FENTON OXIDATION AS A STRATEGY TO PRESERVE THE BIOMASS IN THE ACTIVATED SLUDGE SYSTEM

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***Abstract*– Wastewaters containing biocides constitute an increasing environmental pollution concern. In this work, the feasibility of implementing a pre-treatment based on the Fenton process to minimize the negative impact of biocide compounds, such as benzalkonium chlorides (BAC), on the activated sludge system was studied. The behavior of the microbial community in the presence of a BAC solution untreated (BAC_{100}) or pre-treated by homogeneous Fenton oxidation (BAC_{100}/HF) was analyzed. The addition of BAC_{100} to the activated sludge system caused a deleterious effect. The cellular lysis process caused a 30% decrease in biomass concentration. The inhibition of respiratory activity was 73%. In contrast, BAC_{100}/HF caused no significant decrease in the biomass concentration or detectable inhibition of the respiratory activity. Besides, the consumption of easily oxidizable products was observed. Results indicated that the homogeneous Fenton process as a pre-treatment of wastewaters containing BAC could become a feasible alternative to protect active biomass in biological treatment systems.**

***Keywords*— Benzalkonium chlorides, Fenton oxidation, Iron sludge, Activated sludge, Respirometric tests.**

I. INTRODUCTION

Wastewaters from diverse chemical industries and healthcare establishments frequently contain biocides, which constitutes a growing environmental pollution problem (Rasheed *et al*., 2019). The removal of biocide chemicals is inefficient in conventional wastewater treatment plants and they are consequently released into watercourses and dispersed into the environment (Zhang *et al*., 2015; Mulder *et al*., 2018). Quaternary ammonium compounds (QACs) are biocides extensively used as surfactants, emulsifiers, fabric softeners, disinfectants, pesticides, corrosion inhibitors, and personal care products or as preservatives in pharmaceutical industry (Ismail *et al*., 2010; EPA, 2006). Among the QACs, benzalkonium chlorides (BAC) have been detected in sewage and surface waters, sewage sludge, river sediments and soils (Zhang *et al*., 2015). BAC are characterized by having a positively charged nitrogen covalently bonded to two methyl groups, a benzyl group, and a chain alkyl group of varying length (8-18) balanced by a chloride anion (EPA, 2006). The degradation of BAC in different aerobic microbial communities has been extensively studied (Tezel and Pavlostathis, 2015, Ertekin *et al*., 2016, Chen *et al*., 2018). Though BAC was found to be biodegradable by the activated sludge, their presence could promote changes in microbial diversity and also enhance the risk of developing BAC resistance or generate cross-resistance to antibiotics.

In this context, advanced oxidation processes (AOPs), and also the coupling of AOPs and biological systems represent promising strategies to treat wastewaters containing biocides and/or increase their biodegradability (Lopez Loveira *et al.,* 2012; *Vargas et al*., 2016). Relatively few studies have been published regarding BAC degradation by AOPs, in particular, O_3/H_2O_2 (Khan *et al.*, 2017), persulfate (Wang *et al*., 2018; Hong *et al*., 2017); UV/chlorine (Huang *et al.*, 2017); UV/persulfate (Lee *et al*., 2018); photocatalysis (Lopez Loveira *et al*., 2012; Suchithra *et al*., 2015); photo-Fenton and ozonation (Dantas *et al*., 2009; Carbajo *et al*., 2016) and Fenton (Zhang *et al*., 2016). Among these AOPs, Fenton's oxidation stands out by its simplicity and the use of low price and non-toxic reagents (Babuponnusami and Muthukumar, 2014). This process is based on the reaction between ferrous iron and hydrogen peroxide to produce hydroxyl radicals, which are highly active and non-selective species. Once hydroxyl radicals are formed, they can react efficiently with organic compounds or participate in scavenger reactions by reacting with residual hydrogen peroxide, reactive oxygen species or ferrous ions (Doumic *et al*., 2013). To our knowledge, only the work of Zhang *et al.* (2016) investigated the homogeneous Fenton oxidation of BAC aiming at reducing the solution´s toxicity. These authors analyzed the influence of pH and the molar H_2O_2:Fe^{2+} ratio on the temporal BAC concentration profile in experiments conducted at 25°C.

