Degradation of the mixture of the ketoprofen, meloxicam and tenoxicam drugs using TiO₂/metal photocatalysers supported in polystyrene packaging waste

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ABSTRACT

The solution mixture of the non-steroidal anti-inflammatory drugs ketoprofen, meloxicam and tenoxicam was degraded through systems, composed of different photocatalysts based on TiO₂ (Fe and Cu) and the hydrogen peroxide oxidant. The monitoring was performed by UV-Vis spectroscopy. Under sunlight radiation, a reduction in peaks was observed with the use of impregnated photocatalysts. After 60 min, the sun/H₂O₂/Fe-TiO₂ system reached degradations of 46.5% and 93.2% at 260 and 367 nm, respectively, and was selected for further studies. The degradation kinetic reached 92 and 96% of degradation after 180 min, for the λ of 260 and 367 nm, respectively. The kinetic curve could be represented by the empirical model proposed by Nichela and co-authors, indicating that besides the heterogeneous photocatalysis that occurs at the surface of the TiO₂ there is also the joint effect of the photo-Fenton process. After the treatment, there was no toxicity to cress and lettuce seeds. However, a sensitivity of the thyme seeds to the compounds formed during the treatment was verified. After the fifth treatment cycle, the supported photocatalyst showed degradation higher than 82%. These results indicate that this system is suitable for the treatment of effluents containing pharmaceutical compounds.

Key words | heterogeneous photocatalysis, ketoprofen, meloxicam, tenoxicam

HIGHLIGHTS

- Degradation of the mixture of the drugs meloxicam, tenoxicam and ketoprofen by photocatalysts and hydrogen peroxide together.
- TiO₂ films impregnated with Fe and Cu increase the photocatalytic activity under sunlight radiation when compared to non-doped TiO₂.
- The Fe-TiO₂ film maintained photocatalytic activity after five reaction cycles.
The presence of pharmaceutical compounds in surface waters and groundwater is one of the biggest problems of anthropogenic pollution. Due to the fact that several drugs have already been detected in surface waters, in different concentrations, numerous countries have started monitoring the cycle of active pharmaceutical ingredients (Bagheri et al. 2017; Comber et al. 2018; Della-Flora et al. 2020). However, in general, there is still no regulation regarding effluents from pharmaceutical industries and hospitals, the main sources of drug disposal in the environment (Khan et al. 2020a).

This type of water contamination is associated with the fact that the conventional effluent treatment plants are mostly not able to remove pharmaceutical active ingredients, removing only biodegradable carbon, phosphorous and microorganisms. This treatment gap allows these compounds to reach the recipient bodies, causing damage to aquatic ecosystems (Environmental Protection Agency 2019; Della-Flora et al. 2020; Khan et al. 2020b).

In this way, both the European Union and the United States Environmental Protection Agency have strategically addressed the issue of drugs in the environment. The first aims to identify the actions that address the potential risk of pharmaceutical compounds in the environment and to encourage innovations that help deal with these risks. The United States Environmental Protection Agency regulated the management of pharmaceuticals products with the objective to reduce the concentrations of drugs in surface and drinking water (Environmental Protection Agency 2019; European Commission 2019). To solve this problem, different research has used technologies to treat compounds that are difficult to degrade. Amongst them are the advanced oxidation processes (AOP), which aim at the degradation of these compounds to a complete mineralization (Serpone et al. 2017; Comber et al. 2018; Sinhmam et al. 2020).

There are several types of AOP, which can be divided into the photochemical processes, which use some type of radiation (hv/O3, hv/H2O2, hv/O3/H2O2 and photo-Fenton), and the chemical processes, which do not use radiation; for example, the Fenton process. The subarea that studies the use of a semiconductor as a photocatalyst is called heterogeneous photocatalysis. In this case, the process occurs when the semiconductor is irradiated with photons (hv), whose energy is greater than or equal to the energy difference between the conduction and valence bands (bandgap – Eg), generating electrons (e−) and gaps (h+)(Araújo et al. 2016; Serpone et al. 2017).

