Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Tailored TiO_2 layers for the photocatalytic ozonation of cumylphenol, a refractory pollutant exerting hormonal activity

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1. Film deposition

All chemicals were of the highest purity available and were used as received without further purification. Water purified by a Milli-Q apparatus (Millipore) was used to prepare solutions and suspensions.

The adopted film support was an aluminium lamina (geometric area: 85 cm^2), that had been previously sand blasted and etched in oxalic acid 10%. A well-known commercial TiO_2 powder, Degussa P25 (anatase–rutile composite, specific surface area 50 m^2g^{-1}) was used as the photocatalyst. 0.2 g of the TiO_2 powder were suspended in a 10^{-3} mol L^{-1} solution of sodium dodecyl sulphate in 2-propanol. The homogeneous suspension was deposited by drop casting onto both sides of the aluminium lamina. The solvent was evaporated at 333 K and subsequently the film was calcined in air at 573 K for 2h.

2. Film characterization

The Al lamina and TiO_2 films were morphologically characterized by Scanning Electron Microscopy (SEM) equipped with energy-dispersive X-ray spectroscopy (EDX), and by Atomic Force Microscopy (AFM). SEM and AFM photographs were acquired by LEO 1430 and by NT-MDT Solver PRO-M, respectively.

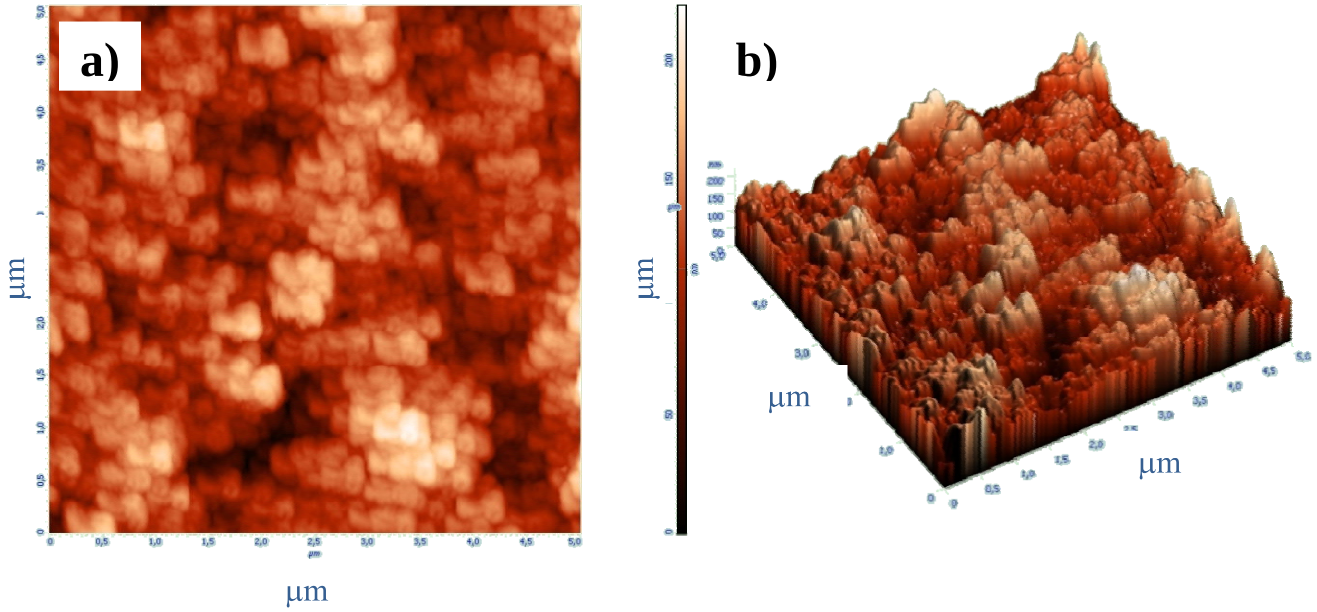

Figure 1 AFM 2D (**c**) and 3D (**d**) images of the TiO_2 film.

