Performance Evaluation of Catalysts of ZnO in Photocatalytic Degradation of Caffeine Solution

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Recent studies has shown that caffeine, a substance present in beverages such as coffee, in pharmaceuticals products and food, it is present in surface water in several countries. In Brazil, a study conducted in 2014, identified caffeine in public water supply in 22 Brazilian cities including the capital of the Federal District with a 93 % detection rate. The degradation of caffeine in aqueous solution has been studied by different methods. The heterogeneous photocatalysis is highlighted by presenting good results in degradation of emerging pollutants. This study focused on the characterization and evaluation of the photocatalytic activity of ZnO (calcined at 400 °C and noncalcined) for the caffeine degradation. The characterization of materials were perfomed by thermogravimetric analysis, Specific surface area (BET method), pore diameter and pore volume, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and spectroscopy photoacoustic. The analysis results as well the materials characterization indicated that the calcination at 400 ºC modified ZnO structure. For the ZnO catalyst (calcined at 400 °C) the photocatalytic activity indicated a caffeine solution degradation of 70 % after around 40 minutes of reaction. On the other hand, for the noncalcined catalyst the degradation, in the same period, was of 40 %. Both catalysts exhibited different kinetic curves, but the calcined ZnO obtained a more sharply response at the beginning of reaction. The reaction was studied in total time of four hours and the results presented a degradation approximately 100 %.

1. Introduction

Caffeine is an organic substance belonging to the class of methylxanthines, its structure is characterized as 1,3,7-trimethylxanthine having its formula and molecular weight as $C_8H_{10}N_4O_2$ and 194.19 g mol^{-1}, respectively (Spiller, 1998; Canela et al., 2014). Caffeine is present in beverages such as coffees, teas, soft drinks, chocolates, some drugs, which makes it a widely consumed substance in the world (Iannone et al., 2015).

When ingested, caffeine has a half-life of approximately 3 to 6 hours in the human body and its moderate consumption does not present risks to human health, however when excreted by urine reaches domestic sewage and its presence in water resources is studied as parameter of the presence of anthropic activity (Trovó et al., 2013; Fagnani et al., 2013).

The concentration of caffeine in raw domestic sewage varies with some aspects such as: consumption profile of the population of the studied area and time of year among others (Canela et al., 2014). Studies have identified caffeine in post-treatment waters and effluent treatment plants and in public water supply (Machado et al., 2016, Canela et al., 2014, Sui et al., 2010, Kosma et al., 2010).

In Brazil, a study identified the presence of caffeine in waters for human consumption in almost all Brazilian capitals, in which in the northeast region detected a frequency of 77 % of caffeine, while in other regions the frequency was 100 %. The concentration of caffeine in nine of the twenty-two capitals studied was above 100 ng L^{-1}, these results reveal the inefficiency of sewage and water treatments employed in the country (Machado et al., 2016).

In this context, researchers are constantly seeking to develop increasingly intelligent and economical processes in the degradation of substances present in surface water and drinking water, such as pharmaceuticals, personal hygiene products, finally compounds called emerging pollutants in which caffeine is classified, since the processes currently used are inefficient in the removal of these compounds (Cunff et al., 2015). Among the investigated processes, there is the heterogeneous photocatalysis, in which the semiconductor used in the reaction plays a very important role, being its structural, morphological and physical characteristics factors that can influence whether or not the pollutant is degraded.

Between the catalysts, zinc oxide (ZnO) is a semiconductor with a strong oxidation capacity and good photocatalytic propertie; in addition, when compared to TiO_2, zinc oxide presents a relatively lower cost and, in relation to its structure, this can be presented in three different forms: rocksalt, cubic, or wurtzite, being the last the most common form due to the greater thermodynamic stability among the others (Lee et al., 2016).

Procedures such as the calcination and addition of additives or metals to the semiconductors can modify the structure, surface area and distribution of sites and thus influence the performance of the catalyst in the reaction (Vaiano et al., 2016). Therefore, the objective of this research was to study the performance of calcined and uncalcined zinc oxide in the degradation of caffeine present in water.

2. Experimental procedure

2.1 Preparation of photocatalysts

The zinc oxide catalyst (supplied by Dinâmica with over 99 % degree of purity) was submitted to the process of calcination in a muffle following the temperature ramp indicated in Figure 1.

The dashed line indicates the used heating rate of 278 K min^{-1} then the temperature remained constant at 373, 473, 573 for 30 min and 673 K for 240 min.

