



Eclética Química

ISSN: 0100-4670

ISSN: 1678-4618

ecletica@journal.iq.unesp.br

Universidade Estadual Paulista Júlio de Mesquita Filho
Brasil

Costa Junior, Ismael Laurindo; Ferreira, Kevin Augusto; Kappes, Cesar Augusto; Giona, Renata Mello
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Eclética Química, vol. 47, núm. 1, 2022, pp. 55-63
Universidade Estadual Paulista Júlio de Mesquita Filho
Araraquara, Brasil

DOI: <https://doi.org/10.26850/1678-4618eqj.v47.1.2022.p55-63>

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Photoperoxidation of ciprofloxacin antibiotic in aqueous medium using $\text{Fe}_{3-x}\text{O}_{4-y}\text{-TiO}_2$ particles as catalyst

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ARTICLE INFO

Article history:

Received: February 04, 2021

Accepted: September 01, 2021

Published: January 01, 2022

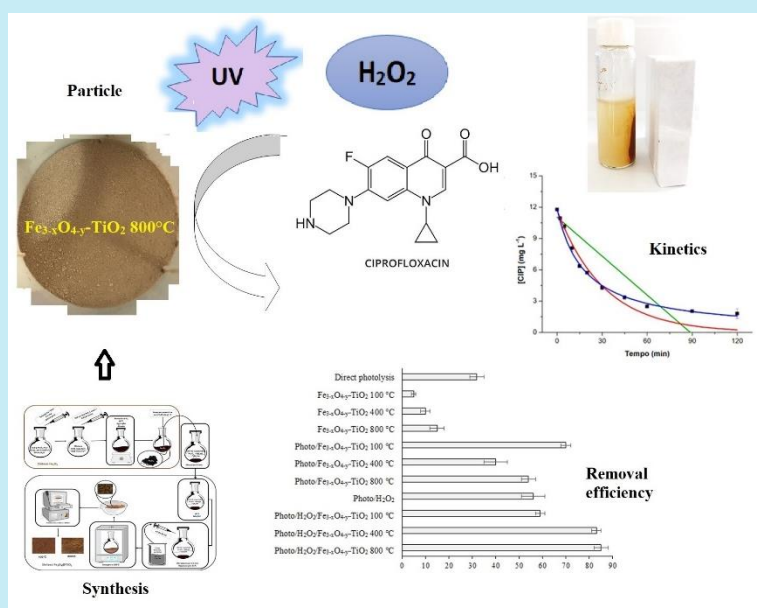
Section Editor: Assis Vicente Benedetti

Keywords

1. photocatalyst
2. emerging pollutants
3. oxidative processes

ABSTRACT: Conventional treatment processes are not effective in removing micropollutants such as antibiotics and other drugs present in wastewater, and degradation methods based on advanced oxidative processes become attractive. Herein, it was synthesized $\text{Fe}_{3-x}\text{O}_{4-y}\text{-TiO}_2$ particles by coprecipitation method and they were heat-treated at 100, 400, and 800 °C. The obtained solids were characterized by X-ray diffraction and thermogravimetric analysis and analytical determinations were performed using ultraviolet-visible (UV-Vis) spectrophotometry. The particles were evaluated in photoperoxidation processes on the degradation of the ciprofloxacin antimicrobial in an aqueous solution. The studies took place at pH 9; with an H_2O_2 concentration of 31 mg L⁻¹ and particle mass 0.22 g L⁻¹ previously defined and, in these conditions, degradation percentages between 40 and 85% were observed, with the removal in the Photo/ H_2O_2 / $\text{Fe}_{3-x}\text{O}_{4-y}\text{-TiO}_2$ 800 °C.

The kinetic study performed for this process revealed the process adjusts to the first-order kinetics during the 120 min of reaction. The use of the catalyst can be attractive with the potential for degradation of the studied antimicrobial.



1. Introduction

Studies on residual drugs in the environment are topics of great relevance today (Costa Junior *et al.*, 2014). With the growth of the world population, the consumption of medicines has increased significantly in the last decades; as a result, these compounds are found in sewage treatment plant effluents, in water supplies, and various environmental compartments (Bound *et al.*, 2006; Luo *et al.*, 2014; Rogowska *et al.*, 2020).

