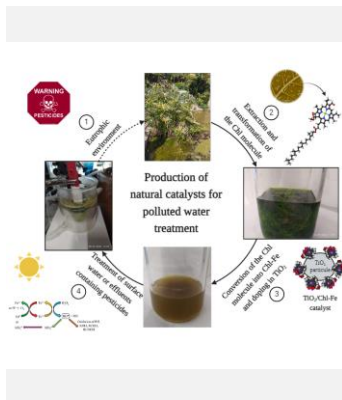


# Enhancing Pesticide Degradation at Neutral pH Using TiO<sub>2</sub> Photocatalyst Modified with Ferric Chlorophyllin

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Prochloraz (PCZ) is an imidazole fungicide that is widely used in Europe, Australia, Asia, and South America. The presence of PCZ in water matrices is associated to environmental and health problems. It is known that conventional water treatment systems are inefficient for pesticide removal, and the use of heterogeneous photocatalysis (HP), photoelectro-Fenton (PEF) of hybrid processes can be a suitable alternative. However, the application of TiO<sub>2</sub> or FeSO<sub>4</sub> is restricted to UV radiation and pH < 4 due to a large bandgap or precipitation, respectively. To overcome these limitations, a promising approach based on modifying TiO<sub>2</sub> with natural dyes is studied. TiO<sub>2</sub> was coated with ferric chlorophyllin (Chl-Fe) to decrease the bandgap, allowing the use of visible light at neutral pH. The results suggest that PCZ is photoresistant because photolysis using a solar simulator was quite inefficient. In contrast, 100% of PCZ was removed at pH 7 in the presence of TiO<sub>2</sub>/Chl-Fe, regardless of the applied catalytic process, being clearly superior to only 24% removal using unmodified TiO<sub>2</sub>.

## Introduction

Since the end of World War II, there has been a noticeable increase in the global population. Nonetheless, food production needs to be accelerated because population expansion is outpacing the increase in cultivable and plantable lands [1]. Synthetic pesticides were created to meet such global need but, unfortunately, pesticides tend to harm the environment and public health [2]. Prochloraz (PCZ) is an imidazole fungicide that is used to protect plants from a wide variety of fungi. Conventional systems do not degrade satisfactorily this compound in wastewater [3].

Photoelectro-Fenton (PEF) process and heterogeneous photocatalysis (HP) have been widely applied to the treatment of aqueous solutions that contain contaminants of emerging concern (CEC), owing to their ability to produce highly oxidizing species [4,5]. However, factors such as the solution pH or the internal recombination of charge carriers play an important role that determine the effectiveness of degradation in both processes.

Therefore, the modification of TiO<sub>2</sub> with ferric chlorophyllin (Chl-Fe) aims to solve these problems [6,7]. The use of TiO<sub>2</sub> catalysts coated with Chl-Fe for degradation of CEC by HP is a very studied topic [7]. In contrast, no work has been found using TiO<sub>2</sub>/Chl-Fe catalysts aimed at degrading pesticides.

Therefore, in this work, Fe-Chl-modified TiO<sub>2</sub> catalyst has been synthesized and then used for the degradation of PCZ solutions via HP and HP-PEF processes.

## Material and Methods

Titanium isopropoxide was used as precursor to obtain TiO<sub>2</sub> nanoparticles. FeSO<sub>4</sub> heptahydrate was used as a source of iron(II). Ultrapure water was employed to prepare all solutions. The TiO<sub>2</sub> catalysts were prepared via sol-gel method by modifying the Changanauqui et al. [9] procedure. The plant *Ceratophyllum submersum* was used

as chelator precursor, being prepared by modifying the Krishnan et al. [5] method. To produce TiO<sub>2</sub>/Chl-Fe, TiO<sub>2</sub> nanoparticles were coated with Chl-Fe at 1%-5% (in wt.% Chl-Fe/Ti).

Diffuse reflectance measurements of TiO<sub>2</sub> and TiO<sub>2</sub>/Chl-Fe catalysts were done on a UV-visible spectrophotometer equipped with an integrated sphere. The Kubelka-Munk function and Tauc plots were used to determine the bandgap energies (E<sub>g</sub>) [10].

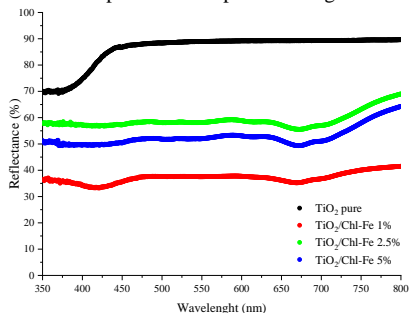
To evaluate the impact of Chl-Fe concentrations as TiO<sub>2</sub> surface modifiers for the CPZ degradation, tests were performed using TiO<sub>2</sub>/Chl-Fe catalysts at concentrations of 1%, 2.5%, and 5% for 1.5 h. Direct photolysis (DP), anodic oxidation (AO), and HP were also performed, serving as control tests. Samples were collected at defined intervals to assess degradation and mineralization (not discussed in this abstract).

