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Evaluation of the removal of *n*-butanol vapor by the poly(lactic acid)-zeolite-TiO₂ composite and formation of by-products

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Abstract

The use of polymeric films incorporated with zeolite-TiO₂ composites associated with UV radiation can be an alternative in the removal of volatile organic compounds (VOCs) through the adsorption and photodegradation processes. This study produced poly(lactic acid) (PLA) films incorporated with 13× zeolite, TiO_2 , and $13 \times -TiO_2$ zeolite composite to remove *n*-butanol and evaluate the by-products generated in the process. The results showed that 13× zeolite and TiO₂ added individually or as a composite to PLA, gave the polymer matrix a significant increase in the removal capacity of *n*-butanol. The best performance was presented by the zeolite-TiO₂, composite, confirming a synergistic effect. However, the formation of CO and CO₂ exceeded the expected values, with the verification that the polymeric matrix underwent photodegradation action by TiO₂. The polymeric film only containing zeolite is the most suitable for the removal of VOCs, as it did not present degradation of the PLA, generating a lower concentration of by-products.

KEYWORDS

adsorption, biopolymers and renewable polymers, composites, films, photochemistry

INTRODUCTION 1

Volatile organic compounds (VOCs) are among the principal air pollutants, characterized by low boiling point and high vapor pressure.¹ VOCs derives from both anthropogenic sources and natural sources.^{1,2} The presence of VOCs severely affects human health, as most of these compounds are toxic, as well as cause serious environmental problems such as the greenhouse effect and depletion of stratospheric ozone.^{2,3} Thermal combustion, catalysis, biofiltration, absorption, adsorption, and photodegradation can remove VOCs present in the

efficiency and low cost.^{2,8} Adsorption with porous materials is one of the most relevant physicochemical processes used to VOCs

removal. There are extensive studies on highly efficient adsorbents, including activated carbon, ordered mesoporous silicon materials, and zeolites.⁵ However, adsorption requires a regeneration step to be economically viable.⁸ Thermal regeneration is the most commercially used method. However, there are other emerging alternatives for the regeneration of adsorbents, including

atmosphere.^{4–7} Among these treatment processes, adsorp-

tion and photodegradation stand out because of its high

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photocatalysis.⁸ Photocatalysis is part of the advanced oxidation processes, where the destruction of contaminants occurs through oxidative reactions.⁹ Usually, photodegradation employs semiconductors as catalysts of oxidative reactions, such as TiO₂, ZnO, ZrO₂, CdS, MoS₂, Fe₂O₃, WO₃, and C₃N₄, with titanium dioxide (TiO₂) being the most widely used for various properties such as high oxidative power, chemically stable, and inexpensive material.^{9–12} However, TiO₂ production is in powder form, which is difficult to recover and easily aggregated, besides having low adsorption capacity.¹³ To overcome these disadvantages, TiO₂ supported on an adsorbent is an attractive alternative, providing a larger specific surface area, favoring the adsorption sites.^{14,15}

Active carbon, alumina, silica, and zeolite are the materials commonly used as support for TiO₂.⁸ Zeolite acts as both electron donors and acceptors of moderate strength to the guest species based on the adsorption site, with excellent absorption ability, high specific surface area, and uniform pores and channels with unique structures.^{16,17} The combination of adsorbents with photocatalysts form materials with great potential for the removal of pollutants because when the properties of both materials are combined, a synergistic effect can occur that increases the speed of the photodegradation.¹⁸

The use of zeolite-TiO₂ composites for photodegradation of pollutants has been increasing in recent years, using both natural and synthetic zeolites as adsorbents and support for TiO₂.^{18,19} It is possible to improve the use of the zeolite-TiO₂ composite by incorporating it into the polymer matrix, thus resulting in new materials for the removal and photodegradation of VOCs.

Currently, there is a growing demand for materials that have a less environmental impact. For example, in the field of polymers, biobased is an alternative to fossil-based polymers.²⁰ Poly(lactic acid) (PLA), a biodegradable polymer, derives from renewable sources²¹ and has been studied by many authors in several application areas,¹⁷ as well as the formation of composites with the introduction of loads.²² The introduction of the fillers in the polymer matrix has the objective of increasing properties to the polymer, depending on the application of interest.²² Some works already use the zeolites as loading in the PLA matrix, improving different properties such as thermal stability.^{23,24}

