TREATMENT OF A LANDFILL LEACHATE BY SOLAR HETEROGENEOUS PHOTOCATALYSIS USING BINARY MIXTURES OF ZNO/TIO_2

DOI: http://dx.doi.org/10.55449/conresol.6.23.XII-009

Nicoly Milhardo Lourenço Nohara, Hélcio José Izário Filho, Evandro Luís Nohara, Marco Aurélio Kondracki Alcântara (*)
* Escola de Engenharia de Lorena – USP – e-mail: marko@usp.br

RESUMO
Lixiviados de aterros sanitários são um problema global que tem atraído considerável atenção de pesquisadores de diversas áreas. É fundamental desenvolver estratégias otimizadas de tratamento de lixiviados de aterros sanitários, dada a necessidade de minimizar ou eliminar impactos ambientais negativos decorrentes do descarte inadequado de resíduos sólidos, conforme determina a legislação. O lixiviado de aterro sanitário é composto principalmente por substâncias húmicas, que podem se associar a outras moléculas tóxicas e são recalcitrantes aos tratamentos convencionais utilizados no Brasil. Este estudo avaliou a degradação fotocatalítica de materiais carbonáceos em chorume coletado do aterro municipal de Cachoeira Paulista, Estado de São Paulo, Brasil. A luz solar foi usada como fonte de energia sem entradas de luz adicionais. Experimentos foram realizados em um reator de leito fixo de filme fino, utilizando placas metálicas revestidas com tintas formuladas para este fim. Investigamos o comportamento fotocatalítico do sistema binário ZnO/TiO_2 incorporado em verniz acrílico na degradação de carbono orgânico não purgável (NPOC) em amostras de ácidos húmicos e ácidos fúlvicos + huminas. As reações foram conduzidas em condições ácidas, neutras ou alcalinas. A degradação do NPOC foi baixa nas amostras de ácido fúlvico + humina, independentemente da concentração do fotocatalisador ou do pH. O processo proposto resultou em alta degradação dos ácidos húmicos, principalmente em condições de baixa estabilidade química, o que facilitou a oxidação. Uma degradação ácida húmica máxima de 65% foi alcançada usando altas concentrações de TiO_2 em meio ácido.

PALAVRAS-CHAVE: Lixiviados de aterros sanitários, Fotocatálise heterogênea, Substâncias húmicas, Ácidos húmicos, Ácidos fúlvidos,

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. We investigated the photocatalytic behavior of the binary system ZnO/TiO_2 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 TiO_2 in acidic medium.

KEY WORDS: Landfill leachate, Heterogeneous photocatalysis, Humic substances, Humic acids, Fulvic acids.

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. For energy optimization in photocatalytic systems, it is recommended to use solely UV radiation instead of visible light (TURKTEN et al, 2020). TiO_2 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 TiO_2 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 TiO_2, ZnO, and a ZnO/TiO_2 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/TiO_2 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/TiO_2 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.

OBJECTIVE

This work investigated the photocatalytic behavior of the binary system ZnO/TiO_2 incorporated into acrylic varnish in the degradation of non-purgeable organic carbon (NPOC) in samples of humic acids and fulvic acids + humins..

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. The Ingredients used in the synthesis of photocatalytic materials were (% in w v^{-1}): acrylic varnish (60.0%), solids (20.0%), water (15%), Ammonium polyacrylate – PAA(NH_4) (4%) and Carboxymethylcellulose (1%).

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).

TiO_2 (99.9% purity) and ZnO (99.5% purity) serve both as photocatalysts and as pigments in paints. Ammonium polyacrylate (PAA(NH_4)) 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 TiO_2 to ZnO (Table 1). 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. TiO_2 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.

Table 1. Proportion of ZnO and TiO_2 in test formulations. Source: Authors of the Work.

Formulation	ZnO (% w w^{-1})	TiO2 (% w w^{-1})
1	65.0	35.0
2	20.0	80.0
3	44.0	56.0
4 (blank)	0.0	0.0

The paints were applied using a spray gun along the galvanized steel plate. 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.

Photocatalytic Tests and Determination of Humic Substances

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 1). 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}.

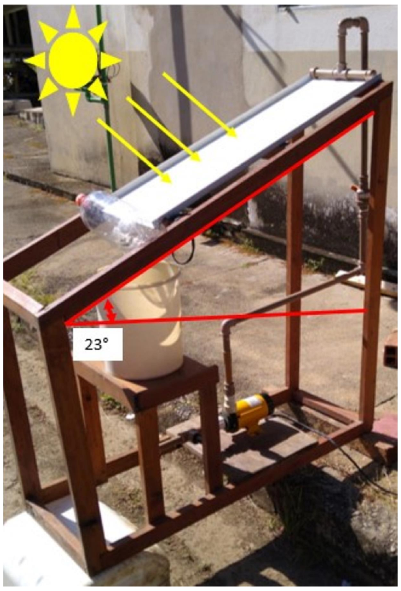

Figure 1. Thin-film fixed-bed reactor used for solar heterogeneous photocatalysis. Source: Authors of the Work.

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 (H_2SO_4, 98% w w^{-1}) under manual agitation. During photocatalytic reactions, pH correction was performed by adding 10 mol L^{-1} H_2SO_4 directly into the reactor reservoir.

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. 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 CO_2. 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.

