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Combination of an anaerobic process with O_3, UV and O_3/UV for cellulose pulp bleaching effluent treatment

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ABSTRACT

Recent studies have shown that partial oxidation by advanced oxidation processes (AOP) is able to transform hard-to-degrade compounds and increase their biodegradability. In this work, anaerobic treatment was followed by ozonation, UV radiation and ozonation in the presence of UV radiation, to treat bleaching effluents from a cellulose kraft pulp plant. The anaerobic reactor (horizontal anaerobic immobilized sludge bed, HAISB) was used as a pretreatment to reduce the effluent organic load before applying AOP. The ozone treatments were applied in three different pH environments (3, 8 and 10) with retention times of 10, 30, 45 and 60 min. COD and adsorbable organic halogens (AOX) removal efficiencies at the HAISB were approximately 50%, while the BOD removal efficiency reached 80%. Ozonation promoted further removal of AOX and COD so that the combined efficiency reached 96% for AOX and 70% for COD. In the oxidation process, BOD was either removed in small quantities or actually increased, as intended, so that a second biological treatment would be able to complete the treatment. The maximum increase in the BOD_5/COD ratio (biodegradability indicator) occurred at pH 8, reaching 104% for ozonation at a dosage of 1540 $mg_{O3}.L^{-1}$. Applying UV radiation alone resulted in lower values: a 34% increase in the BOD_5/COD ratio and a 76% AOX removal efficiency. These results indicate that the combination of anaerobic treatment with ozonation or ozonation/UV radiation improves the treatability of cellulose pulp bleaching effluents and that the resulting wastewater is suitable for further biological treatment under aerobic conditions with a low level of toxic compounds from the halogenated family.

Keywords: Advanced oxidation processes; Ozonation; UV; Bleaching effluent; Anaerobic treatment; Combined wastewater treatment; AOP

1. Introduction

Bleaching is the main source of wastewater discharge in cellulose pulp plants, with a great amount of non-biodegradable organic substances present in the effluents. These persistent compounds are usually dark-brown in colour and result in remaining chemical oxygen demand (COD) in the biologically treated effluent. Some of the compounds found in these effluents are chlorinated organics that can be toxic, mutagenic, carcinogenic and present low degradability [1,2].

Biological wastewater treatments per se do not always remove these recalcitrant and toxic compounds; thus, to meet the stringent regulations that are being considered by environmental agencies [3,4], it may be necessary to combine biological and chemical treatments. One of the

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chemical treatments that can be applied is an advanced oxidation process (AOP). These processes are comprised of a series of technologies using the hydroxyl radical (OH•) to oxidize the contaminants. However, to this day, AOPs have not been economically feasible when used as a single treatment to promote complete degradation of the contaminants. However, cost aside, it has been shown that AOPs can be used to modify organic hard-to-degrade organic compounds into more biodegradable ones. Often, this occurs without a considerable reduction in the COD or total organic carbon (TOC) values, but with a great increase in the five-day biological oxygen demand (BOD_5) to COD ratio, signalling an improvement in the biodegradability of the sample [5]. When these processes are followed by a biological treatment, the newly formed degradable compounds are effectively removed from the water sample.

During an AOP treatment, a reduction of hydroxyl radicals occurs in tandem with oxidation of organic molecules that results in either the withdrawal of a hydrogen atom or addition of this atom to one of the double bonds in the molecule. In this chemical oxidation, the structural and chemical properties of the compounds are changed. The molecules are broken into small pieces and get a higher percentage of oxygen, in the form of alcohol and carboxylic acids and other functional groups. These more oxidized species are usually more biodegradable than the former species [6].

To perform an advanced oxidation treatment several oxidants can be used. The most common oxidants and the ones used in this work are ozone, ultraviolet radiation (UV) and a combination of both.

Ozone decomposes spontaneously in water via a complex mechanism that involves the generation of hydroxyl radicals and can be represented by Eq. (1):

$$2O_3 + H_2O \rightarrow 2HO\bullet + 2O_2 + HO_2\bullet \tag{1}$$

Thus, ozonation is not a direct reaction of the ozone with the pollutant in an aqueous solution. Also, hydroxyl radicals can form from other agents such as hydrogen peroxide.

When UV radiation is applied as an AOP, it usually causes some chemical bonds in the compounds to break and, as a consequence, the organic load decreases. In water, the irradiation produces hydroxyl radicals and hydrogen atoms as described by Eq. (2):

$$H_2O + h\nu \rightarrow HO\bullet + H. \tag{2}$$

When ozonated water is irradiated, hydrogen peroxide (H_2O_2) is produced, which reacts with the excess and ionizes itself to form more hydroxyl radicals. The production of these radicals follows [Eq. (3)]:

$$O_3 + h\nu + H_2O \rightarrow H_2O_2 + O_2 \rightarrow O_2 + 2HO\bullet \tag{3}$$

Although these reactions were known long ago, only after the development of less expensive and more efficient UV lamps and ozone generators did researchers consider the application of these processes to actual wastewater. Some previous works that provided guidance to this project are summarized below.

Hostachy et al. [7] investigated the ozonation process to reduce the pollutant load in effluents from paper and cellulose plants. The toxicity and BOD_5 tests indicated that ozone decreases the toxicity and increases the biodegradability of these effluents. A similar study conducted by Mobius and Cordes-Tolle [5] investigates ozonation followed by biological treatment with anaerobic filters. Ozonation resulted in an increase in BOD_5, which suggests an increase in the effluent biodegradability. According to Mobius and Cordes-Tolle's [5] results, this combined treatment reduces organic load with lower costs than the ozonation process alone. The authors reported 90% colour removal and 67% adsorbable organic halogens (AOX) removal after ozonation.

