

Degradation of Caffeine by Heterogeneous Photocatalysis Using TiO₂ Impregnated with Fe and Ag

Lariana N. B Almeida^{a*}, Giane G. Lenzi^b, Juliana M. T. A. Pietrobelli^b, Onélia A. A. Santos^a

^a State Univ. of Maringá, Chemical Engineering Department, Colombo Av. 5790, 87020-900 Maringá, Paraná, Brazil.

^b Chemical Engineering Department-Federal University of Technology-Paraná, Ponta Grossa Campus, 84016-210 Ponta Grossa, PR, Brazil

beraldolariana@gmail.com

Caffeine, when identified in surface water and drinking water, is classified as a contaminant of emerging concern. The emergence of these compounds occurs due to the direct discharge of sewage into the rivers, as well as through conventional techniques currently applied in the treatment of effluents and drinking water that do not completely remove these contaminants. In this context, the removal of such substances in aqueous solution has been studied by different techniques, standing out heterogeneous photocatalysis. In the photocatalytic reaction, several factors may contribute to the photocatalytic performance of the semiconductor, such as material structure, composition, textural properties, among others. To improve these characteristics, some procedures can be adopted, such as heat treatments and addition of metals to the surface of the material. In this perspective, the objective of this work was to characterize and evaluate the pure commercial TiO₂, also the commercial TiO₂, with the addition of 8% by mass of Fe and Ag, in the degradation of the caffeine contained in the water. The results of the experimental tests and the characterization of the materials indicated that, under the conditions used, 8%Ag-8%Fe/TiO₂ bimetallic catalyst was the material with the highest catalytic activity followed by 8%Ag/TiO₂, 8%Fe/TiO₂ and Pure TiO₂, while pure TiO₂ was similar to the photolysis test, in which there was no satisfactory caffeine degradation. These results emphasize that the composition and structure of the catalysts applied to the heterogeneous photocatalysis has great importance in the yield of the catalyst in the reaction.

1. Introduction

It is not today that the scientific community and the population are concerned about environmental issues, especially when such issues are related to water, availability, contamination among other factors. In recent years, resulting mainly from human activity, several organic compounds, known as "contaminants or pollutants of emerging concerns" have been detected in surface waters. These substances, even in low concentrations, are introduced continuously into the environment, and can affect the entire life of the ecosystem, impacting on water quality and animal health. Among the emerging contaminants found are caffeine, a occurring substance in coffee, in certain teas, cola-based soft drinks, in some drugs among other substances. Caffeine is able to stimulate the central nervous system, and after consumption, its excretion occurs through the urine and also through direct dumping of such beverages, causing the substance to be present in the domestic sewer (Canela et al., 2014). It is also worth mentioning that when present in surface water caffeine exhibits a half-life of 3 days to 3 months (Sauve et al., 2012).

Although conventional treatment in the Wastewater Treatment Plant (WWTP) shows good removal of caffeine, the high concentration of the substance present in the raw sewage still generates residual concentrations of caffeine after treatment, since research has shown the presence of caffeine in WWTPs (Kosma et al., 2010) and also in drinking water (Sodre et al., 2009; Machado et al., 2016), indicating that the techniques commonly used in Water Treatment Stations no remove emerging pollutants such as caffeine.

In order to eliminate such compounds classified as contaminants or pollutants of emerging concern, work has been carried out in order to identify, quantify and degrade such substances, we have as an example, Advanced Oxidative Processes such as the use of heterogeneous photocatalysis with TiO₂, photolysis, peroxidation, photoperoxidation, Fenton reaction or Photo-fenton (Carotenuto et al., 2014; Fagnani et al., 2013; Chaker et al., 2016; Marques et al., 2013; Trovó et al., 2013).

The heterogeneous photocatalysis is presented as an alternative process for the removal of emerging pollutants present in the wastewater. This reaction involves a semiconductor that, when it receives energy greater or equal to its bandgap energy, performs the electronic excitation thus generating intermediates such as •OH, which will later react with the pollutant, oxidizing it (Zioli and Jardim, 1998, Jay and Chirwa, 2018, Shi, 2018).

