# CuO/Activated Carbon for Catalytic Oxidation of Resistant Organics

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## Introduction

When organic pollutants are not biodegradable, it is necessary to employ physicochemical methods for their degradation instead of biological ones. The tested technologies are incineration, chemical oxidation and wet air oxidation [1]. All of them involve high costs to process industrial wastewaters. Nevertheless, wet air oxidation with a catalyst (specially in heterogeneous phase) has an excellent future as a better alternative. Transition metals, such as Cu, Pt, Ni or Fe have been tested with good results [2]. There are technologies that use the active agent supported over a solid such as zirconia or titania.[3], [4]. In that way, the treated water can be separated easily from the catalyst. But the solids and the metals used in those processes are very expensive. There are studies about other supports such as alumina or alumina/ceria [5]. One of the most studied supports now a day, is activated carbon as a support of an active agent, because of its special physicochemical characteristics, that is, shape and distribution of pores and high superficial areas [6], [7], [8].

Since a few years ago, a staff of the Universidad Nacional de San Juan has been developing a reactor to obtain activated carbon (AC) of olive or damask core, poplar, eucalyptus, etc., by water vapor at about 800 K. All carbons come from regional agricultural industries and they have been found to have very good physicochemical properties [9]. In this work, those carbons have been used as a support of CuO to oxidation of organics compounds (methylene blue - MB- and polyvinyl alcohol - PVA-) with oxygen, in aqueous phase. The advance of the reaction is reported as percent of abated organic. Very good results at relatively low temperatures and pressures have been obtained.

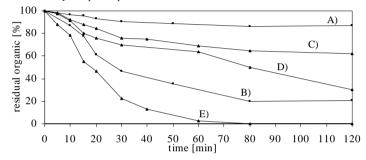
### Materials and Methods

Activated carbons from olive and damask cores were used as supports. Their textural properties have been measured. The catalysts were formulated with cupric nitrate (5% Cu weight) as a precursor of the active agent, using the soaking method, for 30 h. The obtained solid was filtered, dried at 378K and thermal treated to discompose the nitrate salt, at about 830K and  $N_2$  atmosphere for 18 h. The organics tested as prove molecules in catalytic oxidation tests were MB and PVA. The employed oxidant was high purity  $O_2$ . The reactions tests were carried out in a 1 L Parr batch reactor and the composition of no converted organics were measured in a 4001-Wayers UV-visible spectrophotometer. The monitoring of MB concentration was directly made, but to detect PVA, a complex with iodine was necessary. In order to determine the only catalytic reaction, two blank tests were performed. One of them, to determine the adsorption extent, was carried out in  $N_2$  atmosphere. The other one was done with the solution of the organic and  $O_2$  without the catalyst at the same reaction conditions, in order to measure the non catalytic oxidation. The experimental tests were performed at temperatures between 323 and 428K. The partial pressure of  $O_2$  was about 0.2 MPa in all tests. The development of reaction is measured by percent of residual organic; that is, (remnant

organic concentration/initial organic concentration) x 100. In all cases, 500 mg/L of MB or PVA was used, in contact with 200 mg of catalyst. The superficial areas of used carbons are about 800-900  $m^2/g$ .

#### Results and Discussion

As shown in Figure 1, the reaction with MB demonstrated a good response to quite low temperature (353K) given that adsorption is small at a temperature of 323K and decrease at higher ones. To achieve PVA degradation, it was necessary to use higher temperatures, as one can expect, because PVA is more resistant than MB. Good results were obtained, and PVA can be destroyed in 1 h at 428K at relatively low partial pressure of  $O_2$ .



**Figure 1.** Tests for CuO/AC damask core catalyst. Adsorption (N<sub>2</sub> atmosphere): A) MB-323K; Catalytic Reaction (O<sub>2</sub> atmosphere): B) MB-353K, C) PVA-398K, D) PVA-413K, E) PVA-428K.

## Significance

Textile industry is a considerable source of contaminated waters, with organics that are impossible by nature itself to control, at least in a reasonable period. The known methods are expensive because of the chemicals and operation conditions involved. Heterogeneous Catalytic Wet Oxidation with activated carbon as a support seems to be a good technological alternative, with lower operation costs, less expensive chemicals, and supports that come from agricultural industrial wastes.

#### References

- Bhargava, S., Tardío, J., Prasad, J., Föger, K., Akolekar, D. and Grocott, S., Ind. Eng. Chem. Rev. 45, 1221 (2006).
- 2. Lei, L., Hu, X., Chen, G., Porter, J. and Yue, P. Ind. Eng. Chem. Res., 39, 2896 (2000).
- 3. Kolaczkowski, S., Plucinski, P., Beltran, F., Rivas, F. and Mc Lurgh, D. Chem. Eng. J., 73, 143 (1999).
- 4. Luck, F. Catalysis Today, 53, 81 (1999).
- 5. Fortuny, A., Bengoa, C., Font, J., Catells, F. and Fabregat, A. Catalysis Today, 53, 107 (1999).
- 6. Gallezot, P., Laurain, N. and Isnard, P. Applied Catalysis B: Environmental, 9, L11 (1996).
- 7. Rodríguez Reinoso, F. Carbon, 36, 159 (1998).
- 8. Hu, X., Lei, L., Chu, H. and Yue, P. Carbon, 37, 631 (1999).
- 9. Deiana, A., Petkovic, L. and Noriega, S. Información Tecnológica, 9, 89 (1998).