Baig and Liechti [8] applied ozonation to remove the remaining COD from paper mill effluent previously treated using an activated sludge process. The ozonation promoted a significant increase in biodegradability of the effluent because of the partial oxidation of untreated bio refractory compounds left after the biological treatment. An aerobic fixed-bed filter was applied after ozonation. The combined treatment had an efficiency of around 80% for COD removal.

The effect of ozonation on the biodegradability of a single chlorinated compound was studied by Contreras et al. [9]. The authors treated a 100 ppm 2,4-dichlorophenol water solution. The results showed that after an ozone dosage of 0.12 g L^{-1}, the biodegradability increased by 25%.

Mobius and Helble [10] confirmed that ozonation, applied as a partial oxidation, reduces costs associated with expensive chemical oxidants and makes persistent COD more degradable. Substantial elimination of AOX, colour and other substances was observed in all of in their experiments.

The degradation of 4-chlorophenol by a photolytic oxidation with UV radiation and ozone was studied by Esplugas et al. [11]. Their results corroborated findings that UV radiation combined with ozone is more effective than UV radiation or ozone applied alone.

Oéller et al. [12] tested the ozonation process and ozone combined with UV radiation at different temperatures and pH environments to treat wastewater from a pulp and paper plant. They observed a maximum increase of 87% in biodegradability. The use of AOP to segregated effluents from cellulose pulp manufacturing was reported by Yeber et al. [13] who studied the degradation of a bleaching effluent. The wastewater was submitted to six oxidation processes. It was observed that the biodegradability increased significantly in all the tested cases, with the O_3/UV process being the more efficient in transforming the organic matter to more biodegradable forms. The biodegradability increased by a factor of 3.3 times after application of this treatment.

More recently Bijan and Mohseni [14] and Ruas et al. [15] presented results on the use of several AOPs combined with aerobic biological treatments for abatement of recalcitrant effluents.

Although these papers indicate the advantages of combining biological and chemical processes, there is a lack of information on the use of biological treatment preceding the use of advanced oxidation. One can hypothesize that a biological step, applied before the AOP, would remove the biodegradable organic portion and that the AOP promotes an increase in the biodegradability of the effluent. Thus, further biological treatment may be used to purify the wastewater with reduced costs. As the least expensive of the biological treatments and probably the most efficient for toxic compound removal, anaerobic processes are natural choices for combined biological plus AOP treatments. However, the literature is poor in reports on this combination for treating cellulose pulp wastewater, which was the motivation underlying this work.

Ozone is often used in cellulose pulp bleaching plants, and thus, the use of ozone in the wastewater treatment plant will not require the handling of new chemicals in the plant. The goal of this work is to present a screening experiment that shows the benefits of combining a biological treatment (horizontal anaerobic immobilized sludge reactor, HAISB) with ozone, UV radiation and an ozone/UV radiation combination to treat bleaching effluents from a cellulose pulp mill. This work evaluated the preliminary removal of the easy-to-degrade organic portion in the HAISB reactor, the changes in BOD_5 and COD content and the elimination of organochlorines compounds via the AOPs.

2. Procedures

2.1. Wastewater

The wastewater samples used in this study were provided by a pulp and paper mill that employs the bleaching sequence ZD-EOP-D, that is, the application of chlorine dioxide in presence of ozone (ZD) followed by alkaline extraction in presence of oxygen and hydrogen peroxide (EOP) with a final chlorine dioxide (D) stage. The wastewaters from this sequence are of two different types: one is an acid effluent and is produced at the ZD stage, and the other is an alkaline effluent generated in the alkaline extraction, EOP. These effluents are discharged in a ratio of 60% acid to 40% alkaline.

Five samples of each effluent were collected at irregular intervals and mixed in a ratio of three parts acid to two parts alkaline in the laboratory. This mixture was the model for wastewater for this research.

The wastewater pH was corrected to 7 when necessary. The neutralization was carried out with a 1 M sodium hydroxide solution. Nutrient supplementation was provided with nitrogen and phosphorus to keep the usually recommended relation COD:N:P = 500:5:1 for the anaerobic treatment process [16]. This supplementation was performed by adding 2 mL per litre of a stock solution of sodium phosphate ($3.9\ g.L^{-1}$) and ammonium chloride ($25 g.L^{-1}$) to the wastewater.

The wastewater was characterized by its COD, BOD_5, TOC, pH, colour, alkalinity, solids, volatile fatty acids, chlorides, sulphate, phosphorous, nitrogen and AOX concentrations. All parameters, except the AOX and the volatile fatty acids concentrations, were analysed according to the Standard Methods for the Examination of Water and Wastewater [17]. The volatile acids concentration was analysed by the titration method proposed by Dilallo and Albertson [18]. The AOX determinations were done in an AOX analyser ECS1200 - Thermo Electron Dreieich by the batch method DIN EN 1485 [19].

2.2. Experimental design

The model wastewater was submitted to a treatment in two steps. The first one comprised an anaerobic biological pre-treatment, kept unchanged throughout the experiments. At this step, only the natural fluctuations of biological treatment performance were allowed to occur. To minimize their influence on subsequent steps composite samples were used to study the AOPs. All samples were kept refrigerated until needed and none was used if stored for more than 3 days.

The second step involved treatment with an advanced oxidative process. The AOPs examined in this study were ozonation, UV radiation and ozonation in presence of UV radiation. With this set-up, it was possible to individualize the effects of ozone and UV and the synergistic action of their combination when applied simultaneously.

To finalize the experimental program the raw wastewater was submitted to O_3/UV treatment so that the influence of the anaerobic pre-treatment could be evaluated.

When appropriate the results are presented in terms of removed load instead of the usual efficiency performance.

2.2.1. First treatment step—anaerobic process

The anaerobic pre-treatment was performed in a bench-scale HAISB reactor built in boron-silicate glass.