Among the most used semiconductors is titanium dioxide (TiO₂) due to its photostability, not being toxic and presenting low cost (Miranda-García et al., 2014). Researchers use TiO₂ in photoresists for the degradation of contaminants such as caffeine (Carotenuto et al., 2014), methyl orange and wastewater (Chacker et al., 2016), degradation of *Escherichia coli* bacteria (Helali et al., 2014; Miranda et al., 2016), degradation of orange textile dye reactive 122 (Colpini et al., 2008), in the discoloration of the blue dye 5G (Souza et al., 2011) among the others in the reduction of mercury (II) (Lenzi et al., 2011) among others. However, in order to improve the performance of TiO₂ in the degradation of organic and inorganic contaminants, some research has already highlighted the positive influence of the addition of transition metals in their structure (Zhang et al., 2018). Silver-impregnated TiO₂-based catalysts and iron-doped ZnO-based catalysts were successfully applied in the removal of dyes and the photoreduction of Hg (II) (Chacker et al., 2016; Lenzi et al., 2011; Coelho et al., 2015). Thus, the objective of this work was to evaluate the photocatalytic degradation of caffeine, an emerging pollutant, in aqueous solution by heterogeneous photocatalysis using TiO₂ doped with iron and silver.

2. Experimental procedure

2.1 Synthesis of Catalysts

The materials used were: (i) commercial TiO₂ titanium dioxide (supplied by 99% pure Dynamics); (ii) AgNO₃ silver nitrate (supplied by Neon); (iii) Iron nitrate III (ico) (Fe (NO₃)). 9H₂O (supplied by Dynamics). The metal catalysts containing 8 wt% Fe or Ag as well as the bimetallic catalyst containing 8 wt% Fe and Ag were synthesized by the solvent impregnation method as described by Lenzi et al. (2011). The catalysts were oven dried at 100 °C for 24 hours.

2.2 Characterization of Catalysts

Pore properties: The equipment used was the QUANTACHROME - Model Nova 2000 and the analyzes were carried out with the adsorption and desorption of N₂ at 77 K. The calculation of the specific area was performed using the BET method (Braunauer, Emmet and Teller) and the volume and the mean pore diameter were determined at a relative pressure of 0.99.

X-ray diffraction (XRD): The analyzes were performed on a Bruker D8 Advance X-ray diffractometer, 2 θ from 5 to 80°, with 2°/min in the scan, 40 kV and 35 mA that is located in the Complex of Support Centers Research (COMCAP) in EMU. The result obtained was then compared to the standards published by JCPDS (Joint Committee on Powder Diffraction Standards, 1995).

2.3 Experimental Tests of Photocatalysis

The reaction was carried out in a 2 L cylindrical reactor equipped with a cooling jacket with a useful volume of 1 L of aqueous solution containing 20 mg L⁻¹ of caffeine and the amount of catalyst fixed in 0.3 g. The suspension was maintained under constant magnetic stirring and continuous addition of air flow. The temperature of 25 °C was kept constant by means of a thermostated bath. The irradiation was provided by a 125 W mercury vapor lamp coupled just above the reactor. At specific times, samples were collected, filtered on nylon membranes (0.22 μ m pore size and 13 mm diameter) for further analysis in a UV-Vis spectrophotometer (Femto-800 XI).

2.4 Photolysis Test

An assay was performed in the absence of catalyst and presence of photolysis provided by a 125 W mercury vapor lamp to verify the degree of caffeine degradation only by the incidence of radiation in the reaction medium. For the accomplishment of this experiment, the same procedures presented in item 2.3 were followed, however, as already mentioned, without the presence of catalyst.

3. Results

3.1 Characterization of Catalysts

The results obtained with adsorption and desorption of N_2 (pore properties) are shown in Table 1.

Table 1 – Specific area (S_o), pore volume (V_p) e mean pore diameter (d_p).