In our study, the homogeneous Fenton oxidation was evaluated as a pre-treatment stage to preserve the active biomass in the activated sludge process. The influence of the temperature on the evolution of BAC, H_2O_2 and total iron concentrations along the Fenton process was explored. The toxicity and biodegradability of the BAC-containing solutions before and after homogeneous Fenton treatment were evaluated by respirometric tests using non-acclimated activated sludge.

II. METHODS

A. Pre-treatment of benzalkonium chlorides: homogeneous Fenton process.

Fenton oxidation tests were carried out in a thermostated batch Erlenmeyer flask, equipped with a magnetic stirrer (stir bar 4 cm-length). For each test, 540 mL of fresh BAC solution was placed into the reactor. The pH was initially adjusted by using H_2SO_4 1.0 mol L^{-1}. Once the desired temperature was reached, the reaction was initiated by adding calculated amounts of ferrous sulfate and hydrogen peroxide to the reactor. The pH and temperature were continuously monitored, and liquid samples were taken out periodically and analyzed immediately in terms of pH, UV-vis spectrum (190 to 800 nm), and H_2O_2, BAC and total dissolved iron (TDI) concentrations. The total (cumulated) volume reduction was always less than 10%. Additional blank experiments were performed following this procedure but in the absence of BAC or catalyst. The experiments were carried out for 180 minutes and the operating conditions were selected considering results reported by Zhang *et al.* (2016), i.e. pH_0= 3, $[Fe^{+2}]_0$= 0.72 mmol L^{-1} and $[H_2O_2]_0$= 7.2 mmol L^{-1}. The effect of the temperature in Fenton process was evaluated by conducting experiments at T = 30°C, 50°C and 60°C. Outcomes reported here represent the mean of at least three identical runs.

B. Activated sludge

Activated sludge used in this study was cultured in an aerobic laboratory-scale (4.5 L) activated sludge reactor with partial biomass recycle. The sludge age was maintained at 30 d by daily wasting of the mixed liquor directly from the reactor. The hydraulic retention time was 2 d. The reactor was fed with the following synthetic wastewater: dehydrated cheese whey 1.5 g (Chemical Oxygen Demand (COD) = 1500 mg_{COD} L^{-1}), $(NH_4)_2SO_4$ 0.5 g, and $NaHCO_3$ 1.03 g, all dissolved in 1 L of tap water. The operating temperature was 20 ± 2°C. Aeration was provided by an air pump placed near the bottom of the reactor and the dissolved oxygen (DO) concentration was above 4 mg L^{-1}. Under steady-state conditions pH was 7.5 ± 0.4, COD of the effluent ranged from 30 to 80 mg_{COD} L^{-1}, and total suspended solids (TSS) concentration ranged from 3700 to 4500 mg_{TSS} L^{-1}.

C. Respirometric assays

An open respirometer was used to evaluate the impact of untreated 100 mg_{BAC} L^{-1} (BAC_{100}) or a solution of 100 mg_{BAC} L^{-1} pre-treated by homogeneous Fenton oxidation (BAC_{100}/HF) on the microbial community.

Before performing the assays, an activated sludge sample (1 L) from the reactor described in Section II.B was conditioned by washing it three times with phosphate buffer (KH_2PO_4 2 g L^{-1}, K_2HPO_4 0.5 g L^{-1}, pH = 7.0). Then, the conditioned activated sludge was suspended in the same phosphate buffer. Two open respirometers were used, 500 mL of the conditioned activated sludge was poured into each one. Agitation was provided by a magnetic stir-bar; the respirometers were aerated continuously by an air pump. The operation temperature was 25 ± 0.5 ºC. The DO concentration (C) as a function of time (t) was recorded every 5 seconds using an optical DO probe (YSI ProODO).