In heterogeneous photocatalysis, hydroxyl radicals can be formed by reacting the gaps with the adsorbed water, with the OH− surface groups, or by electrons reacting with dissolved oxygen. Gaps can also react directly with the organic compound (Singh et al. 2013; Serpone et al. 2017). TiO2 has been the most studied semiconductor due to its photocatalytic properties, chemical stability, and low toxicity (Ochoa Rodríguez et al. 2019). Anatase and rutile are two types of TiO2 crystalline structure, with its bandgap values being 3.2 eV and 3.0 eV, respectively. Because of its smaller bandgap, the rutile structure can absorb rays slightly closer to the visible light region but has a higher electron/gap recombination rate (Feltrin et al. 2015).

Therefore, in order to increase photocatalytic activity, techniques are being developed and chemical elements are being tested for doping and impregnating TiO2. This process aims to increase the radiation absorption spectrum, as well as to prevent the recombination of the electron pair/gap (Zaid et al. 2016; Ali et al. 2017; Stucchi et al. 2019; Sinhmam et al. 2020). When combined with a metal, the photocatalytic properties of the semiconductor are improved, due to better charge separation at the metal-semiconductor interface and increased absorption of visible light caused by the plasmonic resonance of the metal surface (Fu et al. 2019). Among the transition metals, iron (Fe) and copper (Cu) have properties that give them the ability to be used as dopants, since they
are cheap and available resources. The insertion of these metals in TiO₂ has increased its photocatalytic activity (Zaid et al. 2016; Khaki et al. 2017; Eshaghi & Moradi 2018).

However, sometimes when making use of some AOPs, it is possible to verify that the treated compounds are not completely oxidized, being necessary to evaluate if the formed substances have toxic effects. The seed germination test is a procedure that has been used for this purpose, even without a universally adopted procedure. Lettuce seeds (Lactuca sativa) are used to assess the toxicity of compounds formed in the degradation of non-steroidal anti-inflammatory drugs (NSAIDs). Cress seeds (Lepidium sativum) are also used to assess the toxicity of compounds (Luo et al. 2018; Marchetti & Azevedo 2020).

In view of the above, this work was aimed at evaluating the efficiency of systems, composed of different photocatalysts based on TiO₂ and the hydrogen peroxide oxidant, on the degradation of the drugs ketoprofen, tenoxicam and meloxicam in a multicomponent solution, as well to prepare and characterize TiO₂ impregnated with copper and iron and supported on polystyrene films from post-consumer yoghurt packaging. In addition, the toxicity before and after the selected treatment was evaluated alongside the efficiency of photocatalyst reuse.

**MATERIALS AND METHODS**

**Drug solutions**

The drug solutions were prepared from the active ingredients in ketoprofen, meloxicam and tenoxicam powder, provided by the school pharmacy of the Universidade Federal de Pernambuco according to Santos et al. (2020). To prepare the solution, 10 mg of each drug was diluted together in acetonitrile (Merck, min 99.9%, HPLC) in a 10 mL volumetric flask, which was placed in an ultrasound bath (Eco-Sonics, Q5.9/37A) for 5 min to achieve complete solubilization. From this solution, dilution with distilled water in a 1 L flask was performed for the degradation tests with an initial concentration of 10 mg·L⁻¹ of each drug (working solution).

**TiO₂ impregnation with metals**

The methodology used for impregnating TiO₂ (Dinâmica, 98–100.5%) was adapted from Khan et al. (2013). For the 1% metal impregnation step (mole ratio), 79.1 g of TiO₂ was added in 500 mL of deionized water. For the impregnations with Fe and Cu, 2.78 g of FeSO₄·7H₂O (F. Maia, 99–101%) and 2.4 g of Cu(NO₃)₂·3H₂O (Vetec, min. 99%) were added to this suspension, respectively. For co-impregnation, 0.5% molar proportion of each metal was added.

The suspension was stirred on a shaking table (Fisatom, mod. 753), with the aid of a 3 cm magnetic stick, for 6 h, after which the sample was left to rest for 24 h. It was then dried for 12 h at 100 °C in an oven (Quimis) and the dry solid obtained was crushed in an agate mortar and calcined at 400 °C for 6 h in a muffle furnace (Quimis).

**Imobilization of photocatalysers**

The photocatalysts TiO₂, Cu-TiO₂, Fe-TiO₂ and Cu|Fe-TiO₂ were immobilized in polystyrene materials, obtained from post-consumer yoghurt packaging, with an average surface area equal to 129 cm². The supports were previously washed with neutral detergent and distilled water, then dried at a temperature of 27 ± 2 °C. The method of immobilizing the photocatalysts was carried out as described in Santos et al. (2019).

