

An Acad Bras Cienc (2021) 93(1): e20190137 DOI 10.1590/0001-3765202120190137

Anais da Academia Brasileira de Ciências | Annals of the Brazilian Academy of Sciences Printed ISSN 0001-3765 | Online ISSN 1678-2690 www.scielo.br/aabc | www.fb.com/aabcjournal

ENGINEERING SCIENCES

Photocatalytic Ozonation Performance In Landfill Leachate Treatment

RAFAEL F. CARARD, GILSON JUNIOR SCHIAVON, THIAGO M. DE CASTRO, FLÁVIA V.S. MEDEIROS, GUILHERME DE PAULA, ANA CAROLINA M. LANDGRAF & EUDES J. ARANTES

Abstract: This work aims to identify the best treatment condition for removal of chemical oxigen demand (COD) and increase of biodegradability in an advanced oxidative process of photocatalytic ozonation with titanium dioxide (TiO₂), applied to the remediation of the leachate produced at the municipal landfill of Campo Mourão, Paraná. The experiment was carried out using a photocatalytic chamber and an ozonation system based on the corona effect. A statistical model of the central composite rotatable design (CCRD) was elaborated and three variables (pH, TiO₂ dose and airflow) were analyzed, to define the optimum condition that allows the highest perfomance of the treatment. The statistical model was valid for the data. The best condition identified was: pH = 3.3 TiO₂ dose = 0.012 g and flow = 9.0 L.min⁻¹ (8.79 g, O₃.min⁻¹). The removal of filtrate COD was approximately 30% and increase in biodegradability (BOD/COD) = 0.59 in the optimum condition. Factors such as the complex composition of the leachate and treatment time were considered as possible limitants for better results. The treatment did not allow to reach the permissible limits for disposal of the effluent at the environment, in Brazil.

Key words: Advanced oxidative processes, heterogeneous photocatalysis, Landfill Sanitary, leachate, ozonation, photocatalytic ozonation.

INTRODUCTION

With the increase of the population and the improvement of the quality of life, consumption is boosted by technological development, leading to the generation of a large amount of waste and effluents, such as the leachate. The main sources of this effluent are from the water infiltrated in the soil, the humidity that is already present in the residues and the humidity from the sludge, when present (Guidolini et al. 2005, Tavares 2011).

The leachate has a specific physicochemical composition, according to the original decomposed material, containing components such as dissolved and solubilized organic matter; nutrients; intermediate products of anaerobic digestion of the waste, as volatile organic acids; and chemicals, that include heavy metals like cadmium (Cd) and mercury (Hg), for example. This composition origins an effluent considered extremely damaging to the environment, being responsible for the contamination of soil, surface water bodies and groundwater, on site and in the whole surrounding region, due its toxic caracter. Beside that, the leachate carries pathogenic microorganisms that are harmful to humans, such as *Enterococcus*, *P. aeruginosa*, heterotrophic bacteria, fungi and even thermotolerant coliforms (*E. coli*) (Tavares 2011, Castilhos Junior et al. 2006, Peixoto 2008, Silva et al. 2011, Jucá & Sobrinho 2012). For the treatment of this type of effluent, there is a great diversity of systems, conventionally applied for the degradation and stabilization of pollutants, to promote their safe disposal at the environment. However, Renou et al. (2008) points out that most of the treatments are inefficient to reach the parameters established by the current environmental legislation.

For such, advanced oxidative processes (AOP's) may be a viable alternative. The basic principle of this form of treatment are the hydroxyl free radicals (\cdot OH), with high oxidative power. These, degrades the pollutant molecules decomposing them into stabilized and less harmful substances, leading to the destruction of organic components, such as carboxylic acids and transforming phenolic or chlorinated aromatic derivatives, into more harmless compounds, such as carbon dioxide (CO₂), mineral salts and water (H₂O) (Mehrjouei et al. 2015).

Among the AOP's employed, according to Guidolini et al. (2005), the use of ozonation is common, mainly in the case of leachate, with pollutants in high concentrations, that exceed the limits of the physicochemical parameters accepted by the environmental agencies, being capable of promoting the reduction of chemical oxygen demand (COD), biochemical oxygen demand (BOD), colour, turbidity and odour.

The ozonation process is already mentioned in the literature as a promising technology, with numerous real-scale applications for the treatment of industrial wastewater, using a strong oxidizing agent, ozone (O_3). Thus, it can be applied in the treatment of the compounds present in the landfill leachate, not forming an intrinsic source of pollution (Mahmoud & Freire 2007, Assalin & Durán 2007). Also, the treatment performed with O_3 can be intensified in complement with other forms of treatment, to stimulate the formation of radicals that cause a greater degradation. For this purpose, the use of UV radiation can increase the rate production of •OH radicals and bring more satisfactory results (Kammradt 2004).

From the AOP's currently used with UV radiation, heterogeneous photocatalysis with titanium dioxide (UV/TiO₂) demonstrated as a highly efficient technique. It acts in the total mineralization and destruction of contaminating pollutants present in water and effluents, being economical and environmentally beneficial, also removing microorganisms without generating dangerous by-products. Thus, with the use of AOP's applied simultaneously, it is carried out the transformation of toxic or recalcitrant compounds into biodegradable substances or easily removed by other simple processes, like biological or physico-chemical (Szczepanik 2017, Ahmad et al. 2016, Mehrjouei et al. 2015, Kammradt 2004).

Besides that, the use of O₃ and UV/TiO₂, individually, has limitations on its effectiveness in the degradation of organic pollutants, because UV/TiO, represents a slow process due to the low oxidation rate. Similarly, the oxidation process by molecular O₃, due to its high selectivity, only leads to the partial degradation of organic compounds, generating carboxylic acids and final products that can not be completely mineralized. These limitations end up making such processes economically unviable for treatment of effluents. For this, its simultaneous application resulting in the socalled photocatalytic ozonation, may compose a strong complementation of the processes because of the increased rate of degradation, leading to a more complete and efficient treatment (Mecha et al. 2016).

This process is considered a topic of recent research, and it is suggested in the literature that, the free electrons generated of TiO_2 , in its surface layer, interact with O_3 or O_2 molecules

generating superoxide radicals ($\cdot O_2^{-1}$). Subsequent reactions originate the chemical species called ozonide radical ($\cdot O_3^{-1}$), capable of decomposing into molecules $\cdot OH$ and O_2 , characterizing a synergism between the processes (UV/ TiO₂ and O₃). This synergism allows for the O₃ sequestration effect to avoid the recombination process in the catalyst, a limiting factor of UV/ TiO₂, as well as to form this radical $\cdot O_3^{-1}$, a highly reactive specie in the solution (Moreira et al. 2015, Rey et al. 2014).

With the induction of the photocatalytic process, the pairs (e⁻/h⁺) are generated, from which recombination may occur, causing negative effects of reduction and oxidation on the catalyst surface, reducing its interactions and performance. Because the electronic affinity of O₃ is higher than O₂, it is possible to promote photocatalytic reactions in the presence of O₃, more effectively than in the UV/ TiO_2 process alone, reducing these effects. Also, H₂O₂ formation is favoured through O₃, which also reacts with the catalyst surface to form •OH radicals (Gomes et al. 2017, Mecha et al. 2016, Mehrjoue et al. 2015, Mena et al. 2012).

