Efficient Mineralization of Paracetamol Using the Nanocomposite TiO$_2$/Zn(II) Phthalocyanine as Photocatalyst

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The photocatalytic performance of a composite based on the association of TiO$_2$ and 2.5 wt.% of zinc(II) phthalocyanine (TiO$_2$/ZnPc) was evaluated towards the mineralization of paracetamol and compared to that observed for the bare oxide in different pH and H$_2$O$_2$ concentrations. The results show that the photocatalytic performances were influenced by the pH, with maximum efficiency around the isoelectric point. Mineralization efficiencies between 86-91% was obtained using TiO$_2$/ZnPc in pH 5.5-6.8, with 33 mg L$^{-1}$ of H$_2$O$_2$, ca. 15% higher than that observed with TiO$_2$. The mineralization efficiencies using bare TiO$_2$ and TiO$_2$/ZnPc were respectively 112 and 18% lower in the absence of H$_2$O$_2$. The better performance of TiO$_2$/ZnPc is related to its extended light absorption and non-uniform coating of the TiO$_2$ surface by ZnPc aggregates. Above pH 6.8, the mineralization efficiencies decrease for both photocatalysts, although the consumption of H$_2$O$_2$ remains above 90%, due to its decomposition in alkaline pH.

Keywords: mineralization, paracetamol, heterogeneous photocatalysis, role of pH and hydrogen peroxide, TiO$_2$/zinc(II) phthalocyanine nanocomposite

Introduction

Since initial studies by Fujishima and Honda, heterogeneous photocatalysis has attracted considerable attention due to its many technological applications, such as H$_2$ production, CO$_2$ reduction, environmental remediation, among others.

TiO$_2$ has been widely used in heterogeneous photocatalysis due its low cost, low toxicity, chemical and photochemical stability, usually expressive photocatalytic activity and versatility. Its main limitation as photocatalyst is related to the lack of absorption in the visible region, which limits its use under solar irradiation. Several strategies have been employed to overcome this limitation, including doping and production of nanocomposites.

TiO$_2$-based photocatalysis has been specially used in environmental remediation for the removal of recalcitrant and hazardous organic pollutants in wastewater. The radicals produced from its excitation by light are able to efficiently oxidize organic pollutants leading in some cases to a complete mineralization of the organic matter.

Paracetamol (N-acetyl-p-aminophenol, PCT), Figure 1a, among other pharmaceutical products, their metabolites, pesticides, hormones and herbicides is calling attention due to its persistence in the environment and the inability of the sewage treatment plants in removing this contaminant, which may result in bioaccumulation and harmful consequences for ecosystems.

![Figure 1. Chemical structure of PCT (a) and Zn(II) phthalocyanine (b).](image-url)

Although PCT is metabolized mainly by the liver, up to 68% of this drug tends to be excreted in the urine when ingested within permitted levels. It should be emphasized that one of the routes of paracetamol metabolism produces highly toxic metabolites able to bind covalently to cysteine present in proteins.
Several studies have reported the application of TiO$_2$-based photocatalysis in PCT degradation. In these studies, however, it is found a wide variation in the results due to different experimental conditions employed. Jagannathan et al.,$^{26}$ for example, evaluated PCT degradation by different methodologies, using heterogeneous photocatalysis mediated by TiO$_2$-P25 (1 g L$^{-1}$) at natural pH (approximately pH 6.8) and in experimental conditions similar to those applied in the present study. The authors achieved 71% of PCT mineralization. Yang et al.$^{32}$ achieved 91% of PCT mineralization using heterogeneous photocatalysis also mediated by TiO$_2$-P25 (0.4 g L$^{-1}$) of an aqueous solution containing 604 mg L$^{-1}$ of PCT, at pH 5.6. However, in this case the reactions were performed using quartz reactors and high energy UVC radiation. Dalmázio et al.$^{24}$ achieved only 35% of PCT mineralization, also using UVC.

In the present study, we compared the effectiveness of a photocatalyst based on the association between TiO$_2$-P25 and aggregates of the dye zinc(II) phthalocyanine (Figure 1b) (TiO$_2$/ZnPc 2.5 wt.%), which was shown to be exceptional in promoting the degradation of different substrates.$^{29-31}$ The efficiency of this nanocomposite in promoting PCT mineralization was compared to that presented by the bare TiO$_2$-P25, and the role of pH and addition of hydrogen peroxide was systematically investigated.

