



Photo-anodes based on B-doped TiO₂ for photoelectrocatalytic degradation of propyphenazone: Identification of intermediates, and acute toxicity evaluation

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ABSTRACT

The photoelectrocatalysis (PEC) using B-doped TiO₂ photo-anodes for degradation of the propyphenazone (PPZ) was investigated. For this, four different composites based on TiO₂ and TiO₂-x%B (x = 1, 3 or 5) were synthesized by sol-gel method and supported on titanium substrate by the dip-coating technique. The morphology, optical and electrochemical properties of photo-anodes were evaluated by SEM, TEM, XPS, TGA, DSC, XRD, FTIR, DRS, and sweep voltammetry, respectively. The influence of pH (3, 6 or 9) and electrical potential intensity (+1 V, +2 V or +3 V) used in PEC were evaluated by kinetic study. To understand the synergistic effect of the composition of the photoelectrochemical system, photolysis (PS), electrocatalysis (EC) and photocatalysis (PC) experiments were realized under comparative conditions. Doping 3% of B into TiO₂ promoted a decrease in band gap energy ($E_{bg} = 2.91$ eV), thus providing better radiation absorption and greater generation of charge carriers on the surface of the photo-anode. Characterization analyzes indicate the presence of B₂O₃ coexisting with TiO₂. The most promising results were obtained using Ti/TiO₂-3%B photo-anode (vs a DSA cathode), applying +1 V at pH 6, resulting in 91% of PPZ degradation after 60 min of PEC treatment. Toxicity tests using *A. salina* and *L. sativa* showed that the effluent generated after 2 h of PEC treatment of 30 mg L⁻¹ of PPZ is non-toxic for the studied species. Up to 13 by-products formed during the PEC and PS treatment were detected and a proposal pathway involving possible routes of PPZ degradation were presented.

1. Introduction

Propyphenazone (PPZ, C₁₄H₁₈N₂O, C.A.S.-No. 479–92–5) is a non-steroidal anti-inflammatory drug (NSAID) being derived from the pyrazoline group and incorporated into many analgesic combinations in many countries. Due to its worldwide use, the presence of PPZ in groundwater is already reported at concentrations around 0.092 µg L⁻¹

[1], river at 0.005 µg L⁻¹ [2] and in wastewater treatment plant at a concentration of 0.880 µg L⁻¹ [3,4]. By presenting a high coefficient of danger to the environment [5], methods for the treatment of water contaminated by this type of compound are already being developed [6]. Reports indicate that PPZ degrades rapidly by chlorination [7–9]. Oxidation via ferrate (Fe (IV)) [10], chlorine dioxide [8], cyclodextrin polymer/pulsed light system [11] and ozone [12] are also found as

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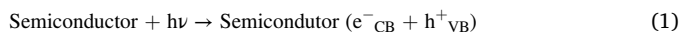
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alternative methods of treating PPZ in aqueous media. In addition to some of these processes that generate chlorinated products [9], there is a high potential for N-nitrosodimethylamine formation [10], raising concerns about potential ecotoxicity.

Advanced oxidation processes (AOPs) are known to be capable of removing various types of pollutants [13–15]. Photocatalysis (PC) [16] and electrochemical oxidation (EO) [17–19] are AOPs widely investigated and applied. Heterogeneous photoelectrocatalysis (PEC) is a hybrid method that combines the advantages of PC with EO, such as minimizing e^-/h^+ pair recombination, and easy removal of the photocatalyst from the electrochemical system. In this system, a thin film semiconductor photo-anode placed in an electrolytic cell is irradiated with photons with energy greater than band gap energy (E_{bg}). As a result, electrons can jump from the semiconductor valence band (h^+_{VB}) to its conduction band (e^-_{CB}), Eq. (1). The generated h^+_{VB} can oxidize water on the surface of the photo-anode to form adsorbed hydroxyl radical ($HO^\bullet$), Eqs. (2–3). In the absence of applied current (i.e. PC conditions), the e^-_{CB}/h^+_{VB} pair disappears rapidly due to recombination reactions, causing a significant decrease in oxidation capacity. This disadvantage is overcome in PEC by applying a small anode potential (E_{bias} or E_{an}) to the photo-anode, which favors the spatial separation of both charge carriers due to the transport of e^-_{CB} to the cell cathode, causing an increase in $HO^\bullet$ generation [20–23].



Titanium dioxide (TiO_2) is the most widely used semiconductor in PEC, as its properties favor its use due to the possibility of activation by sunlight, chemical stability over a wide pH range, low cost, low toxicity and insolubility in water [24]. It can be found in three crystallographic phases anatase, rutile and brookite. In PC and PEC studies, the anatase phase ($E_{bg} = 3.2$ eV) is the most used, due to its easy preparation and greater photocatalytic activity. The photocatalytic activity of TiO_2 can be improved by doping or modification of its crystalline structure and its main objectives are (i) increase the optical absorption of UV radiation in the visible light region (ii) decrease the recombination rate of photo-generated loads, and (iii) increase the amount of adsorbed species on its surface [25]. The first two objectives have been extensively investigated in recent years. For example, doping with transition elements (Ag, Fe, V, Bi, Sn and Mo) [26–34] and non-metallic elements (C, N, S, P and B) [35–38] has been shown to be ways of modifying the electronic structure and decreasing TiO_2 E_{bg} . Doping and/or modification with boron (B) has been shown to improve the photoactivity of TiO_2 , as it can occupy and displace the positions of the interstitial oxygen network, creating intermediate energy levels in TiO_2 E_{bg} [39,40]. TiO_2 doped and/or modified with boron has several applications such as antibacterial activity [41], Dye-sensitized solar cells (DSSC) [42], CO_2 photoreduction [43], and PEC of emerging pollutants [44]. For example, Wang et al. [45] synthesized B- TiO_2 photocatalysts for photodegradation of the herbicide atrazine. As a precursor for doping, they used boric acid in several different concentrations. The authors reported that the presence of boron increases the degradation rate, with the highest efficiency achieved by the photocatalyst with 120 mg boric acid in which the degradation of atrazine in 180 min was 94%. Manasa et al. [46] also synthesized boron-doped catalysts using H_3BO_3 as a precursor. The authors reported that under optimized conditions, the synthesized catalysts showed 90–93% degradation for both ciprofloxacin and norfloxacin.

In previous works, we synthesized B-doped TiO_2 for use in the removal of the metoprolol in pure water [16] and municipal secondary effluent [47]. Additionally, we performed a complete study to investigate the role of active species in the photocatalytic mechanism involving B-doped TiO_2 as a catalyst [48]. The activity of these catalysts was

evaluated in photocatalysis. Seeking strategies to improve the efficiency of the process, this study aims to investigate the application of an electric field to the photocatalyst (known as PEC) to trap h^+ and consequently increasing the lifetime of the electron-hole pairs. To achieve these goals, this work reports to the synthesis of boron doped Ti/TiO_2 photo-anode for PPZ degradation by PEC under UV-vis irradiation and external potential. The electrodes were synthesized by the sol-gel method and the film deposited by dip-coating. To the best of our knowledge, PEC degradation based on boron doped Ti/TiO_2 photo-anode has not yet been reported, and additionally the PPZ degradation has also not been previously reported. Factors such as pH and potential have been investigated. Photolysis (PS), PC and EO experiments were also performed to help in understanding the oxidation process in the study system. Ecotoxicity analysis used *A. salina* and *L. sativa* and possible degradation products were proposed.

This research may provide some new results on the influence of factors such as pH and voltage on PEC in recalcitrant molecules such as PPZ and provide a direction to produce more effective photoelectrocatalysts for water decontamination. It is noteworthy that to the best of our knowledge no study involving photoelectrocatalytic processes has been reported for the removal of PPZ.

2. Material and methods

2.1. Materials

Titanium metal plates (Degussa), titanium isopropoxide 97.0% (Sigma Aldrich), glacial acetic acid 99.7% (Vetec), 2-propanol 99.6% (Merck), nitric acid 65.0% (Vetec), boric acid 99.5% (Dinâmica do Brasil), PPZ Pharmaceutical Secondary Standard (Sigma Aldrich), formic acid 98% (Panreac) and Acetonitrile 99.5% (Sigma). Deionized water (resistivity > 18 MΩ cm) obtained from Gehaka DG500 UF system was used in all experiments.

2.2. Synthesis of Ti/TiO_2 -x%B photoelectrodes

The preparation of Ti/TiO_2 electrodes followed the previously described procedure [16,49]. Titanium metal plates were cut with a geometric area of 10.24 cm² and washed with deionized water and 5% oxalic acid solution in an ultrasonic bath. In the thin film synthesis of TiO_2 , glacial acetic acid was added in a beaker and then titanium isopropoxide in a molar ratio of 1:4 under constant stirring. After homogenization, 2-propanol was added in the ratio 1:1 (v/v) to titanium isopropoxide. After 1 h of stirring, an acidified aqueous solution prepared with 25 mol of deionized water and 0.5 mol of nitric acid was added slowly. The resulting solution was stirred for 2 h, resulting in a thin film. The thin film was deposited by immersing the plates in the suspension produced for 30 s by the dip-coating method (MA 765, Marconi). After immersion and formation of each coating, here called the layer, the electrode was calcined at 450 °C for 4 h. Thin film electrodes were prepared with 1, 3, 5, 7, 10 layers of TiO_2 , named T1, T3, T5, T7 and T10 respectively.

The B-doped electrodes were prepared by the same procedure described above, but boric acid was added as boron precursor in order to prepare samples with different boron weight content (%): 1, 3, and 5 (w/w). Three layers of thin film were applied according to a study of the influence of the layers in the photocurrent tests carried out previously (see Text S1 and Fig. S1 in Supplementary material).

2.3. Characterization

The prepared Ti/TiO_2 and Ti/TiO_2 -x%B electrodes were characterized by X-ray diffraction (XRD) on a LabX XRD - 6100, Shimadzu X-ray diffractometer with Cu Kα radiation. The FTIR spectra were obtained using a PerkinElmer IFTR spectrophotometer, Frontier model, at room temperature and in the 4000–450 cm⁻¹ region. The surface morphology

of the Ti/TiO₂ electrode was observed by Scanning Electron Microscopy (SEM) on a JSM-6380LV JEOL microscope. Diffuse reflectance spectroscopy (DRS) measurements were performed using UV/Vis/NIR spectrophotometer PerkinElmer Lambda 650 operating in the 200–800 nm range.

To complement the characterizations, we synthesized TiO₂ and TiO₂-3%B from the thin film according to topic 2.2. The thin film was kept at 40 °C for 48 h for the gelatinization process. Then, it was dried in an oven at 100 °C for 24 h. The powder obtained was macerated and calcined under the same conditions described for the preparation of electrodes. With the powder obtained under the same synthetic conditions as the electrodes, we performed the following characterization techniques: BET, TGA, DSC, XPS, and TEM.