Besides, the $\cdot O_3$ - radicals formed during O₃ adsorption may react directly with organic contaminants, forming the HO₃.⁻ radical, that also evolves to form O, and •OH. In addition, the reaction of O₃ with the pollutants themselves, such as phenols, amines and humic substances in the leachate, may act as promoters of their decomposition into $\cdot O_3^-$ and $\cdot OH$, thus accelerating the degradation of these pollutants in the solution. This demonstrates a large availability of reactive oxidative molecules (•OH, HO_3^{\dagger} , O_3^{\dagger} , O_3^{\dagger} , O_3^{\dagger} , h^{\dagger}) in the solution for degradation of a greater amount and diversity of pollutants. For this reason, such reconciliation has recently been studied in the degradation of different emerging contaminants (Gomes et al. 2017,

Mecha et al. 2016, Mehrjoue et al. 2015, Mena et al. 2012).

For Mecha et al. (2016) the process is effective in the treatment and detoxification of effluents to reach parameters necessary for its disposal, leading to a higher level of mineralization than that obtained by the sum of the processes used individually. Besides, Mena et al. (2012) evaluated the costs of photocatalytic ozonation in comparison to the individual processes, which showed that the operational costs were always higher than the simultaneous processes, making the photocatalytic ozonation not only attractive in terms of reaction rate, but also by the economy that is obtained.

There are not too many studies of the application of photocatalytic ozonation into landfill leachate treatment, especially in Brazil, where none is reported according to a survey carried out in the Capes journal, Science Direct and Scielo. Also, to evaluate the process in the remediation of leachate, it's necessary to determinate the possibilities of the treatment and the best conditions that allows to reach the maximum performance and the limits of disposal present in the legislation.

This work aims to identify the best treatment condition for removal of chemical oxygen demand (COD) and increase of biodegradability in an advanced oxidative process of photocatalytic ozonation with titanium dioxide (TiO₂), applied to the remediation of the leachate produced at the municipal landfill of Campo Mourão, Paraná.

MATERIALS AND METHODS

Leachate sample collecting

The leachate was collected at the municipal landfill of Campo Mourão. This was done with 50 L polyethene gallons at the entrance of the first treatment lagoon (anaerobic), being hermetically sealed and transported to the laboratory, being allocated in a horizontal refrigerator, with two compartments, at -4 °C, to minimize the biological and chemical reactions.

Analytical methods

To characterize the collected raw leachate, the following parameters were evaluated: pH, temperature, turbidity, crude COD, filtrate COD (COD-F), BOD_5^{20} and biodegradability (BOD/ COD). These parameters were obtained through specific equipment and different methodologies, provided in the Standard Methods for the Examination of Water and Wastewater (APHA 2012), a manual of the Polytechnic School of the University of São Paulo (Garcez 2004) and a manual of the University of São Paulo (Foresti et al. 2005).

To simplify the methods used, the following Table I is presented, establishing the methodology, the equipment and materials used in the determination of physico-chemical parameters.

From those parameters, COD-F and the relation BOD/COD were used to evaluate the treatment. Thus, for those parameters the measure was made before and after the treatment. In case of COD-F, as established by Amr & Aziz (2012), the following equation was used to determinate the efficiency removal provided by the treatment:

Removal (%) =
$$[(Ci - Cf)/Ci] * 100$$
 (1)

In equation (1) Ci and Cf correspond to the initial and final concentration of the parameter monitored, in the sample analyzed. The results of those determinations and the biodegradability measure in each sample were used to create the statistic model proposed. A discussion based in the scientific literature and a comparison with the current environmental legislation was made, to understand better the process and verify if it was possible to meet the levels for the disposal of the effluent "*in natura*".

Photocatalytic ozonation system

The system used to treat the leachate collected, had two distinct structures: heterogeneous photocatalysis and ozonation. The first structure corresponds to an irradiation chamber made of medium density fiberboard (MDF), with dimensions of approximately 50x33x32 (height, width and depth). On the upper external part of the chamber there is a switch, for activating the lamp, and behind it, a 250 W reactor, powered by an extension cord attached to a 220 V power plug. Inside, a vapour lamp of high pressure

 Table I. Methods, equipment and/or materials used to measure physicochemical parameters to characterize crude

 leachate and monitor photocatalytic ozonation process.

Parameter	Method - equipment and materials
Hydrogen potential (pH)	Direct measure - pH meter pH-221 Lutron;
Temperature	Direct measure - digital thermometer WT-1;
Turbidity	Direct measure - turbidimeter HI 93414 Hanna;
Crude and filtrate COD	Spectrophotometric COD < 800 mg O ₂ .L ⁻¹ – vacuum filter <i>Micron;</i> micro membrane of glass fibre GF-3 <i>MN</i> with 47 mm diameter; micro tubes <i>Hach;</i> digester block <i>Policontrol;</i> spectrophotometer <i>DR 500 Hach;</i>
BOD ₅ ²⁰	Five days test – flasks and BOD sensors Velp Científica; incubator stove Nova Técnica;

mercury with 250 W of power is installed in the upper part, connected to the reactor, without the external bulb, removed manually to avoid the effect of UV filter caused by the glass, as established by Schneider et al. (2014).

Under the lamp is placed a 600 mL glass beaker with a magnetic bar, the catalyst (TiO_2) and 250 mL of leachate, inserted into a plastic container upon a magnetic stirrer. The plastic vessel was used for insertion of ice cubes, to reduce the effect of increasing temperature of the solution, caused by irradiation. Together with this, on the side surface of the chamber, there is an entrance, in which is inserted a hose, relating to the second structure.

The second structure is composed of an air compressor, connected to a flowmeter with a capacity of 15 L.min⁻¹, used to regulate the air flow, coupled to a universal support, connected by a hose to the ozone reactor. The reactor consists of a wooden plate with two cylindrical coaxial tubes, of which in one of the tubes the entrance of the air generated by the compressor takes place. This air enters one side of the tube, passing through the inside of it and following to the hose that passes through the side entrance of the photocatalytic reactor, ending in the beaker with leachate.

The generation of O₃ occurs through the electric discharge caused by an electronic circuit located near the tube, which causes the corona effect. This electronic circuit is connected to a source that maintains constant current at 12.5 V and a second power supply that provides 45 W to cause O₃ generation. The system also has fans coolers for cooling effect. Given the excessive heating of the air compressor, a small fan was also directed towards it, to mitigate this effect.

Measure of O, production in the system

Because the air flow of the ozonation system compose an independent variable in the CCRD,

a determination of the amount of O_3 produced in the treatment was carried out using the iodometric titration method, established by the Standard Methods for the Examination of Water and Wastewater (APHA 2012), also used by authors such as Bassani (2010). Based on this methodology, the production of O_3 obtained with the atmospheric airflow applied by the compressor in the proposed system, can be determined by the equation (2) presented:

$$P_{O_3}(g.min^{-1}) = \frac{Ntio * V_{tio} * V_{KI} * 24}{t * V_{am}}$$
(2)

In the equation: $Po_3 = production of O_3$ (g O_3 .min⁻¹); Ntio = normality of thiosulfate; Vtio = volume of thiosulfate obtained in the titration (mL); VKI = volume of potassium iodide (KI) solution (mL); Vam = sample volume; t = bubbling time. This procedure was performed in duplicate, for some outflows foreseen in the CCRD, presented later. In the case of a very large divergence between the volumes obtained in the method, the process was repeated.

Considering the levels established in the CCRD, the results obtained with the iodometric method are presented below (Table II).

Based on the results obtained, a graph was created to observe the O₃ production behaviour

Table II. Determination of the O₃ production generated by the ozonator according to the compressor air flow rate.

Flowmeter flow (L.min ⁻¹)	O₃ (g.min⁻¹)
12	7.18
11	7.26
9.0	8.79
7.0	5.98
6.0	6.68
3.0	4.00

and to obtain the curve equation, allowing the quantification of this production in average and minimum values. Such a question was necessary because the iodometric method is an indirect measure, from which the turning point by titration becomes imperceptible in some values or even the variation is very small between one point and another. Thus, with the elaboration of the curve it was possible to perform reagent saving and the determination of an optimum production point on flow 9.0 L.min⁻¹ (8.79 g.min⁻¹).