To analyze the effect of BAC_{100} on the microbial community, a volume of a stock BAC solution (10 g_{BAC} L^{-1}) was added to the respirometer. When BAC_{100}/HF was evaluated, the total volume of the respirometer (500 mL) was centrifuged; the supernatant was discarded and the pellet (containing the activated sludge biomass) was suspended in 500 mL of the BAC_{100}/HF solution.

Before the addition of the tested compounds (BAC_{100} or BAC_{100}/HF), the oxygen mass transfer coefficient of the respirometer (k_La) was obtained using a non-steady state procedure (Lobo *et al*., 2014).

The oxygen uptake rate (OUR, mg_{O2} L^{-1} h^{-1}) associated with the substrate oxidation (OUR_{Ex}) was calculated from the DO mass balance in the respirometer:

$$\mathbf{OUR_{Ex}} = \mathbf{k_L}a\,(\mathbf{C_e} - C) - \frac{\mathbf{dC}}{\mathbf{dt}} \quad (1)$$

where C_e is the dissolved oxygen concentration in the absence of an oxidizable substrate, and C is the instantaneous DO concentration. In order to compare experiments with different biomass concentrations, the specific exogenous respiration rate (q_{O2}, mg_{O2}/g_{TSS} h) was calculated as the ratio between OUR_{Ex} and the biomass concentration in the respirometer.

In addition, the concentration of biomass as total suspended solids (TSS), dissolved organic carbon (DOC), total ammonia nitrogen (TAN), total benzalkonium chlorides (BAC_T), and pH values were measured as a function of time throughout the open respirometric assay.

D. Toxicity tests.

Toxicity of BAC_{100} and BAC_{100}/HF were determined considering the inhibition of the microbial respiratory activity (%) by using a closed respirometer (ISO 8192, 1995). The contact time of the activated sludge culture with BAC_{100} and BAC_{100}/HF was 30 min.

E. Analytical techniques.

Hydrogen Peroxide concentration was determined by a Glycemia enzymatic test (Wiener Lab.). BAC concentration was determined by a colorimetric method (Tezel *et al*., 2006). Briefly, 2.5 mL of acetate buffer, 1 mL of Patent Blue solution and 5 mL of methylene chloride were added into 1 mL of sample. The anionic dye–BAC ion pair formed was solvent extracted and, 24 h later, the color intensity in the solvent phase at 628 nm was measured using a spectrophotometer Shimadzu UV-1800. Methylene chloride was used as the blank. Prior measurement, samples were centrifuged to determine the "soluble" BAC concentration, or subjected to an extraction procedure with a mixture of $AgNO_3$, acetonitrile and ethylacetate (Tezel, 2009) to evaluate the "total" BAC concentration (BAC_T). TDI concentration was assessed by measuring the total iron content of centri-

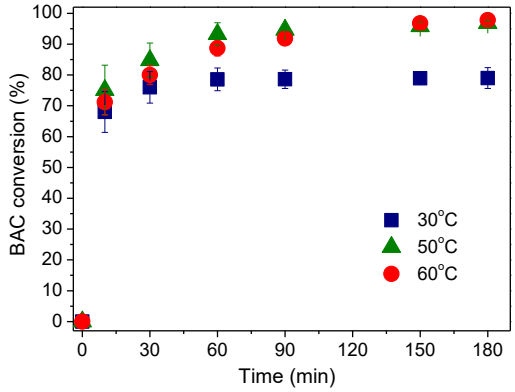

Fig. 1. Evolution of BAC conversion along the Fenton process of BAC_{100} conducted at pH=3, $[Fe^{+2}]_0$= 0.72 mmol L^{-1}, $[H_2O_2]_0$=7.2 mmol L^{-1} and at different reaction temperatures.

