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ORIGINAL PAPER

Alternative for the Treatment of Leachates Generated in a Landfill of Norte de Santander–Colombia, by Means of the Coupling of a Photocatalytic and Biological Aerobic Process

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Abstract
In the present study, the use of heterogeneous photocatalysis TiO2/UV coupled to an activated sludge reactor was evaluated as an alternative treatment for the leachate coming from a Landfill, located in Cucuta (Colombia). TiO_2 (Degussa P-25) between 100 and 600 mg.L^{-1} was used as a catalyst, semi-continuous type reactors for the photocatalysis, a batch for the biological stage, UV light with accumulated energies from 20 to 60 kJ.L^{-1} were also used, a constant concentration of H_2O_2 was used as an adjuvant in all tests. The research consisted of four main phases: leachate characterization, biological treatment, optimization of photocatalytic and AOP-biological coupling. For the optimization of the photocatalytic step, an experimental design was carried out through the statistical program Statgraphics Centurion XV of factorial type 3^2 (3 levels 2 variables), modeling the results by means of a response surface, the variables of the pH and the concentration of the catalyst were included, having this as input for the response of interest the percentage (%) of DOC removal. The biological process itself provided a removal of 38 and 24% for COD and DOC, respectively. The AOP-biological coupling provided a removal of 68 and 76% in terms of COD and DOC, respectively. Thus, the coupling significantly improves the overall efficiency of the process by more than 50%, which represents a promising improvement compared to the removal of organic matter for the treatment of the same type of water using only the biological process. The results show a viable alternative for the treatment of leachate because higher removal levels are achieved in residence times, which are considered shorter than the ones in conventional processes.

Keywords Leachates · TiO_2 · Heterogeneous photocatalysis · Activated sludge · Zahn Wellens Test

1 Introduction

Landfills are one of the most common and frequent alternatives used as deposits of solid waste worldwide. There, leachates are generated as a result of the contact of rainwater with the waste and the percolation of these [1], which contain high amounts of heavy metals, solids (suspended and sedimentable) and organic material, which if it is not properly treated becomes a problem that directly impacts the environment and the population surrounding these sites [2]. Therefore, it is essential to implement methodologies capable of removing the contaminants and avoid generating impacts on the environment or human health by ensuring the conservation of natural resources.

Within these leachate decontamination processes, there is heterogeneous photocatalysis, which is an advanced oxidation process that consists of the use of a semiconductor photocatalyst that, when subjected to specific radiation, allows

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the generation of oxide-reduction processes and makes it possible to remove the contaminants and it produces effluents with lower toxicity [3], which are suitable for continuing their treatment in less complex processes such as biological ones. Several research projects have been carried out based on these technological couplings, such as the case of the Oued Smar landfill, located in Algeria, North Africa, where the treatment of leachates was carried out by means of a heterogeneous photocatalysis coupling (TiO_2/UV) and a biological process of bioreactors sown with different types of inoculums (raw leachate, soil extract and activated sludge). These results were very important because a reduction between 50 and 84% of the initial COD maintained at pH 5 was obtained after the heterogeneous photocatalysis; because of this, the ratio BOD5/COD was favorable for the biological treatment, along with the coupling of advanced oxidation-bioreactor there was a reduction of 90% of the initial BOD5 and 87% of the initial COD of the leachate [4].

Similarly, it is possible to state that after the review of the research material, it was found that other recent research, specifically those combining heterogeneous TiO2/UV photocatalysis with batch activated sludge for leachate decontamination, are limited. However, there are studies which have been developed in the last years such as those made by [5–9], who couple the photocatalytic process using TiO2 as a catalyst in the presence of UV radiation with diverse alternatives of aerobic biological processes, achieving outstanding removals of organic matter and emerging contaminants. These results are achieved through the optimization of experimental variables such as catalyst concentration and pH range.

Now with this project, the aim is to evaluate the efficiency of the removal of contaminants present in the leachates of the El Guayabal Landfill in Cúcuta—Norte de Santander, by coupling a heterogeneous photocatalytic process, using a compound parabolic collector and TiO2 as a catalyst, in coupling with an aerobic biological process (through batch activated sludge reactors—Zahn Wellens Test / EMPA OECD 302B) according to Fig. 1, in order to evaluate the possibility of its use for the removal of organic matter and total suspended solids in the leachates, thus minimizing the negative effects on the environment and human health.

The development of this type of alternatives with solar radiation contributes to the search for economic and environmental sustainability alternatives to advanced oxidation processes [3, 10], promotes the implementation and operation of them by reducing energy costs compared to techniques that use other types of UV radiation. Also, with the results obtained, it is possible to make comparisons with other treatments implemented in the decontamination of leachates and provide information to the scientific world about the usefulness and efficiency of the implementation of couplings between heterogeneous photocatalysis with TiO_2 and activated sludge. Although it is true that these combinations have been implemented on several occasions over time to treat water with complex chemical structures such as pharmaceuticals [11] or pesticides [12], there is not enough recent bibliographic information on their use applied to contaminant removal in leachates, which contributes to reducing the existing knowledge gap and provides innovative solutions capable of giving effect to the sustainable development objectives.