The TiO₂ incorporated in PLA has different functions, Xiu et al.²⁵ used TiO₂ as a filler in the polymer matrix to protect the PLA from UV radiation, obtaining satisfactory results concerning the polymer's photostability, attributing the effect to the absorption of UV radiation by TiO₂. On the other hand, Pillai et al.²⁶ and da Silva et al.²⁷ reported the acceleration of PLA degradation by the photocatalysis action of TiO₂ when incorporated into the polymer matrix. In this study, *n*-butanol was chosen as the representative molecule of VOCs, as it is present in many household products, and olfactometry tests use it as an odorant standard.^{28–30} Adsorption experiments on different materials, such as active carbon³¹ and zeolites,³² uses *n*butanol. Some authors have used *n*-butanol in TiO₂ photodegradation studies,^{28,33,34} such as Benoit–Marquié et al.,³⁴ which suggested a photodegradation mechanism supported by the formation of by-products. Nonetheless, there are still no reports of adsorption and photodegradation of *n*-butanol with zeolite-TiO₂ composites supported on the PLA polymer matrix.

This work aimed to develop biodegradable polymeric films (PLA) incorporated with zeolite-TiO₂, capable of promoting the adsorption and photodegradation of *n*-butanol. Also, to evaluate the formation of photocatalysis by-products and the possible photodegradation of the polymeric matrix of PLA to verify the potential application of the developed material in VOC removal processes.

2 | EXPERIMENTAL

2.1 | Composite

In previous studies,³⁵ the preparation of the zeolite-TiO₂ composite (ZT) followed the sol–gel method in an alcoholic medium with pH correction. In this process, one adds the titanium isopropoxide to the isopropyl alcohol and hydrochloric acid, then corrects the pH to 6.0 with ammonium hydroxide, and finally, includes 13× zeolite (IQE, Spain). Subsequently, the blend is calcined at 500°C to form the composite, remaining at a ratio of 80% zeolite and 20% TiO₂. Likewise, the synthesis of TiO₂ occurred without the presence of zeolite.

2.2 | Films preparation by solvent casting

The poly(acid lactic) utilized was the PLA (NatureWorks LLC, grade 4032D) with $M_n = 133,000$; dispersity ($M_w/M_n = 1.94$); *D* isomer content = 1.4%; relative viscosity = 3.94; residual monomer = 0.14%. In this procedure, firstly PLA pellets (0.8–1.5 g) were dissolved in 30 ml chloroform (Merck, 99%) under magnetic agitation (2 h) and added the load only zeolite (8%), only TiO₂ (2%), and ZT in different percentages (0%, 5%, 10%, and 25% wt) to the PLA solution. Sonication in the US probe (Eco-Sonics, 70 W, 20 kHz, 13 mm diameter ultrasonic probe), using a sonication program (2 min sonication time, power 20%, a maximum temperature of 30°C), followed this step. We put the suspensions in Petri glasses and

evaporated the solvent at ambient temperature during 12 h. The residual solvent was eliminated from films (thickness ~ 100 μ m) in a circulating air-drying oven at the temperature of 60°C for 12 h. Table 1 presents the description and identification of each film used in this study.

2.3 | Generation of *n*-butanol vapor

The vapor of *n*-butanol, with concentrations between 2500 and 3000 ppm, was obtained by the passage of a synthetic air (N₂/O₂, 80/20, Air Products) flow of 1.0 L/s (flowmeter Omega) through a glass flask containing 50 ml of liquid *n*-butanol (Merck, 99.5%), kept at room temperature ($25 \pm 2^{\circ}$ C). We transferred the *n*-butanol airflow mixtures to a collector flask (250 ml) with a septum sampling port through which samples are taken for GC-FID analysis until they reach a stable concentration. The initial vapor concentration of *n*-butanol corresponds to a level of intensity 5 (very strong) in the scale used for olfactometry tests (ASTM E544-10). We chose a high concentration due to the lack of studies at these levels and to verify the adsorption capacity of the films produced.

2.4 | Reactor for photodegradation

We used a borosilicate glass flask with a plastic screw cap (BereichAqualytic, Germany) and a volume of 12 ml as a reactor. The plastic caps were punctured to allow the entry of needles through the septa, installed between it and the body of the borosilicate flask. The double septa (Supelco, Blue \emptyset 13 mm, PTFE/Silicone, and Red \emptyset 13 mm, Butyl rubber/PTFE) were employed as either protective caps or an impermeable barrier to the gases of interest. Abruzzi et al.³⁶ previously validated the sampling protocol using the flask.

The irradiation source used was a 250 W mercury vapor lamp (FLC, Brazil), with its glass shield removed,

TABLE 1 Description and identification of the polymer films used in the adsorption and photodegradation experiments

| ID | Description |
|-------|---------------------------------------|
| NP | Neat PLA |
| PT | PLA with 2% TiO ₂ |
| PZ | PLA with 8% zeolite |
| P5ZT | PLA with 5% composite ZT ^a |
| P10ZT | PLA with 10% composite ZT |
| P25ZT | PLA with 25% composite ZT |

Abbreviation: PLA, poly(lactic acid).