**Experimental**

**Reagents**

All solutions were prepared using ultrapure water. Hydrogen peroxide 30% v/v, sulfuric acid 98%, ammonium metavanadate 99%, sodium hydroxide 99%, methanol UV/high performance liquid chromatography (HPLC) 99.8% and sodium sulfite 97.0% were acquired from Vetec Química Fina. Paracetamol (British Pharmacopoeia (BP) 2008/United States Pharmacopeia (USP) 31) 98.96% was purchased from DEG Importação de Produtos Químicos Ltda.

The nanocomposite TiO$_2$/zinc(II) phthalocyanine 2.5 wt.% (TiO$_2$/ZnPc) was prepared using a methodology previously described, which consists in the adsorption of ZnPc on TiO$_2$ surface at a proportion of 2.5 wt.%. This composite presents a surface area of 35 m$^2$ g$^{-1}$.$^{30}$

**Adsorption assays**

The adsorption of PCT on the surface of the photocatalysts was evaluated at pH 3.00, 5.50, 6.20 and 6.80 using 1 L of suspensions containing 10 mg L$^{-1}$ of PCT and 100 mg L$^{-1}$ of the photocatalysts. These assays were done without addition of H$_2$O$_2$ and protected from light. The suspensions were maintained under stirring for 10 h. Aliquots of 5 mL were collected every 30 min in the first 5 h, and every hour in the remaining time, being measured the absorbance of each aliquot at 243 nm. Prior to the photometric measurements, the collected samples were filtered using 0.45 µm membranes to remove any particulate material. The experiments were carried out at 26 ± 2 °C in triplicate.

**Photodegradation assays**

The experiments were performed using as irradiation source a 400 W high pressure mercury vapor lamp without the protective bulb, positioned at the center of the reactor, as described in a previous study.$^{31}$ The photocatalytic reactor is an annular recipient built in borosilicate glass with a 1 cm optical path jacket and an irradiated volume of 0.850 L, in which the suspension containing the photocatalyst and the compound to be degraded is circulated. The average UVA dose measured for this lamp was estimated as being 1100 W m$^{-2}$,$^{29}$ with a photonic flux of 3.3 × 10$^{-4}$ E s$^{-1}$ between 295 and 710 nm.$^{30}$

The reactions were monitored by the consumption of the organic matter (PCT and its organic degradation products), expressed in terms of dissolved organic carbon (DOC). Four liters of a mixture containing 10 mg L$^{-1}$ of PCT (DOC equal to 6.35 mg L$^{-1}$) and 100 mg L$^{-1}$ of photocatalyst were used in each experiment. The concentration of photocatalyst was defined as being 100 mg L$^{-1}$ since the gain achieved in terms of mineralization is minimal when this concentration ranges from 100 to 1000 mg L$^{-1}$.$^{32}$

After the addition of H$_2$O$_2$ and pH adjustment using aqueous solutions of HCl or NaOH, the suspension, contained in a reservoir, was circulated through the reactor by pumping at a flow rate of 2.37 L min$^{-1}$ for 5 min in the dark. Besides the homogenization promoted by the pump-induced recirculation, the suspension was maintained under magnetic stirring within the reservoir. During the reactions the temperature of the solutions was kept at 25 ± 2 °C, using a thermostatic bath (Tecnal TE-184). All the reactions were limited to 120 min. Aliquots were withdrawn every 20 min of reaction, filtered to remove the solids in suspension, and used for DOC analyses and determination of residual H$_2$O$_2$.

The photocatalytic reactions using the nanocomposite were run in the absence and in the presence of H$_2$O$_2$ at seven different concentrations of H$_2$O$_2$ (16, 33, 66, 99, 120, 166 and 332 mg L$^{-1}$). For the optimal H$_2$O$_2$ concentration, experiments were done at different pH (3.0, 5.5, 6.2, 6.8, 8.0 and 10.0) using the nanocomposite or pure TiO$_2$-P25. Control experiments were performed to evaluate the
photodegradation of PCT in the absence and presence of H$_2$O$_2$ (332 mg L$^{-1}$), and the degradation in the dark in the presence of H$_2$O$_2$.

Analyses

Hydrogen peroxide was quantified spectrophotometrically using ammonium metavanadate, as described by Nogueira et al.$^{33}$

For DOC analyses, the remaining H$_2$O$_2$ was decomposed by the addition of sodium sulfite. The added volume of a solution containing 1.0 mol L$^{-1}$ of Na$_2$SO$_3$ was estimated according to the remaining number of moles of H$_2$O$_2$. The DOC measurements were done using a total organic carbon (TOC) analyzer TOC-VCPH/CPN (Shimadzu), equipped with an ASI-V autosampler.

