

## MBBR evaluation for oil refinery wastewater treatment, with post-ozonation and BAC, for wastewater reuse

E. E. Schneider, A. C. F. P. Cerqueira and M. Dezotti

### ABSTRACT

This work evaluated the performance of a Moving Bed Biofilm Reactor (MBBR) in the treatment of an oil refinery wastewater. Also, it investigated the possibility of reuse of the MBBR effluent, after ozonation in series with a biological activated carbon (BAC) column. The best performance of the MBBR was achieved with a hydraulic retention time (HRT) of 6 hours, employing a bed to bioreactor volume ratio ( $V_B/V_R$ ) of 0.6. COD and  $N-NH_4^+$  MBBR effluent concentrations ranged from 40 to 75 mg L<sup>-1</sup> (removal efficiency of 69–89%) and 2 to 6 mg L<sup>-1</sup> (removal efficiency of 45–86%), respectively. Ozonation carried out for 15 min with an ozone concentration of 5 mg L<sup>-1</sup> was able to improve the treated wastewater biodegradability. The treatment performance of the BAC columns was practically the same for ozonated and non ozonated MBBR effluents. The dissolved organic carbon (DOC) content of the columns of the activated carbon columns (CAG) was in the range of 2.1–3.8 mg L<sup>-1</sup>, and the corresponding DOC removal efficiencies were comprised between 52 and 75%. The effluent obtained at the end of the proposed treatment presented a quality, which meet the requirements for water reuse in the oil refinery.

**Key words** | biological activated carbon (BAC), Moving Bed Biofilm Reactor (MBBR), oil refinery wastewater, ozonation, reuse

E. E. Schneider  
**M. Dezotti** (corresponding author)  
 Chemical Engineering Program – COPPE,  
 Federal University of Rio de Janeiro,  
 P.O. Box 68502,  
 21941-972,  
 Rio de Janeiro,  
 RJ,  
 Brazil  
 E-mail: [elisangela@peq.coppe.ufrj.br](mailto:elisangela@peq.coppe.ufrj.br)  
[mdezotti@peq.coppe.ufrj.br](mailto:mdezotti@peq.coppe.ufrj.br)

A. C. F. P. Cerqueira  
 Petrobras, Horácio Macedo Avenue,  
 950, 21941-915,  
 Rio de Janeiro,  
 RJ,  
 Brazil  
 E-mail: [ana.cerqueira@petrobras.com.br](mailto:ana.cerqueira@petrobras.com.br)

### INTRODUCTION

One-fifth of the world's population has no access to safe drinking water and half of all people have poor water sanitation. Water scarcity will affect more than 1.4 billion people in 48 countries by 2025 (ITT Industries 1999). The decrease in resources in natural waters is inciting authorities to establish and encourage the reuse of wastewater, including industrial wastewater. The obligation to respect the standards of wastewater disposal in the environment and the increase in water costs, compel the industries to rethink their wastewater management practices.

Water in the oil refinery industry is used in large quantities and may contain hydrocarbons, nitrogen and sulfur compounds, phenols and heavy metals. In this way, a new treatment system to the oil refinery wastewater was proposed for producing a high quality effluent, which can be reused in several industrial applications.

The Moving Bed Biofilm Reactor (MBBR) has many advantages when compared with conventional biological treatment systems: high sludge age, no sludge recycling, low

head-loss, use of the whole tank volume for biomass growth, less space, no influence of biomass separation, operational stability, improved mass transfer (Ødegaard 2006; Rusten *et al.* 2006; Aygun *et al.* 2008). MBBR is a completely mixed continuously operated biofilm reactor where biomass grows on small carrier elements that move in the reactor. The reactor may be used for aerobic, anoxic or anaerobic processes, for BOD/COD removal, phosphorous removal and nitrification.

Various techniques are used for the post-treatment of wastewaters for reuse. Because of difficulties in obtaining high quality water by using only biological processes, a hybrid treatment was proposed and investigated: MBBR process followed by ozonation and granular activated carbon columns with biofilm, named biological activated carbon (BAC).

Ozone is a powerful oxidant, and it is well known that ozonation of wastewater would result in considerable COD reduction and biodegradability improvement (Adams *et al.* 1997). Pre-ozonation of source water prior to BAC filtration is a commonly used method, which increases biofilm biological

activity and, as a result, extends GAC media life time (Van der Hoek *et al.* 1999).