^aComposite ZT is constituted of 20% wt TiO₂ on zeolite 13×.

leaving the bulb exposed.³⁷ However, UV-light radiation with wavelengths below 300 nm is filtered out by the glass wall of the reactor, as seen in the UV–VIS spectra of Figure S1 (supplementary material). We used this configuration in accelerated photo-aging tests.³⁸

2.5 | Adsorption/photodegradation tests

We performed the adsorption and photodegradation experiments using polymer composites films with dimensions of 1.5×6.0 cm², totalizing an area of 9.0 cm² and with $100 \pm 20 \,\mu\text{m}$ thickness. The films were arranged in the reactor so that the contact surface with the *n*-butanol vapor molecules made the fillers more concentrated. The reactor was purged with nitrogen (99.9992% purity) and evacuated for 15 min using a pumping system $(1 \times 10^{-4} \text{ m bar}, \text{ Edwards}, \text{ T-Station75})$ immediately before the adsorption/photodegradation tests. The *n*-butanol air mixture is introduced into the reactor from the collector flask, utilizing a gastight syringe, and after the adsorption process reaches equilibrium (50 min in the dark), we place the reactor in a closed hood at a distance of 10 cm from the mercury-vapor lamp. A thermometer was placed in this space (between the reactor and the lamp) to monitor the temperature, and we coupled a ventilation system to avoid heating, and then the system was irradiated. At determined time intervals, aliquots were removed and analyzed by gas chromatography to monitor the concentration of *n*-butanol and byproducts resulting from adsorption and photodegradation steps.

Besides, we carried out the photolysis of *n*-butanol and used an alternative matrix (Copper Conductive Tape, 3 MTM) as support for the ZT composite in the adsorption and photodegradation experiments. Photodegradation blank tests indicated that an alternative matrix does not contribute to the formation of CO_2 or other by-products.

2.6 | Characterization

We obtained the diffuse reflectance spectra (DRS) using a UV–Vis spectrometer (Jasco, V-560), which allows us to obtain spectra at wavelengths in the region between 200 and 850 nm. The X-ray diffractograms (XRDs) patterns were recorded at room temperature on Panalytical Empyrean using Cu K α (45 kV and 40 mA). We identified the crystalline phases present in the samples using the HighScore Plus 3.0 software with the integrated ICDD (International Center for Diffraction Data) PDF4 + (2014) database. The N₂ adsorption–desorption isotherms were obtained using a Micromeritics TristarKr

3020 equipment. The samples were previously heated to 120°C, under vacuum, for 12 h. The specific areas were estimated using the BET method (Brunauer, Emmett and Teller) and the pore size distribution using the DFT method. Scanning electron microscope (SEM) (Hitachi, SU-70) fitted with energy dispersive spectroscopy (EDS) unit was employed to analyze the surface morphology and composition of the synthesized composites and films.

2.7 | Quantification of *n*-butanol and degradation by-products

The *n*-butanol concentration and by-product formation were monitored on a gas chromatograph with FID detector (Shimadzu, GC-2014), using an external calibration curve with liquid standards of *n*-butanol in isopropanol.³⁹ We monitored the formation of CO and CO_2 in a second gas chromatograph with FID detector equipped with methanator (PerkinElmer, Clarus 580). For the identification of by-products, a third gas chromatograph equipped with a mass detector was used (Agilent Technologies, 7890A). The operational parameters of the three chromatographs are in the supplementary material.

3 | **RESULTS AND DISCUSSION**

3.1 | Composites characterization

Figure 1 shows the XRDs obtained for the zeolite, TiO_2 , and zeolite- TiO_2 composite (ZT). For the samples containing TiO_2 , the characteristic peaks of the anatase



FIGURE 1 X-ray diffractograms of zeolite $13\times$, TiO₂, and composite zeolite-TiO₂ [Color figure can be viewed at wileyonlinelibrary.com]

phase are present at 25.2°, 37.7°, and 48.4°, relative to the crystalline planes (101), (004), and (200), respectively. We also verified the presence of crystalline planes characteristic of zeolite 13× of higher relative intensity (111), (533), and (642) at different angles (2 θ) on pure zeolite and in a composite. The incorporation of TiO₂ into the zeolite does not modify its crystalline structure, and it is possible to verify the peak located at 25.2°, referring to the crystalline plane (101) characteristic of the anatase phase. This result suggests that there is a deposit of TiO₂ particles on the surface of the zeolites.