One of the groups of residual drugs that attracts attention is antibiotics due to their potential effect on the development of resistant bacteria in the environment (Barancheshme and Munir, 2019; Karkman *et al.*, 2018). An example of an antimicrobial is ciprofloxacin (CIP), which belongs to the fluoroquinolone class and is widely used in human and veterinary medicine. Its excretion rate can reach 65% in urine and 25% in feces (Frade *et al.*, 2014; Halling-Sørensen *et al.*, 2000).

The discharge of domestic and industrial sewage in surface waters is one of the main routes of dispersion of emerging contaminants, especially drugs. Thus, the effective concentration of emerging pollutants, such as antibiotics, in the various environmental matrices directly depends on the efficiency of the treatment processes applied to wastewater in treatment plants (Leung *et al.*, 2012; Wu *et al.*, 2016).

The treatment methods used in sewage treatment plants are based mainly on conventional processes (physical and biochemical operations), aimed at stabilizing organic matter, removing nutrients, and disinfecting. Thus, effective degradation of these new contaminants is practically nonexistent (Oliveira *et al.*, 2020; Rajasulochana and Preethy, 2016). Some studies have suggested the removal of residual drugs in the treated sewage through the evaluation of input and output parameters in biological treatment systems (Sim *et al.*, 2010; Verlicchi *et al.*, 2012). However, other studies resulted only in the transfer of pollutants to sludge and sediments by sorption mechanisms, with no degradation or effective treatment (Barret *et al.*, 2010; Liu *et al.*, 2019; Piai *et al.*, 2020).

Considering the bioactive and persistent nature of organic micropollutants, the need for advanced treatments for their removal in wastewater is urgent. Some advanced oxidative processes (AOPs), such as ozonation, homogeneous and heterogeneous photocatalysis, are promising for pollutants degradation (Ciccotti *et al.*, 2015; Hörsing *et al.*, 2012; Hyland *et al.*, 2012; Souza *et al.*, 2018).

In heterogeneous photocatalysis, titanium dioxide (TiO₂) based catalysts have great viability and applicability to degrade a wide variety of pollutants. Its main advantages are its electronic properties, chemical stability, nontoxicity, and low cost (Rasalingam *et al.*, 2014; Yang *et al.*, 2005). Catalysts can be applied immobilized on supports or in suspension. When suspended, the separation step is a limitation of the process that involves time and costs. Magnetic particles have been extensively studied as a support for many hybrid materials, like TiO₂ (Borges *et al.*, 2015; Fabbri *et al.*, 2019; Pang *et al.*, 2012).

The association of TiO₂ photocatalytic and Fe₃O₄ magnetic properties has been explored in the proposition of core@shell particles (Ciccotti *et al.*, 2015; Noval *et al.*, 2019; Wei *et al.*, 2009). One of the advantages of using a magnetic material is that the catalyst could be easily removed from the reaction system through the application of an external magnetic field, also facilitating its recovery during the process steps (Dorigon *et al.*, 2017; Wu *et al.*, 2008).

In this work, heat-treated Fe_{3-x}O_{4-y}-TiO₂ magnetic particles were prepared and applied as catalysts in the degradation of the CIP antibiotic by heterogeneous photoperoxidation processes.

2. Materials and Methods

2.1 Reagents: standards and solutions

Ciprofloxacin (CIP) was purchased as an analytical standard for chromatography (C₁₇H₁₉ClFN₃O₃, Sigma-Aldrich) with 99.98% purity. Stock solutions of this drug were prepared at 1000 mg L⁻¹, swollen in ultrapure water and kept at 4 °C under refrigeration, protected from light. In the photocatalysis reactions, hydrogen peroxide (H₂O₂, Alphatec) was used.

Buffer solutions based on potassium phosphate (K₃PO₄, Exodus), anhydrous monobasic potassium phosphate (KH₂PO₄, Exodus), dibasic potassium phosphate (K₂HPO₄, Alphatec) and phosphoric acid were used for the reaction media 85% (H₃PO₄, Moderna). According to the pH ranges of the experiments, adjustments were done using hydrochloric acid (HCl, Dinâmica) and sodium hydroxide (NaOH, Moderna) 0.01 mol L⁻¹. In the synthesis of particles, iron chloride III hexahydrate (FeCl₃·6H₂O, Dinâmica); iron chloride II (FeCl₂, Exodus), ammonium hydroxide (NH₄OH, Anhydrol); absolute ethyl alcohol (C₂H₆O, Dinâmica) and 97% IV titanium isopropoxide (Ti[OCH(CH₃)₂]₄, Sigma-Aldrich) were used.