2.2 Characterization of the photocatalysts

The characterization of the catalysts has great importance to anticipate and explain the behavior of the catalysts in the reactions, in this work in particular, analyzes were performed by the following techniques:

2.2.1 Thermogravimetric analysis (TA)
In this characterization technique was used synthetic air with 30 mL min^{-1} flow with 283 K min^{-1} heating rate.

2.2.2 Pore Properties (B.E.T. Method)
Porous properties such as specific surface area, mean pore diameter, and pore volume were established using a QUANTACHROME Analyzer – Model Nova-1200 with N2 adsorption at 77 K. Both calcined and non-calcined samples were submitted to these analyses. The samples had been previously submitted to a thermal treatment at 573 K, under 2-hourvacuum to eliminate any existing water within the pores of the solids.

2.2.3 X-ray diffraction (XRD)
The samples were measured in a Rigaku-Denki Diffractometer with Cu-Kα radiation (λ= 1.5406 Å) at a voltage of 140 V and a current of 40 mA. The patterns obtained were then compared with the diffraction dataset cards from the Joint Committee of Powder Diffraction Standards.

2.2.4 Fourier transform infrared spectroscopy (FTIR)
For the realization of this characterization, a model of the Vertex 70 v equipment Bruker model with operational data was used: Scans: 128, Range of 4000 to 400 cm^{-1}.

2.2.5 photoacoustic spectroscopy
The photoacoustic spectroscopy measurements in the UV–VIS spectral regions were performed using a lab-made experimental setup. We obtained the monochromatic light through a 1000-Watt xenon arc lamp (Oriel Corporation 68820) and a monochromator model 77250, also by Oriel Instruments. We modulated the light beam using a mechanical chopper – Stanford Research Systems SR540. A lab-made photoacoustic cell was designed to have a very low volume – made of aluminum block, machined to hold samples with dimensions up to 5 mm diameter and 1 mm thickness, which allows light to enter through a high transparent quartz window of 6 mm diameter and 2 mm thickness. The distance of the microphone chamber was 15 mm; it was connected to the sample holder room through a 1-mmdiameter duct. The capacitive microphone used was the 12-mm diameter Bruel&Kjaer model 2639 – very sensitive, presenting a gain of 50 mV/Pa, and flat frequency response between 1 Hz and 10 kHz. We used a lock-in amplifier by EG & G Instruments, model 5110. All of the photoacoustic spectra were obtained at a 20 Hz modulation frequency and recorded between 220 and 720 nm. Data were acquired using a personal computer, and the PAS spectra were normalized with respect to the carbon black signal.

The band gap energies were established through Eq. (1):

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

(1)

Where h is Planck's constant (4,13 x 10^{-15} eV. s), c is the speed of light in the vacuum (3.0 x 10^{17} nm s^{-1}), λ is wave-length (nm) and E_{gap} is the band gap energy in eV units. The direct method was applied to obtain the values, i. e., m=2.

2.3 Photocatalytic experiments

The stock solutions of caffeine (20 mg L^{-1}) were prepared to Caffeine anhydrous (Vetec, 99 % minimum purity) solution water (Milipore Mili-Q water). The reaction was carried out in a 2000 cm³ cylindrical reactor with 1000 cm³ of caffeine solution, to this system 0.3 g of the photocatalyst was added. The reaction was carried out with the jacketed reactor to maintain the constant temperature at an average temperature of 296 K, oxygen air flow, a magnetic stirrer and a medium pressure mercury lamp of 125 W was coupled just above the reactor. At regular time intervals, samples were collected, filtered (0.22 µm pore size filter, diameter 13 mm and membrane type nylon) and the caffeine concentration was determined on a UV-Vis spectrophotometer (Femto-800 XI).
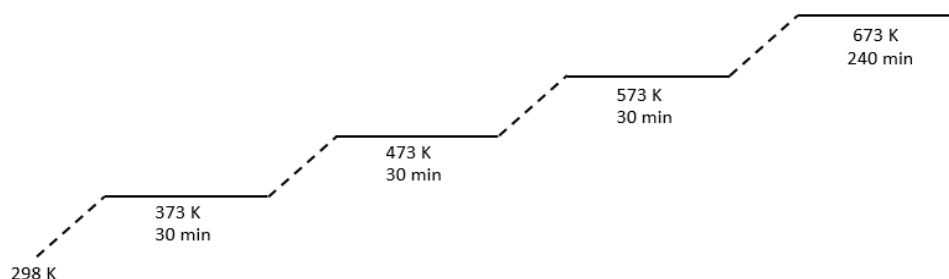

Figure 1: Heating ramp for calcination.

2.4 Adsorption

The adsorption tests were performed applying the same procedure of item 2.3, but without presence of light.