fuged samples with the HACH FerroVer method. The total iron precipitation was estimated from the difference between the initial TDI concentration and that measured at a given time. COD was determined by a closed reflux colorimetric method (Massa *et al.*, 2004). Total suspended solids (TSS) were used to monitor the biomass concentration. Dissolved organic carbon (DOC) and total ammonia nitrogen (TAN) were measured as follows. Samples of 5 mL of the mixed liquor were centrifuged for 5 min at 13000 rpm (Eppendorf 5415C). Then, the DOC concentration of the supernatant sample was measured in a Shimadzu TOC-V_{CPN} analyzer. TAN concentration was measured by the Nessler colorimetric method using commercial reagents (Hach Company, Loveland, CO).

III. RESULTS AND DISCUSSION

A. Pre-treatment stage: homogeneous Fenton process.

The homogeneous Fenton reaction of a solution with initial concentration of 100 mg_{BAC} L^{-1}, which corresponds to a COD of 245.4 mg_{COD} L^{-1} and a DOC of 72.6 mg_{DOC} L^{-1}, was evaluated as an oxidation stage prior to biological treatment.

The effect of reaction temperature on the process performance was explored. Preliminary runs performed for 180 min in the absence of catalyst exhibited BAC conversions of 4.7% and 8.6% with associated oxidant consumptions of 0.7% and 2.5% at 30ºC and 60ºC, respectively. The BAC conversion profiles obtained for the pretreatment conducted at 30ºC, 50ºC, and 60ºC are shown in Fig. 1. The reaction began immediately after the addition of Fenton reagents. At 30ºC, 68.6% of the initial organic content was oxidized within the first 10 min (Fig. 1). Then, the reaction proceeded at a significantly slower rate and it practically stopped after 60 min. Consequently, the BAC conversion attained at 60 min (78.6%) remained almost unchanged.

Figures 2-a and 3-a show the evolution of H_2O_2 consumption and TDI concentration along time at 30ºC, respectively. Outcomes obtained in experiments performed in the absence of BAC were included for comparison purposes. The initial H_2O_2 decomposition rate

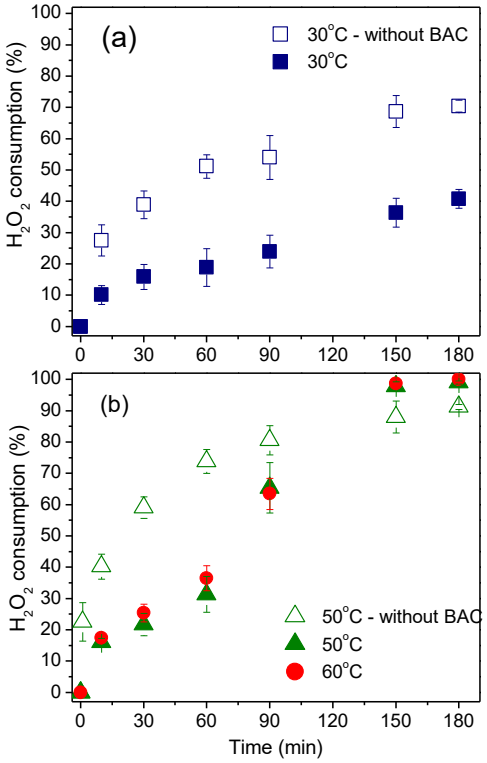

Fig. 2. Evolution of oxidant consumption during the Fenton treatment of BAC_{100} solution (solid symbols) and in blank runs performed in the absence of BAC (open symbols) at: (a) 30ºC; (b) 50ºC and 60ºC. (pH=3, $[Fe^{+2}]_0$= 0.72 mmol L^{-1} and $[H_2O_2]_0$= 7.2 mmol L^{-1}).