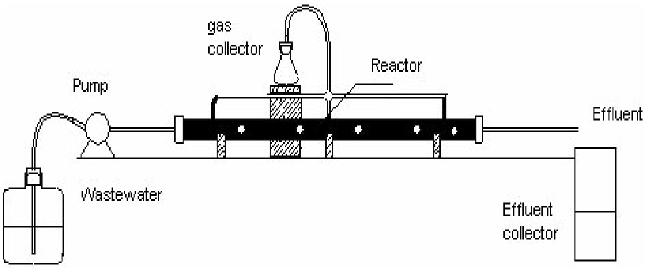

Fig. 1. Diagram of the anaerobic treatment apparatus.

The reactor was 100 cm in length and 5 cm in diameter, with a total volume of 2000 mL (Fig. 1). Previous research has shown that this particular wastewater was responsive to anaerobic treatment [20,21].

The reactor was filled with 25 g of polyurethane foam cubes with 5 mm sides to immobilize the anaerobic biomass, resulting in 800 mL net volume. Inoculation was performed using sludge from an operating upflow anaerobic sludge blanket (UASB) reactor. The sludge was macerated and immobilized in the foam as described by Zaiat et al. [22]. The reactor was kept in an acclimatized chamber set at 27 °C±1 °C.

The reactor was fed by a peristaltic pump (Prominent–Gamma G/4b) and the flow rate was slowly increased during the first 15 days of operation. After 15 days, it was set to give a hydraulic retention time (HRT) of 12 h, based on the net volume of the reactor. This HRT was a compromise between removal efficiency and realistic HRT values for industrial applications. The HAISB reactor was operated continuously for 270 days without any further changes in the hydraulic retention time.

The effluent from the HAISB reactor was characterized by means of its COD, BOD_5, pH, alkalinity, volatile acids concentration, colour and AOX concentration.

2.2.2. Second treatment step – AOP

The effluent from the HAISB reactor was submitted to several oxidation tests with AOPs, with the goal of modifying or removing the toxic and recalcitrant compounds in this effluent and at the same time increasing the BOD_5/COD ratio by converting the COD into BOD.

The AOPs reported in this work were ozone at pH 3, 8 and 10, UV radiation at pH 8 and ozone/UV radiation at pH 3, 8 and 10. These treatments were carried out in a batch oxidation apparatus, which is shown in Fig. 2. The system consisted of a reactor, ozone and UV sources and an ozone retention chamber. The reactor was made of a cylindrical tube of boro-silicate glass mounted inside another glass tube so that a thermostatic bath enclosed the reactor. The external tube diameter was 100 mm while the reactor was 60 mm in diameter. The reactor was 54 cm high with a net volume of 1200 mL.

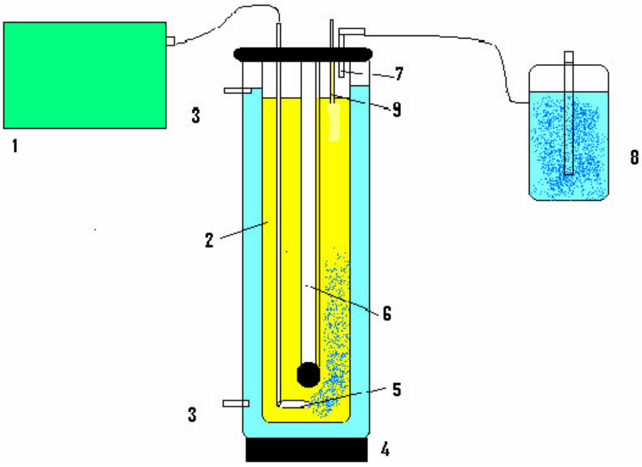

Fig. 2. Diagram of the AOP apparatus. 1 ozone generator, 2 glass reactor, 3 in and out for the cooling water, 4 magnetic stirring, 5 porous plaque, 6 UV lamp, 7 exit for the ozone not consumed,, 8 flash with KI solution, 9 wastewater entrance.

The reactor was mounted above a magnetic stirrer for better mixing of the oxidation batches. At the centre of the reactor a UV radiation lamp, Phillips TUV model (5Wand 45 cm of length) was inserted. The immersed portion of the lamp was 33 cm long.

At the bottom of the reactor, there was a porous disc (80 mesh) for ozone dispersion. The ozone not consumed in the column was transferred to a separated flask that acted as an ozone retention chamber, containing 2% potassium iodide (KI) solution for destruction and quantification of the excess ozone.

Samples from the AOP reactor were collected at 10, 30, 45 and 60 min of treatment for examination. Each sample was 25 mL so that the total volume withdrew from the reactor, 100 mL, corresponded to 10% of the treated volume. The COD, BOD_5, AOX concentration and colour were measured to quantify removal and changes in the biodegradability induced by the AOP. The biodegradability was evaluated by comparing the absolute amount of COD and BOD removal and the ratio BOD_5/COD, a commonly used indicator of wastewater biodegradability, although not a perfect one. All experiments were performed in duplicate and the results shown are the average of the two measurements.

2.3. Ozone experiments

The ozone generator was a Qualid'or (Santa Barbara d'Oeste, Brazil), laboratory model, with a production capacity of 8 $g.h^{-1}$ at 20 $g.m^{-3}$ (2%), directly from air. The chosen flow rate of 80 $L.h^{-1}$ in the ozone generator provided 1.54 g.h^{-1} of ozone, as measured by the consumption of potassium iodide method. Thus, the sampling intervals resulted in dosages of 257, 770, 1155 and 1540 mg.L^{-1}.

Diluted sulphuric acid was employed to reduce the pH value to 3 and sodium hydroxide to raise the pH to 10. The residual ozone in the samples was measured using the Hach Accuvac 25170-25® method (range from 0 to 0.75 mg$_{O3}$.L^{-1}), but the value never reached more than 0.10% of the dosage.