In the modelling of O_3 production values, the trend line closest to the data behaviour was the polynomial of the second order, with R² of 0.79. The results obtained as presented (Table II), were taken into account in the proposed experimental design, in order to contribute for the selection of a flow range corresponding to a viable average production of O_3 , in theory, that would lead to a better degradation of the effluent.

Statistic analyses

To perform a statistical analysis of the data, a factorial design of the type central composite rotatable design (CCRD) was developed. The definition of the independent variables (factors) of pH, TiO₂ dose and ozone dose, as well as their respective levels were established through the revised literature. To compose a process of greater viability, considering also the literature and the high recalcitrance of the effluent, it was evaluated as a response of this planning: the

efficiency of COD-F (%) removal and the increase of biodegradability through the BOD/COD ratio.

For the creation and analysis of the design, the software Statistica 7.0 was used. The planning adopted in this process, having the three independent variables, compose a planning CCRD 2³, this is, corresponding to a total of 8 experiments, 6 axial points and 3 central points, equal to a total of 17 tests, to determinate the optimal operating condition for photocatalytic ozonation process. To be a complete planning 2^3 , the axial points (α) define the coded levels -1,68 and +1,68. As follow, it's presented the independent variables, the levels adopted and the codification of those in the matrix of the experiments design (Table III and Table IV). Worth highlighting that in the CCRD, the variable ozone dose is presented as the variation supplied by the compressor, from which was possible to control in a pratic manner, by the flowmeter.

With all the data from the 17 tests, statistical analyzes were performed to obtain the effects of variables, analysis of variance (ANOVA), to verify the lack of adjustment, plotting of responses and especially, the desirability function of the model for visualization of the best condition for removal of COD-F (%) and increase of biodegradability (BOD/COD).

This optimal condition was repeated experimentally to validate the model prediction, and the complementary parameters were analyzed together to obtain the system response, in this condition, in a better way. Descriptive

Table III. Variables and defined levels for the CCRD (2³) referring to the factors: pH; TiO₂ dose (g) and air flow (L.min⁻¹).

F	Levels						
Factors	-1.68 (-α)	-1	0	1	+1.68(+α)		
рН	1.6	2.0	2.5	3.0	3.3		
TiO ₂ dose (g)	0.003	0.005	0.0075	0.010	0.012		
Air flow (L.min ⁻¹)	3.0	4.0	6.0	8.0	9.0		

Tests	рН	TiO ₂ dose (g)	Air flow (L.min⁻¹)
1	-1	-1	-1
2	+1	-1	-1
3	-1	+1	-1
4	+1	+1	-1
5	-1	-1	+1
6	+1	-1	+1
7	-1	+1	+1
8	+1	+1	+1
9	-1.68	0	0
10	+1.68	0	0
11	0	-1.68	0
12	0	+1.68	0
13	0	0	-1.68
14	0	0	+1.68
15	0	0	0
16	0	0	0
17	0	0	0

Table IV. CCRD planning	matrix (2 ³) with th	e coding of operationa	l variables (factors)
-------------------------	----------------------------------	------------------------	-----------------------

statistics analysis was also performed for the data in which removal was measured (%).

Experimental procedure

The procedure adopted to apply the treatment of photocatalytic ozonation in the leachate consists in the following series of steps:

- The monitoring parameters are measured in the raw leachate sample (250 mL);
- The photocatalytic reactor cover is partially closed and the lamp is switched on and left on for 1 min for irradiation stabilization;
- The air compressor is activated and the flowmeter regulated at the specific flow rate to be tested;
- Both power supplies are switched on and 15
 s are waited for O₃ generation stabilization, the compressor is then switched off briefly;
- 5) The pH of the raw sample is corrected by titration with 0.01 and 1 N sulfuric acid

(H₂SO₄) and sodium hydroxide (NaOH), measured with the pH meter until the adjustment of the value in the condition to be tested;

- 6) In the beaker with the solution, a magnetic bar is inserted, and it is placed inside the photocatalytic chamber, in the plastic container, on the magnetic stirrer;
- 7) The outlet of the hose from the ozonation reactor is position the effluent;
- The TiO₂ catalyst, previously weighed in analytical balance, according to the condition to be tested, in a 25 mL beaker is manually inserted into the solution;
- Ice cubes are placed inside the plastic container, the magnetic stirrer is started and the cover of the photocatalytic reactor is closed;
- 10) Soon after (about 5 s), simultaneously the compressor and the lamp are activated,

initiating the treatment process, measured during its course by a stopwatch.

The treatment applied had a maximum duration of 60 min, in which after its completion, the treated sample was withdrawn to re-measure the physical-chemical monitoring parameters. The commercial chemical catalyst tested was Degussa® TiO_2 P-25 composed of: 80% anthestase and 20% rutile, as a white powder, odourless, with 21 nm particles.

For the photocatalytic treatment, the UV lamp was selected because of its medium pressure, emitting photons of length 253.7 nm and low operating temperature, besides 90% of the emission being foreseen within the minimum absorption range by the catalyst used. Its use provides a more compact and lower cost system (Ilha 2012, Teixeira & Jardim 2004).

RESULTS AND DISCUSSION

Leachate characterization

The characterization of the leachate related to the parameters analyzed is presented below (Table V).

Table V. Physical-chemical characterization of thecrude leachate collected on June 21, 2017 at themunicipal landfill of Campo Mourão, Paraná.

Physicochemical parameters	Min – Max
pН	8.89 - 8.98
Temperature (ºC)	24.5 - 24.83
Turbidity (NTU)	144 – 354
Crude COD (mg O ₂ .L ⁻¹)	995.05 - 1019.80
COD-F (mg O ₂ .L ⁻¹)	987.10 - 1003.90
BOD ₅ ²⁰ (mg O ₂ .L ⁻¹)	216 – 254
BOD/COD	0.22 - 0.25

Taking into account the time of operation of the municipal landfill from Campo Mourão, 14 years (according to the operating license), as well as the considerations made by Souto (2009) and Renou et al. (2008), its possible to classify the leachate collected as being in the phase of methanogenic degradation, that is, "mature" leachate. This fact can be highlighted by the values of parameters such as pH, COD and BOD_5^{20} previously presented. The BOD/COD ratio, between 0.22 and 0.25, confirms that the effluent is in a more advanced state of degradation.

According to Kurniawan et al. (2006a) and Renou et al. (2008), this BOD/COD ratio up to 0.25, between 0.1 and 0.5, is more common in medium/intermediate age leachates, and that a BOD/COD ratio of less than 0.1 represents a more specifically leachate, in the final phase of stabilization. It is possible to consider that the characterized effluent is in a transition phase from the initial methanogen to stabilized. For Renou et al. (2008), the BOD/COD ratio decreases from 0.70 to 0.04 as time passes in the landfills, because large recalcitrant molecules are released by the residues, which consequently renders the landfill leachate "mature" characteristic, presenting low values of BOD/COD, for example.

Lima (2008) performed the characterization of the Campo Mourão landfill leachate, obtaining variations from 1488 to 1738 mg O_2 .L⁻¹ for COD; 696 to 725 mg O_2 .L⁻¹ for BOD₅²⁰; pH ranging from 8.01 to 8.45, with a BOD/COD ratio of 0.41 to 0.46, demonstrating a superior biodegradability in this case. This fact confirms that the leachate collected is in a more advanced phase of degradation, than in 2008, according to the characterization of the author, following to a stabilized methanogenic phase.