Diffuse reflectance spectra for TiO$_2$-P25 and TiO$_2$/ZnPc were taken in the range between 200 and 800 nm using a Shimadzu UV-1650PC spectrophotometer equipped with an integrating sphere. Data were converted to plots of the Kubelka Munk function $F(R)$ vs. photon energy (eV). All of the other absorbance measurements were carried out using the same spectrophotometer.

Results and Discussion

Control experiments

Blank experiments were performed to assure that the process studied occurs mainly via photocatalysis and not by the adsorption of the PCT in the photocatalyst, its photolysis or action of H$_2$O$_2$.

No mineralization was observed in the photolysis of PCT without any additive. However, a mineralization of, at most, 10% was reached after 120 min of photolysis in the presence of H$_2$O$_2$, which can be attributed to the oxidizing nature of this additive. It is noteworthy that, as the reactor was built in borosilicate glass, the radiation that reaches the reaction medium ($\lambda > 290$ nm) is unable to promote the cleavage of hydrogen peroxide. In the dark but in the presence of H$_2$O$_2$, no mineralization was observed.

In a period of 2 h under stirring and in the absence of light, less than 1% of the initial PCT concentration was adsorbed on the bare TiO$_2$, in almost all pH studied, except at pH 6.20, the isoelectric point of this photocatalyst, when this amount was about 8%. It is noteworthy that after the pH adjustment of the suspensions there were no significant changes in this parameter during the course of the reactions, probably due to the formation of carboxylic acids and ammonia.

Using the TiO$_2$/ZnPc nanocomposite the adsorption equilibrium at pH 3.00 is similar to that observed for the bare TiO$_2$. Between pH 5.50 and 6.80 the adsorption equilibrium involved about 7% of the initial concentration of PCT. In this case, the higher adsorption observed occurred at pH 5.5, the isoelectric point measured for this nanocomposite.$^{35}$ At pH 6.80, the interaction between PCT molecules and the surface of both catalysts, negatively charged above the isoelectric point, should be favored through hydrogen bonding. It should be emphasized that, in this pH, PCT is neutral (pKa ca. 9.5).$^{36}$

The kinetics of the heterogeneous photocatalytic reactions is typically correlated to the Langmuir-Hinschelwood model.$^{34,37,38}$ Considering that the concentration of reactive species (RS) formed in the reaction sites must quickly achieve a stationary regimen,$^{39,40}$ remaining nearly constant during all the photocatalytic process, the rate law can be expressed by equation 1:

$$-\frac{d[OM]}{dt} = k' C_S^2 \frac{K_{OM} K_{RS}[OM]}{(1 + K_{OM}[OM] + K_{RS}[RS])^2} \tag{1}$$

where $[OM]$ is the concentration of organic matter; $k' = k'[RS]$ is the apparent reaction rate constant, with $[RS]$ being the concentration of reactive species; $C_S$ is the total number of reactive sites (occupied or not); $K_{OM}$ is the weighted average value of the adsorption/desorption constants of PCT and its organic degradation products, since they are indistinguishable when monitored by DOC measurements; and $K_{RS}$ is the adsorption/desorption constant related to species that interact with the active sites (h$^+$ or e$^-$), giving rise to reactive species.

As the adsorption/desorption equilibrium of OM involves low concentrations, compared to the formation of reactive species, $K_{RS}[RS] >> K_{OM}[OM]$, equation 1 can be rewritten as

$$-\frac{d[OM]}{dt} = k' C_S^2 \frac{K_{OM} K_{RS}[OM]}{(1 + K_{RS}[RS])^2} \tag{2}$$

Although $[RS]$ can be considered constant, it should be very small. Therefore, equation 2 can be reduced to

$$-\frac{d[OM]}{dt} = k' C_S^2 K_{OM} K_{RS} [OM] \tag{3}$$

which, considering that $k' C_S^2 K_{OM} K_{RS}$ is $k_{app}$, the apparent rate constant of the reaction, can be rewritten as

$$-\frac{d[OM]}{dt} = k_{app} [OM] \tag{4}$$
Thus, in global terms, both the degradation and the mineralization of paracetamol can be treated on the basis of a first-order rate law. The consumption of H\textsubscript{2}O\textsubscript{2} follows a similar kinetic model, and can also be described in the same way.