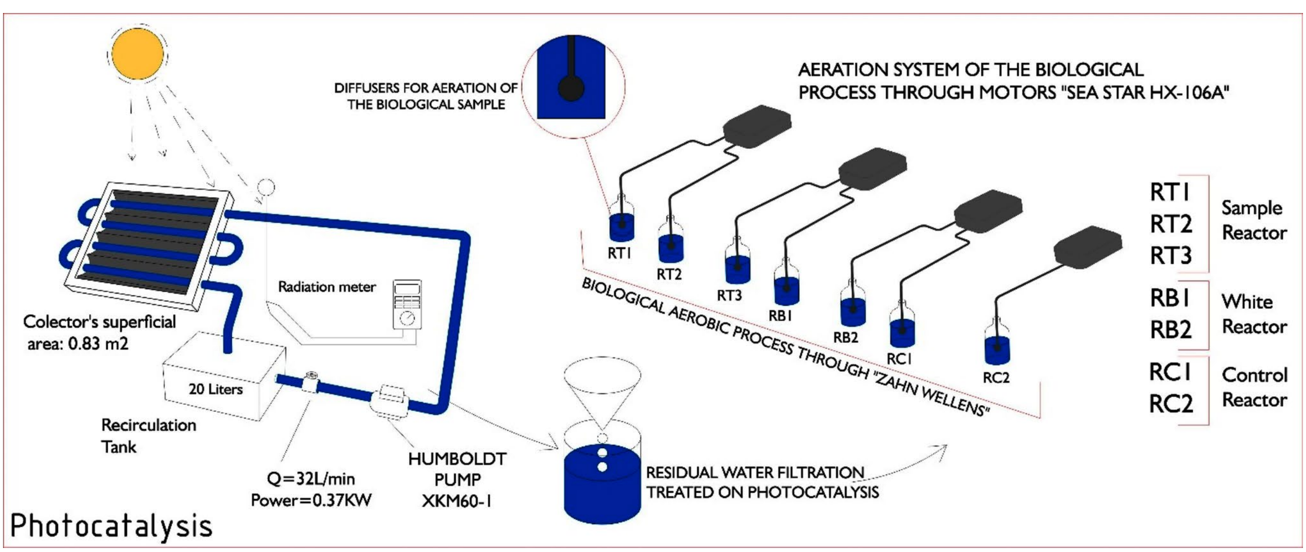

Fig. 1 General scheme of the coupling processes

2 Materials and Methods

The experimental process of the project was based on the scientific approach, the feasibility of the procedures and the application of the results obtained. The analyses were carried out at the Environmental Quality Laboratory of Francisco de Paula Santander University in Campos Eliseos headquarters. The methodology was developed in the following phases:

2.1 Leachate Characterization

The leachate sample from El Guayabal Landfill was characterized by the physicochemical parameters of Chemical Oxygen Demand (COD), Dissolved Organic Carbon (DOC), Total Suspended Solids (TSS) and Volatile Suspended Solids (VSS), the pH and temperature were also part of these characteristics, and they were measured in the field afterwards. The methodologies were carried out taking as reference the Standard Methods for Water and Wastewater Analysis (AWWA—APHA—WPCF).

The COD measurement was carried out using the closed reflow and volumetric method, following the protocol set out in Sect. 5220C. COD measurement was performed by the high temperature combustion method, following the protocol set out in Sect. 5310B. The Teledyne Tekmar TOC Torch equipment was used. Initially, the assembly should be done in the Curve and Calibration Method program, for this, the "Total Organic Carbon Equipment (Teledyne Tekmar TOC Torch) Operating Protocol" was followed. TOS and TOC Torch were performed following the protocol set in Sect. 2540D. The use of analytical balance, porcelain capsule and crucible dryer, Digital Binder Furnace model ED-53 and Electric Ground Muffle model D-8 were used. The temperature and pH parameters were taken in the field at the time of collecting the leachate sample at Guayabal Landfill with a Waterproof PCTestr 35 multiparameter.

2.2 Aerobic Biological Treatment Process

2.2.1 Characterization of the Inoculum Sludge

The inoculum sludge used to carry out the research came from the wastewater treatment plant of Ciudadela "El Country" neighborhood, located in Jamundí, Valle del Cauca, as a result of an aerobic biological treatment process. This mud was fed every other day with wastewater from San Pablo farm which belongs to the Francisco de Paula Santander University in order to ensure its fast activation. This sludge was characterized in physicochemical parameters of Total Suspended Solids (TSS) and Volatile Suspended Solids (VSS). In addition to this, the Sludge Volumetric Index (SVI) and the Oxygen Consumption Rate (OCR) were applied. The Sludge Volumetric Index (SVI) is a parameter that allowed evaluating the behavior of the aerobic sludge according to its good or bad sedimentability (a good sedimentability occurs when the sedimentation rate is higher than the ascension rate of the influent). The method was used to find a standard dilution for the sludge under study, so that after sedimentation it gets a volume of 300 ml in the 1000 ml test tube.

2.2.2 Oxygen Consumption Rate

The Oxygen Consumption Rate (OCR) is a technique based on the measurement of oxygen consumption by microorganisms working on an organic substrate, which is degraded and oxidized to CO_2 [13]. The dissolved oxygen analysis allowed the acquisition of data on oxygen consumption in response to the metabolism of a substrate due to the respiration of the microorganisms. The test was carried out in a Winkler bottle (300 ml capacity) and a range of concentrations related to those allowed in the Zahn Wellens test was handled (100 to 1000 mg COD.L^{-1}), which were 0, 200, 400, 600 and 800 mg COD.L^{-1}, taking into account that the first test mentioned represents the control concentration and the OCR value for the aerobic sludge, because the mixture only contains nutrient solution and the one which was previously mentioned. The amount of aerobic sludge in the tests, depends on the concentration of VSS that is required within each concentration, for this case is 1500 mg VSS.L^{-1}. The content of each test is shown in Table 1.

The dissolved oxygen was measured with an Oxygen Meter model DO -5510 for each study concentration. These measurements were made for 30 min, and the data was recorded every 15 s. A graph of Dissolved Oxygen Vs. Time is made with these values, and the OCR is determined from the slope.

2.2.3 Respiration Inhibition Test

This method determined the effect of the leachate on the microorganisms by measuring the respiration rate of the inoculated sludge under defined conditions in the presence of various concentrations of the test substance. It was carried

Table 1 Volumes used in the OCR

Compound	Concentration (mg.L^{-1} COD)				
	0	200	400	600	800
Aerobic Inoculum Sludge (ml)	27,4	27,4	27,4	27,4	27,4
Nutrients (ml)	272,6	265	257,4	249,9	242,3
Leachate (ml)	0	7,6	15,2	22,7	30,3

out with the purpose of identifying non-leaching inhibitory concentrations that could be used in the Biodegradability Test (Zahn Wellens) [14].

The respiration rate is the oxygen consumption of the microorganisms in an aerobic sludge expressed as mg O_2.mg^{-1} sludge.h^{-1}. The procedure described in the Oxygen Consumption Rate in Sect. 3.2.2 of this document is an input for determining the percentage inhibition, which is calculated by Eq. 1.

$$\%\mathbf{Inhibition} = \left(1 - \frac{\mathbf{R_s}}{\mathbf{R_c}}\right) \times 100 \tag{1}$$

where:

Rs: OCR of each leachate's concentration employed

Rc: OCR of control

2.2.4 Aerobic Biodegradability Test—Zahn Wellens

The objective of the Biodegradability Test, Zahn Wellens Test / EMPA OECD 302B, was to determine the potential for biodegradation of organic substances under aerobic conditions. This test is applicable on non-volatile and water-soluble compounds at least 100 mg/L; which show low adsorption in activated sludge, which have no foaming activity, and which do not inhibit microorganisms at the evaluated concentrations. The contents of each reactor are given in Table 2 [15].