2.2 Synthesis and characterization of Fe_{3-x}O_{4-y}-TiO₂ particles

The synthesis of Fe₃O₄ particles was performed using the modified coprecipitation method (Dorigon *et al.*, 2017; Wu *et al.*, 2008). Briefly, 10.8 g of FeCl₃·6H₂O were added to a reaction flask containing 25 mL of 1.0 mol L⁻¹ HCl aqueous solution and 50 mL of ultrapure water. In another flask, a solution of FeCl₂ was prepared to maintain the proportion of 2:1 in mol (Fe³⁺/Fe²⁺). This solution was transferred drop by drop, with the aid of a syringe, to the reaction flask containing the FeCl₃·6H₂O in acidic solution, resulting in a ratio of 0.04 mol of Fe³⁺ to 0.02 mol of Fe²⁺. Then, 250 mL of a 1.5 mol L⁻¹ NaOH solution was added to the Fe³⁺/Fe²⁺ mixture, followed by constant heating at 60 °C and stirring for 40 min under N₂ atmosphere. The black and magnetic solid obtained composed of Fe₃O₄ was thoroughly washed with ultrapure water until neutral pH, and then it was kept in suspension.

For the TiO₂ coating step, in a round-bottom flask with 250 mL capacity, 20 mL of the Fe₃O₄ suspension obtained in the previous step and 80 mL of absolute ethyl alcohol were added, followed by homogenization in an ultrasonic bath for 5 min. The pH suspension was adjusted to 9 by the addition of concentrated NH₄OH. In another flask, 24 mL of titanium isopropoxide IV 97% were added and diluted in 136 mL of ethyl alcohol, and 20 mL aliquots were added to the Fe₃O₄ suspension under homogenization for 15 min in an ultrasonic bath after each insertion.

The system remained at rest for 24 h and then it was dried in an oven at 100 °C. The solid was broken up into a mortar and divided into three parts, one set aside and the other two portions subjected to heat treatment at 400 and 800 °C, respectively, in a muffle furnace. After cooling, 1 mL of each solid was measured in a 5 mL beaker previously weighted on an analytical balance and the corresponding mass was obtained. Density was calculated by the ratio between mass and volume.

X-ray diffraction (XRD) patterns were measured using an empyrean diffractometer operating from 2 to 50° with a residence time of 2° min⁻¹.

Thermogravimetric analyzes (TGA) were performed on a Perkin Elmer STA 6000 TGA analyzer, with approximately 8 mg of the sample, which was placed on open platinum and preheated to 100 °C for 5 min. The measurements were carried out in a nitrogen atmosphere at a flow rate of 20 mL min⁻¹ and a heating rate of 10 °C min⁻¹, using a heating range of up to 600 °C.

2.3 Analytical measures and photoperoxidation tests

For quantification of CIP, solutions with concentrations ranging from 1 to 25 mg L⁻¹ at pH 9 were prepared for the calibration curve and were used to identify the maximum absorption band of CIP. The measurements were made by using a single beam scanning ultraviolet-visible (UV/VIS) molecular absorption spectrophotometer (PerkinElmer™ LAMBDA XLS), in the range of 200 to 400 nm with a resolution of 2 nm. Quartz cuvettes with an optical path of 1 cm were used.

In the photoperoxidation tests, a reactor was used, consisting of a 57 × 47 × 47 cm³ metal box equipped with four low-pressure mercury lamps (15 W) (OSRAM™ Germicidal), used as a source of UV radiation and fixed at the top about 20 cm away from the solutions. The internal temperature remained around 45 °C after 20 min of stabilization. Inside, four 250 mL glass containers were placed on four magnetic stirrers (Fisatom). The initial CIP concentration was 10 mg L⁻¹, and aliquots of the solution were taken at regular intervals over the 120 min time.

A kinetic study was performed for the best treatment observed. The determination of the rate of degradation of target molecules and their respective concentrations (order of reaction) is an important step in the study of the kinetics of chemical reactions. The order of the reaction is understood as the dependence of the speed of the reaction with the concentration, where C_0 is the initial reagent concentration, and C is the reagent concentration after a reaction time (t) (Sarkar *et al.*, 2015).

