Vol.63:e20180614, 2020
http://dx.doi.org/10.1590/1678-4324-2020180614
ISSN 1678-4324 Online Edition

Article - Engineering, Technology and Techniques

Degradation of Caffeine by Heterogeneous Photocatalysis Using ZnO with Fe and Ag

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Received: 2018.11.02; Accepted: 2020.03.17.

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HIGHLIGHTS

- Fe and Ag were added to the ZnO surface using an excess solvent technique.
- ZnO doped with Fe and Ag is efficient in the Caffeine photoreduction.
- Presence of silver nitrate in ZnO favored the catalytic performance.
- Photolysis and Adsorption did not show significant results.

Abstract: The organic compound caffeine when detected in environmental matrices such as surface waters and groundwater is considered as an emerging contaminant, in which its effects are still unknown. Therefore, in the present research, zinc oxide-based catalysts impregnated with iron and silver were prepared for the reaction of caffeine degradation by heterogeneous photocatalysis. The wet impregnation method with excess solvent was applied to the preparation of the materials, later they were characterized by adsorption of N_2, X-ray diffraction and photoacoustic spectroscopy. Then, the photodegradation, photolysis and adsorption tests were carried out, in which it was observed that only the presence of the radiation or photocatalysts could not sufficiently degrade the caffeine, however when combined radiation with all the catalysts studied here presented degradation above 70% at the end of 300 minutes of the reaction, and the best catalyst studied was that containing 8% Ag in non-calcined ZnO. Thus, these results point out that the methodology employed in this research, both for the preparation of the catalysts and in the process of the photocatalysis reaction, was efficient in the degradation of the emerging contaminant, caffeine, which could later be used for a mixture of other contaminants.

Keywords: Caffeine; ZnO; heterogeneous photocatalysis; photodegradation.

INTRODUCTION

Resulting mainly from human activity, various organic compounds, called "contaminants or pollutants of emerging concern", are being detected in several environmental matrices, such as in effluent from a wastewater treatment plant [1], surface waters [2–4], drinking waters [5,6] and groundwaters [4,7,8].

The term pollutant or emergent contaminant comprises compounds with diverse characteristics and applications, and may be substances already known and that until then there were no analytical techniques to determine them in the environment, as well as those compounds that were recently discovered and classified as contaminants, the main source of disposal of these compounds into the environment are the sewage directly discharged into hydric bodies [8,9].

As an example, there are personal care products, pharmaceuticals, food additives, endocrine disruptors, among other compounds such as caffeine. Caffeine is an organic substance belonging to the class of methylxanthines; which have the ability to stimulate the central nervous system [10]. This substance can be found in various food products, such as coffee, teas, chocolates, which are consumed daily by a large part of the world's population [10,11].

After the consumption of caffeine, the excretion by humans happens mainly through urine or else by the direct dumping of beverages such as teas and coffees that were not consumed completely, thus reaching the domestic effluent [10]. Then, this effluent or goes to wastewater treatment plants or is dumped directly without treatment in surface water, causing caffeine, among other substances, to be detected in aquatic matrices.

Faced with this problem, researchers have studied the possible elimination of this compound present in the water, so that the technique presents complete mineralization of the pollutant. Among which are, advanced oxidative processes such as the use of heterogeneous photocatalysis with TiO_2, photolysis, peroxidation, photoperoxidation, Fenton or Photo-fenton reaction [12–16].

Heterogeneous photocatalysis is considered as a clean technology and use irradiation for the excitation of electrons in a given semiconductor, and thus cause electron transition and generating hydroxyl radicals (HO •), which can then react with the organic pollutant by oxidizing them [17–19]. Thus, among other variables, the photocatalyst or semiconductor is of fundamental importance in heterogeneous photocatalysis. To select the to be used material is a decisive step for the good performance of the reaction. Among the most used semiconductors as photocatalysts are TiO_2, which is a material with good photostability, is non-toxic and is widely found in nature [20]. Another material that has also been investigated as a photocatalyst is ZnO, which, like TiO_2 is non-toxic, and has a strong oxidation capacity, good photocatalytic property [21] and a lower cost when compared to TiO_2-P25. Moreover, ZnO has a band gap energy close to that of TiO_2 (approximately 3.3 eV) and is capable of absorbing a wide range of the UV spectrum [21,22] which makes it very attractive for photocatalysis studies.

In addition, an improvement of the semiconductor can be made, and such enhancement may be affected, for example, by the addition of metals in semiconductors (for example, TiO_2 and ZnO) for the purpose to benefit from the photocatalytic performance of the material [19].