The specific surface areas of the photocatalysts were determined by the TriStar 300 instrument and calculated with the BET model from the N₂ adsorption at 77 K. TEM images of the photocatalysts were obtained from a JEM 2100/JEOL microscope. Elemental composition was determined by X-ray photoelectron spectroscopy (XPS). The experiments were performed in a K-Alpha spectrometer (Thermo Scientific) with a monochromatic X-ray source (AlK α). The carbon contamination C1s peak appearing at 284.80 eV was used as the reference for binding energy calibration. All acquired spectra were treated with CasaXPS software. Thermogravimetric analysis (TGA) was carried out on a Ta Instruments TGA-Q50 instrument. Differential scanning calorimetry (DSC) was performed from an STA 449 F3, Jupiter instrument.

Photoelectrochemical measurements were performed on a conventional three-electrode 200 mL cell connected to a potentiostat/galvanostat (PGSTAT 128 N, The Netherlands) with 0.05 mol L⁻¹ Na₂SO₄ as the electrolyte. As working electrode, the Ti/TiO₂ and Ti/TiO₂-x%B (x = 1, 3 or 5) were used, as counter electrode a dimensionally stable anode (DSA, De Nora®), and reference electrode an Ag/AgCl (KCl 3.0 mol L⁻¹). The illumination was obtained from a 150 W Xenon lamp (Newport Experience Solutions). The lamp was positioned horizontally at a distance of 3 cm from the photo-anode, separated by a quartz wall. The photocurrent curves were registered by linear sweep voltammetry using a scan rate of 10 mV s⁻¹ under the potential range of -0.7 to + 1.2 V vs Ag/AgCl (KCl 3.0 mol L⁻¹). The photoresponse of the photo-anodes was studied by measuring photocurrent densities under chopped light irradiation (light on/off cycles: 30 s) at + 1.0 V vs. Ag/AgCl (KCl 3.0 mol L⁻¹). The experiments were carried out at 25 °C.

2.4. The photoelectrocatalytic system (PEC)

PPZ degradation experiments were carried out in an undivided cell consisting of a Ti/TiO₂-x%B (x = 0, 1, 3, and 5) photoanode and a DSA® cathode, both with 10.24 cm² of geometric area. The study solution was prepared at a concentration of 30 mg L⁻¹ PPZ in 200 mL of deionized water with 0.05 mol L⁻¹ Na₂SO₄. The pH was adjusted according to the sequence of experiments at pH = 3, 6, and 9 with 1.0 mol L⁻¹ NaOH or H₂SO₄ solution with the aid of a Crison GLP 21 pHmeter and monitored during each experiment. The potential difference was provided by a DC power supply (Minipa MPL-1303 M). Illumination was carried out by a 150 W Xenon lamp (Newport Experience Solutions) positioned horizontally at a distance of 3 cm from the photoanode, separated by a quartz window. The studied potentials were + 1 V, + 2 V, or + 3 V. All experiments had a treatment period of 120 min with continuous magnetic stirring, during which time several aliquots were collected. For comparison purposes, PS, PC, and EC, under the same conditions, were also performed.

The PPZ concentration was monitored by reverse-phase HPLC using a Finnigan Surveyor system from Thermo Scientific equipped with a Zorbax Eclipse XDB-C18 5 μ m (250 mm $\times$ 4.6 mm) column from Agilent Technologies and the PDA detector set at 266 nm. Samples were collected at predetermined times, filtered with a 0.22 μ m PTFE filter, then aliquots of 25 μ L were injected and the elution was ensured with an 80:20 (v/v) methanol/water mixture at 0.7 mL min⁻¹ as mobile phase.

Under these conditions, a calibration curve was constructed in the range 0.2–40 mg L⁻¹ with a LOQ = 0.069 mg L⁻¹ and LOD = 0.023 mg L⁻¹ (R² = 0.9998).

The mineralization was followed by the total organic carbon (TOC) analysis using a Shimadzu TOC VCPN analyzer. In this case, 2 mL aliquots were diluted in 5 mL of deionized water and analyzed. The calibration accuracy values with LOQ = 0.180 mg L⁻¹ and LOD = 0.053 mg L⁻¹ were obtained.

Apparent pseudo-first order kinetic constants (k_{app}) (Eq. 4) to PPZ degradation were calculated according to the following:

$$k_{app} = \frac{\ln\left\{\frac{[PPZ]_0}{[PPZ]_t}\right\}}{t} \quad (4)$$

2.5. By-products Generation

UPLC-QToF-MS analyses were carried out on a Waters® Acquity UHPLC H-class liquid chromatograph coupled to a Waters® Xevo® G2-XS QToF mass spectrometer with an electrospray interface (ESI) (Waters Corporation) equipped with a BEH C18 column (dimensions: 2.1 $\times$ 100 mm, 1.7 μ m; Waters Corporation) at a temperature of 40 °C. The mobile phase 0.1% formic acid (HCO₂H) (Panreac) and Acetonitrile (Sigma) at the flow rate was 0.8 mL min⁻¹. The injection volume was 10 μ L with chromatogram acquisition time of 10 min. The mass spectra were acquired in positive mode (M+H), to range of 20–300 Da. The ESI conditions were: 1.2 kV capillary voltage, 30 V cone voltage, 100 °C source temperature, 450 °C desolvation temperature, 50 L h⁻¹ cone gas flow rate and 750 L h⁻¹ desolvation gas flow rate. For internal calibration, a solution of leucine enkephalin (Sigma, 200 pg mL⁻¹) was infused by the lock-mass probe at a flow rate of 10 μ L min⁻¹.

2.6. Toxicity tests

2.6.1. Artemia salina assay

Acute toxicity tests for *A. salina* were performed in duplicate (5 individuals per replicate) at 25 °C in well cell culture plates of 3 mL according to the literature [50,51]. The larvae of microcrustacean were cultivated in synthetic seawater at 30 g L⁻¹, pH 8–9 under aeration for 48 h with a photoperiod of 16 h light and 8 h dark. The median lethal concentrations (LC₅₀) were obtained by dead larvae count after exposure of the organisms for 48 h in the effluents previously diluted (70%, 50%, 25%, 12.5% and 6.25% v/v) obtained from the PEC and PS treatments, using Ti/TiO₂ or Ti/TiO₂-3%B photo-anodes at pH 6.

2.6.2. Lactuca sativa assay

Acute phytotoxicity tests have been adapted from section A.8.7 “Lettuce root elongation (*L. sativa*)” of EPA 600/3-88-029 [52] and previously studies [53]. To this, Lettuce seeds *L. sativa* var. White Boston (Isla Sementes Ltda, lot no. 113273-001 s2, 97% germination, 99.5% purity) was used. The samples tested were the effluents obtained after 2 h PS or PEC treatment (using Ti/TiO₂ or Ti/TO₂-3%B) diluted to 50% (v/v), and compared with a positive control (30 mg L⁻¹ PPZ), and a negative control (deionized water + 0.05 mol L⁻¹ Na₂SO₄). For each solution tested, 20 seeds were distributed in a Petri dish with 3 mL of effluent and exposed for 72 h in the dark at room temperature. The root growth inhibitory concentration for 50% of the seeds (IC₅₀) was determined by measuring the length of the roots [54].

3. Results and discussion

3.1. Characterization of Ti/TiO₂-x%B photo-anodes

The XRD patterns of all Ti substrate, Ti/TiO₂ and Ti/TiO₂-x%B were recorded after calcination (Fig. 1a) in order to confirm the crystalline phase of TiO₂ formed. The substrate diffractogram (Ti) was compared to the ICDD data (00-044-1294) and its peaks refer to the titanium

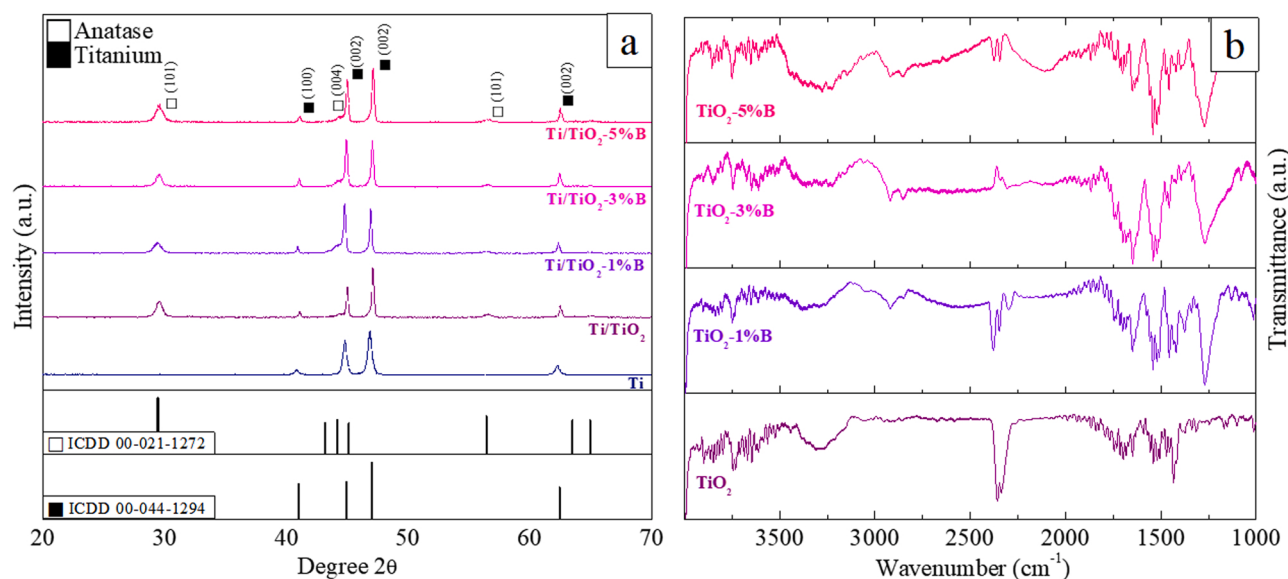


Fig. 1. (a) DRX diffractograms of Ti substrate and Ti/TiO₂ and Ti/TiO₂-x%B (x = 1, 3 or 5) photo-anodes, and, (b): FTIR spectra of TiO₂ and TiO₂-x%B composites.

hexagonal phase planes present in all samples. The peaks generated by the samples (Ti/TiO₂, Ti/TiO₂-1%B, Ti/TiO₂-3%B and Ti/TiO₂-5%B) were compared with ICDD data (00-021-1272) and indicated the formation of the single phase of anatase. The presence of the anatase phase is a satisfactory result as it allows more effective photon absorption than the rutile phase of TiO₂ increasing photo(electro)catalytic performance in practical applications [20].

