

## DETERMINING THE ROLE OF PORE SIZE IN CARBONS FOR THE PHOTOCATALYTIC DEGRADATION OF ORGANIC POLLUTANTS UNDER SOLAR IRRADIATION

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### Introduction

The most important challenges for 21<sup>st</sup> century are minimizing the environmental pollution and the use of a sustainable and clean energy source for the continuous increasing demand. And these complicated tasks are even more difficult with the continuous global population growth. In this context, photocatalysis has emerged as a sustainable process for water pollutant remediation by using a renewable energy source. TiO<sub>2</sub> has been reported as the best photocatalyst but it has important disadvantages, and one of them is the low adsorption capacity due to its low porosity. There are some studies using active carbons with high microporosity as TiO<sub>2</sub> support to be used in photocatalytic reactions<sup>1</sup>. However, in water treatment processes the so called feeder pores may play a relevant role for an optimum procedure and there is a lack of knowledge about the role of these pores in photocatalysis. In this work, synthetic carbons with very well controlled porous structure were produced (i.e. tailored pore diameter from 5 to 100 nm). These materials present analogous surface chemistry and microporosity (and thus specific surface area), being the feeder pore size the only difference. The role of the mean pore size on the adsorption capacity and photodegradation of yellow-5 (Y-5) was evaluated.

### Materials and Methods

Organic xerogels were synthesized from polymerization of resorcinol (R) and formaldehyde (F) mixtures in water under microwave heating. The synthesis is a one-pot process and lasts ca. 5h for polymerization, curing and drying the organic polymer. Porous structure can be design by tuning the synthesis variables<sup>2</sup>, namely the R/F ratio, the dilution, the pH of the precursor solution or the amount of methanol in the F solution. A series of organic xerogels with different pore size (i.e. 5, 10, 20, 40 and 100 nm) were obtained (Figure 1) by means of different combination of these variables. The polymers were carbonized under nitrogen flow at 1000°C and denoted as CX (that stands for Carbon Xerogel) followed by the mean pore size of the sample. The porous properties were evaluated by means of mercury porosimetry and N<sub>2</sub> adsorption-desorption isotherms at -196°C. Preliminary adsorption experiments in the dark were performed for optimizing the procedure and to reach adsorption equilibrium of Y-5 starting from 1 up 10 ppm of initial concentration. Photocatalytic tests were performed at 25°C by using 12.5 mg of sample in 125 mL (loading 0.1 g L<sup>-1</sup>) of 5 ppm Y-5. The influence of lower and higher concentration was also evaluated with and without TiO<sub>2</sub>. The concentration of Y-5 during the adsorption and photodegradation tests was evaluated by UV-spectrophotometry at 664 nm.

## Results and Discussion

Figure 2 shows that there is an optimum feeder pore size for Y-5 adsorption in the dark (i.e. 20 nm). It seems that the narrow mesopores (i.e. 5 nm) inhibit the diffusion, and so the adsorption, of Y-5; while the samples with wider pores (i.e. 40 and 100 nm), although the diffusion should be not limited, show too low adsorption capacity. A maxima surface density of Y-5 adsorbed at equilibrium was found for CX-10 but due to the higher mesopore fraction of CX-20, this carbon was selected for the photocatalytic study. Contrary to nanoporous carbons<sup>1</sup>, carbon xerogels do exhibit very low photocatalytic activity, however an important synergistic effect was found after the combination with commercial TiO<sub>2</sub>-P25, improving the disappearance of Y-5 under the operating conditions studied (Figure 3). It was also found that the synergy effect is highly dependent of the initial concentration of the pollutant. For example, it was found a monotonically decrease in the photocatalytic activity of the binary material (CX-20+TiO<sub>2</sub>) relative to neat TiO<sub>2</sub> from 3.0 down to 1.5 increasing the concentration of Y-5 from 1 to 10 ppm. These results suggest, that mass diffusion from bulk of solution is the driven force for the adsorption and the photocatalytic activity of CX and, accordingly, this behaviour, is highly dependent of the mean pore width and the pores size distribution.

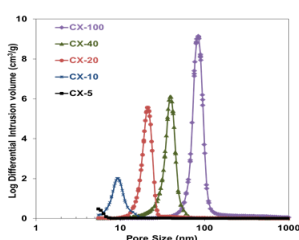


Figure 1. Pore size distribution obtained from mercury porosimetry

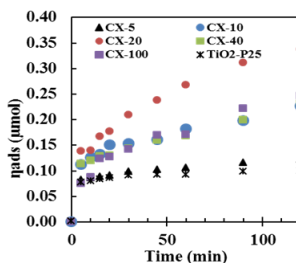


Figure 2. Kinetics of Y-5 adsorption in the dark (2.5 ppm)

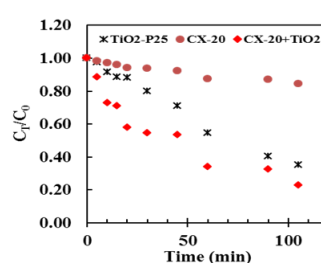


Figure 3. Kinetics of Y-5 disappearance (5 ppm)

## Conclusions

The mean pore diameter of carbon xerogels influences the uptake of Y-5 besides on the surface density of the molecules adsorbed. This is traduced in different photodegradation rates, being the maxima photocatalytic activity in samples with pores of ca. 20 nm which is highly affected by the initial concentration of pollutant. This is an indicative that intraparticle diffusion model can play an important role on the diffusion of Y-5 molecules from the bulk of solution.

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