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Use of ozone in a pilot-scale plant for textile wastewater pre-treatment: Physico-chemical efficiency, degradation by-products identification and environmental toxicity of treated wastewater

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ABSTRACT

In this study, ozonation of raw textile wastewater was conducted in a pilot-scale plant and the efficiency of this treatment was evaluated based on the parameters color removal and soluble organic matter measured as chemical oxygen demand (COD), at two pH values (9.1 and 3.0). Identification of intermediate and final degradation products of ozone pre-treatment, as well as the evaluation of the final ecotoxicity (Lumistox test) of pre-treated wastewater, was also carried out. After 4 h of ozone treatment with wastewater recirculation (flow rate of 0.45 $m^3\ h^{-1}$) the average efficiencies for color removal were 67.5% (pH 9.1) and 40.6% (pH 3.0), while COD reduction was 25.5% (pH 9.1) and 18.7% (pH 3.0) for an ozone production capacity of 20 $g\ h^{-1}$. Furthermore, ozonation enhances the biodegradability of textile wastewater (BOD_5/COD ratios) by a factor of up to 6.8-fold. A GC-MS analysis of pre-treated textile wastewater showed that some products were present at the end of the pre-treatment time. In spite of this fact, the bacterial luminescence inhibition test (Lumistox test) showed a significant toxicity reduction on comparing the raw and treated textile wastewater. In conclusion, pre-ozonation of textile wastewater is an important step in terms of improving wastewater biodegradability, as well as reducing acute ecotoxicity, which should be removed completely through sequential biological treatment.

1. Introduction

Given the large volumes and great chemical complexity and diversity of the wastewater generated, textile mills have searched for innovative wastewater treatment technologies, in order to avoid discharges to the environment causing negative impacts to the biota or public health [1–4]. An important feature of the textile mills is the use of different types of dyes, with multiple color combinations, resulting in fluctuations in wastewater composition. Thus, removal of color is one of the main problems in the treatment of textile dyeing wastewater and dye manufacture wastewater [5]. While traditional methods employed for treating textile wastewater include various combinations of biological and physico-chemical processes, innovative technologies are based on advanced oxidation processes, which have been used to eliminate dyes [6–8] and other organic compounds present in these industrial wastewaters [9,10]. Nevertheless, when advanced oxidation processes are performed, the degradation by-products generated can reduce both the wastewater quality in terms of ecotoxicological effects, and the textile production [11–13]. In Germany, for example, azoic dyes forming amines of MAC (Maximum Allowable Concentration) class III A1 and A2 under reductive conditions are prohibited, as well as textiles with such dyes, according to the revised German ordinance on consumer goods "Deutsche Bedarfsgegenständeverordnung" [11]. Similarly, other European Union countries have approved bans on importing and marketing textiles dyed with dyes capable of reductively splitting carcinogenic amines [14].

Although advanced oxidation processes are generally efficient at reducing organic matter content or degrading dyes, there are some discrepancies (e.g., gas mass transfer) when bench and pilot-scale treatment efficiencies are compared, which can be explained by differences between laboratory and pilot-scale conditions and by spatial variability of samples collected and used in bench-scale tests. While the bench-scale can be used to gain an insight into the feasibility of treatment, pilot-scale treatability studies will provide useful information to help design and plan full-scale technology implementation [15].

Thus, the main objective of this study is to investigate the efficiency of a pilot-scale ozonation system to pre-treat raw textile

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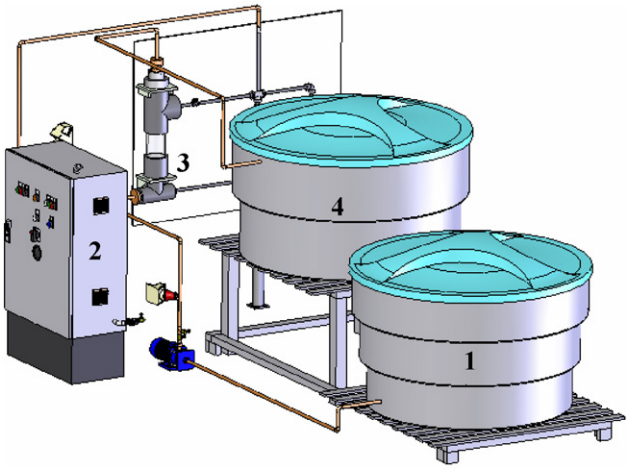