The presence of boron in the TiO₂-x%B composites was confirmed by the FTIR results present in Fig. 1b. Compared with pure TiO₂, it is noted in the spectra obtained from other doped composites the presence of an absorption peak between 1346 and 1126 cm⁻¹, with a maximum of 1270 cm⁻¹ attributed to the B-O stretch vibration of B₂O₃. The widened

bands between 3500 and 3000 cm⁻¹, and 1500–1270 cm⁻¹ are attributed to water and hydroxyl groups adsorbed to the surface of the photocatalyst. The region of 450–1000 cm⁻¹ of FTIR photocatalysts spectra is present in Fig. S2 (Supplementary material), the appearance of absorption band and between 600 and 900 cm⁻¹ differs the B-doped composites with pure TiO₂, attributed to the presence of O-B-O bonds [55].

The surface morphology of Ti/TiO₂-x%B photo-anode is depicted in Fig. 2. By SEM, it can be seen that the film formed is composed of irregular cracks characteristic of thin films. At the edges of the cracks, the detachment of the substrate (Ti) occurs, caused by different surface tensions that occur during the application and drying of the thin film. [56]. The thickness of these detachments is approximately ≈ 597 nm,

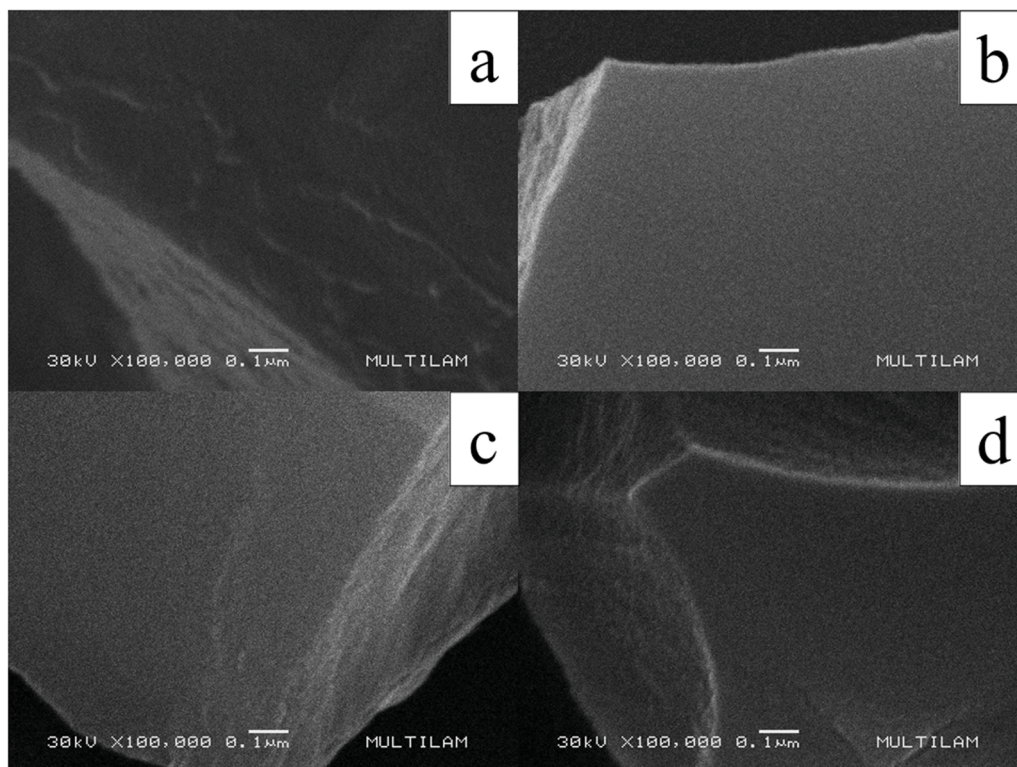


Fig. 2. SEM images of Ti/TiO₂-x%B (a) Ti/TiO₂, (b) Ti/TiO₂-1%B, (c) Ti/TiO₂-3%B, and (d) Ti/TiO₂-5%B.

increasing the surface area of the photo-anodes. The addition of boron did not affect the morphology of the electrodes produced, as can be seen in the micrographs Fig. 2a,b,c, and d.

TEM images and histograms of estimated particle size distributions (using Feret's diameter) of the TiO_2 and TiO_2 -3%B photocatalyst are shown in Fig. 3. The estimated mean particle diameter for TiO_2 is 13.73 nm, Fig. 3a. The presence of boron affects the particle size, as we can see in Fig. 3b, in which TiO_2 -3%B has a particle size of 8.17 nm.

XPS technique was used to analyze the surface chemical structure of the catalysts and to verify the changes in the chemical composition as a function of the presence of boron, Fig. 4. According to the survey spectrum (data not shown) the presence of titanium, oxygen and carbon is evident. For the TiO_2 -3%B catalyst a B1s peak is observed, demonstrating the presence of boron in the catalyst. The origin of carbon is common in XPS analyses, resulting from the strong adsorption of a contaminant layer [57]. The chemical composition of both TiO_2 and TiO_2 -3%B photocatalysts is shown in Table 1.

Fig. 4 shows Ti2p and O1s high-resolution XPS spectra obtained for the TiO_2 and TiO_2 -3%B. The experimental values of binding energies for each Ti2p and O1s component are presented in Table 2. The spectral fit parameters were compiled from the database of the National Institute of Standards and Technology (NIST) [58] and from literature data [59,60]. A titanium-based photocatalyst can be presented as a mixture with different oxidation states (0 to IV) with different binding energies. Deconvolution of Ti2p XPS data (Fig. 4a and b) reveals that titanium is primarily presented as Ti^{4+} (see Table 2), corresponding to relative TiO_2 concentrations of 87.65% and 86.38% for pure and 3%B-doped TiO_2 catalysts. Through the bond energy values obtained for the different components of Ti2p (Fig. 4 and Table 2) it is possible to observe the

presence of small amounts of the reduced species Ti^{3+} and Ti^{2+} in the synthesized catalysts, likely as a result of the charge imbalance caused by B doping [41]. More specifically, for pure TiO_2 the deconvolution of Ti2p XPS showed Ti_2O_3 and TiO at relative concentrations of 6.75% and 5.60%, respectively. For the boron doped photocatalyst, there was a small increase in the relative concentrations of Ti_2O_3 and TiO , reaching values of 7.80% and 5.82%, respectively.

The O1s region of pure TiO_2 (Fig. 4c) is composed of two peaks at 530.02 eV and 530.73 eV, corresponding to the Ti-O and surface-adsorbed O_2/OH groups, respectively. These values are in accordance with the binding energy values described in the literature [60]. For the catalyst composed of TiO_2 -3%B, the presence of a new peak related to the Ti-O-B bond is observed (see binding energy values are inserted in Table 2), confirming the presence of incorporation of B in the crystal structure of the TiO_2 .

Fig. 5 shows the high-resolution XPS B 1s spectra of TiO_2 -3%B catalyst. The standard binding energy of B 1s (for B-O bond) in the form of B_2O_3 and H_3BO_3 is equal to 192.9 eV and 193.3 respectively, and in the form of TiB_2 it is equal to 187.5 eV (for the B-Ti bond) [58,61,62]. From the deconvolution of the XPS B1s it can be seen that the peaks of B1s are divided into three characteristic peaks, at 189.07, 192.07 and 193.05 eV. The peak around 192 eV can be attributed to the O-Ti-B bond formed by the B atoms replacing the O atoms (known as substitutional doping, $\text{BTi}^{\cdot}$) [41]. The peak at 193.05 eV can be attributed to B-O-B bonds in B_2O_3 or H_3BO_3 [61] and the third peak (189.07 eV) can be related to B-Ti bond in TiB_2 . Thus, this indicates the boron atom was probably incorporated into TiO_2 and may also be in the form of precipitates (B_2O_3).

The surface area of TiO_2 and TiO_2 -3%B were obtained through

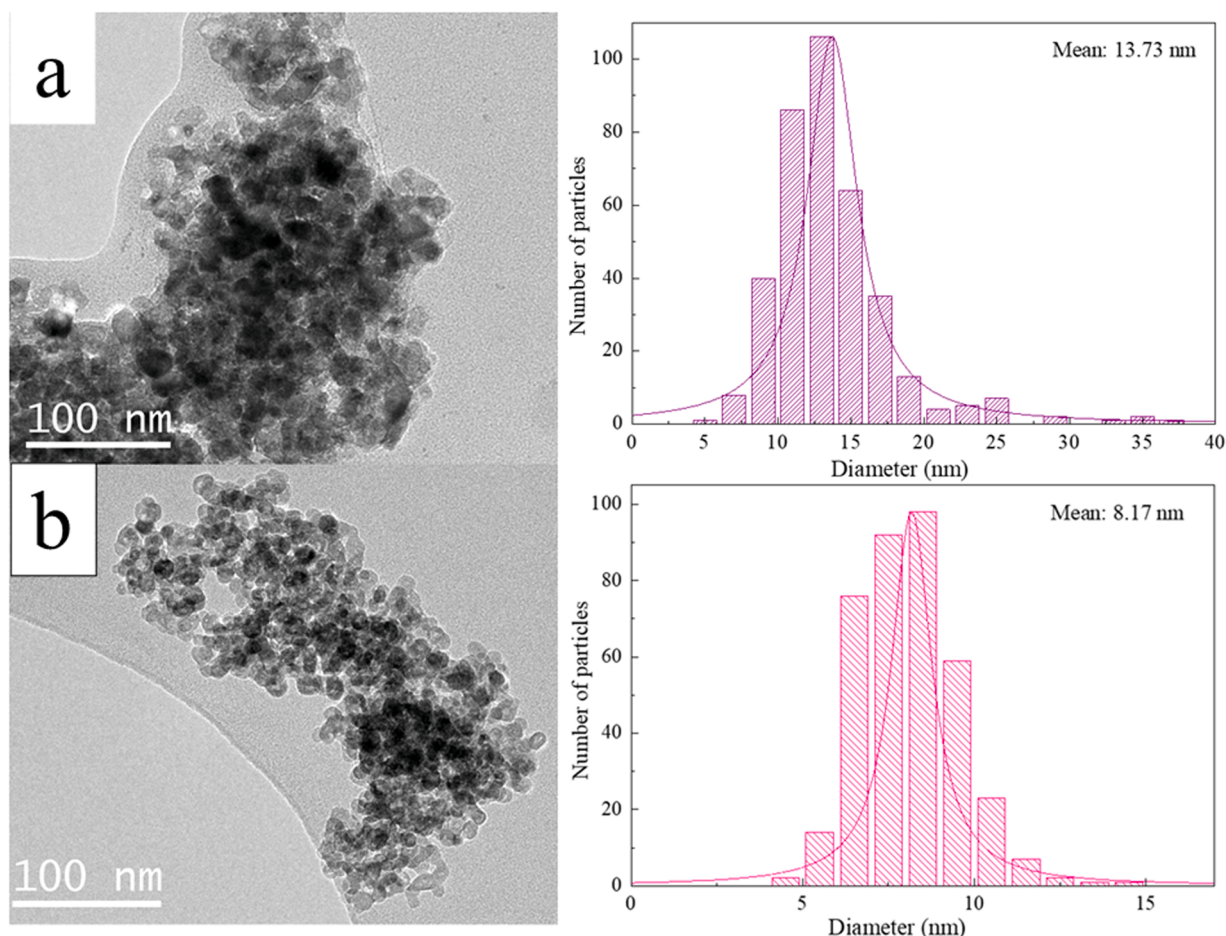


Fig. 3. TEM images and distribution of particles size of photocatalysts (a) TiO_2 , and (b) TiO_2 -3%B.

