

Binary Mixtures of ZnO/TiO₂ for Solar Heterogeneous Photocatalysis of Non-Purgeable Organic Carbon in Landfill Leachate

Misturas Binárias de ZnO/TiO₂ para Catálise Solar Heterogênea do Carbono Orgânico Não-Purgável em Lixiviado de Aterro Sanitário

Mezclas binarias de ZnO/TiO₂ para la catálisis solar heterogénea de carbono orgánico no purgable en lixiviados de rellenos sanitarios

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Abstract

Landfill leachate is a global problem that has attracted considerable attention from researchers in different areas. It is crucial to develop optimized treatment strategies for landfill leachate, given the need to minimize or eliminate negative environmental impacts resulting from the inadequate disposal of solid waste, as determined by legislation. Landfill leachate is primarily composed of humic substances, which may associate with other toxic molecules and are recalcitrant to the conventional treatments used in Brazil. This study assessed the photocatalytic degradation of carbonaceous materials in leachate collected from the Cachoeira Paulista municipal landfill, São Paulo State, Brazil. Sunlight was used as energy source without additional light inputs. Experiments were carried out in a thin-film fixed-bed reactor, using metal plates coated with paints formulated for this purpose. Paints had a low additives loading, including that of photocatalysts. We investigated the photocatalytic behavior of the binary system ZnO/TiO₂ incorporated into acrylic varnish in the degradation of non-purgeable organic carbon (NPOC) in samples of humic acids and fulvic acids + humins. Reactions were conducted under acidic, neutral, or alkaline conditions. NPOC degradation was low in fulvic acid + humin samples, regardless of photocatalyst concentration or pH. The proposed process resulted in high degradation of humic acids, especially under conditions of low chemical stability, which facilitated oxidation. A maximum humic acid degradation of 65% was achieved using high concentrations of TiO₂ in acidic medium.

Keywords: Titanium dioxide; Zinc oxide; Heterogeneous photocatalysis.

Resumo

Lixiviados de aterros sanitários são um problema de abrangência global que têm atraído considerável atenção por parte de pesquisadores de diferentes áreas. É crucial desenvolver estratégias de tratamento otimizadas para esses lixiviados, dada a necessidade de minimizar ou eliminar impactos ambientais negativos resultantes da disposição inadequada de resíduos sólidos, como determinado pela legislação. Lixiviados de aterros são compostos principalmente por substâncias húmicas, que podem estar associadas com outras moléculas tóxicas e recalcitrantes aos tratamentos convencionais utilizados no Brasil. Este estudo estimou a degradação fotocatalítica dos materiais carbonáceos em um lixiviado coletado no aterro sanitário municipal de Cachoeira Paulista, São Paulo, Brasil. Luz solar foi utilizada como fonte de energia, sem utilização de fontes adicionais de energia. Experimentos foram conduzidos em um reator de leito fixo de película fina, utilizando chapas de metal revestidas com tintas formuladas especialmente para essa finalidade. As tintas possuíam baixa carga de aditivos, incluindo fotocatalisadores. Investigamos o comportamento fotocatalítico do sistema binário ZnO/TiO₂ incorporado no verniz acrílico na degradação do carbono orgânico não purgável (NOPC) em amostras de ácidos húmicos e ácidos fúlvicos + huminas. As reações foram conduzidas em condições ácidas, neutra, ou alcalina. A degradação do NOPC foi baixa nas amostras de ácido fúlvicos + huminas, independentemente da concentração dos fotocatalisadores ou pH. O processo proposto resultou em alta degradação dos ácidos húmicos, especialmente sob condições de baixa estabilidade química, as quais facilitaram a oxidação. Foi alcançada degradação máxima de 65% dos ácidos húmicos utilizando concentrações altas de TiO₂ em meio ácido.

Palavras-chave: Dióxido de titânio; Óxido de zinco; Fotocatálise heterogênea.

Resumen

El lixiviado de los relleno sanitario es un problema global que ha atraído una atención considerable por parte de investigadores en diferentes campos. Es fundamental desarrollar estrategias de tratamiento optimizadas para estos lixiviados, dada la necesidad de minimizar o eliminar los impactos ambientales negativos resultantes de la disposición inadecuada de residuos sólidos, según lo determine la legislación. El lixiviado de relleno sanitario está compuesto principalmente por sustancias húmicas, que pueden estar asociadas con otras moléculas tóxicas y recalcitrantes a los tratamientos convencionales utilizados en Brasil. Este estudio estimó la degradación fotocatalítica de materiales carbonosos en un lixiviado recolectado en el relleno sanitario municipal de Cachoeira Paulista, São Paulo, Brasil. La luz solar se utilizó como fuente de energía, sin utilizar fuentes de energía adicionales. Los experimentos se llevaron a cabo en un reactor de reactor de lecho fijo de película fina, utilizando láminas de metal revestidas con pinturas especialmente formuladas. Las tintas tenían una carga aditiva baja, incluidos los fotocatalizadores. Investigamos el comportamiento fotocatalítico del sistema binario ZnO/TiO₂ incorporado en barniz acrílico sobre la degradación del carbono orgánico no depurable (NOPC) en muestras de ácidos húmicos y ácidos fúlvicos + huminas. Las reacciones se realizaron en condiciones ácidas, neutras o alcalinas. La degradación de NOPC fue baja en muestras de ácido fúlvico + húmina, independientemente de la concentración de fotocatalizador o el pH. El proceso propuesto resultó en una alta degradación de ácidos húmicos, especialmente en condiciones de baja estabilidad química, lo que facilitó la oxidación. Se logró una degradación máxima del 65% de los ácidos húmicos utilizando altas concentraciones de TiO₂ en un medio ácido.

Palabras clave: Dióxido de titanio; Óxido de zinc; Fotocatálisis heterogénea.