2.4. UV radiation experiments

To apply the UV radiation, the lamp was turned on 1 h before the introduction of the effluent to be treated into the reactor. The magnetic stirrer was used to mix the sample and the treatment was carried out at a pH of 8. Assuming that all energy emitted by the submersed portion of the lamp was absorbed by the wastewater the UV dosages can be estimated to be 11 W. L^{-1}, resulting in energy inputs equal to 1.83, 5.50, 8.25 and 11 Wh.L^{-1} (or 6.6; 19.8; 29.7 and 39.6 kJ.L^{-1}) after 10, 30, 45 and 60 min of treatment.

2.5. Ozone/UV experiments

These experiments were carried out exactly as the ozone experiments with the exception that the UV radiation was applied simultaneously with the introduction of ozone, using the same protocol of the UV radiation experiment.

3. Results and discussion

Before the results are presented, it is important to remember that the commonly used procedure of comparing removal efficiencies to compare treatment performance may be misleading when one compares treatment effects over a wide range of influent loads. This is especially true in this work as the effect of the applied AOP is compared for pre-treated and untreated effluents. Thus, some comparisons and conclusions in this paper are based on specific pollutant load removal instead of efficiency performance.

3.1. Wastewater characterization

The results of the wastewater characterization are shown in Table 1. Its high colour content and its amenability to biological treatment as suggested by the BOD$_5$/COD ratio are noteworthy as are the low nitrogen concentration and high sulphate content, which are typical characteristics of cellulose pulp plant wastewaters. The AOX concentration is within the expected values for Brazilian plants producing bleached cellulose [1].

Table 1
Wastewater from the bleaching plant[a] and effluent from the anaerobic reactor

Parameter	Value	HAISB Effluent
pH (before neutralization)	4.5–7.8	
pH (after neutralization)[b]	7.6 ± 0.2	8.0 ± 0.7
Total alkalinity (before neutralization) (mg_{CaCO_3}.L^{-1})	53	
Total alkalinity (after neutralization) (mg_{CaCO_3}.L^{-1})	980 ± 190	1200 ± 240
COD (mg_{O_2}L^{-1})	1370 ± 150	700 ± 160
BOD$_5$ (mg_{O_2}L^{-1})	790 ± 130	170 ± 50
BOD$_5$/COD	0.57–0.62	0.13–0.30
TOC (mg.L^{-1})	728	
AOX (mg.L^{-1})	17.3	8.6
Colour (uCoPt)	218	296
Chloride (mg$_{Cl^-}$.L^{-1})	392	
Nitrogen (total) (mg$_N$.L^{-1})	2	
Phosphorous (mg $_P$.L^{-1})	1.8	
Sulphate ($mg_{SO_4^{2}}$.L^{-1})	760	258
Volatile fatty acids (mg$_{Hac}$.L^{-1})	280 ± 45	130 ± 40
Solids (total) (mg.L^{-1})	3390	
Volatile solids (mg.L^{-1})	1440	
Fixed solids (mg.L^{-1})	1920	
Suspended solids (mg.L^{-1})	30	

[a] Mixture of acid and alkaline effluents in the ratio 3:2.
[b] Range.

3.2. First treatment step—anaerobic process

The pH value at the HAISB reactor outlet was approximately 8.0, which is slightly higher than the inlet pH of the reactor, which ranged from 7.2 to 7.8. This is indicative of the buffering effect of the anaerobic process, which is confirmed by higher values of total alkalinity in the reactor effluent, as shown in Table 1. Volatile acid measurements showed a significant reduction of these compounds after the biological treatment with a decrease in concentration from 281±45 mg$_{HAc}$.L^{-1} to 132± 37 mg$_{HAc}$.L^{-1}.

The COD removal at the HAISB reactor was stable at roughly 50% while the BOD$_5$ removal was approximately 80%, a satisfactory result for a pre-treatment step. After the anaerobic treatment, the BOD$_5$/COD ratio decreased from 0.6 to approximately 0.2, with lower values approaching 0.1, as shown in Table 1. This is a clear indication that most of the easy-to-degrade organics were removed during this step. To improve removal, it would be necessary to increase the retention time, as the authors observed during pre-run trials when up to 85% of the COD was removed. However to reach efficiencies at this range, with this particular wastewater, the HRT would be unrealistically high for industrial purposes.

An increase of 78 uCoPt was observed in the colour of the anaerobic treated effluent, which is a normal occurrence when anaerobic processes are used.

The anaerobic treatment removed approximately 50% of the AOX concentration. However, a subsequent treatment step is necessary since the concentration of chlorinated organics was still high for discharge, as shown in Table 1.

3.3. Second treatment step—AOP

3.3.1. Ozone

Treatment with ozone provided high AOX removal, leaving only 0.67 $mg.L^{-1}$ remaining after applying 1540 $mg_{O3}.L^{-1}$. This dosage was achieved after 60 min of treatment with the apparatus used in this work (see Table 2). This corresponds to a removal efficiency of 92% after this step and 96% efficiency after the combined process (HAISB and ozonation). Contrary to the anaerobic pre-treatment, which adds colour to the wastewater, ozonation results in colour removal varying from 42%, to 93% with the highest efficiency occurring with the application of 1540 $mg_{O3}.L^{-1}$ at a pH 3 (see Table 2).

The best specific COD removal was observed at pH 3–0.216 mg_{COD}/mg_{O_3} with a dosage of 1540 $mg_{O3}.L^{-1}$, as shown in Table 2. When the raw wastewater was submitted to ozonation at pH 8 a slightly lower specific COD removal was observed at the end of the treatment than the value observed for the pre-treated wastewater. However, the relative difference is small, −12%, and within the expected uncertainty for this kind of experiment. Thus, in terms of removal capacity, the pre-treatment does not represent a distinct advantage. However, considering the specific removal values reported in Table 2, it can be conclude that the anaerobic treatment is equivalent to dosing approximately 3,500 $mg_{O3}.L^{-1}$. This dosage is more than double the dosage used in this work. Moreover, the variation in the BOD_5/COD ratio shows that for the raw wastewater the increase was 14% while the effluent from the HAISB reactor had an increase of 104%, as shown in Table 3.