Activated carbon adsorption has been widely applied for removing organic matter from wastewater. However, despite its high adsorption capacity, granular activated carbon (GAC) can operate for periods of time limited by its saturation capacity, when columns become saturated with adsorbed organic pollutants. Biological activated carbon (BAC) is a column of granular activated carbon covered with biofilms. The phenomenon of metabolization of adsorbed chemicals is referred to as bioregeneration (Seredyńska-Sobecka *et al.* 2006; Aktas & Çeçen 2007).

## MATERIALS AND METHODS

### Wastewater

The industrial wastewater used for this study was obtained from the treatment plant of Duque de Caxias Refinery (REDUC) - Petrobras, an oil refinery industry. The wastewater was firstly fed to a gravimetric oil separation unit (API tank), followed to a flotation unit. Grab samples of wastewater were collected at the exit of the flotation unit and transferred to our laboratory.

### Experimental arrangement and operational conditions

The laboratory-scale MBBR system consisted of the storage tank, the bioreactor (5 L) and the settler. The MBBR reactor was filled with Kaldnes biomedica K1 in order to operate with a bed/reactor volume ratio of 0.6. A diffuser placed at the bottom of the reactor was used for oxygen supply and mixing. The hydraulic retention time (HRT) was fixed at 12, 9, 6 and 3 hours and for each HRT value operation lasted 2 months. The refinery wastewater was continuously fed to the bioreactor using a peristaltic pump. The relevant operation parameters were monitored daily.

The ozonation experiments were carried out in a 1 L batch-reactor, and ozone was produced in a commercial ozone generator. The operational conditions investigated were ozone concentration (5, 10 and 15 mg L<sup>-1</sup>) and contact time (5, 10, 15, 20, 25 and 30 minutes). Ozone was continuously introduced through a porous diffuser. Samples for analysis were withdrawn from a sampling port at time intervals of 5 minutes.

Columns of granular activated carbon with biofilm (BAC) retained 5.5 g of dry carbon. Each column had an internal

diameter of 3 cm and a height of 2 cm. The influent flow rate was in the range of 0.3–0.8 mL min<sup>-1</sup>. Biofilm from the MBBR was used to inoculate the columns. Two columns of BAC were fed with the MBBR effluent (BAC-MBBR) and two with the ozonated effluent from the MBBR (BAC-MBBR/O<sub>3</sub>). The adsorption of pollutants was assessed through the utilization of GAC columns without microorganisms. Such condition was assured by the addition of sodium azide (8 g L<sup>-1</sup>) to the influent.

### Analytical Methods

Analytical procedures used for COD, N-NH<sub>4</sub><sup>+</sup>, phenol, TSS and VSS determinations were those outlined in *Standard Methods* (2005). DOC (dissolved organic carbon) was analyzed using a Shimadzu, 5000-A, TOC analyzer. Nitrate (N-NO<sub>3</sub><sup>-</sup>) was determined by ionic chromatography in a Dionex equipment (Model ICS-90). Turbidity was determined using a Turbidity-meter, PoliControl (Model AP-2000) and pH was monitored *in situ* with a portable pH-meter, Oakton (Model 110 Series). Absorbance at 254 nm was determined in a UV-VIS spectrophotometer, Shimadzu (Model 1240). The content of polysaccharides in the biofilms, removed from MBBR carries, was determined by the colorimetric method described by Dubois *et al.* (1956), using glucose as standard. Micrographs of the biofilm were obtained using an optical microscope, Hund (Model H500), coupled to a camera (Nikon Coolpix 4500).

## RESULTS AND DISCUSSION

### Wastewater characteristics

The wastewater used in the experiments was obtained from the oil refinery treatment plant at the exit of the flotation unit. During the experimental period of the study twenty four wastewater samples were collected and they presented a huge variability. Table 1 provides a short summary of the wastewater characteristics during the nine months of operation.