1. Introduction

Landfills are an environmentally sound site for the final disposal of municipal solid waste. In Brazil, however, only 46% of municipalities adopt this disposal strategy (ABRELPE, 2019). The combination of organic matter decomposition with rainwater percolation in municipal landfills leads to the formation of leachate, a liquid consisting of a mixture of high molecular weight compounds with a wide variety of functional groups (mainly phenolic and carboxylate groups), which act synergistically with other pollutants. Currently, biological processes are the most commonly used methods for leachate treatment in Brazil, given their low operating and maintenance costs. As leachate matures (5–10 years), however, there is a decrease in the content of biodegradable compounds and an increase in that of recalcitrant substances (e.g., humic substances), rendering biological processes ineffective. In such cases, advanced oxidation processes are indicated (Silva et al., 2017).

Heterogeneous photocatalysis, an important advanced oxidation process, has been successfully used for the degradation of humic substances in landfill leachate (Izário Filho et al., 2018; Brito et al., 2019; Napoleão et al., 2022). Chemlal et al. (2014) observed a 50–84% reduction in dissolved organic carbon concentration in leachate from the Oued Smar landfill, Algeria, via TiO₂/ultraviolet (UV) photocatalysis followed by aeration in a bioreactor. Wiszniowski et al. (2004) studied the degradation of

humic acids using different concentrations of TiO₂ in a compound parabolic collector under solar irradiation. The authors reported that the most influential factor was the presence of hydrogen carbonates (Wiszniowski et al., 2004).

For energy optimization in photocatalytic systems, it is recommended to use solely UV radiation instead of visible light (Turkten et al, 2020). TiO₂ has a high bandgap value but captures only UV radiation. As a strategy to enhance the applicability of this semiconductor, it is common to subject TiO₂ to doping or heterostructure formation with compounds that can act in the spectral range of visible light, as is the case of ZnO (Sun et al., 2018). These processes may enhance the interaction of electron–hole pairs between conduction and valence bands of semiconductors, increasing photocatalytic efficiency (Sun et al., 2018). Turkten and Bekbolet (2020) investigated the photocatalytic performance of TiO₂, ZnO, and a ZnO/TiO₂ system at three weight ratios (1:1, 3:1, and 1:3). The binary mixture was obtained by simple dispersion and tested for the degradation of humic substances under solar irradiation. The best results were obtained with ZnO/TiO₂ at weight ratios of 1:3, 3:1, and 1:1 (in that order).

Heterostructures can be dispersed in solution or fixed on a stationary support. A simple and economically promising method to fixate these materials on supports is by incorporating semiconductors into acrylic paints (Jašková et al., 2013; Islam et al., 2020; Salvadores et al., 2020). In the current study, we innovate by investigating the performance of a ZnO/TiO₂ binary system at different weight ratios incorporated into acrylic varnish and applied using a compressed air gun for the photocatalytic degradation of the main organic components of leachate (humic acids and fulvic acids + humins) under solar irradiation in a thin-film fixed-bed reactor.

2. Methodology

Preparation of Photocatalytic Materials.

Binary mixtures were prepared by a simple mixing method at the Laboratory of Materials and Testing of the Department of Mechanical Engineering, University of Taubaté (UNITAU), and at the Laboratory of Atomic Absorption of the Engineering School of Lorena (EEL/USP), both located in São Paulo State, Brazil. Table 1 describes the materials used to prepare the photocatalysts.

Table 1 - Ingredients used in the synthesis of photocatalytic materials.

Ingredient	Concentration (% w v ⁻¹)
Acrylic varnish	60.0
Solids	20.0
Water	15.0
Ammonium polyacrylate (PAA(NH ₄))	4.0
Carboxymethylcellulose	1.0

Source: Authors.

A colorless, semi-gloss, water-soluble acrylic varnish was obtained commercially. This type of varnish is typically composed of methyl methacrylate (MMA) copolymer, butyl acrylate (BA), 2-hydroxyethyl methacrylate (HEMA), and acrylic acid (AA) at a weight ratio of 60:22.2:10:7.8. The preparation procedure commonly involves free radical-initiated polymerization using an azo primer. The average molecular weight of this type of material ranges from 15,000 to 35,000 (Jones et al., 2017).

TiO₂ (99.9% purity) and ZnO (99.5% purity) serve both as photocatalysts and as pigments in paints. Ammonium polyacrylate (PAA(NH₄)) and carboxymethylcellulose (CMC) are used to modify the rheological properties of paints; the former helps disperse pigments into the matrix and the latter increases the viscosity for easier application with compressed air sprayers.

Four formulations of photocatalytic materials were prepared by varying the weight ratio of TiO₂ to ZnO (Table 2). The first three formulations correspond to the low, central, and high factor levels. The fourth formulation (blank) contains only acrylic varnish and water and was used to assess the occurrence of photolysis.

Table 2 - Proportion of ZnO and TiO₂ in test formulations.

