

## Influence of ZnO Content in Mixed Oxides Catalysts Applied in the Photocatalytic Degradation of Atrazine

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Atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) is an herbicide widely used in agricultural crops and has aroused worldwide concern for high potential pollution in soil, sediments, water and food. As the conventional methods for the persistent degradation of organic compounds are not very efficient, new technologies have been developed to remove those, especially those that use advanced oxidation processes (AOPs) and between AOPs, there is a heterogeneous photocatalysis. In this sense, the use of photocatalysts for water decontamination with organic materials is shown as an efficient alternative due to its oxidative properties. The photocatalytic process involves the activation by sunlight or artificial light of a semiconductor material, resulting in total or partial mineralization of these contaminants.

This study aims to evaluate the performance of the mixed oxide catalysts (ZnO/TiO<sub>2</sub>), with different ZnO contents (5, 8, 10, and 15 wt. %) in the photocatalytic degradation of atrazine in aqueous phase using UV radiation. The catalysts were prepared by wet impregnation and characterized by specific surface area (BET method), pore diameter and pore volume, X-ray diffraction (XRD), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM). The photocatalytic reactions were conducted in a batch-type reactor and the reaction products were analyzed by high-performance liquid chromatography (HPLC) and UV-Vis spectrophotometry at a wavelength of 221nm in order to evaluate the behavior of atrazine throughout the reaction. The results showed that catalysts containing 5%ZnO/TiO<sub>2</sub> and 10%ZnO/TiO<sub>2</sub> were the most efficient presenting a complete degradation of atrazine and a partial mineralization of the products. The degradation of atrazine after 10 minutes of reaction was 97.5 wt.% for the 5%ZnO/TiO<sub>2</sub> catalyst and 94 wt.% for the 10%ZnO/TiO<sub>2</sub> catalyst.

### 1. Introduction

Atrazine, an herbicide of difficult natural degradation, is widely used around the world for the weeds control (Yang et al., 2014). Its main characteristics are: high leaching potential, slow hydrolysis reaction, low vapor pressure and moderate water solubility (30 mg L<sup>-1</sup>) (Santana et al., 2003). Studies have shown the constant presence of atrazine in aquatic environments, causing many diseases in humans and intense environmental pollution, mainly in water and food (Carafa, 2007). For this reason, it is considered as a type of persistent organic pollutant, besides being an endocrine disruptor. Atrazine presence in the water may present risks of affecting the quality of semen and fertility in men, as well as increased breast cancer in women (Gragin, 2011). Due to the harmful effects of atrazine on humans and ecosystems, the World Health Organization (WHO) set the maximum permissible herbicide concentration in drinking water as 0,1mgL<sup>-1</sup> (Who, 2011).

Thus, the heterogeneous photocatalysis, an advanced oxidative process (AOP), has attracted great interest from the scientific community, as an alternative way to degrade organic compounds (Berkani et al. 2015) This process aims the degradation of the pollutant by neutralizing the contaminant, leaving no hazardous waste in the environment, through the thermal activation of the catalysts by sunlight or artificial light (Parra et al., 2004). According to the literature, TiO<sub>2</sub> and ZnO semiconductors have been widely used, as they are both widely available, inexpensive and non-toxic (Vaiano et al., 2014). In this context, the main objective of this

paper is to evaluate the performance of TiO<sub>2</sub>-oxide-based catalysts, containing mass percentages of 5, 8, 10 and 15 of ZnO, in its composition and pure TiO<sub>2</sub> and ZnO, in the photocatalytic degradation of atrazine.

