Revista Facultad de Ingeniería

UNIVERSIDAD DE ANTIOQUIA
1 8 0 3

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DOI: **10.17533/udea.redin.20250365**

To appear in: *Revista Facultad de Ingeniería Universidad de Antioquia*

Received: April 11, 2024
Accepted: March 14, 2025
Available Online: March 14, 2025

Please cite this article as: (Inciales de nombres y apelidos). Título del artículo, *Revista Facultad de Ingeniería Universidad de Antioquia*. [Online]. Available: https://www.doi.org/10.17533/udea.redin.20250365

Effectivity of UV-VIS/H_2O_2/TiO_2 and biological treatments for recovering effluents from an industrial estate

Eficacia de Tratamientos UV-VIS/H_2O_2/TiO_2 y biológicos para la valorización de efluentes de un polígono industrial

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ABSTRACT

In the present study were evaluated a biological treatment and several Advanced Oxidation Technologies (AOTs), including TiO_2/UV-VIS, H_2O_2-UV-VIS and TiO_2/H_2O_2/UV-VIS for industrial wastewater treatment. The experiments were carried out both in a laboratory reactor and in a 120 L/s pilot plant with autonomous operation under solar energy. The individual application of the biological treatment using a commercial bacteria strain led to a significant decrease in total hydrocarbons, sulfates, total organic carbon (TOC), hardness, alkalinity, biochemical oxygen demand (BOD_5), and chemical oxygen demand (COD), in the starting industrial wastewater sample. It was also observed that the application of UV-VIS/H_2O_2/TiO_2 as combined treatments, is more effective than biological treatment and individual AOTs reducing certain quality parameters, such as conductivity, chlorides, nitrates, turbidity, fats and oils, total suspended solids, settleable solids, acidity, TOC, total coliform bacteria and in the removal of heavy metals (Zn, Cu, Cr, Ni, Fe, Pb). In addition, the use of a sequential treatment, initially applying a AOTs and subsequently a biological treatment, resulted in an improvement in the removal of contaminants such as chlorides, heavy metals (Fe, Pb), nitrates and hardness. Thus, the results suggest that the sequential combination of AOTs and biological treatment is an effective strategy for the recovery of industrial wastewater, achieving a greater reduction of contaminants compared to the application of each treatment separately, thus improving the final quality of the treated water.

Keywords: AOTs, photochemistry; biological treatment; wastewater treatment; UV-VIS/H_2O_2/TiO_2.

RESUMEN

En este estudio se evaluó un tratamiento biológico y algunas Tecnologías Avanzadas de Oxidación (TAOs) como TiO_2/UV-VIS, H_2O_2-UV-VIS and TiO_2/H_2O_2/UV-VIS en el tratamiento de aguas residuales industriales. Los experimentos se llevaron a cabo en reactor a escala de laboratorio y en una planta piloto con capacidad de 120 L/s con autonomía de operación bajo luz solar. La aplicación individual del tratamiento biológico usando un cultivo bacteriano comercial permitió obtener una disminución significativa en los hidrocarburos totales, sulfatos, TOC, dureza, alcalinidad, DBO_5, DQO en la muestra de agua residual inicial. Se observó también que la aplicación de los tratamientos combinados UV-VIS/H_2O_2/TiO_2, resultó más efectiva que el tratamiento biológico o las TAOs individuales, llevando a disminuir parámetros como conductividad, cloruros, nitratos, turbidez, grasas y aceites, sólidos suspendidos totales, sólidos sedimentables, acidez, TOC, bacterias coliformes totales y a la remoción de metales pesados (Zn, Cu, Cr, Ni, Fe y Pb). Adicionalmente, el uso del tratamiento secuencial, aplicando inicialmente TAOs y a continuación el tratamiento biológico, llevó a mejorar la remoción de contaminantes como cloruros, metales pesados (Fe y Pb), nitratos y dureza. En general, los resultados sugieren que la combinación secuencial de TAOs y el tratamiento biológico es una estrategia efectiva para la recuperación de aguas residuales industriales, logrando una alta reducción de los contaminantes, comparada con la aplicación de cada tratamiento separado, mejorando así la calidad final del agua tratada.

Palabras clave: TAOs; fotoquímica; tratamiento biológico; tratamiento de aguas residuales; UV-VIS/H_2O_2/TiO_2.

1. Introduction

The rise in industrial effluents globally has had a significant impact, as they are often discharged untreated into natural water bodies [1,2]. This has led to an urgent need for new treatment methods, along with the recovery and recycling of wastewater, and the study of pollutant degradation [3-7], which are pressing issues for both the scientific and governmental sectors.

Biological treatment offers an eco-friendly approach to reducing industrial pollution through bacterial metabolism [8-17]. Bacteria are particularly effective at degrading a wide range of organic pollutants, including chlorinated aromatic compounds, sulfur-based dyes, and many others [18]. Moreover, recent studies have shown that using mixed cultures or microbial consortia enhances the efficiency of pollutant degradation in real environmental contexts [19].

However, the efficiency of contaminant biodegradation can be affected by factors such as salinity, temperature, pH, nitrogen and carbon sources, inoculum concentration, water hardness, chloride concentration, and the presence of metals [20]. These factors are more difficult to control in industrial effluents, which often contain a variety of pollutants. In this study, the effluents analyzed primarily originated from dairy production, food processing, restaurants, car repair shops, and poultry production. In contrast, domestic wastewater, which is also part of the effluents studied, mainly consists of organic carbon, either dissolved or as particulate matter [21]. This mixture of industrial and domestic wastewater creates a complex environment well-suited for biological treatment. Microorganisms degrade complex contaminants, using them as nutrients and converting them into simpler, harmless end products such as CO_2 and H_2O [9]. However, despite biological treatment's effectiveness in breaking down complex toxic substances, it has limitations, including the time required, the need for large facilities, and the potential persistence of heavy metals and certain organic pollutants (such as pharmaceuticals).

To address these limitations, Advanced Oxidation Technologies (AOTs), such as UV-VIS, UV-VIS/H_2O_2, and others, have been recognized as effective tertiary treatment methods for wastewater, particularly in degrading recalcitrant organic compounds [3-5,22,23]. These processes generate reactive oxygen species (ROS) like $^{\bullet}OH$, H_2O_2, and $O_2^{-\bullet}$, which can break down pollutants into CO_2 and water through mineralization [24,25]. Additionally, ROS can deactivate microorganisms by damaging their cell walls, leading to their elimination [26-31]. AOTs offer several advantages over biological treatments, including shorter treatment times and the ability to efficiently remove heavy metals through heterogeneous photocatalysis, where metals are chemically reduced on the surface of semiconductors [27,32-36].