The limited adsorption of PCT on the surface of these photocatalysts suggests that the degradation and mineralization of this substrate and its organic degradation products involve necessarily the electron/hole transfer in the active sites of the photocatalysts to species such as H\textsubscript{2}O\textsubscript{2} and H\textsubscript{2}O\textsubscript{2}\textsuperscript{-}, giving rise to highly reactive species, such as hydroxyl and superoxide radicals, and singlet oxygen.\textsuperscript{41}

Table 1 presents data concerning PCT mineralization mediated by TiO\textsubscript{2}/ZnPc for different concentrations of H\textsubscript{2}O\textsubscript{2}.

<table>
<thead>
<tr>
<th>[H\textsubscript{2}O\textsubscript{2}\textsubscript{aq}] / (mg L\textsuperscript{-1})</th>
<th>PCT mineralization / %</th>
<th>H\textsubscript{2}O\textsubscript{2} consumption / %</th>
<th>k\textsubscript{app} / 10\textsuperscript{3} min\textsuperscript{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>67.0 ± 5.6</td>
<td>–</td>
<td>8.2</td>
</tr>
<tr>
<td>16</td>
<td>63.0 ± 2.6</td>
<td>61.0 ± 9.5</td>
<td>8.7</td>
</tr>
<tr>
<td>33</td>
<td>79.0 ± 0.0</td>
<td>65.0 ± 8.0</td>
<td>12.5</td>
</tr>
<tr>
<td>66</td>
<td>76.0 ± 2.8</td>
<td>84.0 ± 0.4</td>
<td>11.4</td>
</tr>
<tr>
<td>99</td>
<td>78.0 ± 5.0</td>
<td>77.0 ± 6.7</td>
<td>11.2</td>
</tr>
<tr>
<td>120</td>
<td>83.0 ± 1.0</td>
<td>88.0 ± 9.9</td>
<td>15.2</td>
</tr>
<tr>
<td>166</td>
<td>56.0 ± 4.4</td>
<td>54.0 ± 5.9</td>
<td>10.0</td>
</tr>
<tr>
<td>332</td>
<td>57.0 ± 4.8</td>
<td>49.0 ± 4.9</td>
<td>6.4</td>
</tr>
</tbody>
</table>

PCT: paracetamol; k\textsubscript{app}: apparent rate constant for PCT mineralization.

As can be seen, the PCT mineralization rate in the absence of H\textsubscript{2}O\textsubscript{2} is relatively high, suggesting the effectiveness of TiO\textsubscript{2}/ZnPc as photocatalyst. The addition of H\textsubscript{2}O\textsubscript{2} up to 120 mg L\textsuperscript{-1} enhances the mineralization in ca. 40%.

The use of additives with oxidizing characteristics, such as hydrogen peroxide, has been usual to improve the performance of the photocatalytic process.\textsuperscript{39,40,42} Hydrogen peroxide can react with electrons in the conduction band or holes in the valence band, ensuring a higher availability of reactive oxygen species, mainly HO\textsuperscript{*}, also contributing to minimize the electron-hole recombination.\textsuperscript{43,44,45}

However, the amount of hydrogen peroxide needs to be balanced since an excess tends to favor reactions that do not result in the degradation of the organic matter (equations 5-8).\textsuperscript{38,46-48} It must be emphasized that the reactions represented by equations 7 and 8 are very fast, occurring near the diffusion limit in water.\textsuperscript{49}

\[
\begin{align*}
H_2O_2 + H_2O_2 & \rightarrow 2H_2O + O_2 & (5) \\
H_2O_2 + HO^* & \rightarrow H_2O + HO_2 & k = 2.7 \times 10^7 L mol^{-1} s^{-1} (6) \\
HO^* + *OH & \rightarrow H_2O + O_2 & k = 7.1 \times 10^6 L mol^{-1} s^{-1} (7) \\
HO^* + *OH & \rightarrow H_2O_2 & k = 5.2 \times 10^6 L mol^{-1} s^{-1} (8)
\end{align*}
\]

Looking at the consumption of H\textsubscript{2}O\textsubscript{2} as a function of its initial concentration, one can observe that, using 33 mg L\textsuperscript{-1} of H\textsubscript{2}O\textsubscript{2}, 79% of PCT mineralization was reached, a result 5% lower than the one achieved using 120 mg L\textsuperscript{-1}, and resulted in a consumption of 65% of the added H\textsubscript{2}O\textsubscript{2}. On the other hand, the consumption of H\textsubscript{2}O\textsubscript{2} taking an initial concentration of 120 mg L\textsuperscript{-1} was of 88%, a value incompatible with the increment observed in the mineralization, which should be related to side reactions (equations 5-8).\textsuperscript{38,46-48} In view of this, the following experiments were carried out using 33 mg L\textsuperscript{-1} as the minimal concentration of H\textsubscript{2}O\textsubscript{2} capable of improving PCT mineralization.