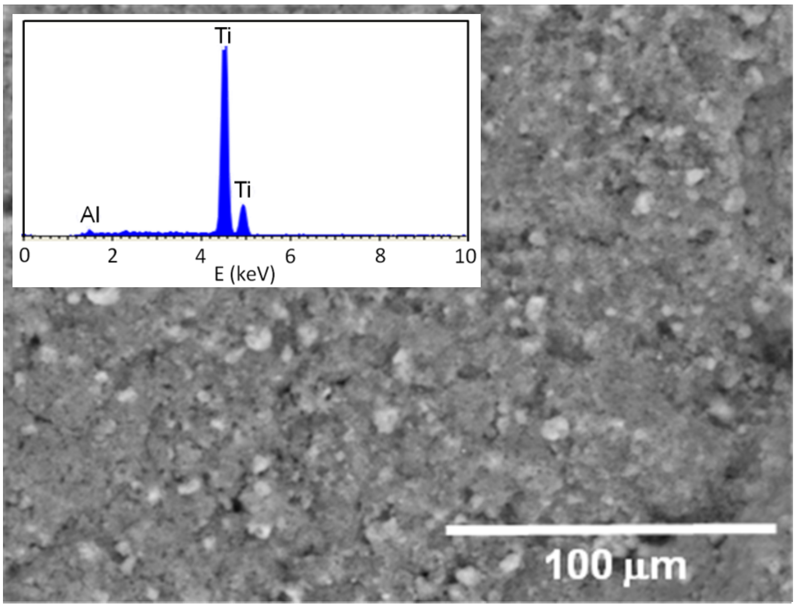

Figure 2 SEM image of the Al-supported TiO_2 film. Inset: the relative EDX spectrum.

A semi-quantitative elemental analysis of the TiO_2 film was obtained by EDX analysis: an Al content of about 1% was detected.

Deposited films showed an optimal stability. No appreciable weight variation of the coated Al laminas was observed after the degradation experiments; no suspended particles were ever observed in the reacting solution.

3. Degradation experiments

All 4-CP degradation tests were carried out at 25°C and at spontaneous pH in the experimental set-up presented in Fig. 1. A 600 mL cylindrical jacketed glass reactor was utilized.

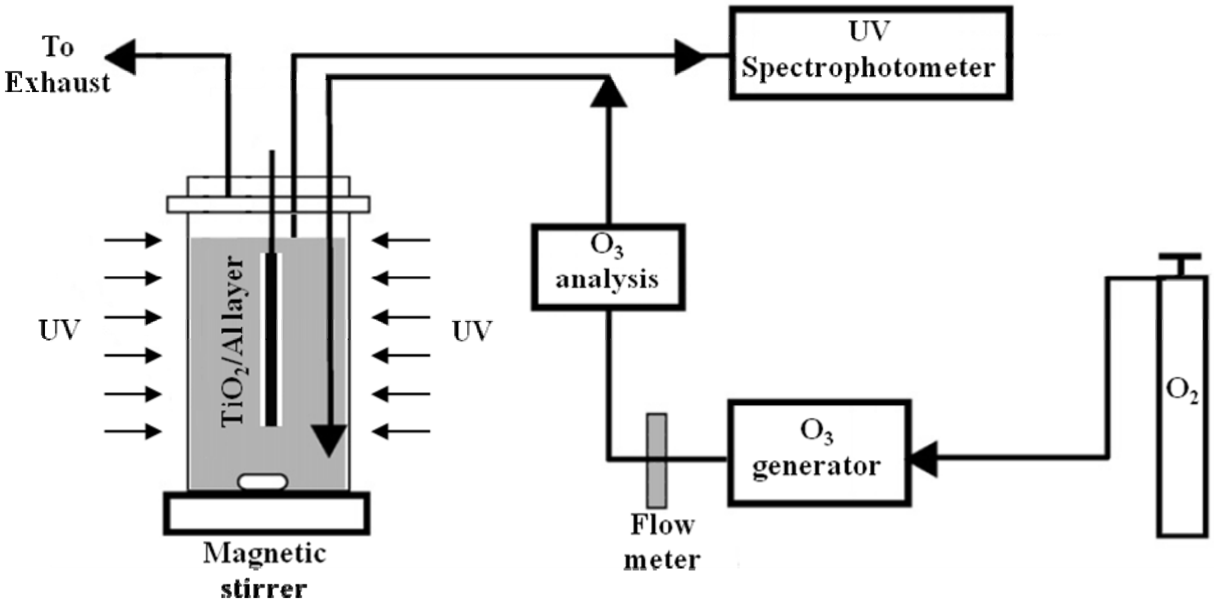

Figure 3 Photocatalytic set up.

