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Caffeine degradation using ZnO and Ag/ZnO under UV and solar radiation

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ABSTRACT

In this study, it was used pure ZnO doped with 1, 3, 5 and 8% wt. Ag was used for the photo catalytic degradation of caffeine, which is a substance classified as a contaminant of potable and underground water of growing concern when present in the surface. The techniques used to characterize the catalysts were: specific surface area, volume and mean pore diameter, X-ray diffraction, SEM, EDS and PAS. The results of the characterization revealed that the thermal treatment had little affected the structural properties of the catalysts, their band gap energy and textural characteristics as well as their specific area. It was also observed that the catalyst with 5% wt. Ag in ZnO (non-calcined) stood out from other materials, as it presented a better performance under artificial and solar radiation. It was also observed that the thermal treatment is important, regarding the catalytic activity for pure ZnO. On the other hand, the results obtained by doping the ZnO with Ag were better for non-calcined catalysts. However, all the catalysts tested showed good performance in the caffeine degradation, and after 180 min all of them degraded 100% of the caffeine present in the water.

Keywords: Caffeine; Degradation; Heterogeneous photo catalysis; Solar radiation

1. Introduction

Over the years, there has been a growing concern about environmental health parallel to the evolution and development of humanity. Studies identified different substances classified as contaminants or pollutants of emerging concern in most diverse environmental matrices. These contaminants are so called “emerging” because they are compounds that have been recently identified in the environment, their properties and their effects are little known, and there has been no legislation yet which allows a maximum of their disposal [1].

Among these contaminants, caffeine, which is widely metabolized by humans, is the most important one considering its structure and characteristics (Table 1). The disposal of the unconsumed coffee and caffeinated soft drinks is a predominant source of caffeine. This caffeine is inevitably released into domestic sewage and introduced into the wastewater treatment system, making its way through the wastewater-treatment plants globally and remaining in the water [2]. It is detected at concentrations from 1.5 to 300 ppm in influent and effluent of sewage treatment plants, while around 0.3 to 106 ppm is found in drinking water and raw water, respectively. Caffeine has also adverse effects such as more frequent headaches and fatigue during Caffeine withdrawal. Nowadays, there is a need for further information on the Caffeine toxicity and its prevalence and mixture with other wastewater components have been of increasing concern [3].

Therefore, research has been being carried out to identify viable and intelligent processes in the degradation of these compounds. Among the techniques already applied for this purpose, there is a heterogeneous photo catalysis that, besides being classified as an advanced oxidative processes (AOP), is a technique that combines catalysis with

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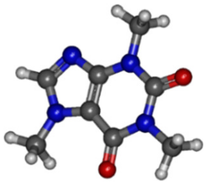
Table 1
Structure and characteristics of Caffeine

Structure	
Solubility in water (kg/m³) (25°C)	20
M_w (g/mol)	194.2
λ_{max} (nm)	275

photochemistry, which involves the use of radiation during the chemical reaction that occurs on the surface of the catalyst [4,5]. Thus, the heterogeneous photo catalysis has been highlighted and widely studied for the degradation of different pollutants, being the TiO_2 photo catalyst the most used one in this process [6,7].

The titanium dioxide (TiO_2) is among one of the most used semiconductors; however, the zinc oxide (ZnO) has been gaining prominence because it presents a good catalytic activity, it has a band gap similar to the TiO_2 one [4,8–10] and it is non-toxic. In addition, the band gap energy for TiO_2 and ZnO is considered reasonable, 3.2 and 3.3 eV respectively [4,11]. Moreover, has high thermal conductivity, high infractive index (2,0041) and excitation binding energy of 60 meV [12]. Another advantage of ZnO is that it absorbs a larger fraction of UV spectrum compared with TiO_2 [13].

In relation to the light absorption range, it is known that its visible region has a wavelength ranging between 700 and 400 nm, and the UV region is between 200 and 400 nm. It is of great importance to know in which region the studied catalyst absorbs energy because it tells us if it is possible, for example, to use sunlight as a light source during the reaction. Among the many advantages of using ZnO in photo catalysis is that ZnO is capable of absorbing a wide range of solar spectrum and greater amount of light than some semi conducting metal oxides [4]. The corresponding threshold of ZnO is 425 nm [13].

However, in order to improve the performance of these catalysts [14], scholars have added various compounds, metals and oxides to them, such as: TiO_2 with metals like copper, silver, zinc, gold, palladium and iron [15,16], ZnO doped with different amounts of Fe^{3+} [17] and Ag-doped ZnO nanorods [14]. In addition, compounds containing, for example, Ag in nanoparticles exhibit effects on the deactivation and inhibition in the growth of certain bacteria, thus the combination of Ag with metal oxides such as ZnO can provide a material with antibacterial properties which expands its application [18].

Pollutant degradation systems obtained significant results with natural radiation and ZnO (photo catalyst): photo catalytic degradation of Congo red by ZnO nanoparticles [19], photo catalytic degradation of nine emerging pollutants and elimination of fecal bacteria by TiO_2 [20], use of solar photo-fenton reaction as a tertiary treatment for liquid effluents containing contaminants and micro-pollutants [21].

The present work evaluated and compared the performance of photo catalysts ZnO pure and ZnO doped with silver (Ag) in the photo catalytic degradation of caffeine, using artificial and solar radiation.

2. Experimental

2.1. Chemicals

The chemicals mentioned here were used in the impregnation process of the photo catalyst: (i) zinc oxide ZnO (supplied by DINAMICA with approximately 99% purity); (ii) $AgNO_3$ silver nitrate (supplied by NEON with approximately 99.9% purity) and (iii) ultra pure water Miliporemili-Q.

2.2. Synthesis of catalysts

Ag photo catalysts in ZnO were synthesized by the wet impregnation method with excess solvent [22]. The nominal metallic charge of silver impregnated to ZnO was 1, 3, 5 and 8% wt. Ag.