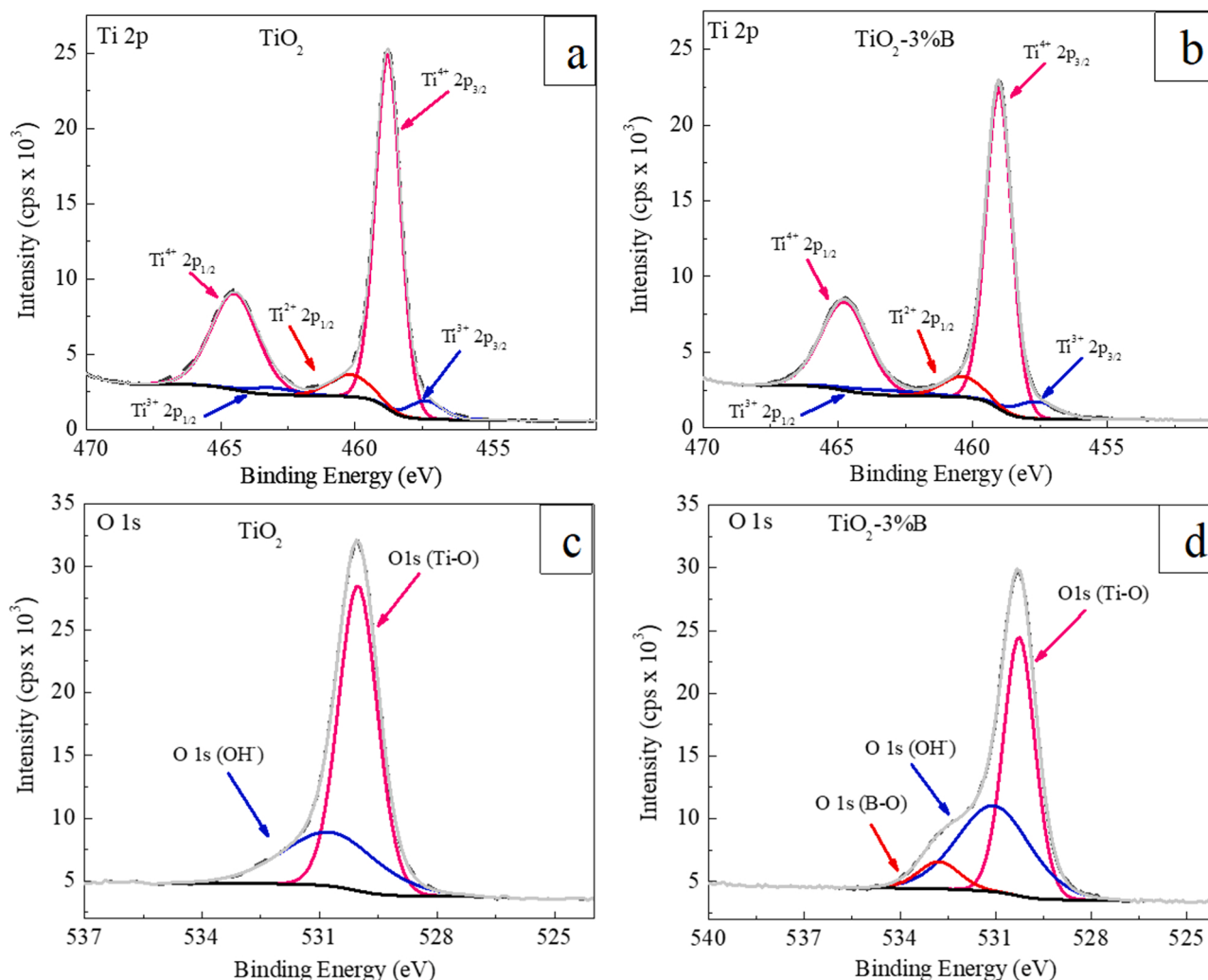


Fig. 4. High-resolution XPS Ti2p and O1s spectra of TiO₂ (a and c) and TiO₂-3%B (b and d).

Table 1

Surface chemical compositions of pure and B-doped TiO₂.

Catalyst	XPS surface chemical composition (%)				
	B	O	Ti	O/Ti	B/Ti
TiO ₂	–	72.25	27.75	2.60	–
TiO ₂ -3%B	9.17	63.44	27.38	2.31	0.33

nitrogen adsorption and desorption experiments (Fig. 6), using the BET mathematical method. TiO₂ has a surface area of 68.11 m²g⁻¹. TiO₂-3%B has a surface area of 103.55 m²g⁻¹. Doping with boron increased the surface area, causing a better photocatalytic response due to the increase in the number of active sites on the catalyst surface for the adsorption of organic molecules. Consequently, mass transport is facilitated, and, as a result, greater application efficiency can be obtained. Fig. 6 shows that the isotherms are by the typical pattern of mesoporous material (Type IV, according to the IUPAC classification of physical adsorption isotherms), indicating the mesoporous nature of the materials [63].

Fig. 7 shows the results of TGA and DSC measurements for TiO₂ and TiO₂-3%B. In Fig. 7a there are no significant mass loss events for both TiO₂ and TiO₂-3%B, which is in agreement with the literature [64,65]. In the DSC measurements, Fig. 7b, both photocatalysts show similar endothermic and exothermic events up to 400 °C. A shallow endothermic peak at 120 °C can be associated with the diffusion-limited adsorbed water evaporation process [66]. A shallow exothermic peak

Table 2

Binding energies (eV) obtained through XPS for TiO₂ and TiO₂-3%B.

Region / sample		TiO ₂	TiO ₂ -3%B
C1s	C-C, C-H	284.80	284.80
	C-OH, C-O-C	286.35	286.73
	O-C=O	289.09	289.34
O1s	Ti-O	530.02	530.27
	Ti-OH	530.73	531.06
	B-O, B ₂ O ₃	n.i.	532.78
Ti2p _{3/2}	TiO ₂	458.78	459.03
	Ti ₂ O ₃	457.38	457.63
	TiO	n.i.	n.i.
Ti2p _{1/2}	TiO ₂	464.50	464.75
	Ti ₂ O ₃	463.10	463.35
	TiO	460.15	460.39
B1s	B-O	–	192.07
	B-O-B, B ₂ O ₃ or H ₃ BO ₃	–	193.05
	B-Ti, TiB ₂	–	189.07

n.i. = not identified

at 192 °C may be associated with pyrolysis of the synthesis precursor [67] present in both photocatalysts. In the TiO₂ curve, there are two additional peaks present, one endothermic at 647 °C and the other exothermic at around 769 °C that may be associated with anatase to rutile phase shift [68]. An endothermic peak at 956 °C and 1010 °C for TiO₂-3%B and TiO₂, respectively. Since no associated weight change could be detected the origin of such peaks could be more appropriately

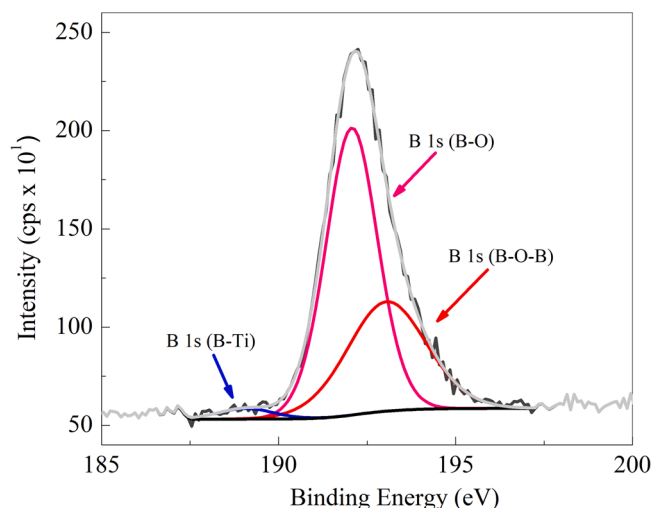


Fig. 5. High-resolution B1s XPS spectrum of $\text{TiO}_2\text{-3%B}$.

associated with crystallization and phase transformation events of the analyzed samples [69].

The photoactivity of $\text{Ti/TiO}_2\text{-x%B}$ electrodes were studied by DRS and the absorbance spectra plot obtained to each photo-anode are presented in Fig. 8. All electrodes showed similar absorption spectra, with intense absorption in the region between 300 and 400 nm, which is characteristic for TiO_2 semiconductors resulting from extrinsic E_{bg} .

Fig. 8b shows the optical band gap was calculated from the Tauc plot. The E_{bg} values for Ti/TiO_2 , $\text{Ti/TiO}_2\text{-1%B}$, $\text{Ti/TiO}_2\text{-3%B}$ and $\text{Ti/TiO}_2\text{-5%B}$ are respectively: 3.17, 3.04, 2.91 and 3.14 eV. For $\text{Ti/TiO}_2\text{-1%B}$ and $\text{Ti/TiO}_2\text{-3%B}$ there is a decrease in E_{bg} with increasing boron content. It is known that the presence of oxygen vacancies is responsible for the optical absorption of redshift [44], causing this decrease. As for $\text{Ti/TiO}_2\text{-5%B}$, E_{bg} increased and this could be related to the continuous migration of CB electrons (TiO_2) over the first excited state of B^{3+} being the maximum energy shift from TiO_2 to B^{3+} ions [42].