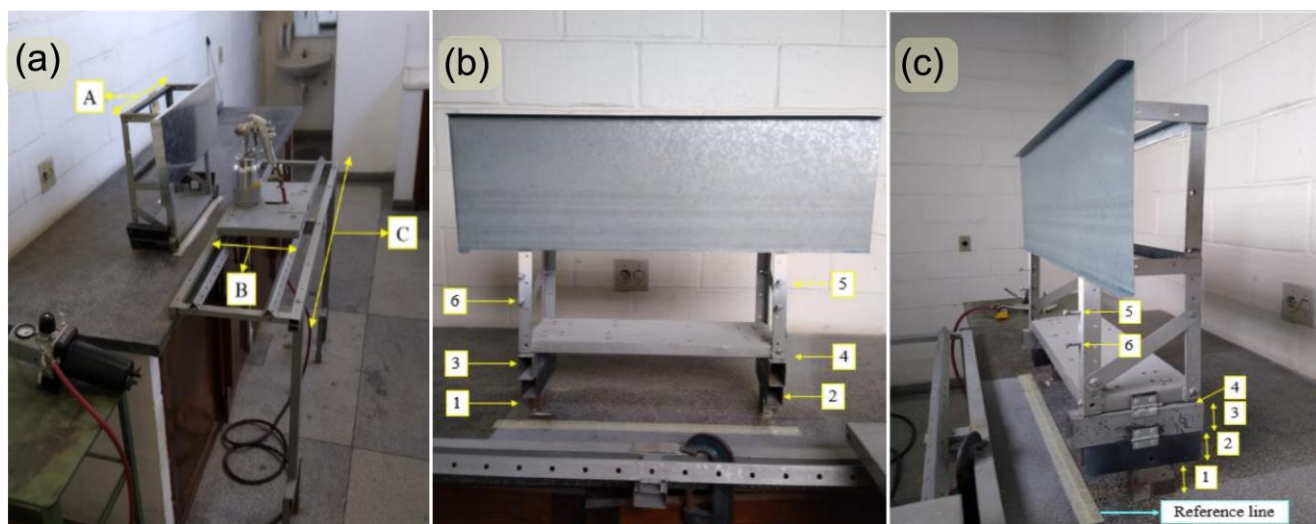
Formulation	ZnO (% w w ⁻¹)	TiO ₂ (% w w ⁻¹)
1	65.0	35.0
2	20.0	80.0
3	44.0	56.0
4 (blank)	0.0	0.0

Source: Authors.

TiO₂ and ZnO were weighed on an analytical scale, mixed together, and homogenized using an IKA A11 basic analytical mill for 60 min. During this period, CMC and PAA(NH₄) were solubilized in deionized water. Subsequently, the solution was mixed with varnish by mechanical agitation with ultrasonication. Finally, the powder mixture was added to the solution, and the mixture was placed under agitation for 15 min.

This study used the paint lab of the Laboratory of Materials and Testing, Department of Mechanical Engineering, University of Taubaté, Brazil. The apparatus (Figure 1a) is equipped with a spray gun (DeVilbiss, model JGA-503), a double air filter/regulator (DeVilbiss, model FRC-600), and an air compressor (Schulz, model Classic Mobile MSL).

Figure 1 - Photographs of the paint lab at the Laboratory of Materials and Testing, University of Taubaté, São Paulo State, Brazil. (a) Painting system: A, sample holder; B, sliding track connected to a paint sprayer; C, frame structure. (b) Frontal view of the sample holder showing the galvanized steel plate ($750 \times 250 \times 0.5$ mm) and six points for height adjustment. (c) Lateral view of the sample holder showing the reference line and six height presets.



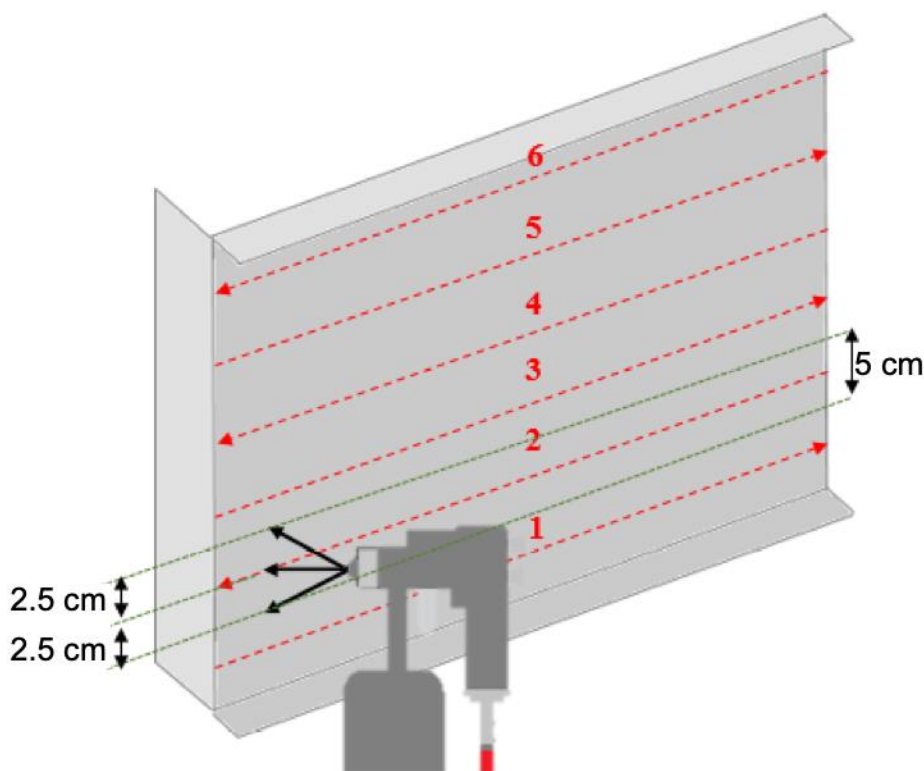
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Figure 1b and c shows the adjustable height sample holder, with six height presets at 5 cm intervals for the application of overlapping strokes. Height position number 1 uses a 2.5 cm thick solid metal support to generate a total distance of 25 cm from the top end of the metal plate to the reference line (marked blue in Figure 1c). The apparatus is set at the second height position by removing the solid metal support of position 1. Position 3 is obtained by removing another metal support. The same applies to position 4. After removing all metal supports, it is possible to set the sample holder to positions 5 and 6 by lowering the plate until it rests on the appropriate position.