The combination of AOTs with biological treatments offers a promising synergistic approach. Biological processes are highly effective at removing biodegradable organic matter [37], while AOTs are remarkably efficient at mineralizing recalcitrant compounds and breaking down pollutants that persist after biological treatment, including heavy metals and pharmaceutical residues [38,39]. This combined approach enhances pollutant removal efficiency, resulting in cleaner effluents suitable for discharge or reuse.

For instance, previous reports demonstrated the potential of this approach in treating landfill leachates by coupling solar TiO_2-UV photocatalysis with an anaerobic biological process (SMA), achieving a 57% mineralization of COD through photocatalysis and a total of 78% mineralization with the combined process [40]. In a similar study, a UV/H_2O_2 system integrated with a biological process for treating industrial wastewater was evaluated, achieving a 49.4% removal in COD and an 85% elimination of TOC after 60 minutes of irradiation [41]. The partially treated wastewater was then mixed with municipal wastewater and further treated biologically, resulting in efficient total nitrogen removal (85%) and significant organic carbon reduction (41.8%), indicating successful denitrification and a final pH suitable for conventional water treatments. These studies demonstrate that the combination of biological treatment and advanced oxidation technologies (AOTs) represents a promising alternative for wastewater recovery.

Besides, over the past decade, various reactor configurations have been employed for AOTs in wastewater treatment. Currently, the development of innovative photocatalytic materials is as relevant as the design and modeling of these reactors [26,42].

In this context, the primary objective of this research was to evaluate the effectiveness of different AOTs at both laboratory and pilot plant levels, and to combine the most effective treatment with a microbiological approach using facultative microorganisms capable of operating under both aerobic and anaerobic conditions. Several studies worldwide have reported the successful removal of contaminants and bacteria from wastewater under laboratory conditions [3-5]. However, under realistic conditions, it is crucial to analyze multiple parameters of water quality control, and the results obtained must be compared with the relevant governmental regulations [43].

In order to make a significant contribution to regional or global communities, this work assessed the effectiveness of the best AOTs in a batch reactor and a patented device. Additionally, two different governmental regulations were considered as quality references: one for the discharge of industrial effluents and another for the recycling of treated wastewater. In line with the objective of this research, the main question this study seeks to answer is: ¿how effective can the combination of UV-VIS/H_2O_2/TiO_2 and biological treatments be for recovering effluents originating from an industrial area?

2. Material and methods

2.1 Industrial wastewater sampling

The wastewater used in this study consisted of a mixture of domestic water and industrial effluents from dairy production, food processing, restaurants, car repair shops, and poultry production. These samples were collected at the sewer outlet box located in an industrial estate (coordinates: 5°47'34"N 73°3'50"W). The Standard Methods for the Examination of Water and Wastewater (SMEWW) [44] was used as the guideline for this procedure. After sampling, the effluents were analyzed according to the methods described below.

2.2 Industrial wastewater characterization

The effluents were analyzed taking into account as main quality parameters, those included in Colombian regulations for industrial discharges (Regulatory Resolution 631-2015) and for crop irrigation water (Regulatory Resolution 1207-2014). The wastewater sampling and other analyses were also performed by the SMEWW [44-45] (Table 1).

Table 1. Methods employed for the characterization of the industrial effluents

Regulatory resolution 1207-2014		
Quality parameter	**Unit**	**Method**
pH	Units of pH	Electrometric method SM 4500-H^+-B
Conductivity	µS/cm	Potentiometric method SM 2510-B

Total phenols	mg/L	UV-VIS Spectrophotometry
Total hydrocarbons		Gravimetric method SM 5520-F
Free cyanide		Titrimetric method SM 4500 CN- B, C, E, I
Chlorides		Argentometric method SM 4500-Cl^--B
Fluorides		Selective ion method SM 4500-F
Sulfates		Turbidimetric method SM 4500-SO_4^{2-}
Aluminum		Aluminum method 8012 HACH
Beryllium		Atomic absorption spectrophotometry (nitrous oxide-acetylene flame) SM 3030F; SM 3111 D
Molybdenum		
Cobalt		Atomic absorption spectrophotometry (nitrous oxide-acetylene flame) SM 3111 B
Manganese		
Sodium		Atomic absorption spectrophotometry (nitrous oxide-acetylene flame) SM 3030F; SM 3111 B
Lithium		
Cadmium		Preliminary treatment by acid digestion nitric acid – sulfuric acid SM 3030-G; Atomic absorption spectrophotometry (nitrous oxide-acetylene flame) 3111-B
Zinc		
Cooper		
Chromium		
Iron		
Nickel		
Lead		
Mercury		
Arsenic		Atomic absorption electrothermal spectrophotometry SM 3030 F, SM 3113 B
Selenium		
Total residual chlorine		Amperometric valoration 4500-Cl D [40].
Boron		UV-VIS spectrophotometry
Vanadium		
Nitrates		Spectrophotometric method SM 4500-NO_3^--B

Regulatory Resolution 631-2015

Tristimulus color (436 nm, 525 nm, and 620 nm)	m^{-1}	Spectrophotometric method SM. 2120-C
Fats and oils	mg/L	Liquid-liquid method, partition-gravimetric SM 5520-B
Chemical oxygen demand (COD)	mg/L O_2	Closed reflux method, colorimetric method SM 5220-D
Biochemical oxygen demand (BOD_5)	mg/L O_2	5 days incubation method and electrometric measurement SM 5210-B
Total alkalinity	mg/L $CaCO_3$	Titrimetric method SM 2320-B
Total suspended solids	mg/L	Gravimetric method SM 2540-B
Sedimentable solids	mL/L	Method SM 2540-F
Total acidity	mg/L $CaCO_3$	Titrimetric method SM 2310-B
Total hardness	mg/L $CaCO_3$	The titrimetric method with EDTA SM 2340- C
Calcic hardness	mg/L $CaCO_3$	The titrimetric method with EDTA SM 3500 Ca-B
Phosphates	mg/L	Ascorbic acid method SM 4500-P-B
Complementary analyzes		
Total Organic Carbon (TOC)	mg/L	High-temperature combustion method SM 5310-B
Total coliforms	CFU/100 mL	Membrane filtration method SM 9222-B

2.3 Biological depuration

The biological treatment was carried out by using commercial facultative microorganisms (BIOMERK®HC). Thus, 5.00 g ($2x10^9$ Colony Forming Units/g) were added to 10 L of effluent sample; then, this suspension was kept under aerobic conditions for 3 months.

2.4 AOTs at lab scale

In a batch reactor containing 250 mL of wastewater was added 1 g/L of TiO_2 (Sigma Aldrich) as a photocatalyst and/or 0.07 M of hydrogen peroxide (Perhydrol™ for analysis EMSURE ISO). These conditions were selected considering previous studies [46,47]. An Osram Ultravitalux lamp was employed as a light source (30 W/m^2). The total reaction time was 4 hours under stirring and oxygen flux. A blank reaction (photolysis) without TiO_2 or hydrogen peroxide was previously performed. It should be noted that all tests were performed twice.