The UV–Vis diffuse reflectance spectrum obtained from the synthesized TiO_2 (results not shown) is characteristic of this material, with maximum absorption of 300–400 nm. The calculated band gap, obtained by extrapolating the tangent to the absorbance curve to the x-axis, presented values of 3.22 eV, following the literature.⁴⁰

Nitrogen adsorption-desorption isotherms and pore size distribution curves of zeolite 13× and composite zeolite-TiO₂ were presented in Figure 2. Zeolite $13 \times$ showed a type I isotherm (Figure 2(a)) that is characteristic for microporous materials (Figure 2(b)), as reported in literature for this zeolite.⁴¹ For the composite 13×-TiO₂ the adsorption also occurs at reduced pressures suggesting a type I isotherm (Figure 2(c)), however an inflection in higher relative pressures indicating a fraction of mesopores.^{42,43} In addition, H1-shaped hysteresis loop confirmed the occurrence of mesopores.⁴⁴ Nevertheless, the contribution to the specific surface area comes from the micropores, because of this, the analysis of pore size distribution was done by the DFT method (Figure 2 (d)). The BET specific surface areas, total pore volume and pore size of the samples were presented in Table 2. As expected, the pore volume of composite is higher than zeolite 13× due to the presence of mesopores. The surface areas of the Zeolite 13× and composite was 652 and $481 \text{ m}^2/\text{g}$, respectively. These results indicate that some of the zeolite pores are blocked or filled with TiO₂ particles, this behavior has already been reported by other authors.45,46 The decrease in surface area indicated that the TiO₂ were fully supported on the zeolite, this was consistent with the XRD and SEM/EDS results.

We evaluated the distribution of TiO_2 on the zeolite surface through SEM images, and it is possible to observe in Figure 3(a) that TiO_2 uniformly covered the zeolite surface as expected. The analysis by EDS (Figure 3(b)) confirmed the presence of Ti, as well as the other elements present in the zeolite (Al, Si, and Na). The presence of C and Cl comes from the compounds used in the synthesis of the ZT composite. Figure 3(c) shows the surface of the unfilled PLA film and Figure 3(d) shows the change in the surface of the polymer with the



FIGURE 2 The N₂ adsorption-desorption isotherm of (a) zeolite $13 \times$ (c) composite zeolite-TiO₂ and pore size distribution (b) zeolite $13 \times$ (d) composite zeolite-TiO₂ [Color figure can be viewed at wileyonlinelibrary.com]

| TABLE 2 Physicochemical narraneters of the zeolite 12x and | Sample | BET $(m^2/g)^a$ | $V(\mathrm{cm}^3/\mathrm{g})^\mathrm{b}$ | D (nm) ^c |
|--|--------------------------------|-----------------|--|---------------------|
| composite zeolite 13×-TiO ₂ | Zeolite 13× | 652 ± 10 | 0.03 ± 0.01 | 1.0–1.5 |
| 1 2 | Composite 13x-TiO ₂ | 481 ± 4 | 0.121 ± 0.001 | 1.0-2.0 |
| | | | | |

^aBET specific surface.

^bTotal pore volume calculated from the desorption branch of the isotherm using BJH method. ^cThe pore diameter calculated using the DFT method.

incorporation of 10% of the ZT composite (P10ZT film). The images obtained for the other films presented similar characteristics, except for the film P5ZT that is more porous than the other ones. We performed a more indepth evaluation of the distribution of the composite in the polymer film through the inspection of the cross-sectional images of the films (with cryogenic rupture). Figure 3(e,f) show that the composite is concentered on the lower surface of the film, probably due to the higher density of zeolite compared to PLA. Therefore, in the adsorption/photodegradation experiments, the films were exposed to the *n*-butanol vapor side of the film with the highest amount of composite.

3.2 | Adsorption and photodegradation of *n*-butanol

Figure 4 shows photolysis and adsorption and photodegradation results of *n*-butanol in the presence of neat PLA (NP), 8% zeolite (PZ), 2% TiO₂ (PT) films, and 10% of the zeolite-TiO₂ composite (P10ZT). The photolysis (without the presence of the films) of *n*-butanol is slow, with a decrease of only 10% after 120 min of reaction, extending to 30% in 240 min (results not shown). The *n*-butanol presents higher and faster (20 min) removal in the presence of the P10ZT film (54%) followed by zeolite containing film (PZ, 51%) and lower adsorption



FIGURE 3 Scanning electron microscopy images of (a) composite zeolite-TiO₂, (b) energy dispersive spectroscopy of composite zeolite-TiO₂, (c) neat poly(lactic acid) (NP) film surface, (d) P10ZT film surface, (e) NP film cross section, and (f) P10ZT cross section [Color figure can be viewed at wileyonlinelibrary.com]

for the film containing the photocatalyst (PT, 43%). This result suggests a synergistic effect of the simultaneous presence of zeolite and TiO_2 and a significant increase (~2×) of *n*-butanol adsorption capacity compared to the neat film-PLA (30% removal).