Process optimization

Based on the experimental design, it was possible to obtain removal efficiencies for

COD-F (%) ranging from 7.85 to 28.95% and increase of biodegradability from 0.36 to 0.64 for the leachate treated. The best result, for both response variables, corresponded to test 10, with a maximum reduction of 28.95% COD-F (%) and increase of the BOD/COD ratio of the effluent to 0.64. Obviously, the increase in biodegradability is related to a greater reduction of COD considering the relation used, however, it is worth mentioning that the behaviour of BOD₅²⁰ was also determinant in this case, justifying tests in which the increase of biodegradability was superior, but the removal of COD-F (%) lower.

The results obtained for the variables studied in each of the 17 tests that compose the CCRD (2³), elaborated for the study of the photocatalytic ozonation process are presented below (Table VI).

To understand the influence of the variables on these results, the effects of the

pH, dose (g) and flow (L.min⁻¹) variables and their interactions, obtained through software Statistica 7.0, are shown below, for COD-F (%) removal and increase of biodegradability (BOD/ COD), at a significance level of 95% (p-value <0.05) in Table VII.

On Table VII, the significant effects (p-value <0.05) are shown in bold. To obtain a more valid fit, most of the insignificant effects on the model were ignored for both COD-F (%) removal and biodegradability increase. Some of the not significant effects, with p-value close or superior from 0.05, and also with the similar linear or quadratic effect significant, were mantained, to keep the high adjustment of the model. For COD-F (%) removal those effects were: pH (L) and air flow (L.min⁻¹) (Q); For biodegradability increase the effects were: pH (L) and TiO₂ dose (g) (L).

		Factor	5	Responses						
Tests	pH TiO		Air flow	COD-F (mg O ₂ .L ⁻¹)		COD-F removal	BOD ₅ ²⁰ (mg O ₂ .L ⁻¹)		Biodegradability (DBO/DQO)	
		4656 (3)	(/	Raw	Treated	(%)	Raw	Treated	Raw	Treated
1	2.0	0.005	3.0	744.12	671.37	9.78	259	338	0.35	0.50
2	3.0	0.005	3.0	786.21	688.48	12.43	236	327	0.30	0.48
3	2.0	0.01	3.0	818.30	622.15	23.97	130	221	0.16	0.36
4	3.0	0.01	3.0	811.17	605.74	25.33	130	251	0.16	0.41
5	2.0	0.005	9.0	821.16	626.43	23.71	244	311	0.30	0.50
6	3.0	0.005	9.0	826.86	663.52	19.75	244	288	0.29	0.43
7	2.0	0.01	9.0	756.25	570.08	24.62	244	346	0.32	0.61
8	3.0	0.01	9.0	778.36	594.33	23.64	235	338	0.30	0.57
9	1.6	0.0075	6.0	766.95	573.64	25.20	235	348	0.31	0.61
10	3.3	0.0075	6.0	761.24	540.83	28.95	235	346	0.31	0.64
11	2.5	0.003	6.0	744.83	686.34	7.85	243	252	0.33	0.37
12	2.5	0.012	6.0	800.47	690.62	13.72	243	342	0.30	0.50
13	2.5	0.0075	4.0	809.03	654.25	19.13	243	326	0.30	0.50
14	2.5	0.0075	8.0	794.77	678.50	14.63	234	261	0.29	0.38
15	2.5	0.0075	6.0	744.83	661.38	11.20	259	308	0.35	0.47
16	2.5	0.0075	6.0	806.89	669.94	16.97	234	283	0.29	0.42
17	2.5	0.0075	6.0	746.26	628.57	15.77	259	281	0.35	0.45

Table VI. Factors and responses obtained according to the variation of the decoded levels and the predicted tests in the factorial planning for photocatalytic ozonation treatment.

By the obtained values, most of the factors present a synergistic effect, indicating that as the increase of these factors cause the increase in removal of COD-F (%) and biodegradability. The only significant antagonistic effect, that is to say, opposite to better results, was the interaction air flow versus TiO_2 dose (L), indicating that the interaction between these variables is negative, so even if a superior air flow is used, the negative effect of the catalyst dosage may prevail, leading to a decrease in COD-F (%) removal (Barros Neto et al. 2001). For biodegradability increase the antagonistic effect obtained was pH (L), but not significant in the model.

It is worth mentioning in this case, that the interaction air flow x TiO_2 dose (L) is considered synergistic in biodegradability increase, inverse to that obtained in the removal of COD-F (%), probably because it considers the BOD₅²⁰ data. It can also be inferred that the TiO_2 dosage exerts little influence on the biodegradability results.

To establish the validity of the statistical model of the presented data, based on the significant effects, a variance analysis (ANOVA) was performed considering the pure error, allowing to detect if the lack of fit was significant in the model adopted (Table VIII).

For both cases, the p-value less than 0.05 indicates that the regression factors, or at least one of them has a significant impact on the mean response obtained. Also, this value also establishes the probability of Fcalculated (Fcal) being close to the Ftable (Ftab), to be lower than 0.05, considering a 95% confidence interval, indicating that the model is valid. The Fcal superior to Ftab presents, in of regression, that the mathematical model can be considered predictive for the data, in both cases. The p-value for lack of adjustment was greater than 0.05, so the lack of adjustment is not significant, which is also portrayed by the Fcal lower than the Ftab, in this case.

COD-F removal (%)							
Factors/Interactions	Effect	Mean	t(10)	p-value			
Main Interactions	13.34	1.22	10.94	0.00			
рН (L)	0.80	1.52	0.52	0.61			
рН (Q)	10.22	1.61	6.36	0.00			
Air flow (L.min ⁻¹) (L)	4.07	1.52	2.67	0.02			
Air flow (L.min ⁻¹) (Q)	2.96	1.61	1.84	0.09			
TiO ₂ dose (g) (L)	6.09	1.52	3.99	0.00			
Air flow x TiO ₂ dose (L)	-5.60	1.99	-2.81	0.02			
	Biodegradability	increase (BOD/COD)				
Main Interactions	0.43	0.01	39.27	0.00			
рН (L)	-0.003	0.02	-0.15	0.88			
рН (Q)	0.12	0.02	6.70	0.00			
Air flow (L.min ⁻¹) (L)	0.08	0.02	4.48	0.00			
TiO ₂ dose (g) (L)	0.04	0.02	2.07	0.06			
Air flow x TiO ₂ dose (L)	0.11	0.02	4.78	0.00			

 Table VII. Significant effects and interactions, standard error, degrees of freedom and p-value significance level of

 95% for COD-F removal and biodegradability increase.

With the estimation of effects and analysis of ANOVA, it was possible to construct a predictive statistical model for the COD-F (%) data with a R² of 0.88 and R-adjusted of 0.80, indicating that 80% of the variation of the presented data can be explained by this. Likewise, in the case of increased biodegradability (BOD/COD), the R² was 0.89 and an adjusted R-value of 0.84, indicating that the model can cover 84% of the variation in the data obtained by the treatment.

Based on the statistical model presented, the equations that govern the relationship between the factors and the response variables for modelling the COD-F (%) removal (y_1) and biodegradability increase (BOD/COD) (y_2) data, are as follows on (3) and (4):

$$y_1 = 13,33 + 0,40.x_1 + 5,11.x_1^2 + 2,03.x_2 + 1,48.x_2^2 + 3,04.x_3 - 2,80.x_2.x_3$$
(3)

$$y_2 = 0,43 - 0,0014.x_1 + 0,06.x_1^2 + 0,04.x_2 + 0,02.x_3 - 0,05.x_2.x_3$$
(4)

In (3) and (4) the variables x_1 , x_2 and x_3 correspond to:

- x₁ = pH: 1.6 (-1.68); 2.0 (-1); 2.5 (0); 3.0 (+1);
 3.3 (1.68);
- x₂ = TiO₂ dose (g): 0.003 g (-1.68); 0.005 g (-1); 0.0075 g (0); 0.01 g (+1); 0.012 g (+1.68);
- x₃ = air flow (L.min⁻¹): 3.0 L.min⁻¹ (-1.68); 4.0 L.min⁻¹ (-1); 6.0 L.min⁻¹ (0); 8.0 L.min⁻¹ (+1); 9.0 L.min⁻¹ (+1.68).