The photoelectrochemical behavior of $\text{Ti/TiO}_2\text{-x%B}$ electrodes under UV-Vis light irradiation is shown in Fig. 9a. During irradiation, voltametric curves exhibit the same behavior, where photocurrent density increases with the applied potential. The photocurrents generated correspond to a residual current density that is constituted by a faradaic current, derived from redox processes (electroactive species and

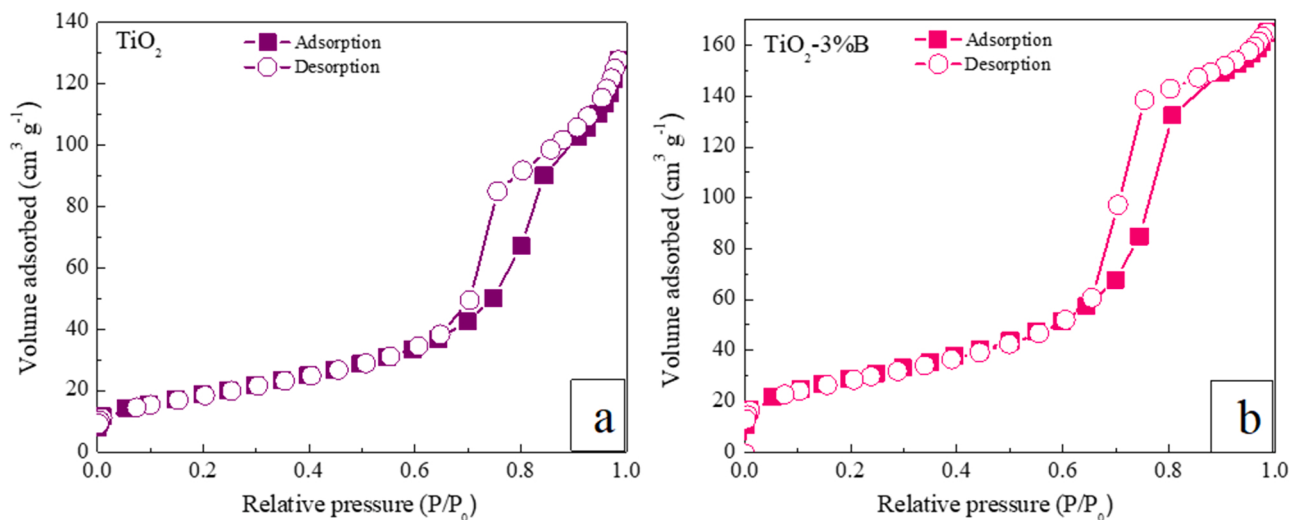


Fig. 6. Nitrogen adsorption-desorption isotherms of (a) TiO_2 and (b) $\text{TiO}_2\text{-3%B}$.

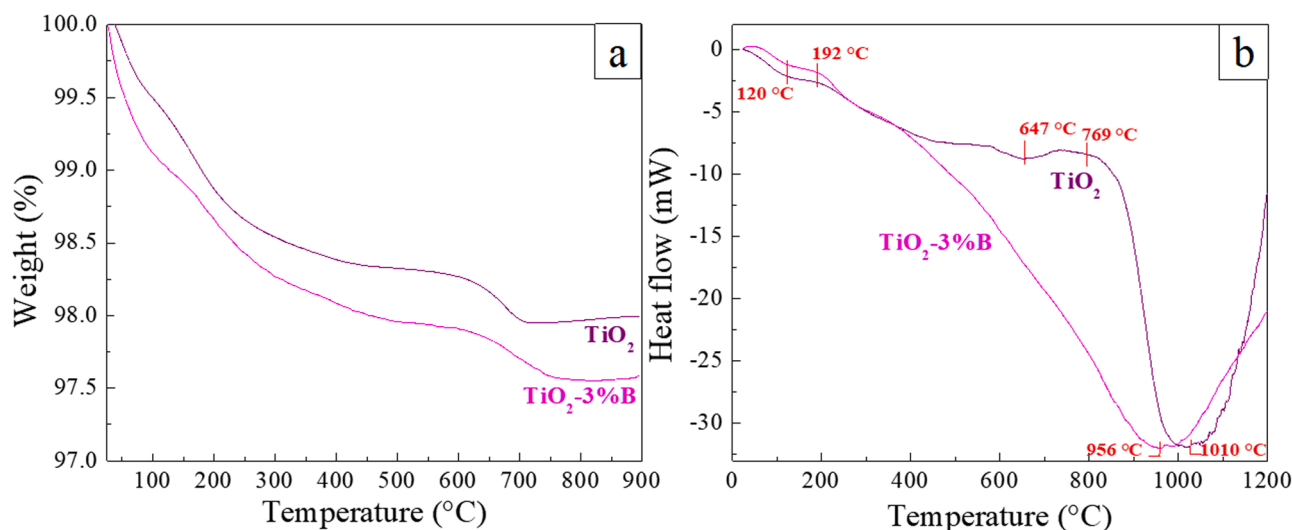


Fig. 7. (a) – TGA signals of TiO_2 and $\text{TiO}_2\text{-3%B}$ under nitrogen, with a heating rate of $10\text{ }^\circ\text{C/min}$. DSC curves of TiO_2 and $\text{TiO}_2\text{-3%B}$.

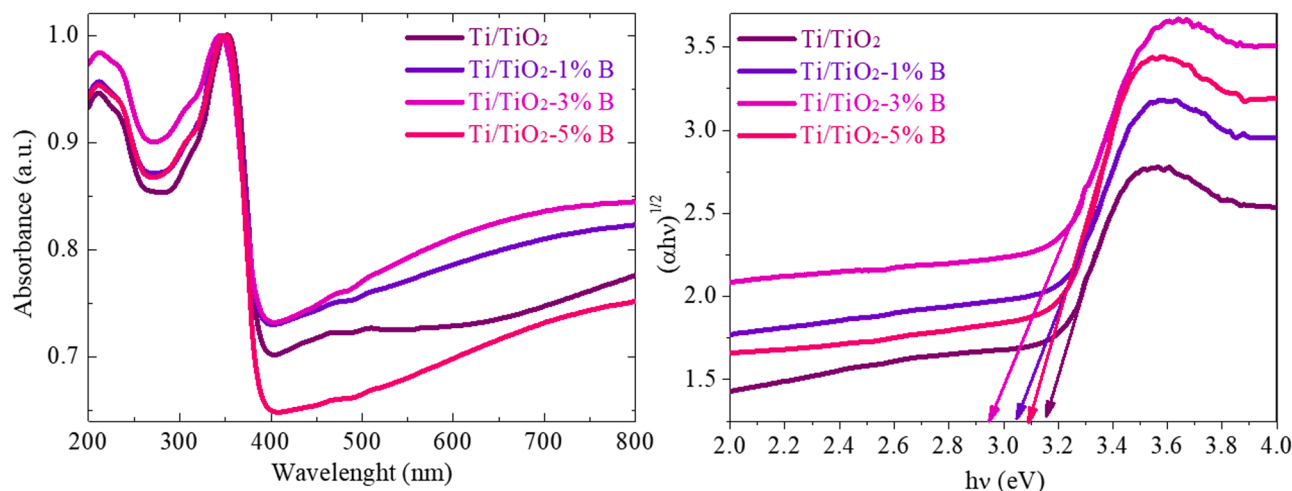


Fig. 8. (a) Optical absorption spectra of electrodes. (b) Tauc plot for the determination of E_{bg} .

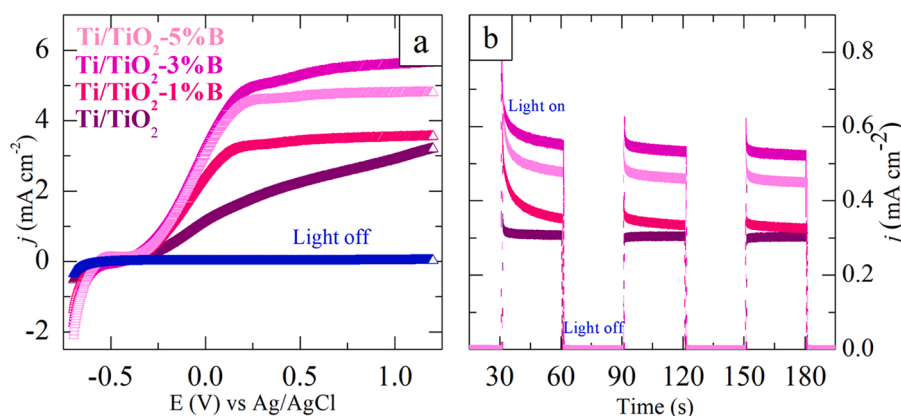


Fig. 9. (a) – Linear sweep voltammetry obtained in $0.05 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ electrolyte at scan rate of 10 mV s^{-1} . (b) – Photocurrent transient applying a potential of $+1 \text{ V}$, both using Ti/TiO_2 or $\text{Ti/TiO}_2\text{-x}\% \text{ B}$ photo-anodes under 150 W of UV/Vis irradiation.

dissolved oxygen) and capacitive current from the charging process of the double electric layer. Under UV-Vis irradiation, the $\text{Ti/TiO}_2\text{-3}\% \text{ B}$ electrode has a limiting current density of 0.53 mA cm^{-2} followed by 0.46 mA cm^{-2} , 0.34 mA cm^{-2} and 0.25 mA cm^{-2} for $\text{Ti/TiO}_2\text{-5}\% \text{ B}$, $\text{Ti/TiO}_2\text{-1}\% \text{ B}$ and Ti/TiO_2 electrodes, respectively.

The transient current experiment is considered an effective measure to investigate the efficiency of photoinduced charge separation in nanomaterials and thereby determine the stability of the investigated material. As shown in Fig. 9b, the photoactivity responses present in all cases a rapid rise and fall with intermittent lighting. By comparison $\text{Ti/TiO}_2\text{-3}\% \text{ B}$ had a current density of 0.527 mA cm^{-2} considerably higher than $\text{Ti/TiO}_2\text{-5}\% \text{ B}$ (0.451 mA cm^{-2}), $\text{Ti/TiO}_2\text{-1}\% \text{ B}$ (0.327 mA cm^{-2}) and Ti/TiO_2 (0.302 mA cm^{-2}) electrodes. These performances demonstrate that the presence of boron in the developed material improves the separation of charge carriers and, consequently, decreases charge recombination [70].

3.2. PEC degradation of propyphenazone

To understand the synergistic contribution of PEC elements: photoanodes, UV-vis irradiation, and potential difference, degradation experiments of 30 mg L^{-1} of PPZ in 0.05 mol L^{-1} and Na_2SO_4 were also carried out by: (i) PS in pH 3, 6 or 9; (ii) EC applying $+1 \text{ V}$ at pH 6; (iii) and PC at pH 6. The results are shown in Fig. S3 (PS) presented in the Supplementary material and Fig. 10 (EC and PC).

Fig. S3a shows decay curves obtained of PPZ degradation by PS, note

that photodecomposition of the drug can be accelerated under acidic conditions. However, only 45% drug degradation is observed after 120 min of treatment at pH 3. In the Fig. S3b the pseudo-first-order kinetics (k_{app}) obtained from linear regression of the first 30 min, are also presented, and their values with the quadratic linearity coefficients (R^2) are presented in Table S1 (see Supplementary material).

As little as the degradation of the total amount of PPZ, the TOC was not satisfactorily removed by PS, Fig. S3c. These results indicate that only UV-vis radiation was not able to degrade and mineralize PPZ in the studied system.