After their synthesis the thermal treatment of calcination was carried out under a synthetic air flow of 35 $mL\cdot min^{-1}$ (21% O_2 and 79% N_2) to 400°C (thermal ramp of 10°C min^{-1}) for 4 h.

2.3. Characterization of the catalysts

2.3.1. Photo acoustic spectroscopy (PAS)

This analysis allowed to determine the minimum energy required to excite the electron. The photo acoustic spectroscopic measurements in the UV-VIS spectral regions were performed using an experimental configuration made in the laboratory. Monochromatic light was obtained from a 1000 W xenon arc lamp (Oriel Corporation 68820), a monochromator, and also from a 77250 model Oriel Instrument. The light beam was modulated with a mechanical chopper, a SR540 model Stanford Research System. The photo acoustic cell was made of an aluminum block, machined to store samples with maximum dimensions of 5 mm in diameter and 1 mm in thickness, allowing light to enter through a transparent quartz window of 6 m in diameter and 2 mm of thickness. The microphone chamber was 15 mm apart and connected to the sample holder compartment by means of a 1 mm diameter duct. It was used a capacitive microphone with 12 mm in diameter, a Bruel & Kjaer model 2639 with a high gain of 50 mV/Pa and a flat frequency response of 1 Hz to 10 kHz. The blocking amplifier was a 5110 EG&G Instruments model. All photo acoustic spectra were obtained at a modulation frequency of 20 Hz and recorded between 220 and 720 nm. The data were obtained by a personal computer and the PAS spectra were normalized regarding the carbon black signal [22]. The Band gap energies were determined using Eq. (1):

$$\lambda = \frac{hc}{E_{gap}} = \frac{1240}{E_{gap}} \tag{1}$$

where h is the Planck constant (4.13×10^{-15}eV · s), c is the velocity of light in the vacuum ($3.0 \cdot 10^{17}$ nm · s^{-1}), λ is the wavelength (nm), and E_{gap} is the band gap energy in eV. The direct method was applied to obtain the values, i. e., $m = 2$.

The photo acoustic spectroscopy tests were performed only with calcined samples while with the non-calcined ones, the material was burned during the three tests.

2.3.2. Specific surface area (BET method)

The porous properties of calcined and non-calcined catalysts were established using a QUANTACHROME-Model Nova-1200 analyzer with N_2 adsorption at 77 K. The samples were previously subjected to a thermal treatment at 150°C under vacuuming for 3 h to eliminate any water inside the pores of the solids

2.3.3. X-Ray diffraction (XRD)

The equipment used in this characterization technique was a D8 Advance diffractometer (Bruker), with initial theta of 5, final of 80, step 0.018 and 0.59 s per step. The obtained patterns were then compared with the diffraction data cards of the Joint Committee of Powder Diffraction Standards (JCPDS) [23].

2.3.4. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS)

The surface morphology of the four best photo catalysts were characterized by SEM (Tescan; VH3 model) and EDS (Oxford x act).

2.4. Experimental tests

2.4.1. Photo reduction

The caffeine solution (20 mg·L^{-1}) was prepared in ultra pure water (Miliporemili -Q) and the catalyst concentration used in the experiments was fixed at 0.3 g·L^{-1}. The reaction mixture was maintained in a cylindrical 2 L jacketed reactor with 1 L of caffeine solution. The pH of the solution (~ 6.5), defined by preliminary tests, was not adjusted; since the degradation of the pollutant at basic pH was close to the solution natural pH and the its degradation was lower at acid pH according to Fincur et al. [24], who describe that at acid pH, the ZnO can dissolve and thus, decrease the rate of degradation of the pollutant. The reaction was conducted with the reactor open to air with air flow of 0.5 L·min^{-1}. The system also had a magnetic stirrer to keep the mixture of the reaction homogeneous. The tests were carried out with mercury vapor lamps of 125 W and 250 W, which were coupled just above the reactor. At specific times, samples were collected and filtered through a syringe filter (0.22 μm pore size, 13 mn diameter and nylon membrane) and the caffeine concentration was analyzed in a UV-Vis (Femto-800 XI) spectrophotometer. A test with solar radiation was performed in this experiment and the system used counted on a cone wrapped to the reactor which was coated with reflective paper. Figs. 1a and b show the systems used.

A first order model [25,26] was applied to evaluate the kinetics of the caffeine degradation, which is expressed by Eq. (2).

$$\ln = \frac{C_0}{C} = kt \tag{2}$$

where C_0 is the initial concentration and C is the concentration at any t time.

2.4.2. Adsorption

The purpose of the adsorption test was to verify if the catalysts adsorbed the pollutant (caffeine) without the presence of a radiation source. The system contained the same characteristics of the system indicated in item 2.4.1, however, without any radiation.

