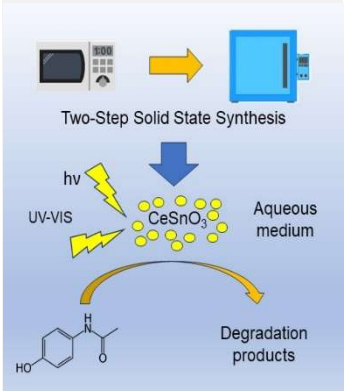
Catalytic and Photocatalytic Degradation of Paracetamol Intermediated by a Novel Catalyst of Empirical Formula $CeSnO_3$

ORAL/POSTER
Ph.D. Student: Y
Journal: ESPR

L. Hansen[1], *D. U. Rizzana*[2], *M.A.R. Siqueira*[2], *D. Weibel*[1] . *(1) Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves 9500, Porto Alegre , Brazil, hansen.lcs@gmail.com (2) Universidade Feevale, RS-239 2755, Novo Hamburgo, Brazil.*



In this work, we describe the characterization of a novel catalyst of empirical formula $CeSnO_3$, as well as its performance in the degradation of paracetamol (PCT, acetaminophen). Regarding the characterization of the catalyst, EDS yielded an empirical formula $Ce_1Sn_{1.16}O_{3.02}$. XPS showed the superficial presence of Ce(IV) and possibly Ce(III) as well, and also confirmed the presence of Sn and O on the surface of the catalyst. The bandgap of the material, determined via UV-VIS diffuse reflectance spectroscopy, was found to be 2.70 eV. XRD evidence suggests the presence of CeO_2 and SnO_2 in the catalyst. As for the degradation experiments, the catalyst was able to remove 44.5% of paracetamol from a 1 ppm solution upon 6 hours of UV-VIS irradiation. The catalyst was also able to remove 33.5% of PCT in a dark reaction in 6h. Further characterization of the catalyst is under way.

Introduction

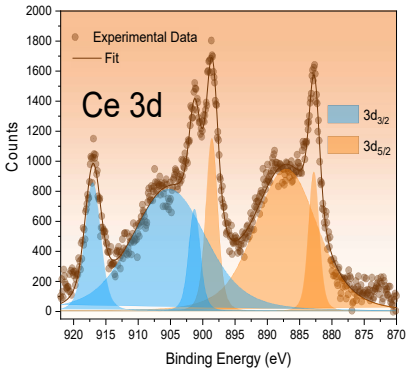
Paracetamol (PCT), also known as acetominophen, is a common over-the-counter drug used to treat fever and mild to moderate pain. Due to its excessive usage, PCT has been found in concentrations ranging from 0.1 to 300 mg L^{-1} in effluents of many countries worldwide [1]. PCT is regarded as an emerging pollutant, and its increasing concentrations result in the possiblity of occurence of toxic phenomena in organinsms in receiving water bodies [2]. In this sense, the development of materials that may help in removing PCT from the environment is a necessity. The objectives of this work are thus 1) to characterize a novel catalyst synthesized using a simple two-step method via Energy Dispersive X-Ray Spectroscopy (EDS), X-Ray Photoelectron Spectrosopy (XPS), UV-VIS diffuse reflectance spectroscopy and X-Ray Diffraction (XRD), and 2) to evaluate the performance of the synthesized catalyst in removing PCT from aqueous solutions via photocatalysis and non-radiative catalysis.