**Photocatalyst characterization**

To determine the surface morphology of the supports, the films were analyzed using a scanning electron microscope (SEM) (Jeol JSM-6460 Scanning electron microscope). The samples were deposited on carbon adhesive tape and covered with a thin layer of graphite in a chamber (Cressington carbon contains 108 carbon/A). The samples were then placed in a vacuum chamber and analyzed according to the magnification lens chosen.

In order to verify the presence of TiO₂ in the support and the possible differences of the metals’ impregnations, analysis by Fourier transform infrared spectroscopy (FTIR) in the medium infrared (4,000–500 cm⁻¹), 16 scans, resolution of 2 cm⁻¹ with attenuated total reflectance, with UATR accessory, were applied. For this, the surfaces of the polymers were evaluated, before and after deposition.

To obtain the metal content incorporated into TiO₂, the photocatalyst was subjected to acid digestion by the addition of HNO₃ p.a. (Química Moderna, 65%) and HCL p.a. (Química Moderna, 37%), following standard methodology according to the American Public Health Association (APHA 2012). The readings were taken on the atomic absorption spectrophotometer (Varian, AA240FS) at wavelengths of 248.3 and 324.7 nm for iron and copper, respectively.

The composition of the crystalline phase of the photocatalyst was examined on an X-ray diffractogram (Bruker, D8 Advance), with the scanning angles (2θ) ranging from 5° to
90°, using the step size and the scan rate of 0.021 (degree) and 1.33° per minute, respectively.

**Evaluation of the advanced oxidation processes**

The degradations of non-steroidal anti-inflammatory drugs, ketoprofen, tenoxicam and meloxicam were evaluated by comparing different advanced oxidation processes (AOP) in two bench reactors, the first with three UV-C lamps (Philips, 30 W each) (Figure 1(a)) and the second with sunlight lamp (Sun) (Osram, 300 W) (Figure 1(b)). Therefore, the following AOPs were evaluated: $h\nu/H_2O_2$, $h\nu/H_2O_2/TiO_2$, $h\nu/H_2O_2/Cu-TiO_2$, $h\nu/H_2O_2/Fe-TiO_2$, $h\nu/H_2O_2/Cu|Fe-TiO_2$. In which $h\nu$ represents radiation, be it sunlight or UV-C. These experiments were also carried out in the absence of radiation, to assess the contribution of the adsorptive process. In addition to these, the drugs were degraded by the sun/TiO$_2$ and sun/Fe-TiO$_2$ systems, in the absence of H$_2$O$_2$.

Measurements of incident radiation intensities were performed using light meter MRU-201 and ultraviolet MRUR-203, from Instrutherm Ltda. While the identification of the degradation was carried out through spectral scanning analysis from 190 to 500 nm in a UV/Vis spectrophotometer (Thermo Scientific), before and after each process.

For each experiment, 250 mL of the working solution were placed in cylindrical Pyrex glass cells with 300 mL of

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**Figure 1** | Scheme of reactors with radiation lamps (a) UV-C and (b) sunlight, with dimensions in cm.
capacity and each test conducted for a period of 60 min. The concentration of H$_2$O$_2$ (Química moderna, 30% v/v) applied was 500 mg·L$^{-1}$. The total volume of hydrogen peroxide added was divided in three aliquots at 0, 10 and 20 min. In the experiments with photocatalysts, the addition of hydrogen peroxide was only done after 30 min in the dark and under agitation, to stabilize the adsorptive process as recommended by Ali et al. (2017) and Tayade et al. (2006). The cell used in these processes is illustrated in Santos et al. (2019).

**Kinetic study**

The kinetic study was carried out according to operational conditions described in the previous item, for the system that presented the best degradation. 2 mL samples were taken from 0 to 180 minutes and analyzed on a UV/Vis spectrophotometer (Thermo Scientific), at the characteristic wavelengths (260 and 367 nm). Analytical curves were built, which resulted in detection limits of 0.23 and 0.17 mg·L$^{-1}$, and quantification limits of 0.69 and 0.52 mg·L$^{-1}$ for the respective wavelengths of 260 and 367 nm.