2.5 AOTs at the pilot plant

The pilot plant assays were carried out in a sunlight reactor using a patented design with 120 L of capacity operating with continuous flow (Figure 1) [48]. The main operation parameters were a volumetric flow rate of 0.50 L/s, length of 22.5 m, total residence time of 36 s (recirculation cycle), and 7 h of reaction. The pilot plant features a main storage tank where the wastewater is treated and the necessary chemical products are added. For these tests, the AOTs that showed the best performance in wastewater recovery at the lab scale were selected.

Figure 1. Pilot plant for wastewater treatment [48].

Finally, a comparison by simultaneous application of the best AOTs and biological depuration was also attempted. For this stage, to remove the TiO_2 after treatment at the pilot plant level the treated water sample was previously filtered (Whatman® quantitative filter paper, ashless, Grade 40), and then, this sample was submitted to biological depuration as described in section 3.3. The effectiveness of the treatments applied was evaluated by the parameters included in Table 1 and by duplicate.

3. Results and discussion

3.1 Starting industrial effluent characterization

The main results obtained in the starting characterization for the effluents under study are summarized in Table 2. As can be seen in this table, the effluents present values that are not compliant with the Colombian regulations for crop irrigation water, as indicated in the regulatory resolution number 1207 of 2014, for treated wastewater recycling in crop irrigation [49]. In the present research is very important to consider this norm, mainly because the effluents in the study, are discharged directly into a river, and then the water of this affluent is conventionally used for agricultural activities. Likewise, one of the objectives of the present study was to analyze the recycling potential of the wastewater after treatment and recovery in agreement with government regulations.

To analyze the effectiveness of the treatments applied and to achieve a better quality of the wastewater before it is discharged into the drain, the regulatory resolution for industrial discharges [49] and other parameters were also considered.

3.2 Biological purification of industrial wastewater

The results obtained from the biological treatment of the effluents over three months are summarized in Table 2.

Table 2. Results obtained in the starting industrial effluents characterization and after treatments, comparison with Colombian regulations.

Water Quality Control Parameters	**Units**	**Maximum permissible limit in regulatory resolution 1207-2014** [39]	**Starting Industrial effluent**	**Biological depuration**	**AOTs at the lab scale**				**Pilot plant**	**UV-VIS/ H_2O_2/ TiO_2 and Biological depuration**
					UV-VIS Photolysis	**UV-VIS/ TiO_2**	**UV-VIS/ H_2O_2**	**UV-VIS/ H_2O_2/ TiO_2**	**UV-VIS/ H_2O_2/ TiO_2**	
pH	pH scale	6.00-9.00	7,40 ± 0,141	8.33 ± 0.125	8.65 ± 0,102	8.45 ± 0.090	8.85 ± 0.062	8.90 ± 0.035	8.52 ± 0,110	8.14 ± 0
Conductivity	μS/cm	1500	1940 ± 0,102	2660 ± 42.4	N.D	N.D	N.D	1070 ± 21.2	750 ± 31.8	1164.5 ± 24.7
Total Hydrocarbons	mg/L	1.00	13.30	<2.00	N.D	N.D	N.D	N.D	<2.00	N.D
Free cyanide	mg/L	0.20	<0.024	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Chlorides	mg/L	300	212.4 ± 0.707	225 ± 7.07	N.D	N.D	N.D	148 ± 0.500	99 ± 0.710	33.5 ± 0.707
Fluorides	mg/L	1.00	0.22 ± 0.009	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Sulfates	mg/L	500	152	12.20	N.D	N.D	N.D	41	35	N.D
Aluminum	mg/L	5.00	0.16	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Beryllium	mg/L	0.10	<0.08	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Molybdenum	mg/L	0.07	<0.05	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Cobalt	mg/L	0.05	<0.043	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Manganese	mg/L	0.20	0.18 ± 0.011	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Sodium	mg/L	200	125 ± 5.65	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Lithium	mg/L	2.50	<0.100	N.D	N.D	N.D	N.D	N.D	N.D	N.D

Cadmium	mg/L	0.01	5.90 x 10^{-3} ± $8.00\text{x}10^{-4}$	<3.00 x10^{-3} ± $1.00\text{x}10^{-4}$	<3.00 x10^{-3} ± $1.00\text{x}10^{-4}$	<3.00 x10^{-3} ± $1.00\text{x}10^{-4}$	<3.00 x10^{-3} ± $1.00\text{x}10^{-4}$	<3.00 x10^{-3} ± $1.00\text{x}10^{-4}$	<3.00 x10^{-3} ± $1.00\text{x}10^{-4}$	N.D
Zinc	mg/L	3.00	12.2 ± 0.045	5.83 ± 0.150	8.50 ± 0.280	5.40 ± 0.270	6.51 ± 0.088	0.33 ± 0.078	0.80 ± 0.164	1.02 ± 0.164
Cooper	mg/L	1.00	0.15 ± 0.020	0.14 ± 0	0.14 ± 0.020	0.10 ± 0.006	0.14 ± 0.002	0.11 ± 0.033	0.15 ± 0.015	0.210 ± 0.093
Chromium	mg/L	0.10	0.58 ± 0.050	0.520 ± 0.062	0.62 ± 0.022	0.23 ± 0.030	0.56 ± 0.050	0.39 ± 0.025	0.33 ± 0.161	0.350 ± 0.093
Iron	mg/L	5.00	4.74 ± 0.350	5.50 ± 0,170	4.08 ± 0.210	1.23 ± 0.056	2.74 ± 0.270	0.028 ± 0	1.55 ± 0.630	1.30 ± 0.046
Nickel	mg/L	0.20	1.52 ± 0.273	1.70 ± 0,210	1.26 ± 0.100	1.16 ± 0.030	1.25 ± 0.015	0.026 ± 0.012	0.55 ± 0.092	0.800 ± 0.110
Lead	mg/L	5.00	5.84 ± 0.172	6.43 ± 0.051	2.90 ± 0.017	0.67 ± 0.120	1.01 ± 0.085	0.27 ± 0	0.67 ± 0.232	0.410 ± 0.091
Mercury	mg/L	0.002	<1.00 x10^{-5} ± $2.00\text{x}10^{-6}$	<$1.00\text{x}10^{-5}$ ± $1.00\text{x}10^{-6}$	<$1.00\text{x}10^{-5}$ ± $1.00\text{x}10^{-6}$	<$1.00\text{x}10^{-5}$ ± $1.00\text{x}10^{-6}$	<$1.00\text{x}10^{-5}$ ± $1.00\text{x}10^{-6}$	<$1.00\text{x}10^{-5}$ ± $1.00\text{x}10^{-6}$	<$1.00\text{x}10^{-5}$ ± $1.00\text{x}10^{-6}$	N.D
Arsenic	mg/L	0.10	<7.37 x 10^{-3}	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Selenium	mg/L	0.02	<0.010	N.D	N.D	N.D	N.D	N.D	N.D	N.D
Total residual chlorine	mg/L	<1.00	>3.00	>3.00	N.D	N.D	N.D	>3.00	>3.00	>3.0
Nitrates	mg/L	5.00	13.20 ± 0.780	10.3 ± 0.640	N.D	N.D	N.D	5.30 ± 0.092	9.15 ± 0.057	0.900 ± 0.071
Regulatory Resolution 631 of 2015 [50]										
Tristimular color (436 nm)	m^{-1}	N.R	14.60	3.86	N.D	N.D	N.D	N.D	0.052	N.D
Tristimular color (525 nm)		N.R	11.50	3.20	N.D	N.D	N.D	N.D	0.047	N.D