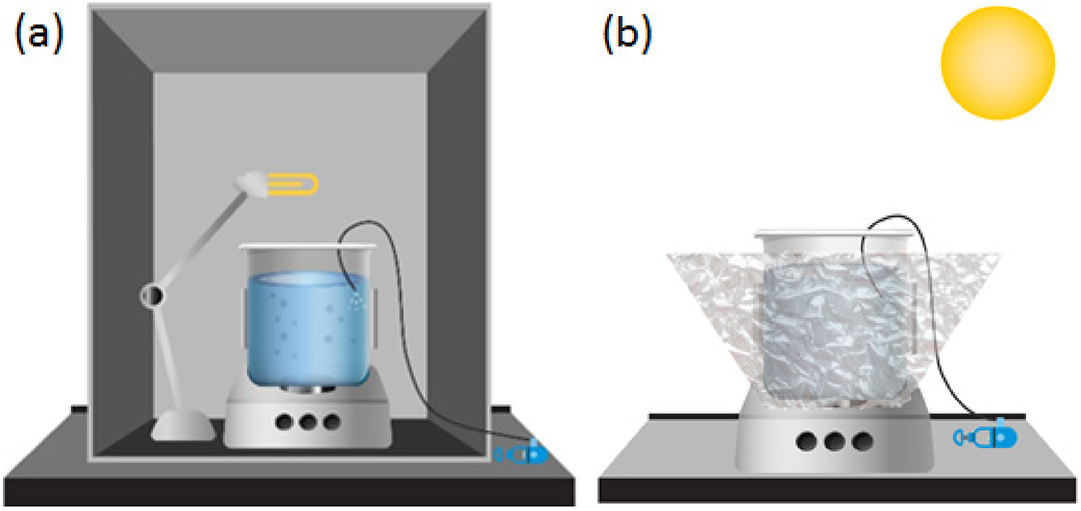


Fig. 1. Photo catalysis test (a) with the lamps 125 and 250 W (b) solar test.

2.4.3. Photolysis tests

Photolysis tests were performed using only the radiations applied in this study (artificial radiation by mercury vapor lamp of 125 and 250 W and solar radiation) with the synthetic solution of caffeine. The procedure was the same showed in item 2.4.1, however, without any catalyst.

3. Results and discussion

3.1. Characterization of the catalysts

The band gap results of each catalyst and their respective wavelengths of absorption are shown in Fig. 2. Analyzes indicated that the addition of Ag to the surface of ZnO, with any mass studied here in the calcined samples, led to an increase in the band gap energy when compared to pure calcined ZnO. The addition to some elements such as Ga and In, Mg can affect the shift of the optical adsorption edge of the crystals increasing its band gap value [27], so the same phenomenon possibly occurred with ZnO and silver. Although the addition of silver has altered the band gap of the calcined samples, it was noticed that for samples with quantities of 1, 3 and 5% wt. Ag, there was no significant change in the electronic properties of the materials. This phenomenon may be related to the small percentage of silver incorporated to the ZnO, whereas when compared to 8% wt. Ag, a greater increase was observed in relation to the other materials. Results in the literature with Zr-doped TiO_2/clay catalysts also found few changes in the band gap of the samples and concluded that they were due to the low amount of Zr (0–2%) incorporated to the semiconductor [5].

In relation to the wavelength (λ) calculated from Eq. (1) described in item 2.3.1, it can be verified that all the catalysts had values in the ultraviolet region, that is, $\lambda < 400$ nm.

In Table 2, the textural analysis of the catalysts indicated that for the pure commercial ZnO, the thermal treatment process was calcination at 400ºC, which slightly increased the specific area (S_o) of the material (from 8 $m^2 \cdot g^{-1}$ to 10 $m^2 \cdot g^{-1}$). An increase that may be related to the elimination of possible residues present in the pores of the material [22]. It can also be verified that after this thermal treatment, the pore volume (V_p) increased and there was a decrease in the mean pore diameter (d_p), these differences in the S_o, V_p and D_p after thermal treatment were not significant. Fincur et al. [24] characterized the ZnO, and detected the surface area S_o = 6.5 $m^2 \cdot g^{-1}$ and pore volume V_p = 0.016 $cm^3 \cdot g^{-1}$, values close

