22º Congresso Brasileiro de Catálise
25 a 29 Setembro de 2023
Bento Gonçalves / RS

SBCAT
SOCIEDADE BRASILEIRA DE CATÁLISE

Ferric chlorophyllin as TiO_2 surface modifier for visible light-responsive heterogeneous photocatalysis

Louidi Lauer Albornoz[1,2,3*], **Lucas Bohnenberger**[2], **Pere Cabot**[1], **Enric Brillas**[1] **Salatiel Wohlmuth da Silva**[2], **Andrea Moura Bernardes**[3], **Ignasi Sirés**[1]

[1] Laboratori d'Electroquímica dels Materials i del Medi Ambient, Departament de Ciència de Materials i Química Física, Secció de Química Física, Facultat de Química, Universitat de Barcelona, Martí i Franquès 1-11, 08028 Barcelona, Spain
[2] Laboratório de Desenvolvimento de Tecnologias, Instituto de Pesquisas Hidráulicas, Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves, 9500, Porto Alegre, Brazil
[3] Universidade Federal do Rio Grande do Sul (UFRGS) – Programa de Pós-Graduação em Engenharia de Minas, Metalúrgica e Materiais (PPGE3M), Av. Bento Gonçalves, 9500 Porto Alegre, RS, Brazil.
** Corresponding author: Louidi Lauer Albornoz; E-mail address: louidi.lauer@ufrgs.br*

Resumo/Abstract

RESUMO - O uso de pesticidas é essencial para a segurança alimentar da população mundial, mas seu uso/aplicação inadequada no solo causa sérios problemas ambientais para a fauna, a flora e os seres humanos. Esses pesticidas, entre eles o Procloraz (PCZ), não são degradados/removidos nas estações convencionais de tratamento de água e esgoto. O uso de processos oxidativos avançados, como a fotocatálise heterogênea (FH), tem como objetivo gerar radicais $HO^{\bullet}$ durante o processo de degradação do PCZ, porém, ao usar TiO_2 puro uma de suas principais limitações é o uso apenas de radiação UV devido ao seu alto *bandgap* (3,26 eV). Para reduzir esse valor, o processo de dopagem do TiO_2 com corantes naturais pode ser realizado. Neste trabalho, o TiO_2 foi dopado com clorofilina férrica (Chl-Fe), o que permitiu a diminuição do *bandgap* (2,65 eV) e, consequentemente, um aumento significativo da degradação do PCZ (24% - TiO_2 puro e 98,3% - TiO_2/Chl-Fe 1%), ao utilizar uma fonte de radiação solar simulada durante a FH.

Palavras-chave: fotocatálise heterogênea, TiO_2, clorofila, dopagem, radiação solar

ABSTRACT - The use of pesticides is essential for the food security of the world's population, but their inappropriate application to the soil causes serious environmental problems to fauna, flora and humans. These pesticides, as for example prochloraz (PCZ), are not degraded in conventional sewage and water treatment plants. The use of advanced oxidation processes like heterogeneous photocatalysis (HP) aims to generate $^{\bullet}OH$ radicals during PCZ degradation. However, when using pure TiO_2, one of its major limitations is the use of only UV radiation due to its large bandgap (3.26 eV). In order to reduce this value, the process of doping TiO_2 with natural dyes seems a promising approach. In this work, TiO_2 was doped with ferric chlorophyllin (Chl-Fe), which allowed the decrease of the bandgap to 2.65 eV and, consequently, a significant increase in PCZ degradation (24% for pure TiO_2 vs 98.3% for TiO_2/Chl-Fe(1%)), when using a simulated solar radiation source during HP.

