Application of O_3 and O_3 /H_2O_2 for post-treatment of Horizontal-Flow Anaerobic Immobilized Biomass (HAIB) effluent, treating hospital wastewater

Aplicación de O_3 y O_3/H_2O_2 como postratamiento del efluente de un reactor anaerobio de flujo horizontal y Biomasa Inmovilizada De Flujo Horizontal (RAFABI) tratando aguas residuales hospitalarias

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Resumen

Introducción— En los últimos años, se ha incrementado la atención a la presencia de "contaminantes emergentes" en aguas residuales urbanas, industriales y cuerpos de agua superficial. En la mayoría de los casos, estas sustancias, corresponden a contaminantes que aún no ha sido reglamentados a nivel nacional por las autoridades ambientales. Los hospitales son considerados como la mayor fuente de estos compuestos, resultado de diferentes actividades. No existe en la actualidad un consenso sobre cuál o cuáles son los tratamientos adecuados para tratar las aguas residuales que contienen estos compuestos. En general, los procesos biológicos convencionales por sí solos no alcanzan a cumplir con los valores de los límites de descarga, siendo necesario aplicar postratamientos como los Procesos de Oxidación Avanzada (POA), conocidos como una tecnología apropiada no sólo por aumentar la biodegradabilidad de los compuestos recalcitrantes, sino también por contribuir con la remoción de ciertas sustancias que son difíciles de tratar en un proceso biológico.

Objetivo— Por tal razón, en este estudio se evaluó la aplicación de Ozono (O_3) y O_3/H_2O_2 al efluente de un Reactor Anaerobio de Flujo Horizontal y Biomasa Inmovilizada (RAFABI).

Metodología— Los oxidantes fueron aplicados en un reactor de vidrio de borosilicato tipo batch en escala de laboratorio. El tiempo de reacción fue de 60 min y se tomaron muestras a intervalos de 15 min. Para evaluar el desempeño del tratamiento se midieron parámetros tales como la absorbancia a una longitud de onda de UV_{254}, la relación de biodegradabilidad expresada como DQO/DBO_5, y el color como VIS_{436}. Todas las muestras fueron analizadas por duplicado.

Resultados— Los resultados mostraron que la aplicación de O_3 y O_3/H_2O_2 produjeron un incremento en la biodegradabilidad del 25% y del 67% respectivamente. En relación con el color, se observó una eficiencia del 85 % para el Ozono y el 100 % para el O_3/H_2O_2. Adicionalmente, los dos POA aplicados también mostraron ser efectivos para remover orgánicos aromáticos medidos como UV_{254}, para lo cual se obtuvieron remociones entre el 40% y 50% de UV_{254}.

Conclusiones— Finalmente, es importante mencionar que la aplicación de procesos de oxidación avanzada como postratamiento de efluentes anaerobios, aumentan la biodegradabilidad principalmente por la transformación que sufren los compuestos recalcitrantes.

Palabras clave— Oxidación avanzada; biodegradabilidad; compuestos emergentes; efluentes hospitalarios; recalcitrancia

Abstract

Introduction— In recent years, the "emerging pollutants" in urban, industrial, and surface water bodies have called the attention worldwide. In many cases, these substances correspond to pollutants that have not been yet regulated by the environmental authorities. Hospitals are considered the main source of these contaminants as a result of different activities. However, there is no consensus about the appropriate treatments for removing this kind of pollutants in the wastewaters; independent conventional biological processes do not reach the desirable values of discharge limits. Advanced Oxidation Processes (AOP) are known as an appropriate technology, not only to improve the biodegradability of recalcitrant compounds, but also to contribute to the removal of certain substances that are difficult to treat during the biological process.

Objective— Thus, this study evaluated the application of O_3z and O_3 /H_2O_2 to the effluent of an Anaerobic Horizontal Flow Reactor and Immobilized Biomass (HAIB).

Methodology— The oxidizers were applied in a lab-scale batch borosilicate glass reactor. The reaction time was 60 min and samples were taken at intervals of 15 min. Parameters such as absorbance at UV_{254}, biodegradability ratio expressed as COD/BOD_5, and color as VIS_{436} were measured. All samples were analyzed in duplicate.

Results— The results showed that the application of Ozone and O_3/H_2O_2 results in an increase in the biodegradability of 25% and 67% respectively. Concerning color, an efficiency of 85 % for Ozone and 100 % for O_3 /H_2O_2 was observed. Besides, the AOPs applied also showed their effectiveness in removing aromatic organics, removing 40% to 50% of UV_{254}.

Conclusions— Finally, it is important to mention that the application of advanced oxidation processes as a post-treatment of anaerobic effluents increases biodegradability mainly due to the transformation suffered by recalcitrant compounds.

Keywords— Advanced oxidation; biodegradability; emerging compounds; hospital effluents; recalcitrance

I. Introduction

Hospital wastewater contains a wide variety of toxic and persistent substances, such as pharmaceutical residuals, radionucleidos solvents, and disinfectants generated by laboratory activities, research, and excretion of medicines in patients. Most of these compounds belong to the group called "emerging compounds". The difficulty in removing these contaminants, especially the pharmaceutical residues, is because their concentration ranges are low (*e.g.* 10^{-3} – 10^{-6} $mg.L^{-1}$) compared to macrocontaminant concentrations (*e.g.* nitrogen, phosphorus, COD). Also, the behavior of these substances is affected by the treatment systems, because of changes in their physical properties, such as solubility, volatility, biodegradability, polarity, and stability.