The distance between the reference line and the nozzle of the spray gun was 20 cm. Suspensions were applied by horizontal spraying on four different galvanized steel plates, each measuring $750 \times 250 \times 0.5$ mm (Figure 1 b). The vertical fan of the spray gun was set at a height of 5.0 cm. Application of the first stroke of the first coating would involve the following steps: (i) adjust the galvanized steel plate to height position 1, (ii) securely attach the paint sprayer to the sliding track (placed at 90° to the plate); (iii) bring the sliding track to the left side (beginning) of the fixed structure; and (iv) move the sliding track to the right side, covering a distance of 750 mm in 4.0 s at constant speed, with the trigger pulled to the desired pressure. After this procedure, the galvanized steel plate is set to height position 2, and the second stroke is applied in the opposite direction (from right to left). Each coating consisted of six strokes.

Figure 2 demonstrates the six preset positions of the spray gun along the galvanized steel plate and the direction of each stroke. The figure also highlights the area covered by stroke 2. Note that each stroke overlaps 50% of the area covered by the previous stroke. Nine coatings of suspension were applied per sample. The first coating was semi-wet and applied at 40 psi. This procedure ensured the deposition of a uniform coating without coalescence of droplets. The remaining eight coatings were wet and applied at 20 psi, forming a continuous, uniform film of coalescent droplets. At the end of the procedure, thickness was measured using a Mitutoyo digital micrometer. Films had a mean thickness of 600 ± 80 μm .

Figure 2 - Schematic (not to scale) showing the horizontal motion of the spray gun along the galvanized steel plate to complete the six strokes.



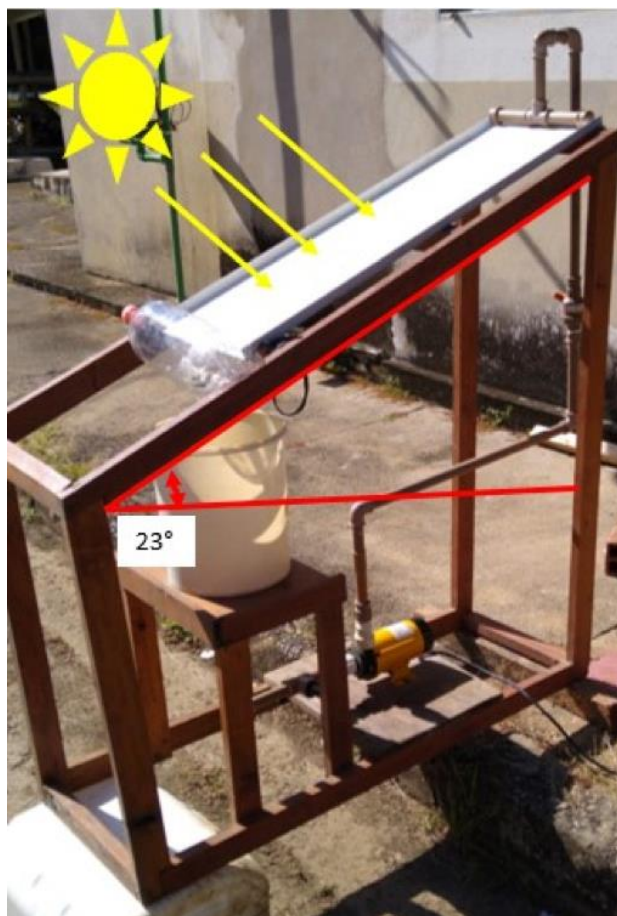
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Photocatalytic Tests.

For photocatalytic tests, 100 L of leachate was collected from a landfill (22°39'4"S 45°3'18"W) in Cachoeira Paulista, São Paulo State, Brazil. After collection, leachate samples were homogenized by mechanical agitation and stored in a cold chamber at 4 °C until use. Photocatalytic tests were carried out in thin-film fixed-bed solar reactors operated in semi-continuous mode on bench scale. The reactor was positioned at an inclination angle of 23° facing the equator (Figure 3). Further details of a similar reactor can be found in Izário Filho et al. (2021). The volume of raw leachate used in each run was 3 L. Reactions were performed at a flow rate of 12 to 13 mL min⁻¹ between 11:00 and 15:00 h for five consecutive days in the autumn, under sunny weather, with temperatures ranging from 28 to 32 °C and solar irradiation of 750 to 872 mJ cm⁻². The mean evaporation rate of raw leachate during an experimental cycle was 160 mL; therefore, water was added during photocatalysis to replace this loss.

Before each run, the pH of raw leachate samples was measured (between 7.8 and 8.0) and adjusted by adding small volumes of sulfuric acid (H₂SO₄, 98% w w⁻¹) under manual agitation. During photocatalytic reactions, pH correction was performed by adding 10 mol L⁻¹ H₂SO₄ directly into the reactor reservoir. Aliquots were collected every 20 min for monitoring and adjustment of the operation. At these predetermined times, temperature readings were taken from the plate and the leachate in the reservoir.

Figure 3 - Thin-film fixed-bed reactor used for solar heterogeneous photocatalysis.



Source: Authors.

To assess the occurrence of leachate degradation by photolysis, we carried out a blank test using plate 4 (without oxides or additives). For the blank test, samples were collected only at the beginning and end of the reaction period (240 min). Experimental conditions (temperature, leachate volume, and solar irradiation) were similar to those of test runs. The blank test indicated absence of photolytic degradation.

Determination of Humic Substances

Analytical characterization of humic substances was performed on a Shimadzu TOC-V analyzer, in which samples are subjected to total combustion (680 °C) followed by non-dispersive infrared detection. The equipment is capable of analyzing total carbon, inorganic carbon, total organic carbon, and non-purgeable organic carbon (NPOC) at concentrations ranging from 2.0 to 1,000 mg L⁻¹ in aqueous media. Total organic carbon is estimated by subtracting inorganic carbon from total carbon. Inorganic carbon, in turn, is obtained by sample acidification and conversion of carbonates into CO₂. Preliminary analysis showed that CO₂ concentrations were negligible. Finally, NPOC is obtained after this last step. It should be noted that humic acids were evaluated separately from fulvic acids + humins. During photocatalysis, aliquots of treated leachate were collected every 5 min for the first 20 min and then every 10 min for the following 240 min, totaling 26 samples per experiment.