For a better visualization of the results obtained by the statistical modelling, the behaviour of the COD-F (%) removal and biodegradability (BOD/COD) data, according to the factors used, are plotted in response surfaces as follows in Figure 1. It is emphasized that the variation in these surfaces corresponds to the decoded levels. The regions, with different tones, suggest in what condition superior results were obtained and the dots are equivalent to the results obtained in the tabulated tests, already presented.

As shown in Figure 1, the model demonstrates that the use of a high O_3 flow, corresponding to 9.0 L.min⁻¹ (8.79 g O_3 .min⁻¹) favours higher removals, together with the association of a

Variation source	SQ	DF	MQ	Fcal	Ftab	p-value (Fcal/Ftab)				
	COD-F(%) removal									
Regression	571.04	6	95.17	11.99	3.01	0.00				
Waste	79.39	10	7.94							
Lack of fit	60.64	8	7.58	0.81	6.09	0.66				
Pure error	18.75	2	9.37							
Total	650.43	16	40.65							
R ²	0.88									
R-adjusted	0.80									
	Biode	egradability in	crease (BOD/0	COD)						
Regression	0.103	5	0.021	18.443	3.012	0.00				
Waste	0.012	11	0.001							
Lack of fit	0.011	9	0.001	2.595	6.094	0.31				
Pure error	0.001	2	0.000							
Total	0.115	16	0.007							
R ²	0.89									
R-adjusted	0.84									

Table VIII. Analysis of variance (ANOVA) of the statistical model to increase biodegradability (BOD / COD).

higher TiO_2 dosage (0.01 and 0.012 g) (a, b). The pH in this case is presented as a more flexible factor, that is, in both lower value (1.6) and higher (3.3), the higher removals in COD-F (%) can be obtained. For biodegradability increase, in the case of the TiO_2 dosage and the O_3 flow (d,e), values taken as central, in both cases, provided the best results based on their location near the darker region on the surfaces. In these cases, pH is a determinant factor for this, so that its variation in 1.6 and 3 would also lead to a higher performance. This can be seen, in both cases, considering that the pH having only significant quadratic effects.

The model also reflects for the factors such as catalyst dose and airflow, that the use of a larger quantity would lead to better results. It is noteworthy that in this cases, pH prevailed as a determining factor to obtain a superior performance according to the presented surfaces. Thus, considering the versatility of the photocatalytic ozonation system as regards the pH factor, as the model itself showed, changes could be made that would bring better performance, considering the PCZ of the catalyst.

Based on these considerations, obtain the optimal condition of the model, with a focus mainly on the increase of biodegradability, it is presented the result of the desirability function of the statistical model, according to Figure 2.

In this function, it was chosen to give a greater weight to the increase of the BOD/ COD ratio. As indicated, based on the statistical model previously presented, the best condition would correspond to the maximum levels defined in the CCRD for all factors. Thus, the



Figure 1. Response surfaces obtained by statistical model for COD-F (%) removal and biodegradability increase (BOD/COD). For COD-F (%) removal: (a) pH versus air flow; (b) pH versus TiO₂ dose (g); (c) Air flow versus TiO₂ dose. For biodregadability increase: (d) pH versus air flow; (e) pH versus TiO₂ dose; (f) Air flow versus TiO₂ dose.

pH of 3.3, the TiO₂ dosage of 0.012 g and an air flow of 9.0 L.min⁻¹ (8.79 g O₃.min⁻¹) would allow a removal of approximately 29% of COD-F (%) and the increase of the biodegradability of the effluent, BOD/COD ratio, to 0.64, approximately.

Considering the obtained employing the function, a last test was carried out examining which were the answers of the system regarding to the pre-established optimal condition. The results predicted by the model and those obtained experimentally are presented below (Table IX).

By the response of the desirability function, it is possible to consider that the model was shown to be predictive. The pre-established efficiency of 29% according to the presented conditions, resulted in the practice, in a response of 30.13% of removal of COD-F (%), value even more positive than that established by the model. The biodegradability of the treated leachate resulted in a predicted, but lower value of BOD/COD = 0.59, post-treatment.

Sense high R² values were obtained: 0.88 and 0.89, it is expected that the model corresponds to the reality verified. Despite of this, it is important to emphasize that the high R-adjusted is more significant for analysis of the fit of the model, because it considers the degrees of freedom, that must be higher than the number of coefficients of the model, composing



Figure 2. Results of the model desirability function regarding the removal of COD-F (%) and biodegradability increase (BOD/COD) of the data obtained for the process of photocatalytic ozonation in leachate landfill.

a more statistically faithful coefficient. The R-adjusted values were also high, 0.80 and 0.84, confirming that the model is predictive for the data and range studied. The variation obtained occurs because the model predicts only 80% and 84% of COD-F (%) removal and increase of biodegradability (BOD/COD) data.

COD-F removal and increase of biodegradability discussion

It can be seen from Table VI that the treatment did not allow for high COD-F reductions, achieving maximum efficiency of 28.95% in test 10 and a minimum of 7.85% in the test 11. Even test of validation, with maximum levels of all the variables studied, corresponding to the best condition, resulted in a maximum of 30.13%, as previsouly presented.

Considering the scientific literature, high values were expected in both heterogeneous photocatalysis and ozonation, applied individually, demonstrate high performances in the COD removal. Despite this, in these studies generally higher treatment times are noticed, which was not applied in this work, due to the limitations of the ozonization system used, because of the heating of the compressor.

As for BOD₅²⁰, all the tests carried out made it possible to increase this parameter in the raw leachate, being more evident in tests 9 and 10. This associated with the reduction of COD-F made it possible to increase the biodegradability

Table IX. Expected results and obtainedexperimentally for optimal condition established bythe statistical model.

Variable response	Experimental results	Predicted results
COd-F (%) removal	30.13%	29%
Biodegradability increase (BOD/ COD)	0.59	0.64

of the effluent from a minimum of 0.16 (tests 3 and 4), indicating a need for more advanced treatment, up to a minimum ratio of 0.36 (in test 3) and a maximum of 0,61 and 0,64 (tests 9 and 10), high, considering the recalcitrance of the leachate.

According to Kurniawan et al. (2006b), for a BOD/COD ratio of 0.3 or higher, the biological treatment is more indicated because the organic compounds in the leachate have already been transformed into more biodegradable compounds. Chemlal et al. (2014) states that in a BOD/COD ratio of 0.6, a complete degradation of the leachate occurs naturally through the action of microorganisms.Taking into account the data in Table VI, the following descriptive statistics are presented (Table X).

Based on the previous table, it can be seen that the COD-F of the raw leachate showed little variation, from 744.12 to 826.86 mg O_{2} .L⁻¹, with a mean value of 783.49 mg $O_2.L^{-1}$ and a standard deviation of approximately 29.96 mg O₃.L⁻¹. This small variation is considered since the samples comprise replicates with each other, considering that the measurement of this parameter in the raw effluent, occur on average on the same day, for at least three tests at a time. With the treatment it was possible to reduce the COD-F to a range of 540.83 to 690.62 mg O_3 .L⁻¹, with an average value of 636.83 mg O_2 .L⁻¹ considering the 17 tests performed. The standard deviation of 46.42 mg O_3 . L⁻¹, higher, ranged from variation of results and different removal performances according to factor variation in CCRD and the treatment process.