The ozonation at pH 10 did not show good efficiency, as would be expected since there is a greater production of hydroxyl radicals at this pH. However, at the same time bicarbonate and carbonate ions concentrations increase with higher pH and their radical scavenger effect surpasses the advantage of having more radicals in solution. Tanaka et al. [23] have studied the carbonate effects in several AOPs and inferred that these ions promote a decline in the efficiency of all the AOPs tested.

Further discussion of biodegradability increase results requires a hypothesis to explain the outcomes. Contrary to biochemical oxidation, which shows a clear distinction between the classes of chemicals that are removed first—the BOD inducing compounds — chemical treatment does not have such a distinction, as ease-to-oxidize compounds are not necessarily biodegradable. Thus, one can hypothesize that, in an ideal oxidation treatment of a complex wastewater, the oxidant would react with COD and BOD inducing compounds in the same proportion that these chemicals appear in the mixture. In this case, the BOD_5 to COD ratio would remain constant. However, if COD

Table 2
Main results for ozonation at 1540 $mgO_3.L^{-1}$ and for ozonation/UV at 1540 $mgO_3.L^{-1}$ and 11 $Wh.L^{-1}$ of UV

Ozonation

pH	COD ($mg_{O2}.L^{-1}$)		BOD ($mg_{O2}.L^{-1}$)		Colour		Specific removal[a]	
	In	Out	In	Out	In	Out	COD	BOD
Ozonation								
3	648	316	224	169	344	25	0.216	0.04
8[b]	545	307	139	164	575	267	0.155	0
8[c]	1386	1177	503	480	253	149	0.136	0.02
10	706	514	301	300	667	133	0.125	0
Ozonation in the presence of UV								
3	980	414	236	192	816	15	0.368	0.03
8[b]	760	549	101	139	280	40	0.137	0
8[c]	1375	1105	660	627	531	328	0.175	0.02
10	732	392	238	174	677	86	0.221	0.04

[a] COD or BOD mass removed per unit mass of ozone applied at the treatment. Negative values indicate an increase in BOD instead of a reduction.
[b] Pre-treated wastewater. [c] Raw wastewater.

Table 3
COD/BOD ratios at the end of treatment for O_3 and O_3/UV[a]

pH	Ozone treatment		Ozone/UV treatment		Relative increase (%)	
	In	Out	In	Out	O_3	O_3/UV
3	0.35	0.53	0.24	0.46	51	94
8	0.26	0.53	0.13	0.25	104	92
8[b]	0.36	0.41	0.46	0.48	14	4
10	0.46	0.58	0.32	0.44	26	38

[a] Results for 1540 $mgO_3.L^{-1}$ and 11 $Wh.L^{-1}$ of UV.
[b] Raw wastewater.

decreases but BOD_5 continues at the same level, decreases in a lesser proportion or even increases, one may conclude that part of the COD chemicals became biodegradable and are being measured as BOD_5. This would seem to be the case in our experiments. For instance, at pH 8 the COD decreased by 238 $mg_{O2}.L^{-1}$ at the end of the experiment while the BOD increased by 26 $mg_{O2}.L^{-1}$. At pH 3, these figures were a 332 $mg_{O2}.L^{-1}$ decrease for COD and a 55 $mg_{O2}.L^{-1}$ decrease for BOD_5, as shown in Table 2. The evolution of these parameters over the progression of treatment is shown in Fig. 3 for ozone and ozone/UV treatment at pH 8. Table 3 presents the BOD_5/COD and its relative changes at the end of the treatment for the three pH values used in this work. As observed in Table 3, the BOD_5/COD ratio increased after all AOP treatments, contrary to what is observed when biological processes are applied. As this is one of the important points of this work, these results will be discussed further and compared to the O_3/UV treatment.

No residual ozone was detected in the samples at the end of the ozonation. After comparing all ozonation treatments at all pHs investigated, one can see that the process carried out at pH 3 was most efficient in removing the remaining COD and colour from the HAISB reactor, reaching efficiencies of 51% and 93%, respectively. However, the purpose of ozonation was not to degrade the remaining COD from the first treatment step, but to change the structure of the compounds to increase the biodegradability so that the further application of a second biological treatment would result in the water quality necessary for discharge. Thus, ozonation at pH 8 seems to be a better option as it does not require as many additional chemicals to adjust the pH. In addition, it should be considered that the process performed at pH 8 causes the highest increase in biodegradability of the effluent previously treated at the HAISB reactor.

3.3.2. UV radiation

UV radiation, when applied to the HAISB effluent at pH 8, produced some unexpected results that may be unique to this case. COD measurements for samples taken after 10, 30, 45 and 60 minutes of treatment show that this parameter had a steady and small decrease, from 680 to 636 $mg_{O2}.L^{-1}$. However, it is difficult to be sure that these changes actually occurred, since these differences fell within the expected experimental error for this measurement. However, the BOD showed an increase of 30%, a value well above the experimental error. This increase may be explained by changes in the composition of COD inducing chemicals that became biodegradable. This result is consistent with the findings of Alnaizy and Akgerman [23], who subjected phenol solutions to UV radiation. They observed a low degradation of this compound and the emergence of intermediate aromatic compounds. The increase of BOD may also be a consequence of the observed AOX removal, close to 50% at this stage, and reaching 76% in combination with the anaerobic pretreatment.