Accordingly, the presence of pharmaceutical waste in natural water bodies because of hospital effluents is a serious environmental problem. These compounds are extremely resistant to biological degradation and usually they escape intact from conventional treatment systems, what provoke adverse effects in humans and other living organisms. Due to the identification of these dissolved pollutants require sophisticated methods, the academy is dedicated to develop new analytical techniques. Also, several studies are focused to analyze the toxic effects of these emerging pollutants, their degradation and/or transformation using non-biological treatment technologies, such as the advanced oxidation processes [1].

These emerging contaminants are not fully regulated, turning them into ideal candidates to analyze their effect on human-environment health, occurrence in water treatment systems, and final destination into the environment. Despite they do not persist for a long time in the environment, their discharge into to the soil or water is constant [2].

The COVID-19 pandemic has generated special attention in the scientific community mainly for the development of the concept "Wastewater-Based Epidemiology" (WBE). This definition permits the identification of the sources of contagion before the traditional tests in the health centers. As a consequence, the technologies for hospital wastewater treatment have also become an object of study, to preserve and protect the environment, improve the sanitation and ensure a clean and safe water for a wide range of activities, in line with the United Nations Sustainable Development Goals [1].

Considering that the COVID-19 pandemic has increased the use of medicines [3], [4], [5], the receiving waters are more exposed to a rise of the concentrations of these emerging pollutants. In this sense, the current concern is: what would be the appropriate treatments in the hospital centers to reduce the emerging compounds, especially those that are resistant to antibiotics? In an extensive review of new approaches and perspectives in the management of HWW, [2] highlights that combining HWW with Urban Wastewaters (UWW) is not appropriate. However, this practice can be considered as a mitigation measure for countries like India, Colombia, Nepal, Pakistan, where the wastewater discharge directly without treatment remains.

Biological processes are a limited option for the removal of recalcitrant compounds present in Hospital Wastewater [6]. Therefore, the application of Advanced Oxidation Processes (AOPs) such as a post-treatment could be considered a viable option to improve the physical-chemical quality of the system's effluents, that could prevent the discharge of emerging pollutants to receiving sources [7].

According to University of California [8], AOPs are defined as a series of oxidation processes that might generate hydroxyl radicals (OH•) in sufficient quantity to improve the water treatment. The first POA was discovered by Fenton in 1894 [9], since then, numerous chemical and non-chemical processes have been developed to produce hydroxyl radicals. Hydroxyl radical (OH•) is an agent with high oxidation power, short lifetime, which attacks not selectively several organic molecules, with constant velocities in the range of 106 – 109 M^{-1} s^{-1} [10], [9], [11]. Its oxidation potential is higher than other oxidants including O_3 and hydrogen peroxide [12].

Ozone is an agent with high oxidation potential, capable of participating in many reactions of organic and inorganic compounds. Among the oxidizing agents, Ozone is only overcome by fluoride and hydroxyl radical. The chemistry of ozonation is complex and is characterized by the action of two mechanisms: direct reaction, with dissolved molecular Ozone, and indirect reaction with radical species (OH•), formed when Ozone decomposes in water [13], [14]. The combination of the two mechanisms in the removal of substances depends on their nature, the pH of the medium, and the applied dosage of Ozone [15].

The Ozone power can be improved in the presence of hydrogen peroxide and UV irradiation, metal cations such as ferrous and ferrous ions, alumina, or catalysts such as titanium dioxide [16], [17]. The decomposition of O_3 is influenced by pH, temperature, UV radiation, concentration, and presence of inhibitors [13]. According to M.U.I.C.T [11], if the operating pH is higher than the *pK* value of the compound when the compound is not in a molecular state, the probability of an increment of speed degradation will decrease. Universität des Saarlandes [18] performed a wide review of combined processes, who included biological processes and chemical oxidation. The study indicated that apparently oxidation with Ozone at high pH is faster, with a high efficiency of the process when pH is neutral, a fact observed due to the amount of Ozone needed to oxidize organic molecules. The research emphasized that the aforementioned behavior is favorable during the combination of Ozone and biological processes, then it would not require modifying the pH between these two processes.

The O_3 application in wastewater treatment has been used as an alternative to help the degradation of those compounds that are not eliminated in conventional treatments. The Ozone application does not produce odors and does not generate non-toxic residual elements such as the O_2 y H_2O. Furthermore, Ozone is easily produced by electrical discharge over a volume of air. Ozone can transform dissolved pollutants in water samples into simpler compounds [19].

Hydrogen peroxide (H_2O_2) is considered a versatile oxidant, superior to chlorine, chlorine dioxide, and potassium permanganate. Weak, colorless acid with *pKa* value from 11.75 K to 293 K, molar absorption coefficient from 19.6 M^{-1} cm^{-1} to 253.7 nm. The density of a 35% hydrogen peroxide solution is 1,113 kg/m^3 at 293 K and the value of the Henry constant is 1 Pa. L. mol^{-1} [20]. As hydrogen peroxide applied alone is not the ideal oxidant for various organic compounds, it is recommended to combine it with other substances such as metal salts and Ozone or UV irradiation.

The integration of advanced oxidation processes with biological processes is recognized by the reduction of recalcitrant compounds in wastewater. For example, NCSU [21] reviewing 58 studies, mostly on a bench scale, identified 4 types of wastewater, depending on the type of contaminant present, which could be treated through integrated processes: (a) with high concentrations of recalcitrant compounds; (b) with good biodegradability and low concentrations of recalcitrant compounds; (c) containing inhibitory compounds and (d) containing recalcitrant compounds and inhibitors at intermediate levels. The effect of process integration is based on increasing the biodegradability of the compounds studied by the application of AOPs in cases (a), (c), and (d). For case (b) the purpose is to improve the water quality of biological effluents [22].