The sample reactors were taken in triplicate, the target and reference compound reactors were taken in duplicates. The concentration (mg.L^{-1} COD) within the sample reactors was determined from the results obtained in the Oxygen Consumption Rate and the Respiration Inhibition Test. Similarly, the ratio was maintained for the concentration of the sludge in mg.L^{-1} VSS (3:1). In the case of the reference compound (Ethylene Glycol).

The test lasted 28 days. The monitoring parameters were the pH and the temperature, in order to guarantee optimal conditions for the development of the biological process. The samples were taken on days 0, 4, 8, 12, 16, 20, 24 and 28, each of them filtered and characterized in terms of COD and DOC, to determine the percentages of biodegradation based on Eq. 2.

$$\%\mathbf{Biodegrability} = \left(1 - \frac{\mathbf{R_T} - \mathbf{R_B}}{\mathbf{R_{t0}} - \mathbf{R_{B0}}}\right) \times 100 \tag{2}$$

where:

R_T: is the quantity in mg/L of DOC or COD at time t in the test vessel

R_B: is the quantity in mg/L of DOC or COD at time t in the blank test

R_{T0}: is the quantity in mg/L of DOC or COD of the test vessel after 3.5 h

R_{B0}: is the quantity in mg/L of DOC or COD of balnk test after 3.5 h

Table 2 Composition of the biological reactors

Reactor	Composition	Amount (ml)
Sample	Inoculum Sludge	73
	Nutrient solution	676,5
	Leachate	50,5
Blank	Inoculum Sludge	73
	Nutrient solution	727
Reference Composite	Inoculum Sludge	73
	Nutrient solution	726,45
	Ethylene glycol	0,55

2.3 Optimization of Photocatalysis

The leachate sample from El Guayabal Landfill was submitted to the heterogeneous photocatalysis process, using TiO_2 (Degussa P25) as catalyst, which [16] has shown high efficiency when it is used in leachate decontamination treatments due to the generation of hydroxyl radicals, especially when photolysis is submitted. Besides, it has been used in numerous studies oriented to the removal of recalcitrant contaminants or with structures difficult to treat, and it obtains efficiencies of more than 70% [17–21]. Furthermore, according to [22] who carried out a similar wastewater treatment employing TiO_2 (Degussa P25), this has a band gap energy from 2.90 to 3.15 eV, [23]. The BET of this catalyst has a value between 51 and 56 m^{2}g^{-1}[24]. TiO_2 (Degussa P25) is mainly composed of Anatase (80%) and Rutile Crystallites (20%) and its particle size is between 20 and 30 nm.[25–27].

Subsequently, H_2O_2 is used as an oxidation coadjutant, since having previous research as reference such as that carried out by [28–30] has shown that the use of this type of oxidant promotes the formation of OH radicals, helping the degradation of contaminating compounds. A Compound Parabolic Collector (CPC) was used at laboratory scale, with a system that allowed the measurement of accumulated energies in kJ × L-1. The use of this kind of Collector allows the concentration of solar energy, and it generates a higher intensity radiation [31], which results in a high degradation capacity of the system [32].

This CPC has a surface area of 0.83 m^2. It is composed of two aluminum structures (UV light-reflective film), each equipped with a set of borosilicate tubes (material sensitive to UV adsorption), and a 20 L capacity storage tank, where the treatment mixture is prepared. In addition, it is equipped with a Humboldt pump (Qmax: 32 L.min^{-1}) which is responsible for recirculating the treatment throughout the system. The connections and pipes

Table 3 Independent variables and their coded levels for the experimental design

Parameter	Level of the variable		
	− 1	0	1
pH	3	6	9
TiO_2	100	350	600

Table 4 Design of experiments—photocatalysis process

No. Assay	[mg.L^{-1}] TiO_2	pH
1	100 (− 1)	9 (1)
2	350 (0)	6 (0)
3	350 (0)	9 (1)
4	600 (1)	9 (1)
5	100 (− 1)	6 (0)
6	600 (1)	6 (0)
7	600 (1)	3 (− 1)
8	100 (− 1)	3 (− 1)
9	350 (0)	3 (− 1)
10	350 (0)	6 (0)

are made of half inch PVC tube, as well as accessories that allow the operation of the prototype.

To optimize the photocatalytic process, an experimental design was carried out through the statistical program Statgraphics Centurion XV of factorial type 3^2 (3 levels 2 variables), modeling the results by means of a response surface. The ranges of the independent variables and their coded levels are shown in Table 3 having + 1 as the maximum level and -1 as the minimum level.

H_2O_2, is a variable that remained constant throughout the process. The working concentration was of 300 mg. L^{-1}, this value was optimized by [33], under acidic pH conditions (4 units), applying a heterogeneous photocatalytic treatment process (TiO_2/UV) for leachates, where it obtained percentages of biodegradation higher than 94.7%.

The accumulated energy was used in a range from 0 to 60 kJ.L^{-1}, it was considered that in heterogeneous photocatalytic processes high accumulated energies are used: 111 kJ.L^{-1} [34]; 1850 and 250 kJ.L^{-1} [35] that allow high removal percentages of the evaluated pollutants, and as the intention of the project is not to totally degrade the leachate, but to make a partial transformation where subsequent biodegradability in biological reactors is promoted, the range of work is justified.

With the ranges of the independent variables already established, we proceed to model the program, for which we have the design of experiments set forth in Table 4.

2.3.1 Calculation of the Accumulated Energy

For the calculation of the accumulated energy (UV radiation), a system was assembled that would allow the measurement of the total solar radiation, and to be able to determine at each moment of measurement the energy in the units of interest (kJ L^{-1}) an equation and basic conversions were used.

This system consisted of a multimeter (Uni-T UT71C) connected to a pyranometer (SP-110) which, when it comes into contact with the radiation, marks a value sequentially in millivolts (mV). The precise data acquisition is defined by timescales in which the information will be given, which in this case is every 10 min (600 s).