For BOD₅²⁰, the variation was in a range of 130 to 259 mg O₂.L⁻¹, with a mean of 230 mg O₂.L⁻¹, a standard deviation of 38.53 mg O₂.L⁻¹, a median of 304 mg O₂.L⁻¹ and a slightly higher standard deviation of 40.14 mg O₂.L⁻¹ were obtained for a range of 221 to 348 mg O₂.L⁻¹. In the case of BOD₅²⁰, the fact that the raw samples correspond to the

Descriptive statistics								
Parameter	Mean	Minimum	Maximum	Stardard Deviation				
COD-F (raw)	783,40	744,12	826,86	29,96				
COD-F (treated)	636,83	540,83	690,62	46,42				
BOD ₅ ²⁰ (raw)	230	130	259	38,53				
BOD_{5}^{20} (treated)	304	221	348	40,14				

Table X. Descriptive statistics for COD-F and BOD,²⁰ data for raw leachate and post-treatment.

average of duplicates, may have contributed to a lower standard deviation.

The increase in BOD_5^{20} was evident in all tests, as well as in the study by Monje-Ramirez & Velásquez (2004), which associated this effect with the transformation of recalcitrant organic compounds into biodegradable intermediates. The authors noted an increase of up to 265% in the values of BOD_5^{20} in the leachate by promoting ozonization, including in other studies in which the same effect was observed.

It is not considered that the low removal of COD-F is associated with the variation of the pH range, even if small, taking into account also that only its quadratic interaction was significant, according to the CCRD. As discussed by Cho et al. (2002) the photocatalysis process should be conducted at a pH range lower than 4.5, considering that the extraction of alkalinity and bicarbonate ions present in the leachate, since together with inorganic carbons, can compete with organic materials and cause scavenging effects on photogenerated gaps. The authors obtained removals in COD of 60 to 80% in the conditions of pH 2.0 and 4.0, after 12 h of treatment with 3.0 g.L⁻¹ of TiO₂.

Besides, under acidic conditions below the PCZ of the catalyst, the attractive forces between the surface of the TiO_2 , from which it is positively charged, producing •OH radicals and negatively charged materials such as Cl⁻, PO₄³⁻, SO₄²⁻, NO₂⁻, among others, favours its adsorption, decreasing the photocatalytic activity, hindering the production of the radicals and preventing other compounds from approaching the active sites in the catalyst. Especially the Cl⁻ ion, in addition to the PO_4^{3-} and SO_4^{2-} ions, can react with the radicals or the generated h⁺ gaps, forming radicals with lower oxidative power, resulting in a lower rate of degradation (Cho et al. 2002, Ramdhani 2018). This may have been one of the factors due to the low efficiencies obtained.

Cho et al. (2004) obtained the reduction of an initial concentration of 706 mg.L⁻¹ to the maximum of 315 mg O_2 .L⁻¹, about 52% removal efficiency, after 5 h of treatment with 3,0 g.L⁻¹ of TiO₂ of which, for the authors, did not show an increase after this period. The authors considered that complete photocatalytic mineralization in the case of leachate is difficult and that the catalyst deactivation process is evident because of the adsorption of non-photodegradable materials, remaining in the solution after treatment, such as siloxane compounds. These compose inactive species that are deposited on the surface of the catalyst and block the adsorption of O₂, for example, directly injected with ozonation, in the case of photocalytic ozonation treatment.

As for the dosage of the applied catalyst, it is worth noting that it was selected according to the preliminary tests, in a range that made possible the removal of COD-F (%). Also, Wiszniowski et al. (2003) presented that the removal of humic substances in leachate is superior to low TiO_2 dosages, corresponding to 0.1 and 0.3 g.L⁻¹, allowing reductions of 20 to 60% with these, while dosages from 0.5 g.L⁻¹ showed low performance due to the opacity effect on the effluent, which in the case of this work, was not observed.

The reaction time may also have been low in the treatment, as Thuong & Binh (2015) obtained removals close to 40% COD with 60 min of reaction, reaching 52.9% in 90 min treatment with 0.5 gL⁻¹ of TiO₂. Although time is an important factor, based on that established by Shaykhi & Zinatizadeh (2014), it did not demonstrate effects on the photocatalytic ozonation, in terms of COD removal, on effluent containing amoxicillin submitted to the 240 min reaction. According to the authors, one of the factors that may have contributed to the low efficiency of COD removal (11.7%) may have been its initial concentration (1200 mg O₂.L⁻¹). However, the authors demonstrate that the reaction time factor was paramount to achieve a higher BOD/ COD ratio.

No longer irradiation periods were applied, since the factor was not considered in the CCRD and because of the system limitation regarding the heating of the compressor, which was verified in all the tests.

From the considerations presented, regarding the role of the photocatalytic process, the applied ozonation also did not increase the efficiency of the process in an evident way. This question can be verified according to Rivas et al. (2003) from which it obtained similar removals, about 30% for COD with ozonation in 60 min of treatment, not observing significant improvement effects when also using O_3/UV ; O_3 with hydrogen peroxide (H_2O_2); $O_3/UV/H_2O_2$ and O_3 /heterogeneous catalyst, with 120 min of treatment. The authors conclude that the composition of the "mature" leachate, with

considerable fractions of high molecular weight substances and recalcitrant characteristics may be responsible, since the oxidizing molecules are more resistant, with a complex structure devoided of reactive functional groups (Bassani 2010, Morais & Peralta-Zamora 2005).

The authors present similarities in the results, even varying the pH, considering that the removals independent of this factor was associated with the substances present in the effluent to be degraded, mainly by direct (molecular O_3). Thus, •OH radicals, by their non-selective nature, are likely to be wasted in parallel reactions with hijackers of low or zero COD content. Despite this, the authors also showed an increase of BOD_5^{20} in the leachate, after ozonization, evolving from approximately 450 to 800 mg O_2 .L⁻¹ resulting in a BOD/COD evolution of 0.1 to 0.25, allowing post biological treatment.

The increase of the O_3 flow did not seem to promote significant changes, since similar efficiencies were observed for the flow rates: 3.0, 4.0, 6.0 and 8.0 and 9.0 L.min⁻¹ (4.00, 4.91, 6.68, 7.43, 8.79 g O_3 .min⁻¹), although the best removal condition corresponded to the maximum dosage adopted.

Cortez et al. (2010) noted an increase in efficiency by ozonation, with a flow rate of 0.83 to 2.5 L.min⁻¹, with removal of 23% COD after 60 min of treatment. According to the authors, in the case of leachate, it is noted that the removal efficiency for COD in the initial 30 min increases rapidly, due to the oxidation of compounds such as phenols, quinones and aromatic acids occur faster. However, as the reaction proceeds, the formation of by-products such as aliphatic, oxalic and aldehyde acids (responsible for pH change, as already discussed), make the treatment difficult, since they are more complex to decompose (Ntampou et al. 2006). Bila et al. (2005) used similar dosages as those used in this study, ranging from 0.5 to 9.0 g O_3 .L⁻¹ of which obtained high COD reductions with flow rates of 7.0 and 9.0 g O_3 .L⁻¹, with the higher consumption of the gas, noting the same difficulty of degradation as the reaction progresses. In both studies presented above, the authors obtained increase of BOD/COD, making possible the use of biological post-treatment.

Amaral-Silva et al. (2016) obtained low removals of 10% COD with 60 min of treatment, which suggests that the reaction time of 60 min is characterized by the transformation of organic molecules into smaller intermediates, without significant changes in COD. The authors also show that even increasing the dosage from 5 to 20 mg O_3 .min⁻¹, the efficiency increases are very mild (~ 10%), so that the oxidation time of 3 h allowed more significant removals for COD (up to 43%). This may establish that the treatment time used for photocatalytic ozonation, considering ozonation, may also have been insufficient to promote the necessary changes to the extent of COD-F (%) removal.