The EC process proved to be the most incapable of degrading PPZ. In Fig. 10a symbols filled with dashed lines represent PPZ degradation. The EC process was carried out by applying $+1 \text{ V}$ to the photoanode ($\text{Ti/TiO}_2\text{-x}\% \text{ B}$) without UV-Vis radiation. The low efficiency of the EC process can be related to the low current generated in the system ($0.25\text{--}0.53 \text{ mA cm}^{-2}$, Fig. 9a), being insufficient to produce $\text{HO}^\bullet$ [71]. In the same graph (Fig. 10a), the degradation results for PC process (empty symbols with solid lines) are also shown. Here we confirm the dependence of UV-Vis radiation for PPZ degradation. When irradiated by UV-vis light, the TiO_2 or $\text{TiO}_2\text{-x}\% \text{ B}$ adhered to the Ti plate is activated. The valence band electrons are promoted to the conduction band, leaving gaps capable of oxidizing the water present in the medium. As a product of water oxidation, we have the generation $\text{HO}^\bullet$ radicals, among other reactive oxygen species (ROS), that attack the PPZ molecule, degrading it, Eqs.1–3.

Around 79% PPZ degradation and 8.5% TOC reduction (Fig. 10b) is

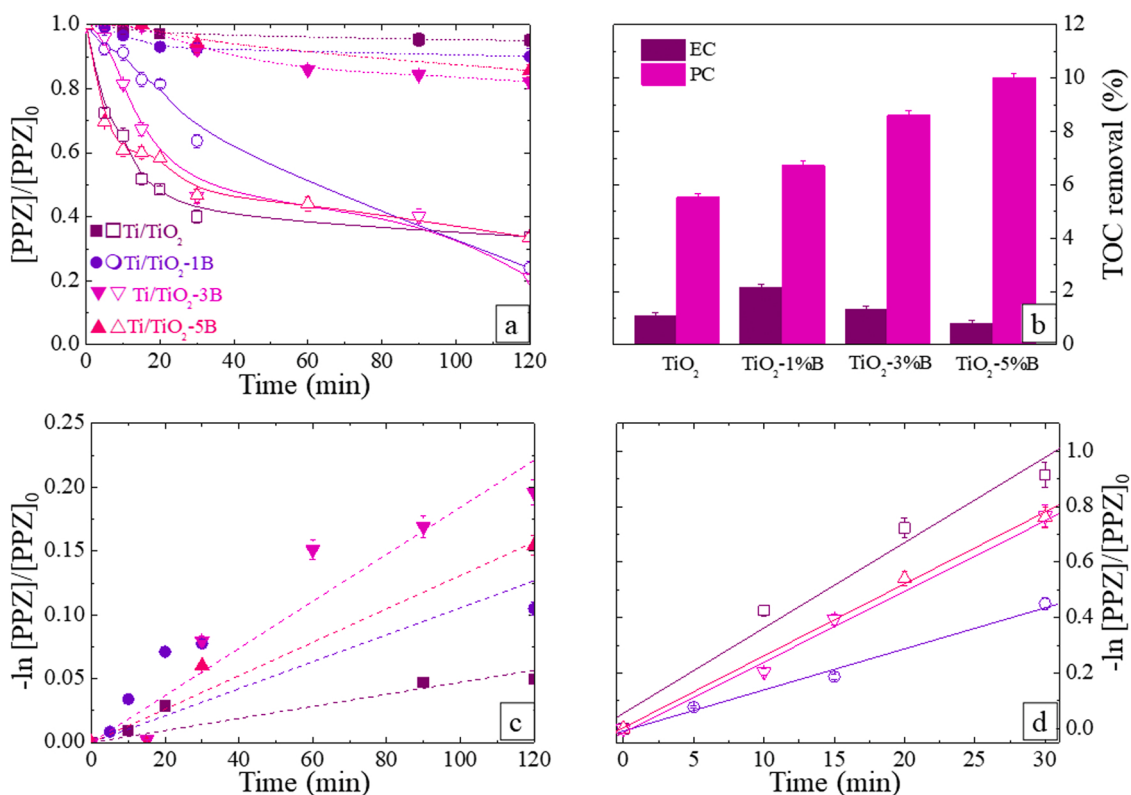


Fig. 10. (a) – Normalized decay curves obtained from EC treatment (filled symbols, dashed lines) of 200 mL of 0.05 mol L⁻¹ Na₂SO₄ solution containing 30 mg L⁻¹ PPZ at pH 6, using DSA cathode and Ti/TiO₂ or Ti/TiO₂-x%B photo-anodes applying ddp + 1 V. And PC treatment (empty symbols, solid lines) using the same solutions and photoanodes, irradiated by a 150 W UV-Vis xenon lamp. (b) – TOC removal obtained after 120 min of respective EC and PC treatment. (c) and (d) – Pseudo-first order kinetic degradation curves to EC and PC treatment, respectively.

observed using Ti/TiO₂-3%B after 120 min of PC. The degradation kinetics for EC and PC are shown in Fig. 10c and d respectively, and the k_{app} values obtained in Table S1 (see Supplementary material).

3.2.1. pH effect on PEC

For the four different photo-anodes, three pH values were tested during PPZ degradation, and the results are shown in Fig. 11. Note that for all electrodes tested, no significant influence of pH on PPZ degradation was observed. Comparing the PPZ degradation obtained using pure Ti/TiO₂ (Fig. 11a) and Ti/TiO₂-1%B (Fig. 11b), a higher decay rate is observed up to 30 min for the boron-doped electrode. Under the same conditions, with Ti/TiO₂-3%B (Fig. 11c) or Ti/TiO₂-5%B (Fig. 11b), around 94% PPZ degradation is obtained after 120 min of PEC at pH 6. In 120 min of the experiment, all degradation values converge to almost 100% elimination of PPZ. In a 60 min experiment, we can see in Fig. 11c that the Ti/TiO₂-3%B electrode degraded 91% of the PPZ at pH 6. And this value remained constant up to 120 min (see Table S1 in the supplementary material). The k_{app} value for Ti/TiO₂-3%B in was 0.0377 min⁻¹ ($R^2 = 0.9710$) being a faster reaction than Ti/TiO₂ at pH 6, k_{app} 0.0155 min⁻¹ ($R^2 = 0.9929$).

The interest of this study is the possibility of interference of the pH of the reaction medium in the formation of ROS on the surface of photo-electrocatalysts. There is also the existence of different solvated species of PPZ at different pHs (protonated or deprotonated). Considering that TiO₂ has its isoelectric point (pH value where the semiconductor has zero electric charges) around pH 4.24 [16] and that the PPZ molecule (Fig. 12) has pKa 0.87, at pH 3 both will be positively charged. The electrostatic attraction provides a significant improvement in degradation due to direct oxidation of molecules by gaps generated on the photocatalyst surface [72]. However, the results at pH 3 indicate that the high efficiency does not depend on PPZ adsorption. Thus, it is believed that the degradation of PPZ would be governed preferentially

by reactions with HO• radicals generated from the oxidation of adsorbed water molecules on the electrode surface [73]. These radicals act as electrophiles preferentially attacking the regions with the highest electron density, as we can see in Fig. 12 at pH > 3.4 and electron density is found in the benzene ring and pyrazoline group.

The values of k_{app} , Table S1 (Supplementary material) showed fast superiority of the Ti/TiO₂-3%B electrode at pH 3 or 6 compared to the other electrodes tested. This better efficiency of Ti/TiO₂-3%B at acidic pHs is confirmed by observing the TOC results shown in Fig. 13c. A TOC reduction of up to 18% TOC has been achieved. The pH 6.0 of the working solution was adopted for further studies because it is the natural pH of the solution, not requiring correction, and because of the similarity of the results in relation to pH 3.0.

3.2.2. Effect of voltage

To verify the influence of voltage, experiments were carried out using the voltages of + 2 V and + 3 V in which the pH was adjusted to 6. Fig. 14 shows the PPZ degradation graphs for the voltages studied. Fig. 14a shows the results obtained for the Ti/TiO₂ electrode. Applying a voltage of 3 V, 79% PPZ removal was obtained. The Ti/TiO₂-1%B electrode, Fig. 14b, degraded 69% of the PPZ in 30 min of the experiment and from 60 min onwards the degradations were similar regardless of the applied voltage. In Fig. 14c, it is shown that for the experiment carried out using the Ti/TiO₂-3%B electrode and applying a voltage of + 1 V, 91% of PPZ removal was obtained in 60 min. The better performance of the + 1 V potential is evident by analyzing the k_{app} values displayed in Table S1. From these values, we can see that the voltage + 1 V had a $k_{app} = 0.0377$ min⁻¹, greater than the other experiments. The Ti/TiO₂-5%B electrode degraded 87% of the PPZ in 60 min of the experiment applying a voltage of + 3 V, while at + 1 V and + 2 V the values were 70% and 77%, respectively.