According to UBC [23], it is recommended to remove the initial fraction of Low Molar Mass (LMW) in a biological treatment before the application of Ozone. Thus, one can have an increase in the reduction of the recalcitrant part of High Molar Mass (HMW) when the oxidant is applied. In this sense, this study evaluates the application of O_3 and O_3/H_2O_2 to treat the effluent of a Horizontal-Flow Anaerobic Immobilized Biomass (HAIB), without adjustment of the pH.

II. Material and Methods

A. *Hospital Wastewater (HWW)*

The HWW was obtained from a University hospital located in Bogotá city (Colombia). The sample comes from different medical activities such as surgical interventions, outpatient consultations, laboratories, excretion of patients, general services (cleaning and disinfection), research, and teaching activities. The HWW was collected from the Parshall flume placed at the entrance of the wastewater treatment. This wastewater was treated in an a HAIB reactor at bench-scale

The HWW was collected twice per week during 2019. As received, the samples were preserved and stored at 4°C and fully characterized by total Suspended Solids (SST), Total Dissolved Solids (SDT), Total Solids (ST), alkalinity, Color (VIS_{436}), UV_{254}, sulfates, phosphates, nitrogen (TKN), COD, BOD_5, and pH according to the methods described by [24] and [25].

B. *Experimental design and analytical determinations*

The effluent from the HAIB reactor was subjected to Ozone and O_3/H_2O_2 tests without prior pH adjustment. The pH of the HAIB reactor effluent was close to 7.7. With the purpose of identifying chromophore compounds with conjugated double bonds, responsible for the color of these effluents, was measured the absorbance at wavelength of 254 nm [26], [27], [25].

For these measurements, the samples were filtered in Millipore membrane, cellulose acetate, with 0.45 µm pore, and diluted to reach absorbance values of up to 0.9 cm^{-1}. The HACH UV-VIS DR 5000 spectrophotometer and quartz buckets of optical length of 1.00cm were used.

Each experiment was repeated five times for each AOP treatment. An ANOVA test was applied with a significance level of $p < 0.05$, to determine the statistical influence between the applied treatments. To determine the effect over biodegradability were evaluated the ratio COD/BOD_5. The parameters evaluated were pH, COD, BOD_5, UV_{254}, Color as absorbance at a wavelength of 436 nm (VIS_{436}), and total alkalinity [24]. All analyses were performed in duplicate and were reported as average values.

C. *O_3 and O_3/H_2O_2 applications*

O_3 and O_3/UV H_2O_2 experiments were conducted in a bench-scale reactor made of a cylindrical tube of bore-silicate glass with an external tube diameter of 100 mm, internal tube diameter of 60 mm, a height of 54 cm, resulting in a net volume of 1 200 mL. Ozone was provided by a Microzone generator (*Clearwater Tech*, LLC) with a top production of 233 mgO_3/h. The gas was injected at the bottom of the reactor using a fine bubble plate diffuser of 200 mesh. The not-consumed Ozone in the column was transferred to a separate flask-containing potassium iodide solution at 2%.

For O_3/H_2O_2, an effective dose of H_2O_2 of 150 mg/L was applied in accordance with the recommendations of [8]. The determination of H_2O_2 residual was measured using test strips *Quantofix* with a range of 0.5 mg/L - 25 mg/L de H_2O_2. The reaction of the chemical process was stopped by adding to each sample an amount of sodium sulfite determined by stoichiometry according to [28].

For every experiment, the treated volume was 1 000 mL, then, the reaction time for Ozone was 60 minutes and the samples were taken at intervals of 15 minutes. The schematic diagram of the bench-scale oxidation reactor is depicted in Fig. 1.