Despite the results for COD-F, the increase of biodegradability in the leachate was evident and possibly higher than the one obtained with the use of the separated processes, as observed by Rajeswari & Kanmani (2009) in effluent containing Carbaryl, with a dose of 1.0 g.L⁻¹ of TiO₂ and 0.28 g O₃.h⁻¹, with an increase in relation to BOD/COD = 0.38, of which the authors already consider the effluent as biodegradable in nature and suitable for secondary biological treatment.

Based on that obtained by the treatment of photocatalytic ozonation for landfill leachate, considering the current legislation (CONAMA nº 430/2011 and CEMA nº 70), the disposal of the treated effluent could still cause harmful alterations to the environment. Despite this, the resulting high BOD/COD ratio suggests that the effluent, previously unfit for biological treatment, can proceed to a subsequent treatment, due to its current biodegradability, to reach the established limits.

CONCLUSIONS

With the physical-chemical characterization of the leachate produced in the municipal landfill, considering the operation time, it was achievable to classify the effluent in "mature" leachate, possibly in a transition phase to stabilized methanogenic. Considering the scientific literature and the reduction of the BOD/COD ratio, there is a need for a more advanced treatment, due to the high recalcitrance the effluent can present in the future, for the biological treatment, currently applied.

It was verified, through the CCRD and the treatment tests, that the factors pH, TiO_2 dose and O_3 flow have significant effects on the removal of COD-F (%) and increase of biodegradability (BOD/COD) of the leachate. The statistical model, considered valid and without a significant lack of fit, contributed to establishing the best operational condition of the treatment, corresponding to the maximum levels defined: pH = $3.3 TiO_2$ dose = 0.012 g and flow = 9.0 L.min^{-1} (8.79 g, $O_3 \text{.min}^{-1}$). The validation of the prediction of the model allowed to reach close results for COD-F (%) and BOD/COD ratio, making a valuable tool for studies involving the treatment of leachate.

The limitations observed during the treatment may have occurred because of the composition of the leachate, with complex compounds, recalcitrant and scavengers that impair the performance of the process. Also, it may be considered that limited conditions, such as the maximum treatment time of 60 min, may have contributed to this issue, since other

RAFAEL F. CARARD et al.

studies establish longer treatment periods to obtain better results.

Based on the current environmental legislation (CONAMA 2011 and CEMA 2009), none of the analyzed parameters, would hypothetically allow the disposal of treated effluent in the environment, requiring complementary treatment.

REFERENCES

AHMAD RETAL. 2016. Photocatalytic systems as an advanced environmental remediation: Recent developments, limitations and new avenues for applications. J Environ Chem Eng 4: 4143-4164.

AMARAL-SILVA N ET AL. 2016. Ozonation and perozonation on the biodegradability improvement of a landfill leachate. J Environ Chem Eng 4: 527-533.

AMR SS & AZIZ HA. 2012. New treatment of stabilized leachate by ozone/Fenton in the advanced oxidation process. Waste Manag 32: 1693-1698.

APHA - AMERICAN PUBLIC HEALTH ASSOCIATION. 2012. Standard Methods for the examination of water and waste water. 22 ed. American Public Health Association, 1360 p.

ASSALIN MR & DURÁN N. 2007. Novas tendências para aplicação de ozônio no tratamento de resíduos: ozonização catalítica. Revista Analytica, São Paulo, n. 26.

BARROS NETO B, SCARMINIO IS & BRUNS RE. 2001. Como fazer experimentos: Pesquisa e desenvolvimento na ciência e na indústria. 2 ed. Campinas: Editora da Unicamp, 401 p.

BASSANI F. 2010. Monitoramento do lixiviado de aterro controlado de Maringá, Paraná, e avaliação da tratabilidade com coagulantes naturais, radiação ultravioleta (UV) e ozônio. Dissertação (Mestrado em Engenharia Urbana) — Programa de Pós-Graduação em Engenharia Urbana, Universidade Estadual de Maringá. Maringá, 127 p. (Unpublished data).

BILA DM ET AL. 2005. Ozonation of a landfill leachate: evaluation of toxicity removal and biodegradability improvement. J Hazard Mater B117: 235-242.

CASTILHOS JUNIOR AB ET AL. 2006. Gerenciamento de resíduos sólidos urbanos com ênfase na proteção de corpos d'água: prevenção, geração e tratamento de lixiviados de aterros sanitários. Rio de Janeiro: ABES, p. 494. CEMA. 2009. Resolução № 70, de 01 de Outubro de 2009. Dispõe sobre o licenciamento ambiental, estabelece condições e critérios e dá outras providências, para Empreendimentos Industriais. Diário Ofícial da União. n. 8068. Curitiba, Paraná.

CHEMLAL R ET AL. 2014. Combination of advanced oxidation and biological processes for the landfill leachate treatment. Ecol Eng 73: 281-289.

CHO SP, HONG SC & HONG SI. 2002. Photocatalytic degradation of the landfill leachate containing refractory matters and nitrogen compounds. Appl Catal B: Environ 39: 125-133.

CHO SP, HONG SC & HONG SI. 2004. Study of the end point of photocatalytic degradation of landfill leachate containing refractory matter. Chem Eng Technol 98: 245-253.

CONAMA. 2011. Resolução № 430, de 13 de Maio de 2011. Dispõe sobre as condições e padrões de lançamento de efluentes, complementa e altera a Resolução no 357, de 17 de março de 2005, do Conselho Nacional do Meio Ambiente - CONAMA. Diário Oficial da República Federativa do Brasil, Brasília, nº 92.

CORTEZ S ET AL. 2010. Ozonation as polishing treatment of mature landfill leachate. J Hazard Mater 182: 730-734.

FORESTI E ET AL. 2005. Métodos de Análises Físico-Químicas de Rotina de Águas Residuárias Tratadas Biologicamente. São Paulo: Universidade de São Paulo.

GARCEZ LN. 2004. Manual de procedimentos e técnicas laboratoriais voltado para análises de águas e esgotos sanitário e industrial. São Paulo: Escola Politécnica da Universidade de São Paulo.

GUIDOLINI J ET AL. 2005. Arranjos alternativos para o pré-tratamento do chorume do depósito municipal de Aracruz. Revista Educação e Tecnologia, Aracruz, n. 1.

ILHA J. 2012. Degradação fotocatalítica de fenol utilizando nanofios de dióxido de titânio modificados com nitrogênio. Dissertação (Mestrado em Engenharia Química) — Programa de Pós-Graduação em Engenharia Química, Universidade Federal de Santa Catarina. Florianópolis, 88 p. (Unpublished data).

KAMMRADT PB. 2004. Remoção de cor de efluentes de tinturarias industriais através de processo de oxidação avançada. Dissertação (Pós-Graduação em Engenharia de Recursos Hídricos e Ambiental) – Universidade Federal do Paraná, Paraná, 92 p. (Unpublished data).

KURNIAWAN TA, LO WH & CHAN GYS. 2006a. Physico-chemical treatments for removal of recalcitrant contaminants from landfill leachate. J Hazard Mater B129: 80-100.

KURNIAWAN TA, LO WH & CHAN GYS. 2006b. Radicalscatalyzed oxidation reactions for degradation of recalcitrant compounds from landfill leachate. Chem Eng Technol 125: 35-57.

LIMA SB. 2008. Pós-tratamento de chorume com wetlands construídos utilizando macrófitas aquáticas emergentes da região de Campo Mourão-PR. Tese (Doutorado em Ciências) — Programa de Pós-Graduação em Química, Universidade Estadual de Maringá, Maringá, 86 p.