Experimental Design

Two factors were investigated: [ZnO/TiO₂] (ZnO/TiO₂ weight ratio) and [pH] (pH range). Each factor was tested at three levels (-1), (0) and (+1). For [ZnO/TiO₂], the ratio levels were 20.80, 44.56 and 65.35. For [pH], the levels were 4.5-5.0 (acidic), 6.0-6.5 (here denominated “neutral”) and 7.5-8.0 (basic).

Runs were conducted following a 2² factorial completely randomized design, with two replications of each test condition (I to IV) and two replications of the center point (condition V), totaling 10 runs (Table 3).

Table 3 - Experimental conditions, runs, factors, and levels used in the study of photocatalytic properties.

Condition	Runs	Factor	
		[pH]	[ZnO/TiO ₂]
I	1 and 5	-1	-1
II	2 and 6	-1	+1
III	3 and 7	+1	-1
IV	4 and 8	+1	+1
V	9 and 10	0	0

Source: Authors.

The efficiency of NPOC removal from humic acid and fulvic acid + humin samples was calculated using Eq. (1). Results were plotted using DataGraph software version 4.6.1, and data were subjected to analysis of variance (ANOVA) using Minitab software version 16.

$$NPOC_0 \text{ removal efficiency} = \frac{NPOC_0 - NPOC_f}{NPOC_0} \times 100 \quad (1)$$

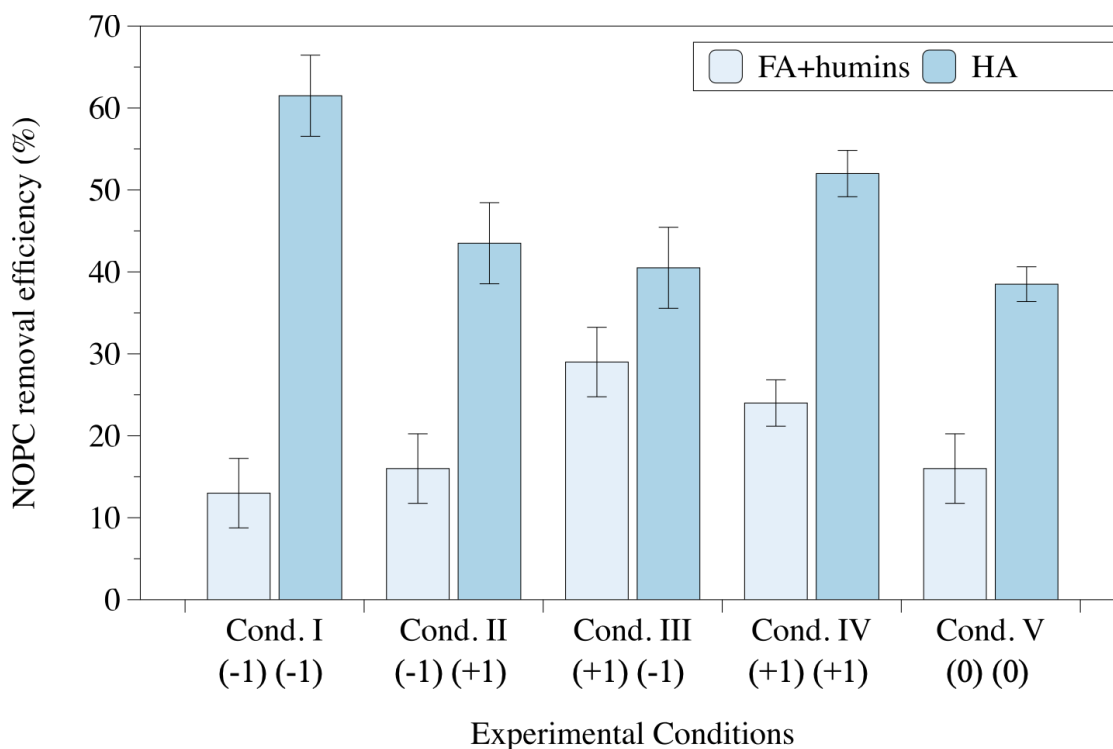
where NPOC₀ is the initial NPOC concentration and NPOC_f is the final NPOC concentration.

3. Results and Discussion

By overlapping coatings, it was possible to obtain films with high thickness (600 ± 80 μm), in compliance with the recommendations of Samanamud et al. (2012). According to the authors, high thickness allows for greater coat durability and reduced production and operation costs, although no study has yet assessed film durability. The paints formulated for the thin-film fixed-bed reactor (galvanized steel test bodies) were obtained by an unprecedented method and had low additive concentration and good load distribution.

Figure 4 depicts the results of humic acid and fulvic acid + humin removal efficiencies. The highest humic acid removal efficiency was achieved in acidic medium containing high TiO₂ concentrations, whereas the highest fulvic acid + humin removal efficiency was obtained with high ZnO concentration and acidic conditions.