If dC/dT satisfies Eq. 1, n is the order of the reaction.

$$\frac{dC}{dt} = -k \cdot C^n \quad (1)$$

When $n = 0$ (zero order reaction), $n = 1$ (first order reaction) and $n = 2$ (second order reaction), Eq. 1 will lead to Eqs. 2–4, respectively.

$$C = C_0 - k_0 \cdot t \quad (2)$$

$$C = C_0 \cdot e^{-k_1 \cdot t} \quad (3)$$

$$C = \frac{C_0}{1 + C_0 \cdot k_2 \cdot t} \quad (4)$$

In the photodegradation studies involving organic micropollutants, employed to assess persistence and susceptibility to ultraviolet radiation, the models

represented in Eqs. 2–4 are commonly applied for kinetic evaluation (Carlson *et al.*, 2015).

The experimental data obtained in the photoperoxidation tests catalyzed by the synthesized particles were evaluated in terms of the adjustments of the kinetic models (Eqs. 2–4) using the originPro 8.0 software. The decay of the CIP concentration was verified during the test and the half-life times were determined.

3. Results and discussion

3.1 Catalyst characterization

From the synthesis, it was obtained 7.9 g of $\text{Fe}_{3-x}\text{O}_{4-y}\text{-TiO}_2$ particles and they presented densities of 0.35 g mL^{-1} for the particles treated at 100°C , 0.5 g mL^{-1} for 400°C , and 0.6 g mL^{-1} for 800°C (Fig. 1). This increase in density possibly resulted from the modification of the particle structure and the elimination of residual inputs from the synthesis. The magnetism of the particles was qualitatively evaluated in the presence of a neodymium magnet and, as shown in Fig. 1, $\text{Fe}_{3-x}\text{O}_{4-y}\text{-TiO}_2$ with heat treatments of 100 and 400°C is magnetic, while the solid treated at 800°C has lost its magnetic property upon heat treatment.

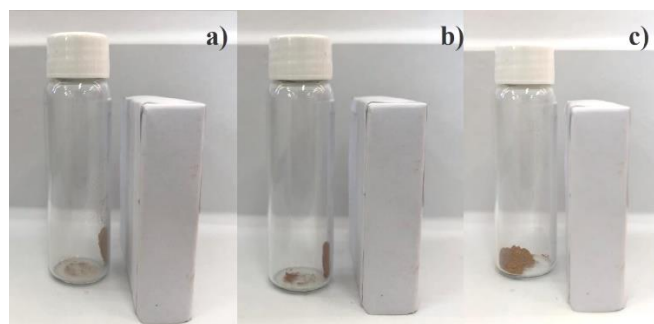


Figure 1. $\text{Fe}_{3-x}\text{O}_{4-y}\text{-TiO}_2$ being attract by a neodymium magnet. Treatments at (a) 100°C (b) 400°C and (c) 800°C .

The crystallographic structures of the products were analyzed by powder XRD. The particles treated at 100°C do not show peaks of a crystalline structure, suggesting an amorphous structure (Fig. 2a). Interestingly, the increase in temperature directly influenced the crystallinity of the system, with a predominance of $\alpha\text{-Fe}_2\text{O}_3$ particles derived from the amorphous magnetite of the system, which is also reflected in the reduction of magnetism when heated to 800°C (Fig. 1c).

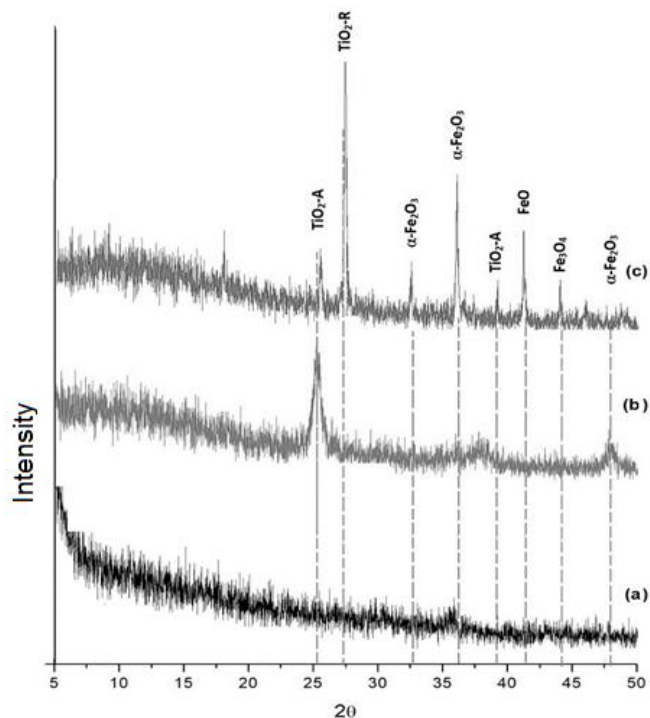


Figure 2. $\text{Fe}_{3-x}\text{O}_{4-y}\text{-TiO}_2$ XRD patterns in treatments at (a) 100°C (b) 400°C and (c) 800°C .