Iron is one the most abundant metals on Earth and the use of this metal in science is very diversified, being that in catalysis and adsorption when impregnated in supports can improve the behavior and performance of the catalyst, and this happens due to its redox and textural characteristics [23,24].

Still in this context, in a given study [25], the researches verified that among the metallic ions that were added to the TiO_2, the iron with the percentage of 0.5% showed an improvement in the photoefficiency in relation to the pure TiO_2 P-25 Degussa, in this way the evaluation of the impregnation of iron in substrates like ZnO becomes interesting because the cost of iron is relatively low in relation to other, more noble, such as gold.

Silver, on the other hand, has the lowest resistivity of metals, high resistance to oxidation and is non-toxic. Using silver in ZnO, for example, can lead to an improvement in surface charge distribution, optical properties and can prevent recombination of the electron-hole pair [26].

Some studies have reported improvement in the degradation of some contaminants such as Rhodamine B, water disinfection with E. coli, when using Ag in TiO_2 in the photocatalysis reaction [27], as well as the reduction of mercury (II) when was utilized Ag/TiO_2 catalyst [28].

Thus, this study evaluated the photocatalytic performance of ZnO impregnated with iron and silver, on the degradation of caffeine in aqueous medium by heterogeneous photocatalysis.

MATERIAL AND METHODS

Synthesis of Catalysts

Pure commercial ZnO (DINAMICA Ltda) and Fe and Ag impregnated were tested as catalysts. The impregnation of Fe and Ag in ZnO was carried out by means of the wet impregnation technique with excess solvent. The methodology proceeded with the following steps: the oxide used (ZnO) and the aqueous solution containing the metal precursor ($AgNO_3$ or Fe $(NO_3).9H_2O$) were mixed and kept under constant stirring for 24 hours at room temperature. The metal solution was made so that the Fe or Ag nominal load was of 8% of the ZnO total weight by previously described in the literature [29]. After obtaining the mixture, the excess solvent (water) was removed by vacuum evaporation in the rotavaporation system with heating, at 90 °C and then the catalyst was dried at 100 ºC for 20 hours. Subsequently, half of the already dried catalysts were calcined at 400 °C in a muffle.

Characterization of the Catalysts

Texture properties: The porous properties of the catalysts, such as specific surface area (B.E.T method), pore volume and mean pore diameter were determined using QUANTACHROME - Nova-1200 with adsorption of N2 at 77 K. The samples were previously subjected to a thermal treatment at 573 K under vacuum of 2 hours to eliminate possible water within the pores of the solids.

X-Ray Diffraction (XRD): Was used a D8 Advance diffractometer (Bruker), with initial theta of 5 and final of 80. The obtained patterns were then compared with the diffraction data cards of the Joint Committee of Powder Drifraction Standards [30].

Photoacoustic spectroscopy (PAS): Technique that allows to determine the minimum energy necessary for excitation of the electron, that is, its band gap energy. The conditions used were: 20Hz modulation frequency and recorded between 220 and 270 nm. The spectra were standardized with charcoal sample. The band gap energy was then calculated by Equation 1:

$$\lambda = \frac{hc}{E_{gap}} = \frac{1240}{E_{gap}} \quad (1)$$

Experimental tests of photocatalysis

Caffeine solutions (20 mg L-1) were prepared using caffeine (Vetec, 99% purity) with ultra-pure water. The reactions were carried out in a 2000 mL cylindrical reactor with 1000 mL of caffeine solution and 0.3 g of photocatalyst. The reactor was jacketed to keep the water at constant temperature ~ 23 °C, the system still contained oxygen flow (0.5 L min-1) and magnetic stirring and to obtain a homogeneous mixture. The lamp used for these experiments was installed approximately 20 cm above the aqueous solution (mercury vapor lamp with medium pressure of 125 W) and the tests were run with a time of 300 minutes. The radiations emitted by the lamp are UVA and UVB (280 to 400 nm) and the radiation incidence was measured at 5.32 mW cm^{-2}, information collected by means of a Uv light meter radiometer (Sentry ST-500).

Figure 1 shows the scheme of the experimental system. At established times, samples were collected, filtered (0.22 μm syringe filter, 13 mm diameter and nylon membrane), followed by determination of the caffeine concentration by means of a UV-Vis spectrophotometer (Femto-800XI), where at first a calibration curve was made and the wavelength of 275 nm was defined.