## 2. Experimental procedures

### 2.1 Synthesis of catalysts

In the preparation of the titanium-based catalysts containing different loads of zinc, by the method of impregnation with excessive solvent, pure commercial TiO<sub>2</sub> and ZnO were used, manufactured by Synth and Dinâmica respectively. The method basically consists of mixing the TiO<sub>2</sub> with deionized water; leaving the resulting mixture under slow stirring; adding the zinc oxide, previously dissolved in deionized water, in the amount requested to prepare the material in the proposed composition (5, 8, 10 and 15 wt.% Zinc). Thereafter, the solution was kept under stirring for 12 hours, which is the time to impregnate TiO<sub>2</sub> with ZnO. Immediately afterwards, the excess solvent was removed by vacuum evaporation, in a rotary evaporator, while heated at 80°C, and later, the solution was kept in the oven at 100°C for 24 hours to complete drying. Finally, the synthesized catalysts were subjected to calcination in a muffle, in an oxidizing atmosphere (air), for 4 hours at 400°C, under the conditions determined by thermogravimetric analysis (Santos, 1999).

### 2.2 Characterization of catalysts

After the synthesis, both the precursors and the impregnated catalyst were characterized by measurements of adsorption/desorption of N<sub>2</sub>, X-rays diffraction (XRD), thermogravimetric analysis (TGA) and electronic scanning microscopy. In respect of the analyses of the measurements of adsorption/desorption of N<sub>2</sub>, the specific surface area, specific volume and average pore diameter, as well as the adsorption isotherms, were determined using the Quanta Chrome equipment, model Nova 1200, using N<sub>2</sub> at 77 K. Previously to the analyses, the calcined samples were submitted to a heat treatment at 460 K, under vacuum for 8 hours, in order to eliminate water and adsorptive materials in the pores of the samples during their manipulation.

In order to determine the best calcination temperature, the TGA of the oxides was performed after the drying step, using the Shimadzu Thermogravimetric Analyser equipment, model TGA-50M, and Mettler Toledo Analytical Microscales, model MX5. About 1g of sample was used, which was placed in an aluminum crucible. The conditions of the analyses were the following: flow rate of N<sub>2</sub> was 50 mL/min, from room temperature to 1273 K and heating rate of 10°C/min. On the other hand, the diffractograms were obtained on a Bruker D8 Advance X-ray diffractometer, using CuK $\alpha$  radiation (V= 40 KV, I= 35 mA). The parameters used were following: angle (2 $\theta$ ) between 20 and 80°; step of 0,01°; speed of 0.28°/min. Data were analysed using the X'Pert HighScore program, and with the standards published by JCPDS (1995).

The Scanning Electron Microscope (SEM) was performed in order to determine the morphology of the synthesized materials. For the sample coating, the Sputter Coater Emitech metallic coating equipment, model K450, was used, and the gold layer thickness was estimated at 200 Å. For the micrographs measurements, an electronic scanning microscope with a detector of X-ray dispersive energy was used, Leo Electron Microscopy, model MEV Leo 440i. For the X-ray spectra measurements, the acceleration voltage was 20 kV and the beam current equal to 700 pA

### 2.3 Experimental Method

The atrazine (Sigma-Aldrich) was previously dissolved in Methanol (J. T. Baker) forming a stock solution of 1000mg/ L. From the stock solution a synthetic solution of 5mg/ L in deionized water was prepared to evaluate the catalytic activity of the materials in batch reactor containing 750ml. In the solution containing the herbicide, 10mg of the catalyst was added and the resulting mixture was kept under constant stirring for 30 min in the dark for the adsorption process, and then this solution remained for 60 min under irradiation. To control the temperature, the reactor was wrapped in a steel jacket containing a temperature-controlled bath. A 250 W UV mercury vapor lamp was used as the light source. All reactions were performed at the constant temperature (25°C), ambient pressure and natural solution pH. To evaluate the degradation of atrazine, samples were withdrawn at time regular intervals (0, 5, 10, 20, 30 and 60 minutes), filtered with a 0.45  $\mu$ m Millipore membrane to remove the catalysts, and were sent for analysis. Figure1 shows a schematic of the experimental module where the experimental tests were conducted.

Effluent samples from the reactor were analyzed by a Shimadzu UV-vis spectrometry and later analyzed by a high performance liquid chromatography (HPLC), equipped with an UV detector at 221 nm, C18 column, 5 $\mu$ , length of 250 mm and diameter of 4.6 mm, flow rate of 1mL and mobile phase composed of 55% of volume aqueous acetonitrile solution (Parra et al., 2004).