MAHMOUD A & FREIRE RS. 2007. Métodos emergentes para aumentar a eficiência do ozônio no tratamento de águas contaminadas. Quím Nova 30(1): 198-205.

MECHA AC ET AL. 2016. Synergistic effect of UV–vis and solar photocatalytic ozonation on the degradation of phenol in municipal wastewater: A comparative study. J Catal 341: 116-125.

MEHRJOUEI M, MÜLLER S & MÖLLER DA. 2015. Review on photocatalytic ozonation used for the treatment of water and wastewater. Chem Eng Technol 263: 209-219.

MENA E ET AL. 2012. On ozone-photocatalysis synergism in black-light induced reactions: Oxidizing species production in photocatalytic ozonation versus heterogeneous photocatalysis. Chem Eng Technol 204-206: 131-140.

MONJE-RAMIREZ I & VELÁSQUEZ MTO. 2004. Removal and transformation of recalcitrant organic matter from stabilized saline landfill leachates by coagulation– ozonation coupling processes. Water Res 38: 2359-2367.

MORAIS JL & PERALTA-ZAMORA P. 2005. Use of advanced oxidation processes to improve the biodegradability of mature landfill leachates. J Hazard Mater B123: 181-186.

MOREIRA NFF ET AL. 2015. Fast mineralization and detoxification of amoxicillin and diclofenac by photocatalytic ozonation and application to an urban wastewater. Water Res 87: 87-96.

NTAMPOU X, ZOUBOULIS AI & SAMARAS P. 2006. Appropriate combination of physico-chemical methods (coagulation/ flocculation and ozonation) for the efficient treatment of landfill leachates. Chemosphere 62: 722-730.

PEIXOTO ALC. 2008. Ozonização catalítica homogênea do chorume proveniente do antigo aterro da cidade de Guaratinguetá – SP utilizando os íons Fe₂⁺, Fe₃⁺, Zn₂⁺, Mn₂⁺, Ni₂⁺ e Cr₃⁺. Dissertação (Mestrado em Engenharia Química) —Universidade de São Paulo, Lorena, 211 p. (Unpublished data).

RAJESWARI R & KANMANI S. 2009. A study on synergistic effect of photocatalytic ozonation for carbaryl degradation. Desalination 242: 277-285. RAMDHANI MY, SURURI MR & AINUN S. 2018. Leachate Treatment from Sarimukti Landfill using ozone with sludge from water treatment plant as a catalyst. MATEC Web Conf 147: n. 04006.

RENOU S ET AL. 2008. Landfill leachate treatment: Review and opportunity. J Hazard Mater 150(3): 468-493.

REY A ET AL. 2014. Photocatalytic Decomposition Of Gaseous Toluene By TiO2 Nanoparticles Coated On Activated Carbon. IJEHSE 5(4): 305-310.

RIVAS FJ ET AL. 2003. Stabilized leachates: ozone-activated carbon treatment and kinetics. Water Res 37: 4823-4834.

SCHNEIDER MV ET AL. 2014. Degradação fotocalítica de bentazona com TiO₂. Eng Sanit Ambient 19(1). Disponível em: <http://www.scielo.br/pdf/esa/v19n1/1413-4152-esa-19-01-00061.pdf>. Acesso em: 02 fev. 2018. (Unpublished).

SHAYKHI ZM & ZINATIZADEH AAL. 2014. Statistical modeling of photocatalytic degradation of synthetic amoxicillin wastewater (SAW) in an immobilized TiO₂ photocatalytic reactor using response surface methodology (RSM). J Taiwan Inst Chem Eng 45(4): 1717-1726.

SILVA CAMC ET AL. 2011. Caracterização microbiológica de lixiviados gerados por resíduos sólidos domiciliares e de serviços de saúde da cidade do Rio de Janeiro. Eng Sanit Ambient 16(2). (Unpublished).

SOUTO GDB. 2009. Lixiviado de aterros sanitários brasileiros – estudo de remoção de nitrogênio amoniacal por processo de arraste com ar. Tese (Doutorado em Engenharia Hidráulica e Saneamento) — Programa de Pós-Graduação em Engenharia Hidráulica e Saneamento, Universidade de São Paulo. São Carlos, 371 p.

SZCZEPANIK B. 2017. Photocatalytic degradation of organic contaminants over clay-TiO₂ nanocomposites: A review. Appl Clay Sci 141: 227-239.

TAVARES BFD. 2011. Tratamento de chorume: Análise dos efluentes da evaporação forçada. Trabalho de Conclusão de Curso (Graduação em Engenharia Ambiental) — Universidade Federal do Rio de Janeiro, 71 p.

TEIXEIRA CPAB & JARDIM WF. 2004. Caderno Temático Volume 03: Processos Oxidativos Avançados. Campinas: Universidade Estadual de Campinas.

THUONG NTL & BINH NT. 2015. Small scale landfill leachate treatment using photocatalytic oxidation process. JST 53(3A): 49-54.

WISZNIOWSKI J ET AL. 2003. Photocatalytic mineralization of humic acids with TiO₂: Effect of pH, sulfate and chloride anions. Int J Photoenergy 5: 69-74.

How to cite

CARARD RF, JUNIOR SCHIAVON G, CASTRO TM, MEDEIROS FVS, PAULA G, LANDGRAF ACM & ARANTES EJ. 2021. Photocatalytic Ozonation Performance In Landfill Leachate Treatment. An Acad Bras Cienc 93: e20190137. DOI 10.1590/0001-3765202120190137.

Manuscript received on February 6, 2019; accepted for publication on August 23, 2019

RAFAEL F. CARARD¹

https://orcid.org/0000-0002-2929-0801

GILSON JUNIOR SCHIAVON³

https://orcid.org/0000-0002-5642-078X

THIAGO M. DE CASTRO² https://orcid.org/0000-0002-6027-368X

FLÁVIA V.S. MEDEIROS²

https://orcid.org/0000-0001-6490-8876

GUILHERME DE PAULA² https://orcid.org/0000-0003-1928-1677

ANA CAROLINA M. LANDGRAF²

https://orcid.org/0000-0001-6754-5978

EUDES J. ARANTES²

https://orcid.org/0000-0002-7684-3069

¹ Universidade Tecnológica Federal do Paraná, Campus Campo Mourão, Rua Rosalina Maria Ferreira, 1233, Zona Urbanizada I, 87301-899 Campo Mourão, PR, Brazil

² Universidade Tecnológica Federal do Paraná, Departamento Acadêmico de Ambiental/DAAMB, Campus Campo Mourão, Rua Rosalina Maria Ferreira, 1233, Zona Urbanizada I, 87301-899 Campo Mourão, PR, Brazil

³ Universidade Tecnológica Federal do Paraná, Departamento Acadêmico de Eletrõnica/DAELN, Campus Campo Mourão, Rua Rosalina Maria Ferreira, 1233, Zona Urbanizada I, 87301-899 Campo Mourão, PR, Brazil

Correspondence to: Eudes José Arantes

E-mail: eudesarantes@utfpr.edu.br

Author contributions

RAFAEL F. CARARD Lead author, contribution to laboratory research and analysis of work discussion. GILSON JUNIOR SCHIAVON Responsible for ozonation equipment, contribution to the calibration of ozonation equipment and the control of ozone dozation. THIAGO M. DE CASTRO Contribution to statistical analysis of the article. FLÁVIA V.S. MEDEIROS Contribution to physico-chemical laboratory analysis. GUILHERME DE PAULA & ANA CAROLINA M. LANDGRAF Contribution with assistance in laboratory analysis. EUDES JOSÉ ARANTES Advisor, contribution to the definition of methodologies, analysis and discussion of results.