The following step is to make the mathematical conversion of mV to W × m-2 for which 1 mV represents 5 W.m^{-2}. Finally, what remains is to apply the Eq. 3 for the calculation of the energy:

$$Q_n = Q_{n-1} + \Delta t_n \times I_n \times A_f \times V_T^{-1} \tag{3}$$

where:

Q_n: total accumulated energy kJ.L^{-1}.
Q_{n-1}: previous accumulated energy kJ.L^{-1}.
Δt_n: irradiation time (600 s).
I_n: Average irradation (W.m^{-2} UV).
A_f: irradiated reactor surface (0,83 m^2).
V_T: volume discussed (20 L).

2.4 CPC Effluent Coupling—Zahn Wellens Test

With the obtained results in the optimization of the photocatalysis process, the coupling took place which consisted of the sequential operation of the Compound Parabolic Collector and the aerobic biological process of treatment (biodegradability test). This coupling is based on the fact that different researchers have applied photocatalysis (TiO_2/UV) as a pre-treatment for landfill leachate, in order to improve the biodegradability of the organic compounds present in this waste liquid and thus consider the application of a subsequent treatment that allows a discharge of waste with less impact on the environment [16].

The degradation of the pollutants is monitored in terms of the percentage of COD and DOC removal at the end, compared to the start of the test.

In the biological coupling process, the sample coming from the optimal photocatalytic treatment was used, and with this, 3 reactors with mineral medium and activated aerobic sludge were adapted, as well as two white reactors (aerobic sludge and mineral medium) and 2 reference compound reactors (activated aerobic sludge + mineral medium + ethylene glycol). In addition to this, each of them

Table 5 Leachate characterization

Parameter	Units	Value
COD	mg $O_2.L^{-1}$	7920
DOC	mg $C.L^{-1}$	2767
TSS	mg $TSS.L^{-1}$	19,941
VSS	mg $VSS.L^{-1}$	8587
pH	–	7,29
Temperature	°C	33,2

Table 6 Results characterization of the inoculated sludge

Parameter	Measurement	Units
TSS	45,529,33	mg $TSS.L^{-1}$
VSS	16,450,67	mg $VSS.L^{-1}$
SVI	66,16	$mg.L^{-1}$
OCR	14,64	$mg.g^{-1}$ $VSS.h^{-1}$
Ethylene glycol Degradation (8 days)	100	%

was monitored in terms of COD and DOC on days 0, 4, 8, 12, 16, 20, 24, 28, and TSS and VSS on days 0, 16 and 28, in order to provide a percentage of biodegradation and to determine the efficiency of the coupled treatment.

3 Results and Analysis

3.1 Leachate Description

Following the methodologies proposed in the methodological design to characterize the leachate, the obtained results are represented in Table 5.

It is concluded that the leachates from "El Guayabal" Landfill have a COD of 7920 mg O2*L-1, which according to the consolidated classification by [31], It is listed as a leachate of average age, since it is in the range of 5000—10,000 mg $O_2.L^{-1}$.

It was determined that the leachate sample from "El Guayabal" Landfill has a concentration of 2767 mg $C.L^{-1}$, and taking into account its COD/DOC ratio (0.35), it is categorized as having low biodegradable properties [16].

The concentration of suspended solids in the leachate coming from "El Guayabal" Landfill is of 19,941 mg $TSS.L^{-1}$ and 8587 mg $VSS.L^{-1}$, which is interpreted as a high content of them, and the VSS contributes with a great amount of microorganisms due to the high contribution of organic matter in this residual liquid.

The leachate sample has a pH of 7.29, which indicates a value close to neutral, and it allows the development of a biological treatment process. The temperature recorded as 33.2 °C is consistent with the normal temperature of the location area (Max. 33 °C; Min. 24 °C).

3.2 Aerobic Biological Treatment Process

3.2.1 Description of the Inoculum Sludge

Table 6 consolidates the results obtained from the analyses carried out on the inoculum sludge.

According to the results presented above, the sludge comes from the treatment plant of the "El Country" neighborhood, it has a volumetric index of sludge of 66.16 $mg.L^{-1}$, a value that places it within the range of sludge with good sedimentation characteristics, considering that a sludge with good sedimentation characteristics should present a value of VIS in the low range [36]. This parameter is very important to consider because in a biological treatment the organic matter is transformed into microorganisms that become part of the slurry, and if it is not removed in the spillage before being discharged, in fact, it transforms the organic materials into slurry and it is discharged as an effluent avoiding the polluting agents to be removed. Therefore, the idea of having a settled slurry is beneficial because after the biological process in real conditions, a settler can be available where this slurry is removed (as settled solids), providing the discharge of an effluent free of pollution.

The Oxygen Consumption Rate of 14.64 $mg.g^{-1}.h^{-1}$ indicates an adequate development of microbial metabolism and a high biological activity of the sludge, and places it in the range of 12 and 20 $mg.g^{-1}.h^{-1}$, for which they are considered under normal conditions and capable of degrading pollutants [37].

The result obtained in the degradation of a reference compound such as ethylene glycol, shows a high biological activity and microorganisms capable of degrading organic material, as well as having optimal conditions for the development of them, which are relevant when performing the biological treatment, The methodology proposed by the Zahn Wellens Test / EMPA OECD 302B establishes that this compound must be degraded in less than 14 days, which guarantees the viability of using this sludge as inoculum in the biodegradability tests.

3.2.2 Oxygen Consumption Rate

In Table 7, the Oxygen Consumption Rate data is reported for each concentration. According to the studies, a OCR is considered low when it shows values lower than 12 mg $O_2.g^{-1}.VSS.h^{-1}$, indicating that there are too many solids or the presence of toxics elements, because a high toxicity of the leachates is corroborated, due to the large amount of contaminating constituents that form the waste that the landfill in study has.

Table 7 Oxygen consumption rates

Concentration (mg $O_2.L^{-1}$)	Slope of the graph (mg $O_2.L^{-1}.S^{-1}$)	OCR (mg $O_2.g^{-1}$SSV.h^{-1})
0	0,0061	14,64
200	0,0027	6,48
400	0,0026	6,24
600	0,0026	6,24
800	0,0026	6,24

3.2.3 Respiration Inhibition Test

According to Fig. 2, from the concentration of 400 mg $O_2.L^{-1}$, a trend associated with the percentage of inhibition of 57% begins to occur, indicating that 43% of microorganisms are available to give rise to biodegradability in the biological process.

That is the reason why it is decided to work with an intermediate concentration, in which the biological process is not affected by the toxicity of the residual liquid. Therefore, a concentration of 500 mg COD.L^{-1} is selected for the biodegradability test (Zahn Wellens).