The pseudo-first order kinetic models proposed by Chan & Chu (2003) and proposed by Nichela et al. (2010) were adjusted to the experimental data. All described kinetic models were adjusted applying the non-linear regression method (least squares method), using Origin software (version 8.0). The performances of the models that best fit were compared using the F test, where $F_{\text{calculated}}$ was defined from Equation (1).

$$F_{\text{calculated}} = \frac{S_R^2(A)}{S_R^2(B)}$$  \hspace{1cm} (1)

where $S_R^2(A)$ and $S_R^2(B)$ are the standard deviations of models A and B, respectively, for $S_R(A) > S_R(B)$. If $F_{\text{calculated}} > F_{\text{tabulated}}$, model B has a better fit than model A for a 95% confidence level.

**Toxicity**

The acute toxicity test was performed for cress seeds (*Lepidium sativum*, cv *Barbara verna*), thyme seeds (*Thymus vulgaris*) and Lettuce seeds (*Lactuca sativa*, cv *Veneranda*) by exposing them to distilled water (negative control) and to the drug solution before and after treatment by the AOPs. The effects of the iron reagents were also evaluated, with a concentration of 1 mg·L$^{-1}$, which is higher than that dissolved in the solution and H$_2$O$_2$, with a concentration of 25 mg·L$^{-1}$, concentration of residual hydrogen peroxide in the solution after treatment.

The tests, in triplicate, were conducted for a period of 120 h, at a temperature of 22 ± 2 °C, in the absence of light. In each Petri dish, 20 seeds were placed on filter paper (support) and moistened with 4 mL of solution, as according to Young et al. (2012) and Marchetti & Azevedo (2020).

At the end of the incubation time, the radicle length of each seed was measured with a caliper. The calculation of relative growth index (RGI) is shown in Equation (2).

$$\text{RGI} = \frac{\text{RLS}}{\text{RLC}}$$  \hspace{1cm} (2)

where RLS and RLC is the average radicle length of the sample and of the control, respectively.

**Photocatalyser reuse**

The reuse study of the selected photocatalyst was carried out for five reaction cycles. The operating conditions were the same as in the kinetic study; after 180 min the sample was immediately quantified. Between each cycle, the photocatalyst was expected to dry at room temperature and weighing was carried out to monitor the loss of mass.

**RESULTS AND DISCUSSION**

**Photocatalyst characterization**

To analyze the morphologies of the support surface before and after the immobilization of TiO$_2$ and TiO$_2$ impregnated with the metals copper and iron, the scanning electron microscopy (SEM) technique was used. The morphology of the materials is shown in Figure 2.

When looking at Figure 2, a morphological modification of the surface is observed, which indicates the immobilization of the photocatalysts, distributed as a layer (Figure 2(b)–2(e)) on the surface of the polystyrene support (Figure 2(a)). The addition of ions to the photocatalyst through the wet impregnation process does not modify the morphology of the TiO$_2$ particles according to Tayade et al. (2006), Zaid et al. (2016) and Ochoa Rodríguez et al. (2019). Despite this, there is a difference in the aspect of impregnation on the polymer.

Figure 3(a) shows the spectra obtained in the analysis of Fourier transform infrared spectroscopy. Figure 3(b) shows the X-ray diffractograms of the photocatalytic materials.
This type of analysis is used to investigate the type of crystallinity of the material.

It can be seen in Figure 3(a) that the spectrum of the support showed peaks in the bonds present in the polystyrene molecule (peaks 1–6), as according to Solomons & Fryhle (2012) and Velásquez et al. (2012). It can also be seen that TiO$_2$ was immobilized on the support surface, being impossible to observe typical absorption bands, such as that observed around 700–500 cm$^{-1}$ regarding the O–Ti–O bond (Ali et al. 2017; Eshaghi & Moradi 2018).

The spectra of the supports impregnated with the photocatalysts, in addition to the peaks referring to TiO$_2$, also
showed peaks characteristic of the polystyrene, even in lesser intensity, indicating that there may be small areas of the material not covered by the photocatalyst.

The analysis of the amount of metal incorporated into TiO₂ was carried out through acid digestion and quantification in the flame atomic absorption spectrometer. It was found that the actual amount of metal impregnated with copper (0.84) was greater than with iron (0.63), in mole ratio (%). This may be due to the fact that Cu(II) has a smaller radius (0.69 Å) in relation to the Fe(II) ion (0.76 Å), thus facilitating its impregnation on the surface of TiO₂. The impregnation with two metals simultaneously, theoretical quantity (0.5), decreased the yield in relation to both ions, with Cu (0.36) and Fe (0.21).