The mineralization reached using TiO\textsubscript{2}-P25 at pH 3.0 without H\textsubscript{2}O\textsubscript{2} was of about 33% in 120 min of reaction, approximately 112% lower than that reached using 33 mg L\textsuperscript{-1} of this additive (Table 2). Using the nanocomposite TiO\textsubscript{2}/ZnPc under similar conditions, the difference was of only 18%, suggesting that the photocatalytic reactions mediated by TiO\textsubscript{2}-P25 are more favored by the addition of H\textsubscript{2}O\textsubscript{2}. Similarly, a decrease of performance of about 12% was verified in the reactions using TiO\textsubscript{2}-P25 at pH 10.0 with addition of H\textsubscript{2}O\textsubscript{2}, and only of 5% when the nanocomposite was used. The different behaviors should be related to differences in the reaction chains triggered by these photocatalysts.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>pH</th>
<th>Mineralization / %</th>
<th>Variation / %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Without H\textsubscript{2}O\textsubscript{2}</td>
<td>With H\textsubscript{2}O\textsubscript{2}</td>
</tr>
<tr>
<td>TiO\textsubscript{2}-P25</td>
<td>3.00</td>
<td>32.7 ± 1.0</td>
<td>69.2 ± 4.2</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>75.7 ± 7.9</td>
<td>66.8 ± 6.7</td>
</tr>
<tr>
<td>TiO\textsubscript{2}/ZnPc</td>
<td>3.00</td>
<td>67.0 ± 5.6</td>
<td>79.0 ± 4.0</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>72.5 ± 3.1</td>
<td>69.1 ± 2.8</td>
</tr>
</tbody>
</table>

It is well known that the relaxation of excited states in aggregates of metal phthalocyanines is predominantly due to very fast thermal deactivation processes, committing the occurrence of other processes, such as the intersystem crossing.\textsuperscript{50-53} When associated with bulk TiO\textsubscript{2}, the electron transfer from excitons of metal phthalocyanine aggregates to the oxide surface has been reported as a preferential way, giving rise to (ZnPc\textsubscript{agg})\textsuperscript{**} and TiO\textsubscript{2} / e\textsubscript{CB} (equations 9-11).\textsuperscript{54}
The coupling effects of the allowed transitions of these aggregates and electronic states of the bare TiO$_2$-P25 leads to an improvement in the charge carrier mobility, favoring the electron transfer. 

\[ \text{TiO}_2 + h\nu \rightarrow \text{TiO}_2 / h_g^+ + \text{TiO}_2 / e_g^- \]  

(9) 

\[ \text{ZnPc}_{agg} + h\nu \rightarrow (\text{ZnPc}_{agg})^* \] \( \forall \nu_2 < \nu_1 \)  

(10) 

\[ (\text{ZnPc}_{agg})^* + \text{TiO}_2 \rightarrow (\text{ZnPc}_{agg})^* + \text{TiO}_2 / e_g^- \]  

(11) 

The increased number of electron-deficient sites due to the formation of \((\text{ZnPc}_{agg})^*\) and \(\text{TiO}_2 / h_g^+\), equations 12-15, should improve the oxidative processes mediated by the nanocomposite, favoring PCT mineralization. Using \(h^+\) to designate \(\text{TiO}_2 / h_g^+\) and \((\text{ZnPc}_{agg})^*\), the reactions related to the production of reactive oxygen species can be expressed as shown in equations 12-15, 

\[ h^+ + \text{H}_2\text{O}_{ads} \rightarrow \text{HO}^* + H^+ \]  

(12) 

\[ h^+ + \text{HO}_2^-_{(ads)} \rightarrow \text{HO}^* \]  

(13) 

\[ h^+ + \text{H}_2\text{O}_2-(ads) \rightarrow \text{HO}_2^* + H^+ \]  

(14) 

\[ h^+ + \text{PCT} \rightarrow (\text{PCT})^* + H^+ \]  

(15) 

Reactions induced by \(\text{TiO}_2 / e_g^-\) and secondary reactions that result in reactive species, mainly hydroxyl radicals, complement the process, as shown in equations 16-21, 

\[ \text{TiO}_2 / e_g^- + \text{O}_2(g) \rightarrow \text{O}_2^* \]  

(16) 

\[ \text{TiO}_2 / e_g^- + \text{H}_2\text{O}_2 \rightarrow \text{HO}^* + \text{HO}^- \]  

(17) 

\[ \text{O}_2^* + \text{H}^+ \rightarrow \text{HO}_2^* \]  