3.2.4 Biodegradability Test—Zahn Wellens

This biodegradability test by Zahn Wellens simulates an aerobic biological treatment process of activated sludge in a laboratory scale. It was carried out following the protocol established by EMPA OECD 302B. It should be clarified that the COD of the leachate from "El Guayabal" Landfill was 7920 mg.L^{-1}, but the concentration of 500 mg $O_2.L^{-1}$ in the sample reactors was chosen because the working range established by the test is 100 to 1000 mg $O_2.L^{-1}$, and taking as a reference the results obtained in the respiration inhibition test, where the use of such concentration is supported.

The test establishes that the method is validated when the reference compound, in this case ethylene glycol, is degraded by more than 70% within 14 days from the beginning of the test. After 4 days, this compound had already fulfilled this condition, in terms of COD and DOC, which supports optimal conditions of the inoculum used for the treatment, as well as the correct application of the test under the established minimum conditions and requirements, which validate the accuracy of the obtained results.

The degree of volatilization that could occur in the test was evaluated, because it was considered that the compounds present in the leachate may be of a volatile type, and that in an activated sludge process where there is constant airflow the compounds may go into the atmosphere. That is the reason why a reactor was prepared with the same leachate concentration, calibrated to 800 ml with a nutrient solution and in the absence of inoculum slurry, where there are no microbiological biodegradation processes. This reactor was evaluated in terms of COD and DOC at the beginning and end of the test (28 days), and a percentage of volatilization of the compound was determined through these values, which must be adjusted to the percentages of biodegradation determined during the test. These results are presented in Table 8.

A percentage of volatilization is determined in the test of 47 and 55%, for COD and DOC respectively. According to Fig. 3, with the percentages of biodegradation adjusted to volatilization, we determined a maximum biodegradation for COD of 38% and 24% for DOC. This Zahn Wellens test establishes a limit of biodegradation of more than 70% after 28 days of the test, in order to consider a substance as biodegradable. It is concluded that the treated leachate sample is not biodegradable under the requirements of this test, for this reason it is important to carry out previous treatment processes that allow the transformation of the compound into simpler substances, capable of breaking down and degrading the toxic constituents, and thus be able to apply subsequent

Fig. 2 Breathing Inhibition Test

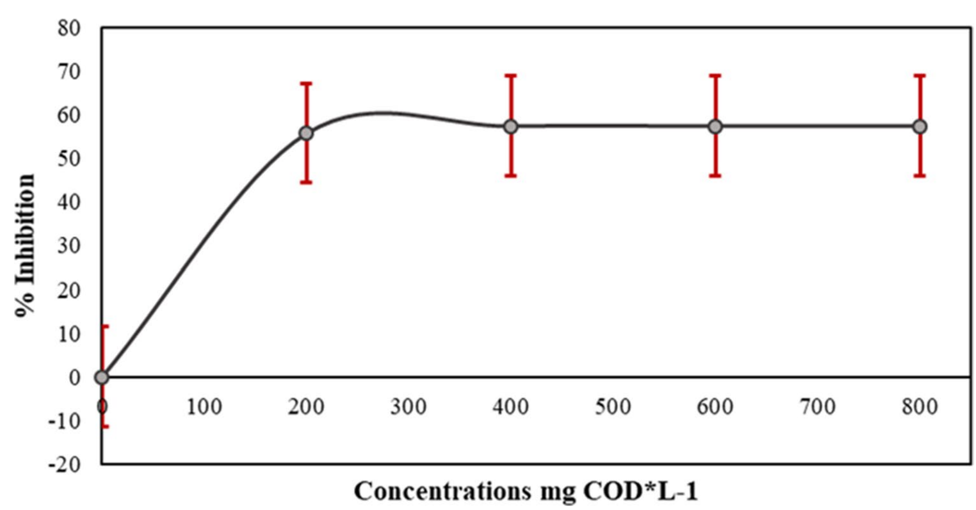

Table 8 Volatilization results biodegradability test

Time (Days)	COD (mg. L^{-1})	Volatilization (% COD)	DOC (mg. L^{-1})	Volatilization (% DOC)
0	1152	47	358	55
28	608		160	

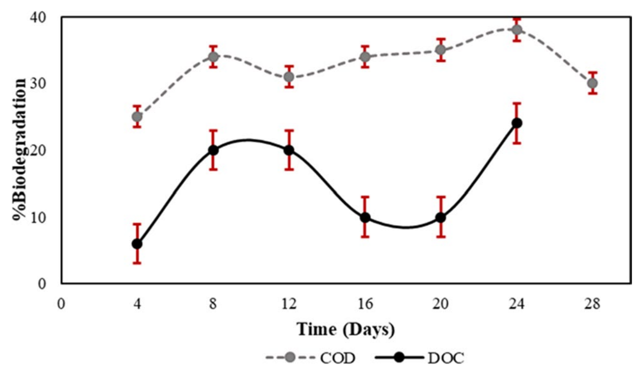

Fig. 3 Percentage (%) Biodegradation COD and DOC on Zahn Wellens test

biological processes that have the ability to remove contaminants [13].

Similarly, the results mentioned above are comparable to those obtained in the study done by [38], where a similar process for the treatment of leachate from Mermuelo Landfill in Spain was carried out, in which a 57% biodegradation using the same biological process was obtained, and it also failed to exceed the percentage of degradation required by the methodology, which implies the need to couple this system with another treatment alternative. The mentioned study obtained a higher biodegradation due to the initial characteristics of the leachate, which presented a COD and a DOC notably lower than those coming from "El Guayabal" Landfill.

During the test, a pH between 7.03 and 7.13 (adjusted from buffer solutions) was handled in the reactors, as well as temperatures ranging from 24.5 to 25.7 °C, which allowed optimal conditions for the development of metabolic activities by the microorganisms during the biological treatment, and contributed to the biodegradation of the contaminating compounds provided by the leachate.