3. Results

3.1 Characterization

The results of the specific surface area (S_o), the pore volume (V_p) and the average pore diameter (d_p) of the calcined and uncalcined ZnO are presented in Table 1. Table 2 indicates the results referring to the photoacoustic spectroscopy, that is, band gap values obtained for calcined and non-calcined catalysts. Figures 2, 3 and 4 present the results obtained by TA, XRD and FTIR, respectively.

3.2 Evaluation of photocatalytic activity

The results of the photocatalysis test are shown in Figure 5 where it is possible to identify the behavior of the caffeine concentration over time.

Table 1: Specific surface area (S_o), pore volume (V_p) and average pore diameter (d_p) of the ZnO calcined and non-calcined.

Catalysts	Specific surface area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (Å)
ZnO (non-calcined)	7.895	0.01154	29.23
ZnO (calcined)	9.835	0.01285	26.12

Table 2: The band gap result for the ZnO calcined and non-calcined.

Catalyst	Band gap (eV)	Absorption threshold (mm)
ZnO Non-Calcined (commercial)	3.12	398
ZnO Calcined	3.11	399

3.3 Adsorption

The results of the adsorption performed with calcined and non-calcined ZnO catalysts are shown in Figure 6.
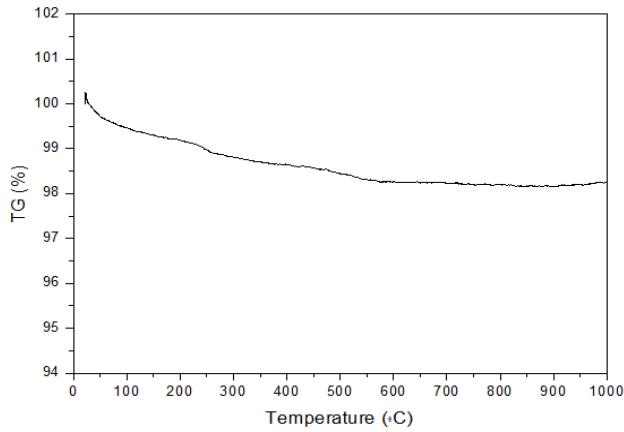

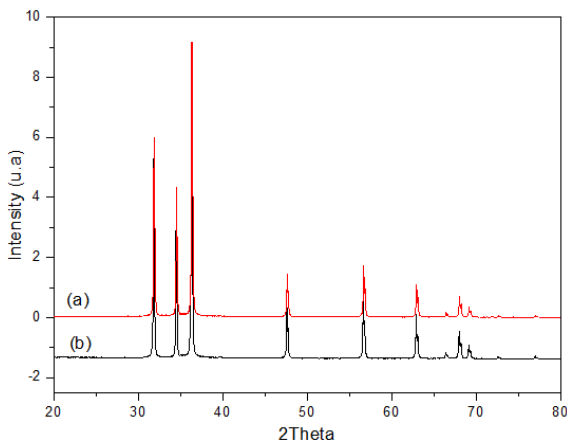Figure 2: thermogravimetric analysis for photocatalyst ZnO non-calcined.

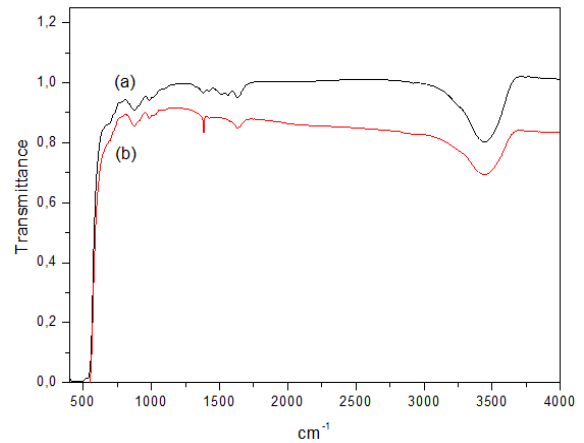Figure 3: XDR patter of the ZnO (a) calcined and (b) non-calcined

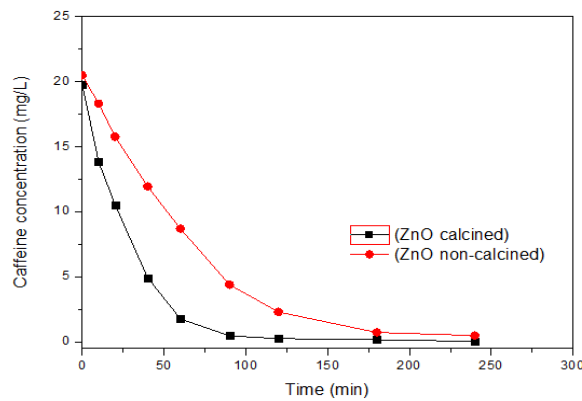Figure 4: FTIR of the ZnO (a) non-calcined (b) calcined.