Figure 1. System for Photocatalysis Reactions.

The photolysis and adsorption test were performed with the same characteristics of the photocatalysis test, however, without light presence and catalysts, respectively.

RESULTS AND DISCUSSION

Synthesis of catalysts

In relation to the textural properties, the results obtained by N2 adsorption analysis are shown in Table 1 and the adsorption isotherms are showed in Figure 2, in which all the catalysts are calcined (cal) and not calcined.

Figure 2 shows that for all catalysts the adsorbed amount tends to infinity when p/po →1, which, according to the literature [30], corresponds to the overlap of multilayer adsorption characterizing macroporous solids, non-porous or mesopore. Moreover, verified that the Fe or Ag addition in the ZnO surface did not change the isotherm shape. Flores and coauthors [32] analyzing ZnO nanomaterials synthesized by ultrasound-assisted hydrolysis identified adsorption isotherms similar to those found in this paper.

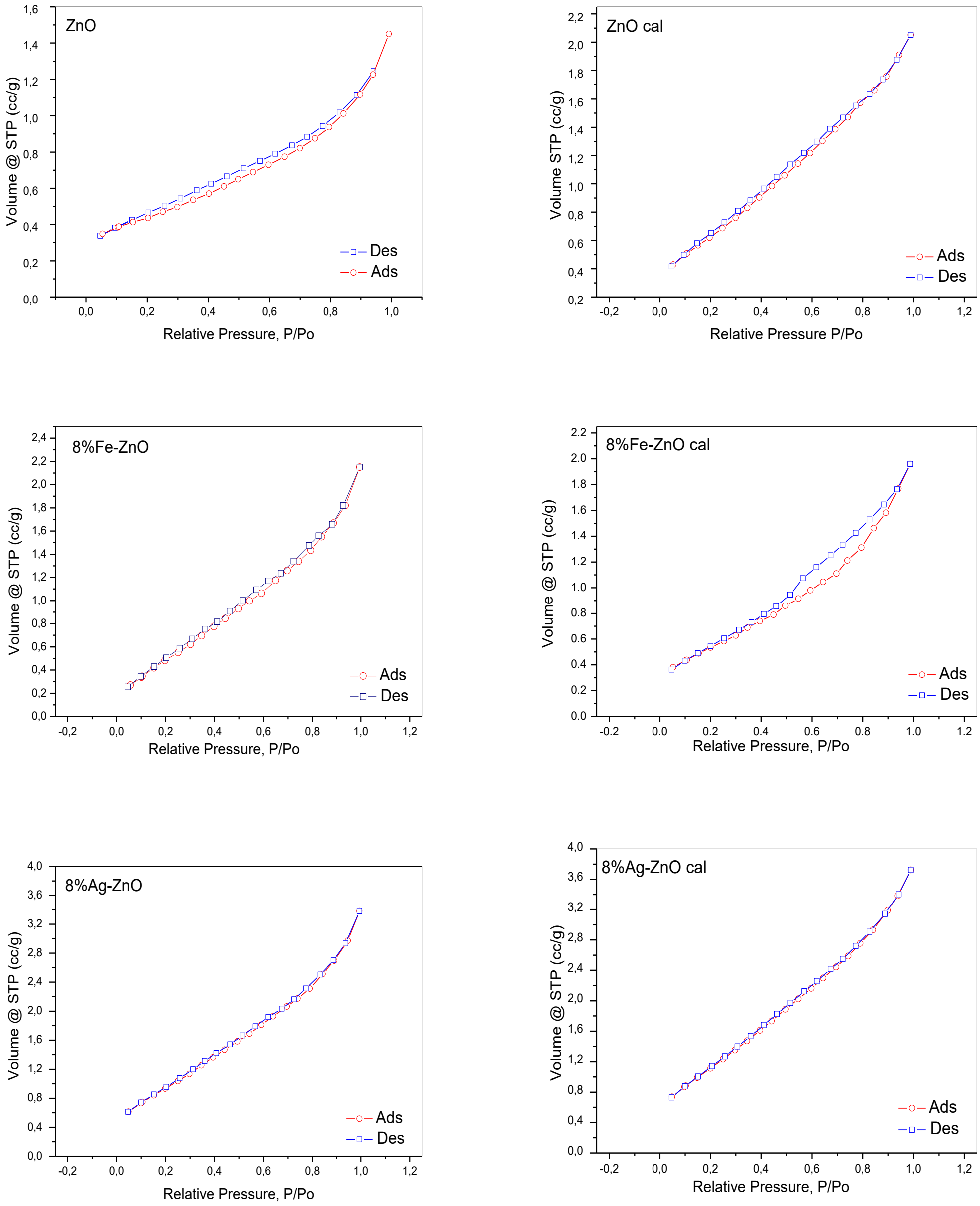

Figure 2. Adsorption isotherms.