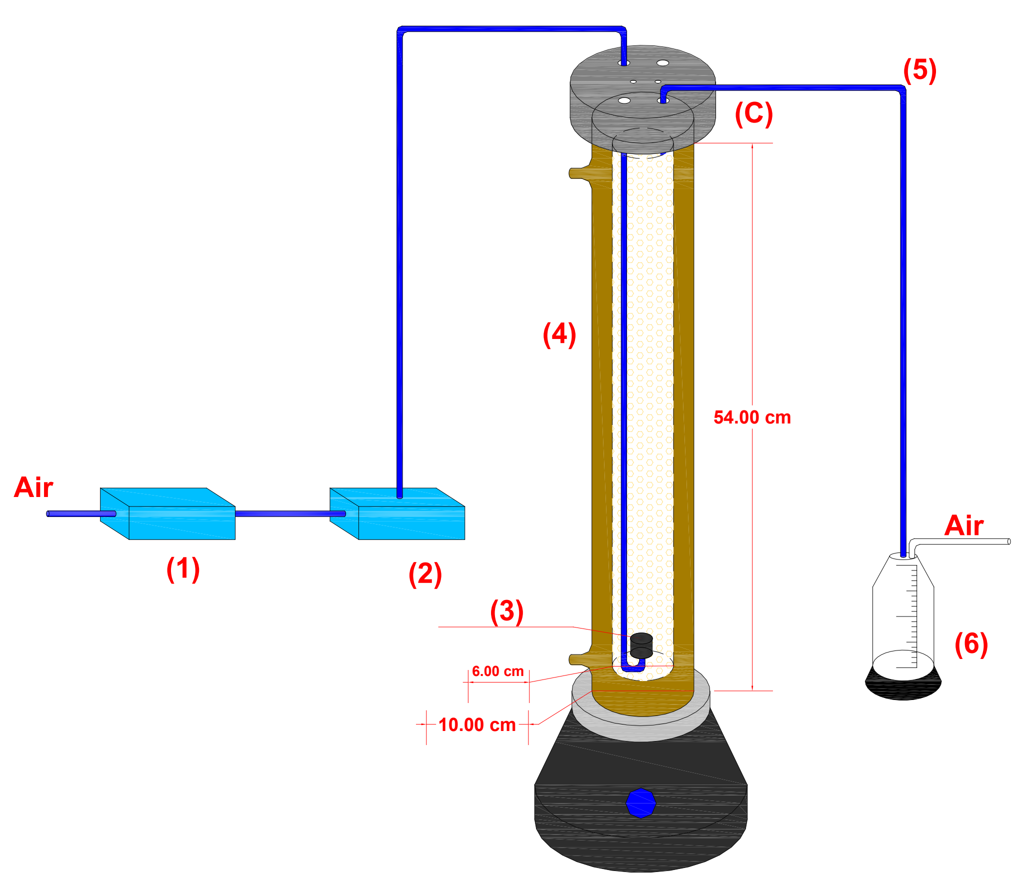

Fig. 1. Experimental setup of the AOP application. (1) Oxygen separator, (2) Microzone generator, (3) Ozone disperser, (4) Ozone reactor, (5) Exhaust gas line, (6) Flask with Iodine Solution (2%), (C) Sampling point.
Source: Authors.

III. Results and Discussion

A. *Characterization of HWW treated in the HAIB reactor*

The Table 2 shows the main characteristics of the hospital wastewater treated in the HAIB reactor. It can be seen that the values did not differ significantly from each other, therefore, the quality of the effluent kept stable during the study period, an aspect that facilitated the comparison of the tests carried out applying the AOP.

Table 2. Characteristics of the effluent from the immobilized biomass anaerobic reactor.

Parameter	Unit	Mean ± S.D
pH		7.7 ± 0.3
COLOR (VIS_{436})	cm^{-1}	0.02 ± 0.004
UV_{254}	cm^{-1}	0.25 ± 0.03
COD	mg/L	43 ± 21
BOD5	mg/L	8 ± 2
COD/BOD5	-	5.6 ± 2.2
Total Alkalinity	mg $CaCO_3$/L	192 ± 59
Estándar Deviation (SD)	n = 5	

Source: Authors.

During the application of the biological process (HAIB), easily degradable compounds are eliminated, while recalcitrant compounds are still present in the effluent because they are difficult to break down by the microorganism. As a result, the ratio (COD/BOD_5) was superior to 4, and the value of pH was 7.7 ± 0.3 in the effluent of the HAIB reactor.

It is worth mentioning that, as the interest of this research is the removal of recalcitrant compounds through the integration of anaerobic processes and advanced oxidation, the objective of the use of HAIB was the removal of the biodegradable fraction present in this type of effluent and probably some fraction of recalcitrant organic matter. Thus, the application of the AOPs would have as its sole objective, the transformation of the recalcitrant organic fraction.

The combination of anaerobic processes with advanced oxidation processes is a matter of interest to treat waters that contains emerging compounds. In a study conducted by ITU [29] in wastewater from the textile industry, found not only that this strategy reduced recalcitrant compounds but also removed the toxicity. These authors conclude that toxicity and mutagenicity assays are necessary and a complementary tool when these two processes are combined.

RWTH Aachen University [30] evaluated the effect of applying Ozone to the effluent of a system MBR equipped with ultrafiltration membranes, treating wastewater from a psychiatric hospital in Germany. Although they found optimal values for Ozone dose and contact time, 5 mg O_3/L and 12.8 min, respectively, a poor removal of dissolved organic carbon was obtained. This indicated that in this case the emerging pollutants were not completely removed and there was no good mineralization. It is important to mention that similar studies in which Ozone and its combinations are applied to anaerobic effluents are scarce in the literature [31].

B. *Effect in the UV_{254} and Color.*

The UV_{254} is a measure of the organic matter that indicates the presence of aromatic and unsaturated compounds in the wastewater, which are precursors of trihalomethanes and other organochlorine compounds. In other words, the measure of the absorbance at a wavelength of 254 nm, indicates how aromatic is the carbon present in the water [25].

Fig. 2 shows the effect of applying Ozone (Condition 1) and O_3/H_2O_2 (Condition 2) on the natural organic matter, measure as UV_{254}. Condition 1 shows a decrease in the absorbance as the Ozone dose increased. In minute 60, for an applied dose of 233 mgO_3/L was obtained an efficiency of removal of 49% ± 11.05.

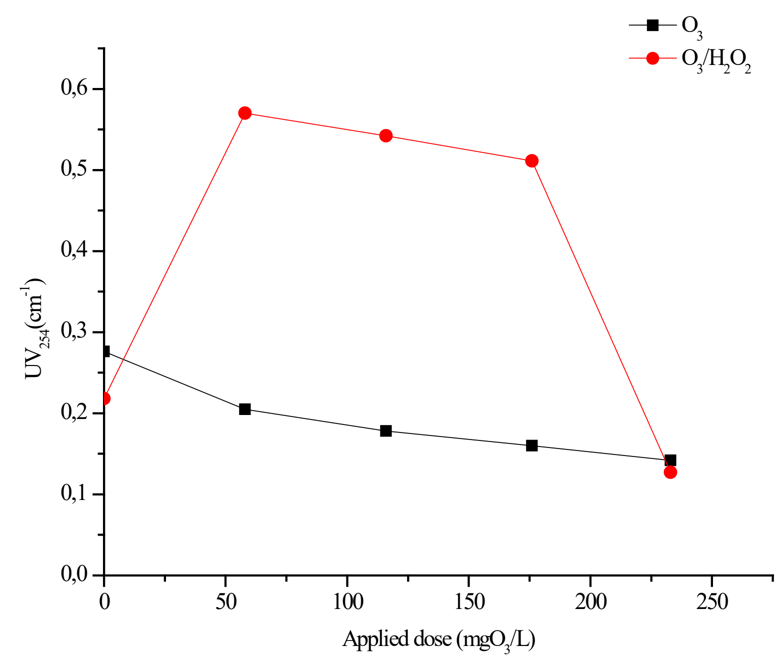

Fig. 2. Decay of absorbance at UV254 vs applied dose of ozone.
Source: Authors.