attained in the first 10 min was no longer maintained. Oxidant was then progressively decomposed at a slower rate, reaching a conversion of 40.8% at 180 min. This might be attributed to the occurrence of iron precipitation, evidenced from the beginning of the reaction (Fig. 3-a). TDI concentration significantly decreased along time. It decayed from 40 to 26 mg L^{-1} in 10 min (35%), and attained a value of 13 mg L^{-1} at the end of the run. The iron precipitate was free of BAC since the measured "soluble" and "total" BAC concentrations were almost identical. In experiments performed without BAC, almost the same decay in TDI was observed; evidencing that iron solubility was not influenced by the presence of BAC. Furthermore, the presence of BAC significantly reduced the oxidant decomposition rate, probably due to the promotion of reactions between hydroxyl radicals and organics yielding a reduction in the extent of scavenger reactions which further consumed H_2O_2 (Doumic *et al.*, 2015).

The oxidation of BAC was enhanced when the temperature was increased from 30 to 50°C (Fig. 1). At 50ºC, BAC conversions of 75% and 93% were accomplished in 10 and 60 min, respectively.

TDI concentration suffered an initial steep decay (75% in 10 min) and then decreased gradually until it reached a value of 7 mg L^{-1} in 60 min. Beyond ~60 min, an increase in TDI content was observed, reaching a value of 18.5 mg L^{-1} at 180 min (Fig. 3-b). In contrast, this trend was not observed in the experiment carried

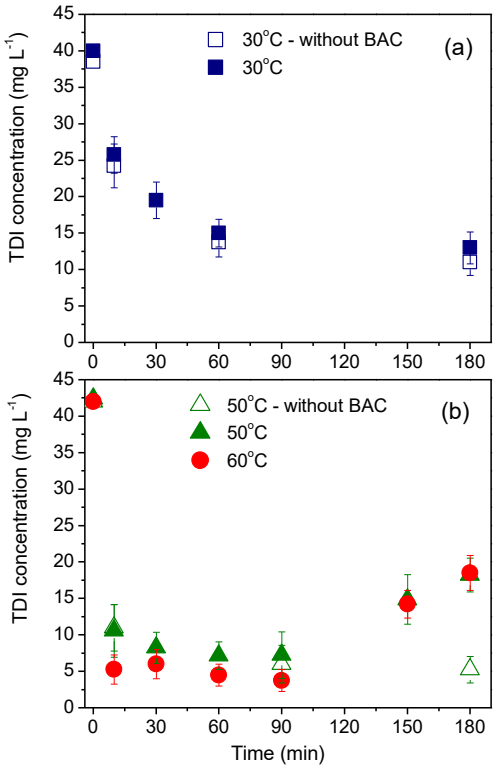

Fig. 3. Total dissolved iron (TDI) concentration profiles attained in the Fenton treatment of BAC_{100} solution (solid symbols) and in blank experiments performed in the absence of BAC (open symbols) at: (a) 30ºC; and (b) 50ºC and 60ºC. (pH=3, $[Fe^{+2}]_0$= 0.72 mmol L^{-1} and $[H_2O_2]_0$= 7.2 mmol L^{-1}).

out without BAC at 50°C, in which TDI exhibited a similar initial decay but followed by a progressive decrease until reaching a value of 5 mg L^{-1} at the end of the run. These interesting outcomes suggest that the formation of soluble iron complexes with species generated from BAC oxidation process occurred.

From the comparison of the H_2O_2 consumption (Fig. 2) and TDI content (Fig. 3) profiles obtained for homogeneous Fenton oxidation at 30°C and 50°C, it arises that during the first 60 min, oxidant was decomposed at a higher rate at 50°C, despite the lower TDI values. In addition, at 50°C, a further enhancement in the H_2O_2 consumption rate was clearly observed beyond 60 min. This improvement might be probably associated with the increase in TDI content, particularly considering that this behavior was not evidenced in the oxidant consumption profile obtained in the absence of BAC.

