:6	1010 ± 45	86 ± 2[a]	159 ± 41[a]
3	64–93	OS + PW	1:240	765 ± 187	12 ± 23	124 ± 14

[a] The peak values for the first day of addition of PW were not taken into account.

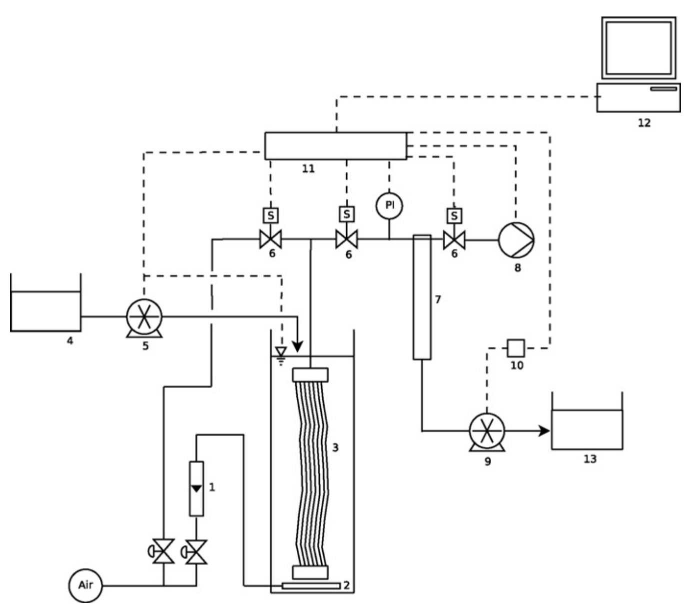

Fig. 1. Schematic diagram of the SMBR: (1) flowmeter, (2) air diffuser, (3) membrane skein, (4) reservoir, (5) peristaltic pump, (6) solenoid valves, (7) air separation tank, (8) vacuum pump, (9) positive displacement pump, (10) frequency inverter, (11) control and data acquisition system, (12) personal computer, (13) permeate tank.