### Moving Bed Biofilm Reactor

Activated sludge from a municipal sewage treatment plant was used to inoculate the MBBR. The start-up period lasted about 1 month for biofilm growth on the biomedias. After that, the reactor was operated during a period of 8 months. Oxygen supply was adjusted in order to maintain the concentration of dissolved oxygen (DO) at a non-limiting

**Table 1** | Characteristics of the industrial wastewater fed to the MBBR

Parameter	Unit	Min	Max
COD	mg L <sup>-1</sup>	125	1095
DOC	mg L <sup>-1</sup>	28.9	158.8
Phenol	mg L <sup>-1</sup>	1.0	21.3
N-NH <sub>4</sub> <sup>+</sup>	mg L <sup>-1</sup>	5	51
TSS	mg L <sup>-1</sup>	9	93
VSS	mg L <sup>-1</sup>	7	48
Turbidity	NTU	4.2	108.0
pH	-	6.9	10.0

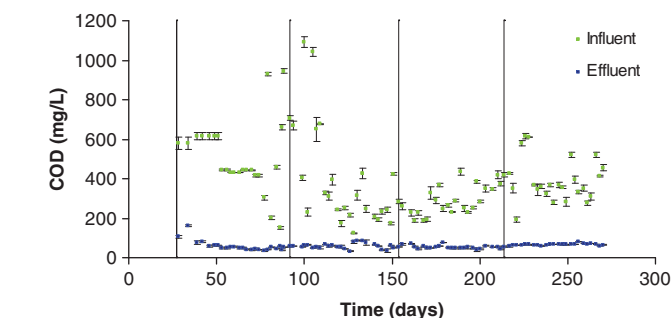
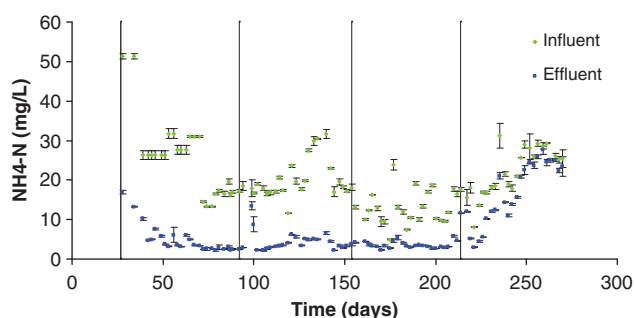
**Table 2** | Experimental runs corresponding to different organic loads

Run	HRT (h)	Organic Load (g DQO m <sup>-2</sup> d <sup>-1</sup> )
I	12	1.0–6.3
II	9	1.1–9.7
III	6	2.5–5.8
IV	3	5.2–16.4

level for the biological activity and to keep biomedias in suspension.

The organic loads applied to the MBBR during the operation period are indicated in Table 2. MBBR operation was very stable and the removal of organic compounds was high for the investigated conditions. The effluent COD was around 30–90 mg L<sup>-1</sup> for all applied organic loads, as shown in Figure 1.

The results shown in Figure 1 reveal that the MBBR had a good stability, even when submitted to different organic loads. The stability seems to be a positive MBBR attribute as already outlined by Ødegaard (2006) and Rusten *et al.* (2006).

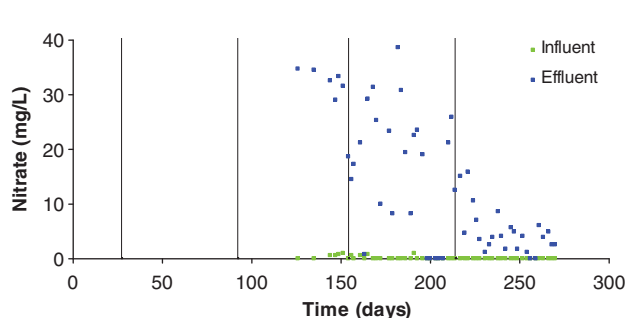
**Figure 1** | COD variation during reactor operation: influent and effluent values. Subscribers to the online version of *Water Science and Technology* can access the colour version of this figure from <http://www.iwaponline.com/wst>.

Hosseini & Borghei (2005) reported that MBBR can handle phenolic wastewaters with up to 220 mg L<sup>-1</sup> of phenol concentration without any inhibition. High phenol removal was observed in the present study. Removals in the range of 89 to 99% were achieved, and the effluent phenol concentration was comprised between 0.08 and 0.23 mg L<sup>-1</sup>.

The N-NH<sub>4</sub><sup>+</sup> content of the MBBR effluent remained practically constant in the first three runs (Figure 2). However, N-NH<sub>4</sub><sup>+</sup> removal efficiency dropped to low levels when HRT was reduced to 3 hours. The evidence of nitrification process was confirmed through the determination of effluent nitrate content for runs II and III. For run IV, nitrate concentration in the reactor effluent decreased significantly, revealing that nitrification collapsed for the highest range of applied organic loads (Figure 2).