Experimental Design

Two factors were investigated: [ZnO/TiO_2] (ZnO/TiO_2 weight ratio) and [pH] (pH range). Each factor was tested at three levels (–1), (0) and (+1). For [ZnO/TiO_2], 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 2).

Table 2: Experimental conditions, runs, factors, and levels used in the study of photocatalytic properties. Source: Authors of the Work.

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

The efficiency of NPOC removal from humic acid and fulvic acid + humin samples was calculated using Eq. (1). In this equation, $NPOC_0$ is the initial NPOC concentration and $NPOC_f$ is the final NPOC concentration. Results were plotted using DataGraph software version 4.6.1.

$$NOPC_0 \text{ removal efficiency} = \frac{NOPC_0 - NOPC_f}{NOPC_0} \cdot 100 \qquad \text{equation (1)}$$

RESULTS

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 2 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 TiO_2 concentrations, whereas the highest fulvic acid + humin removal efficiency was obtained with high ZnO concentration and acidic conditions.

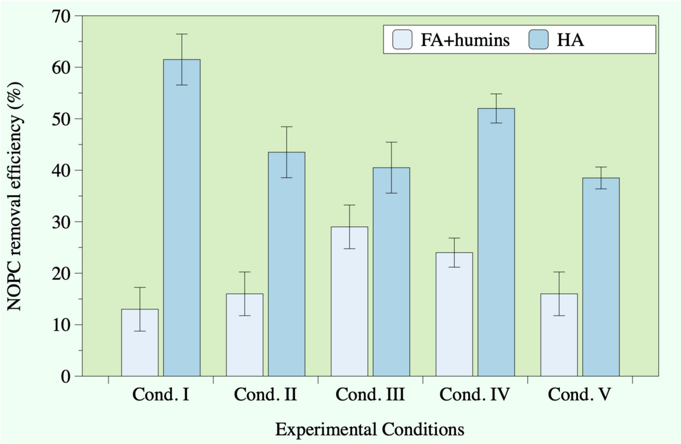

Figure 2. Removal efficiency of humic acids (HA) and fluvial acids (FA) + humins. Numbers in parentheses on the X–axis indicate [pH] and [ZnO/TiO_2] levels for each Experimental Condition, respectively. Source: Authors of the Work.

RESULTS

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/TiO_2 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 TiO_2 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.

It is suggested, for future works, the study of other binary combinations between ZnO-TiO_2 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.

REFERÊNCIAS BIBLIOGRÁFICAS

1. ABRELPE – Associação Brasileira de Empresas de Limpeza Pública e Resíduos Especiais. (2020). **Panorama dos resíduos sólidos no Brasil 2019/2020**. Abrelpe. https://abrelpe.org.br/panorama-2020/
2. Islam, Md. T., Dominguez, A., Turley, R. S., Kim, H., Sultana, K. A., Shuvo, M., Alvarado-Tenorio, B., Montes, M. O., Lin, Y., Gardea-Torresdey, J., & Noveron, J. C. (2020). Development of photocatalytic paint based on TiO_2 and photopolymer resin for the degradation of organic pollutants in water. **Science of The Total Environment**, *704*, 135406. https://doi.org/10.1016/j.scitotenv.2019.135406
3. Jašková, V., Hochmannová, L., & Vytřasová, J. (2013). TiO_2 and ZnO Nanoparticles in Photocatalytic and Hygienic Coatings. **International Journal of Photoenergy**, *2013*, 1–6. https://doi.org/10.1155/2013/795060
4. Jones, F. N., Nichols, M. E., & Pappas, S. P. (2017). **Organic coatings: Science and technology** (Fourth edition). John Wiley & Sons, Inc.
5. Salvadores, F., Alfano, O. M., & Ballari, M. M. (2020). Kinetic study of air treatment by photocatalytic paints under indoor radiation source: Influence of ambient conditions and photocatalyst content. **Applied Catalysis B: Environmental**, *268*, 118694. https://doi.org/10.1016/j.apcatb.2020.118694
6. Samanamud, G. R. L., Loures, C. C. A., Souza, A. L., Salazar, R. F. S., Oliveira, I. S., Silva, M. B., & Izário Filho, H. J. (2012). Heterogeneous Photocatalytic Degradation of Dairy Wastewater Using Immobilized ZnO. **ISRN Chemical Engineering**, *2012*, 1–8. https://doi.org/10.5402/2012/275371

7. Silva, T. F. C. V., Soares, P. A., Manenti, D. R., Fonseca, A., Saraiva, I., Boaventura, R. A. R., & Vilar, V. J. P. (2017). An innovative multistage treatment system for sanitary landfill leachate depuration: Studies at pilot-scale. **Science of The Total Environment**, *576*, 99–117. https://doi.org/10.1016/j.scitotenv.2016.10.058
8. Sun, W., Meng, S., Zhang, S., Zheng, X., Ye, X., Fu, X., & Chen, S. (2018). Insight into the Transfer Mechanisms of Photogenerated Carriers for Heterojunction Photocatalysts with the Analogous Positions of Valence Band and Conduction Band: A Case Study of ZnO/TiO_2. **The Journal of Physical Chemistry C**, *122*(27), 15409–15420. https://doi.org/10.1021/acs.jpcc.8b03753
9. Turkten, N., & Bekbolet, M. (2020). Photocatalytic performance of titanium dioxide and zinc oxide binary system on degradation of humic matter. **Journal of Photochemistry and Photobiology A: Chemistry**, *401*, 112748. https://doi.org/10.1016/j.jphotochem.2020.112748