From Figure 3(b), no significant changes were observed in the diffractograms, indicating that the impregnation performed at a temperature of 400 °C did not significantly influence the crystallinity of the catalyst, not least because the main crystalline phase detected in the TiO₂ used was rutile. It was not possible to visualize characteristic peaks of metals, the metal particles were possibly dispersed on the surface of TiO₂ or the concentration was below the detection limit, as also evidenced by Varadharajan et al. (2016) and Zaid et al. (2016).

Preliminary evaluation of the processes

In the initial analysis, the drugs ketoprofen, tenoxicam and meloxicam, in a multicomponent solution, were subjected to degradation in bench reactors with a sunlight lamp (photon emission: UV-C - 8.96·10⁻⁴ W·cm⁻², UV-A/UV-B – 5.90·10⁻³ W·cm⁻², visible – 13.8 W·cm⁻²) and UV-C (photo emission: 1.50·10⁻³ W·cm⁻²). The spectra of the samples before (initial) and after degradation, after 60 min, are shown in Figure 4(a) and 4(b), while the solution of the drugs studied separately, and the mixture, are seen in Figure 4(c). The degradation rates of systems with and without radiation are shown in Figure 4(d).

The experiments in the absence of radiation were not efficient in the degradation of the studied compounds. In Figure 4(a) it is observed that heterogeneous photocatalysis, under UV-C radiation is less efficient when compared to the UV-C/H₂O₂ process, which obtained 76.7% and 99.8% peak degradation at the λ of 260 and 367 nm, respectively.

The decrease in degradation of the heterogeneous process in relation to the UV/H₂O₂ in the present study can be attributed to the competition of the photocatalyst for the available photons. Thus, in this process, there is a decrease in the performance of hydrogen peroxide in the reaction, this oxidizing agent being the main one responsible for the generation of radicals and thus for the degradation in these systems.

Results that corroborate with this study were obtained by Janssens et al. (2019), who found a degradation rate for the UV/H₂O₂ process of an order of magnitude higher than that obtained for UV/TiO₂ (P25), in the degradation of anti-cancer drugs, as well as the results obtained by Somathilake et al. (2018), who obtained a kinetic rate for the UV/H₂O₂ process seven times higher than for the UV/TiO₂ (P25) process to degrade carbamazepine in drinking water.

Based on these results, the treatment using sunlight radiation was passed (Figure 4(b)). The sun/H₂O₂ (no degradation at 260 nm and 74.1% at 367 nm) and sun/H₂O₂/TiO₂ (5.5% at 260 nm and 74.9% at 367 nm) systems
showed similar results, indicating that TiO₂ did not act significantly in the degradation of these drugs, under the conditions studied. Therefore, probably the observed decay of the peak at 367 nm is mainly due to the breakage of bonds directly by radiation and hydroxyl radicals formed by the use of hydrogen peroxide.

In Figure 4(b), a reduction in the peaks can also be seen with the use of impregnated photocatalysts (Fe-TiO₂, Cu-TiO₂, Cu|Fe-TiO₂). According to Ali et al. (2017) and Khaki et al. (2017), TiO₂ requires the use of radiation at a wavelength lower than 400 nm, which explains its low performance under the solar spectrum. When impregnated with metal ions, this performance improves, as, as verified by Bhardwaj & Pal (2020), in a photocatalytic process, the impregnated metal ions are excited under visible irradiation, transferring electrons to the conduction band, while the positive gaps in metal ions are used for various oxidation reaction. In addition, the additional surface charge provided by the metal cations attracts a larger number of molecules to be degraded, depending on the nature of the charge of the adsorbed substrate.

The objective of this work was the analysis of the use of TiO₂ and the performance of the impregnation of metals. It was found that the inclusion of photocatalysts under UV-C radiation did not increase photocatalytic activity, with the UV-C/H₂O₂ system being the one that showed the highest degradation of the drugs. On the other hand, the best performance of the heterogeneous systems was obtained by the photocatalyst Fe-TiO₂, under sunlight radiation, which is similar to solar radiation, a type of radiation with high availability over much of the Earth’s continental surface (World Bank Group 2019).

It is also important to note that the fact that greater efficiency was obtained for the photocatalyst Fe-TiO₂ may be associated with leaching of iron in the sample. Thus, the solution after treatment was analyzed on an atomic absorption

![Figure 4](image_url)
spectrometer, with an iron concentration below 0.3 mg·L\(^{-1}\) being verified.

