

# O<sub>3</sub>/BAC filter performance to remove organophosphates and toxicity during urban wastewater treatment

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The increase in emerging contaminants in surface water has become a major problem for the environment. Flame retardants, such as organophosphates (OPFRs) are the new type of extremely toxic contaminants and are present in daily life. In this work it was tested the combination of Ozone and Biologically activated carbon (BAC) for removing OPFRs in urban wastewater and the ecotoxicity of this effluent during treatment. The removal performance of OPFRs was 100%, indicating concentrations below the limit of detection (LOD) through GC-MS analysis. The toxicity test was carried out using *Eruca sativa* and *Artemia salina* and showed that the BAC treatment was not sufficient ( $p > 0.05$ ) to reduce toxicity for the tested microcontaminants. The combination of O<sub>3</sub> and BAC was able to reduce effluent toxicity by more than 40%.

## Introduction

Flame retardants (FR) are used in construction materials such as polymers used in electrical and electronic equipment, building materials and furniture, polyurethane foam, textiles, and some chemical formulations (paints, resins) [1]. Due to their complex structure are not effectively eliminated by conventional water and sewage treatment and, consequently, with the increase in toxicity and persistence of these compounds, changes in metabolism can occur and cause various diseases in living beings [2]. In addition, these pollutants are present in surface water, groundwater, and discharges from wastewater treatment plants (WWTPs). In this context the present work aims to investigate the performance of biological filters in the post treatment of secondary effluents from a commercial GAC. The effluent present in the work comes from the secondary post treatment and presents high amount of organic matter stimulating the growth and biological activity in the biofilters. Furthermore, the influence of microorganisms on the surface of the GACs and the performance of OPFRs: tris (2-chloro-1-(chloromethyl) ethyl) phosphate (TDCIPP) and tributylphosphate (TNBP) removal through the optimization of parameters (filtration and contact time) was investigated and compared.

## Material and Methods

The effluent was collected from the WWTP "Águas da Serra" located in the city of Limeira- SP, immediately after the secondary treatment. It was collected every 2 months, for 1 year. After collection, the characterization of the effluent was performed for physical-chemical parameters [3]: pH, Alkalinity, Turbidity, TSS, COD, BOD, UV<sub>254nm</sub>, Conductivity and Color.

The BAC columns were assembled in laboratory scale glass tubes of 1 m height and 20 mm internal diameter. The granular activated carbon (GAC) was used to pack the columns, purchased Sigma Aldrich (Darco®, 12-20 mesh) and BFilters (12-20 mesh) was packing 50cm of high. Before packing, both GACs were manually inoculated with activated sludge, collected from the WWTP "Águas da Serra" Limeira-SP, for 15 days, to accelerate the microbial colonization process. An ozone generator produced ozone with a maximum 12 g O<sub>3</sub> h<sup>-1</sup> capacity. The reaction was initiated with 10 mgL<sup>-1</sup> of ozone measured by indirect iodometry. The BAC characterization was performed by Scanning Electron Microscopy (SEM), Surface Area and Porosity (BET) and the determination of OPFRs was performed by gas chromatography coupled to mass spectrometry (ITQ 900 Ion Trap Mass Spectrometer, Thermo Scientific). The toxicity during the treatments was carried out with *Eruca sativa* and *Artemia salina*.

## Results and Discussion

The SEM images of BAC samples after biofilm formation (75 days) as shown in figure 1.

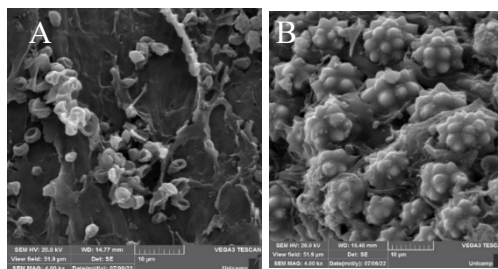
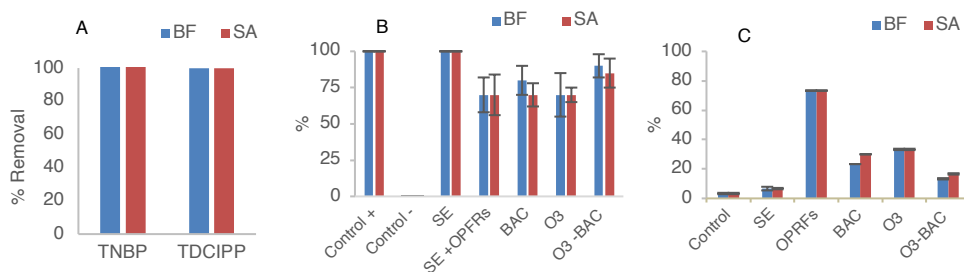


Figure 1. SEM images of BAC, resolution up to 5.00kx. A) BF, B) SA.

Through the N<sub>2</sub> adsorption and desorption experiments, the BET surface area of Fresh GAC and GAC after biofilm formation was obtained (Table 2).

**Table 1**-Surface properties of GAC (BFilters), GAC (Sigma-Aldrich) and their respective BACs.

Properties	GAC (B-F)	GAC (S-A)	BFilters	Sigma-aldrich
			50 cm	50 cm
Particle Size (mesh)	12 x 25	12 x 20	-	-
Surface Area BET (m <sup>2</sup> g <sup>-1</sup> )	481.603	627.07	544.145	629.157
Average Pore diameter (nm)	1.553	1.326	1.519	1.284
Total pore volume (cm <sup>3</sup> .g <sup>-1</sup> )	0.187	0.208	0.207	0.202



**Figure 2**- Removal of OPFRs (A), Relative germination of *E. sativa* seeds (B), *Artemia salina* mortality (C) in the secondary effluent for BF and SA.

## Conclusions

The SEM images showed a change in the surface of the GAC after biofilm formation, indicating an increase in porosity. Colonies with fungal characteristics were detected in the SEM images of both the BF and SA GAC, with a greater predominance of the species on the BF carbon. Surface area and pore volume increased, and pore diameter decreased with biofilm growth for both types of GAC (BF and SA). However, the BF GAC showed a greater increase in surface area, ranging from 481.60 m<sup>2</sup> g<sup>-1</sup> to 692.05 m<sup>2</sup> g<sup>-1</sup> (an increase of 43.70%) after biofilm formation. The removal of OPFRs was approximately 100%, as shown by the spectrometric results (GC-MS) where the concentration values were below the limit of quantification (LOQ) and detection (LOD). Through the RG and mortality by *Artemia salina* tests, the t-test showed that the O<sub>3</sub>/BAC system was efficient in reducing the toxicity of the effluent after treatment.

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