Tristimular color (620 nm)		N.R	10.00	2.46	N.D	N.D	N.D	N.D	0.050	N.D
Fats and oils		N.R	30.00	4.28	N.D	N.D	N.D	<4.00	<4.00	N.D
COD	mg/L	N.R	400	158.90	N.D	N.D	N.D	359	266.05	N.D
BOD_5		N.R	277.80	90.70	N.D	N.D	N.D	230.20	155.40	N.D
Total alkalinity	mg/L $CaCO_3$	N.R	480	220	N.D	N.D	N.D	416	373	N.D
Total suspended solids	mg/L	N.R	37.50	171	N.D	N.D	N.D	2.00	1.50	N.D
Sedimentable Solids	mL/L	N.R	1.00	4.00	N.D	N.D	N.D	0.10	0.10	N.D
Total Acidity	mg/L $CaCO_3$	N.R	120	226	N.D	N.D	N.D	20	11	N.D
Total hardness	mg/L	N.R	192	120	N.D	N.D	N.D	184	128	59.0
Calcic hardness	mg/L	N.R	126	84	N.D	N.D	N.D	158	90	N.D
Phosphates	mg/L	N.R	8.72	4.00	N.D	N.D	N.D	6.16	6.87	N.D
** TOC	mg/L	N.R	81.5 ± 2.40	46.90 ± 1.60	72.98 ± 2.32	51.47 ± 7.01	58.97 ± 5.87	38.2 ± 4.41	20.3 ± 0.742	44.1 ± 4.94
**Total coliforms	CFU/100 mL	N.R	43304	N.D	N.D	N.D	N.D	200	100	100

*N.R: Not applicable

*N.D: Not determined

** Complementary analysis

Considering the high number of required physicochemical analyses, this study focused solely on those that are essential for the recycling of treated water. The results are described, explained, and discussed carefully below.

- First, by comparing the results obtained after biological treatment with the maximum permissible limits for water used for crop irrigation and other quality parameters (experimental section), it was found that the tristimulus color of the effluent samples measured at 436, 525 y 625 nm decreased until 73.6, 72.2 and 75.4%, respectively; as it was reported by different specialized authors [51-52], this behavior indicates that the vegetable extracts and the organic and inorganic compounds have been effectively employed for the microorganisms metabolism.
- The pH value slightly increases after treatment, because of the transformation of organic compounds into water and CO_2 [53].
- Parameters such as BOD_5, COD, and TOC significantly decrease at 67.35, 60.28 and 42.45%, respectively. To understand these results, is important to indicate that the COD corresponds to the oxygen content requested for organic matter degradation by chemical routes [54]; in contrast, the BOD is the oxygen content necessary for organic matter degradation by biological mechanisms (i.e. microorganisms such as bacteria, fungi, and/or plankton) [55]. Thus, the results obtained indicate that microorganisms have used dissolved oxygen as a source of organic matter degradation [54-56]. It is also important to observe that the values obtained for COD were higher than those observed for BOD, it is mainly due to the oxidation of non-biodegradable compounds [57]. Besides, is relevant to consider that the COD/BOD ratio is also a water quality control parameter; in this work the value of the ratio was 1.44, indicating a high fraction of biodegradable material available for biological treatment [58].
- On the other hand, as expected, other parameters such as total hydrocarbons, fats, and oils, were decreased by 84%. This result is mainly due to the action of the microorganisms provided by BIOMERK®HC. Thus, as this commercial trademark indicates [59], the microorganisms create their bio-surfactants for the emulsion of fat and oils. Simultaneously, the fraction of remaining organic compounds is consumed by the microorganisms, thus obtaining CO_2 and water from the biological metabolism as the final products.
- Besides organic matter, microorganisms also need some macronutrients such as phosphorous and nitrogen [60]. Firstly, phosphorous is assimilated as phosphates; then, nitrogen can be processed as ammonium or nitrate [60]. In general, in the present study, the nitrates were eliminated at 21.97%, indicating that it is necessary to apply a complementary treatment to obtain a better remotion of this pollutant. The facultative organisms are responsible for denitrification, in this mechanism, nitrites act as electron acceptors and the carbon present in organic matter acts as a substrate, this process is described in Equation 1 [61].

$$C_6H_{12}O_6 + O_2 + HNO_3 + NH_3 + other\ nutrients \rightarrow C_5H_7\,O_2N + CO_2 + H_2O + N_2$$
Equation 1

- On the other hand, the removal of phosphate was 54.13%, thus showing a high consumption of this nutrient by microorganisms. In the case of sulfates, it was achieved at 91.97% of removal, this behavior can be explained by the presence of sulfate-reducing bacteria in the biological inoculant; this kind of bacteria can chemically reduce the sulfates to sulfides and H_2S [62].

- Total suspended solids and sedimentable solids significantly increased in the wastewater after biological treatment. This is mainly due to the sedimentation of non-biodegradable material, because of microorganism metabolism [63].

- The increase observed in the acidity value after treatment, was due to the production of H_2CO_3 by the CO_2 coming from the organic matter degradation [64] (Equation 2).

$$CO_{2(g)} + H_2O_{(l)} \rightarrow\ H_2CO_3$$ Equation 2

After the formation of H_2CO_3, it can be partially dissociated as bicarbonate and protons (Equation 3). The content of bicarbonate species, carbonates, and hydroxyls is responsible for the observed decrease in the alkalinity value (by displacing the mechanism to the left in Equation 3) [64] and a slight increase in the pH value, as it was reported in Table 2.

$$H_2CO_3 \leftrightarrows HCO_3^- + H^+$$ Equation 3

After treatment, a decrease in total and calcic hardness values was observed, mainly due to the consumption of Ca^{2+} and Mg^{2+} ions as micronutrients of the microorganisms, which act as enzymatic co-factors [65]. The content of chromium and copper slightly decreased at <10% and Zn removal was close to 52.14%. It has been reported that this behavior may be due to the intra or extracellular chelating properties in the bacteria [66]. The loading of other metals such as iron, nickel, and lead, and anions such as chlorides slightly increases after treatment, it can be due to a possible concentration of these metals in the wastewater as an effect of the evaporation during the aerobic treatment. This increase in the loading of electrically charged species is responsible for the conductivity value increasing.