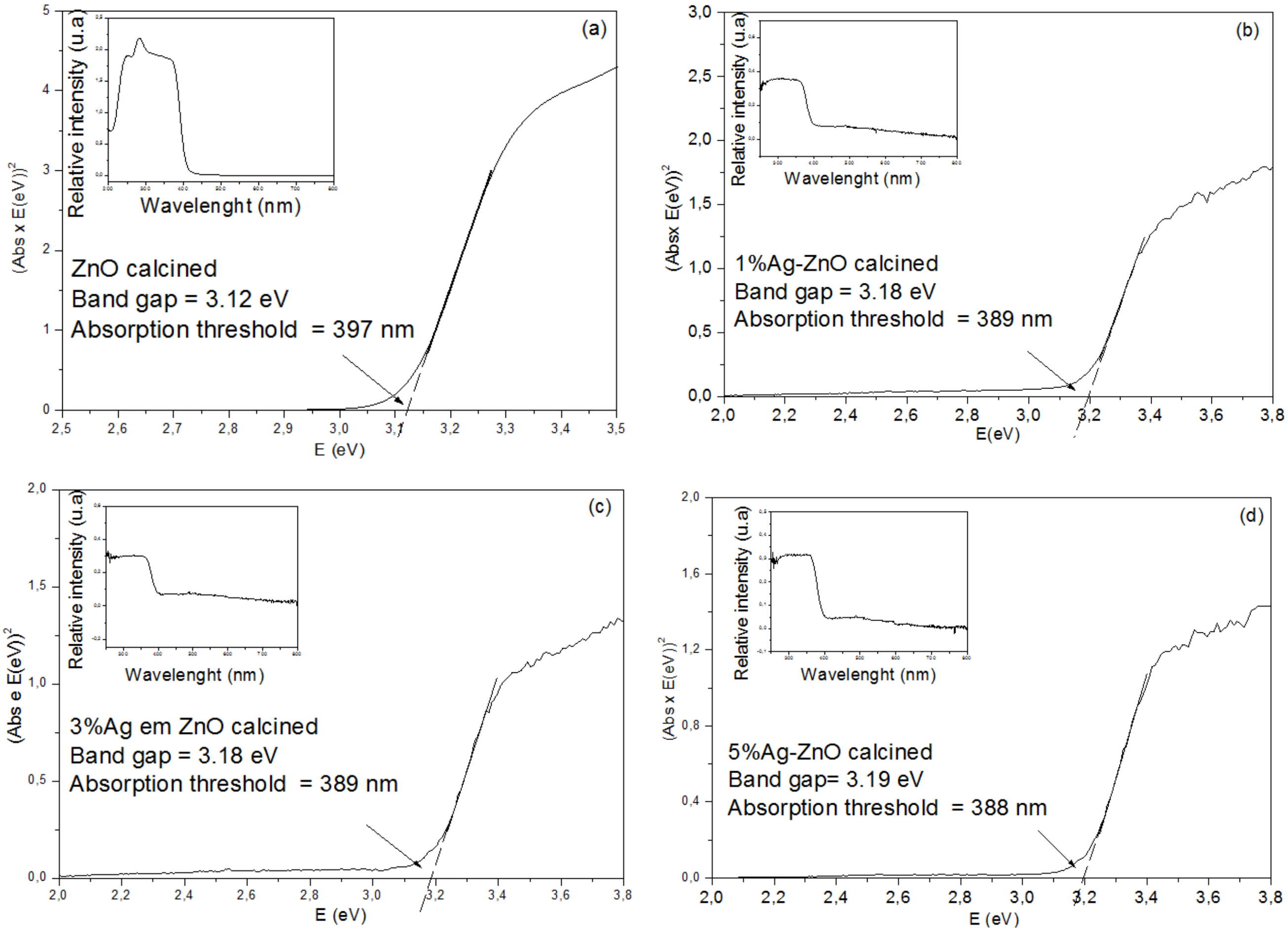


Fig. 2. Band gap of the catalysts with 1, 3, 5 and 8% wt. Ag in ZnO calcined (in detail the UV-Vis spectrum).

Table 2
Specific surface area (S_o), pore volume (V_p) and mean pore diameter (d_p) of the catalysts studied

Catalyst	Specific surface area S_o ($m^2 \cdot g^{-1}$)	Pore volume V_p ($cm^3 \cdot g^{-1}$)	Mean pore diameter d_p (Å)
ZnO non-calcined	8	0.0115	29
ZnO calcined	10	0.0128	26
1%Ag-ZnO non-calcined	8	0.0120	27
1%Ag-ZnO calcined	7	0.0092	27
3%Ag-ZnO non-calcined	8	0.0114	28
3%Ag-ZnO calcined	7	0.0091	27
5%Ag-ZnO non-calcined	8	0.0106	26
5%Ag-ZnO calcined	7	0.0087	25
8%Ag-ZnO non-calcined	8	0.0113	29
8%Ag-ZnO calcined	8	0.0101	27

to those found in this work, and in relation to the mean pore diameter, they also found a diameter smaller than 100 nm (1000 Å).

By adding the metal (nominal metal loading of 1, 3, 5 and 8% wt. Ag) to non-calcined catalysts, the specific area exhibited values of 8 $m^2 \cdot g^{-1}$, and when calcined, the specific area showed values of 7 $m^2 \cdot g^{-1}$, that is, they remained unchanged. When there is a considerable decrease in the specific area this phenomenon may be related to particle agglomeration by sintering and loss of surface hydroxyl groups or may have removed organic materials with calcination at 400°C [11,22]. In addition, the pore volume and the average pore diameter of the characterized materials also show that there were not considerable changes in the values presented for calcined and non-calcined catalysts.

In the analysis of the obtained XRD spectra, it is observed that for the ZnO calcined and non-calcined (Fig. 3) photo catalysts, crystallinity characteristics in hexagonal wurtzite form [9] were found, which is the most common for this material. The characteristic peaks are located at approximately $2\theta = 32, 34, 36, 47, 57, 62$ and 68°. Thus, the thermal treatment did not alter the crystalline structure of the material. Similar results have already been found in the literature [28] in which, although the calcination temperature of ZnO varied between 350 and 450°C, it was not identified any change in the typical peaks of the hexagonal wurtzite ZnO form. The authors also verified that, with an increase in the temperature of the ZnO calcination, the peaks showed higher intensity, indicating an increase in the particle size and in the crystallinity of the semiconductor. However, in the present research it was not possible to notice any considerable difference between the intensity of the peaks of the calcined and non-calcined samples. Kumar et al. [29] using XRD analyzed ZnO samples at different temperatures (100, 300, 500, 700 and 900°C). All samples were found to have the same diffraction peaks, and the intensity of the peaks increased as the temperature increased, indicating greater crystallinity, however the greatest differences among the peak intensities observed were for materials with calcination at 700 and 900°C. For the other samples there was little difference [29], as observed in the present study.

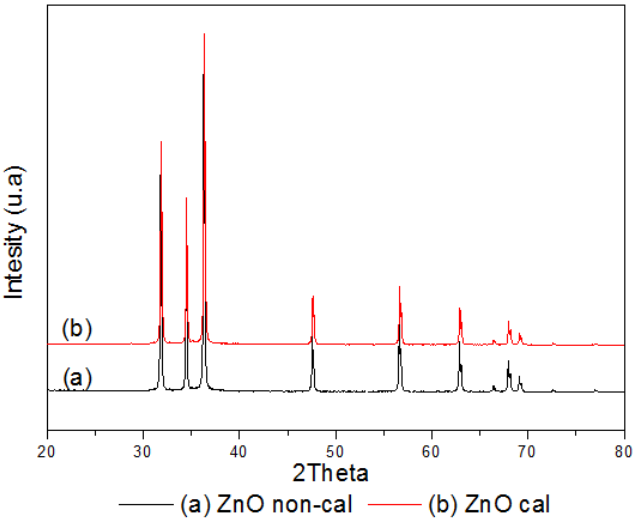


Fig. 3. XRD for calcined and non-calcined ZnO.

