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Oxidation process by ozonization aplied in post-treatment of pulp and paper industry wastewaters

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Abstract

Restrictions imposed by environmental legislation, the water crisis and economic challenges are all factors that have recently contributed to the proliferation and application of advanced oxidation processes as an alternative method of wastewater treatment. The purpose of this study was to assess the use of ozone in the post-treatment of a pulp and paper mill's wastewater, already treated using an activated sludge biological process. The ozonation process yielded high levels of oxidation of organic substances, corroborated by an almost immediate reduction in COD and BOD_5 loads. By the end of the treatment, the wastewater's biodegradability had increased by 70%. Color removal percentages ranged from 52% to 91%. In terms of turbidity, the removal rate attained a 78% level. Total solids removal reached a 63% level. These results are evidence of the effectiveness of the ozonation process in the post-treatment of biologically treated wastewater generated by pulp and paper mills.

Keywords: *Advanced Oxidation Process; Ozone; Industrial Wastewater; Pulp and Paper.*

Nomenclature

BOD_5	Biological Oxygen Demand ($mg.L^{-1}$)	***Greek symbols***	
COD	Chemical Oxygen Demand ($mg.L^{-1}$)	*V*	volt
O_3	ozone ($mg.L^{-1}$)	*pH*	ionic hydrogen potential
TS	total solids ($mg.L^{-1}$)		

1. Introduction

In today's world, the pulp and paper industry is extremely relevant to the economic and social environments of industrialized countries. Technological innovations have significantly contributed to the growth and increased production in the industry. In essence, modern equipments have considerably increased the speed of manufacturing processes, escalating that growth. In the Brazilian market, there are over 500 different types of paper being produced and distributed nationally and internationally [1]. In the coming years, the trend is that paper consumption will increase, especially due to its correlation to increased demographics, which is directly responsible for an increase in the demand for goods and services.

Although its economic and social importance is irrefutable, the pulp and paper industry is among the worst environmental polluting sources in the world. Along with the chemical and metallurgical industries, pulp and paper is part of a group classified as the three biggest sources of wastewater [2,3]. Such classification characterizes those activities as potential causative agents of the degradation of the environment.

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Apart from its elevated toxicity and distinct color, wastewater generated by the pulp and paper industry has a high concentration of COD, BOD, suspended solids, lignin, chlorinated compounds, fatty acids and acidic resins. A few of these elements, such as lignin and acidic resins, are naturally occurring by-products of wood, while others are produced during the many phases of paper manufacturing, as is the case with phenols, dioxins, furans and chlorinated lignin [4,5].

In general, this type of wastewater is disposed of into our waterways and, when not adequately treated, tend to jeopardize the quality of the water at the receiving end [6].

Most pulp and paper companies treat their wastewater through biological processes. This preference is justified by the fact that these processes are fairly easy to implement and operate, and incur relatively low costs [7]. These processes are also mostly implemented using activated sludge and aerated ponds, and are rather efficient in terms of the removal of biodegradable organic material. Their disadvantages, however, lie in the fact that they are rather susceptible to the composition of the wastewater and shock loads, and require strict control of its nutrients, temperature and pH, as well as constant monitoring of its microbial activities. In addition, they also produce high volumes of sludge [8]. Other negative aspects that need to be considered include their low effectiveness in the removal of color, COD and refractory compounds. All these issues make it necessary to implement other additional treatment methods so as to "polish" the final wastewater [9].

In the past decade, new Advanced Oxidation Processes (AOPs) have emerged as promising sources of wastewater treatment, especially due to their capacity to break down several polluting compounds in a short period of time. Such processes induce a chemical structure change in recalcitrant compounds, making them less toxic and reducing their molar mass [10, 11,12, 13].

For several types of wastewater, O_3 a gas with high oxidative capacity, is an attractive treatment option [14,13]. It's instability allows for rapid decomposition upon contact with the water, causing a number of reactions. The most relevant of these reactions is the formation of hydroxyl radicals, or •OH [15], a highly reactive species that delivers a reduction potential of 2.80 V. Because they're not selective, •OH are capable of oxidizing and breaking down several pollutant compounds [16].

In the pulp and paper industry, ozonation processes have proven to be rather effective in terms of oxidation of refractory compounds, color and toxicity removal, and in increasing the biodegradability of the wastewater [17,18].

Its use induces chemical structure changes at the molecular level, allowing for the conversion of high molecular weight compounds into organic acids with reduced molar mass [11]. With all that in mind, the purpose of this study was to assess the use of O_3 as applied to the treatment of a pulp and paper mill's wastewater, after its regular biological process treatment.