During ozonation and photocatalytic ozonation tests, an ozone generator (Ozono Elettronica Internazionale S.r.l.) was employed to produce the ozone feed from pure oxygen. In photocatalytic ozonation, the ozone feed was started 90 min before switching on the lamp in order to allow a complete ozone solubilization. The ozone flow rate (30 L h^{-1}) was maintained through all the duration of the degradation test in order to keep a constant dissolved ozone concentration of 3 mg L^{-1} (determined by iodometric analyses).

Tests of photolysis, photocatalysis and photocatalytic ozonation were performed under UV-A irradiation. The photon sources were provided by two 500W iron halogenide lamps (Jelosil, model HG 500) emitting in the 315-400 nm wavelength range (UV-A), photon flux 2.4×10^{-5} E $dm^{-3}s^{-1}$, determined by actinometry.

During photocatalysis and photocatalytic ozonation, the TiO_2/Al layer described above was employed as the photocatalyst.

4-Cumylphenol (purity > 99%), used as the target compound, was purchased from Sigma-Aldrich. The initial concentration of the 4-CP solution was varied in the range 0.2 - 0.4 mM.

The progressive disappearance of 4-CP was monitored by measuring the absorbance at 275 nm using a Beckman DU 640. The degree of mineralization was instead determined by means of chemical oxygen demand (COD) analysis kit (Spectroquant Merck), using the following equation:

$$\%\ \text{mineralization} = \frac{COD_0 - COD_t}{COD_0}$$

where COD_0 and COD_t represent the initial COD value and the COD at time “t”, respectively.

Blank experiments performed with pure oxygen instead of O_3 showed no significant improvement with respect to plain photocatalysis.

5. Mineralization data (COD)

Table 1 Mineralization data of separate and combined test (t_{fin} = 90 min; * t_{fin} = 240 min).

	$[4\text{-}CP]_0$ mM	COD_{in} mg O_2/L	COD_{fin} mg O_2/L
Ozonation	0.3	151	127
Photocatalysis*	0.3	151	123
Photocatalytic ozonation	0.2	103	0
	0.3	151	21
	0.4	186	56