The limiting factor for the choice of the best operation condition is nitrification efficiency. In run IV, although some small degree of nitrification was observed, it was not enough to produce an effluent meeting the discharge requirements. It is important to remark that the operating biological treatment system in the oil refinery has a hydraulic retention time of 80 hours, and the effluent nitrogen content does not always meet the discharge standards.

Biomass accumulation in the MBBR was followed through the determination of biofilm polysaccharides

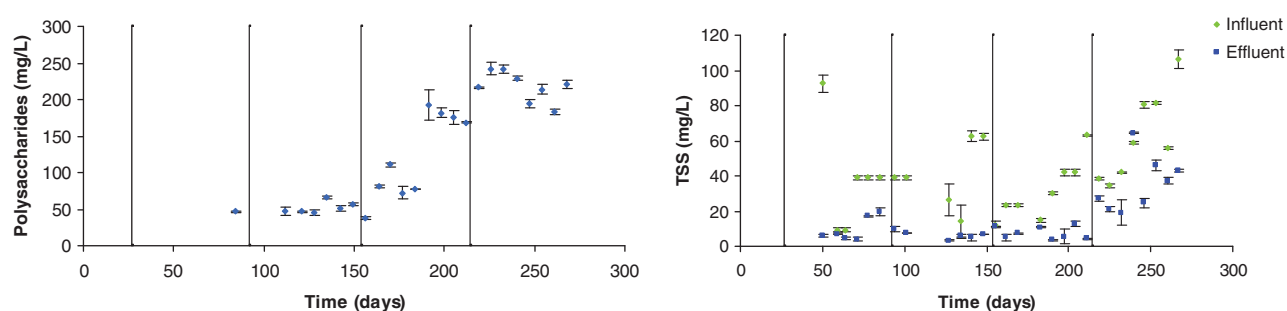
**Figure 2** | Variation of ammonia and nitrate concentration (influent and effluent) in different operation runs. Subscribers to the online version of *Water Science and Technology* can access the colour version of this figure from <http://www.iwaponline.com/wst>.

content. As shown in Figure 3, biofilm accumulation increased with organic load. The suspended biomass in the effluent, expressed as TSS, was low in the first three runs but increased significantly in the last run.