Fig. 1. Experimental apparatus for pilot-scale ozone pre-treatment of textile wastewater (1—raw textile wastewater tank; 2—ozonator; 3—semi-batch column reactor; 4—treated textile wastewater tank).

wastewater at two different pH values (9.1 and 3.0) with a view to improving the biodegradability and reducing wastewater toxicity, allowing subsequent microbiological treatment of the effluent. In this regard, the data generated in this investigation will be used to help in the design and planning of a full-scale technology implementation. Evaluation of ozonation efficiency was based on the parameters color removal and soluble organic matter measured as chemical oxygen demand (COD). Furthermore, identification of degradation by-products during and after ozone treatment, as well as the evaluation of the final ecotoxicity (Lumistox test) of post-treated wastewater, was also carried out.

2. Materials and methods

2.1. Wastewater collection and ozone pilot-scale treatment design

Raw textile wastewater was collected daily during a 1-week period from the equalization storage tank of a textile mill located in the city of Blumenau (SC State—Brazil), where cotton and polyester fabrics are dyed using reactive, dispersive dyes. Classical wastewater treatment methods are based on microbiological and physico-chemical processes, including a coagulation/flocculation step and dye complexation by polymers. The raw wastewater was pump aspirated to a fiberglass tank, which was transported to the university campus where the ozone treatment system was assembled. The experimental set-up for ozone treatment consisted of an air dryer, compressor, ozone generator and semi-batch reactor (Fig. 1). The air dryer consisted of a column which was filled with highly adsorptive anhydrous SiO_2. Ozone was generated using an ozonator model OZ 20-Econoto (ProMinent® Brasil Ltda.) at a concentration of 20 g m^{-3} (ozone:air). A water-cooling jacket was used to keep the reactor contents at constant temperature (20 °C) and an ozone trap containing 4% potassium iodide solution was connected at the top of the reactor to collect all remaining ozone gas passing through the reactor. The ozone–air mixture (1 m^3 h^{-1}) was fed into the reactor through a micro-porous plate gas sparger located at the base of the semi-batch reactor. All experiments were carried out in triplicate in an 18-L cylindrical semi-batch reactor. The reactor consisted of a polyvinyl chloride/polyethylene column of 0.15-m diameter, 1.0-m height and the flow rate of the textile wastewater was 0.45 m^3 h^{-1}. Ozonation at pH 3.0 was carried out after pH adjustment of the textile wastewater with 5 M H_2SO_4. To maximize ozone transfer to the wastewater, the gas was sparged in countercurrent in relation to the textile wastewater circulation. Ozonation treatment/wastewater recirculation was carried out for 4 h, and after this period the color removal was lower.

2.2. Physico-chemical analysis

All experiments were carried out in triplicate and coefficient of variation was below 15%. For color measurements, wastewater samples (5 mL) were taken at regular time intervals (30 min) and analyzed for visible absorbance at 455 nm (maximum absorbance) using a UV/visible double beam Spectrophotometer (Varian, model Carin Win UV 50). Measurement of the color samples from the three independent treatments was based on the comparison of the absorbance of the sample with the absorbance of a standard solution of cobalt hexachloroplatinate at 455 nm [16]. For the chemical oxygen demand determination the test method HACH 800 (DR2010 Spectrophotometer/Hach Company, USA) was used. Determination of biological oxygen demand (BOD) was carried out according to a standard method [16]. In the BOD tests with ozonated effluents, a small amount of filtered activated sludge from a municipal wastewater treatment plant was used as the bacterial seed. Separation of intermediates as well as end by-products in the ozone treated wastewater samples was performed in a Varian CP 3800 GC instrument equipped with a DB-WAX column (60 m × 0.25 mm i.d., 0.25 μm film thickness) according to the USEPA protocols, using dichloromethane as the extractor solvent [17]. The injector temperature was 280 °C (splitless). Chromatographic conditions included an initial oven temperature of 50 °C, with a 2 h 50 min isotherm and a program rate of 7 °C min^{-1} and a final oven temperature of 240 °C with an isotherm of 8 min. The gas carrier was N_2, with a column flow of 1 mL min^{-1}. Identification of GC separated compounds was carried out with a Varian mass spectrometer (model Saturn 2000).

2.3. Ecotoxicological analysis (Lumistox test)

The bacterial (*Vibrio fischeri*) luminescence inhibition (Lumistox, Dr. Bruno Lange, Düsseldorf, Germany) test was conducted according to ISO guidelines [18] at 15 ± 1 °C on water samples with salinity adjustment to 35‰ at pH 7. The exposure time was 30 min. The lyophilized bacterial reagent was obtained from Deutsche Sammlung von Mikroorganismen und Zellkulturen (DSM N# 7151, Braunschweig, Germany). Each sample dilution (or control) was performed in triplicate.