To better assess this issue, the sun/Fe-TiO\(_2\) system experiment was carried out, without the presence of H\(_2\)O\(_2\). This showed degradation of 23.9% and 56.4% for the \(\lambda\) of 260 and 367 nm, respectively, after 60 min. On the other hand, the sun/TiO\(_2\) system obtained 5.7% and 35.6% for the mentioned \(\lambda\), respectively; indicating that in fact there is a photocatalytic contribution of Fe-TiO\(_2\) in the process. Therefore, for the sun/H\(_2\)O\(_2\)/Fe-TiO\(_2\) system, with degradations of 46.5% and 93.2% at 260 and 367 nm respectively, a kinetic, toxicity and reuse study was carried out.

**Kinetic study**

In general, direct photolysis, photo assisted peroxidation, photo-Fenton processes and photocatalysis are described by first order equations (Giannakis et al. 2017; Della-Flora et al. 2020; Janssens et al. 2019, Somathilake et al. 2018).

Photocatalytic degradation is generally described by the Langmuir Hinshelwood model for various organic compounds (Equation (3)).

\[
\frac{d[C]}{dt} = -kK[C] \frac{1}{1 + K[C]}
\]  

(3)

where \(r\) is the rate of photocatalytic degradation, \([C]\) the concentration of the compound, \(k\) is the reaction speed constant and \(K\) is the adsorption equilibrium constant. This equation represents a mechanism in which there is a pre-equilibrium of adsorption and a slow surface reaction. When the concentration of the compound is small (\([C] < 1\)), this equation can be simplified to a pseudo-first order equation (Equation (4)) (Kasanen et al. 2011; Regulska et al. 2016).

\[
\frac{d[C]}{dt} = k_{ap}[C]
\]

(4)

in which \(k_{ap}\) is the pseudo-first order velocity constant of the reaction (min\(^{-1}\)). The integration of Equation (3) results in Equation (5).

\[
\frac{[C]}{[C]_0} = e^{-k_{ap}t}
\]

(5)

Another model, non-linear of pseudo-first order, which can be adjusted to experimental kinetic data of AOP, is the one proposed by Chan & Chu (2003), developed in Fenton-type reactions (Equation (6)).

\[
\frac{[C]}{[C]_0} = 1 - \frac{t}{\rho + \sigma t}
\]

(6)

This model was developed to describe the reaction kinetics in two stages, the first being formed by rapid degradation, followed by a slow phase. The model uses two simple parameters: the initial contaminant decay rate (\(\rho\)) in min and the final oxidation capacity (\(\sigma\)), which is dimensionless (Chan & Chu 2003).

However, knowing that Fenton-type systems can result in kinetic profiles in which there is a slow decay stage, followed by rapid decay, Nichela et al. (2010) proposed an empirical equation by modifying the OriginLab 7.5 logistic curve (OriginLab Corporation, Northhampton, MA 01060, USA), to adjust the normalized decay profiles (Equation (7)). This kinetic model was also evaluated for the degradation of the drug mixture in the present study.

\[
\frac{[C]}{[C]_0} = \frac{1 - a \cdot t - d}{1 + \left(\frac{b}{t}\right)^c} + d
\]

(7)

In this equation, the parameter \(a\) (min\(^{-1}\)) represents the average oxidation rate (apparent initial rate), \(b\) (min) the time required to reach half the initial concentration (apparent half-life), and the mean slope during the fast phase and the final residue value, these last two parameters are dimensionless.

Figure 5 shows the monitoring of drug degradation kinetic by sun/H\(_2\)O\(_2\)/Fe-TiO\(_2\) system obtained through UV/Vis spectrophotometry. In this figure, it is possible to verify the adjustments of the kinetic models of pseudo first order, Chan & Chu (2003) and Nichela et al. (2010), to the experimental data.

As can be seen in Figure 5, the decay of drug concentration presented a slow initial phase in the first minutes of the process. This behavior can be attributed to the formation on intermediate products associated with the addition of the oxidant. After this period, a more pronounced decay occurred, reaching 92% degradation after 180 min, in relation to \(\lambda\) 260 nm (Figure 5(a)). The kinetic curve for \(\lambda\) 367 nm (Figure 5(b)) showed a more rapid decay, stabilizing after 120 min of treatment with 96% degradation. The parameters of the adjusted models are shown in Table 1.