Figure 5: Evolution of the concentration of caffeine for the photocatalytic process with ZnO calcined and non-calcined.
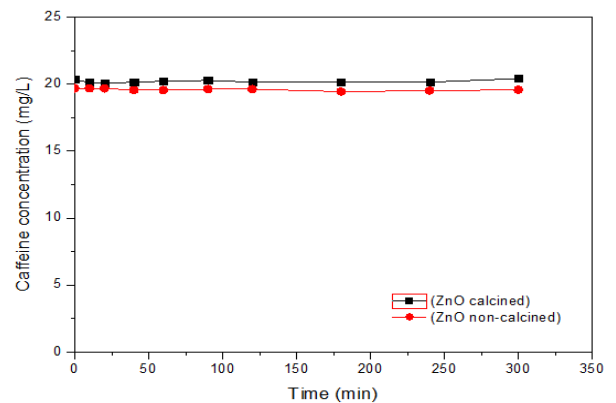
Figure 6: Concentration of caffeine for ZnO calcined and non-calcined – adsorption test.

4. Discussion

4.1 Characterization

By the analysis of Table 1, it was observed that with the thermal treatment (calcination) the release of residues that were adsorbed on the surface of the catalyst occurred and as a consequence an increase in the surface area was observed. Fincur et al., (2017) found a surface area for the ZnO (9 m²/g and 6 m²/g) similar with these study, another study that synthesized ZnO by the hydrothermal method found a surface area of 5.69 m²/g (Kansal et al., 2011).

In the thermogravimetric analysis (Figure 2) the y-axis indicates the mass variation of ZnO as a function of temperature (x-axis), thus, this analysis was performed only with uncalcined zinc oxide, since this technique aimed to identify the best calcination temperature. In response to this test it can be seen that for ZnO there was a small percentage of mass loss, in which up to 373 K had a loss of water and in the above temperatures the loss of other compounds possibly adsorbed on the surface of the catalyst particles.

The results of the photoacoustic spectroscopy revealed little difference between the band gap energy for the two catalysts analyzed, in which the lowest value was of the calcined ZnO catalyst.

In the evaluation of the XRD spectra it can be verified that in both catalysts the same peaks were observed, corresponding to the hexagonal wurtzite crystalline structure, which is the structure commonly found for ZnO, similar results were found by Kumar et. Al., (2013) in the characterization of zinc oxide calcined at different temperatures.

According to Pan et al. (2016) varying the calcination temperature of ZnO between 350 and 450 °C, all samples showed the typical peaks of the hexagonal wurtzite form of ZnO. The authors also verified that with the increase of the ZnO calcination temperature the peaks showed higher intensity, and this indicates an increase in the semiconductor particle size and crystallinity. In the present research, it can be observed that with the calcination there was also a higher intensity of the peaks between 30 and 40 cm^{-1} and an increase in the surface area.

In relation to the curve obtained by the characterization of the FTIR, the peaks located before and near 600 cm^{-1} correspond to the Zn-O metal oxide binding, while the peaks between 1400 and 1500 cm^{-1} are related the C=O bonds, the band near the 1625 cm^{-1} is attributed to OH binding and the band near 3500 cm^{-1} is probably attributed to the presence of water in the KB matrix (Kulkarni; Shirsat, 2015; Khalil et al., 2014).

Characterizations showed that calcination had an influence on the specific surface area and pore volume, however this thermal treatment (calcination) has little or no influence on the band gap energy of the two catalysts and on their crystalline structures shown in XRD and FTIR.

4.2 Photocatalysis test

The Figure 5 presents the result obtained by the photocatalysis test, in which it can be observed that the two curves (ZnO calcined and not calcined) reaches the detection limit of the equipment of the axis corresponding to the concentration of caffeine. However, the calcined ZnO exhibits a better result with a total caffeine degradation of about 100 % in 120 min and the uncalcined ZnO catalyst reaches at the same time a degradation of approximately 89 % caffeine degradation. It is also noted that, for the calcined ZnO, after 120 minutes, the degradation of the pollutant is constant, while the uncalcined ZnO continues to degrade the caffeine, and when it reaches a time of 180 min the degradation remained constant in approximately 97 %.

Although the two photocatalysis systems can achieve a good degradation of the caffeine present in the water (above 96 %), with curves of the same behavior, the calcined catalyst presents a better reaction kinetics and consequently a better performance of the catalyst that probably has relation with its characteristics, such as band gap energy, morphology, surface area, porosity, among others (Band et al., 2006).