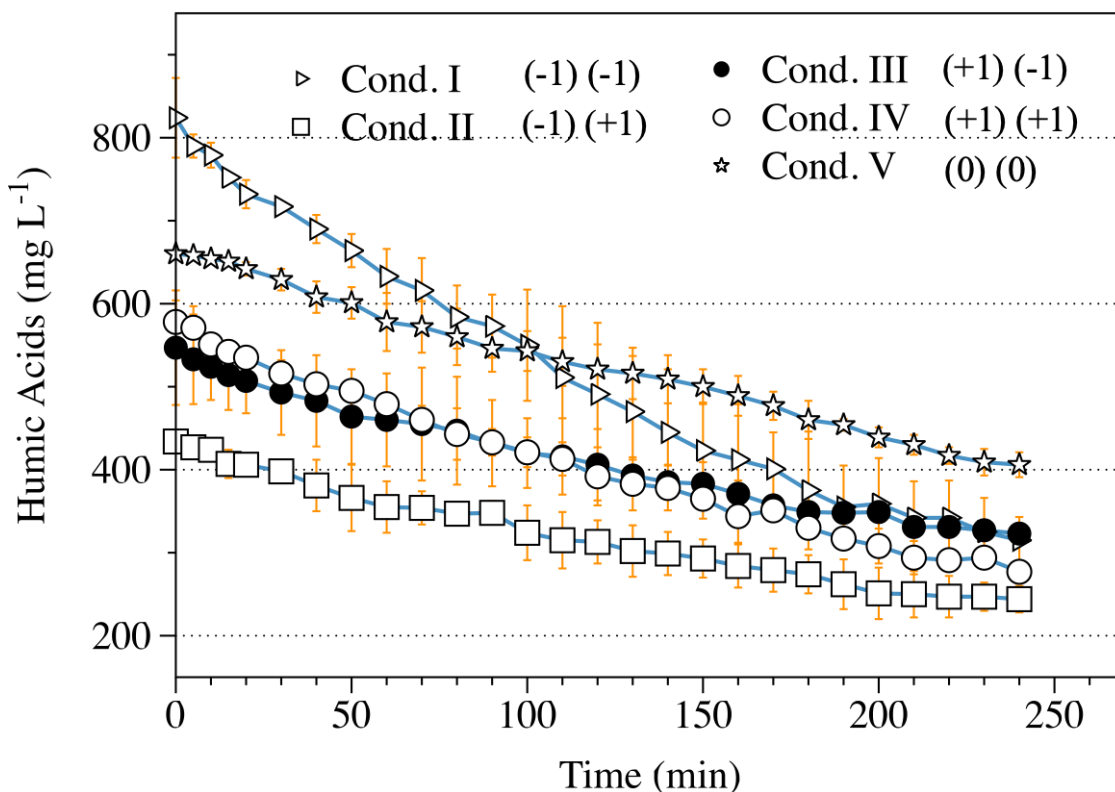
Figure 4 - Removal efficiency of humic acids (HA) and fluvial acids (FA) + humins. Numbers in parentheses on the X-axis indicate [pH] and [ZnO/TiO₂] levels for each Experimental Condition, respectively. NOPC: Non-Purgeable Organic Carbon.



Source: Authors.

Figure 5 depicts the NPOC concentrations in humic acid samples according to experimental conditions I to V. A higher initial humic acid concentration and mean degradation rate (62.0%) were obtained under condition I, with [pH] = (-1) and [ZnO/TiO₂] = (-1). The lowest mean degradation rate (38.5%) was achieved under condition V, with [pH] = (0) and [ZnO-TiO₂] = (0) (center point). Absence of photolytic reaction was observed in the blank test.

Figure 5 - Concentration and standard deviation of non-purgeable organic carbon in humic acid samples according to experimental conditions. Numbers in parentheses indicate [pH] and [ZnO/TiO₂] levels for each Experimental Condition, respectively.



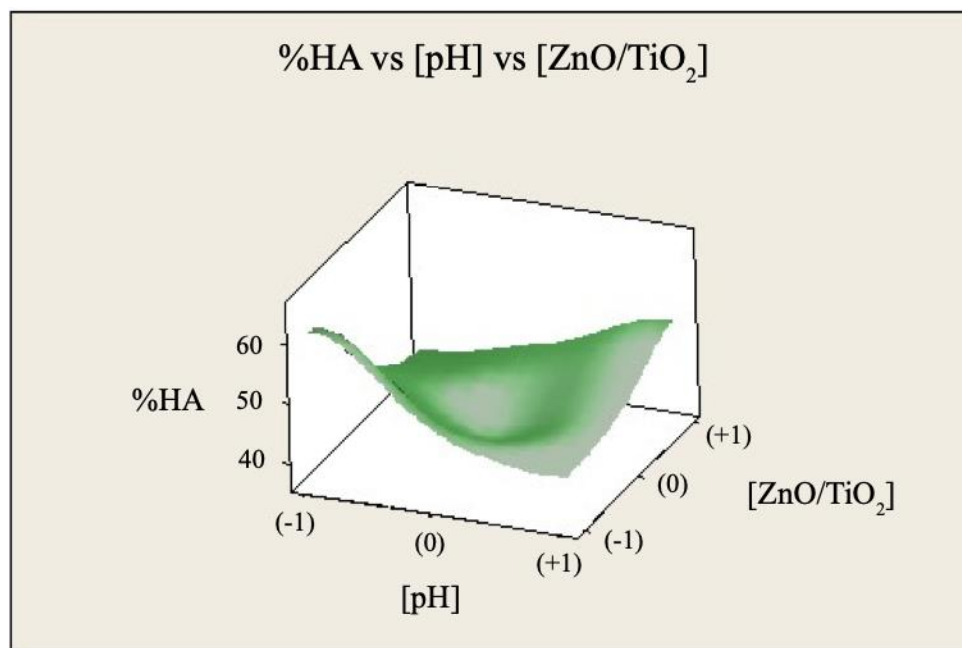
Source: Authors.

Main and interactions effects were assessed by ANOVA. Eq. (2) shows the statistical model for the evaluated factors and their interaction. R^2 and adjusted R^2 values were 89.38% and 80.88%, respectively. Results are expressed as percentage of humic acid degradation (%HA).

$$\%HA = 49.38 - 1.62[pH] - 3.21[ZnO/TiO_2] + 7.37[pH][ZnO/TiO_2] \quad (2)$$

Analysis of the mathematical model showed that no individual factor exerted a significant effect on humic acid degradation at the 95% confidence level. On the other hand, $[pH] \times [ZnO/TiO_2]$ effects on the response variable were significant ($P = 0.004$) compared with main effects ($P = 0.318$), revealing a catalytic synergism between the studied factors. The surface plot of humic acid degradation as a function of pH and photocatalyst concentration (Figure 6) confirms the results of ANOVA, predicting 60–65% humic acid degradation under condition I.