It was identified as non-calcined, ZnO catalysts with 1, 3, 5 and 8% wt. Ag (Fig. 4), in addition to the characteristic peaks of zinc oxide with wurtzite hexagonal crystallinity and silver nitrate related peaks ($AgNO_3$) in orthorhombic crystalline form ($2\theta = 20, 22, 24$, and 43°). As calcined ones, it was identified related peaks of silver (Ag) with crystalline cubic system ($2\theta = 38, 44$ and 64°), showing the efficiency of the calcination process in eliminating the organic compounds present on the surface of the catalysts originated from the salt precursor. There were no significant or considerable changes in any ZnO diffraction peaks, however, the appearance of Ag-related peaks indicates agglomeration of Ag crystals in the porous ZnO. Moreover, similar results were defined [30], when silver-doped ZnO nanocatalysts were developed, the researchers identified Ag in the cubic phase in the same characteristic peaks which are here defined as well as zinc oxide in hexagonal wurtzite format. Zarei and Behnajady [31] also found that the ZnO nanoparticles remained with the same crystal structure after doping with Mg by the sol-gel method.

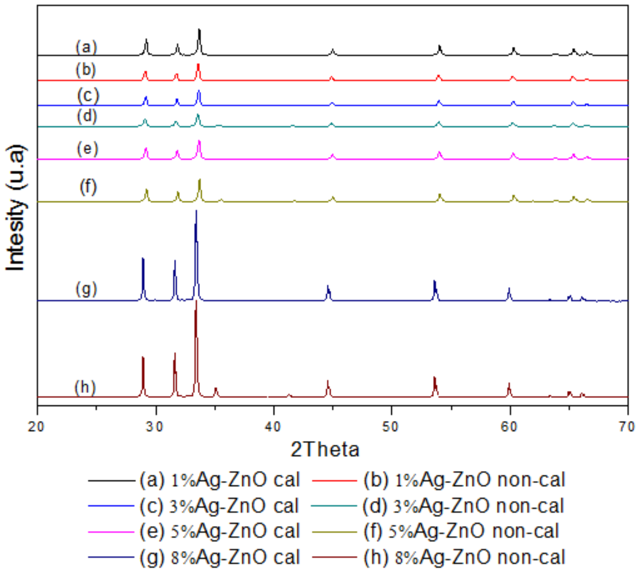


Fig. 4. XRD for catalysts 1, 3, 5, and 8% of Ag in ZnO calcined and non-calcined.

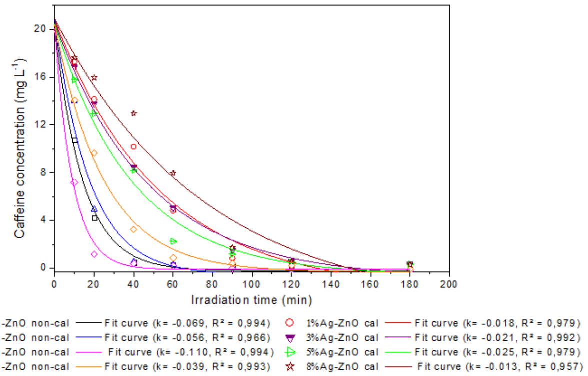


Fig. 5. Photo catalytic tests with mercury vapor lamp with power of 125 W and catalysts with 1, 3, 5, and 8% of Ag in ZnO calcined and non-calcined.

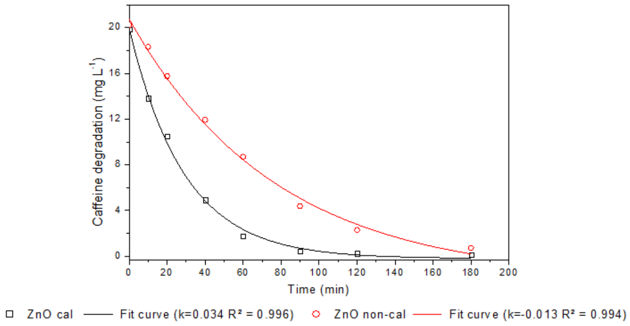


Fig. 6. Photo catalytic tests with lamp of 125 W and catalysts of pure ZnO calcined and non-calcined.

3.2. Experimental tests

3.2.1. Photo reduction

The evolution of the caffeine concentration over the time for the tests with a mercury vapor lamp of 125 W and with all the catalysts prepared is shown in Figs. 5 and 6.

In Fig. 5 it can be seen that all the catalysts had a caffeine degradation higher than 96% at the end of the reaction (180 min). However, in the presence of the catalyst containing 5 wt %. Ag, supported by non-calcined ZnO (5% Ag-ZnO non-calcined), caffeine degradation was approximately 100% within the first hour (60 min) of the reaction.

Thus, the amount of silver has a certain influence on the activity of the photo catalyst when it is applied to the caffeine degradation. It is noticed that by increasing the amount of Ag added to the surface of ZnO, the catalytic activity shows some improvement. However, for the catalyst containing 8 wt %. Ag, the kinetic curve was softer than the other curves for both calcined and non-calcined catalysts, indicating that the catalytic activity increased with the silver content and passed through a maximum in fill of about 5 wt %. Ag. In fact, Van Nghia et al. [32], while studying different silver contents (1, 2, 3, 4 and 5 wt.% Ag) in ZnO-supported catalysts in the degradation of the methylene blue dye by heterogeneous photo catalysis, found that the optimum amount of the metal to be added to the surface of ZnO was 4%, because 5% showed practically the same result. The authors also observed that an increase above 5%, in the amount of the metal ion may favor the recombination of the electron-gap pair and, thus, reduce the activity of the photo catalyst.