In this study, the performance difference of the catalysts analyzed is probably related to the heat treatment (calcination), where a considerable increase in the specific surface area can be noticed. According to Pan et al., (2016) greater surface area and larger porous structure favor the adsorption of reagents in ZnO which may facilitate the reaction at the interface, and the porous structure improves optical absorption through light scattering.

5. Conclusions

The result of the evaluation of the photocatalytic reaction indicated that the caffeine degradation was directly influenced by the thermal treatment used to the ZnO catalyst. The calcined catalyst exhibited a higher specific surface area thus favoring an increase in the reaction rate when compared to the non-calcined ZnO. The photocatalytic process proved to be efficient for the degradation of 100 % of the caffeine, using the ZnO calcined at 673 K in 120 min

Reference

Canela M. C., Jardim W. F. Sodré F. F. Grassi M, T., 2014, Cafeína em águas de abastecimento público no Brasil / Instituto Nacional de Ciências e Tecnologias Analíticas Avançadas. São Carlos: Editora Cubo.

Cunff J. L., Tomasic V., Gomzi Z., 2015, Preparation and Photoactivity of the Immobilized TiO_2/chitosan Layer. Chemical Engineering Transactions, 43, 865-870, DOI: 10.3303/CET1543145

Fagnani E., Guadagnini R. A., Silva G. A., Guimarães J. R., 2013, Degradação da cafeína e azul de metileno por processos oxidativos avançados (POA). Holos Environment, Campinas,13, 85-97.

Fincur N. L., Krstíc J. B., Sibul F. S., Sojic D. V., Despotovíc V. N., Baníc N. D., Agbaba J. R., Abramovíc B. F., 2017, Removal of alprazolam from aqueous solutions by heterogeneous photocatalysis: Influencing factors, intermediates, and products. Chemical Engineering Journal, 307, 1105-1115.

Iannone R., Miranda S., Riemma S., Marco I., 2015, Combined Semi-continuous and Discrete Simulation Model to Optimize a Decaffeination Process Based on Supercritical CO_2. Chemical Engineering Transactions, 43,1453-1458, DOI: 10.3303/CET1543243

Kansal S. K., Ali A. H., Kapoor S., Bahnemann D. W., 2011, Synthesis of flower like zinc oxide nanostructure and its application as a photocatalyst. Separation And Purification Technology, 80, 125-130.

Khalil M I., Al-Qunaibit M. M., Al-zahem A. M., Labis J. P., 2014, Synthesis and characterization of ZnO nanoparticles by thermal decomposition of a curcumin zinc complex. Arabian Journal Of Chemistry, 7, 1178-1184.

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.

Kulkarni S., Shirsat M. D., 2015, Optical and Structural properties od Zinc Oxide Nanoparticles. International Journal Of Advanced Research In Physical Science (IJARPS), 2, 14-18.

Kumar S. S., Venkateswarlu P., Rao V. R., Rao G. N., 2013 Synthesis, characterization and optical properties of zinc oxide nanoparticles. International Nano Letters, 330, 1-6.

Lee K. M., Lai C. W., Ngai K. S., Juan J. C., 2016, Recent developments of zinc oxide based photocatalyst in water treatment technology: A review. Water Research, 88, 428-448.

Machado K. C., Grassi M .T., Vidal C., Pescara I. C., Jardim W. F., Fernandes A. N., Sodré F. F., Almeida F. V., Santana J. S., Canela M. C., Nunes C. R. O., Bichinho K. M., Severo F. J. R., 2016, A preliminary nationwide survey of the presence of emerging contaminants in drinking and source waters in Brazil. Science Of The Total Environment, 572, 138-146.

Pan L., Muhammad T., Ma L., Huang Z., Wang S., Wang L., Zou J. J., Zhang X., 2016, MOF-derived C-doped ZnO prepared via a two-step calcination for efficient photocatalysis. Applied Catalysis B: Environmental, 189, 181-191.

Spiller, Gene A., 1998, Caffeine. Los Altos, California: Crc Press.

Sui Q., Huang J., Deng S., Yu G., Fan Q., 2010, Occurrence and removal of pharmaceuticals, caffeine and DEET in wastewater treatment plants of Beijing, China. Water Research, 44, 417-426.

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.

Vaiano V., Iervolino G., Sannino D., 2016, Photocatalytic Removal of Tartrazine Dye from Aqueous Samples on $LaFeO_3$/ZnO Photocatalysts. Chemical Engineering Transactions, 52, 847- 852, DOI: 10.3303/CET1652142