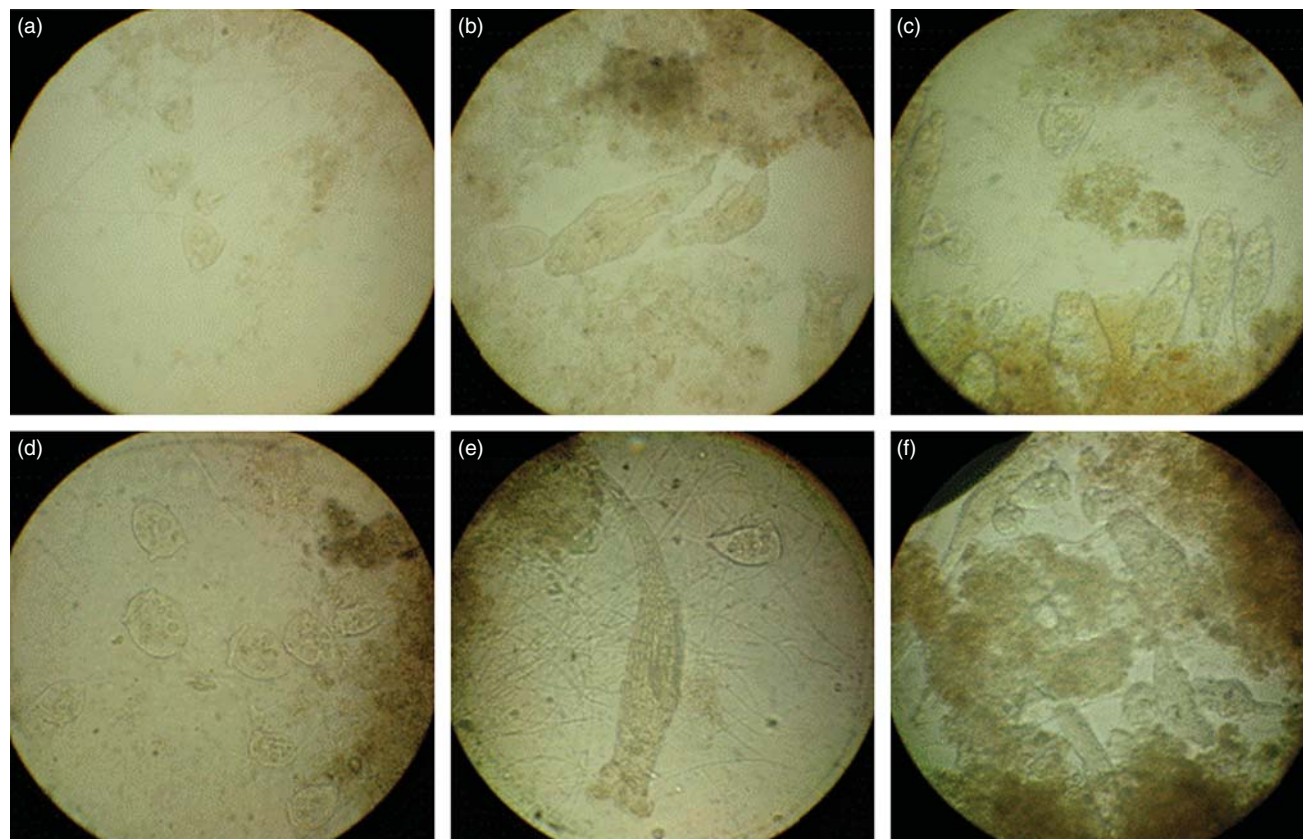
### Microscopic examination of biofilms

During the experiments, optical microscope observations were carried out by taking samples from biofilm adhered

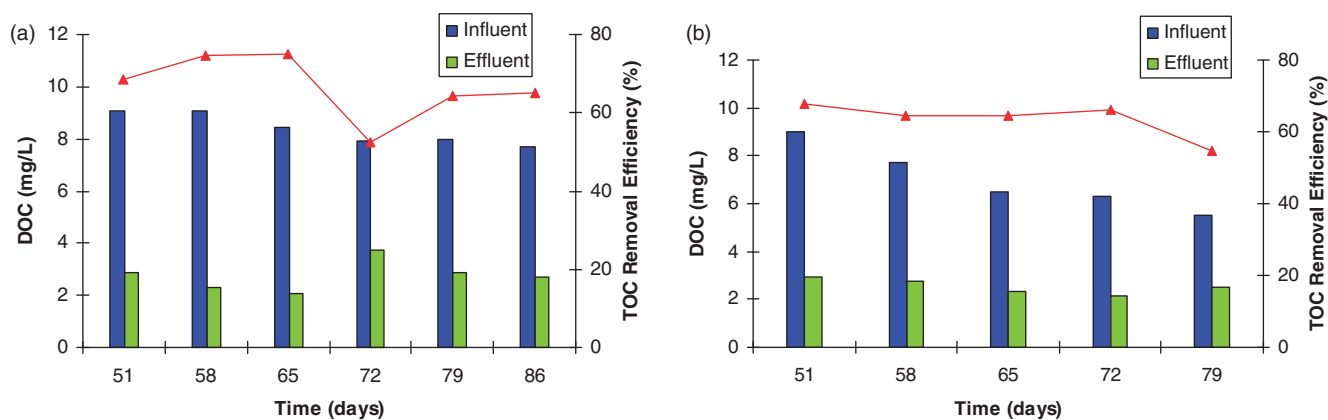
to the carrier elements. Photomicrographs showed a large number and variety of microorganisms in the biofilm, i.e. rotifers (the population increased during the operation), filamentous bacteria (only in HRT = 3 h), mobile and fixed protozoa (more observed in the HRT = 12 and 9 h). Micrographs also revealed the biomass accumulation during MBBR operation. Photomicrographs illustrating the aspects above commented are shown in Figure 4.



**Figure 3** | Content of polysaccharides in biofilms and suspended solids in the MBBR for different operation runs. Subscribers to the online version of *Water Science and Technology* can access the colour version of this figure from <http://www.iwaponline.com/wst>.



**Figure 4** | Photomicrograph of biofilm from the MBBR, magnified 400 ×. (a) Fixed protozoa (HRT = 12 h); (b) Rotifers and mobile protozoa (HRT = 9 h); (c) rotifers and fixed protozoa (HRT = 6 h); (d) fixed protozoa (HRT = 6 h); (e) rotifer, fixed protozoa and filamentous bacteria (HRT = 3 h); and (f) high microbial diversity (HRT = 3 h). Subscribers to the online version of *Water Science and Technology* can access the colour version of this figure from <http://www.iwaponline.com/wst>.