We investigated three different loadings of the ZT composite in the PLA polymer matrix. The adsorption and photodegradation experiments presented different results for each loading, as can be observed in Figure 5. The adsorption step was very similar for the 5% and 10% composite loads, with 54% and 56% removals, respectively (Table 3). The explanation to this result can be that the P5ZT film had an unexpected higher porosity than

the P10ZT film, as suggested by SEM analysis. However, n-butanol photodegradation was faster in the presence of the P10ZT film, suggesting that the catalyst content plays a significant role at this stage of the removal process. The results with the 25% loading film were different from the others. The adsorption of n-butanol by P25ZT film was quickly, and the removal was higher than 95% of the initial concentration at the end of the adsorption step (50 min). After 10 min of the lamp activation, the n-butanol concentration showed a slight increase (2%), indicating possible desorption of the adsorbed vapor from the film matrix. We can justify this behavior by the low increase in temperature that occurs in the



FIGURE 4 Photolysis and adsorption/photodegradation of *n*-butanol in the presence of the neat poly(lactic acid) (NP), PT, PZ, and P10ZT films



FIGURE 5 Adsorption and photodegradation of *n*-butanol in the presence of the P5ZT, P10ZT, and P25ZT films

photodegradation step. The *n*-butanol concentration decreased slowly over the first 60 min (270–240 ppm). As a result, this test was extended up to 240 min, observing a slow drop in *n*-butanol concentration, which reached 40 ppm at the end of the experiment.

3.3 | Photodegradation kinetics

Usually, the heterogeneous reactions of organic compounds' photodegradation follow the model of Languimir–Hinshelwoodh $(L-H)^9$:

$$r = -\frac{dC}{t} = \frac{kKC}{1+KC},\tag{1}$$

where r is the initial rate of the photodegradation reaction, C is the gas phase reagent concentration, t is the

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irradiation time, k is the constant rate of the reaction, and K is the reagent adsorption coefficient.

At low concentrations (on a molar basis), KC < < 1, one can use the simplified form of the L–H equation:

$$\ln \frac{Co}{C} = kKt = K_{app}t,$$
(2)

where K_{app} is the apparent constant rate of pseudo-firstorder, obtained by the interpolation of $\ln C_0/C$ versus t, C_0 , and C being the reagent concentrations in the gas phase at time zero and time *t* of the *r*.

Figure 6 shows the photodegradation kinetics of *n*-butanol in the presence of the PZ, PT, P5ZT, and P10ZT films. It is possible to observe that the P10ZT film has the fastest kinetics with $K_{app} 0.064 \text{ min}^{-1}$ (Table 3), followed by the P5ZT (0.049 min⁻¹), and the PT (0.010 min⁻¹) films. On the other hand, PZ and NP films showed very slow photodegradation kinetics (0.002 min⁻¹). As previously reported, the P25ZT film showed a distinct behavior. In the first 10 min of UV exposure, we observed desorption of *n*-butanol (<2%), probably the light increase in the temperature of the reactor. With the extension of exposure time, we noticed a decrease in *n*-butanol concentration, and a kinetic constant was calculated ($K_{app} = 0.005 \text{ min}^{-1}$).

3.4 | Adsorption/photodegradation cycles

We carried out experiments to verify the reusability of the polymer composite. In this study, we performed five cycles with the P10ZT film, which presented the best performance in *n*-butanol adsorption/photodegradation. Figure 7 shows the obtained results, indicating the potential reuse of the film. However, inspecting the kinetic constants obtained for each cycle, we observed a linear decrease over *n*-butanol photodegradation (from 0.064 to 0.033 min^{-1}). On the other hand, *n*-butanol removal during the 50 min wherein the system remains in the dark showed an increase from the third (59%) and fourth (69%) cycles compared to the first cycle (54%). However, a significant decrease was observed in the fifth cycle (47%), suggesting that exposure to UV radiation also affects the adsorption equilibrium in addition to the photodegradation kinetics. The loss of efficiency in the removal processes of *n*-butanol may be linked to catalyst activity, however the structure of the catalyst after the reaction is not easily accessible. The catalyst is dispersed in the zeolite, which in turn is introduced into the polymeric matrix (PLA). It should be noted that the concentration of TiO₂ in the polymeric composite is a maximum