The EC_{50} values for the Lumistox test were calculated by graphical interpolation, according to the ISO guidelines [18].

3. Results and discussion

The preliminary experiments in bench-scale with the raw textile wastewater at different pH values, together with consideration of the operational costs, allowed the selection of the pH values for the pilot-scale experiments. Furthermore, the literature shows that ozonation under acidic conditions allows direct oxidation by molecular ozone, while at high pH value hydroxyl free radical production is favored and hydroxyl oxidation starts to dominate [19]. Since the ozone mechanism of action is related to the pH conditions, pilot-scale experiments were carried out under acidic and basic pH to evaluate the influence of pH on the ozonation efficiency. The characteristics of the raw and ozonated textile wastewater under basic pH are given in Table 1.

This textile wastewater is characterized mainly by high organic content and high salinity, while environmentally hazardous (transition) metals were not found in the samples within the quantification limits.

Table 1
Mean physico-chemical values of parameters measured on raw and ozonated textile wastewater ($n = 3$).

Parameters	Raw wastewater	Ozonated wastewater pH 9.0
Chemical oxygen demand ($mg\,O_2\,L^{-1}$)	1505	1126
Biochemical oxygen demand ($mg\,O_2\,L^{-1}$)	91.2	458.9
Surfactants ($mg\,L^{-1}$)	1.18	0.07
Color (A_{455})	0.754	0.240
pH	9.10	6.98
Conductivity (mV)	109	101
Hardness ($mg\,L^{-1}$ as $CaCO_3$)	86.5	81.2
Cyanide ($mg\,L^{-1}$)	0.2	0.05
Phenolic compounds ($mg\,L^{-1}$)	0.090	<0.0047
Total iron ($mg\,L^{-1}$)	0.77	0.26
N-Nitrate ($mg\,L^{-1}$)	2.0	1.8
Sulfate ($mg\,L^{-1}$)	345.3	332.1
Phosphate ($mg\,L^{-1}$)	12	2.3
Fluoride ($mg\,L^{-1}$)	0.64	0.26

(<) Analyte not quantified at/or above the presented value (quantification limit).

3.1. Ozone oxidation and raw wastewater color and COD removal

The efficiency of pre-ozonation in the removal of color and COD from textile wastewater is important to achieve to discharge limits, as well as to degrade complex chemical structures to more easily degradable molecules, since dyes were intentionally designed to resist degradation and conventional biological wastewater treatment methods are ineffective in removing the color [2,7]. Thus, Fig. 2 presents the decolorization efficiency as a function of the ozonation time applied to the textile wastewater. The results indicated that ozonation treatment was more effective at degrading wastewater dyes under basic pH than acidic pH. As described above, under conditions favoring hydroxyl free radical ($HO^{\bullet}$) production (e.g., high pH), the more powerful hydroxyl oxidation starts to dominate [19]. Thus, the average efficiencies for color removal were 40.6% for pH 3.0 and 67.5% for pH 9.1. Since the oxidation potential of ozone reportedly decreases from 2.07 mV (acidic pH) to 1.4 mV (basic pH) [20], it is clear that another more powerful oxidant ($HO^{\bullet}$) is responsible for the increase in the dye degradation, with a consequent color absorbance decrease. Besides being pH-dependent, ozonation efficiency is also influenced by the dye structure and solubility. In this regard, reactive dyes are very soluble in water, and thus ozone can easily react with them, while disperse dyes are present as particles in solution and considerably longer treatment times are therefore required for wastewater decolorization.

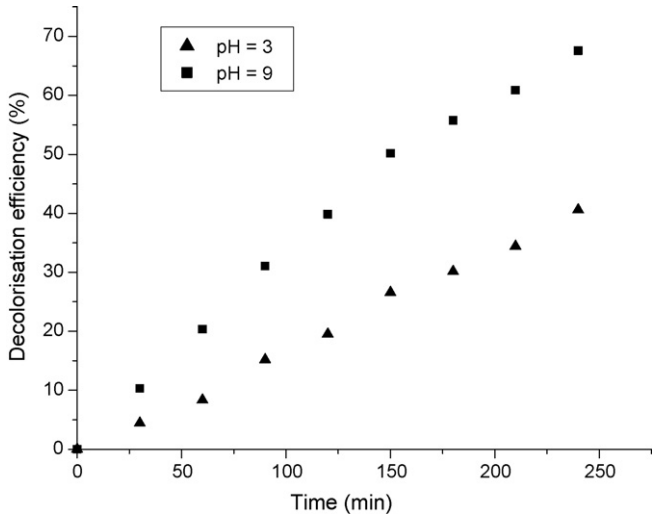

Fig. 2. Decolorization efficiency in function of time ozonation of textile wastewater under acidic and basic pH conditions. Data are the mean of three experiments.