In another research, also carried out on the degradation of methylene blue, Zhang et al. [33] found that catalysts flower-like Ag/ZnO nanocomposites with different percentage of Ag (1.92 wt%, 2.71 wt%, 3.82 wt%, 5.6 wt%, and 9.8 wt%) were efficient in the degradation of the dye , and with the increase in the amount of Ag, the photo catalytic performance also increased. However, the catalyst with 5,6% wt. Ag was the best, since the catalyst with 9.8 wt.% Ag caused a decrease of the specific area and there was aggregation of Ag particles which made it difficult for the photocatalytic reaction.

It should be noted in the present work that under the conditions studied, although 5% Ag-ZnO supported catalyst was chosen as the best catalyst to continue with the mercury vapor lamp of 250 W and the solar test, the catalyst containing 1 wt %. Ag, could also have been used in the treatment of water containing caffeine because it had less silver and reduced costs when compared to the catalyst containing 5 wt %. Ag. Moreover, the difference in the percentage of caffeine degradation was maintained at approximately 2%, which would justify its use.

Elhalil et al. [34] studied the caffeine degradation using a UV mercury lamp 400 W with Ag-ZnO-Al_2O_3 nanocomposite, they found that the addition of 5 wt%. Ag to the nanocomposite calcined at 500ºC improved the semiconductor photo catalytic activity in the caffeine degradation, which completely occurred in 55 min which is in agreement with the results of this research.

The addition of metals to the surface of semiconductors, such as zinc oxide, has been widely applied, since they can alter characteristics such as specific area, band gap energy, and thus improve the performance of the catalyst. Furthermore, by means of the metal-semiconductor interface there may be modifications of the electronic and atomic structure of the semiconductor surfaces induced by the adsorption of metallic atoms. When a semiconductor is placed in contact with a given metal, its bands align to establish a common chemical potential. This usually leads to an upward shift of the semiconductor bands (due to energy decay of the gap energy) forming a barrier on the surface, termed the Schottky Barrier [35]. According to Yu et al. [36], this barrier formed at the metal-semiconductor interface can considerably impede the recombination between the electrons present in the ZnO and the gaps in the metallic nanoparticles, increasing the possible successive chemical reactions and, thus, affecting the performance of the photo catalyst positively.

Semiconductors of commercial calcined and non-calcined ZnO showed good performance in the pollutant degradation. However, the calcined material exhibits a better result with caffeine degradation close to 100% in only 120 min of reaction, since the non-calcined ZnO reaches a degradation of approximately 89% at the same time. This difference is probably related to oxide characteristics, even though, the values obtained in the present work, for the band gap energy, porous properties and the crystalline structure of ZnO, were practically unchanged with the calcination. It may be that with the thermal treatment there have been qualitative changes that could not be observed with the characterization techniques available for this research.

Bitenc et al. [37] carried out a study investigating the degradation of caffeine by heterogeneous photo catalysis in the presence of ZnO prepared by the solvothermal process. This catalyst, besides being a good semiconductor in the degradation reaction, was also stable, as the authors evaluated its reuse and found that ZnO showed little change in its catalytic activity after reusing it, which favors its use in the degradation of pollutants.

The SEM and EDS analysis with the catalysts ZnO calcined and non-calcined, and with 5%wt. Ag in ZnO calcined and non-calcined are shown in Fig. 7.

Fig. 7 shows the SEM micro graphs images and the energy dispersive spectra of the samples selected for the tests with solar radiation and with the lamp of 250 W. Apparently, both calcination and impregnation of Ag on the surface of ZnO did not modify the initial morphology of ZnO that presents as irregular particles. Also, with this analysis it was verified that the distribution of Ag did not happen homogeneously, that is, there were areas where the amount of Ag was higher and in others the amount was lower, probably due to the small amount of Ag used in doping.

Zhang et al. [33] synthesized of flower-like Ag/ZnO nanocomposites with different levels of Ag in ZnO, verified by scanning electron microscopy analysis that even increasing the amount of Ag deposited, the ZnO structure remained practically the same, indicating that the surface morphology of ZnO was not modified. In addition, the authors verified that it was not possible to identify Ag particles on the surface of ZnO which suggests that the Ag particles may be involved by ZnO nanoparticles.

The photo catalytic tests with the pure, calcined and non-calcined ZnO catalysts, as well as with the metal-charged Ag catalyst that showed the best catalytic activity is shown in Figs. 8a and b for tests with a 250 W lamp and solar test, respectively.

In the tests with the lamp of 250 W and with solar radiation, it is also possible to verify that, in general, all the studied materials presented a significant caffeine degradation. However, the non-calcined 5% Ag-ZnO photo catalyst stood out in relation to the others, that is, the other photo catalysts presented in only 120 min a degradation of approximately 100% of the caffeine with the power lamp of 250 W, whereas 5% Ag-ZnO non-calcined had degraded the same percentage in 60 min for the test with a 250 W lamp and solar test.

The radiation intensity influences the speed of the reaction. The kinetics of the reaction varies with the radiation intensity, since it is closely linked to the formation of the electron-gap pair. However, when the formation of the electron-gap pairs reaches a limit, even if the radiation intensity is increased, it is not possible to generate these pairs anymore, and thus, there is no more influence in the amount of the pollutant that will be removed from the reaction medium [25].

It is noticed that caffeine degradation exhibits a tendency to first-order kinetics, since in 91% of the cases the correlation coefficient was > 0.928. Al-Qaim et al. [26] carried out electrochemical oxidation experiments on caffeine with the presence of NaCl also concluded that the kinetics of caffeine degradation presented a tendency to the first order with a $R^2 > 0.915$ in all the tests performed.

Similarly to what was observed with the mercury vapor lamps of 125 and 250 W, the catalyst that presented the best performance when the reaction was carried out in the presence of solar radiation was the non-calcined 5% Ag-ZnO supported catalyst, showing that this catalyst was positively highlighted in relation other materials in all sources of light, evidencing that the metallic load of 5 wt %. Ag favored the performance of the catalyst.