Mineralization was also monitored, Fig. S4 (see Supplementary

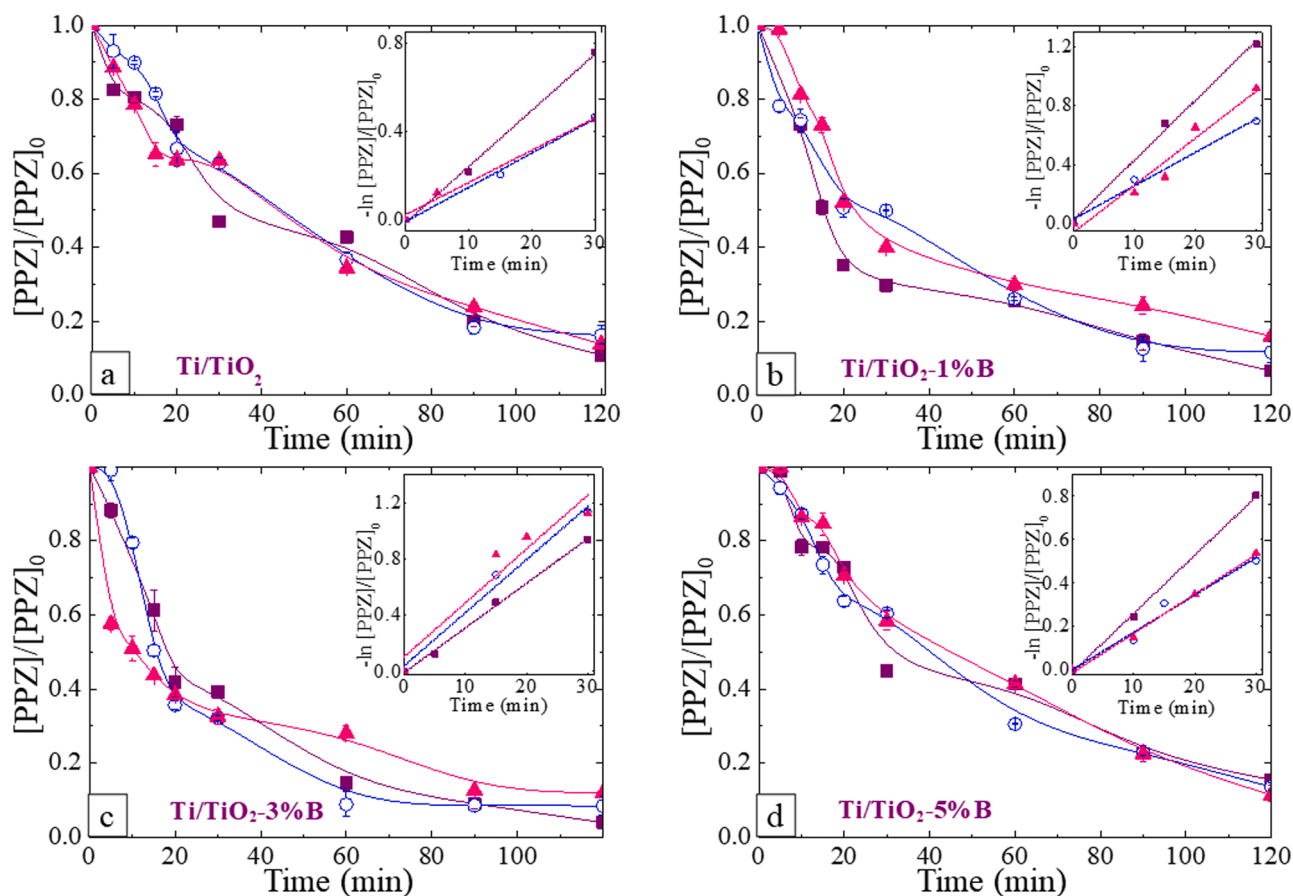


Fig. 11. (a), (b), (c) and (d) – Normalized decay curves obtained from PEC treatment of 200 mL of $0.05 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solution containing 30 mg L^{-1} PPZ, using DSA cathode and Ti/TiO_2 or $Ti/TiO_2-x\%B$ photo-anodes, irradiated by a 150 W UV-Vis xenon lamp, applying ddp + 1 V, at pH = 3 (■), pH = 6 (○) or pH = 9 (▲). In the inserted graphics, respective pseudo-first order kinetic degradation curves.

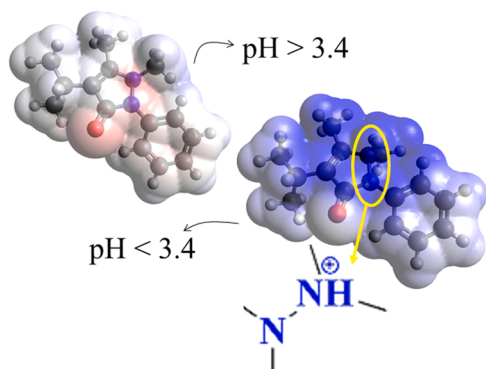


Fig. 12. Electrostatic map of the PPZ molecule in relation to pH.

material). The mineralization rate did not increase over the + 1 V voltage. Fig. S4a shows the results for PPZ mineralization using the Ti/TiO_2 electrode. It is possible to verify that in 120 min of reaction, 14% of mineralization was obtained for the experiment carried out with + 3 V. This value is not very significant since at + 1 V and + 2 V the TOC removal was 13%. From Fig. S4b, it is possible to verify that $Ti/TiO_2-1\%B$ electrode mineralized 15%, 14% and 11% for voltages + 1 V, + 3 V and + 2 V, respectively in 120 min. While for $Ti/TiO_2-3\%B$ electrode, Fig. S4c, the mineralization was similar for the + 1 V and + 2 V experiments, with a percentage of 19%. The $Ti/TiO_2-5\%B$ electrode, Fig. S4d, mineralized 17% at voltage + 2 V. It is worth noting that the addition of boron slightly increased the mineralization rate. However,

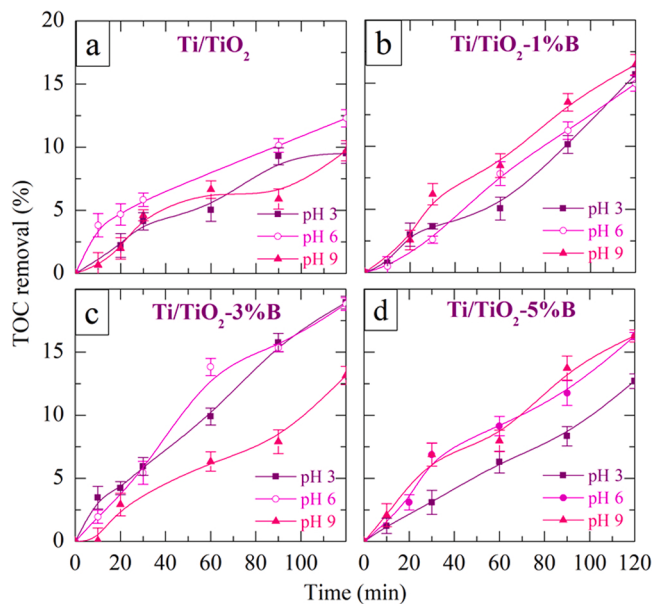


Fig. 13. (a), (b), (c) and (d) – TOC removal percentage as a function of time obtained of PEC treatment described for Fig. 11.

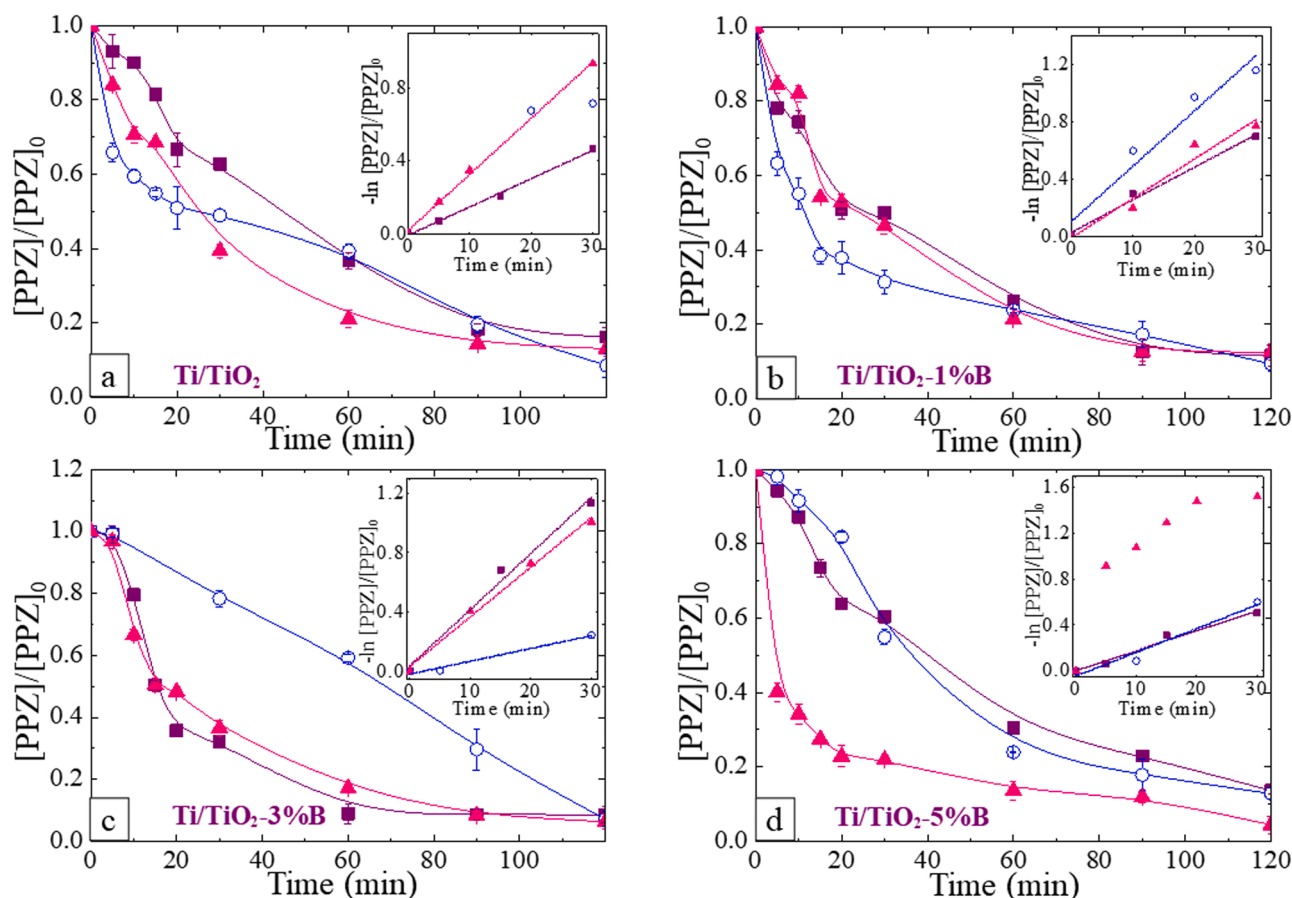


Fig. 14. Normalized decay curves obtained from PEC treatment of 200 mL of 0.05 mol L⁻¹ Na₂SO₄ solution containing 30 mg L⁻¹ PPZ, using DSA cathode and Ti/TiO₂ or Ti/TiO₂-x%B photo-anode, irradiated by a 150 W UV-Vis xenon lamp, at pH = 6.0, applying ddp + 1 V (■), + 2 V (○) or + 3 V (▲). In the inserted graphics, respective pseudo-first order kinetic degradation curves.

the effect of pH and voltage was not significant in removing TOC.

3.3. Identification of degradation products

During PFZ photoelectrodegradation processes, different by-products resulting from its oxidation can be formed. The samples submitted for analysis were obtained from photolysis and PEC experiments using Ti/TiO₂-3%B electrode at the end of 2 h of experiment. The masses of the different products were determined from the peaks corresponding to the protonated molecule, [M + H]⁺. The chromatograms for the PPZ photolysis and PEC experiments are shown in Fig. S5 (Supplementary material). From the analysis performed 8 PPZ degradation products were detected in the ion photolysis experiment of *m/z* = 125, 139, 192, 217, 249, 306, 430 and 550, Fig. S5a. Already for the PEC experiments were 6 products with ion of *m/z* = 125, 139, 192, 217, 306 and 460, Fig. S5b.

Knowing that the *m/z* of PFZ (C₁₄H₁₈N₂O) is 231, hydroxylated intermediate compounds corresponding to the binding of HO• radicals in the aromatic ring were detected, such as the C1 and C12 compounds shown in Fig. 15. In the photolysis experiment, compound C1 and C12 can polymerize resulting in compounds C9 (*m/z* = 430) and C13 (*m/z* = 550) respectively, which are absent in photoelectrodegradation with the Ti/TiO₂-3%B electrode. Also in photolysis, the presence of *m/z* ions with values 430 (C9) and 550 (C13), which may be dimers of the initial molecule. These polymeric compounds may be the causes of the acute toxicity presented by this solution, as we will discuss in Section 3.4, since they are not present in the photoelectrocatalytic treatment. Evidence of pyrazole ring opening by oxidative cleavage of N-N bond is reported in the literature [74]. Compound C5 (*m/z* = 192) is a possible

product generated by N-N bond disruption. Intermediates C2, C3 and C4 come from the loss of a methyl group (-CH₃) from the initial structure. In the literature [75] there are reports that compound C2 is the most likely to be generated, indicating that PPZ loses a group -CH₃ from isopropyl group, this compound is considered quite stable. Compound C6 is a proposed structure where there is pyrazole ring opening (loss of propyphenazone C₂HN) resulting in a possible aliphatic carbon chain [75]. From compound C2 we suggest compounds C7 (*m/z* = 139) and C8 (*m/z* = 125) as resulting from successive oxidation in the medium. Compound C10 (*m/z* = 249) results from partial or complete oxidation of the double bond C = C [76]. From the rupture of the C = C bond present in the pyrazole ring caused by the attack of HO• radicals, was proposed the C11 structure (*m/z* = 460) present only in the PEC experiment. The reaction mechanisms proposed in this study, although with some similarities, differ from others previously reported in the literature [51,74–76] for the PPZ degradation process.