Catalysts	S_o ($m^2 \cdot g^{-1}$)	V_p ($cm^3 \cdot g^{-1}$)	d_p (Å)
TiO ₂	17	0,0223	27
8%Ag/TiO ₂	11	0,0170	31
8%Fe/TiO ₂	16	0,0159	20
8%Ag-8%Fe/TiO ₂	15	0,0216	30

Regarding the XRD of the synthesized materials, the result is shown in Figure 1.

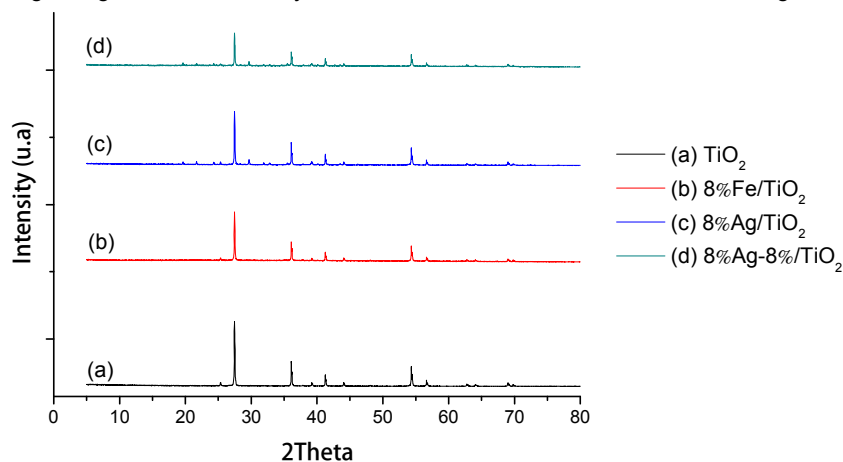


Figure 1: X-ray Diffractograms for catalysts.

3.2 Experimental Tests

The experimental results obtained with the experiments are shown in figure 2, where the variation of the caffeine concentration can be analyzed along the time of the photocatalytic reaction.

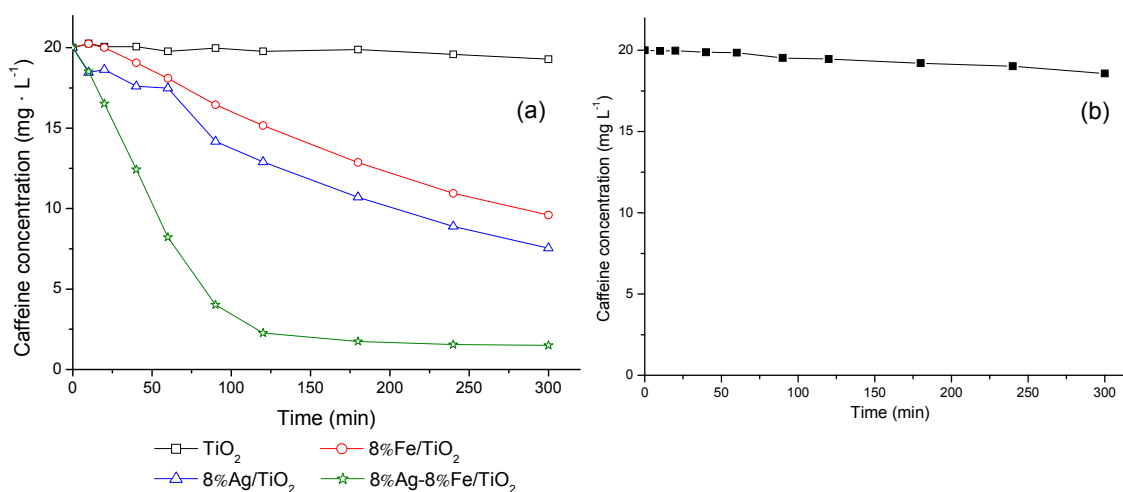


Figure 2: Experimental testes: (a) Photocatalytic tests of caffeine degradation with pure TiO₂ and impregnated with Fe and Ag (b) Photolysis test..