For both wavelengths \(F_{\text{cal}} > F_{\text{lab}}\), which means that the model proposed by Nichela et al. (2010) (the model with less...
variance) has a higher statistical reliability than the other models presented in Table 1, for a 95% confidence level.

It is known that in the system under study, several processes occur at the same time; that is, there is direct photolysis, in which the compounds are directly degraded by radiation; the photo-assisted peroxidation given the presence of H2O2 and the heterogeneous photocatalysis that occurs on the surface of TiO2.

Allied to this, the insertion of iron by impregnation on the TiO2 surfaces increased its photocatalytic activity, due to the better separation of charges at the metal-semiconductor interface and the greater absorption of visible light. It must also be considered that the metal interacted with the H2O2 available in the system, leading to an irradiated Fenton reaction (photo-Fenton process). This fact may be confirmed by the better fit of the model proposed by Nichela et al. (2010), which foresees different behaviors considering the slow and fast stages. These reactions can occur on the surface of the photocatalyst and in the middle of the solution, due to leaching of the metal.

Finally, it is worth noting that in the model proposed by Nichela et al. (2010), the parameter \( a \) (min\(^{-1}\)), which represents the apparent initial rate, was negative for \( \lambda \) of 260 nm; this was caused by the slight increase in the kinetic curve in the initial minutes, which, as already discussed, can be attributed to the formation of intermediates that absorb in this wavelength. The apparent initial rate for \( \lambda \) of 367 nm was positive, accompanied by the kinetic decay of the experimental data. At this wavelength, the time required to reach half of the initial concentration \( b \) (min) was half that observed at 260 nm, with a greater mean slope during the fast phase (c). Thus, the final residual value (d) for the \( \lambda \) of 367 nm was predicted with greater precision.

**Toxicity**

Aiming to evaluate the efficiency of the AOPs used in terms of toxicity, since intermediates can be formed during the treatment, the toxic effect caused to different seeds was evaluated. On Table 2, the data related to the toxicity analysis against the cress, thyme and lettuce are shown.

In Table 2, it is observed that the initial solution did not inhibit radicle growth for the cress and lettuce seeds. The solution treated by the sun/H2O2/Fe-TiO2 system had no significant effect on the root growth of the studied seeds.

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**Table 1** | Adjustment parameters of the pseudo-first order models, proposed by Chan & Chu (2003) and by Nichela et al. (2010) for the degradation kinetics

<table>
<thead>
<tr>
<th>Model/Parameters</th>
<th>260 nm</th>
<th>367 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chan &amp; Chu (2003)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( K_{ap} ) (min(^{-1}))</td>
<td>0.010 ± 0.002</td>
<td>0.026 ± 0.004</td>
</tr>
<tr>
<td>( S_{R}^{2} )</td>
<td>0.914</td>
<td>0.935</td>
</tr>
<tr>
<td><strong>Nichela et al. (2010)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( a ) (min(^{-1}))</td>
<td>0.007 ± 0.002</td>
<td>0.031 ± 0.009</td>
</tr>
<tr>
<td>( 1/\rho ) (adm)</td>
<td>4.306 ± 4.387</td>
<td>1.270 ± 0.177</td>
</tr>
<tr>
<td>( S_{R}^{2} )</td>
<td>0.066</td>
<td>0.113</td>
</tr>
<tr>
<td>( R^{2} )</td>
<td>0.942</td>
<td>0.901</td>
</tr>
<tr>
<td><strong>Test F</strong></td>
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</tr>
<tr>
<td>( F_{calc} )</td>
<td>6.00</td>
<td>21.50</td>
</tr>
<tr>
<td>( F_{tab} )</td>
<td>4.88</td>
<td>4.82</td>
</tr>
</tbody>
</table>

*The F test was applied considering the two models with the lowest \( S_{R}^{2} \), in each wavelength.*

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**Figure 5** | Degradation kinetics of drugs on sun/H2O2/Fe-TiO2 system and the kinetic adjustment to \( \lambda \) (a) 260 nm and (b) 367 nm. C\(_{0}\) = 10 mg·L\(^{-1}\) of each drug; \([\text{H}_2\text{O}_2]\) = 500 mg·L\(^{-1}\); [photocatalyst] = 100 mg by 250 mL of solution ([Fe] \(\approx\) 1.75 mg), pH 5.
according to Young et al. (2022), since the RGI index presented values between 0.8 and 1.2. For the reagents analysis, \( \text{H}_2\text{O}_2 \) (25 mg·L\(^{-1}\)) was evaluated, which had no influence on radicle growth, and iron solutions (1 mg·L\(^{-1}\)) which showed a light inhibition for cress seeds, indicating that they do not add a toxic effect to the process in relation to these seeds.