TABLE 3 N-butanol removal by adsorption and photodegradation, in the presence of neat PLA and PLA composites

| Film | | Dark Adsorption | UV-lamp on photodegradation | | | Total removal ^a |
|-------|-------|-----------------|---|-------|-------------|----------------------------|
| Code | Cycle | Removal (%) | $\overline{K_{\mathrm{app}}} \ (\mathrm{min}^{-1})$ | R^2 | Removal (%) | % |
| NP | | 30 | 0.002 | 0.859 | 2 | 32 |
| PZ | | 51 | 0.002 | 0.974 | 1 | 52 |
| PT | | 43 | 0.029 ^b | 0.965 | 52 | 96 ^b |
| P5ZT | | 56 | 0.049 | 0.913 | 42 | 98 |
| P10ZT | | 54 | 0.064 | 0.991 | 45 | 99 |
| P25ZT | | 95 | 0.005 ^c | 0.988 | 4 | 99 ^c |
| P10ZT | 1st | 54 | 0.064 | 0.991 | 45 | 99 |
| | 2nd | 52 | 0.060 | 0.990 | 47 | 99 |
| | 3th | 59 | 0.051 | 0.962 | 38 | 98 |
| | 4th | 67 | 0.038 | 0.934 | 30 | 97 |
| | 5th | 47 | 0.033 | 0.976 | 45 | 93 |

Abbreviation: PLA, poly(lactic acid).

^aTotal removal considering adsorption and photodegradation steps. ^bData calculated at time interval from 0 to 60 min.

^cData calculated at time interval from 10 to 120 min (K_{aDD}).



FIGURE 6 Kinetics of *n*-butanol photodegradation in the presence of the PZ, PT, P5ZT, and P10ZT films



FIGURE 7 Adsorption and photodegradation of *n*-butanol in five cycles with the P10ZT film

of 5%. In addition, the PLA matrix causes difficulties in verifying changes in the catalyst structure by SEM or XRD analyzes. According to Mo et al.,²⁹ several factors interfere with the activity of the photocatalyst, as regards its surface, such as photopolymerization of some substances, the presence of particulate material, which may block the pores, besides the intermediate by-products that may also deposit on the surface of the photocatalyst. Sauer et al.⁴⁷ emphasize the deactivation of the active sites by the by-products generated. This phenomenon occurs in both batch and flows reactors, regardless of the VOC understudy or the photocatalyst used.

3.5 | By-products generated

3.5.1 | Photodegradation of PLA films

We did a preliminary test with the neat PLA film exposed to UV radiation (120 min) in the presence of synthetic air. We detected acetaldehyde, acetone, and chloroform as gaseous by-products, but at low concentrations (3.9, 3.0, and 11 ppm, respectively), at the end of the reaction. The presence of chloroform is due to its use as a solvent in the films' preparation, even though it evaporated in the preparation, it retained a small amount, and released it with radiation exposure. To eliminate residual chloroform, we extended the drying time (up to 48 h) to all other films prepared. On the other hand, we could associate acetaldehyde and acetone with the degradation of the polymer matrix. PLA photodegrade under UV and

sunlight exposure through the mechanism of Norrish II reaction, whereby chain scission occurs, and the formation of C=C double bonds takes place along with carboxyl end groups.²⁰ According to this mechanism, a diversity of by-products, including acetaldehyde and acetone, could be formed as the polymer chain cleavage result. In addition to the organic by-products, PLA photodegradation also generates CO (27 ppm) and CO₂ (179 ppm). Despite the low concentrations, the presence of these compounds, especially acetaldehyde and CO, should be carefully considered, given their higher toxicity. For instance, Lyulyukin et al.⁴⁸ indicated limit values of 25, 20, and 200 ppm for CO, acetaldehyde, and acetone, respectively, for a calculation of a total hazard index during the photocatalytic oxidation of VOCs by zeolite-TiO₂. Vapors and gas exposure limits in the workplace form industrial standards are the bases for these values.⁵¹ We highlight that in the indoor air of non-occupational environments, the exposure limits for these pollutants should be more restrictive.

We also exposed PT and P10ZT films that presented the best performance in *n*-butanol photodegradation to UV radiation in synthetic air. The CO₂ and CO concentration profiles observed during these experiments, in addition to the neat PLA (NP) data, are shown in Figure 8(a,b). A significant linear increase in CO₂ concentration with a time of exposure (up to 120 min) was observed for both films containing TiO₂, with concentrations reaching 5500 and 7300 ppm for the films P10ZT and PT, respectively. These values are 30 and 40 times greater than the concentration observed in the experiment with NP film. We observed similar behavior for CO, but with higher concentrations (900 ppm) in the presence of P10ZT compared to PT (800 ppm) at the end of the reaction. These results evidenced a significant photodegradation of the polymer matrix induced by the action of TiO₂. We also observed acetone and acetaldehyde as by-products but at low levels, and only in the presence of PT film, reached maximum concentrations of 7 and 8 ppm, respectively, after 60 min of reaction. However, increasing the reaction time, the concentration of both compounds decreased, reaching values close to zero after 120 min of UV exposure. No oxygenated byproducts were observed during the test with the P10ZT film, suggesting that the presence of zeolite in the polymeric matrix inhibits the formation of such by-products and or they do not desorb from the film.