This results are similar to reports by different authors [32], who studied the influence of Ozone application in the treatment of domestic wastewater, using the analysis of Chemical Oxygen Demand (COD) and UV_{254}. These authors conclude that increasing the applied dose of O_3 decreased the absorbance values at a wavelength of 254 nm, derived from the reaction of molecular Ozone with the unsaturated and aromatic compounds present in the effluent.

The condition 2 showed an irregular behavior in 15, 30, and 45 minutes of reaction time, probably due to the intermediaries that are produced when the Ozone reacts with the hydrogen peroxide [33]. These intermediaries can absorb the light at the wavelength of 254 nm and consequently altering the measure of UV_{254} [34], observed that, in high concentrations, the H_2O_2 reacts with the intermediate oxotriperomolybdate, producing the intermediate tetraperoxomolybdate, which does not generate the O_2 and during the reaction, it acts as an inhibitor.

Finally, for an applied dose of 233 mgO_3/L and 150 mgH_2O_2/L, in a reaction time of 60 minutes, the removal of organic double bond compounds was 42% ± 15.05. Hence, it can be inferred that when the combination of O_3/H_2O_2 is applied, the intermediaries play an important role that influences the selection of the optimal time of the reaction. However, in this experiment was not possible to verify precisely what intermediaries were formed because many organic compounds were absorbed in the UV_{254}.

As can be seen in Fig. 3, the results of the two conditions studied were similar. From condition 1 at 15 minutes of the reaction was observed a decrement of the color (VIS_{436}), resulting in a removal efficiency close to 55% what correspond to an applied O_3 dose of 58 mgO_3/L.

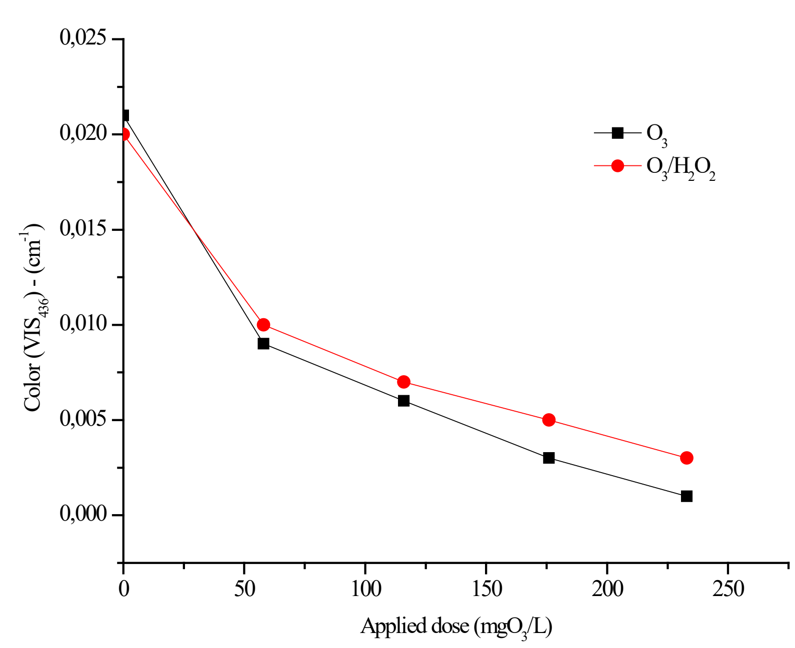

Fig. 3. Decay of Color vs applied dose of ozone.
Source: Authors.

Moreover, for this condition at minute 60 and a dose of 233 mgO_3/L, it was observed the maximum removal efficiency of ca. 95%. Similarly, the condition 2 was obtained the higher efficiency with 60 minutes of the reaction of O_3 combined with 150 mgH_2O_2/L. These results were similar to the findings of other studies [35], [36], [26], what validated the results of this study regarding to the effectiveness of the performed treatments in the discoloration of the wastewater.

The color measured as the absorbance value at wavelength 436 nm, is a clean, fast and complementary measure of the water quality monitoring [25]. The efficiency of color removal in conventional wastewater treatment is very low, therefore, it is necessary to apply treatments such as Advanced Oxidation Process, capable to break the double chain of the aromatic compounds. In particular, the AOPs are recognized to be proper for removing the precursors of the color that are generally associated with the presence of toxic and recalcitrant compounds [37].

Joint research between different countries [1] evaluate the effect of different AOPs based on Ozone, in an aqueous solution containing nine pharmaceutical compounds. The authors found that applying independently the Ozone was more efficient in the attenuation of the compounds than the application of combined $O_3/_2O_2$. The dose of the applied Ozone was 110 mg/L and H_2O_2 was 2.5 mg/L. Furthermore, was observed that the combination O_3/H_2O_2, is good but it is not economically viable, then, it is necessary to develop more studies especially evaluating the lifetime of Ozone, which disappears in the first minute of the reaction. Finally, this study also showed that the most effective biological pretreatment was the Membrane Bioreactor (MBR).

Although this study did not evaluate the effect of applying the AOP based on Ozone as a disinfectant, it's possible to state based on the cited research that hospital effluents till now are not properly disinfected and are contributing to the dissemination of antibiotic-resistant microorganisms. However, the application of oxidants as post-treatment of any technology can also contribute to the above-mentioned. In their report on the health emergency situation arising from COVID-19 [36], italian institutions indicated that the current health emergency derived from the COVID-19 revealed the urgent need to investigate the disinfection of raw or treated wastewater in health centers.