In this case, there was no colour removal, but a colour increase from 575 uCoPt to 770 uCoPt at the end of the treatment, representing a 34% increase. When the UV radiation was applied to the raw wastewater, the changes in COD and BOD_5 were negligible but the AOX removal was 26%.

3.3.3. Ozone/UV radiation and comparison of results

From a qualitative point of view, the results of O_3/UV treatment are similar those of the ozonation experiment, but the absolute values of specific COD removal increased by 70% at pH 3 and 10 while remaining relatively constant at pH 8. Again, the highest efficiencies were achieved at pH 3, with 60% COD and 98% colour removals. However, as observed previously, when treatment costs are taken into consideration it is possible that treatments at pH 8 would be a better option

An inspection of the UV treatment results shows that the O_3/UV outputs cannot be explained as an additive effect of both treatments occurring simultaneously. They are better explained as an effect of UV radiation on the hydroxyl radical reaction chain [Eqs. (1) to (3)]. It seems that if sufficient UV radiation is provided each mol of O_3 furnishes two moles of hydroxyl radicals instead of only one, as occurs when decomposition occurs in water alone.

AOX removal for the O_3/UV treatment was similar to the ozone treatment. The final concentration of 0.74 $mg.L^{-1}$ cannot be considered significantly distinct from the 0.67 $mg.L^{-1}$ achieved with ozonation only. Similarly to the ozone treatment, when the raw wastewater was submitted to the O_3/UV radiation treatment the BOD_5/COD ratio showed an increase of only 4% while the effluent of the HAISB showed a 92% increase in this ratio. In this case, the COD decreased by 211 $mgO_2.L^{-1}$ while the BOD increased by 38 $mg_{O2}.L^{-1}$. It is worth noting that for the raw

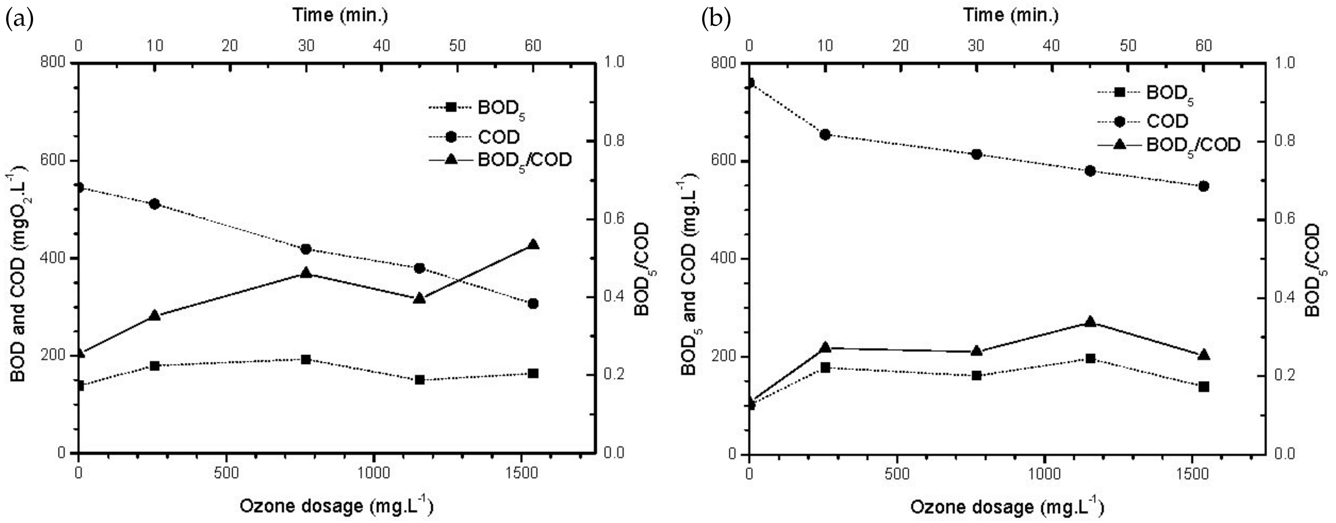

Fig. 3. COD, BOD_5 and BOD_5/COD ratio at pH 8 for (a) ozone treatment and (b) ozone/UV treatment.

effluent, the oxidation occurs in the same proportion for both, COD- and BOD-inducing compounds, as in an ideal oxidative treatment.

For an acidic environment, the colour removal reached 98% however, a more realistic expected value would be 85%, as observed under alkaline conditions. This is because, in an industrial plant, it would be more cost effective to carry out the wastewater treatment under alkaline conditions than acidifying the wastewater. Again, the best COD removal was observed at pH 3–0.368 mg_{COD}/mg_{O3}, or 70%, with a dosage of 1540 $mg_{O3}.L^{-1}$ and 11 $Wh.L^{-1}$ of UV energy.

An examination of the specific COD removal shows some results that the authors could not easily explain. At pH 3 and 10 there is a clear increase in the specific COD removal when UV radiation was added to the treatment, as shown in Table 3. However, at pH 8, this increase was not observed. Moreover, an inversion in behaviour occurred. While with ozone a higher specific COD removal was observed with the effluent of the anaerobic reactor, when ozone/UV radiation were used, the raw effluent presented a higher specific removal, as shown in Table 2. This change in behaviour is a clear indication that even though the treatment process is almost the same, a reaction with hydroxyl radicals produced by ozone, there are particularities that have unknown influences and great care should be taken when extrapolating results.

The behaviour of load removal at pH 8 and 10 with the use of O_3/UV treatment also differs from the pure ozonation treatment. While ozonation alone provided higher COD removal at pH 8 than at pH 10, with the combined treatment the results were reversed—a higher removal was observed at pH 10, although the highest removal was still at pH 3, as shown in Table 2. A possible explanation for this result may be that the increase in hydroxyl radical production, that occurs when UV radiation is present, is sufficient to overcome the higher concentration of bicarbonate and carbonate ions at pH 10, despite their scavenger effect.