3.3 Optimization of Photocatalysis

Based on the percentages (%) of removal determined in each of the tests, and when the established accumulated energies were accomplished, it was determined that the maximum degradations were recorded when 60 kJ.L^{-1} was reached. Table 9 consolidates the results of photocatalysis

Table 9 Removal of DOC—Optimization of photocatalysis

Assay	[TiO_2] (mg*L^{-1})	pH	Percentage (%) of final removal COD
1	100 (− 1)	9 (1)	1,4
2	350 (0)	6 (0)	7,2
3	350 (0)	9 (1)	5,5
4	600 (1)	9 (1)	22,4
5	100 (− 1)	6 (0)	23,9
6	600 (1)	6 (0)	5,0
7	600 (1)	3 (− 1)	12,5
8	100 (− 1)	3 (− 1)	57,9
9	350 (0)	3 (− 1)	29,8
10	350 (0)	6 (0)	11,9

optimization, highlighting for each test the percentages of final removal in terms of the parameter of DOC.

Considering the response surface of Fig. 4, the optimal region is between the orange and red zone, which represents a desirability of 0.9 and 1.0 respectively, therefore, this region is limited between the TiO_2 concentration of 100 and 200, and the pH of 3 to 4.

It is also concluded that the optimal test is No. 8, since it presents the highest DOC removal (57.9%) with the lowest catalyst concentration evaluated of 100 mg TiO_2.L^{-1}, at an acid pH of 3 units. Becerra et al.[39] found that photocatalytic treatment with TiO_2 provided a removal of more than 80% of the contaminants present in the leachate, under acidic pH conditions (4 units) and with the lowest dose of catalyst evaluated, which is in accordance with the results obtained in this investigation.

The hydraulic retention times for each one of the tests varied, due to the fact that they were carried out in sunny and cloudy days, where the accumulated energies were reached faster or slower, respectively. We conclude that for a hot climate like the city of Cúcuta, Norte de Santander, in sunny days the accumulated energies of 60 kJ.L^{-1} are reached in HRT in less than 3 h, and for cloudy days in HRT greater in more than 3 h. According to [7], the amount of illumination falling on the catalyst leads to a high rate of photocatalytic degradation, because as irradiation times increase, so does the removal of contaminants. It should be noted that this optimal test obtained one of the highest irradiation times (4.3 h), which is consistent with the obtained results.

Considering the application of treatment on a real scale, the leachates can be mixed with domestic wastewater, in the necessary quantities to maintain the working concentrations carried out in the investigation. In addition to this, the physicochemical characteristics of these domestic wastewater (COD and DOC), allow their mixing to maintain the concentrations at the required dilution, and thus apply the techniques described above.

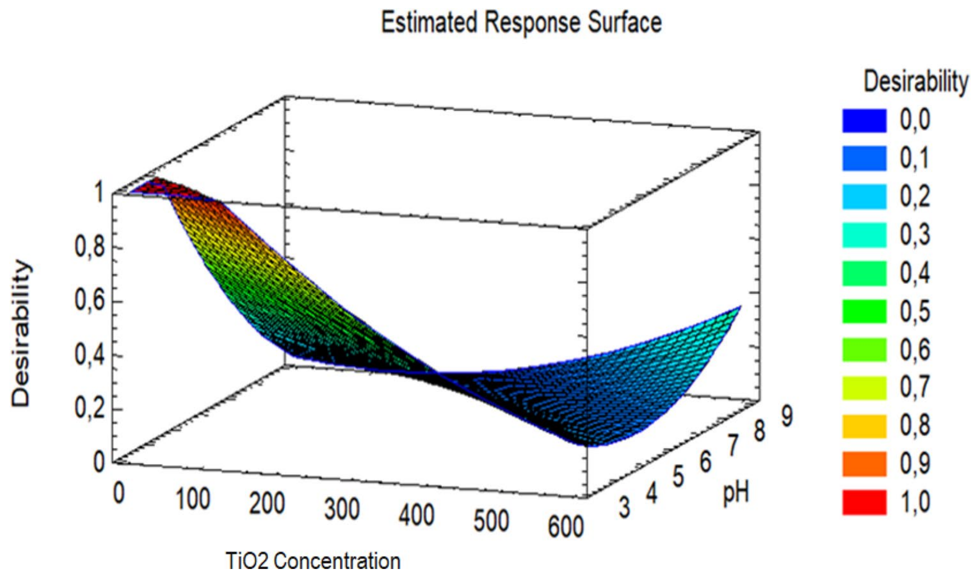

Fig. 4 Response surface for photocatalysis optimization

It must be concluded that for the concentrations represented by 100 and 350 mg $TiO_2.L^{-1}$ the highest removal percentages (in terms of DOC) occur when in the treatment the pH is controlled in 3 units, which is consistent with the work done by [40] which showed that photodegradation of the leachate that was strongly favored at a higher acidic pH than the neutral and alkaline solutions.

Similarly, several studies [41–44], prove that this treatment alternative produces better results when it is developed at acidic pH, since at acidity levels, the surface of the catalyst is positively charged which leads to the attraction of negatively charged organic pollutants generating an important photocatalytic activity [45, 46]. That is why, the closer the pH is to the alkalinity, the removal behavior throughout the treatment is usually very dispersed, and it is not possible to determine a reliable reduction of the contaminants. It must also be argued that at pH near neutrality (pH = 6), removal maintains a consistent trend line, although it does not present degradation results that are relevant, since they are very low.

The behavior of the removal at each concentration shows that not necessarily the best treatment is not necessarily the one that uses the highest concentration of the catalyst. Generally, what can be concluded with (from) the behavior of the treatment under the different configurations is that, in high concentrations of catalyst (600 mg.L^{-1} TiO_2), there are better removal levels at basic pH, and in the case of low catalyst concentrations (100 mg.L^{-1} TiO_2) or with average values (350 mg.L^{-1} TiO_2), the best removal levels are given at acidic pH levels.

Photocatalytic degradation using TiO_2 as a catalyst has revealed great potential for economical and environmentally consistent, non-toxic, chemically stable, high photoactivity treatment [16]. Its main advantage is the possibility of incorporating solar energy in the photoactivation of the catalyst, so the degradation process acquires a significant additional environmental value and it becomes a sustainable technique [47]. The use of sunlight in the photodegradation of wastewater pollutants makes it an economically viable process, particularly for large-scale applications [19].

Losada et al. [35], determined that the addition of H_2O_2 in a TiO_2/UV photocatalytic treatment, improves the process notably, since it contributes positively to the speed of degradation of the contaminants, which is related to the chemical action of this element as an oxidizing agent. Thus, for the same period of time, in the absence of H_2O_2, 50% of the contaminants present were degraded, while in the presence of peroxide, more than 90% were removed, which shows a high contribution to the efficiency of the treatment. For this reason, with each accumulated energy, a concentration of hydrogen peroxide was maintained, which was determined from an optimal dose as a reference for a research project.