Keywords: heterogeneous photocatalysis, TiO_2, chlorophyll, sensitization, solar radiation

Introduction

The world population has shown considerable growth since the end of World War II. However, as population growth is higher than the rise in cultivable and plantable areas, the productivity of food production must be significantly increased (1). To achieve the needed increase in food worldwide, synthetic pesticides were synthesized. Nevertheless, many of these cause serious environmental and health problems to the population and the environment (2). Among the pesticides, prochloraz (PCZ) is an imidazole fungicide used to protect plants against a broad spectrum of fungi. Conventional systems do not degrade satisfactorily this compound in wastewater (3). Heterogeneous photocatalysis (HP), which uses a semiconductor like TiO_2 as a catalyst, has been widely used in the treatment of effluents that contain contaminants of emerging concern (CEC) (4). However, the disadvantage is the rapid internal recombination leading to a decrease in catalytic activity (4). This recombination can be reduced by doping TiO_2 with natural dyes and this process is known dye sensitization (5). One can cite chlorophyll (Chl) which has great potential as macrophyte from eutrophic environments, since Chl-sensitized TiO_2 catalysts showed absorption peaks in the visible range (5). However, Chl has low stability and an alternative to provide robustness to the Chl molecule consists in replacing the Mg atom by Fe, leading to the formation of ferric chlorophyllin (Chl-Fe) (5,6). The use of TiO_2 catalysts doped with Chl and Chl-Fe in the HP process for the degradation of CEC is a very studied topic (5). However, no work has been found using TiO_2/Chl-Fe 1% catalysts in the HP process aimed at degrading pesticides.

Experimental

Titanium isopropoxide (Sigma-Aldrich) was used as a precursor to TiO_2. $FeSO_4$ heptahydrate (Sigma-Aldrich) was used as a source of iron (II). High-purity water (Millipore Milli-Q) was employed to prepare the solutions. The TiO_2

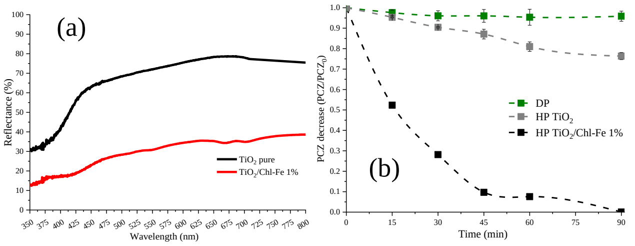
catalysts were prepared by the sol–gel method by modifying a previous procedure (7). For the preparation of a natural chelating agent, the plant *Ceratophyllum submersum* was collected at Barcelona, Spain. After the cleaning procedure, the process of extracting the Chl molecule was carried with 70:30% ethanol:acetone for 24 h at a temperature of 4ºC. The transformation of the Chl molecule to the Chl-Fe molecule was carried out by saponification with NaOH of extracted Chl solution. The vacuum drying process was carried out until the total evaporation of solution. The Chl solid was then solubilized in Milli-Q water and centrifuged to separate solids. After was carried out the acidifying of the aqueous solution with glacial acetic acid and heating under stirring. Iron (II) sulfate was used as a source of iron in the proportion of 1.5 mol of Fe^{2+} to 1 mol Chl. The concentration values of Chl, in mg L^{-1} of the extracted Chl and Chl-Fe samples were calculated according to Krishnan, Shriwastav (5). The TiO_2 nanoparticulate catalysts were doped by adding 50 mg L^{-1} of Chl-Fe in 0.5 g L^{-1} of the TiO_2 nanoparticulate catalyst to produce the TiO_2/Chl-Fe 1%, in % ww Chl-Fe/Ti. Diffuse reflectance and bandgap energies of TiO_2 and TiO_2/Chl-Fe 1% catalysts were recorded with UV-visible diffuse reflectance spectroscopy (Specord 210 Plus), equipped with an integrated sphere and using $BaSO_4$ as a reflectance reference standard. The Kubelka–Munk function and Tauc plots were used to determine bandgap energies (Eg) (8). The experimental system used for the HP evaluation consists of a glass cell jacketed reactor filled with 0.5 g L^{-1} of the prepared catalysts, 0.150 L^{-1} solution of 25 mg L^{-1} of PCZ at 25 ºC. As a source of radiation, a solar simulator equipped high a pressure 300 W xenon short arc lamp (LOT-QuantumDesign) was used, placed at 15 cm from the catalyst. The PCZ solutions were quantified by HPLC (Shimadzu) with DAD detector.