In the particles treated at 400°C (Fig. 2b), two main peaks were identified, the first referring to the TiO_2 anatase phase (25°) and the second to $\alpha\text{-Fe}_2\text{O}_3$ phase (48°) (Khashan *et al.*, 2017). For the treatment at 800°C , several peaks were observed, with the occurrence of TiO_2 anatase (25 and 39°), and rutile TiO_2 (27°), $\alpha\text{-Fe}_2\text{O}_3$ (33 and 35°), FeO (42°) and Fe_3O_4 (44°) (Noval *et al.*, 2019).

The results of XRD indicate that the thermal treatments performed caused a structural modification in the synthesized particle, and the decrease in the magnetic property is due to the conversion of magnetite (Fe_3O_4) in oxides, such as $\alpha\text{-Fe}_2\text{O}_3$ and FeO . Thus, it was assumed that the particles have a complex mixed composition of these compounds and, therefore, were denoted as $\text{Fe}_{3-x}\text{O}_{4-y}\text{-TiO}_2$. These hypotheses are reinforced by the TGA curves (Fig. 3).

From the TGA curves, it was determined a mass loss of approximately 25% of $\text{Fe}_{3-x}\text{O}_{4-y}\text{-TiO}_2$ particles synthesized at 100°C . The first loss occurred between $50\text{--}150^\circ\text{C}$ and is related to the evaporation of alcohol and water residues adsorbed in the system. In the range of 150 to 350°C , there is a loss that resulted from the decomposition of organic substances, and from 350°C , total decomposition occurred, with crystallization beginning at high temperatures, generating a stable coating for the particles (Khashan *et al.*, 2017).

The particles treated at 400 and 800 °C did not show significant mass loss since they were previously subjected to a higher temperature. From TGA curves and XRD, it is possible to infer that the mass losses in the particles treated at 400 and 800 °C are lower than particles treated at 100 °C because the heating in the thermal treatment promoted structural changes. In addition, the TGA curves corroborate the predominance of the stable iron oxides identified in the XRD for the treatment of 800 °C.

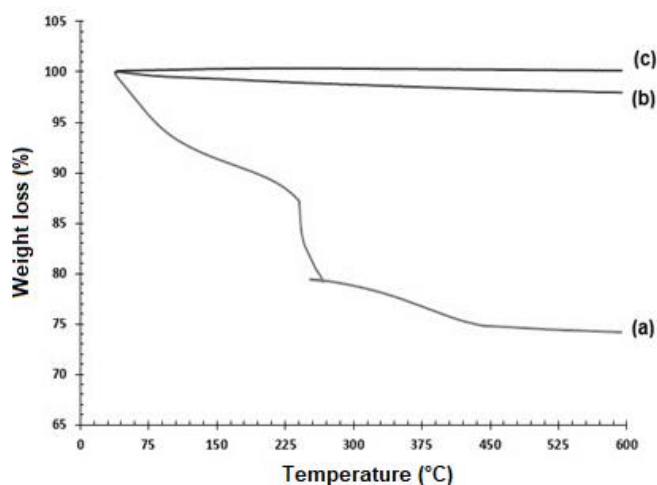


Figure 3. Thermogravimetric analyzes curves obtained for $\text{Fe}_{3-x}\text{O}_{4-y}\text{-TiO}_2$ synthesized in treatments (a) 100 °C (b) 400 °C and (c) 800 °C.

3.2 Application of synthesized particles in the photoperoxidation of ciprofloxacin

The absorption spectrum of the CIP drug with a concentration of 5 mg L⁻¹ and pH 9 has a maximum absorption band at 278 nm, which is covered in the medium ultraviolet (Fig. 4).