Table 1. Specific surface area (S_0), pore volume (V_p) and mean pore diameter (d_m).

Catalyst	**S_o (m^2/g)**	**V_p (cm^3/g)**	**d_m (Å)**
ZnO	08	0.0115	29
ZnO cal	10	0.0128	26
8%Fe-ZnO	11	0.0161	31
8%Fe-ZnO cal	07	0.0099	31
8%Ag-ZnO	08	0,0113	29
8%Ag-ZnO cal	08	0,0101	27

In Table 1, it can be verified that the values obtained for the specific areas are of the same order of magnitude as those obtained for ZnO, indicating that the method of preparation of the catalysts by impregnation maintains the textural characteristics of the material used as support. Also regarding specific area, with regard to the calcination process, it is observed that this thermal treatment exerts little or no influence. However, the small increase observed in the value of the specific area with the calcination of the ZnO catalyst may be related to the release of adsorbed residues on the surface of the catalyst during the manipulation of the samples, or even that they were not totally eliminated during the drying process.

For the 8% Fe -ZnO catalyst, the thermal treatment of calcination caused a decrease in the value obtained for the specific area, indicating that for this catalyst the calcination at 400 ºC could have caused the agglomeration of the particles, for sintering, and loss of surface hydroxyl groups [28,30,33]. The results of the XRD are shown in Figure 3.

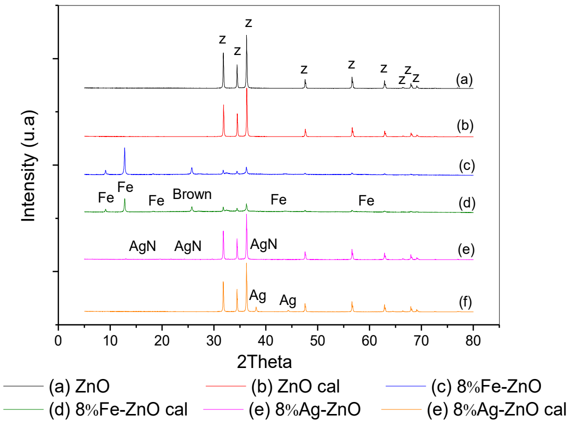

Figure 3. XRD for catalysts with ZnO calcined and non-calcined.

As shown in Figure 3, it can be seen that for pure, non-calcined and calcined zinc oxides, the characteristics of crystallinity in wurtzite hexagonal form are the most common for this material. Characteristic peaks for this material are located at approximately 2Θ= 32, 34, 36, 47, 57, 62, 66, 68 and 69º (JCPDS:19-0206). So, the thermal treatment did not alter the crystalline structure of the material. Similar results were found in literature [34] that, varying the calcination temperature of the ZnO between 350 and 450 °C did not identify change in the typical peaks of the hexagonal wurtzite of ZnO.

About the catalysts containing 8% Ag-ZnO non-calcined, besides the characteristic peaks of zinc oxide with wurtzite hexagonal crystallinity, silver nitrate (AgNO3) peaks were also identified in orthorhombic crystalline form 2Θ = 19, 22, and 36º (JCPDS:43-0649). On the other hand, silver-related peaks (Ag) with cubic crystalline system 2Θ=38, 44 and 64º (JCPDS: 87-0597) were identified for the calcined catalyst. Similar results were found by [35], when studying silver-doped ZnO nanocatalysts. The researchers identified Ag in cubic phase, with characteristic peaks located in the same position as those found in this work as well as zinc oxide in hexagonal wurtzite format.

As for the catalysts containing 8% iron (8% Fe-ZnO), the presence of characteristic peaks relative to hexagonal ZnO was observed, however, with lower intensity. For the catalysts, calcined and not calcined, iron oxide (Fe_3O_4) was found with crystalline orthorhombic system 2θ = 9, 12, 18 and 43º (JCPDS: 76-0958), more was identified in 2θ = 25º a peak related to Pigment Brown 38 (JCPDS: 47-2148).