Results and discussion

The diffuse reflectance of the TiO_2 pure catalyst, in black in Fig. 1.a, shows that there is an abrupt change in the reflectance values above 400 nm, which is explained due to the optical absorption of the material at $\lambda < 400$ nm (8).

The TiO_2/Chl-Fe catalysts at $\lambda > 400$ nm the catalyst presents a behavior closer to that presented by the natural Chl molecule, that is, exhibits a red shift of absorption band in comparison to pure TiO_2, which can explain the better photocatalytic activity of TiO_2/Chl-Fe under solar visible-light exposition (8). The Eg values found showed that the value of Eg = 3.26 eV for the pure TiO_2 sample indicates that the predominant crystalline form is anatase (5). The results found for the TiO_2/Chl-Fe 1% catalyst showed a decrease in the Eg value (Eg = 2.65 eV) which indicates that radiation below 467.9 nm can excite the e^- da valence band to the conduction band and, subsequently, formation of $HO^\bullet$ radicals during the HP process (5). The DP results showed low degradation (4%, Fig. 1.b) of the PCZ molecule when using the solar simulator as a radiation source and this indicates that the degradation of the PCZ during HP was not due to the photolysis of the PCZ molecule by the radiation. The HP, using pure TiO_2 as a catalyst, results showed degradation (24%) results superior to those found in the DP assays. The degradation (98.3%) results after the HP test using the TiO_2-Chl-Fe 1% catalysts were superior than pure TiO_2 catalyst evidence that doping with Chl-Fe increased the absorbance of the catalyst in visible regions where TiO_2 does not present absorption which allows the generation of $HO^\bullet$ radicals in greater quantity (5).

Figure 1. (a) Reflectance values, in %, in nm, for pure TiO_2 and TiO_2/Chl-Fe 1% samples; (b) values of degradation of DP and HP using TiO_2 and TiO_2/Chl-Fe 1%.



Conclusions

The doping process of TiO_2 with Chl-Fe 1% showed that the prepared catalyst presented a great absorption of radiation in the visible region which led to a significant increase in the degradation of PCZ when compared with the pure TiO_2. Therefore, the TiO_2/Chl-Fe 1% catalyst presents a great potential for the degradation of CEC.

Acknowledgments

The authors acknowledge support from CNPq, CAPES, FINEP, FAPERGS and project PID2019-109291RB-I00 (MCIN/AEI/10.13039/501100011033, Spain).

References

1. WWAP, The United Nations World Water Development Report 2019: Leaving No One Behind, Paris, 2019.
2. M. Tudi, H.D. Ruan, L. Wang, J. Lyu, R. Sadler, D. Connell, C. Chu, D.T. Phung, *Int. J. Environ. Res. Public Health*. 2021, 18, 1–24.
3. A. Masiá, J. Campo, P. Vázquez-Roig, C. Blasco, Y. Picó, J. Hazard. Mater. 263 (2013) 95–104.
4. L.L. Albornoz, S.W. da Silva, J.P. Bortolozzi, E.D. Banús, P. Brussino, M.A. Ulla, A.M. Bernardes, , Chemosphere. 268 (2021) 128858.
5. S. Krishnan, A. Shriwastav, Environ. Res. 216 (2023) 114568.
6. L. Wang, P. Jin, S. Duan, J. Huang, H. She, Q. Wang, T. An, Environ. Sci. Nano. 6 (2019) 2652–2661.
7. K. Changanaqui, E. Brillas, H. Alarcón, I. Sirés, Electrochim. Acta. 331 (2020).
8. G.D. Gesesse, A. Gomis-Berenguer, M.F. Barthe, C.O. Ania, J. Photochem. Photobiol. A Chem. 398 (2020) 112622.