The experiments were conducted in a jacketed glass reactor with a capacity of 250 L. The system was equipped with a DSA<sup>®</sup> anode and a commercial C-PTFE-coated carbon cloth as the cathode (both with a geometric area of 3 cm<sup>2</sup> and a gap of ~1 cm). Air was continuously fed through the cathode at a flow rate of 3 L min<sup>-1</sup>. For photoirradiated processes, a solar simulator equipped with a 300 W xenon lamp was used and positioned 15 cm away from the solution. The experiments were conducted using solutions of 15 mg L<sup>-1</sup> of PCZ + 15 mg L<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub> at 25 °C under magnetic stirring. A constant current density (*j*) = 30 mA cm<sup>-2</sup> was used in AO, PEF, and HP-PEF. In HP, PEF, and HP-PEF, 0.5 g L<sup>-1</sup> of catalyst were suspended in the medium.

## Results and Discussion

The diffuse reflectance analysis of raw TiO<sub>2</sub> shows an abrupt change at values below 400 nm, which is explained by its optical absorption (Fig. 1) [10]. In contrast, TiO<sub>2</sub>/Chl-Fe catalysts exhibit shifting in the red-light

absorption band, confirming their ability to absorb visible light [10]. The estimated  $E_g$  values suggest that the primary crystalline structure of pure  $\text{TiO}_2$  is anatase, with a corresponding ( $E_g = 3.26$  eV) [7]. On the other hand, lower  $E_g$  values were obtained for the  $\text{TiO}_2/\text{Chl-Fe}$  1% (2.65 eV), 2.5% (2.96 eV), and 5% (2.97 eV) catalysts, corroborating the potential viability of sunlight-powered HP and HP-PEF processes for pesticide degradation [5].



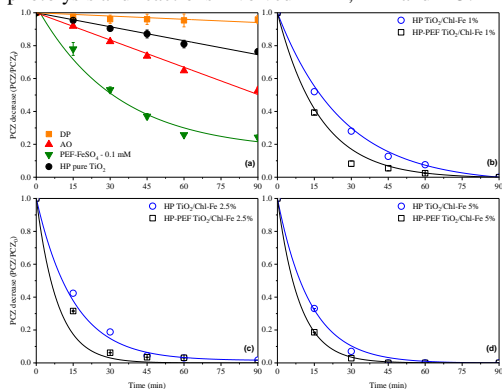
**Figure 1.** Diffuse reflectance values obtained for pure  $\text{TiO}_2$  and  $\text{TiO}_2/\text{Chl-Fe}$  1%, 2.5%, and 5%.

It can be observed in Fig 2a that DP was inefficient for PCZ degradation, whereas in the presence of unmodified  $\text{TiO}_2$ , slow degradation (24%) and mineralization (11%) were found. The superior results can be associated to the generation of  $\cdot\text{OH}$  radicals. AO led to higher degradation (47%) and mineralization (17%) than HP with  $\text{TiO}_2$ , which can be associated with a greater generation of  $\cdot\text{OH}$  radicals on the surface of the DSA<sup>®</sup>. Analyzing the PEF in Fig. 2a, it can be concluded that this process is more effective, reaching higher degradation (47%) and mineralization (17%), thanks to  $\cdot\text{OH}$  generation at the anode surface as well as in the bulk upon  $\text{H}_2\text{O}_2$  activation, thus reducing mass transport limitations.

The results show that  $\text{TiO}_2/\text{Chl-Fe}$  has a higher photocatalytic activity (as shown in Fig 2b-d) when compared to unmodified  $\text{TiO}_2$  (Fig 2a). This can be attributed to the absorption of visible light by  $\text{TiO}_2/\text{Chl-Fe}$  [11], providing a greater accumulation of  $\cdot\text{OH}$  that led to complete CPZ abatement. Furthermore, it is observed that

increasing the percentage of Chl-Fe accelerated the CPZ abatement.

The best CPZ abatement was found using HP-PEF process with  $\text{TiO}_2/\text{Chl-Fe}$  due to the synergistic effects of photolysis and reactions involved in HP, PEF and AO.



**Figure 2.** PCZ degradation by: (a) DP, AO, PEF ( $\text{FeSO}_4$ ), and HP (raw  $\text{TiO}_2$ ), at pH 2.8 and 25 °C. (b-d) HP and HP-PEF using  $\text{TiO}_2/\text{Chl-Fe}$  1%, 2.5%, and 5%, at pH 7, 25°C, and 30 mA  $\text{cm}^{-2}$ .

## Conclusions

$\text{TiO}_2/\text{Chl-Fe}$  catalyst demonstrated a notable increase in PCZ degradation due to its high visible radiation absorption when irradiating with simulated sunlight, which led to  $\cdot\text{OH}$  production. Additionally, the use of a supported Fe(II) effectively prevented the precipitation of Fe(III) at pH > 4, which is a significant drawback of the Fenton process. The best CPZ abatement was found in HP-PEF process due to the synergistic effects of reactions involved in HP, PEF and AO. All percentages of Chl-Fe tested were able to lead to complete PCZ removal and hence, for pilot or real-scale applications,  $\text{TiO}_2/\text{Chl-Fe}$  1% catalyst can be selected.

## Acknowledgments

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