Recent research [36] - which studied ZnO based catalysts doped with different amounts of iron, with the XRD analysis it was possible to verify that the intensity of the ZnO peaks was also smaller/less due to the addition of the metal. In the same way, they observed a decrease of the intensity of the peaks with the increase of the amount of the metal in the sample, besides, there was even small displacement of these same peaks, which was not observed in this work. For the results of the PAS, Table 2 shows the values obtained.

Table 2. Band gap and absorption threshold (λ) of the catalysts calcined and non-calcined

Catalyst	Band Gap (eV)	λ (nm)
ZnO	3.12	397
ZnO cal	3.11	398
8%Fe/ZnO	3.37	367
8%Fe/ZnO cal	3.65	339
8%Ag/ZnO	3.92	316
8%Ag/ZnO cal	3.88	319

The band gap obtained for the non-calcined ZnO was approximately 3.12 eV and for the calcined ZnO was 3.11 eV, this small difference indicates that the calcination process at 400 ºC exerted little or no influence on the ZnO band gap energy. On the other hand, in general, both iron and silver addition led to an increase in ZnO band gap energy. According to Rodnyi and Khodyuk [37] the addition of some elements, such as Ga, In, Mg, can cause a shift of the optical adsorption edge of the crystals causing the band gap value to increase, which may have happened in this work. With respect to the wavelength (λ) calculated from Equation (1) it can be verified that all the photocatalysts are in the ultraviolet region λ <400 nm.

Experimental tests of photocatalysis

The concentration curves of caffeine versus reaction time are shown in Figure 4.

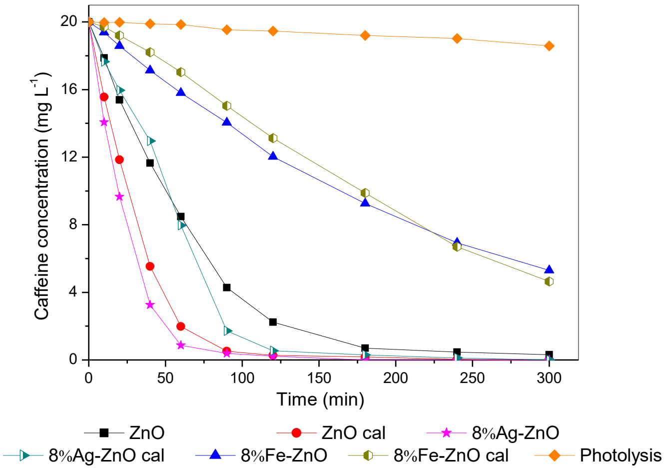

Figure 4. Photolysis and photocatalytic degradation of caffeine, ph= 6.5; T=23 ºC; Concentration of catalysts = 0.3 g L-1 and 125 W lamp.

In general, all the catalysts studied showed good caffeine degradation, that is, above 70% at the end of the 300 minutes of reaction.

In order to evaluate the kinetics of caffeine degradation not only visually the first order model expressed by ln(C0/C)=kt. In the tests, 83.3% of the cases the correlation coefficient (R²) was above 0.99. The k velocity constant values are presented according to the sequence in order of decreasing performance: 8%Ag-ZnO non-cal (k=-0.039) > ZnO cal (k=-0.034) > 8%Ag-ZnO cal (k=-0.013) > ZnO non-cal (k=-0.012) > 8%Fe-ZnO cal (k=-0.003) > 8%Fe-ZnO non-cal (k= 6.4 x10-6). The catalyst with 8%Ag-ZnO non-cal, in 120 minutes already showed a degradation of the caffeine of 100%.

For the catalysts of calcined and non-calcined ZnO, it was verified that both the band gap energy and the crystalline structure of ZnO were practically unchanged with the calcination, an increase in the specific area (8 to 10 m² g-1) which may have favored the performance of the catalyst. According to Pan and coauthors [34] larger specific area and larger porous structure favor the adsorption of the reagents on the surface of the ZnO that can facilitate the reaction at the interface, in addition the porous structure improves the optical absorption through the dispersion of light.

Still in analysis of Figure 3, we note that the addition of iron did not favor the performance of the ZnO catalyst, since 8% Fe in ZnO non-calcined and 8% Fe in ZnO calcined presented at the end of 300 minutes a degradation of 73.5% and 76.8%, respectively.