(18) 

\[ \text{H}_2\text{O}_2 + \text{O}_2^* \rightarrow \text{HO}^* + \text{HO}^- + \text{O}_2 \]  

(19) 

\[ 2\text{HO}_2^* + \text{O}_2 \rightarrow \text{HO}^* + \text{HO}^- + 2\text{O}_2 \]  

(20) 

In short, 

\[ \text{PCT} + \text{RS} \rightarrow \text{oxidation products} \]  

(21) 

For the nanocomposite the synergism between \(\text{TiO}_2 / h_g^+\) and \((\text{ZnPc}_{agg})^*\) should be the reason of the minor dependence of this catalyst on additional sources of hydroxyl radicals such as hydrogen peroxide. Eventually ZnPc can suffer degradation (equation 22), but at the time scale of the experiments no evidence of this side reaction was observed. 

\[ (\text{ZnPc}_{agg})^* + \text{O}_2 \rightarrow \text{degradation products} \]  

(22) 

Singlet oxygen, \(1\text{O}_2(\Delta_s)\), is a reactive oxygen species that can be produced during the photocatalytic process mediated by the nanocomposite. High quantum yields of \(1\text{O}_2\) production have been reported in photocatalytic reactions. Its production may involve the oxidation of \(\text{O}_2^*\) by \(h^+\) (equation 23), the combination of two \(\text{O}_2^*\) (equation 25), or by the reaction of \(\text{O}_2^*\) with \(\text{H}_2\text{O}_2\) (equation 26) or \(\text{HO}^*\) (equation 27). Another possibility is the direct energy transfer to molecular oxygen from the electronically excited TiO$_2$ (equation 28). 

\[ \text{O}_2^* + h^+ \rightarrow 1\text{O}_2 \]  

(23) 

\[ \text{O}_2 + 2e^- + 2\text{H}^+ \rightarrow \text{H}_2\text{O}_2 \]  

(24) 

\[ \text{O}_2^* + \text{O}_2^* + 2\text{H}^+ \rightarrow \text{H}_2\text{O}_2 + 1\text{O}_2 \]  

(25) 

\[ \text{O}_2^* + \text{H}_2\text{O}_2 \rightarrow 1\text{O}_2 + \text{HO}^- + \text{HO}^* \]  

(26) 

\[ \text{O}_2^* + \text{HO}^* \rightarrow 1\text{O}_2 + \text{HO}^- \]  

(27) 

\[ \text{TiO}_2 + h\nu \rightarrow [\text{TiO}_2]^* + 1\text{O}_2 \rightarrow \text{TiO}_2 + 1\text{O}_2 \]  

(28) 

However, due to its short lifetime in solution, it has been reported that the contribution of \(1\text{O}_2\) in photocatalytic reactions is limited in most cases. It has been reported that the effective participation of singlet oxygen is strongly dependent on the morphology of the photocatalyst. While in the TiO$_2$ nanopowder its participation is limited, in TiO$_2$ nanotubes this reactive species shows a significantly better photocatalytic activity, being suggested that this occurs due to the confinement of the oxidizable substrate into the nanotubes, compensating for the short lifetime of \(1\text{O}_2\). 

The participation of \(1\text{O}_2\) produced by photosensitization mediated by ZnPc in PCT oxidation promoted by TiO$_2$/ZnPc is very unlikely to occur, since this species is not in the monomeric form but as aggregates, which minimize considerably the efficiency of \(1\text{O}_2\) production. It is noteworthy that the coating thickness of the ZnPc aggregates varies between 5 and 10 nm on the surface of the TiO$_2$/ZnPc nanocomposite, suggesting a remote possibility of occurrence of ZnPc in the monomeric form in this material.

The additional electrons transferred from ZnPc to TiO$_2$ increases the number of electron-rich sites \((\text{TiO}_2 / e_g^-)\) favoring the reduction of chemical species, as for example in the production of H$_2$ by water decomposition (equations 29 and 30): recent results obtained in our research group show that the rate of hydrogen production mediated by TiO$_2$/ZnPc is about 38% higher than the one reached using TiO$_2$-P25. 

\[ 4h^+ + 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ \]  

(29) 

\[ \text{TiO}_2 / e_g^- + 2\text{H}^+ \rightarrow \text{H}_2 \]  

(30) 