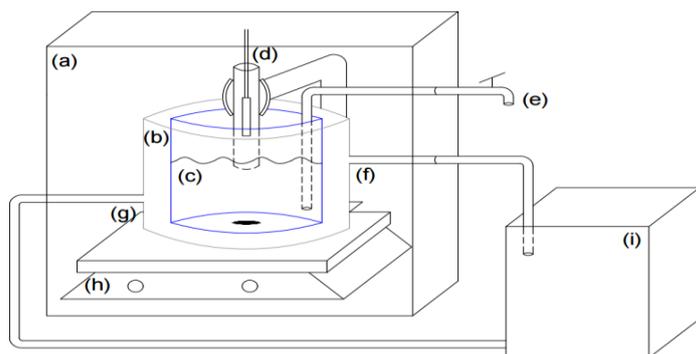


Figure 1- Experimental module: (a) steel box, (b) steel jacket, (c) atrazine solution, (d) lamp wrapped by quartz tube, (e) sample collection, (f) For cooling, (g) cooling water outlet, (h) magnetic stirrer and (i) thermostatic bath.

### 3. Result and discussion

#### 3.1 Characterization of catalysts

The crystalline structures obtained with XRD are shown in Figure 2 for the TiO<sub>2</sub> samples containing mass percentages of 5, 8, 10 and 15 of ZnO. The diffractograms of all the synthesized catalysts showed TiO<sub>2</sub> in the Anatase form (25.4°, 37.9°, 48.1°, 54.0° and 55.1°), with a tetrahedral crystallographic arrangement, and ZnO in Wurtzite form (31.9°, 34.5°, 36.3° and 56.7°), with a hexagonal crystallographic arrangement, according to database JCPDS PDF # 73-1764 and # 75-0576 respectively. These results are in agreement with those obtained by Nirmla et. Al., 2010, and Souza et. 2013. The peaks corresponding to ZnO become more intense as the zinc content in the structure increases, proving a high efficiency in the synthesis process.

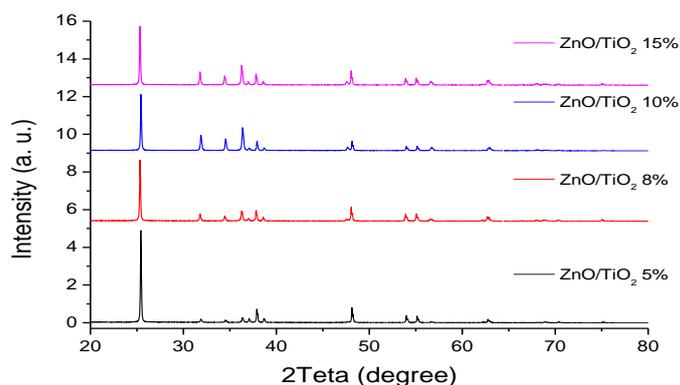


Figure 2 - XRD of synthesized catalysts.

With respect to the textural analysis obtained by N<sub>2</sub> adsorption / desorption measurements, the results indicated mesoporous structures, as they had an average particle diameter of 3 nm, according to the IUPAC classification, for all catalysts analyzed, commercial and synthesized. However, all the samples indicated the presence of areas and volumes of micropores, confirming their existence among the mesoporous media. The synthesized catalysts obtained 31, 24.5, 32, 17.8 m<sup>2</sup>/g as specific surface area for Zinc mass of 5, 8, 10 and 15%, respectively. The specific pore volume, in turn, was in the order of 0.02129, 0.09043, 0.01901, 0.08448 cm<sup>3</sup>/g, to 5, 8, 10 and 15 wt.% zinc, respectively. Both the values of the surface area and the specific volume were higher than those found for the industrialized TiO<sub>2</sub> and ZnO, which presented 16.8 and 13 m<sup>2</sup>/g as surface area and 0.02177 and 0.01053 cm<sup>3</sup>/g of specific volume respectively.