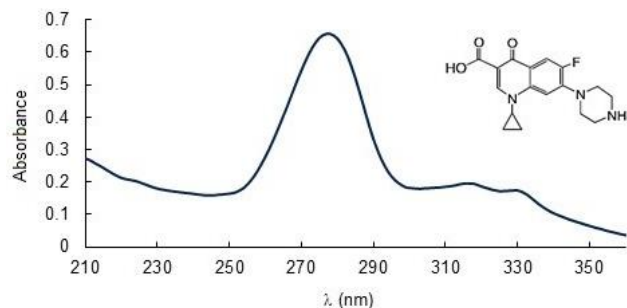


Figure 4. Ultraviolet-visible absorption spectrum in aqueous solution with a concentration of 5 mg L⁻¹ of CIP and pH = 9.

Because of the molecular structure of CIP, its ionic forms depend on the pH. A cationic form is predominant in solution pH below 5.9 (up to pK_a = 5.9), zwitterionic form is present in a neutral medium (5.9 < pK_a < 8.9), and the anionic form is dominant at alkaline pH (pK_a > 8.9) (Carabineiro *et al.*, 2012). Given that the photoperoxidation experiment was conducted at pH 9, the predominance of the anionic form of CIP is expected.

As for the surface of the photocatalyst, the pHP_{PCZ} of the TiO₂ was 7.5 (Borges *et al.*, 2016). Under the conditions studied, the surface charge will also be negative, indicating that the possible removal of CIP by adsorption is unlikely, thus possibly not contributing to the results obtained through the photoperoxidation catalyzed by $\text{Fe}_{3-x}\text{O}_{4-y}\text{-TiO}_2$ particles. It is possible that, if adsorption phenomena still occur, the CIP molecules might be oxidized by reacting directly with the positive gap of the semiconductor valence layer, although this reaction is less likely (Mourão *et al.*, 2009; Nogueira and Jardim, 1998).

To evaluate the particles, the processes of direct photolysis, homogeneous photocatalysis (Photo/H₂O₂), and heterogeneous photocatalysis (Photo/ $\text{Fe}_{3-x}\text{O}_{4-y}\text{-TiO}_2$ and Photo/H₂O₂/ $\text{Fe}_{3-x}\text{O}_{4-y}\text{-TiO}_2$) were compared (Fig. 5). It was observed that the removal of the CIP antibiotic occurred in all tested processes.

No differences were observed between the process of direct photolysis and photocatalysis in the presence of particles without peroxidation. Thus, in these processes, the removals ranged from 36 to 56%. This behavior is possibly related to the mass of particles used (0.22 g L⁻¹) that may have impaired irradiation or also due to the need for more than 120 min for degradation.

The systems (Photo/H₂O₂/ $\text{Fe}_{3-x}\text{O}_{4-y}\text{-TiO}_2$) with the heat treatments of 400 and 800 °C were the photocatalysts that presented the best performance, showing a percentage of degradation greater than 80%. This system was 30% more efficient than the direct photolysis process, indicating that the materials improved the photoperoxidation process (68%). Also, results showed that the particles with heat treatment of 100 °C presented low degradation efficiency, indicating that the absence of crystalline structures of the particles in the Photo/H₂O₂/ $\text{Fe}_{3-x}\text{O}_{4-y}\text{-TiO}_2$ particle impairs the degradation of the CIP in the medium tested.