4. Photocatalytic ozonation tests with different initial pollutant concentrations

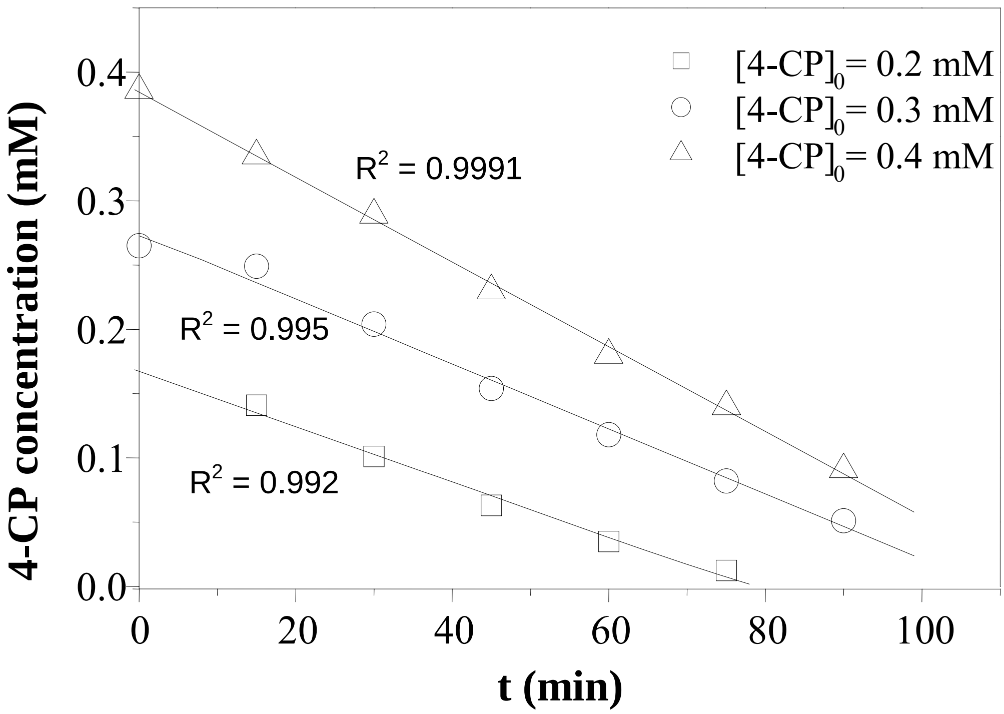

Figure 4 4-CP removal as a function of the irradiation time during photocatalytic ozonation tests with different initial pollutant concentrations (initial 4-CP concentration 0.2-0.4 mM, ozone concentration 3 mg L^{-1}, initial ozone equilibration step 90 min).

6. Identification of the oxidation intermediate products

Intermediate products of 4-CP oxidation during photocatalytic ozonation were identified by high performance liquid chromatography-mass spectrometry (HPLC/MS) determinations on solutions sampled at different reaction times and by Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) analyses of the used catalyst at the end of the reaction.

The HPLC/MS analyses were performed using an Agilent 1100 chromatographic system (quaternary pump, autosampler, thermostated column holder) equipped with a diode array detector and a Bruker ion-trap Esquire 3000+. The column was a Supelco Ascentis-Express (50x4.6 mm, 2.7

μm). A two phase mixture was used as the mobile phase with a flow-rate of 1 mL/min in gradient mode. Phase A was Milli-Q water containing 0.05 % (v/v) TFA or 10 mM ammonium acetate in the case of ESI+ or ESI- respectively; phase B was Acetonitrile (LC-MS grade), containing 0.05 % TFA only in the case of ESI+. The adopted gradient was the following: from 5 % B to 95 % B in 6 min, washing at 100 % B for 1 min, equilibration at 5 % B in the next 3 min. Peak UV detection was carried out at 220 and 254 nm (reference at 500 nm, 40 nm bandwith). Mass spectrometry was performed with an electrospray ionization (ESI) source in either positive or negative mode with the following parameters: detection in the 50-2000 m/z range with alternating MS/MS, capillary voltage ± 3500 V, drying gas temperature 365 °C, nebulizer pressure 50 psi, drying gas flow 10 L/min. All other tuning parameters were optimized with the standard tuning mix provided by Bruker for a generic detection in the above mass range.

The chemical structure of organic compounds adsorbed on the used TiO_2 surface was analyzed by using a Jasco 4200 FTIR, accessorized with an ATR module.