As previously mentioned, some authors^{26,27} reported the degradation of PLA by TiO₂, but for much longer irradiation time (several days) and without the identification of the generated by-products. TiO₂, when irradiated by UV light in the presence of oxygen, generates reactive radicals such as O₂•, HOO•, and HO•, which initiate the



FIGURE 8 Concentrations profiles of (a) CO_2 and (b) CO in the photodegradation experiments of neat poly(lactic acid) (NP), PT, and P10ZT films in synthetic air

PLA photodegradation, generating other radicals (CH_2 •, $CHCH_2$ •, among others). These radicals are introduced into the polymer chain and results in their cleavage into volatile compounds such as CO and CO₂ that desorb, while others by-products with low volatility become attached to the polymer matrix.^{27,49,50}

Although no by-product formation, other than CO_2 and CO, has been observed in the photolysis of film P10ZT, the evaluation of its use must be cautious. The presence of *n*-butanol in the gas phase may influence the photodegradation and adsorption/desorption mechanisms involving PLA composites, which we discuss below.

3.5.2 | Photodegradation of the *n*-butanol

In the presence of the NP film, the photodegradation of n-butanol only results in the formation of CO₂ at the maximum concentration of 480 ppm. The CO₂ generation corresponds to 4% of n-butanol, considering its initial concentration expressed in C ppm. These results suggest that the removal of n-butanol from the gas phase occurs mainly by adsorption on the polymer film. Butanol

adsorption on NP film seems to decrease the generation of photodegradation by-products of the polymeric matrix since it generated any organic by-products.

The presence of the zeolite in the polymeric film (PZ) favored the formation of CO_2 and CO at more significant concentrations (1300 and 180 ppm, respectively) compared to the NP film after 120 min of photolysis. It was observed the formation of acetaldehyde (45 ppm), acetone (7 ppm), and butanal (65 ppm), as well as higher adsorption of *n*-butanol (51%), compared to NP film (32%), as reported in Table 3. The presence of zeolite increases not only the adsorption of *n*-butanol but also its photodegradation. The formation of butanal, which is undoubtedly a specific by-product of the *n*-butanol photodegradation, ^{28,34,51} supports this finding.

3.5.3 | Films with TiO_2

Figure 9 shows the GC-FID chromatograms (Method 1) obtained at different reaction times of *n*-butanol in the presence of the P10ZT film. We observed the significant formation of butanal, and in smaller proportions of acetone and acetaldehyde, already from 10 min of exposure to UV radiation, with the rapid and concomitant removal of *n*-butanol from the gas phase. As the reaction progresses, the butanal concentration decreases while occurs the generation of other by-products (acetone; acetaldehyde; formic acid, and butyl ester). The concentration profile of the main by-products generated, including CO₂ and CO, are shown in Figure 10. We verified that CO₂ and CO generation already occurs from the beginning of the photolysis, increasing continuously and reaching high concentrations (16,600 and 850 ppm, respectively)

at the final time of the experiment (120 min). We obtained similar results in the photodegradation of *n*-butanol with PT film, with the formation of acetaldehyde, acetone, propanol, butanal, and formic acid, butyl ester, as shown in Figure 11(a). However, the by-product levels are lower, and the maximum concentrations arrive in longer reaction times when compared to composite film, despite the same TiO_2 loading (2%) for both films. This result confirms the best photodegradation performance of composite film compared to PT film.

For comparison, Figure 11(b) also indicates the results obtained in *n*-butanol photodegradation in the presence of the PZ film. In the presence of zeolite, the photodegradation by-products generated are the same as those observed for other films (P10ZT and PT). Despite the slower formation and lower concentrations of by-products, the generation of butanal confirms the role of zeolite (PZ) in the photodegradation of *n*-butanol.

Figure 12 shows the mass balances, expressed in carbon basis (C ppm), for the experiments in the presence of PT, P10ZT, and PZ films for comparison. The concentrations of CO_2 and CO found in the experiments with the PT and P10ZT films were higher than the stoichiometric concentration according to the initial concentration of *n*-butanol. In contrast, for the film containing only the zeolite (PZ), the carbon balance is not exceeded. As previously discussed, these results suggest the photodegradation of the polymer matrix in the presence of TiO₂, with essentially CO and CO₂ generation.