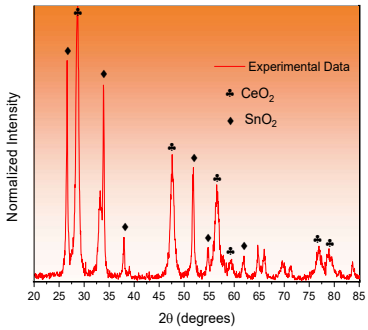
Materials and Methods

EDS analysis was performed in a Scanning Electron Microscope, with a beam energy of 20 kV, after metallization of the sample with gold. Twenty-five randomly chosen points of the sample were probed, and an elemental map of each point was acquired, as well as the mass and atom % of each element detected.XPS was performed using a non-monochromated Al Kα radiation as the excitation source and a conventional electron spectrometer (Omicron Gmbh, Germany). UV-VIS diffuse reflectance spectroscopy analysis was conducted by scanning the surface of the sample with wavelengths from 1800 to 200 nm, with a source bandwitdth of 2.0 nm. XRD was performed with a monochromated Cu Kα source at a 2θ interval of 3-90° with a pace of 2θ = 0.05°. The degradation experiments were carried out in a custom made reactor. The outer part of the reator is cooled in a thermostatized water bath (5°C). A commercial 400 W medium-pressure mercury vapor lamp, without its external bulb was employed. The radiation was filtered by a water filter, being the water supplied by an ultrathermostatized bath (Marconi, Brazil) kept at 2°C.Therefore, only UV and visible light reached the photocatalyst. Two dark catalysis experiments were conducted at room temperature in 500 mL Erlenmeyer flasks under agitation for 6h with a 1 ppm paracetamol solution with 0.1% of the catalyst in suspension. Two photocatalytic degradation experiments were sequentially conducted with an irradiation time of 6h after a 1h equilibration step. Agitation was provided by a magnetic stir bar placed inside the reactor. Four hundred-fifty mL of solution were loaded into the reactor for each experiment. Two photolysis experiments were also conducted under the same conditions as the photocatalysis experiments. Paracetamol was quantified in a Shimadzu LC-20 liquid chromatograph (Shimadzu Corp., Japan) using the external standard method (concentrations of 0.125, 0.250, 0.500, 0.750, and 1.000 mg L^{-1}). Conditions were the following: flow rate = 1.500 mL/min, column temperature = 32.0 °C, UV-VIS detector set at 243 nm, isocratic elution (60:40 acetonitrile:water)

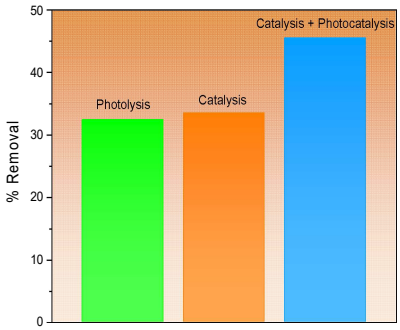
Results and Discussion

Figure 1 shows the fit of the obtained XPS data for Ce. Figure 2 shows the X-Ray diffractogram of the catalyst :





The Ce 3d spectrum (Figure 1) is consistent with Ce (IV). The broad features, however, suggest the presence of Ce(III) as well. The presence of Sn is confirmed by its XPS spectrum (not shown) with its characteristic spin-orbit splitting of 8.40 eV, the peaks being located at 487.10 and 495.50 eV. The oxygen 1s spectrum (not shown) shows a metal oxide component at ~530 eV, thus confirming the presence of O bound to metals, as well as an adsorbed O/OH component at 531.72 eV, which can be attributed to adsorbed water. The XRD diffractogram (Figure 2) suggests the presence of both CeO_2 and SnO_2 [3,4]. $CeSnO_3$ peaks may be coincident with the oxides' peaks. Only Ce, Sn and O were conistently detected in all scanned points of the sample in the EDS analysis. Other, unconsistently detected, elements include Al, Cl and C, which amounted to less than 5% of the sample in mass.The empirical formula obtained by EDS was $Ce_1Sn_{1.16}O_{3.02}$. The bandgap of the material obtained via the Tauc plot of the UV- VIS diffuse reflectance data yielded a bandgap of 2.70 eV, showing that the material is indeed a semiconductor and absorbs partly in the visible spectrum. The catalyst exhibited both catalytical and photocatalytcal activity in the degradatation of PCT, as shown in Figure 3:



The catalyst was able to remove 33.5% of PCT upon 6h of agitation at room temperature (24°C) without irradiation, compared to 32.4% of removal of PCT from solution upon 6h of UV-VIS irradiation. Irradiation of the PCT/catalyst solution/suspension for 6h yielded 44.5% removal of PCT, thus showing that the catalyst also has photocatalytical activity in the removal of paracetamol from an aqueous solution.

Figure 1. Ce 3d XPS spectrum of the synthesized catalyst
Figure 2. XRD diffractogram of the synthesized catalyst
Figure 3. Removal of PCT via photolysis, catalysis and catalysis plus photocatalysis

Conclusions

A catalyst of empirical formula $Ce_1Sn_{1.16}O_{3.02}$ was synthesized and characterized by a variety of methods. Further characterization is under way. The catalyst exhibited both catalytic and photocatalytic activity in the degradation of Paracetamol from aqueous solutions, being able to remove 33.5 and 44.5% of PCT from aqueous media, respectively.

References

[1] J.M. Peralta-Hernández, E. Brillas, *Chemosphere*, 313 (2023) 137411.
[2] J. Zur *et al*. *Environmental Science and Pollution Research*, 25 (2018) 21498.
[3] A. Debataraja *et al*. *Procedia Engineering*, 170 (2017) 60.
[4]S A.A.R. Sayyed *et al*. *Bulletin of Materials Science* , 39 (2016) 1381.