C. *Effect on aerobic biodegradability*

The values of COD are related to BOD_5 in proportions that vary according to the associated components with the organic matter. This ratio is important to determine the type of water pollution and the biodegradability of the organic matter [38].

The results showed that the Ozone application to the HAIB effluent had a positive effect on the biodegradability ratio, also, there was observed a decrease from 7.2 to 5.8 what pointed a rise of 25% in the biodegradability; this change is related to the COD by 29%. China [39] and Germany [40] found that the effect of Ozone is manifested mainly as a result of the reduction in the COD and the decay in the BOD_5 in an order between 60 and 70% respectively. Venezuela [41] studied the effect of the application of Ozone on the biodegradability of waters from the petroleum industry, thorough the measure of ratio BOD_5/COD. These authors concluded that the application of Ozone in the range of 0-100mg/L improves its biodegradability as a consequence of the decrease in COD when is close to 50%.

The O_3/H_2O_2 in our study showed a decrease of COD/BOD_5 ratio from 4.1 to 2.4, then, the biodegradability increased by 67%. This response was a consequence of an BOD_5 increment of 47% with a concomitant decrease in COD close to 12%. An explanation of the aforementioned would be that the organic matter did not fully degrade (*ie.* it does not mineralize), and just got transform into a more biodegradable state as established by other studies [42]. Therefore, the combination of these two oxidants (O_3 + H_2O_2) provided the most efficient way for treating this kind of effluent, what generates a better-quality wastewater into the receiving sources.

The present study focused on the post-treatment of the effluent from a HAIB reactor, then, for future research is important to perform a wide study that considers the associated biological process and the post-treatment with Ozone and O_3/H_2O_2. Also, it is necessary to include more parameters such as alkalinity, TOC, and heavy metals, for a better understanding of this kind of wastewater. In addition, an economic evaluation (cost/benefit) may be done to identify feasible engineering designs, considering that the cost using H_2O_2 could be high without an optimization study.

The ANOVA analysis showed that for a significance level of $p < 0.05$, the removal efficiency and the increase in biodegradability were not statistically significant between the treatments. However, it was observed that the combination of Ozone with Hydrogen Peroxide increased the biodegradability of this type of effluent in a high proportion.

IV. Conclusions

Independent Biological treatments are not sufficient to reduce the COD of anaerobically treated wastewater from the health care centers, what could limit the achievements of the Sustainable Development Goal 5 - 10 (water and sanitation). The Advanced Oxidation Processes (AOPs) based on Ozone and O_3/H_2O_2 treatments are alternatives that can reduce the toxic content of recalcitrant compounds, improving the quality of the effluent and mitigating the impact over the human health and the environment due to untreated discharges.

This study showed that the synergy produced between O_3/H_2O_2 generated an improvement on the biodegradability of 67%, better than the 42% of biodegradability reached by the independent Ozone treatment. The results of the aromatic organic content measured as the absorbance at UV_{254} was similar in the two analyzed conditions. The application of AOP based on ozone demonstrated the effectiveness in the discoloration of the hospital wastewaters. Further studies are needed which consider variations of the pH of effluent during the biological treatment, and the dose of the oxidants applied to determine the optimal conditions.

Finally, due to the nature of the hospital wastewater and the possibility that by-products (more dangerous than the originals) could be produced during the application of the oxidative processes, it is essential to include toxicity tests as a complementary tool to the traditional testing.

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References

[1] A. Husain, N. A. Khan, S. Ahmed, A. Dhingra, Ch. Pratap Singh, S. U. Khan, A. A. Mohammadi, F. Changani, M. Yousefi, S. Alam, S. Vambol, V. Vambol, A. Khursheed & I. Ali, "Application of advanced oxidation processes followed by different treatment technologies for hospital wastewater treatment," *J. Clean. Prod*, vol. 269, pp. 1–4, 2020. https://doi.org/10.1016/j.jclepro.2020.122411

[2] P. Verlicchi, "Trends, new insights and perspectives in the treatment of hospital effluents," *Curr. Opin. Environ. Sci. Heal.*, vol. 19, 2020. https://doi.org/10.1016/j.coesh.2020.10.005

[3] A. Cheudjeu, "Correlation of D-xylose with severity and morbidity-related factors of COVID-19 and possible therapeutic use of D-xylose and antibiotics for COVID-19,," *Life Sci.*, vol. 260, no. August, pp. 118335, 2020. https://doi.org/10.1016/j.lfs.2020.118335

[4] L. Heesom, L. Rehnberg, M. Nasim-Mohi, A. Jackson, M. Celinski, A. Dushianthan, P. Cook, W. Rivinberg & K. Saeed, "Procalcitonin as an antibiotic stewardship tool in COVID-19 patients in the intensive care," *J. Glob. Antimicrob. Resist.*, vol. 22, pp. 784–784, 2020. https://doi.org/10.1016/j.jgar.2020.07.017

[5] S. K. Pathak, A. A. Salunke, P. Thivari, A. Pandey, K. Nandy, H. V. K. Ratna, S. Pandey, J. Chawla, J. Mujawar, A. Dhanwate & V. Menonb, "No benefit of hydroxychloroquine in COVID-19 : Results of Systematic Review and Meta-Analysis of Randomized Controlled Trials " Diabetes & Metabolic Syndrome : Clinical Research & Reviews No bene fi t of hydroxychloroquine in COVID-19 : Results of Systema," *Diabetes Metab. Syndr. Clin. Res. Rev.*, vol. 14, no. 6, pp. 1673–1680, 2020. https://doi.org/10.1016/j.dsx.2020.08.033