With the results obtained from the tests carried out in the presence of 250 W radiation, the percentage of caffeine degradation, at the end of the reaction, was slightly higher than that obtained when the tests were carried out in the presence of solar radiation. However, both tests had excellent caffeine degradation. The little difference can be attributed to the possible targeting of the radiation incidence, since with the 250 W lamp, the radiation was well directed to the caffeine solution. Yet, for the test with solar radiation, although there was the reflective surface structure wrapped in a conical support to the reactor, there was no such exclusive direction of radiation.

For the best catalyst, 5% Ag-ZnO non-calcined using the solar radiation is justified by the energy savings, since even on partially cloudy days, in which the radiation presents great variation, there is an expressive degradation of the pollutant in question as can be observed in detail in Fig. 8b on the first day of the test. Bernabeu et al. [20], analyzed the water after an effluent treatment and, identified the presence of emerging contaminants, performing heterogeneous photo catalysis with TiO_2 P-25 Degussa and solar radiation for 3 h. Using this system, it was obtained a significant removal of the contaminants and it was also achieved the disinfection of the water. The present study, besides reinforcing the idea of the use of solar radiation for the degradation of caffeine, presents an alternative catalyst to TiO_2 P-25, widely used in research around the world, but which has a much higher cost than the ZnO used in this work which in future studies could be tested for the degradation of a mixture of emerging contaminants

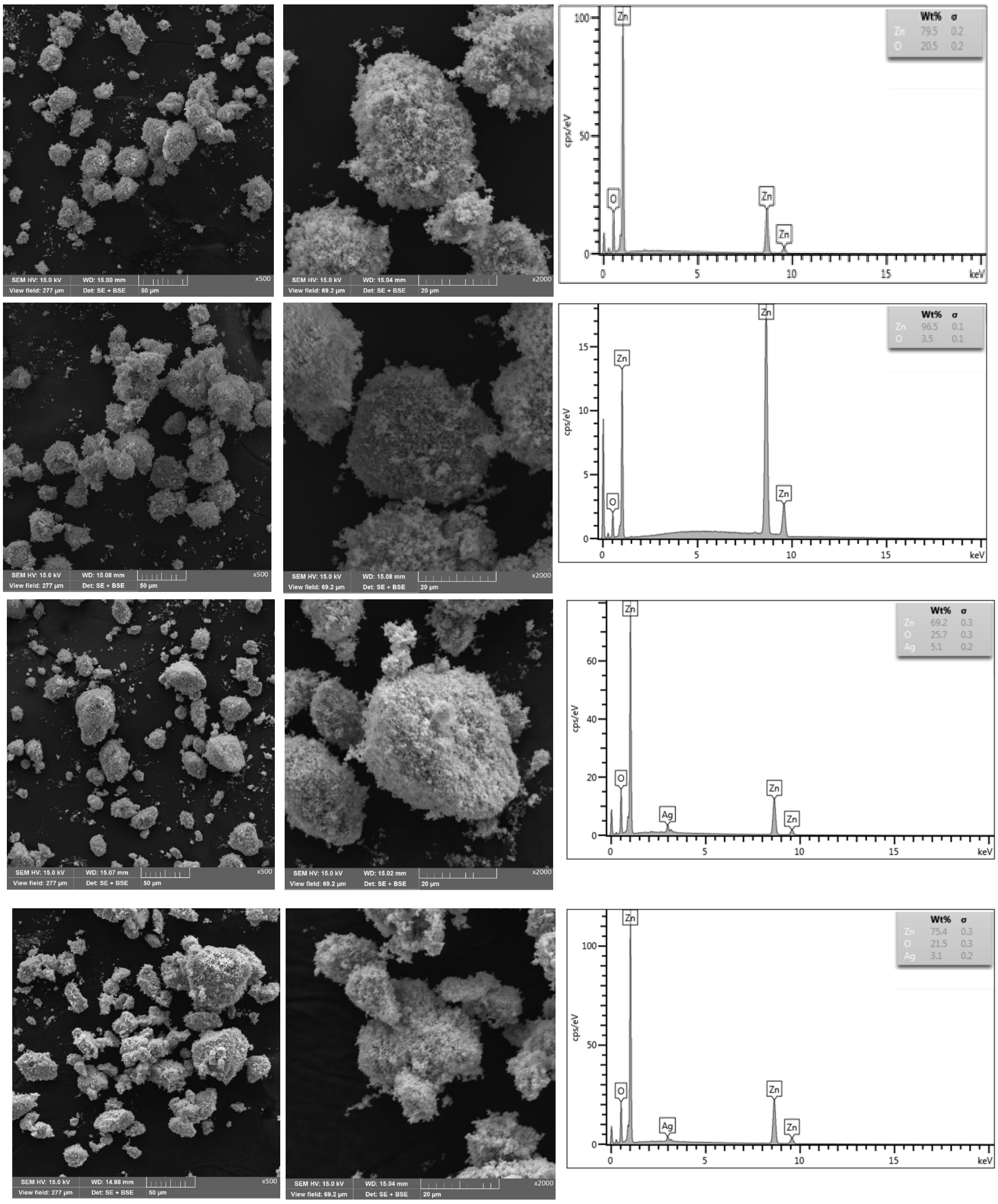


Fig. 7. Scanning electron micrographs and energy dispersive spectra: (a) ZnO non-calcined (b) ZnO calcined (c) 5%Ag-ZnO non-calcined and (d) 5%Ag-ZnO calcined.