Figure 6 - Surface plot of humic acid concentration *versus* ZnO/TiO₂ weight ratio *versus* pH.

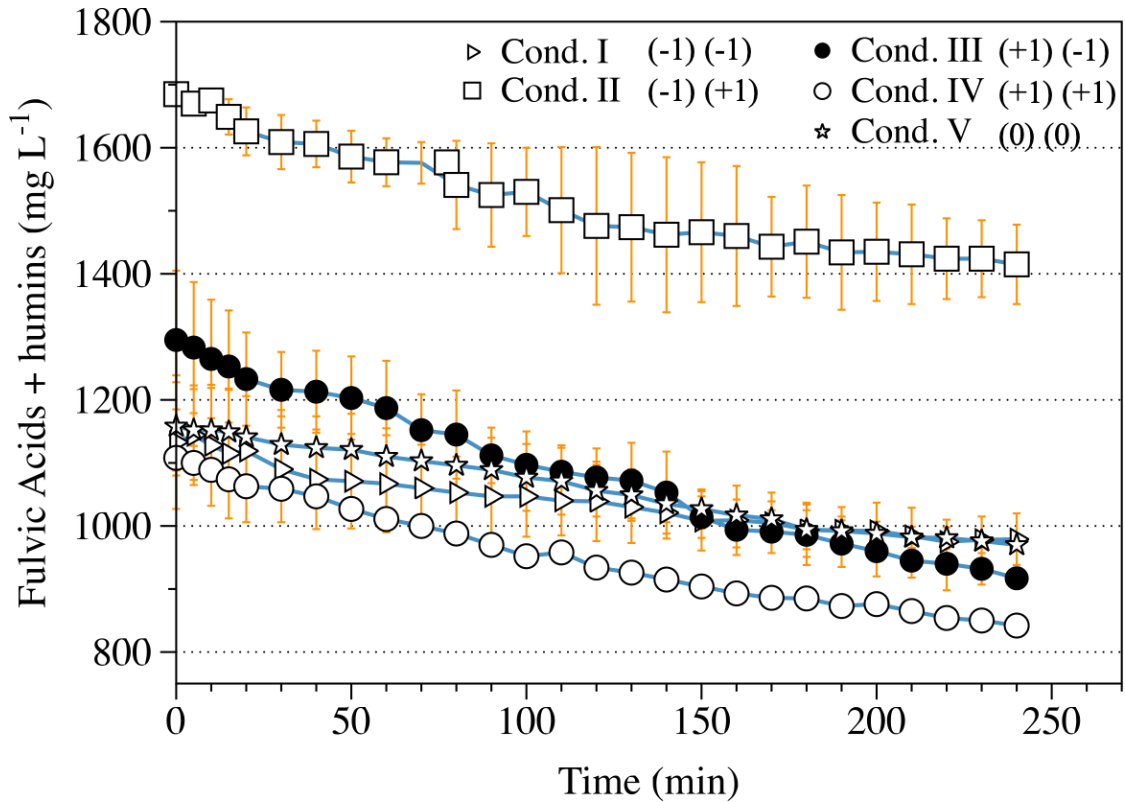


Source: Authors.

One of the factors with the greatest influence in heterogeneous photocatalysis is solution pH (Azeez et al., 2018). This is due to the fact that pH alters the surface characteristics of semiconductors, thereby modifying the adsorption capacity of contaminants and promoting hydroxyl radical generation (Azeez et al., 2018). Another important parameter is the point of zero charge, defined as the pH at which the semiconductor surface has a neutral charge. According to Kosmulski (2006), the point of zero charge of TiO₂ ranges from 5.1 to 6.9 and that of ZnO, from 8.6 to 9.8. The closer the medium pH is to the point of zero charge, the greater the photocatalytic efficiency. It is important to mention that humic acids have a higher concentration of carboxylic acids that dissociate at pH greater than 4 (Klučáková, 2018). For this reason, the highest humic acid degradation efficiency was achieved under condition I.

As shown in Figure 7, fulvic acid + humin samples had a markedly higher initial NPOC concentration than humic acid samples. Some variations in initial concentrations were observed as a result of random errors in sample preparation. The highest mean degradation rate (29.18%) was obtained under condition III, with [pH] = (-1) and [ZnO/TiO₂] = (+1), followed by condition IV (24.04%), with [pH] = (+1) and [ZnO/TiO₂] = (+1). The worst oxidative performance was achieved under condition I, [pH] = (-1) and [ZnO/TiO₂] = (-1), with a mean degradation rate of 13.54%. It was observed that the highest fulvic acid + humin degradation rates were obtained under conditions that were the least favorable for humic acid degradation. We highlight that, during the photocatalytic reactions, surfactant byproducts were formed because of the addition of H₂SO₄ for pH control. The surfactant elements likely hindered the incidence of photons on the photocatalyst surface, decreasing degradation efficiency.

Figure 7 - Concentration and standard deviation of non-purgeable organic carbon in fulvic acid + humin samples according to experimental conditions. Numbers in parentheses indicate [pH] and [ZnO/TiO₂] levels for each Experimental Condition, respectively.