The results of the thermogravimetric analyses showed a mass loss up to approximately 400°C, considered as the calcination temperature for the catalysts after drying. It was also observed that the mass loss decreased with increasing zinc content, while 10% loss for the catalyst containing 15 wt.% zinc and 34% loss for the 5 wt.% zinc. The losses of mass in the process are due to the release of H<sub>2</sub>O and O<sub>2</sub> originally contained in the samples.

Figure 3 shows the micrographs, obtained by SEM, for TiO<sub>2</sub>-based materials, doped with 5, 8, 10 and 15 wt.% zinc, with a 20,000 times magnification. It can be seen from the micrographs that the supported catalysts showed an irregular structure, quite porous and granular, thus confirming the presence of mesopores at the surface, noticeable by the dark spots in the images. In addition, the sphericity of the particles is evident, as it is also observed in industrialized pure zinc and titanium oxides, confirming an effective mixture of those oxides. The synthesis favored the formation of solid structures in the form of crystals, present in the catalysts containing 10 and 15 wt.% zinc.

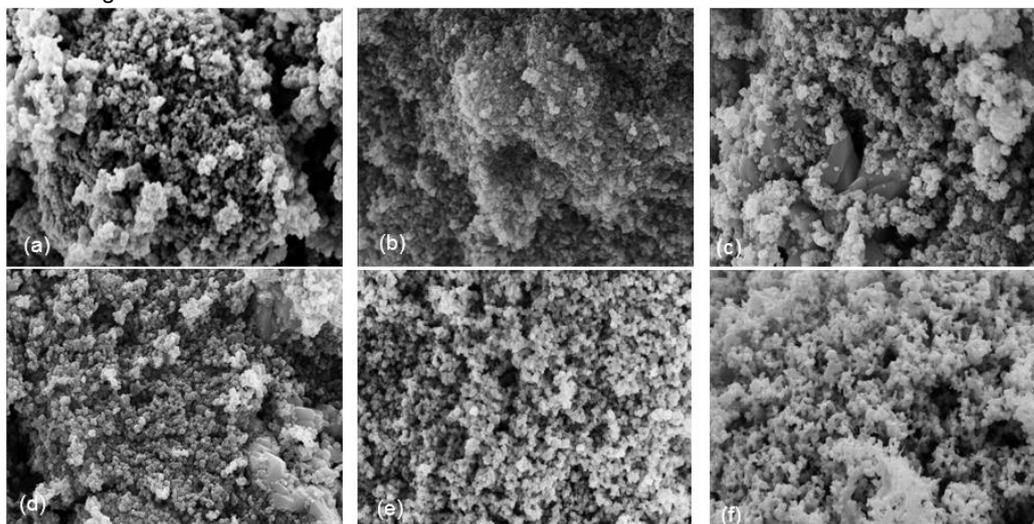


Figure 3 - Scanning Electron Microscopy: (a) 5% ZnO/ TiO<sub>2</sub>, (b) 8% ZnO/ TiO<sub>2</sub>, (c) 10% ZnO/TiO<sub>2</sub> and (d) 15% ZnO/TiO<sub>2</sub>. Magnification 20,000 times.

### 3.2 Reaction tests

The efficiency of the supported catalysts (5% ZnO / TiO<sub>2</sub>, 8% ZnO / TiO<sub>2</sub>, 10% ZnO / TiO<sub>2</sub>, 15% ZnO / TiO<sub>2</sub>), as well as the pure commercial oxides (ZnO, TiO<sub>2</sub>) was evaluated in degradation of atrazine. In order to verify if the target herbicide was degraded in the heterogeneous photocatalytic process, experiments were performed in the absence of light and in the presence of the catalyst (adsorption tests). In particular, the tests performed under dark conditions did not show any oxidation activity. In addition to that, additional control tests were performed in the presence of atrazine, in which the photoreactor was irradiated by the mercury vapor lamp in the absence of a photocatalyst (photolysis reaction). Although the photolytic system had reached about 60% atrazine degradation, the residual level after 60 minutes of treatment (0.4 mg/L) was above the human threshold of 0.1 mg/L allowed by the World Health Organization (Who, 2011).