The diffuse reflectance spectrum of the nanocomposite (Figure 2) shows that the association between ZnPc and TiO$_2$ results in the extension of the light absorption up to visible region. The unstructured band with maximum near 680 nm is attributed to a red shifted Q band. This shift is related to strong intermolecular interactions in the ZnPc aggregates, with main characteristics of Frenkel’s J aggregates. The coupling effects of the allowed transitions of these aggregates and electronic states of the bare TiO$_2$-P25 leads to an improvement in the charge carrier mobility, favoring the electron transfer.
The mineralization of the organic matter follows an exponential decay as a function of the irradiation time. Figure 3 exemplifies this, presenting the decay and the integrated form of the rate law (equation 4), considering that the DOC expresses the amount of organic species in the aqueous medium, including the remaining PCT, as the reaction progresses. The results suggest that the mineralization occurs in two stages: a faster one, within the first 80 min, followed by a slower decay at longer reaction times. The fast step should occur due to the higher availability of reactive species, formed by the consumption of hydrogen peroxide and other oxygenated species. In the second stage, the mineralization involves the oxidation of the remaining PCT as well as more persistent organic derivatives, such as carboxylic acids,[71] formed in the first step. Thus, the existence of two distinct mineralization rate constants is associated with the higher consumption of H$_2$O$_2$ in the first stage of the reaction that leads to a lower availability of reactive species in the second stage of the reaction and, additionally, to the formation of persistent organic derivatives.

In studies involving the mineralization of the Ponceau 4R dye (trisodium (8Z)-7-oxo-8-[(4-sulfonatonaphthalen-1-yl) hydrazinylidene]naphthalene-1,3-disulfonate) in reactions performed at pH 3.00 under irradiation conditions similar to those applied in the present study,[31] but without addition of hydrogen peroxide, it was also observed that the reaction occurs in two stages, with the first one also occurring within the first 80 min of reaction. However, different from the results presented in this work, the mineralization rate in the first stage was lower than in the second one. In this case, the availability of reactive species becomes proportionally higher as the concentration of Ponceau 4R decreases, since the source of reactive species is limited to O$_2$ and H$_2$O, whose concentrations are virtually constant throughout the course of the reaction.

The influence of pH on PCT mineralization (Table 3 and Figure 4) was evaluated using 33 mg L$^{-1}$ as initial H$_2$O$_2$ concentration. The charge correlation between the surface of the photocatalyst and the oxidizable substrate defines the effectiveness of the adsorptive processes and influences the mineralization rates, since the establishment of electrostatic attractions tends to favor the adsorption. As example, in a set of experiments in the absence of hydrogen peroxide and at pH 3.0, using aqueous suspensions of the dye Ponceau 4R dye (4.0 × 10$^{-5}$ mol L$^{-1}$), a negatively charged azo compound, due to the presence of sulfonic groups in its structure, a mineralization about 200% higher than that obtained with TiO$_2$-P25 was reached using a TiO$_2$/ZnPc nanocomposite containing 1.6 wt.% of ZnPc.[31] In another study, the mineralization of 150 mg L$^{-1}$ of a pre-degraded sodium

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**Figure 2.** Diffuse reflectance spectra of (a) TiO$_2$-P25 and (b) TiO$_2$/ZnPc nanocomposite. Barium sulfate was used as reference.

**Figure 3.** Exponential decay of the ratio DOC/DOC$_0$ during the mineralization of paracetamol and organic species formed during its degradation: (a) reaction mediated by the TiO$_2$/ZnPc composite, at pH 6.2 and 33 mg L$^{-1}$ H$_2$O$_2$; (b) reaction mediated by TiO$_2$-P25 at pH 5.5 and 33 mg L$^{-1}$ H$_2$O$_2$. Inset in both figures: integrated form of the rate law for the mineralization of the organic matter.
lignosulfonate in suspension at pH 3.0, using 50 mg L\(^{-1}\) of a TiO\(_2\)/ZnPc nanocomposite containing 10 wt.\% of ZnPc and about 300 mg L\(^{-1}\) of H\(_2\)O\(_2\), was 19% higher than the one achieved using TiO\(_2\)-P25.\(^{29}\) In the solar photocatalytic degradation of a sodium lignosulfonate (160 mg L\(^{-1}\)) in aqueous suspension containing 300 mg L\(^{-1}\) of H\(_2\)O\(_2\), at pH 3.0, and 100 mg L\(^{-1}\) of the nanocomposite with 2.5 wt.\% of ZnPc as photocatalyst, 95% of the chemical oxygen demand (COD) was removed using an accumulated UVA dose of 900 kJ m\(^{-2}\), while using TiO\(_2\)-P25 under the same conditions the removal was of about 60%.\(^{30}\)

For the TiO\(_2\)/ZnPc nanocomposite, a better performance is observed in a wider range of pH. This should be related to its better capability to uptake photons (Figure 2) and the non-uniformity of the coating of the surface of TiO\(_2\)-P25 by ZnPc aggregates, favoring the coexistence between regions coated by these aggregates, with coating thickness ranging between 5 and 10 nm,\(^{30}\) and non-coated, which should keep characteristics of the pure oxide. A relevant fact is that the nanocomposite has a specific surface area 33% lower than the measured for TiO\(_2\)-P25,\(^{30}\) suggesting that its photonic efficiency is much higher than that of bare TiO\(_2\).