The increase in temperature from 50 to 60°C did not yield significant differences. TDI profiles obtained at 50°C and 60°C followed a similar trend (Fig. 3-b). A more pronounced drop in TDI was evidenced (88% in 10 min) at 60°C, due to the decrease in solubility of iron compounds at increasing temperature. However, the H_2O_2 consumption profiles were similar in experiments performed at both temperatures (Fig. 2). The expected enhancement in BAC conversion due to the higher temperature was not observed as a result of the lower TDI concentration. Moreover, BAC oxidation proceeded at a

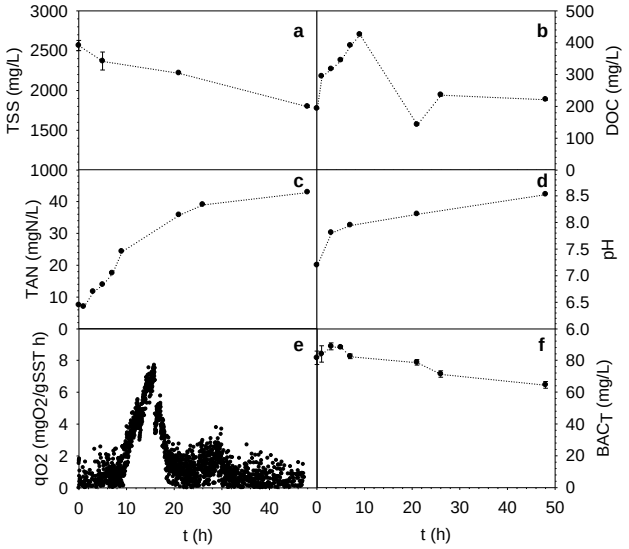

Fig. 4. Addition of BAC_{100} to the activated sludge system. Temporal profiles of a) TSS; b) DOC; c) TAN; d) pH; e) Specific oxygen uptake rate (q_{O2}), and f) BAC_T.

slightly slower rate at 60°C (Fig. 1). The similar oxidant decomposition rate along with a lower BAC oxidation rate pointed to an inefficient H_2O_2 consumption since scavenger reactions could be further favored at higher temperatures (Doumic *et al.*, 2013).

The BAC_{100} solution treated by Fenton oxidation conducted for 180 min at 50°C, pH_0= 3, $[Fe^{+2}]_0$= 0.72 mmol L^{-1} and $[H_2O_2]_0$= 7.2 mmol L^{-1} was subjected to further biological treatment. Under these operating conditions, the oxidant was completely depleted, 97% of the initial BAC load was oxidized, 65% of the initial COD concentration was removed and 28.3% of DOC abatement was achieved. The treated solution pH was adjusted to 7 by using NaOH 1 mol L^{-1}, centrifuged and cooled down to ambient temperature (BAC_{100}/HF). After this procedure, BAC concentration and the content of COD and DOC did not change, whereas TDI concentration was 8 mg L^{-1}.

B. Effect of BAC_{100} and BAC_{100}/HF on microbial community

Figure 4 shows the results obtained by adding BAC_{100} into the activated sludge system. Figure 4-a shows that the addition of BAC to the microbial community caused a decrease in the biomass concentration of 30%. Consequently, a gradual increase in the concentration of DOC (Fig. 4-b), TAN (Fig. 4-c) and pH (Fig. 4-d) were observed, reflecting the process of cellular lysis. However, after a period of ~ 9 hours, the respiratory activity was evidenced, along with the decrease in the DOC concentration (Fig. 4-e and 4-b). It is important to note that only BAC was added as carbon source. Fig. 4-f shows that BAC concentration remained almost constant for up to 20 hours. Therefore, the respiratory activity (evidenced during the first ~ 20 hours) was attributed to the degradation of carbonaceous substrates released as a result of the breakdown of the cells during the cellular