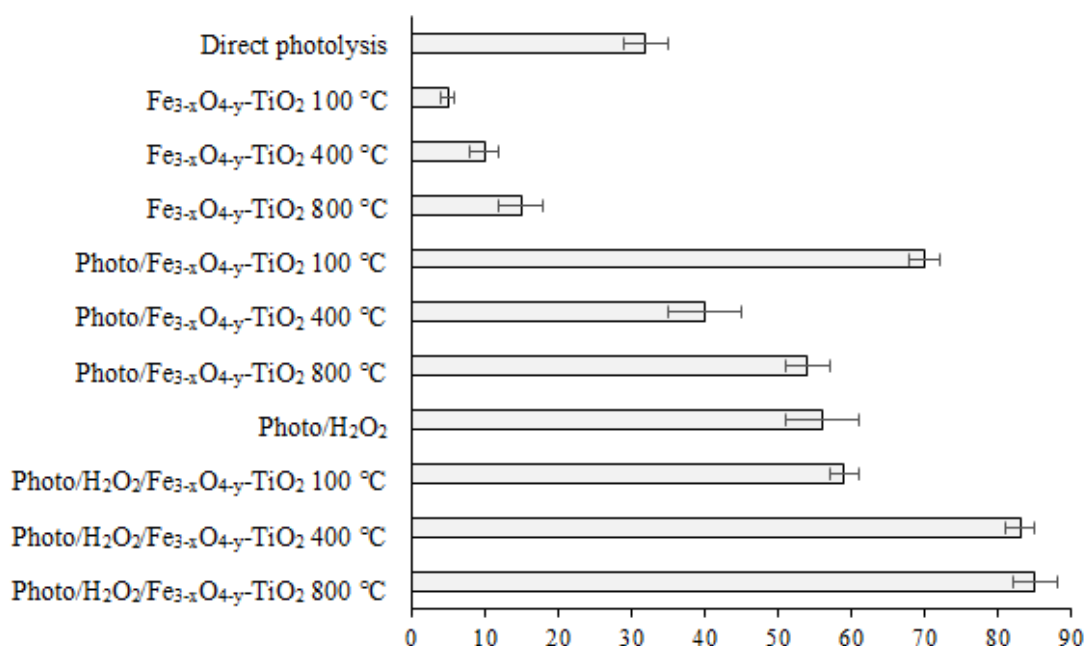


Figure 5. Ciprofloxacin removal during the tested degradation processes. Experimental condition: $t = 120$ min, $[CIP]_0 = 10$ mg L⁻¹, pH = 9, H₂O₂ = 31 mg L⁻¹ and $[Particles] = 0.22$ g L⁻¹.

Hence, direct photolysis alone could not be used as an important procedure for the removal of CIP from aqueous solutions. As can be seen in Fig. 5, the removal of CIP via adsorption onto Fe_{3-x}O_{4-y}-TiO₂ (6 to 14 %) was lower in comparison to the photocatalysis process.

Fe₃O₄@SiO₂@TiO₂ particles with heat treatment of 500 and 600 °C were evaluated as a heterogeneous photocatalysis with H₂O₂ in a reactor composed of six lamps of 8 W, pH of 5.5, and CIP degradations of 83 and 95%, respectively, were reported over a test time of 90 min (Teixeira *et al.*, 2017). These results were similar to those obtained in this study.

Considering the photocatalyzed peroxidation process by the particles synthesized in the 800 °C heat treatment exhibited the best performance (Fig. 4), this system was evaluated through the kinetic study (Fig. 6).

It was observed that the most intense degradation of the CIP occurs in the first 60 min; this time interval corresponds to the dynamic range and might be related to factors such as the maximum amount of H₂O₂ favorable to the mechanism or the competition with by-products that were formed (Fiores *et al.*, 2014). After 60 min, low degradation rates were observed, indicating that the system tends to stabilize, keeping the concentration of residual CIP constant.

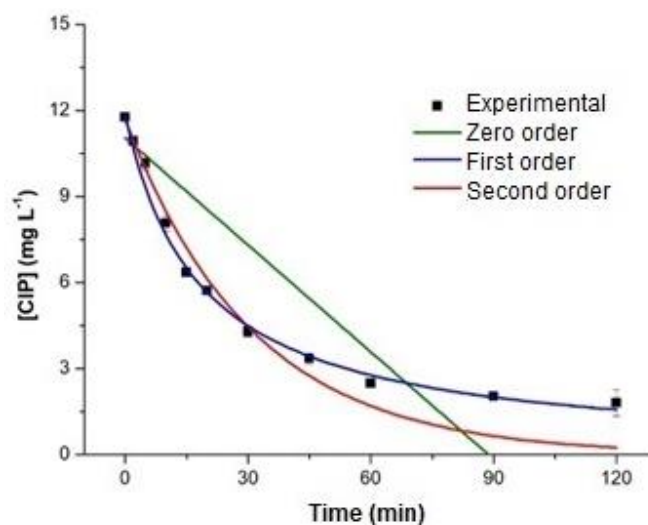


Figure 6. Kinetic study of the photo/H₂O₂/Fe_{3-x}O_{4-y}-TiO₂ process applied to CIP degradation. T = 120 min, $[CIP]_0 = 12$ mg L⁻¹, pH = 9, H₂O₂ = 31 mg L⁻¹ and $[Particles] = 0.22$ g L⁻¹.

From the R² coefficients (Tab. 1), it was possible to determine that the model that presented the best fitting of experimental data was the first order with R² of 99.7%; such a model assumes that, in a speed reaction, it is directly dependent on the concentration of the reagents.