In general, it was observed that biological treatment is effective for wastewater recovery. However, some pollutants that remained after treatment were still detected with high values, this is a limiting factor for wastewater recycling. In the next section, the application of AOTs is presented as a potential complementary treatment for the effluents under study.

3.3 AOTs for wastewater treatment at batch reactor lab scale

Table 2 summarizes the results obtained in the wastewater treatment by using different AOTs such as UV-VIS (photolysis), UV-VIS/TiO_2, and UV-VIS/H_2O_2. The selection of the best treatment in this step was based on the pH value, TOC, and heavy metal contents; then, the treatment that showed the highest effectiveness was evaluated by following all the parameters included in the experimental section.

The TOC content reduction after treatments reported in Table 2, evidences the mineralization of organic compounds by AOTs [67]. First, UV-VIS light can induce chemical and structural changes in the organic pollutants; however, this treatment had low effectiveness in TOC removal, which was close to 10.41%.

The global tendency of TOC removal by the different AOTs applied was UV-VIS< UV-VIS/TiO_2< UV-VIS/H_2O_2< UV-VIS/H_2O_2/TiO_2. As can be observed, the effectiveness of the AOTs in the TOC removal increased by a combination of two or more treatments. Thus, the highest TOC removal was achieved by combining the AOTs labeled as UV-VIS/H_2O_2/TiO_2. This effectiveness is mainly due to: (i) the presence of UV-VIS light available for photochemical processes [68,69]; (ii) the generation of ROS, which is responsible for the degradation of organic compounds [26, 70-72]; (iii) the highest ROS generation, which is more favored by combining the presence of hydrogen peroxide and TiO_2 as a source of these species [5,29,30,73,74].

Figure 2 shows the evolution of the concentration of heavy metals after different AOTs. As can be seen in this figure, after photolysis and/or H_2O_2/UV-VIS treatments, a slight decrease in the metal contents was obtained; this is probably due to the chemical reduction of these metals in the glass reactor walls [75], which was evidenced by the changes of color observed in the reactor after the treatments applied.

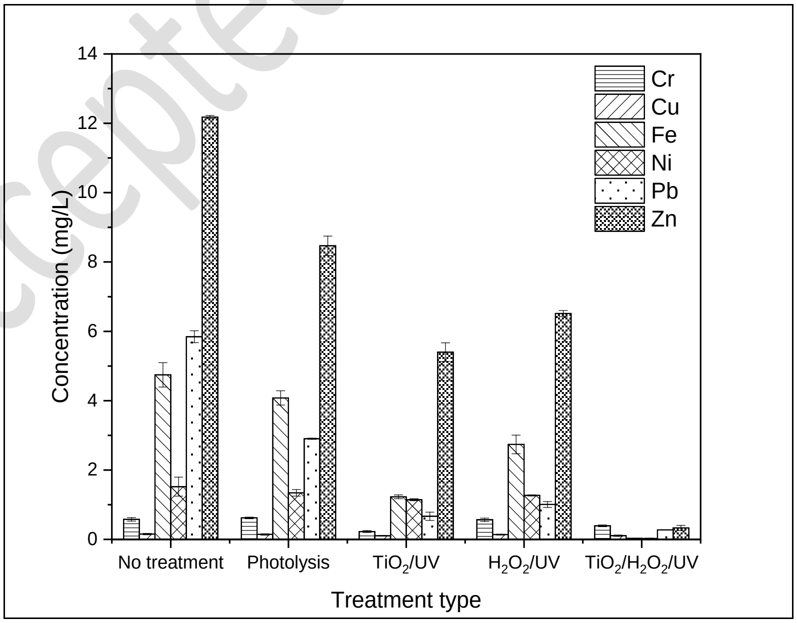

Figure 2. Heavy metals content before and after industrial wastewater treatment

As expected, the presence of TiO_2 in the reaction system significantly contributes to the metal content decreasing. It is a direct consequence of the photochemical reduction of the metals on the titania surface, thus leading to the removal of the metals from the fluid phase [76]. In addition, it was found that by using the combining treatments UV-VIS/H_2O_2/TiO_2, the Fe, Ni, Pb, and Zn removal was above 95%. This behavior can be explained, taking into account that these metals can be present in the wastewater as positive species. Under the reaction conditions of the present study, a slightly basic pH was measured, so, in this case, the TiO_2 surface can be negatively charged, thus favoring the adsorption and reduction of the positive metallic species on the semiconductor surface [77]. However, the pH of the starting wastewater sample is close to neutrality, so, the effectiveness of the treatment by AOTs does not depend directly on the pH value.

The pH value is one of the main factors affecting both, the formation of hydroxyl radicals and the surface charge properties on TiO_2 [78-79]. Due to the amphoteric character of TiO_2, under acidic or basic conditions, this semiconductor can be protonated or deprotonated, as indicated in Equations 4 and 5 [80].

$$TiOH + H^{+} \rightarrow TiOH^{2+} \qquad \text{Equation 4}$$

$$TiOH + OH^{-} \rightarrow TiO^{-} + H_2O \qquad \text{Equation 5}$$

As can be seen in Figure 2, the combination of the AOTs evaluated is a good alternative in the removal of organic pollutants and heavy metals such as Zn, Cu, Fe, Ni, Pb, and Hg from industrial wastewater, which led to achieving the maximum permissible limits for crop irrigation water.

It is also important to observe that the total coliforms bacteria content significantly decreases in the industrial effluent after UV-VIS/H_2O_2/TiO_2 treatment, thus leading to achieving 99.5% of coliforms bacteria elimination at the natural pH of the starting effluent (i.e 7.40). It can be explained by oxidative stress induced by both H_2O_2 and AOTs, thus leading to coliform inactivation [29-81]. It has been reported that in some cases the combination of UV light and H_2O_2 is more effective for bacteria inactivation than the individual UV or peroxide application [3]. Thus, for example, the efficiency of AOTs using the combination of UV and H_2O_2 in the fecal coliforms inactivation from industrial effluent was studied [3]; leading to determine that pH and H_2O_2 concentration are important factors affecting the global effectiveness of the antibacterial effect of these treatments, thus, under a pH value of 3.0 was achieved the increase of bacteria inactivation in 40 s of contact with 35 mg/L of peroxide. This is a valuable result, however, that authors modified the pH for the different assays; in the case of our work, the pH was not modified after or during the treatments applied, it is because, under real applications, the addition of external compounds for pH modification could lead to include a new pollutant in the treated effluent, which also increase the treatment stages.