3.4 Photocatalysis Coupling–Aerobic Biological Process.

Once the optimal conditions are set to develop the photocatalytic treatment, with a concentration of TiO_2 of 100 mg.L^{-1} and a pH of 3, the treatment of the leachate in the compound parabolic collector (CPC) is carried out again until it gets to 60 kJ.L^{-1} of accumulated energy.

Once it is completed, the resulting effluent is subjected to a filtration process, in order to eliminate the excess TiO_2 present to avoid any effects on the microorganisms, and it is ready to begin the coupling with the biological treatment.

To start the biological treatment, the methodology proposed by the Zahn Wellens Test / EMPA OCDE 302B was followed, showing 3 reactors containing inoculum sludge + mineral medium + phototreated effluent previously filtered, 2 white reactors with mineral medium + inoculum sludge and 2 control reactors with mineral medium + inoculum sludge + reference compound. A reactor capacity of 800 ml and a concentration of VSS by the slurry of 1500 mg $VSS.L^{-1}$ (ratio 3:1) was handled. The degradation in COD and DOC parameters was monitored for 28 days, with measurements on days 0, 4, 8, 12, 16, 20, 24, 28 and TSS and VSS on days 0, 16, 28.

Considering Fig. 5, in terms of COD, the highest degradation is evident, with a value of 68% of the compound analyzed. As for DOC, it shows a maximum level of degradation equivalent to 87%. In both parameters, a remarkable improvement in degradation within the biological process is seen after treating the sample with photocatalysis, which shows that photocatalytic processes can either decompose or reorganize the molecular structures of non-biodegradable organic materials into more easily biodegradable products, and it improves the efficiency and it allows biological post-treatments [48]. In addition, the requirement set out by the EMPA OECD 302B methodology is accomplished, and at the end of the test, biodegradation results of more than or close to 70% have been obtained.

The suspended solids results are listed in Table 10. According to the results presented above, a final removal of 54% and 6% is obtained, in terms of VSS and TSS, respectively. This removal is provided by the biological process, for which the solids are settle in the reactors, this is a real-scale process which is evident in a subsequent settler.

A better behavior of the compound after coupling is detailed, since much higher degradation percentages are evidenced than those of the initial biodegradability test, which corroborates that this heterogeneous photocatalysis process (TiO_2/UV and H_2O_2) provides a much more stabilized effluent with adequate characteristics for degradation in biological reactors under controlled aerobic processes.

Table 10 Solid results suspended in the coupling

Time (days)	TSS (mg.L)	Removal (%)	VSS (mg.L)	Removal (%)
0	3932	–	2048	–
16	3786	3,71	1344	34,38
28	3688	6,21	928	54,69

Finally, the results of removal for coupling, register percentages of 61 and 74%, for COD and DOC of the leachate respectively, in relation to the input in the photocatalysis process and the output in the biological process. It is estimated that the efficiency of the coupling is more than 50%, which supports the hypothesis that the leachates coming from the El Guayabal Landfill, by the coupling of a heterogeneous photocatalytic and biological activated slurry process, allow a considerable removal of the constituents present in this liquid residual, and that it is considered a viable alternative for the treatment on a real scale of them.

Dacosta et al. [49] found that two leachate samples from different landfills had low aerobic biodegradability (65% and 30%) after 28 days under the Zahn Wellens test, and that after applying advanced oxidation pretreatment, the effluent within the biological process showed higher biodegradability characteristics, increasing in final removals by 89% and 69% respectively. Silva et al. [50] determined a similar efficiency in the evaluation of leachate biodegradability improvement by applying the same method (Zahn-Wellens Test), which after an advanced oxidation process, increased its degradation to 70%, in relation to the initial values of between 4 and 20%. This supports and evidences the need to couple this type of treatment towards the reduction of contaminants and toxics present in leachates, because due to their harmful characteristics, they do not allow a removal of contaminants under conventional treatment processes,

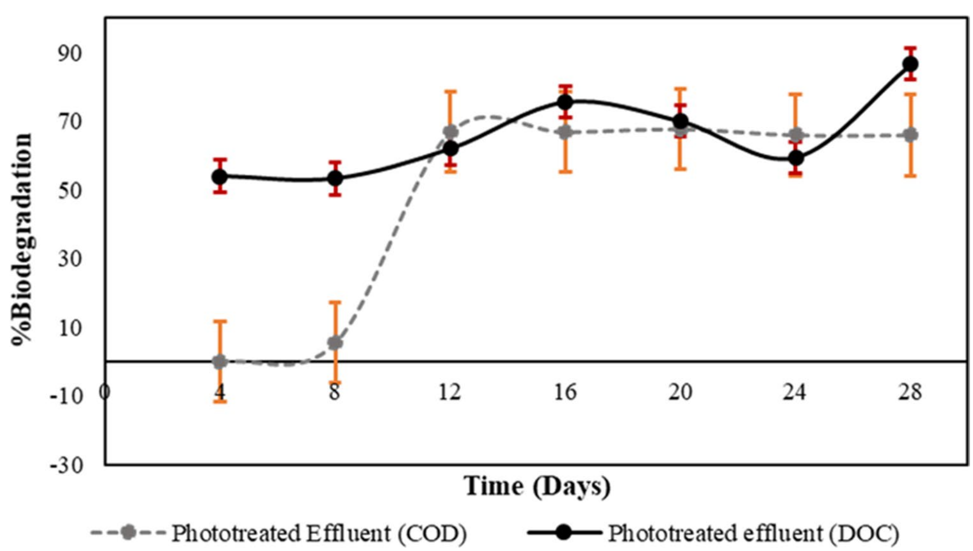

Fig. 5 Percentage (%) of Biodegradation of COD and DOC—Coupled biodegradability test

requiring the application of these new techniques that have proven to be an efficient alternative, as well as applicable in real settings, besides their easy application, such as low operation costs.