Table 1. Kinetic data for Photo/H₂O₂/Fe_{3-x}O_{4-y}-TiO₂ process. t = 120 min, [CIP]₀ = 12 mg L⁻¹, pH = 9, H₂O₂ = 31 mg L⁻¹ and [Particles] = 0.22 g L⁻¹.

Zero order			First order			Second order		
<i>k</i> ₀ (mg L ⁻¹ min ⁻¹)	<i>t</i> _{1/2} (min)	R ²	<i>k</i> ₁ (min ⁻¹)	<i>t</i> _{1/2} (min)	R ²	<i>k</i> ₂ (L mg ⁻¹ min ⁻¹)	<i>t</i> _{1/2} (min)	R ²
0.12 (± 0.02)	44.5	80.9	0.05 (± 0.002)	16.9	99.7	0.03 (± 0.003)	23.1	97.9

Based on the first-order model, it was observed that, in 16.9 min, the CIP concentration was reduced to half of its initial value. The rate constant (*k*) was 0.05 min⁻¹. Similarly, a study using Fe₃O₄@SiO₂@TiO₂ in CIP photodegradation presented the first-order constant of 0.017 min⁻¹ (Teixeira *et al.*, 2017). Also, the degradation of CIP with an initial concentration of 20 mg L⁻¹ was studied by the photocatalysis process using a Fe₃O₄@TiO₂@C-dot particle exposed to a mercury vapor lamp. The kinetic model followed first-order with a *k* = 0.0154 min⁻¹ during 150 min of testing (Das *et al.*, 2016).

A heterogeneous photocatalysis study using TiO₂ obtained 57% efficiency in CIP removal over 120 min of testing in a reactor equipped with 16 W UV lamps. The reported model was also first-order with a rate constant of 0.0063 min⁻¹ (Hassani *et al.*, 2015).

Comparing the data obtained here for the photodegradation of CIP with studies reported in the literature, it is clear that Fe_{3-x}O_{4-y}-TiO₂ heat-treated at 800 °C is a promising catalyst for CIP degradation.

4. Conclusions

Here, the facile and reproducible preparation of Fe_{3-x}O_{4-y}-TiO₂ particles was reported, combining the use of the TiO₂ catalyst with the magnetic properties of iron oxide.

In the conditions explored, the photocatalysts showed degradation percentages between 40 and 85%, in which the Photo/H₂O₂/Fe_{3-x}O_{4-y}-TiO₂ process with the particles synthesized in the 800 °C heat treatment exhibited the best performance.

The kinetic study revealed that Fe_{3-x}O_{4-y}-TiO₂ catalyst followed first-order kinetics during the 120 min reaction. The use of a large amount of catalyst has some limitations, such as low degradation, for example, possibly because the dispersed particles interfere with the incident radiation. Despite this, the process is attractive, since it eliminates the need for a robust wastewater post-treatment step to remove the suspended catalyst.

Thus, although other factors must be evaluated for real scale usage, such as the analysis and removal of by-products formed, using, for example, chromatography liquid techniques coupled to mass spectrometry, the

heterogeneous photocatalysis process using the synthesized particles is a promising treatment in the CIP degradation.

Authors' contribution

Conceptualization: Costa Junior, I. L.; Giona, R. M.; Ferreira, K. A.; Kappes, C. A.

Data curation: Costa Junior, I. L.; Giona, R. M.

Formal Analysis: Costa Junior, I. L.; Ferreira, K. A.; Kappes, C. A.

Funding acquisition: Not applicable

Investigation: Costa Junior, I. L.; Giona, R. M.; Ferreira, K. A.; Kappes, C. A.

Methodology: Costa Junior, I. L.; Giona, R. M.

Project administration: Costa Junior, I. L.

Resources: Not applicable

Software: Not applicable

Supervision: Costa Junior, I. L.

Validation: Costa Junior, I. L.; Ferreira, K. A.; Kappes, C. A.

Visualization: Giona, R. M.

Writing – original draft: Costa Junior, I. L.; Giona, R. M.; Ferreira, K. A.; Kappes, C. A.

Writing – review & editing: Costa Junior, I. L.; Giona, R. M.

Data availability statement

All data sets were generated or analyzed in the current study.

Funding

Not applicable.

Acknowledgments

We are grateful to the Federal Technological University of Paraná for their assistance in the course of this study.

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