2. Experimental Rig

2.1 Materials

The wastewater used in this study was collected at the backend of a secondary settling tank belonging to a pulp and paper mill in the midwest of the State of Santa Catarina. It had already been treated by an activated sludge biological process consisting of an initial grating operation, an equalization tank, aeration tanks, and primary and secondary settling tanks. The experiments were conducted in an oxidation system consisting of a portable ozone (O_3) generator (Corona Discharge, model ID-05 CD) connected to a PVC tubular reactor, with a diameter of 200 mm, 1.50 meters in height, and a capacity of 45 liters. A peripheral pump, model IDB-35, with a ¼ HP motor, was used to pump the wastewater into the reactor. The O_3 generator was configured to generate 2.1 $g.O_3.h^{-1}$, in accordance with its production and flow of oxygen. Generator calibration was done using of iodometric titration as described in APHA's, 1997, 2350 OXIDANT DEMAND/REQUIREMENT method. Figure 1 shows the ozonation system's schematic diagram.

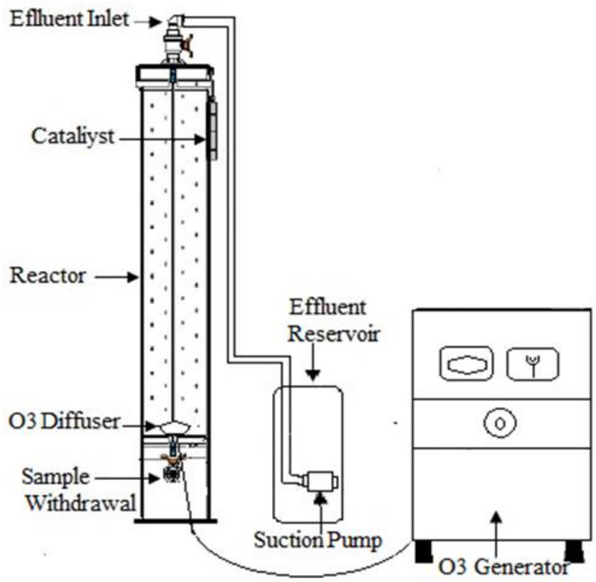

Figure 1. Ozonation system's schematic diagram.

The wastewater was kept in the reactor for 60 minutes. On the 15th, 30th, 45th, and 60th minutes, a 50 mL aliquot of wastewater was collected so as to analyze it for the following parameters: BOD_5, COD, color, turbidity and total solids (TS), all according to instructions contained in APHA's 2005 documentation. The pH for the samples was not adjusted; the process was, therefore, applied with the wastewater's natural pH, which was 7.3.

3. Results and Discussion

Table 1 shows the results pertaining to the physicochemical and biological parameters that characterized the raw and bio-treated wastewater.

Table 1. Characterization of the wastewater generated by a pulp and paper mill.

Parameter	Raw Waste-water	Bio-treated Waste-water	Unit
Color	278	147	PtCo
COD	1045	606.3	$mg.L^{-1}$
BOD_5	489.9	201	$mg.L^{-1}$
pH	7.32	7.1	-
TS	2040	1265	$mg.L^{-1}$
Temperature	41	39.5	ºC
Turbidity	4.20	2.68	NTU

It was determined that the biological processes used by the pulp and paper industry to treat their wastewater is removing only 58% of the BOD_5, when the current Brazilian environmental legislation requires a minimum BOD_5 removal rate of 60%. For COD, on the other hand, the same biological processes yield a removal rate of 42%. Figure 2 shows the rate variations for BOD_5 and COD, after ozonation. The use of this oxidation process resulted in an almost immediate reduction of the wastewater's COD and BOD_5 loads.

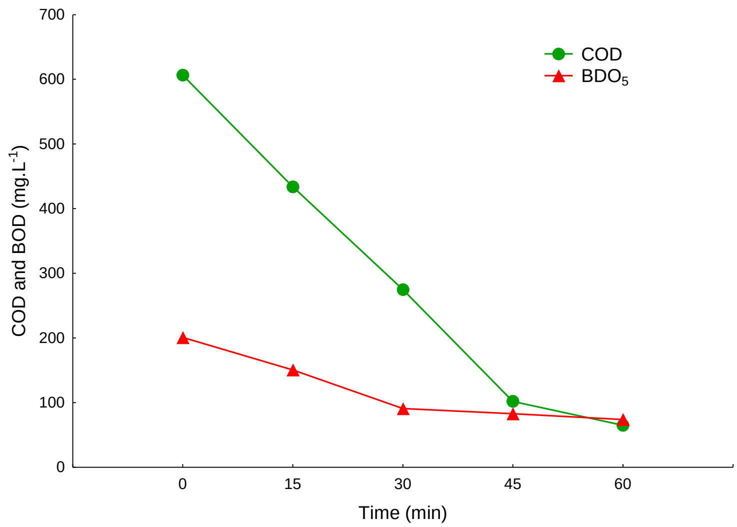

Figure 2. Wastewater BOD_5 and COD variations as a function of time in ozonation.