Further exploring the subject of COD conversion, Fig. 3 shows a comparison of the BOD_5/COD ratio as a function of the ozone dosage promoted by O_3 and O_3/UV treatment applied at pH 8. This pH was chosen for comparison purposes as it is thought that this condition would promote the best overall results in an industrial environment, as previously discussed. The O_3/UV process promoted the highest relative BOD_5/COD increase at a dosage around 1155 $mg_{O3}.L^{-1}$. As the treatment progressed, the BOD_5/COD ratio decreased, as shown in Fig. 3. In Fig. 3b, a point exists where compounds that were converted in BOD were also oxidized, thus decreasing the BOD_5/COD ratio. One may speculate that this process may continue in a cyclical fashion if the treatment progresses until it achieves complete mineralization of the organic compounds. When ozone is used alone, the same behaviour was observed, however the BOD_5 consumption began at 770 $mg_{O3}.L^{-1}$ and reverted to production around 1155 $mg_{O3}.L^{-1}$ while the COD continued to decrease. As several phenomena occur simultaneously, it is difficult to isolate a single cause for this shift in the O_3 concentration required to start the consumption of BOD. If a decision concerning the end point of the AOP treatment was required, a cost analysis would be an adequate tool for the decision taking process. Such analysis would combine the cost of the AOP treatment with the costs of the final biological treatment. One can predict that it may be more advantageous to stop the treatment at the point where the biodegradability is highest and then apply a biological process to finish the treatment.

With respect to colour removal induced by the AOP at pH 8, the results are shown in Fig. 4. Although O_3/UV treatment was the most efficient, the difference between it and ozonation does not become significant for up to 45 min of treatment. After this time, a reversal in colour content was observed, indicating a decrease in removal efficiencies in the ozone treatment while the O_3/UV treatment continued to remove colour. It is important to note that UV radiation alone does not remove colour; on the contrary, there is an increase in its content for up to 45 min of treatment when the colour is close to 50% higher. After that, the colour content starts to decrease.

The results of the AOX removal tests show that when the AOPs at pH 8 were combined with the anaerobic treatment, there was a total removal of 96% for the O_3 and O_3/UV processes and 76% for the UV process. When these processes were applied to the untreated bleaching effluent, the AOX removal efficiencies were around 46% for O_3 and O_3/UV and 26% for the UV, as shown in Fig. 5. In terms of load, the anaerobic treatment represents a dosage of 1700 $mg_{O3}.L^{-1}$, considering that O_3 and O_3/UV remove about 5.1×10^{-3} mg_{AOX}/mg_{O3}.

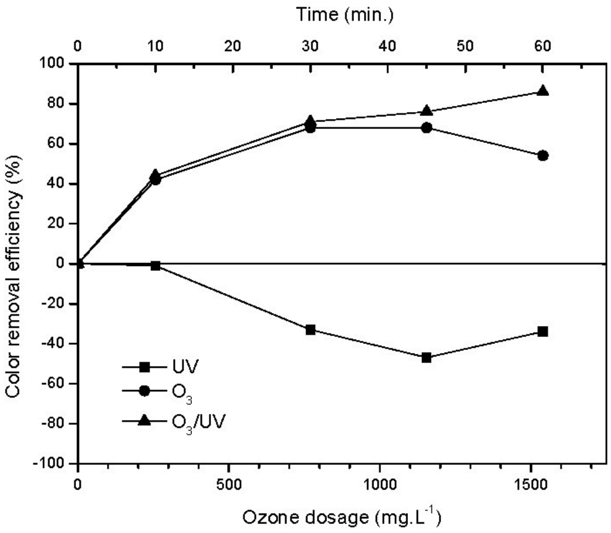

Fig. 4. Comparison of colour removal by ozone, ozone/UV radiation and UV radiation treatment at pH 8. (For UV radiation treatment consider only the time axis).

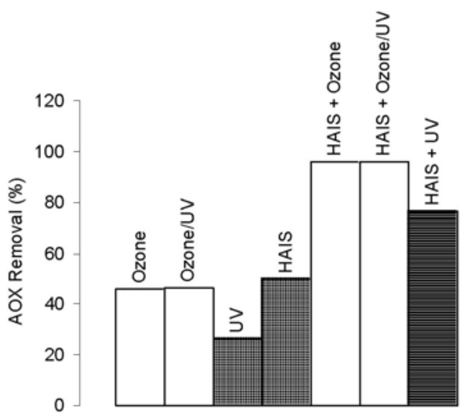

Fig. 5. AOX removal at pH 8.

4. Conclusions

The wastewater from the cellulose bleaching plant had a high organic load and contained toxic compounds. Fortunately, it was amenable to an anaerobic biological treatment that removed 80% of the BOD in 12 h of retention time.

The three AOPs tested promote changes in the biodegradability of the effluent from the HAISB reactor as indicated by the BOD_5/COD ratio, and are thus useful for enhancing the biodegradability of some wastewaters.

Although pH 8 does not provide the best removal efficiencies, when costs are considered, it may provide the most adequate cost-effective treatment solution in an industrial environment, as fewer chemicals are needed to adjust the pH. It should also be noted that further biological treatment would be necessary to reach discharge limits so that a small gain of efficiency in the AOP phase of the treatment may be offset in the final treatment phase. Usually, the bleaching plants in pulp and paper mills have an ozone production unit that could make the use of this chemical in the wastewater treatment attractive.

Although the combination of O_3 and UV results in a more efficient treatment when COD and BOD are considered, further studies should be performed to determine the best dosage for each process and the balance between removal efficiency gain and energy consumption.

The UV radiation promotes transformations in the compound structure, changing the biodegradability of the samples, but with a maximum increase of only 34%. When this treatment was applied, significant changes were not observed in COD content, although the AOX was removed and BOD increased by 30%.