**Figure 5** | DOC values and DOC removal efficiency versus time: (a) BAC-MBBR and (b) BAC-MBBR/O<sub>3</sub>. Subscribers to the online version of *Water Science and Technology* can access the colour version of this figure from <http://www.iwaponline.com/wst>.

## Ozonation

The effluent from the MBBR was filtered, in order to simulate a sand filter operation, before ozonation. For different ozone concentrations and contact times the following variables were monitored: pH, DOC removal and UV<sub>254</sub> absorbance. DOC removal efficiency was low (approximated 10%) after 30 minutes of contact time, for all tested ozone concentrations. UV<sub>254</sub> absorbance was moderately reduced after ozonation. Using an ozone concentration of 5 mg L<sup>-1</sup> and 15 minutes of contact time, 40% of UV<sub>254</sub> reduction was achieved.

## Columns of granular activated carbon with biofilm (BAC)

Biological activity of carbon filters was assessed during 40 days of operation. According to [Seredyńska-Sobecka \*et al.\* \(2006\)](#), microorganisms are present on the external surface and inside the macropores of GAC. For this reason, the presence of microorganisms in the columns was confirmed using the entire particle of granular activated carbon and the method of successive dilutions with subsequent plating. After incubation for 72 hours at 303 K,  $1.88 \times 10^7$  ufc of bacteria per milliliter and  $5.10 \times 10^5$  ufc of fungi per milliliter were found.

BAC columns work as bioreactors in which two parallel processes take place: biodegradation and adsorption on activated carbon. To assess the removal of pollutants by adsorption, control experiments were performed, using GAC columns fed with sodium azide to avoid microbial growth. These columns were early saturated in comparison BAC columns. Thus, colonization with microorganisms is an

alternative method to extend GAC columns life time. As illustrated in [Figure 5](#), DOC concentrations of the BAC effluent were constantly around 2 to 4 mg L<sup>-1</sup>.

As show in [Figure 5](#), the columns of BAC-MBBR and BAC-MBBR/O<sub>3</sub> showed similar DOC removal efficiencies (52–75%). Thus, ozonation was not anymore considered as a treatment technique for the specific wastewater used in the present work. In turn, BAC columns showed to contribute to polish the MBBR effluent, producing water that can be reused in industrial applications.

## CONCLUSIONS

MBBR operation with HRT ranging from 12 to 3 h had a stable COD removal performance (removal efficiencies of 89 to 69%) and produced an effluent presenting COD concentrations comprised between 40 and 75 mg L<sup>-1</sup>. Such concentrations are fairly smaller than the local discharge requirement (COD < 250 mg L<sup>-1</sup>).

The experimental results in MBBR indicated that the best HRT was 6 hours, because it provided good N-NH<sub>4</sub><sup>+</sup> removal efficiency. Ammonia concentrations in the MBBR effluent were in the range of 2 to 6 mg L<sup>-1</sup>. MBBR operation with a HRT of 3 hours was not effective to promote nitrification. The MBBR effluent N-NH<sub>4</sub><sup>+</sup> concentrations were below the local discharge standard (< 20 mg L<sup>-1</sup>). Nitrification was confirmed by the presence of nitrate in the MBBR effluent.

Biofilm examination by optical microscopy revealed presence of rotifers, filamentous bacteria and mobile and fixed protozoa. Biomass accumulation increased with applied organic load and suspended solids reached up to 60 mg L<sup>-1</sup>

when the MBBR was operated at the highest organic load range.

The MBBR process showed to be an efficient alternative to the conventional biological treatment for organic matter and N-  $\text{NH}_4^+$  removal. Also it can be utilized for upgrading the existing facilities achieving high efficiency with reduced HRT values.

Ozonation reduced the  $\text{UV}_{254}$  absorbance of the wastewater but was not effective to remove DOC. BAC columns were able to reduce DOC to a low level: 2–4  $\text{mg L}^{-1}$ . Furthermore, they operated for longer periods in comparison with GAC columns, showing that the use of BAC is an alternative method to extend GAC columns life time. The effluent obtained at the end of the treatment presented the necessary characteristics to be reused in the oil refinery.

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