Different reactor configurations have been employed for AOTs worldwide [37,82-86]. Currently, focused on the further industrial application of AOTs it is very important to compare the performance of these technologies not only at lab scale, but also to abroad research by using pilot plant devices. To follow this tendency in the present work, both lab and pilot plant reactors were evaluated and the results obtained are presented below.

3.4 UV-VIS/H_2O_2/TiO_2 treatment at solar reactor pilot plant

It is important to take into account that the configuration of the reactors employed in this work at the lab or pilot plant level is different, so, a fit comparison is not possible, however; it is interesting to analyze the behavior of the UV-VIS/H_2O_2/TiO_2 system by using different reaction volumes and room or environmental conditions. The results obtained in these assays are presented in Table 2.

As was observed in section 3.3, the treatment system composed by the presence of UV-VIS light, TiO_2, and H_2O_2, led to obtaining the highest effectiveness in the recovery of industrial effluents at the lab scale. This behavior is directly related to the increase of hydroxyl radicals rate generation, which is more favored in the simultaneous presence of peroxide and titania in the reaction medium. These mechanisms for the formation of ROS are described in equations 6, 7, and 8 [87,88].

$$TiO_2 + hv \rightarrow TiO_2(e^- + h^+) \qquad \text{Equation 6}$$

$$TiO_2h^+ + OH^- \rightarrow TiO_2 + OH^\bullet \qquad \text{Equation 7}$$

$$H_2O_2 + e^- \rightarrow OH^\bullet + OH^- \qquad \text{Equation 8}$$

The effectiveness of the combined AOTs treatments is analyzed in detail for lab and pilot plant level, considering each control quality water parameter, as follows:

pH: As indicated in Table 2, after treatment a pH value close to neutrality was obtained. This value agrees with the maximum permissible limits included in regulations normative [50]. The pH increase observed after treatment is mainly due to the *in-situ* generation of hydroxyl ions during the photocatalytic process, which indicates that the reaction medium favored the formation of $^\bullet OH$ radicals [79]. These species were responsible for the efficient oxidation of organic pollutants and color degradation observed in the effluents [88]. pH increases after photolysis or reactions on AOTs can be also explained due to the formation of by-products coming from protein oxidation during the bacteria inactivation [46].

Hydrocarbons, fats, and oils: The removal of these compounds from the wastewater was close to 85%. This result is like that obtained by biological depuration, which is very interesting taking into account that the biological consortium employed is specialized in hydrocarbon degradation [58], however, by AOTs was also possible to obtain comparable results, in this case, the effectiveness of these technologies is mainly due to the mineralization of the hydrocarbons, fats and oils by ROS [20,89].

COD and BOD_5: The results obtained in these parameters led to determine that the pollution of the effluent given by organic matter decreases to 33.49 and 44.06%, for COD and BOD_5, respectively.

TOC: The TOC value significantly decreased at 75.08% after treatment, thus indicating high mineralization of organic compounds [90]. This is in good agreement with the results obtained in the hydrocarbons, fats, and oils degradation, previously explained. On the other hand, it is important to note that by using the pilot plant device was possible to increase the removal ratio for COD, BOD$_5$, and TOC, compared with the results obtained in the lab batch reactor. It can be explained due to the improved absorption of both diffuse and direct solar radiation [90,91], and the highest reaction time at pilot plant level tests (7 h) is a determining factor for the effectiveness of treatment.

Total suspended solids and sedimentable solids: The solids present in the effluent considerably decreased after treatment, (i.e. 90%), thus showing the elimination and mineralization of organic particulate material such as proteins, carbohydrates, and fats [92].

Ions: The ions present in wastewater can be very active in redox reactions, these ionic species can be adsorbed on semiconductor surfaces [47], thus leading to a decrease in the content of NO_3^-, Cl^-, SO_4^{2-} y PO_4^{3-} in the fluid phase, as it can be observed in Table 2. These ions can be efficiently removed from the effluent by photocatalysis; however, these can also represent an important source of inhibition in the surficial activity of the photocatalyst [93]. Thus, the reaction of CO_3^{2-}, HCO_3^- and Cl^- with $^\bullet OH$ radicals, can generate fewer active radicals as described in equations 9 to 11 [88,94]:

$$Cl^- + HO^\bullet \rightarrow Cl^\bullet + OH^- \qquad \text{Equation 9}$$

$$CO_3^{2-} + HO^\bullet \rightarrow CO_3^{-\bullet} + OH^- \qquad \text{Equation 10}$$

$$HCO_3^- + HO^\bullet \rightarrow CO_3^{-\bullet} + H_2O \qquad \text{Equation 11}$$

Cl^- ions can also have an additional detrimental effect on photoactivity, by interaction with positive vacancies, leading to produce low reactive radicals such as $Cl^\bullet$ and $Cl_2^{-\bullet}$ (Equations 12 and 13) [95]:

$$Cl^- + h_{vb}^+ \rightarrow Cl^\bullet \qquad \text{Equation 12}$$

$$Cl^- + Cl^\bullet \rightarrow Cl_2^{-\bullet} \qquad \text{Equation 13}$$

As previously indicated, and taking into account the COD and BOD$_5$ values, it appears that the lower organic matter degradation achieved by AOTs application compared with that obtained by biological treatment (Table 2), is mainly due to the negative effect of ionic species on the global effectiveness of AOTs [95].

Alkalinity: As represented in equations 9 to 11, the interaction of $^\bullet OH$ radicals with carbonates and bicarbonate ions, and the *in-situ* generation of these radicals, led to a decrease in the alkalinity value of the effluent after treatment (90.83%).

Total and calcic hardness: The removal percentages for these parameters were 33.33% and 28.57%, respectively, which can be due to the adsorption of Ca^{2+} and Mg^{2+} over the TiO_2 surface [93].

Metals: The metallic species can participate in redox reactions with the electron-hole pairs generated during the photocatalytic process. In this way, the metal content in the effluent decreases by photoreduction on the semiconductor surface. As it had been deeply reported, these redox processes take place by the action of holes (h^+) and $^\bullet OH$, the electrons in the conduction band which can oxidize or reduce the metals, respectively [75].