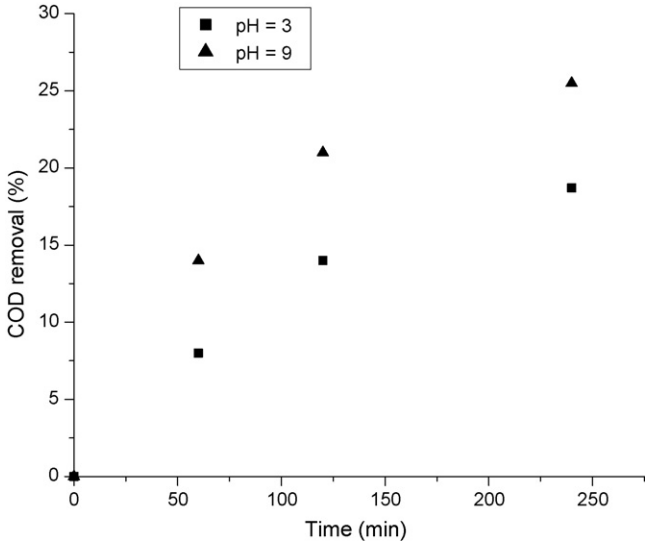

Fig. 3. Percentual removal of COD in function of time ozonation of textile wastewater under acidic and basic pH conditions. Data are the mean of three experiments.

In relation to the degradation of soluble organic matter measured as COD, Fig. 3 gives the percentage removal of COD as a function of treatment time under acidic and basic pH conditions.

After 240 min of pre-ozonation the values of COD decreased by 25.5 and 18.7% for pH 9.1 and pH 3.0, respectively, as shown in Fig. 3. The literature shows that COD and color removal efficiencies are mainly dependent on dye/organic matter contents, pH, temperature, ozone transfer to the wastewater solution, and other factors [21–23]. Thus, it is reported that ozonation reduces COD and color by up to 51% and 98%, respectively [24], while other study reached removal percentages of 86–96% for color, and 33–39% for soluble COD [25]. Optimal process conditions in a bench-scale reactor for biotreated effluent (pH 8 and temperature 25 °C) resulted in 100% color and 96% COD removal for 10 min ozonation (100 mg O_3/104 mg COD) [26].

Along with direct organic matter oxidation, the biodegradability potential of ozonated textile wastewater can be established by BOD_5/COD ratio. Thus, the samples were analyzed for COD and BOD_5 in order to establish changes in the biodegradability profile during ozonation. The results obtained are shown in Fig. 4. Ratios of BOD_5/COD higher than 0.4 (or biodegradability of 40%) indicate a high biodegradability of the sample, while values lower than 0.4 indicate low degradability [27]. In this respect, a more careful consideration should be made when the samples are not oxidized or are only partially oxidized in the COD or BOD_5 assays, which could lead to false BOD_5/COD ratio results [28]. In this regard,

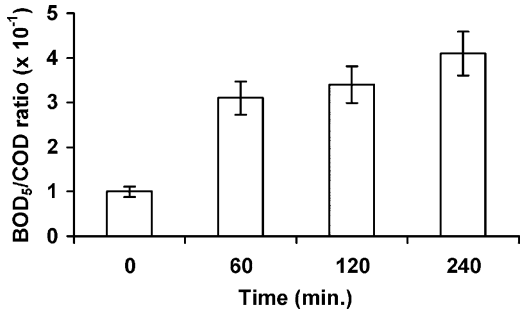

Fig. 4. BOD_5/COD ratios in function of time ozonation of textile wastewater. Data are the mean of three experiments. Vertical bars are standard deviation.