All by-products identified in this study are reported in the literature as the intermediate or end-products of the *n*-butanol photodegradation,^{28,34,51} except for formic acid, butyl ester. Several samples analyzed by GC-MS suggested the structure of this by-product. However, the



FIGURE 9

Chromatograms of *n*-butanol photodegradation by-products with P10ZT film at different adsorption (0–50 min) and photodegradation (50–110 min) times [Color figure can be viewed at wileyonlinelibrary.com]

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FIGURE 10 Removal of *n*-butanol and generation of by-products profiles in the presence of P10ZT film. In detail profiles of concentration in the photodegradation step [Color figure can be viewed at wileyonlinelibrary.com]



FIGURE 11 Removal of *n*-butanol photodegradation concentration and generation of by-products profiles in the presence of: (a) PT and (b) PZ films [Color figure can be viewed at wileyonlinelibrary.com]

confirmation of its formation as an end-product should be observed with caution since its formation implies mechanisms not yet reported in the literature for the *n*-butanol photodegradation.

On the other hand, Benoit-Marquié et al.³⁴ found butyric acid as a by-product of *n*-butanol photodegradation, in addition to the other by-products previously mentioned. However, butyric acid has not been identified in any tests, neither by GC-FID nor by GC-MS. Kirchenova et al.²⁸ state that there was an aldolization of the butanal formed from *n*-butanol photodegradation and found crotonaldehyde as a by-product, in addition to the other compounds already reported. These authors related their findings with the particular characteristics of the TiO_2 employed. All authors confirm butanal as a significant by-product of photodegradation of *n*-butanol, which in turn is photodegraded, resulting in the other minor chain by-products. The photodegradation reaction could proceed until complete mineralization resulting in H₂O and CO₂.

We carried out a complementary experiment to verify the action of the zeolite-TiO₂ composite on photodegradation of *n*-butanol without the interference of the polymer matrix

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FIGURE 12 Carbon balance of *n*-butanol photodegradation by-products in the presence of the films: (a) PZ, (b) PT, and (c) P10ZT [Color figure can be viewed at wileyonlinelibrary.com]

since it contributed to the by-product formation. The composite was placed on an adhesive surface (copper adhesive tape) for fixation and introduced into the glass reactor. Previously it was found that the adhesive tape used was inert and would not interfere with the results obtained. Figure 13(a) shows the decay of the *n*-butanol concentration, as well as the formation of CO and CO_2 . The other by-products generated are acetaldehyde, acetone, propanol, butanal, and acid formic, butyl ester. The results obtained confirmed that the presence of acetaldehyde and acetone are not only byproducts of photodegradation of PLA but are part of the photodegradation mechanism of *n*-butanol. We highlight



FIGURE 13 (a) Removal of *n*-butanol photodegradation concentration and generation of by-products profiles and (b) carbon balance *n*-butanol and by-products in the presence of ZT composite impregnated in the alternative matrix [Color figure can be viewed at wileyonlinelibrary.com]

that the carbon balance was within the expected range, as can be seen in Figure 13(b).

4 | CONCLUSION

Zeolite 13× and TiO₂ added individually or in composite form give the polymer matrix an increased *n*-butanol adsorption capacity, with better Zeolite-TiO₂ composite performance than the individual fillers, suggesting an important synergistic effect. The use of the Zeolite-TiO₂ composite compared to the other films evaluated, improved the *n*-butanol photodegradation capacity.

We obtained pseudo-first-order kinetics with K_{app} proportional to the added loading (0%–10%) and differentiated behavior for higher loading tested (25%). The reuse of the TiO₂-containing composite films (up to five cycles) indicated an increase in the adsorption capacity of butanol, but with a decrease in its photodegradation. This behavior is related to the probable surface modification of the polymer matrix induced by its photodegradation by TiO_2 .

The *n*-butanol photodegradation tests resulted in the formation of CO, CO₂, and several oxygenated organic by-products, with butanal as the most relevant intermediate formed. The mass balance of carbon during the photodegradation reaction evidenced the significant attack of the polymer matrix by TiO_2 , with values much higher than expected for the photodegradation of *n*-butanol.

Tests with polymeric films in the presence of synthetic air evidenced the susceptibility of PLA to the photodegradation, intensified by the presence of TiO_2 . Despite the absence or low concentrations of organic byproducts (acetone and acetaldehyde), the generation of high concentrations of CO, due to its high toxicity, indicates that the evaluation of the use of PLA composites with TiO₂ in VOC photodegradation should be cautious.

The presence of the zeolite $13\times$ seems to inhibit the formation of undesirable by-products and to increase the photodegradation of *n*-butanol. These results suggest a possible application of PZ film in the removal and photodegradation of *n*-butanol in indoor air, with lower risks of photodegradation of the polymer matrix, as observed in films containing TiO₂.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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