Figure 4 shows the evolution of the degradation of atrazine as a function of the time of exposure to UV light, in the presence of the commercial photocatalysts TiO<sub>2</sub> and ZnO, as well as in the presence of TiO<sub>2</sub> based supported photocatalysts with different mass proportions of zinc, besides the reaction For 60 min of reaction. Under dark conditions, a decrease in atrazine concentration was observed during the first 20 minutes of the test, and it was practically unchanged during the last 10 min, showing that the adsorption equilibrium of the herbicide on the catalyst surface was reached. After this period, the solution was irradiated with UV light, and the actual photocatalytic reaction started.

In addition, a significant decrease in contaminant concentration can be observed in the presence of both pure ZnO and TiO<sub>2</sub> commercial catalysts and of the catalysts supported by the impregnation method with different zinc charges (ZnO / TiO<sub>2</sub>), since our five minutes of reaction. However, the reactions in the presence of the synthesized catalysts were better than those with the industrialized ones, thus showing that the addition of zinc in the TiO<sub>2</sub> structure contributed to an increase in the photocatalytic activity, although the catalysts containing 8 and 15 wt.% zinc had shown a photocatalytic activity close to the industrialized photocatalysts.

In particular, a degradation of 97.5% and 94% was observed, for the synthesized catalysts containing 5 and 10 wt.% zinc, respectively, in just 10 minutes of treatment, thus being the most active catalysts. At the end of the reaction, all the synthesized catalysts showed approximately 99% removal of the herbicide, while the industrialized ones reached approximately 96%, proving that the mixture of the oxides in the degradation of atrazine guaranteed greater efficiency in the process. All the reactions performed with the synthesized catalysts showed concentrations of around 0.005mg/L after 60 minutes of radiation, values lower than the ones allowed by the World Health Organization (0.1 mg/L).

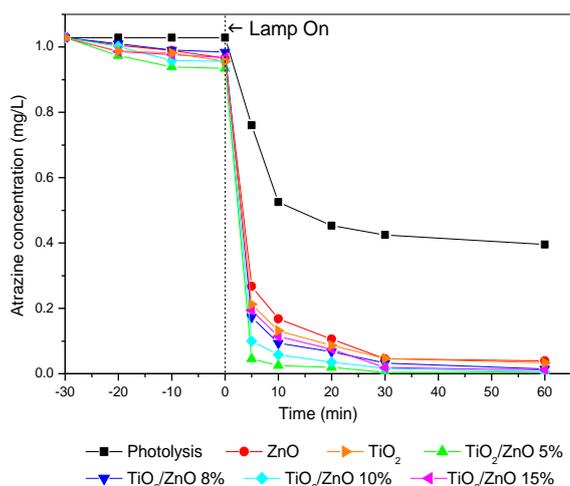


Figure 4 - Degradation of atrazine in the presence of photocatalysts and by photolysis.

The spectrophotometric result of the photocatalysis process with an atrazine solution of  $1 \text{ mg L}^{-1}$ , in the presence of the  $\text{TiO}_2$ -based catalyst containing 5 wt.% zinc, using wavelength scanning after exposure to UV radiation is shown in Figure 5 (a). This figure shows the decrease of the peak corresponding to Atrazine, which presents maximum absorbance at 221nm, due to the increase of the exposure time to UV radiation, followed by the appearance of the absorbance signal at approximately 240 nm, within the first 10 minutes of reaction, as shown in the delimitation in figure 5 (a).