After 15 minutes, the COD removal rate was already at 28%, a rate that became even more significant after 30 minutes of oxidation treatment, with rates reaching 54%, 80% and 89%. After 60 minutes of applying ozonation to wastewaters generated by pulp and paper mill and already treated with biological processes using activated sludge, [19] reported results similar to that attained in this study, with COD removal rates ranging between 36% and 76%. The change in the oxidation state of carbon bonds present in organic materials results in the reduction of COD [20].

A similar behavior was observed for BOD_5, with removal rates ranging between 25% and 63%. The ozonation process altered the wastewater's biodegradability. An increase of 40% and 70% was attained for samples collected at 45 and 60 minutes of treatment, respectively. Such results indicate that the O_3 treatment was effective in removing recalcitrant species, inducing mineralization and converting recalcitrant compounds into CO_2 and H_2O.

Ozonation escalated the removal of color from the wastewater, with rates ranging from 52% to 91%. As had already been determined by [22], industrial wastewater color removal is rather effective when using the O_3 treatment process. Results attained in this study also show that the O3 concentrations applied were not excessive. An excess of O_3 does not increase its color removal capability. If the O_3 concentration is above the ideal dosage, the quantity of OH and the O_3 itself in the solution are practically unchanged [23]. Turbidity displayed a similar behavior, with its removal from the wastewater due to ozonation ranging from 58% to 78%. Additionally, the biologically treated wastewater had a total solids (TS) average concentration of 1.265 mg.L^{-1}. Figure 4 shows the wastewater's total solids concentration as a function of time in ozonation.

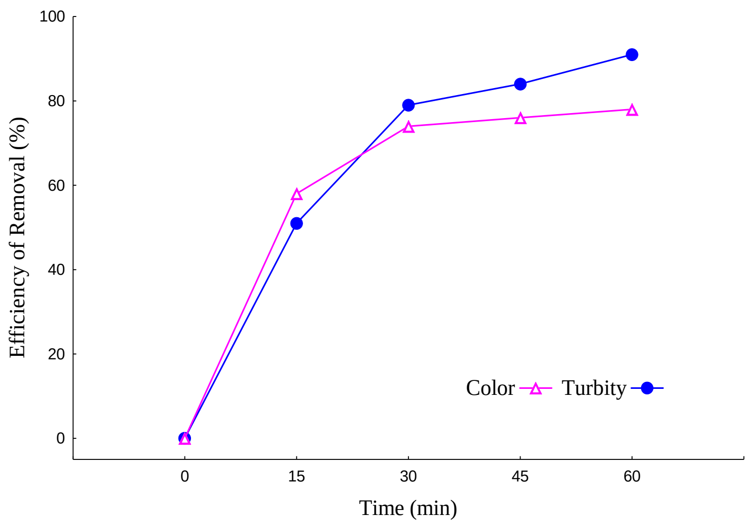

Figure 3. Color and turbidity removal efficiency as a function of time in ozonation.

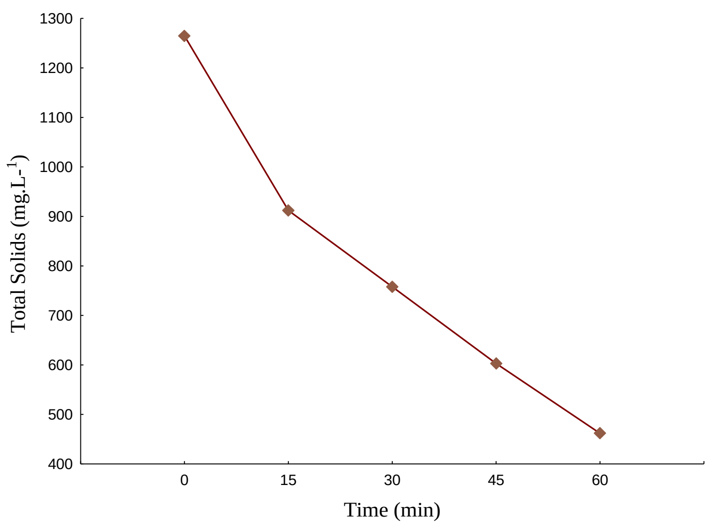

Figure 4. Reduction of TS concentration as a function of time in ozonation.

The longer the wastewater was in contact with the O_3 in the reactor, the better the results; TS removal rates at 15, 30, 45 and 60 minutes were 28%, 40%, 52% and 63%, respectively.

4. Conclusions

Wastewater generated by the pulp and paper industry is loaded with chemical pollutants and refractory compounds, both of which are often resistant to conventional treatment. Oxidation produced during the ozonation process was capable of removing the organic material present in the wastewater, increasing its biodegradability by up to 70%, and improving its final quality before proper disposal. The oxidation treatment also yielded high color and turbidity removal rates, with percentages of 91% and 78%, respectively. Removal of total solids was also escalated by the O_3 process, with its rates ranging from 52% to 63%. By virtue of these results, one can conclude that ozonation is an effective method of wastewater treatment; one that can potentially be used for the treatment of wastewater generated by the pulp and paper industry, after its initial treatment with biological processes using activated sludge.

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