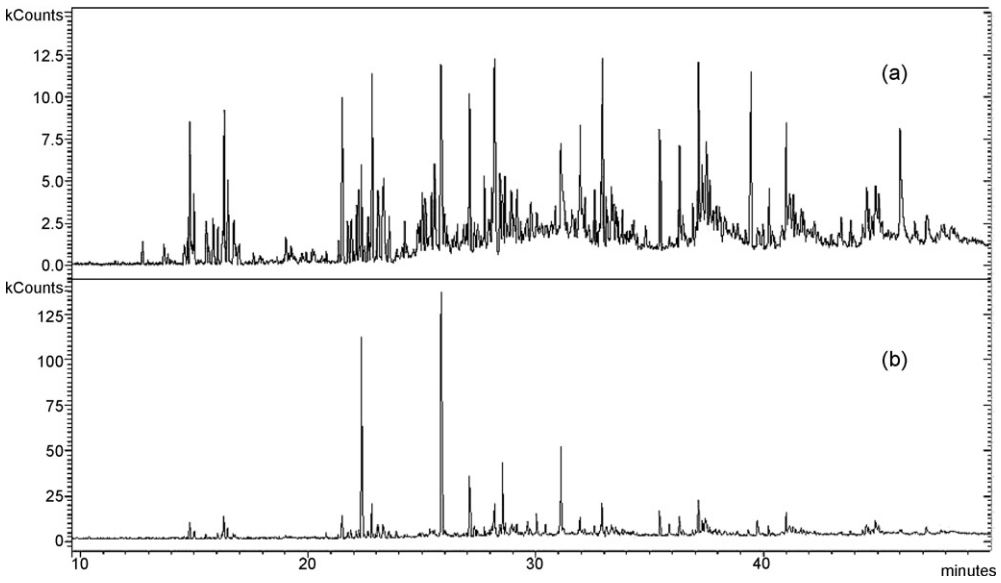

Fig. 5. GC chromatograms of the (a) raw (pH 9.10) and (b) ozonated textile wastewater (pH 6.98).

when assays were carried out with wastewater at pH 3.0, bacterial growth was negligible and no BOD_5 values were obtained under this pH condition. Fig. 4 shows an increase in the biodegradability for the treatment at pH 9.1 in relation to the initial time. Thus, after the ozonation, samples became more biodegradable. Raw textile wastewater showed a low BOD_5/COD ratio (0.06), that is, these samples have a low biodegradability, which could be attributed to the toxicity and/or low solubility of compounds present in this sample [29]. After 240 min of ozonation, this ratio reached an acceptable value (0.41), which could ensure good sample biodegradability. In fact, Wodzinski and Coyle [30] have shown that dissolved compounds can be more easily biodegraded. The increase in sample biodegradability observed in Fig. 4 could be associated with the more soluble/biodegraded by-products of ozonation. Therefore, an increase in the treatment time increases both biodegradability and mineralization of the wastewater samples. Since the ozonation represents a significant cost, partial oxidation is of interest because microorganisms can be used in a post-treatment process for the complete mineralization of contaminants in a water matrix. Therefore, the use of chemical oxidation followed by microbiological degradation may provide more economical and effective process conditions than oxidation or biodegradation alone.

Nevertheless, dyes and organic matter are not completely destroyed in the pre-ozonation scheme used in the present study, and formation of intermediates and final products was observed.

3.2. Intermediates and final degradation products of ozonation

It is preferable that ozonation degraded products be innocuous, but the intermediates and final products of the ozonation reaction of the dyes could have toxic effects [4,25,31]. Thus, identification and/or ecotoxicological evaluation of these products must be carried out to avoid problems with sequential biological degradation treatment. Literature data show that the intermediates and final products of ozonation depend on the chemical structure of parent compounds, as well as the ozonation conditions [11,14,32].

Among the intermediates, phenols, quinones, hydroquinones, phthalic, muconic, fumaric, maleic were identified, but they disappeared completely after 60 min of ozone treatment. Fig. 5a and b show the GC chromatograms of the raw (pH 9.10) and ozonated textile wastewater (pH 6.98). The presence of some aliphatic alcohols originated from the partial hydrolysis of nonylphenol ethoxylated (NPE) molecules, which are widely used in textile mills as dispersants, humectants and emulsifiers, are observed in the raw textile wastewater. From Fig. 5a and b, it is clear that ozonation decreased significantly the contents of the organic textile wastewater extracts. It should be noted that ozonation normally leads to more polar compounds, but the solvent used in the extraction (CH_2Cl_2) gathers mid-polar or non-polar compounds. Also, GC-MS methods are not appropriate for the detection of polar or large molecular weight compounds. Thus, it is very probable that some polar degradation products were generated which could not be detected with the analytical method used.