3.3 Photolysis Test

The result obtained with the photolysis test applied in the degradation of caffeine is shown in Figure 2 (b).

4. Discussion

4.1 Characterization of Catalysts

With respect to the textural characteristics of the materials, it is possible to verify that the values obtained for the specific areas of the supported catalysts (Table 1) are of the same order of magnitude as that obtained for pure TiO_2 . However, there is a small decrease in the specific area with the addition of the metal, for both silver and iron. Probably the partial blockade of some micropores occurred with the incorporation of the metal. Similar results were obtained by Lima and Perez-Lopez (2018) when studying the addition of metals (Ni, La, Ca and Li) on the zeolite surface.

According to Figure 1, it is possible to observe that for all TiO_2 -based catalysts containing silver and zinc, as well as for pure oxide, the rutile tetragonal form was identified by the characteristic peaks in $2\theta = 27, 36, 41, 54, 56$ and 69° . These peaks showed a higher intensity than those observed for the other peaks, indicating that the commercial titania used as support for the metallic and bimetal catalysts is mainly composed by the rutile form. Typical peaks found in $2\theta = 25, 38, 48^\circ$, related to the anatase form were also identified, however, with lower intensity.

The titanium-supported bimetallic catalyst containing 8 wt.% of iron and silver (8%Fe-8%Ag/ TiO_2) and the titanium supported bimetallic catalyst containing 8 wt% silver (8%Ag/ TiO_2), presented silver nitrate (AgNO_3). For the 8%Fe/ TiO_2 catalyst, in turn, it was not possible to identify the presence of iron on the titania surface when submitted to XRD analysis. These results demonstrate that the catalyst preparation method, or iron-containing precursor salt type, may not have been sufficiently effective for the impregnation of the metal on the surface of the semiconductor in both the preparation of the metal catalyst (8%Fe/ TiO_2) and in the preparation of the bimetallic catalyst, containing iron and silver (8%Fe-8%Ag/ TiO_2). On the other hand, iron impregnation on the titania surface may have occurred, however in smaller percentages than expected, or the amount of iron (8% by mass) used in the impregnation process was not sufficient to allow its identification in XRD characterization. Coelho et al. (2015) identified peaks related to iron oxide in samples with 8, 10 and 15% Fe in TiO_2 , but iron was not observed in the sample with 5%Fe in TiO_2 . Mahy et al. (2016) studied TiO_2 catalysts doped with different metals prepared by the sol-gel method, did not observe any peak corresponding to the studied metals (Fe, Pt and Cu) added to the titania surface when performing the XRD analysis.

4.2 Experimental Tests

It was found that commercial TiO_2 was the least active in the caffeine degradation reaction, probably because of its crystalline form (rutile), because although the other characteristics presented here, such as the specific area, may have influenced the performance of TiO_2 , Wang et al. (2017) report that the crystalline structure is the factor that most influences the photocatalytic performance of TiO_2 .

The addition of iron and silver on the surface of TiO_2 improved the performance of the photocatalyst. The 8%Ag/ TiO_2 catalyst presented better performance than the Fe-promoted catalyst. Mahy et al. (2016) when studying TiO_2 catalysts promoted with iron and silver, observed that the presence of iron in low concentration (0.5 mol%) increases the catalytic activity of TiO_2 , the authors attributed this event to the fact that Fe^{3+} reacts with water and in the presence of radiation produces $\text{OH}\cdot$ radicals that can degrade the studied pollutant (p-nitrophenol). Already with the addition of Ag, Mahy et al. (2016) noted that photocatalytic activity increased with both added amounts of Ag (0.5 and 2 mol%). The authors report that the action of silver was to prevent the recombination of the electron-gap pair, thus increasing the useful life of photoexcited electrons and gaps. For the bimetallic catalyst containing iron and silver on the titania surface, the catalytic activity was much higher than that observed for its monometallic pairs. Thus, at the end of 300 min of the reaction, caffeine degradation was approximately 92.5% for the 8%Ag-8%Fe/ TiO_2 catalyst, 62.3% for the 8%Ag/ TiO_2 catalyst and 52% for the 8%Fe/ TiO_2 catalyst, thus evidencing the synergistic effect between the two metals.