For metals with high concentrations in the starting effluent such as lead, zinc, iron, nickel, and chromium, a decrease in the initial concentration after treatment close to 88.5, 93.4, 67.3, 63.1 and 43.1%, respectively, was observed. A hypothesis to explain these results can be that the metals with high loading in the effluent can have the major probability of being involved in redox reaction on the semiconductor surface [96], for this reason, these heavy metals were more effectively removed from the effluent, compared with those with low concentration.

Total coliforms: Figure 3 includes some pictures of the microbial culture from the effluent under study (dilution factor 100) before and after treatment. In Figure 3 (A), it is possible to identify by color, three main bacteria species such as *Citrobacter freundii* (salmon, red and purple), *Escherichia coli* (dark blue), and *Salmonella spp* (white bone) [75]. As can be seen in Table 2 and Figure 3, after treatment by combined AOTs, at the lab or pilot plant scale, was possible to achieve 99.8% bacteria removal. Total removal was achieved for *Citrobacter freundii* and *Escherichia coli* after treatment. These results demonstrate the bactericidal effect of the AOTs employed, which is mainly due to the bacteria inactivation given by the ROS; these oxidant species attack the polyunsaturated fosfolypids in the lipidic membrane of the bacteria cell, thus leading to the bacterial death [97,98]. However, it is important to note that some CFU of *Salmonella spp* (white bone) [75] remains after treatment. Taking into account the potential danger of these bacteria for human health it is necessary to apply further treatment to ensure the total elimination of them.

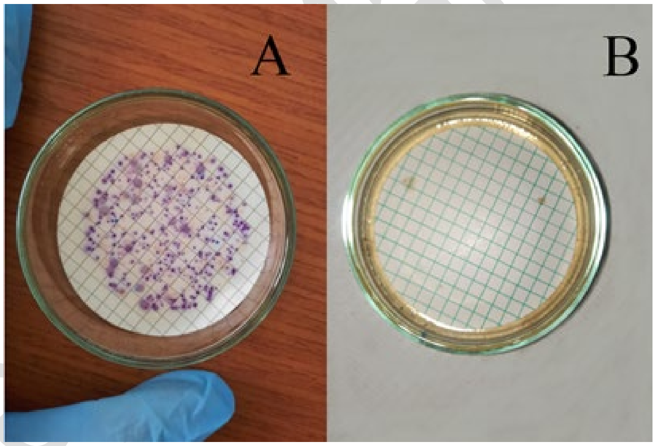

Figure 3. Bacteria culture for industrial wastewater before (A) and after (B) AOTs.

From this concern, it is also important to consider previously reported works, where it has been found that processes like UV/H_2O_2 combination are not enough efficient to eliminate antibiotic resistance microorganisms, which is a relevant factor for the treated wastewater recycling and final disposal for irrigation of soils and/or crops [29,31].

Finally, it was observed that the AOTs employed for the industrial wastewater recovery are effective at the lab and pilot plant; however, as expected, in the pilot plant the effectiveness of the treatments slightly decreases for some water quality parameters, such as nitrates, phosphates, and some metals (Zn, Cu, Fe, Ni, and Pb). It can be explained by taking into account that the pilot device works in environmental conditions, where the light intensity changes during the day.

It is important to take in mind that, as previously commented, the configuration of the lab reactor and pilot plant solar reactor is different, for that reason a reliable comparison was not attempted in this research; however, this work represents an interesting starting point for further studies focused in the employ of AOTs at real scale, with volumes of effluent near to 120 L.

3.5 Simultaneous treatment AOTs and biological depuration

To find a possible synergic effect, after the individual evaluation of photochemical and biological treatment, the simultaneous combination of them was attempted; thus, firstly, the effluent samples were submitted to AOTs (UV-VIS/H_2O_2/TiO_2) for 7 hours, then these samples were maintained under biological treatment for four months. The results obtained in these experiments are summarized in Table 2.

In general, it is observed from Table 2 that the successive application of AOTs and biological depuration led to achieving the best effectiveness in the elimination of some pollutants, compared with that obtained from the individual treatments, thus leading also to achieve values much lower than the reported in the regulations for the maximum permissible limits in parameters [50] such as pH, chlorides, nitrates, Pb and Zn. In the case of other parameters, the observed behavior was represented as follows:

Total hardness: This parameter also decreases after treatments, which, as previously indicated, is mainly due to the adsorption of Ca^{2+} and Mg^{2+} ions on the semiconductor surface [88] and due to the micronutrient consumption by facultative microorganisms [80].

TOC: After combined treatment (biological and photocatalytic treatments), it was observed that the effectiveness in the TOC removal is lower than that obtained after the application of UV-VIS/H_2O_2/TiO_2 only. This behavior is due to the solid organic waste inside the reactor after biological depuration.

Total coliforms: As expected, the CFU counting after combining treatments was like that obtained after the photochemical process, which is due to the biological nature of the bacteria consortium employed in the biological depuration [59]. It is important to say that an ideal recovering treatment for wastewater, should lead to total bacteria elimination, however, in agreement with Colombian regulations a certain content of bacteria is permissible for irrigation crops water [50].

Residual chlorine: It was observed that this pollutant remains after all the treatments applied in the effluent with values >3,0 mg Cl_2/L. This substance represented by sodium hypochlorite and/or calcium hypochlorite, is a contaminant usually present in wastewater, which comes from primary treatments for the elimination of bacteria or as a bleacher additive [95]. The chloride species are solved in water, thus leading to some dissociations as indicated as follows in equations 14 to 16 [99]:

$$NaClO + H_2O \rightarrow NaOH + HClO \qquad \text{Equation14}$$

$$Ca(ClO)_2 + H_2O \rightarrow Ca(OH)_2 + 2HClO \qquad \text{Equation 15}$$

$$HClO \leftrightarrows H^+ + ClO^- \qquad \text{Equation 16}$$

pH value is a determinant factor for the presence of HClO or ClO^-, thus, at pH 7.5, both of these species coexist in similar content [99]. At lower pH prevails HClO, and at higher pH is preferentially present ClO^-. The pH value in the effluent under study was close to 7.40, at this value is possible that chloride species were less reactive, thus leading to a low removal after treatments [95].

Heavy metals: As expected, after combining treatments the results obtained indicated that the metal content remains almost similar to that achieved by using only UV-VIS/H_2O_2/TiO_2 processes. This is because the microbial consortium employed in the biological treatment is not able to process all the metals present in the effluent. However, a similar behavior was observed for the metals at the highest concentration (Pb and Zn).

From the results obtained, it is possible to indicate that biological depuration could work as a complementary treatment to AOTs in the recovery of industrial wastewater. However, from the outcomes observed, two hypotheses can be stated:

It is important to take into account that, as previously commented: (i) during the biological depuration, H_2O_2 could still be present in the sample, which remains from previously applied AOTs, and (ii) biological depuration treatment takes place under environmental conditions and solar light. Therefore, AOTs can continue in the fluid phase. These factors may contribute to obtaining the best performance observed by simultaneous treatments.