These results are in agreement with those reported by Marchetti & Azevedo (2020) and Nascimento et al. (2020) who evaluated toxicity after the degradation of non-steroidal anti-inflammatory drugs by the photo-Fenton processes and did not verify toxicity against lettuce seeds, while Feliciano et al. (2020) observed growth inhibition for species of \( L. \text{ sativa} \) and \( E. \text{ sativa} \), when subjected to the degradation compounds of the drug lamivudine treated by photoperoxidation.

Regarding thyme seed, a seed not commonly used in toxicity tests, the initial solution did not impact radicle growth. However, it was observed that after the 180 min treatment the impact on growth was high, indicating that the compounds formed are potentially toxic to this seed. The result of the seed germination test is a parameter that depends on the seed species used, as the species have different sensitivities to the contaminant, according to Luo et al. (2018), which corroborates with the result presented above since the thyme seed showed greater sensitivity to the compounds formed during the treatment.

**Photocatalyser reuse**

In addition to eliminating the step of separating the photocatalyst used to treat the effluent at the end of the process, the supported application of the photocatalyst facilitates its reuse in the process. To assess whether Fe-TiO\(_2\) was able to maintain photocatalytic activity for several cycles, the reuse test was performed, the results of which are shown in Figure 6(a). The characterizations after the fifth cycle are shown in Figure 6(b)–6(d).

It is observed in Figure 6(a) that after five cycles there was a reduction of approximately 9% in the degradation percentage for the wavelength of 260 nm, whereas for \( \lambda \) of 367 nm there was no difference in the percentage of degradation. The photocatalyst showed high rates of degradation for the mixture of the studied drugs after the five treatment cycles. The stability of the photocatalyst in the support material is an important parameter in its application for the treatment of contaminants. Although in this study an average loss of 4% of mass was observed between each cycle, despite this loss the surface of the polystyrene film remained covered by Fe-TiO\(_2\), as seen in Figure 6(b). The supported Fe-TiO\(_2\) spectra, after five reaction cycles (Figure 6(d)), resembles the initial spectra (Figure 3(a)), confirming that no significative change on the chemical structure of the photocatalyst happened. This loss of mass can be associated with two factors: poor adhesion of the photocatalyst in some regions of polystyrene and dissolution of the photocatalyst throughout the experiments, since the use of agitation can lead to the detachment of regions where there was no complete adhesion of the material used.

Figure 6(c) shows that after five cycles, the composition of the photocatalyst remained similar to that obtained before use in the AOP, being predominantly composed of TiO\(_2\). The presence of iron is observed at a small peak in the spectrum, in agreement with the results observed by Khan et al. (2013) and Shi et al. (2019) for small amounts of inserted metals. It is also worth noting that the most intense peak observed in this figure refers to element C, present in the graphite used to perform the SEM-EDS analysis.

**CONCLUSION**

The best performance of the heterogeneous system was obtained by the photocatalyst Fe-TiO\(_2\) under sunlight radiation. The sun/\( \text{H}_2\text{O}_2/\text{Fe-TiO}_2 \) system reached 92 and 96%
degradation after 180 min for the $\lambda$ of 260 and 367 nm, respectively. The model proposed by Nichela et al. (2010) presented a lower variance and the better adjustment between the models considering the slow and fast stages observed in the kinetic curve of the present study. It is also important to highlight that in the process applied in this study, homogeneous and heterogeneous reactions can occur at the same time, since even in small quantities there is still some release of iron to the solutions submitted to the photolytic reactions. The treated solutions did not show toxicity to the cress and lettuce seeds, and a sensitivity of the thyme seed to the compounds formed during the treatment was verified. The supported photocatalyst showed high degradation rates for the drugs studied even after five treatment cycles, indicating that the use of this system is promising for the treatment of pharmaceutical effluents.

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**DATA AVAILABILITY STATEMENT**

All relevant data are included in the paper or its Supplementary Information.

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