On the other hand, the addition of silver increased the catalytic activity in relation to the pure ZnO, however the calcination negatively influenced the performance in the first hour of reaction, since the caffeine degradation was approximately 96% and 60% respectively for the samples non-calcined and calcined. Although the non-calcined and calcined 8% Ag-ZnO catalysts reach 100% caffeine degradation at the end of the 300 min reaction. Still on the catalysts with Ag, when we observe the XRD spectra, it is noted that there is difference in composition of the catalyst structure (8%Ag-ZnO) calcined and non-calcined, that is, AgNO3 for the catalyst non-calcined and just Ag for the catalyst calcined. Possibly the presence of AgNO3 favored the catalytic activity of ZnO.

Elhalil and coauthors [38] studied ZnO-$La_2O_2CO_3$ nanomaterials as catalysts and found that catalysts when doped with Ag showed better experimental results compared to pure ZnO and P-25, the best result was obtained with 5% Ag with degradation 99.4% after 40 minutes of reaction.

Chuang and coauthors [39] investigated the degradation of caffeine by TiO2 nano-powders through a modified HPPLT and found that there was a total pollutant degradation within 360 min of reaction. Sacco and coauthors [40] used a vanadium-doped TiO2 catalyst synthesized by the sol-gel method in caffeine degradation and found that the amount of 1 mg of Vanadium in TiO_2 significantly increased catalyst performance showing 96% degradation in 360 min. The catalysts studied in this study, besides being synthesized by a simple methodology, showed good results of caffeine degradation when compared to those already presented in the literature.

The result obtained with the photolysis test showed that the caffeine degradation only in the presence of the irradiation of the lamp of 125 W, reached a percentage of the degradation, at the end 300 minutes of reaction of only 7% , and in the first 120 minutes the degradation remained below 2.5%, which demonstrates the need to the introduce a photocatalyst.

The adsorption test is shown in Figure 5. Thus, as the photolysis test, the adsorption test was not efficient for caffeine degradation complete. This leads to the need for the presence of radiation and catalysts for the complete degradation of pollutant.

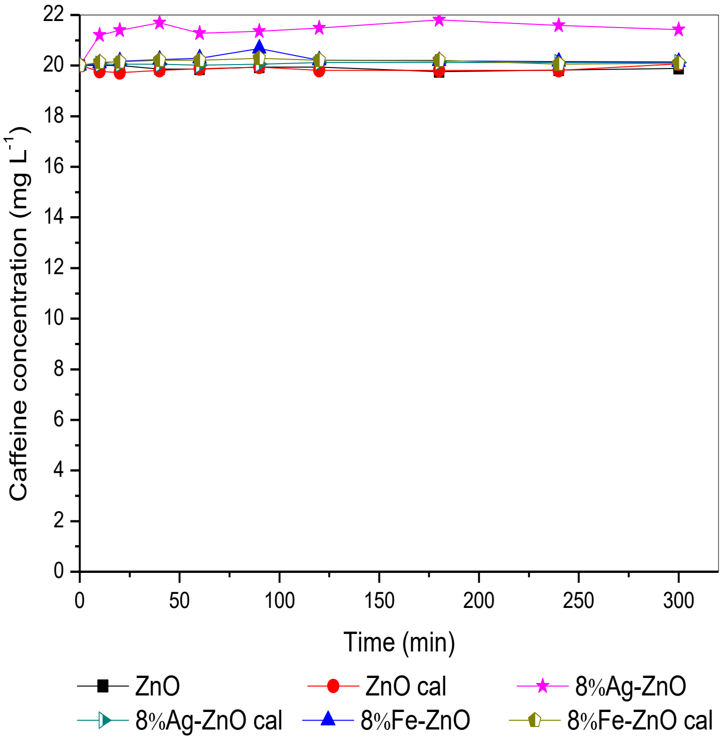

Figure 5. Adsorption tests**.**

CONCLUSION

In the present work, in general, the catalysis based on ZnO promoted with iron and silver, showed a good degradation of caffeine, the difference in the performance of each catalyst can be better understood with the help the characterization techniques that presented important results with respect to its textural and structural characteristics, showing, for example, that the presence of the silver nitrate favored the degradation caffeine reaction.

In relation the experimental photolysis test it was possible to conclude that only in the presence of the irradiation was not efficient to satisfactorily remove the caffeine present in aqueous solution. Soon, the 8%Ag-ZnO, which presented itself as the best catalyst, could be applied in degradation studies of a mixture of emerging contaminants and on a larger scale tested here.

Acknowledgments: The authors wish to thank the Brazilian Agencies CNPq and CAPES for the financial support of this study, UTFPR and COMCAP – UEM for the analyzes carried out.

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