Thus, a preliminary analysis (including mass spectrometry—data not shown) of the raw textile wastewater samples showed an important absorption peak with a retention time of 14.5 min, which was identified as being 5-n-butyl-nonane. Other absorption peaks were those with retention times of 15.5 min (2-ethyl-1,4-dimethyl-benzene) and 22.3 min (2-methyl-5-s-propyl-phenol). On the other hand, ozonated textile

Table 2
Percent inhibition of the bacterial luminescence test with *Vibrio fischeri* exposed to raw and ozonated textile wastewater during 30 min. ($n = 3$).

		Textile wastewater present in dilution (%)									Result (%)	
		Control	0.4	0.8	1.5	3.1	6.25	12.5	25.0	50.0	EC20	EC50
Raw wastewater	X[a]	0.0	15.0	22.5	34.2	48.6	60.1	73.1	81.1	88.5	0.5	3.4
	CV[b]	5.3	6.2	7.2	6.6	5.1	8.5	4.8	5.7	8.3	6.7	7.3
Ozonated wastewater	X[a]	0.0	–	–	–	8.3	16.6	29.3	48.0	61.2	6.9	28.6
	CV[b]	5.3				6.1	4.8	7.2	6.4	5.3	6.8	6.6

[a] Mean of luminescence inhibition or mean of EC values.
[b] CV, coefficient of variation (%).

wastewater (pH 6.98) showed the presence of the same 2-methyl-5-s-propyl-phenol (retention time 22.3 min), as well as absorption peaks of 4-hydroxyoctahydronaphthalen-1(2*H*)-one (retention time 27.0 min) and 7-isopropyl-7-methyl-nona-3,5-diene-2,9-dione (retention time 28.5 min). Some aromatic compounds react relatively slowly under ozonation and will require longer treatment times to be oxidized under the experimental conditions used in this study.

3.3. Ozone oxidation and raw wastewater ecotoxicity removal

Efficiency of expensive textile wastewater treatment methodologies can be optimized by ecotoxicological tests, such as those using *V. fischeri* bacteria or *Daphnia magna* cladoceran crustacean. This optimization is related to the final toxicity of the treated wastewater, which has direct implications with regard to discharge permits. Table 2 gives the toxicity results of the raw and ozonated textile wastewater.

The results obtained with the bacteria ecotoxicity test showed that the raw textile wastewater was more toxic than the ozonated wastewater. In this respect, Table 2 clearly demonstrates a significant reduction in the toxicity of wastewater samples after ozonation, probably due to the partial elimination of the toxic organic fraction oxidized during this treatment process. The remaining toxicity could be attributed to the recalcitrant compounds, and also to the inorganic fraction. Taking into account that the final goal of this pilot-scale ozonation pre-treatment was the partial oxidation of recalcitrant organic matter, a moderate toxicity reduction would be expected. To achieve total toxicity elimination, the ozonation time must be increase, which will increase the treatment cost. The variability in the results of this study, expressed as the coefficient of variation, is acceptable and comparable with results published by Rosa et al. [33]. Furthermore, if we consider that pre-ozonated textile wastewater will be treated by sequential microbiological treatment, bacterial toxicity evaluation is important to ensure the feasibility of this sequential wastewater treatment.

4. Conclusions

This pilot-scale treatment of textile wastewater was designed to evaluate pre-ozonation efficiency for removal of color and soluble COD, as well as to identify ozone recalcitrant molecules and evaluate acute toxicity abatement. All of these wastewater aspects are important to ensure optimization of treatment and to achieve discharge limits. Thus, after 4 h of ozone treatment with wastewater recirculation, the average efficiencies for color removal were 67.5% (pH 9.1) and 40.6% (pH 3.0), while COD reduction was 25.5% (pH 9.1) and 18.7% (pH 3.0) with an ozone production capacity of 20 g h^{-1}. Ozonation enhances the biodegradability of textile wastewater (BOD_5/COD ratios) by a factor of up to 6.8-fold. A GC-MS analysis of the pre-treated textile wastewater showed that some products were present at the end of the pre-treatment time. In spite of this fact, the bacterial luminescence inhibition test (Lumistox test) showed a significant toxicity reduction on comparing the results of the raw and ozonated textile wastewater. It is clear that mineralization of the total organic content of the textile wastewater is not economical during ozonation in a pilot-scale, but partial oxidation altering the original product can have beneficial effects by reducing toxicity effects of wastewater and enhancing the biodegradability of organic wastewater contents in a sequential microbiological treatment of textile wastewaters.

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