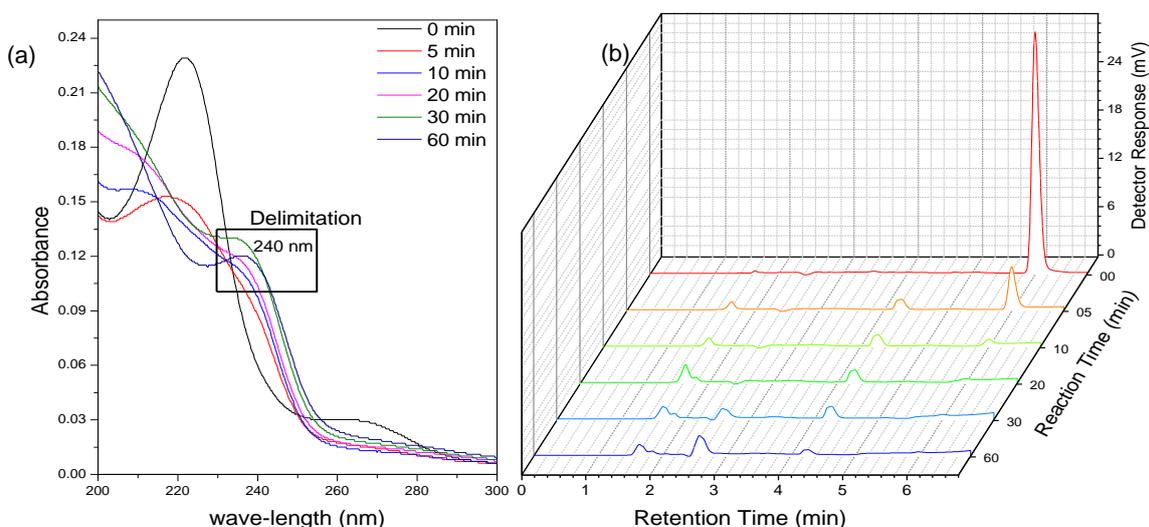


Figure 5 - Degradation of atrazine in the presence of 5% ZnO /  $\text{TiO}_2$ : (a) Spectral scan at different times; (b) Chromatogram of atrazine degradation samples collected during the reaction.

The appearance of a new peak at 240 nm, the formation of an intermediate with a degradation of the attraction, since 97% of the degradation of the herbicide was obtained in the presence of 5% ZnO /  $\text{TiO}_2$  for 10 min of reaction. According to Moreira, 2016, the compound appearing at the wavelength of 240 nm is an Atrazine-2-hydroxy, one of the most common by-sub products of Atrazine and possibly less toxic due to the hydroxylation of the triazinic ring along the halogenated carbon.

Figure 5 (b) shows a typical chromatogram obtained with the development of the photocatalytic degradation reaction of atrazine ( $1 \text{ mg.L}^{-1}$ ) at different reaction times in the presence of  $\text{TiO}_2$  containing 5 wt.% zinc in its structure. From this chromatogram, it is observed that the herbicide shows a period of retention within the chromatographic column of approximately 6 min. In this period of retention, the decrease of the amount of herbicide present in the reaction medium is evident, showing a considerable drop of the corresponding peak

already in the first 5 minutes, and a total degradation after the 30 minutes of reaction, demonstrating that the effective action of the radiation UV in the process occurs after this period.

However, together with the decrease of the herbicide peak, small peaks are formed in other periods of retention, which may indicate a possible formation of intermediates as byproducts of the reaction, thus proving the changes in wavelength behavior already shown in Figure 5 (a). From what the results of this research show and according to the literature, the decrease of the Atrazine peak may have been due to the increase of the Atrazine-2-hydroxy peak, among other products (Moreira, 2016). In addition, the peaks identified as reaction products appear in low quantity and low intensity, proving a possible partial mineralization of the products.

#### 4. Conclusion

In this work, the photocatalytic degradation of the Atrazine contaminant using TiO<sub>2</sub> based catalysts with 5, 8, 10 and 15% by mass of zinc, synthesized from commercial oxides by the solvent impregnation method, has been approached for the first time. In particular, the insertion / deposition of ZnO in the TiO<sub>2</sub> structure improved the catalytic activity of the catalyst in the treatment of atrazine-containing water, since the mixed oxides presented higher results than the pure commercial oxides. The characterization results show that the deposition of zinc on the surface of the titanium caused an increase in the surface areas and the specific volumes of pores, thus making the surface of the catalysts more accessible to ultraviolet light. In addition, it was possible to identify, through SEM analysis, massive structures in the form of crystals, due to the deposition of zinc in the structure of TiO<sub>2</sub>, especially in the samples containing 10 and 15% of zinc. An ideal composition, among those studied in this work, was found in 5% by mass of ZnO in TiO<sub>2</sub>, as it obtained a degradation higher than 97% in 5 minutes of reaction with this catalyst. The mixed oxides ZnO/TiO<sub>2</sub> exhibited good photoactivity in the degradation of atrazine in the presence of UV light, evidencing a good performance both in the degradation of the herbicide and in the mineralization of the products.