4.3 Photocatalysis test

According to the result, the degradation of caffeine only in the presence of radiation evidenced the need for the presence of the photocatalyst for a more efficient process, since the percentage of degradation by photolysis at the end of the 300 minutes of reaction was only 7% and in the first 120 minutes the degradation remained below 2.5%.

5. Conclusions

The presence of silver nitrate on the TiO₂ surface combined or not with iron nitrate favored the caffeine degradation reaction, evidencing that caffeine is probably easier to adsorb on the surface of the catalyst containing this metal (Ag). In descending order, the catalyst that presented the best performance was 8%Ag-8%Fe/TiO₂, followed by 8%Ag/TiO₂, 8%Fe/TiO₂ and finally the commercial TiO₂, with which it was not possible to remove caffeine present in aqueous medium as well as with the photolysis test.

Acknowledgments

The authors are grateful to COMCAP-UEM, UFPR-PALOTINA and UTFPR-Ponta Grossa for their analyzes, as well as to CAPES and CNPq for financial support

Reference

- Canela M. C., Jardim W. F., Sodr  F. F., Grassi M. T., 2014, Caffeine in Waters for public consumption in Brazil/ Intituto Nacional de Ci ncias e Tecnologias Avan adas – INCTAA, S o Carlos: Editora Cubo.
- Carotenuto M., Lofrano G., Siciliano A., Alibert F., Guida M., 2014, TiO₂ photocatalytic degradation of caffeine and ecotoxicological assessment of oxidation by-products. *Global Nest Journal*, 16,463-473.
- Chacker H., Cherif-Aouali L., Khaoulani S., Bengueddach A., Fourmentin S., 2016, Photocatalytic degradation of methyl orange and real wastewater by silver doped mesoporous TiO₂ catalysts. *Journal of Photochemistry and Photobiology A: Chemistry*, 318, 142-149.
- Coelho A. L.S., Almeida neto A. F., Jorge L. M. M., Santos O. A. A., 2015, S ntese e Caracteriza o de part culas a base de tit nia e zinco dopadas com ferro. XXXVII ENEMP – Congresso Brasileiro de Sistemas Particulados, S o Carlos.
- Colpini L. M. S., Alves H. J., Santos O. A. A., Costa C. M. M., 2008, Discoloration and degradation of textile dye aqueous solutions with titanium oxide catalysts obtained by the sol–gel method. *Dyes And Pigments*, 76,525-529.
- Fagnani E., Guadagnini R. A., Silva G. A., Guimaraes J. R., 2013, Degradation of caffeine and methlene blue by advanced oxidation process (AOPs). *Holos Environment*, 13, 85-97.
- Helali S., Polo-L pez M. I., Fern ndez-Ib nez P., Ohtani B., Amano F., Malato S., Guillard C., 2014, Solar photocatalysis: A green technology for E. coli contaminated water disinfection. Effect of concentration and different types of suspended catalyst. *Journal Of Photochemistry And Photobiology A: Chemistry*, 276, 31-40.
- Jay, L.; Chirwa, E. E. M. N., 2018, Pathway Analysis of Phenol Degradation by UV/TiO₂ Photocatalysis Utilising the C-13 Isotopic Labelling Technique. *Chemical Engineering Transactions*, 70, 181-186.
- Joint Committee on Powder Diffraction Standards (JCPDS): International Center of Diffraction Data, Pensilv nia, 1995.
- Kosma, C. I.; Lambropoulou D. A.; Albanis T. A., 2010, Occurrence and removal of PPCPs in municipal and hospital wastewaters in Greece. *Journal of Hazardous Materials*, 179, 804-817.
- Lenzi G. G., F vero C. V. B., Colpini L. M. S., Bernabe H., Baesso M. L., Specchia S., Santos O. A. A., 2011, Photocatalytic reduction of Hg (II) on TiO₂ and Ag/TiO₂ prepared by the sol–gel and impregnation methods, *Desalination*, 270, 241-247.
- Lima D. S., Perez-Lopez O. W., 2018, Convers o catal tica do etanol sobre catalisadores suportados em ZSM-5, *Cer mica*, 64, 1-9.
- Machado K. C., Grassi M. T., Vidal C., Pescara I. C., Jardim W. F., Fernandes A. N., Sodr  F. F., Almeida F. V., Canela M. C., Nunes C. R. O., Bichinho K. M., Severo F. R.J., 2016, A preliminar Nationwide survey of the presence of emerging contaminants in drinking and source Waters in Brazil. *Science of The Total Environment*, 572, 138-146.
- Mahy J. G., Labert S. D., Leonard G. L-M., Zubiatur A., Olup Y., Mahmoud A., Boschini F., Heinrichs B., 2016, Towards a large scale aqueous sol-gel synthesis of doped TiO₂: Study of various metallic dopings for the photocatalytic degradation of p-nitrophenol. *Journal of Photochemistry and Photobiology A: Chemistry*, 329, 189-202.
- Marques R. R. N., Sampaio M J., Carrapi o P. M., Silva C. G., Morales-Torres S., Drazic G., Faria J. L., Silva A. M. T., 2013, Photocatalytic degradation of caffeine: Developing solutions for emerging pollutants. *Catalysis Today*, 209, 108-115.
- Miranda-Garc a N., Su rez S., Maldonado M. I., Malato S., S nchez B., 2014, Regeneration approaches for TiO₂ immobilized photocatalyst used in the elimination of emerging contaminants in water. *Catalysis Today*, 230, 27-34.