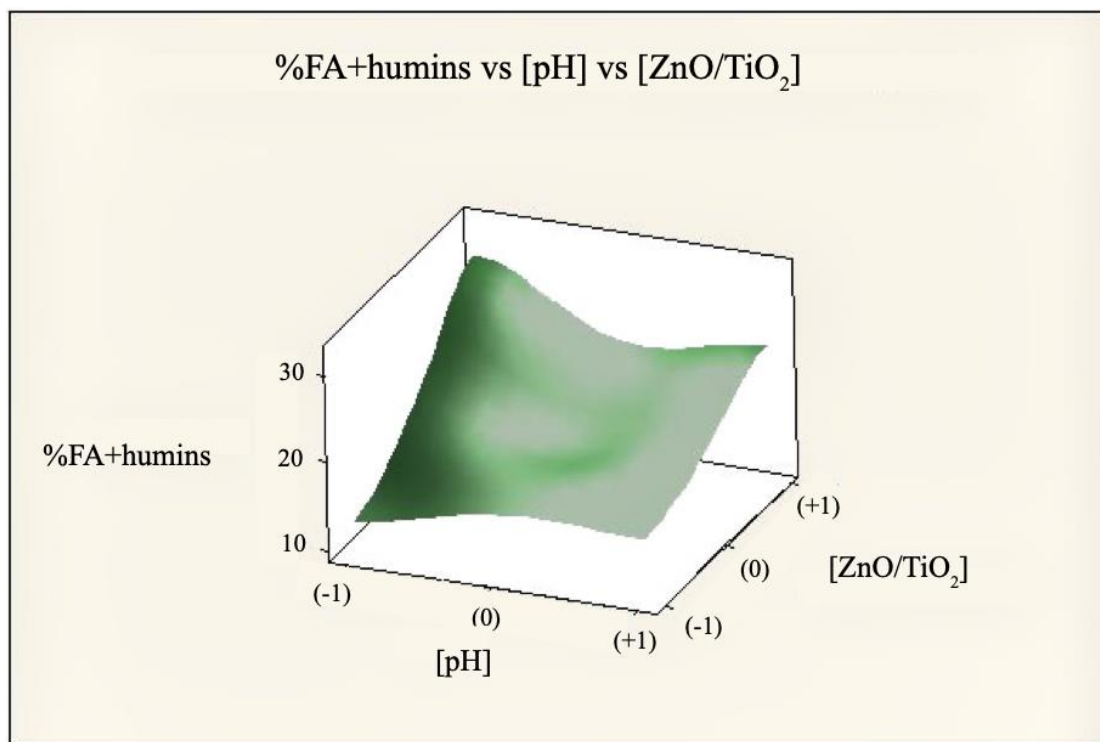
Source: Authors.

The statistical model explaining the relationship between fulvic acid + humin degradation and factors is shown in Eq. (3) ($R^2 = 81.58\%$). Results are expressed as degradation percentage of fulvic acids + humins (%FA + humins).

$$\%FA+humins = 20.5 - 0.5[pH] + 6.0[ZnO/TiO_2] - 2.0[pH][ZnO/TiO_2] \quad (3)$$

Only [ZnO/TiO₂] was significant ($p = 0.022$) at the 95% confidence level. [pH] and the interaction between factors, [pH] × [ZnO/TiO₂], were not significant. The surface plot of fulvic acid + humin degradation as a function of pH and photocatalyst concentration (Figure 8) confirms the results of ANOVA. A degradation efficiency of 25 to 30% was predicted for condition II.

Figure 8 - Surface plot of fulvic acid (FA) + humin concentration *versus* ZnO/TiO₂ weight ratio *versus* pH.



Source: Authors.

During photocatalysis, humic and fulvic acids can be converted into lower molecular weight compounds, that is, into humins. These hydrophilic substances are composed predominantly of phenols that dissociate at pH greater than 8 (Klučáková, 2018). This fact may explain the high NPOC degradation rates in fulvic acid + humin samples under conditions III and IV, with [pH] = (-1) or (+1) and [ZnO/TiO₂] = (+1). The pH range used in the experiments did not exert significant effects on the fulvic acid + humin fraction. Possibly, to improve the significance of this parameter, it would be necessary to increase ZnO concentration. Previous studies have shown that it is difficult to achieve high photocatalytic efficiency in samples with high humin concentrations (Dia et al., 2017; Vithanage et al., 2017).

Center point runs did not have satisfactory results for any of the carbonaceous samples, in agreement with the findings of Turkten and Bekbolet (2020). This is due to the fact that the point of zero charge of the mixture was shifted to an unfavorable range for humic acid and fulvic acid + humin degradation. Future studies should explore mixtures with a greater concentration of ZnO and TiO₂ at pH ranges closer to the point of zero charge.

4. Conclusion

The paint mixtures formulated for this study were obtained using an unprecedented and successful method. Paints were applied by overlapping coat layers on the experimental plates, resulting in films with high thickness. Separation of humic substances into humic acids and fulvic acids + humins allowed differentiated analysis of the results for the ZnO/TiO₂ binary system at different pH values. Humic acids were more susceptible to degradation under all tested conditions, regardless of the initial concentration. The maximum degradation rate (65%) was obtained in acidic medium using the paint mixture with high TiO₂ content. The highest fulvic acid + humin degradation rate (29.18%) was obtained under high ZnO concentration and acidic conditions. The highest degradation efficiency for fulvic acids + humins was lower than the minimum for humic acids. This

finding is associated with the conversion of acid fractions into humins during photocatalysis as well as with the correlation between medium pH and the point of zero charge of materials. Our results agree with those of several studies characterizing dissolved organic materials of landfill leachate. As also observed in previous studies, a 1:1 ZnO/TiO₂ ratio is not the most suitable for degradation of humic substances.

It is suggested, for future works, the study of other binary combinations between ZnO-TiO₂ in extreme pH ranges (less than 4.0 or greater than 8.0). There will probably be an experimental condition that comes even closer to the optimal region. Another possibility would be the separation of organic fractions before the photocatalytic process, in order to evaluate the effects of these substances when submitted individually to the treatment.

Competing interests

We have no conflict of interest to declare. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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