[6] N. A. Khan, S. U. Khan, S. Ahmed, I. H., Farooqi, M. Yousefi, A. A. Mohammadi & F. Changanie, "Recent trends in disposal and treatment technologies of emerging-pollutants- A critical review," *TrAC - Trends Anal. Chem.*, vol. 122, pp. 115744, 2020. https://doi.org/10.1016/j.trac.2019.115744

[7] J. P. Scott and D. F. Ollis, "Integration of chemical and biological oxidation processes for water treatment: Review and recommendations," *Environ. Prog.*, vol. 14, no. 2, pp. 88–103, 1995. https://doi.org/10.1002/ep.670140212

[8] W. H. Glaze, J.-W. Kung & D. H. Chapin, "The Chemistry of Water Treatment Processes Involving Ozone, Hydrogen Peroxide and Ultraviolet Radiation," *Ozone: Sci Eng*, vol. 9, no. 4, pp. 335–352, 2008. https://doi.org/10.1080/01919518708552148

[9] R. Andreozzi, V. Caprio, A. Insola & R. Marotta, "Advanced oxidation processes (AOP) for water purification and recovery," *Catal. Today*, vol. 53, no. 1, pp. 51–59, 1999. https://doi.org/10.1016/S0920-5861(99)00102-9

[10] C. P. H. C. Dong & Z. Tang, "Advanced chemical oxidation: Its present role and potential future in hazardous waste treatment," *Waste Management*, vol. 13, no. 5-7, pp. 361–377, 1993. https://doi.org/10.1016/0956-053X(93)90070-D

[11] P. R. Gogate & A. B. Pandit, "A review of imperative technologies for wastewater treatment I: Oxidation technologies at ambient conditions," *Adv. Environ. Res.*, vol. 8, no. 3-4, pp. 501–551, 2004. https://doi.org/10.1016/S1093-0191(03)00032-7

[12] O. Legrini, E. Oliveros, & A. M. Braun, "Photochemical Processes for Water Treatment," *Chem. Rev.*, vol. 93, no. 2, pp. 671–698, 1993. https://doi.org/10.1021/cr00018a003

[13] J. Staehelin, R. E. Bühler & J. Hoigné, "Ozone decomposition in water studied by pulse radiolysis. 2. OH and HO4 as chain intermediates," *J Phys Chem*, vol. 88, no. 24, pp. 5999–6004, 1984. https://doi.org/10.1021/j150668a051

[14] J. Hoigne & H. Bader, "Ozonation of Water: Selectivity and Rate of Oxidation of Solutes," *Ozone Sci Eng*, vol. 1, pp. 73–85, 1979. https://doi.org/10.1080/01919517908550834

[15] F. J. Beltrán, J. F. García-Araya, J. Frades, P. Álvarez & O. Gimeno, "Effects of single and combined ozonation with hydrogen peroxide or UV radiation on the chemical degradation and biodegradability of debittering table olive industrial wastewaters," *Water Res*, vol. 33, no. 3, pp. 723–732, 1999. https://doi.org/10.1016/S0043-1354(98)00239-5

[16] M. Pera-Titus, V. García-Molina, M. A. Baños, J. Giménez & S. Esplugas, "Degradation of chlorophenols by means of advanced oxidation processes: A general review," *Appl Catal B Environ*, vol. 47, no. 4, pp. 219–256, 2004. https://doi.org/10.1016/j.apcatb.2003.09.010

[17] T. E. Agustina, H. M. Ang & V. K. Vareek, "A review of synergistic effect of photocatalysis and ozonation on wastewater treatment," *J Photochem. Photobiol C Photochem Rev*, vol. 6, no. 4, pp. 264–273, 2005. https://doi.org/10.1016/j.jphotochemrev.2005.12.003

[18] M. Jeworski & E. Heinzle, "Combined chemical-biological treatment of wastewater containing refractory pollutants," *Biotechnol. Annu Rev*, vol. 6, pp. 163–196, 2000. https://doi.org/10.1016/S1387-2656(00)06022-1

[19] W. Glaze, F. Beltran, T. Tuhkanen & J. W. Kang, "Chemical models of advanced oxidation proces," *Water Pollut Res J Canada*, vol. 27, no. 1, pp. 23–42, 1992. https://doi.org/10.2166/wqrj.1992.002

[20] I. L. De Mattos, K. A. Shiraishi, A. D. Braz & J. R. Fernandes, "Peróxido de hidrogênio: importância e determinação," *Quím Nova*, vol. 26, no. 3, pp. 373–380, 2003. https://doi.org/10.1590/S0100-40422003000300015

[21] J. P. Scott & D. F. Ollis, "Integration of Chemical and Biological Oxidation Processes for Water Treatment : Review and Recommendations," *Environ Prog*, vol. 14, no. 2, pp. 88–103, 1995. https://doi.org/10.1002/ep.670140212

[22] A. Ried, J. Mielcke, A. Wieland, S. Schaefer & M. Sievers, "An overview of the integration of ozone systems in biological treatment steps," *Water Sci Technol*vol. 55, no. 12, pp. 253–258, 2007. https://doi.org/10.2166/wst.2007.413

[23] L. Bijan & M. Mohseni, "Using ozone to reduce recalcitrant compounds and to enhance biodegradability of pulp and paper effluents," *Water Sci Technol*, vol. 50, no. 3, pp. 173–182, 2004. https://doi.org/10.2166/wst.2004.0190

[24] APHA, *Standard Methods for examination of water and wastewate*, WA: APHA, 2012.