#### Reference

- Berkani. M., Bouhelassa M., Bouzaza A., Bouchareb M. K., Kadmi Y., Soutrelle I., 2015, Optimization of Photocatalytic Decolourization of Cationic Azo Dye in Thin Film Fixed Bed Photoreactor, *Chemical Engineering Transactions*, 32, 2275-2280. DOI: 10.3303/CET1543161.
- Carafa R., Wollgast J., Canuti E., Ligthart J., Dueri S., Hanke G., Eisenreich S. J., Viaroli P., Zaldívar J. M., 2007, Seasonal variations of selected herbicides and related metabolites in water, sediment, seaweed and clams in the Sacca di Goro coastal lagoon, *Chemosphere*, 69, 1625-1637, Northern Adriatic.
- Cragin, L. A.; Kesner, J. S.; Bachand, A. M.; Barr, D. B.; Meadows, J. W.; Krieg, E. F., 2011, Menstrual cycle characteristics and reproductive hormone levels in women exposed to atrazine in drinking water. *Environmental Research*, 111, 1293-1301, DOI: 10.1016/j.envres.2011.09.009
- Lopes O. F., Mendonça V. R., Silva F. B. F., Paris E. C., Ribeiro C., 2014, Niobium oxides: an overview of the synthesis of Nb<sub>2</sub>O<sub>5</sub> and its application in heterogeneous photocatalysis, *Química nova*, 38, 106-117.
- Moreira, A. J., Pinheiro B. S., Araújo A. F., Freschi G. P. G., 2016, Evaluation of atrazine degradation applied to different energy systems, *Environmental Science And Pollution Research*, 23, 18502-18511.
- Nirmala, M., Nair, M. G., Rekha, K., Anukaliani, A., Samdarshi, S. K., Nair, R. G., 2010, Photocatalytic activity of ZnO nanopowders Synthesized by DC Thermal Plasma, *African Journal of Basic & Applied Sciences*, 2, 161-166.
- Parra S., Stanca S. E., Guasaquillo I., Thampi R. K., 2004, Photocatalytic degradation of atrazine using suspended and supported TiO<sub>2</sub>. *Applied Catalysis B: Environmental*, 51, 107-116.
- Santana, H., Bonancêa, C. E; Takashima, K., 2003, Fotocatálise eletroquímica de atrazina sobre dióxido de titânio: efeito de diferentes parâmetros experimentais. *Química Nova*, 26, 807-811, Brazil.
- Santos, O. A. A. Hidrogenação seletiva do ácido oleico em catalisadores de rutênio, 1999, PhD Thesis, State University of Campinas, Brazil.
- Souza, D. A. R., Gusatti M., Sanches C., Moser, V., M., Kuhnen N. C., Riella H. G., 2013, Initial studies of photocatalytic discolouration of methyl orange by using zno nanostructures, *Chemical Engineering Transactions*, 32, 2275-2280. DOI: 10.3303/CET1332348.
- Vaiano, V.; Sacco, O.; Sannino, D.; Ciambelli, P., 2014, Increasing the photoactivity of N-doped TiO<sub>2</sub> photocatalysts using phosphors as light carriers *Chemical Engineering Transactions*, 39, 619-624, DOI: 10.3303/CET1439104.
- Yang Y., Cao H., Peng P., Bo H., 2014, Degradation and transformation of atrazine under catalyzed ozonation process with TiO<sub>2</sub> as catalyst, *Journal of Hazardous Materials*, 279, 444-451.
- Who (World Health Organization), 2011. Guidelines for drinking-water quality - 4th ed. <apps.who.int/iris/bitstream/10665/44584/1/9789241548151\_eng.pdf> accessed 20.12.2016.