7. HPLC/MS spectra

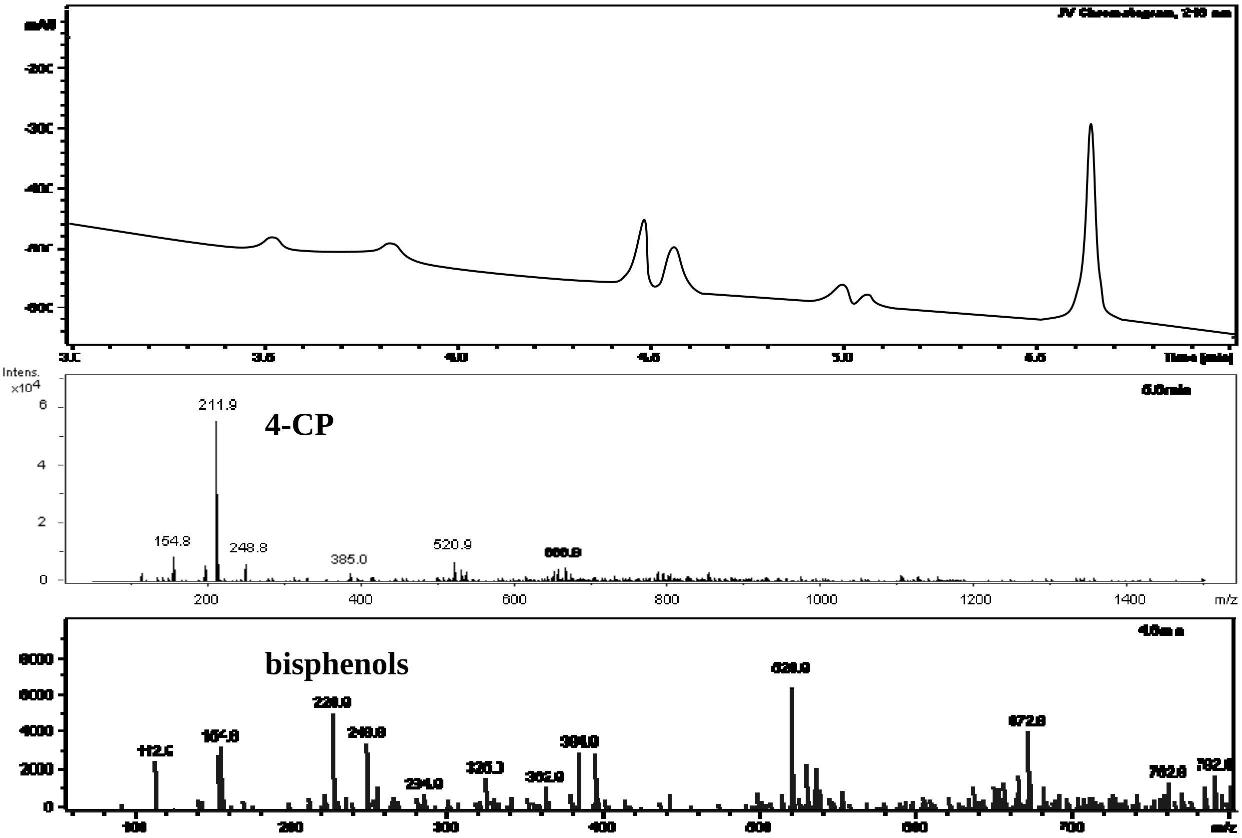

Figure 5 a) HPLC peaks for different retention times and **b)** relative mass spectra of 0.4 mM 4-CP solution at the end of the combined ozonation and photocatalysis.

The peak at the retention time of 5.6 min can be attributed to 4-CP by comparison with the pure 4-CP mass spectrum. The chromatographic peaks at a retention time of about 4.5 min certainly correspond to a mixture of oxidation products of 4-CP. Even when the polarity of the eluent was changed, it was not possible to obtain a better separation for the corresponding compounds. The attribution of the HPLC peaks at about 4.5 min was performed using the method of the internal calibration by addition of a known compound (bisphenol A). The peak at 4.6 min can be attributed to bisphenols bearing the second hydroxyl group on the non-phenolic aromatic ring, such as bisphenol A (BPA). The peak at 4.4 min can instead be attributed to isomers of BPA bearing the second hydroxyl group in orto or para positions with respect to the 4-CP hydroxyl group. This attribution is based on the proximity of this peak to the one of BPA-type compounds and on the grounds of spectrophotometric considerations. In both cases, the attribution of precise chemical structures was not feasible since several isomers might occur. As shown in Fig. 5, some chemical structures were proposed according to their mass spectra. In addition to the previously described degradation products, few minor chromatographic peaks were also observed. Because of the very low retention time, these compounds certainly corresponded to smaller and more polar molecules such as acids or aldehydes, as confirmed by FTIR analyses and in agreement with literature results on other ECDs (M. Deborde, S. Rabouan, P. Mazellier, J.-P. Duguet, B. Legube, *Water Res*., 2008, **42**, 4299).