The biological reactor most often combined with advanced laboratory-scale oxidation processes for leachate treatment is the Sequential Biological Reactor (SBR) that simulates an activated sludge process, and the anaerobic biodegradability analyses are less common [51]. However, [52] evaluated an aerobic (rotary biological contactor) and anaerobic (upflow anaerobic sludge reactor) biological process for leachate treatment, finding 54% and 62% removals of contaminants present in terms of COD respectively [53]. evaluated the performance of a pilot-scale anaerobic biofilm digester (ABD) for leachate treatment, determining that, despite the complex characteristics of this residual liquid, the system demonstrated high performance in maintaining removal levels in terms of COD of 96%, at hydraulic retention times of 10 days. With the above, it is possible that in later studies a coupling of heterogeneous photocatalysis with an anaerobic biological process can be evaluated, in which the process with the efficiencies found by the alternative developed in this research can be compared, this later studies can also determine which one can be more viable, starting from the high organic loads of the leachate.

3.5 Catalyst Comparison

One of the main challenges faced by researchers working with heterogeneous photocatalytic processes is the selection of the catalyst, because with this type of alternatives the research has not been as broadly developed as for other advanced oxidation processes [3]. There are several variables that influence the performance of catalysts, such as the pH of the treating wastewater, inorganic ions, dissolved oxygen, radiation and the hydraulic retention time of the treatment, which leads to the use of optimization processes that allow reproducible and accurate results [16]. This activity that was carried out in the current project allowed us to know the optimal dose of the catalyst used.

From bibliographical revision, it was determined that several catalysts based on metal oxides are frequently implemented in photocatalytic treatments, and they are focused on the removal of contaminants present in wastewater, such as Iron Oxide (Fe_2O_3) [54], Cerium Oxide (CeO_2) [55], Zinc Oxide (ZnO) [54], Titanium Dioxide (TiO_2) [56], this being the one that has shown the best results, When it is irradiated with UV light, electrons are propelled into the conduction band of the catalyst from the valence band which in turns, generates holes that leads to the production of OH radicals, while the electron located in the conduction band by its negative charge repels oxygen molecules generating a significant amount of OH radicals.[57, 58]. Among its advantages, it is mentioned that it is cheap, it has a good band position, it is non-toxic and it has an adequate biocompatibility [59].

Diez et al. [60], compared the removal efficiencies and kinetic behavior of Fe_2O_3 and TiO_2 when subjected to a photocatalysis process, found that although with iron oxide higher degradations are achieved in terms of TOC, iron leaching occurs, which would require a subsequent treatment. Besides, the TiO_2 achieves a better bond with the reactor surface favoring the reaction kinetics. Additionally, it is proven that the addition of oxidants such as H_2O_2 favors the efficiency of the treatment, which is also validated by [29, 61] and it was applied to the heterogeneous photocatalytic process developed in numbers 3.3 and 3.4 of the present document. Another catalyst frequently used in photocatalytic processes and that has evidenced high removals is Zinc Oxide (ZnO) [12, 62, 63], however it has been shown that the photocorrosion generated is considered to be the main disadvantage of this catalyst and according to [64, 65], it presents lower photocatalytic activity compared to TiO_2.

The statement made by the authors mentioned above is true, because by implementing a heterogeneous photocatalytic process using TiO_2, COD and TOC removals higher than 57% are obtained using small doses of it, a similar event to the results was obtained by [66–68] who also achieved removals higher than 60% of organic materials, metals and contaminants emerging from leachates when they used the same catalyst.

It should be noted that the product used was not chemically or laboratory scale modified, but it is for commercial use and easily accessible for anyone wishing to repeat the experiments. As for new alternatives when applying this type of treatment, there is the modification of the chemical structures of the catalyst, in this case, of the TiO2. An example of the this is the fact that [69], who combined cerium oxide with titanium dioxide found that the heterostructure generated can enhance the degradation of recalcitrant contaminants through photocatalysis processes. It is also possible to conclude that future research should focus on catalyst doping in order to favor oxide reduction processes as to increase the kinetics reaction for the removal of emerging and recalcitrant contaminants [70, 71], which are present in large quantities in landfill leachate.

4 Conclusions

Based on the characterization of the leachate from the Guayabal Landfill, in terms of COD, DOC, TSS and VSS, it can be classified as a middle-aged leachate, whose COD/DOC ratio illustrated low biodegradable characteristics, therefore, in a biological process very low levels of degradation can occur, making it necessary to implement a previous phase that allows a more stable effluent and with more appropriate conditions to carry out this process.

The sludge coming from the treatment plant of El Country neighborhood, located in Jamundí, Valle del Cauca, provided the optimal and necessary characteristics to carry out the biodegradability test, since it showed a concentration of SVI (66.16 $mg.L^{-1}$), which categorizes it with good sedimentability, according to its use in a biological process.

Based on the biodegradability test (Zahn Wellens / EMPA OECD 302B), the leachates are not biodegradable, as less than 70% biodegradation rates were obtained, indicating that a process is needed prior to biological treatment, allowing for a more stable effluent with more consistent conditions so that significant removal levels exist and the test can be validated.

Taking into account the OCR (14.64 $mg.g^{-1}$ $VSS.h^{-1}$) indicating an adequate development of the microbial metabolism and a high biological activity of the sludge, it allowed the total degradation of ethylene glycol, used as a reference compound. Therefore, the fact that a considerable removal was not obtained in the biological process is due to the characteristics and toxic components that make up the leachate.

Heterogeneous photocatalysis (TiO_2/UV), provides higher removal percentages in acidic pH, and low TiO_2 concentrations, since taking into account the latter; the higher the catalyst concentrations, the incidence levels of UV rays decrease on the sample, which is reflected in the fact that the 600 mg $TiO_2.L^{-1}$ concentration for this project has provided the lowest removal percentages.

The results obtained in the coupling showed that after treating the leachate sample through the photocatalysis process, a much more stable effluent was available for the biological process, since within the biodegradability test, the efficiency in the removal of the contaminants increased by 50%, which improved the treatment conditions.

The need to couple this type of treatment for the reduction of contaminants and toxins present in the leachates is evident, since due to their harmful characteristics, they do not allow a removal of the contaminants present under conventional treatment processes, making it necessary to apply these new techniques that have proven to be an efficient alternative, as well as applicable in real scenarios.

In accordance with the country's current regulations, Resolution 0631 of 2015, issued by the Ministry of the Environment and Sustainable Development, taking into account the concentration of 500 mg $COD.L^{-1}$ of leachate used in this research, the final effluent from the coupled treatment process meets the characteristics for discharge in the COD (160 $mg.L^{-1}$) and pH (7.0 and 7.3) parameters. As for the suspended solids, high loads are still maintained, so in a real process, already having a sedimentation mechanism available, the values of these solids would begin to be significantly removed.

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