However, it is well known that both H_2O_2 and AOTs can induce oxidative stress and lead to microbial inactivation [3,26,29,75,81,100-102], thus affecting the commercial bacteria consortium employed in the biological depuration. It is possible that the remaining peroxide and the AOTs can conduce to the death of good bacteria, and the best performance observed could be due only to the long exposure of the wastewater at AOTs.

To probe one of these facts, it was interesting to test the simultaneous process starting with the bacteria depuration and then, completing the treatment of the effluents by the combined AOTs (UV-VIS/H_2O_2/TiO_2), so, further treatments and analyses were carried out in equivalent periods; the results obtained in these assays are presented in Table 3.

Table 3. Comparison of the results obtained by the application of biological and AOTs treatment in different chronological order.

Water Quality Control Parameters	Units	Starting	UV-VIS/ H_2O_2/TiO_2 and Biological depuration	Biological depuration and UV-VIS/ H_2O_2/TiO_2
pH	Units of pH	7,40 ± 0,141	8.14 ± 0	8.03 ± 0.067

Conductivity	μS/cm	1940 ± 0,102	1164.5 ± 24.7	3648 ± 53.0
Chlorides	mg/L	212.4 ± 0.707	33.5 ± 0.707	256.5 ± 0
Zinc		12.2 ± 0.045	1.02 ± 0,164	1.12± 0,076
Cooper		0.15 ± 0.020	0.210 ± 0.093	0.10 ± 0.018
Chromium		0.58 ± 0.050	0.350 ± 0.093	0.353 ± 0.041
Iron		4.74 ± 0.350	1.30 ± 0.046	1.76 ± 0.082
Nickel		1.52 ± 0.273	0.800 ± 0.110	0.69 ± 0.067
Lead		5.84 ± 0.172	0.410 ± 0.091	0.58 ± 0.034
Nitrates		13.20 ± 0.780	0.900 ± 0.071	0.650 ± 0.103
TOC		81.5 ± 2.40	44.1 ± 4.94	136.0 ± 5.89
Total coliforms	CFU/100 mL	43304	100	2.00

As can be seen, in Table 3, the global effectiveness in the treatment of industrial effluents is very similar, no matter what treatment (i.e. biological depuration or AOTs) was carried out first. Thus, similar results were obtained in the concentration of Cr, Cu, Fe, Ni, Pb, Zn, and nitrates.

However, an increase in the value of parameters such as conductivity, chlorides, and TOC was evidenced. The increase in conductivity may be due to a possible concentration of anions such as chlorides in the wastewater as an effect of water evaporation during aerobic treatment. Besides, the increase in TOC value may be due to the incomplete mineralization of the organic matter present in the wastewater sample [103], thus, applying the biological treatment as a first step, could contribute to the formation of new organic matter by microbial metabolism, confirmed by a high value of dissolved oxygen in the sample [104].

Finally, it was evidenced that by application of AOTs after biological depuration was possible to significantly increase the bacteria elimination, thus achieving almost the total removal of coliform bacteria in the industrial wastewater (2 UFC/100 mL).

4. Conclusions

Effluents coming from an industrial estate with intense and diverse industrial activities were analyzed in the present study. It was found that a potential combination of biological treatment, by using a commercial microorganisms consortium, and advanced oxidation processes (UV-VIS/H_2O_2/TiO_2) can be an excellent alternative for environmental remediation, by treating wastewater recycling as an irrigation source. The simultaneous application of these treatments led to obtaining a good recovery of the industrial effluents and it also demonstrated the effectiveness of the AOTs under realistic conditions at the pilot plant level.

By a sequential combination of biological and AOTs treatments was possible to achieve the values requested in the Colombian regulations for recycling treated wastewater in agricultural activities. For a better comprehension of this behavior, a comparison between the legal requested values, the starting sample effluents, and the values obtained after treatment, respectively, are presented as follows for selected quality control water parameters: pH [6.00-9.00, 7.40, and 8.14], Conductivity [1500, 1940 and 1164.5 µS/cm], Chlorides [300, 212.40 and 33.5 mg/L], Zn [3.00, 12.20 and 1.02 mg/L], Cu [1.00, 0.15 and 0.21 mg/L], Cr [0.10, 0.58 and 0.35 mg/L], Fe [5.00, 4.74 and 1.30], Ni [0.20, 1.52, and 0.80 mg/L], Pb [5.00, 5.84 and 0.410 mg/L], Nitrates [5.00, 13.20 and 0.900 mg/L].

To understand the positive impact of the treatments applied, other parameters not requested in Colombian regulations are also worth considering. Thus, the values of the starting effluents and the treated effluents, respectively, are summarized as follows: Total hardness [192 and 59.0 mg/L] and TOC [81.46 and 44.1]. By these comparisons, it is possible to observe the relevant contribution of the present work by testing the combination of conventional and modern treatments for industrial wastewater recovery and recycling.

Despite the good results observed in the present work, one disadvantage of biological depuration is the generation of more suspended solids and microorganisms loading after treatment. Based on the results obtained, for further work, it is recommended to apply firstly biological depuration and then AOTs, it is because the last treatment led to a significant decrease in the bacteria loading. Thus, demonstrating the synergistic effect of the treatments applied.

This study led to advances in the search for efficient strategies for the treatment and recovery of industrial wastewater, mainly focused on mitigating the environmental impact them and at the same time employing clean and renewable energies like solar light. Finally, in economic terms, to treat 1 m^3 of wastewater, 7.2 L of H_2O_2 and 1 kg of TiO_2 are required, resulting in a cost of 2016 dollars and 325 dollars for H_2O_2 and TiO_2, respectively. Regarding energy cost, there is no expense once the pilot plant is installed and operational, as it operates only on solar energy.

Declaration of competing interest

We declare that we have no significant competing interests including financial or non-financial, professional, or personal interests interfering with the full and objective presentation of the work described in this manuscript.

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Acknowledgments

This work was funded by the Ministerio de Ciencia, Tecnología e Innovación – Minciencias and Ministerio de Salud y Protección Social, Project 110991891727, and Universidad Pedagógica y Tecnológica de Colombia (UPTC) Project SGI 3393.

Author Contributions

Conceptualization, investigation, writing—original draft preparation: J. J. Murcia-Mesa; methodology, investigation: M. A. Gil-Agudelo; methodology, investigation, writing—original draft preparation: J. S. Hernández-Niño; conceptualization, investigation, writing—original draft preparation: C. P. Castañeda-Mesa

Data available statement

The authors confirm that the data supporting the findings of this study are available within the article [and/or] its supplementary materials.

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