The organochlorine compound removal was indicated by the AOX concentration. The anaerobic process promoted a 50% removal of these compounds and further oxidation with ozone or ozone/UV provided approximately 96% removal.

In conclusion, this work confirmed the initial hypothesis that to combine an anaerobic process, in this case an HAISB reactor, followed by ozonation or ozonation in the presence of UV radiation, improves the treatability of bleaching effluents. This results in wastewater with higher biodegradability and less toxic compounds. Thus, after the use of the AOPs, an aerobic biological treatment process could be applied to complete treatment, removing the modified remaining organic load.

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References

[1] J. Rosa, Evaluation of methanogenic activity in the effluents from the cellulose industry determined by short duration essay with *Salmonella typhimurium*, AMES test. M.Sc. Thesis, EESC-USP, Dept. of Hydraulics and Sanitary Engineering, São Carlos, Brazil, 1997 [in Portuguese].

[2] A.M. Springer, ed., Industrial Environmental Control: Pulp and Paper Industry, 3rd ed., Tappi Press, Atlanta, 2000.

[3] J. Carey, E. Hall and N. McCubbin, Review of scientific basis for AOX effluent standard in British Columbia, Minister of Water, Land and Air Protection in British Columbia, www.llbc.leg.bc.ca/Public/PubDocs/bcdocs/352023/aoxpanelreport.pdf, 2002.

[4] D.V. Savant, R. Abdul-Rahman and D.R. Ranade, Anaerobic degradation of adsorbable organic halides (AOX) from pulp and paper industry wastewater. Biores. Technol., 97 (2006) 1092–1104.

[5] C.H. Mobius and M. Cordes-Tolle, Enhanced biodegradability by oxidative and radiative wastewater treatment. Water Sci Technol., 35(2–3) (1997) 245–250.

[6] A. Marco, S. Esplugas and G. Saum, How and why combine chemical and biological processes for wastewater treatment. Water Sci. Technol., 35(4) (1997) 321–327.

[7] J.C. Hostachy, G. Lenon, J.L. Pisicchio, C. Coste and C. Legay, Reduction of pulp and paper mill pollution by ozone treatment. Water Sci. Technol., 35(2–3) (1997) 261–268.

[8] S. Baig and P.A. Liechti, Ozone treatment for biorefractory COD removal. Water Sci. Technol., 43(2) (2001) 197–204.

[9] S. Contreras, M. Rodriguez, F. Al Momani, C. Sans and S. Eesplugas, Contribution of the ozonation pre-treatment to the biodegradation of aqueous solutions of 2,4-dichlorophenol. Water Res., 37 (2003) 3164–3171.

[10] C.H. Mobius and A. Helble, Combined ozonation and biofilm treatment for reuse of paper mill wastewaters. Water Sci. Technol., 49(4) (2004) 319–323.

[11] S. Esplugas, P.L. Yue and M.I. Pervez, Degradation of 4-chlorophenol by photolytic oxidation. Water Res., 28(6) (1994) 1323–1328.

[12] H.J. Oéller, I. Demel and G. Weinberger, Reduction in residual COD in biologically treated paper mill effluents by means of combined ozone and ozone/UV reactors stages. Water Sci. Technol., 35(2–3) (1997) 269–276.

[13] M.C. Yeber, J. Rodríguez, J. Freer, J. Baeza, N. Durán and H.D. Mansilla, Advanced oxidation of a pulp mill bleaching wastewater. Chemosphere, 39(10) (1999) 1679–1688.

[14] L. Bijan and M. Mohseni, Integrated ozone and biotreatment of pulp mill effluent and changes in biodegradability and molecular weight distribution of organic compounds. Water Res., 39(4) (2005) 3763–3772.

[15] D.B. Ruas, A.H. Mounteer, A.C. Lopes, B.L. Gomes, F.D. Brandão and L.M. Girondoli, Combined chemical biological treatment of bleached eucalypt kraft pulp mill effluent Water Sci. Technol., 55(6) (2007) 143–150.

[16] R.E. Speece, Anaerobic Biotechnology for Industrial Wastewater, Archae Press, Nashville, TN, 1996.

[17] Standard Methods for Examination of Water and Wastewater. American Public Health Association (APHA), 19th ed., Washington, DC, 1995.

[18] R. Dilallo and O.E. Albertson, Volatile acids by direct titration. J. WPCF, 33(4) (1961) 356–365.

[19] Water quality—Determination of adsorbable organically bound halogens (AOX), DIN EN 1485.

[20] T.J. Momenti, Obtaining a synthetic effluent from the bleaching process in the pulp and paper industry. M.Sc. Thesis, EESC-USP, Dept. of Hydraulics and Sanitary Engineering, São Carlos, Brazil, 2002 [in Portuguese].

[21] X. Wang, T.H. Mize, F.M. Saunders and S.A. Baker, Biotreatability test of bleach wastewaters from pulp and paper mills. Water Sci. Technol., 35(2–3) (1997) 101–108.

[22] M. Zaiat, A.K. Cabral and E. Foresti, Reator anaeróbio horizontal de leito fixo para tratamento de águas residuárias: concepção e avaliação preliminar de desempenho [Fixed bed horizontal anaerobic reactor for wastewater treatment: design and preliminary performance evaluation]. Revista Brasileira de Engenharia Química, 11 (1994) 33–42 [in Portuguese].

[23] T. Tanaka, K. Tsuzuki and T. Tagati, Chemical oxidation of organic matter in secondary-treated municipal wastewater by using methods involving ozone, ultraviolet radiation and TiO_2 catalyst. Water Sci. Technol., 43(10) (2001) 295–302.

[24] R. Alnaizy and A. Agerman, Advanced oxidation of phenolic compounds. Adv. Environ. Res., 4 (2001) 233–244.