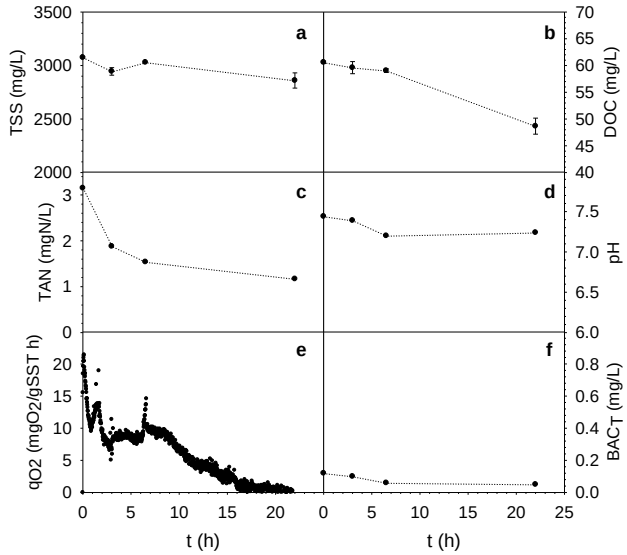

Fig. 5. Addition of BAC_{100}/HF to the activated sludge system. Temporal profiles of a) TSS; b) DOC; c) TAN; d) pH; e) Specific oxygen uptake rate (q_{O2}), and f) BAC_T.

lysis process. In addition, the inhibition of respiratory activity was 73%, indicating that BAC had a negative effect on microbial metabolism.

The results obtained after the addition of the BAC_{100}/HF solution to the activated sludge system are shown in Fig. 5 (a-f). In contrast to that observed when BAC_{100} was added (Fig. 4), no significant decrease in the biomass concentration was observed (Fig. 5-a). Besides, the consumption of DOC and TAN were observed from the beginning of the assay (Fig. 5-b and 5-c), and the pH values were almost constant (Fig. 5-d). Thus, there were no indicators of the occurrence of cellular lysis. On the other hand, in agreement with the consumption of DOC (Fig. 5-b), respiratory activity did not show a lag phase and was observed from the beginning of the assay (Fig. 5-e). Because the concentration of BAC_T (Fig. 5-f) in the BAC_{100}/HF solution was almost zero, the respiratory activity was attributed to the existence of easily oxidizable products generated by the homogeneous Fenton pretreatment.

In contrast to the 73% inhibition observed for the addition of BAC_{100}, the pre-treated solution caused no detectable inhibition of the respiratory activity. Hence, the addition of BAC_{100}/HF to the microbial community caused neither an increase in the cellular lysis process nor inhibition of the microbial respiration activity, suggesting that the homogeneous Fenton oxidation process to pre-treat wastewaters containing BAC could become a feasible alternative to protect active biomass in biological treatment systems.

III. CONCLUSIONS

In this study, a BAC solution (100 mg L^{-1}) was effectively oxidized by the homogeneous Fenton process. Among the operating conditions studied, best results were attained in experiments performed for 180 min at 50°C, pH0= 3, $[Fe^{+2}]0$= 0.72 mmol L^{-1} and $[H_2O_2]0$= 7.2 mmol L^{-1}, in which the oxidant was completely depleted, and the reduction in BAC concentration and COD were 96% and 65%, respectively.

Unlike untreated BAC_{100}, which exerted a deleterious influence on the microbial community, the pre-treated solution (BAC_{100}/HF) caused neither an increment on the cellular lysis process nor inhibition on the microbial respiratory activity.

Based on these results, Fenton oxidation could be considered as a pre-treatment stage to minimize the impact of biocide compounds, such as BAC, on the activated sludge system. Further research is currently underway aiming to effectively contribute to the future application of this technology. Specifically, the efforts are focused on the influence of key operating variables (pH, H_2O_2:Fe^{+2} and BAC:H_2O_2 ratios, reaction time) on the Fenton process as well as on the feasibility of the implementation of a heterogeneous "Fenton-type" process as a pre-treatment stage.

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