- Miranda A. C., Lepretti M., Rizzo L., Caputo I., Vaiano V., Sacco O., Lopes W., Sannino D., 2016, Surface water disinfection by chlorination and advanced oxidation processes: Inactivation of an antibiotic resistant *E. coli* strain and cytotoxicity evaluation. *Science Of The Total Environment*, 554-55, 1-6
- Sauvé S., Aboufadi K., Doner S., Payment P., Deschamps G., Prévost M., 2012, Fecal coliforms, caffeine and carbamazepine in stormwater collection systems in a large urban area. *Chemosphere*, 86, 118-123.
- Shi, J., 2018. Research on Photochemical Catalytic Sewage Degradation Property Based on Photovoltaic Technology. *Chemical Engineering Transactions*. 71, 601-606.
- Sodré F. F., Locatelli M. A. F., Jardim W. F., 2009, Occurrence of Emerging Contaminants in Brazilian Drinking Waters: A Sewage-To-Tao Issue. *Water Air and Soil Pollution*. 57-67.
- Souza M. C. P., Lenzi G. G., Colpini L. M. S., Jorge L. M. M., Santos O. A. A., 2011, photocatalytic discoloration of reactive blue 5g dye in the presence of mixed oxides and with the addition of iron and silver. *Brazilian Journal Of Chemical Engineering*, 28, 393-402.
- Trovó A. G., Silva T. F. S, Gomes Jr O., Machado A. E. H., Neto W. B., Muller Jr P S., Daniel D., 2013, Degradation of caffeine by photo-Fenton process: Optimization of treatment conditions using experimental design. *Chemosphere*. 90,170-175.
- Zhang, J.; Wang, S.; Xie, Y.; Gao, J., 2018, Characterization of N-doped TiO₂ Pillared Clay and Its Photocatalytic Performance under Visible Light. *Chemical Engineering Transactions*, 71, 217-222.
- Ziulli R. L., Jardim W. F., 1998, Mechanism Reactions of Photodegradation of Organic Compounds Catalyzed by TiO₂. *Química Nova*, 21, 319-325.
- Wang H., Wang C., Chen Q., Ren B., Guan R., Cao X., Yang X., Duan R., 2017, Interface-defect-mediated photocatalysis of mesocrystalline ZnO assembly synthesized in-situ via a template-free hydrothermal approach. *Applied Surface Science*, 412, 517-528.