3.4. Acute toxicity

The results obtained for the acute toxicity parameters evaluated in each organism were expressed as percentages and compared with the control group. For evaluation purposes, for the above organisms and parameters, was considered as toxic all treatment whose value obtained caused mortality effect greater than 50% in relation to the control group in the case of tests with *A. salina*. Already in the tests with *L. sativa* the percentage of root growth was evaluated, considering toxic when germination index (GI) was equal or less than 50%.

Fig. 16a presents the results for the tests with *A. salina*, were evaluated the solutions from photolysis and PEC with the Ti/TiO₂ and Ti/

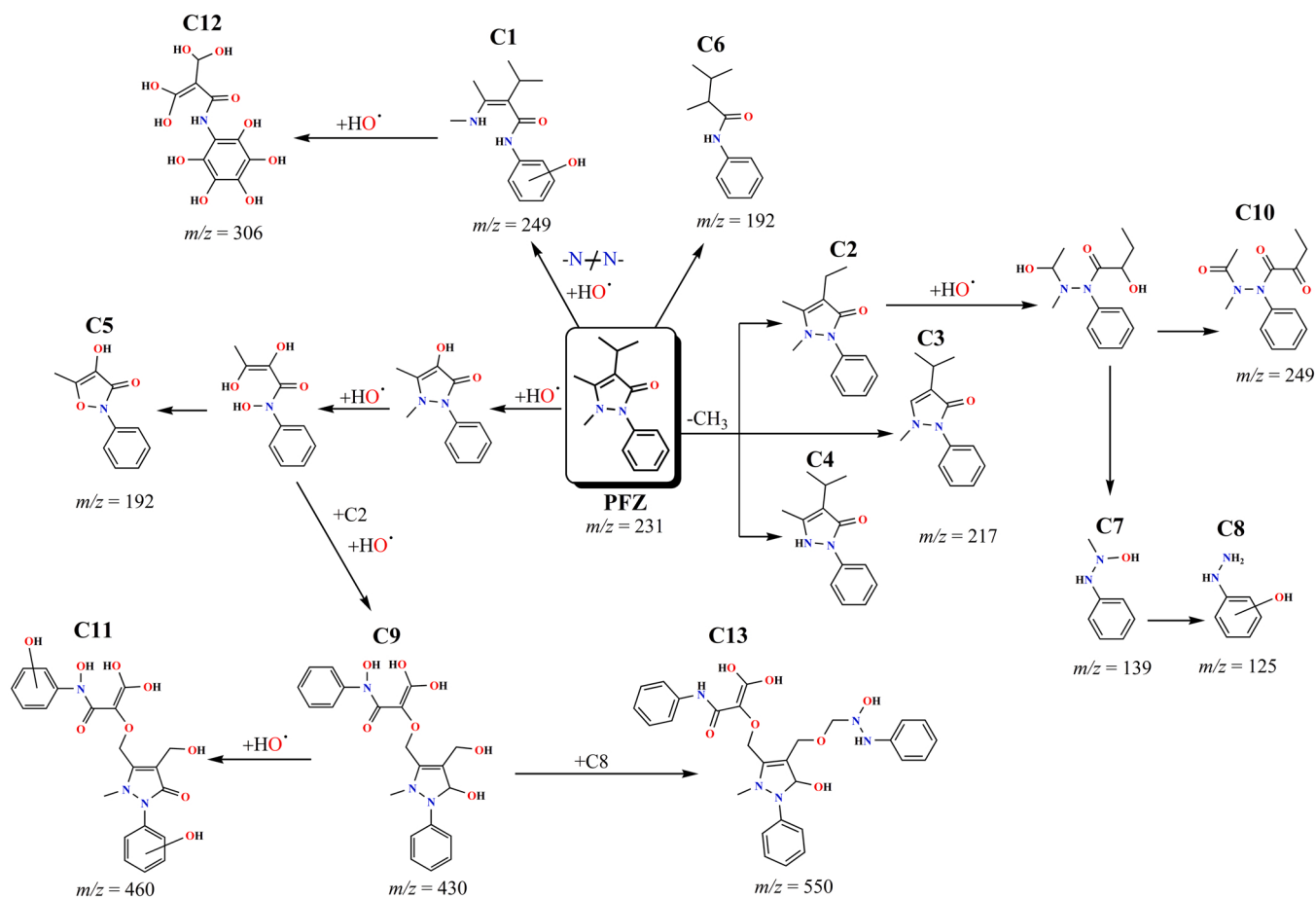


Fig. 15. Proposed PPZ degradation pathway through photolysis and PEC.

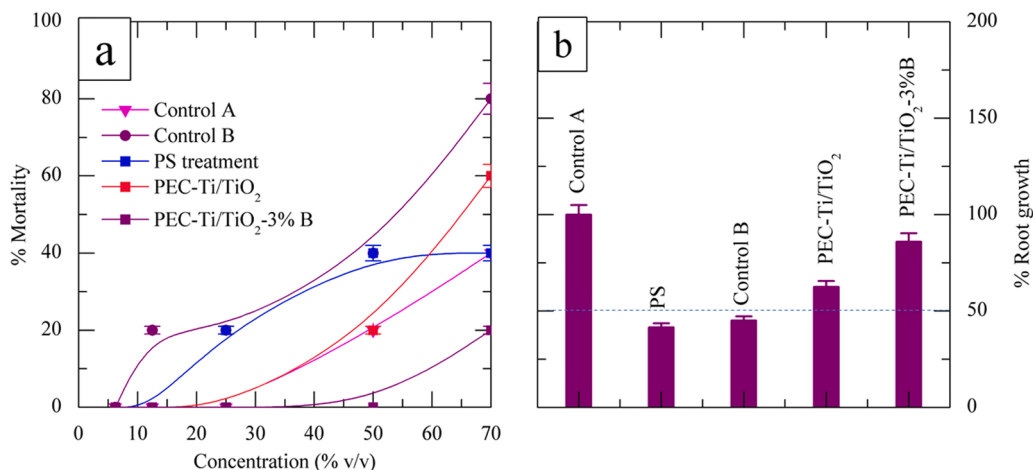


Fig. 16. Acute toxicity. (a) *A. salina* toxicity test. (b) *L. sativa* test.

TiO₂-3%B electrodes. For comparison, tests were also performed with the initial 30 mg L⁻¹ PPZ solution and 0.05 mol L⁻¹ Na₂SO₄ electrolyte solution as a negative control. In the graph we have the percentage of individuals mortality by concentration between 70% and 6.25% (v/v) as described in experimental Section 2.6.1. The tests were not performed with 100% of the solutions because the electrolyte concentration is high for the nauplii, making the experiments impossible. Higher mortality with increasing PPZ concentration was found for the untreated solution, indicating that it has a toxicity. For PPZ an LC₅₀ value of 14.95 mg L⁻¹ was determined. This value corresponds to 2.0 units of toxic units (TU =

(1 / LC₅₀) × 100), which is within the range of 1–10 that reports a highly toxic chemical [77]. The products generated by photolysis were more toxic than the initial solution, presenting an LC₅₀ of 12.61 mg L⁻¹. The TU for photolysis is also within the range of 1–10, being a highly environmentally toxic product. In contrast, solutions treated with the Ti/TiO₂ and Ti/TiO₂-3%B electrodes did not show any remarkable acute toxicity since the nauplii mortality was similar to those found for the negative control samples, thus not allowing the determination of LC₅₀ values [51,77].

For *L. sativa*, test results are shown in Fig. 16b. Results are expressed

in terms of percentage comparison with the control group A (deionized water + 0.05 mol L⁻¹ Na₂SO₄). Tests with the 30 mg L⁻¹ PPZ solution (control group B) and the by-products generated by photolysis showed 45% and 41% inhibition, respectively, of the root growth parameter, indicating the presence of acute toxicity. Both the by-products generated by the experiments with the Ti/TiO₂ and Ti/TiO₂-3%B electrode had no toxicity showing root growth values of 62% and 86%, respectively.

4. Conclusions

In this work we investigate the use of PEC as a viable alternative for the treatment of contaminated water with the non-steroidal anti-inflammatory propyphenazone. The Ti/TiO₂-x%B electrodes showed a decrease in E_{bg} due to boron doping. XPS and FTIR analyze indicated the presence of B₂O₃ coexisting in the TiO₂ structure. Electrochemical analyzes indicated that the Ti/TiO₂-3%B electrode showed an increase in current density of 50% more than the electrode made without boron. Under optimized conditions, the result of the PPZ photoelectrodegradation applying a +1 V potential at pH 6.0 showed a degradation of 92% in just 1 h of experiment for the Ti/TiO₂-3%B electrode. The intermediates generated by itself being composed polymers, were non-toxic to the organisms tested.

Considering the widespread use of medicines by the population, a large amount of waste generated can reach surface water or sewage stations, so our results are an important step in evaluating an efficient and promising method of treating contaminated water.

CRediT authorship contribution statement

Thalita Ferreira da Silva: Experiment, Conceptualization, Methodology, Data analysis, Writing – original draft, Writing – review & editing. **Rodrigo Pereira Cavalcante:** Conceptualization, Supervision, Revision, Writing – review & editing. **Diego Roberto Vieira Guelfi:** Methodology, Data analysis, Writing – review & editing. **Silvio César de Oliveira:** Conceptualization, Methodology, Revision. **Gleison Antonio Casagrande:** Conceptualization, Methodology, Revision. **Anderson Rodrigues Lima Caires:** Conceptualization, Methodology, Revision. **Felipe Fernandes de Oliveira:** Investigation, Methodology. **Juliana Regina Gubiani:** Investigation, Methodology. **Juliano Carvalho Cardoso:** Conceptualization, Supervision, Revision, Writing – review & editing. **Amilcar Machulek Jr:** Conceptualization, Project administration, Funding acquisition, Supervision, Revision, Writing – review & editing. All authors listed have made a substantial, significant and intellectual contribution to the development of the manuscript.

Declaration of Competing Interest

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

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2022.107212.

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