[25] F. Çeçen, "Investigation of substrate degradation and nonbiodegradable portion in several pulp bleaching wastes," *Water Sci Technol*, vol. 40, no. 11–12, pp. 305–312, 1999. https://doi.org/10.1016/S0273-1223(99)00732-5

[26] T. R. Chaparro & E. C. Pires, "ost-treatment of anaerobic effluent by ozone and ozone/UV of a kraft cellulose pulp mill," *Water Sci Technol*, vol. 71, no. 3, pp. 382–9, 2015. https://doi.org/10.2166/wst.2014.527

[27] B. Roig, C. Gonzalez & O. Thomas, "Simple UV/UV-visible method for nitrogen and phosphorus measurement in wastewater," *Talanta*, vol. 50, no. 4, pp. 751–758, 1999. https://doi.org/10.1016/S0039-9140(99)00203-9

[28] D. Botelho, T. Rodríguez & E. Cleto, "Advanced oxidation process H2 O2/UV combined with anaerobic digestion to remove chlorinated organics from bleached kraft pulp mill wastewater," *Rev Fac Ing*, no. 63, 2012. Disponible en https://revistas.udea.edu.co/index.php/ingenieria/article/view/12485

[29] I. A. Alaton & S. Teksoy, "Acid dyebath effluent pretreatment using Fenton's reagent: Process optimization, reaction kinetics and effects on acute toxicity," *Dye Pigment*, vol. 73, no. 1, pp. 31–39, 2007. https://doi.org/10.1016/j.dyepig.2005.09.027

[30] J. Mousel & D. Pinnekamp, "Ozonation of nursing home wastewater pretreated in a membrane bioreactor," *Water Sci Technol*, vol. 78, no. 2, pp. 266–278, 2018. https://doi.org/10.2166/wst.2018.288

[31] M. Punzi, F. Nilsson, A. Anbalagan, B.-M. Svensson, K. Jönsson, B. Mattiasson & M. Jonstrup, "Combined anaerobic – ozonation process for treatment of textile wastewater : Removal of acute toxicity and mutagenicity," *J Hazard Mater*, vol. 292, pp. 52–60, 2015. https://doi.org/10.1016/j.jhazmat.2015.03.018

[32] E. Bataller, M. Véliz, E. Fernández, L. Hernández, C. Fernández, I. Álvarez & C. Sánchez, "Influencia de la Ozonización en el Tratamiento de un Efluente Secundario," *Rev AIDIS Ing Cienc Amb*, vol. 5, no. 2, pp. 28–36, 2005. Disponible en http://www.journals.unam.mx/index.php/aidis/issue/archive

[33] D. Paternina, E. Arias & J. Barragan, "Estudio cinético de la descomposición catalizada de peróxido de hidrógeno sobre carbón activado,"*Quim. Nova*, vol. 32, no. 4, pp. 934–938, 2009. https://doi.org/10.1590/S0100-40422009000400020

[34] C. E. Diaz, F. León, F. Martínez & M. Daza, “Oxidacion de antraceno con oxigeno singulete generado quimicamente por el sistema molibdato de sodio/peroxido de hidrogeno,” *Rev Col Quim*, vol. 37, no. 1, pp. 45–53, 2008. http://dx.doi.org/10.15446/rev.colomb.quim

[35] D. Grisales, J. Ortega & T. Rodríguez, “Remocion de la materia organica y toxicidad en aguas residuales hospitalarias aplicando ozono ,” *DYNA*, vol. 79, no. 173 PART I, pp. 109–115, 2012. Disponible en https://revistas.unal.edu.co/index.php/dyna/article/view/30753

[36] P. Foladori, F. Cutrupi, N. Segata, S. Manara, F. Pinto, F. Malpei, L. Bruni & G. La Rosa, “SARS-CoV-2 from faeces to wastewater treatment: What do we know? A review ,” *Sci. Total Environ.*, vol. 743, pp. 1–12, 2020. https://doi.org/10.1016/j.scitotenv.2020.140444

[37] S. Rodríguez, R. Bermúdez, M. Serrat & A. Kouroma, “Selección de cepas de Pleurotus ostreatus para la decoloración de efluentes industriales,” *Rev Mex Micol*, vol. 23, pp.9–15, 2006. Disponible en https://www.scientiafungorum.org.mx/index.php/micologia/article/view/973

[38] C. Chernicharo, “,” *Anaerobic Reactor*, 1st ed. LDN, UK: IWA, 2007.

[39] Z. Qiu, J. Sun, D. Han, F. Wei, Q. Mei, B. Wei, X. Wang, Z. An, X. Bo, M. Li, J. Xie & M. He, “Ozonation of diclofenac in the aqueous solution: Mechanism, kinetics and ecotoxicity assessment,” *Environ Res*, vol. 188, no. February, pp.109713, 2020. https://doi.org/10.1016/j.envres.2020.109713

[40] E. Gilbert, “Biodegradability of ozonation product as a function of COD and DOC elimination by examples of substitude aromatic substances,” *Water Res*, vol. 21, no. 10, pp. 1273–1278, 1987. https://doi.org/10.1016/0043-1354(87)90180-1

[41] Z. Gutiérrez, E. Fernández, N. Herrera, L. Sepúlveda & J. Mármol, “Efecto de la aplicación de ozono sobre la biodegradabilidad de aguas de formación,” *Multiciencias*, vol. 2, no. 1, pp. 50–54, 2002. Disponible en https://produccioncientificaluz.org/index.php/multiciencias/article/view/16564

[42] A. H. Mounteer, R.O. Pereira, A.A. Morais, D.B. Ruas, D.S.A. Silveira, D.B. Viana & R.C. Medeiros, “Advanced oxidation of bleached eucalypt kraft pulp mill effluent,,” *Water Sci Technol*, vol. 55, no. 6, pp. 109–116, 2007. https://doi.org/10.2166/wst.2007.218

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