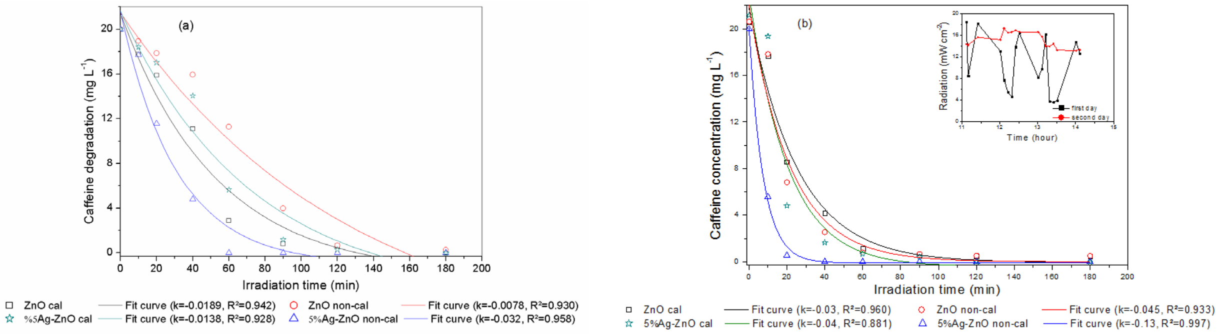


Fig. 8. Photo catalysis tests (a) Mercury vapor lamp with power of 250 W and (b) Solar test (in detail the radiation of the days that the tests were performed).

3.2.2. Adsorption

Fig. 9 shows the results of the adsorption test.

The adsorption results for the four catalysts are presented in Fig. 9. It was observed that only the catalysts without the presence of artificial radiation are not able to absorb the caffeine present in the water, maintaining its initial concentration of 20 mg·L^{-1} for 180 min of reaction.

3.2.3. Photolysis tests

Fig. 10 shows the results of photolysis with artificial radiation and solar radiation.

The results obtained with the photolysis test applied in the degradation of caffeine performed in the presence of 125 W, 250 W and solar irradiation are shown in Fig. 10. According to the results, the degradation of caffeine only in the radiation presence evidenced the need of photo catalyst for a more efficient process. Thus, the percentage of caffeine degradation by photolysis using artificial irradiation (125 W) was only 4%. For the artificial irradiation 250 W, it was noticed that the caffeine degradation in 180 min was 21%, and the solar irradiation experiment indicated at the caffeine degradation of approximately 1%.

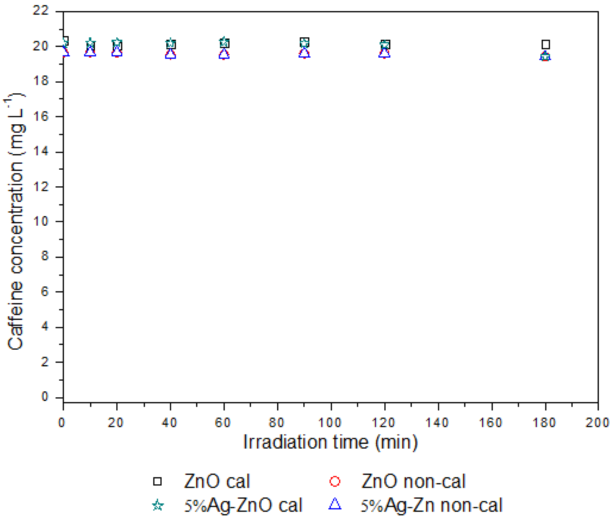


Fig. 9. Adsorption test.

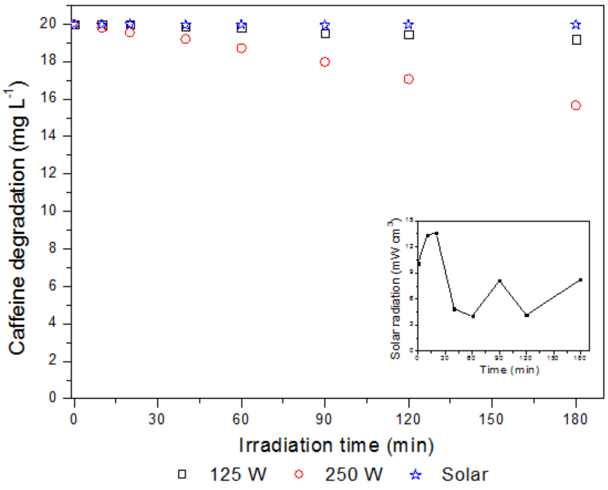


Fig. 10. Photolysis tests (detail: solar irradiation intensity).

4. Conclusion

Generally, the increasing order of the best catalysts for the degradation of caffeine under the conditions studied is ZnO non-calcined<ZnO Calcined<8% Ag-ZnO calcined <3% Ag-ZnO calcined <1% Ag-ZnO calcined <5% Ag-ZnO calcined <8% Ag-ZnO non-calcined <3% Ag-ZnO non-calcined <1% Ag-ZnO non-calcined <5% Ag-ZnO non-calcined. However, Calcine should be used when using pure zinc oxide, for a better catalytic behavior.

With the addition of the metal in the support (ZnO) when performing the thermal treatment of calcination, the results are not as efficient as compared to the non-calcined ones. When calcined, silver nitrate (NO_3Ag) is converted to Ag.

It was also observed by the optimization of the metallic load (1, 3, 5 and 8 wt.% Ag) that when we increase the amount of Ag, a small loss of efficiency occurs. On the other hand, when we reach 5%wt. Ag, it is found the great optimal metallic charge for the studied process.

However, by analyzing the results obtained using the non-calcined 1% Ag-ZnO catalyst, the result compared to pure zinc oxide is higher than 55% in the first 40 min, that is, 97% and 41% for 1% non-calcined Ag-ZnO and non-calcined ZnO in caffeine degradation, respectively.

The results obtained using solar radiation were highlighted because they presented good degradation and did not require either energy consumption or a cooling system, making it quite attractive. In addition, the efficiency of the photo catalytic process was confirmed by adsorption and photolysis results where no caffeine removal occurred.

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