Between pH 3.00 and 6.80 the consumption of H\(_2\)O\(_2\) is compatible with the observed increase in mineralization. For pH higher than 6.80 the performance of both photocatalysts tends to decrease, while the consumption of H\(_2\)O\(_2\) remains above 90%. In part, the loss of efficiency is related to the increase of H\(_2\)O\(_2\) decomposition, producing, for example, perhydroxyl ions (equation 31), without generating species able to mineralize and/or degrade the oxidizable substrate.\(^{70,71}\) The decomposition of H\(_2\)O\(_2\) under alkaline pH reaches a maximum in a pH range between 11 and 12 (the pKa of hydrogen peroxide is 11.75).\(^{72}\)

\[
2H_2O_2 + HO^- \rightarrow 2HO_2^- + H_2O
\]

(31)

**Conclusions**

In this study we compared the performances of the nanocomposite TiO\(_2\)/ZnPc 2.5 wt.\% (ZnPc is zinc(II) phthalocyanine) and TiO\(_2\)-P25 photocatalysts in PCT mineralization, evaluating the role of pH and the effect of addition of H\(_2\)O\(_2\).

The nanocomposite mediates more efficiently the PCT mineralization, being less dependent on the addition of H\(_2\)O\(_2\) than TiO\(_2\)-P25. At pH 3.00, even in the absence of H\(_2\)O\(_2\), 67.0% of PCT mineralization was achieved using the nanocomposite. For TiO\(_2\)-P25, under the same conditions,
only 33% mineralization was reached. With the addition of 33 mg L\(^{-1}\) of \(\text{H}_2\text{O}_2\), the PCT mineralization mediated by TiO\(_2\)-P25 was of 69%, an increase of approximately 112%. Under the same conditions, the result using the nanocomposite was 18% better.

With the addition of \(\text{H}_2\text{O}_2\) in the pH range between 3.00 and 6.80 the mineralization reached using the nanocomposite is about 15% higher, except at pH 6.2, where the mineralization promoted by both photocatalysts is equivalent. The reason for the better performance of the nanocomposite should be related to its capability to uptake photons in a large range of wavelengths and to the non-uniformity of the coating of the TiO\(_2\) surface by ZnPc aggregates, favoring the coexistence of regions completely coated by ZnPc aggregates with non-coated regions, which should keep characteristics of the pure photocatalyst. The improved light harvesting along with a better charge mobility in TiO\(_2\)/ZnPc nanocomposite should lead to a decrease in charge recombination, accelerating the mineralization of PCT.

For both photocatalysts the reaction is influenced by the pH of the reaction medium with maximum nearby their respective isoelectric points. The highest level of mineralization using the nanocomposite, with addition of \(\text{H}_2\text{O}_2\), occurs between pH 5.50 and 6.80, with maximum mineralization between 86 and 91%, while using TiO\(_2\)-P25 the best result occurred only at pH 6.20 (91% mineralization). Above pH 6.80 the mineralization decreases but the consumption of \(\text{H}_2\text{O}_2\) remains higher than 90% due to decomposition reactions.

The highest level of mineralization using the nanocomposite in presence of \(\text{H}_2\text{O}_2\) was reached with an initial concentration of this additive equal to 120 mg L\(^{-1}\), when PCT mineralization was about 83% with the consumption of 88% of the added \(\text{H}_2\text{O}_2\). However, with an initial concentration of only 33 mg L\(^{-1}\) PCT mineralization was only 5% lower with the consumption of 65% of the added \(\text{H}_2\text{O}_2\), suggesting that in the former case most of the \(\text{H}_2\text{O}_2\) added was consumed in side-reactions that do not result in the degradation of the organic matter.

The results presented here show that the TiO\(_2\)/ZnPc nanocomposite is an effective catalyst to promote PCT mineralization under a wide pH range.

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**References**

Efficient Mineralization of Paracetamol Using the Nanocomposite TiO2/Zn(II) Phthalocyanine as Photocatalyst


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