# **Electronic Supporting Information**

# Emerging pollutant mixture mineralization by TiO<sub>2</sub> photocatalysts. The role of the water medium.

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Table S1 – The studied pollutants.

## Experimental procedures

# Catalyst preparation

Reactants, purchased from Sigma-Aldrich, were used without further purification. Doubly distilled water obtained by a Milli-Q apparatus was used to prepare solutions and suspensions.  $TiO_2$  nanostructured powders were prepared by a sol-gel synthesis. Water was added dropwise to a 1:1 mixture of titanium(IV) isopropoxide (TTIP) and acetic acid at 0 °C, while stirring vigorously. The water : TTIP molar ratio was fixed at 200. The as-prepared sol was aged for 24 h and successively dried at 70°C for 3 h, then 100°C overnight. Finally, the powder was calcined at 400 °C for 6 h under  $O_2$  flux (9 NL h<sup>-1</sup>).

## Characterization methods

Information about the crystalline structure of the  $TiO_2$  sample were retrieved by X-ray Powder Diffraction (XRPD) experiments. A Philips PW 3710 Bragg-Brentano goniometer was used. Graphite-monochromated Cu K $\alpha$  radiation at 40 kV × 40 mA nominal X-ray power was employed.  $\theta$ :2 $\theta$  scans were performed between 20° and 90°. The Quanto software was adopted to perform the Rietveld refinement of the diffractogram. The Scherrer equation on the (101) anatase peak was applied to estimate the average crystallite sizes.

The morphological properties of the photocatalyst such as specific surface area and porosity were determined by recording adsorption-desorption isotherm of  $N_2$  in subcritical conditions (-196 °C), using a Coulter SA3100 apparatus. Data were elaborated according to the Brunauer-Emmett-Teller (BET) method for the specific surface area determination, while the Barrett-Joyner-Halenda (BJH) method was employed to determine pore size distribution from the desorption isotherm.

The morphology of the Ti-TiO<sub>2</sub> mesh was analyzed by SEM using a Leo 1430 Zeiss instrument.

## Photocatalytic activity tests

In tests with single pollutants, two different initial concentrations were selected ( $C_0 = 8.75$  and 35 mg L<sup>-1</sup>); the TiO<sub>2</sub> surface area for pollutant molecule was kept constant by adopting a TiO<sub>2</sub> slurry concentration of 0.5 g L<sup>-1</sup> for tests with high  $C_0$  (35 mg L<sup>-1</sup>) and of 0.125 g L<sup>-1</sup> for tests with low  $C_0$  (8.75 mg L<sup>-1</sup>). In the case of pollutant mixtures, an initial concentration of 8.75 mg L<sup>-1</sup> for each molecule and a slurry concentration of 0.5 g L<sup>-1</sup> were adopted, in order to keep in principle the same photocatalyst surface area available for each pollutant molecule. The here adopted pollutant concentrations are well above the environmental levels; however, they were selected to allow a sound analytical approach, especially concerning the final mineralization of the pollutants.

Tests were carried out at 20 °C, using magnetic stirring and  $O_2$  bubbling. In tests with ultrapurewater, the solution pH was not corrected, being 5.5 in all cases except for the most concentrated TC solution, which had a pH of about 4 due to the nature of the salt. Before the test, the photocatalyst was pre-treated with UV light for 1 h in order to promote surface hydroxylation, activation and cleaning. Then, it was dispersed in the pollutant solution and, before irradiation, the system was kept in the dark for 30 min until adsorption equilibrium was achieved. The photocatalytic degradation was monitored for 6 h. Adsorption and photolysis kinetics were also performed.

The pollutant disappearance was monitored by UV-vis spectroscopy (Shimadzu UV-2600 spectrophotometer) as well as high performance liquid chromatography (HPLC) analyses (Agilent Eclipse XDB, equipped with C18 column and a UV-vis detector). Acetonitrile (A) and phosphoric acid 0.1% (B) were

used as eluents. A linear gradient elution was performed in 40 min from 90% A - 10% B to 100% B. The detection of TC, CF, PC and AT was carried out by monitoring the absorption at 357, 277, 246, and 224 nm, respectively. Prior to analysis, the suspension was sampled with a syringe and filtered with a Millipore MF-membrane filter (0.45  $\mu$ m-HA). In the case of the P25 photocatalyst, three subsequent filtration steps were needed to obtain a clear surnatant.

Electrospray Ionisation Mass Spectrometry (ESI-MS) analyses were performed by using a Thermo Finnigan (MA, USA) LCQ Advantage system MS spectrometer with an electrospray ionization source and an 'Ion Trap' mass analyzer. The samples were solubilised in methanol. Formic acid was added in order to enhance the sample volatility. MS spectra were obtained by direct infusion of the sample solutions under ionization, ESI positive by applying +3.0 kV at the entrance of the capillary with the drying gas heated to 350 °C. Full-scan mass spectra were recorded in the mass/charge (m/z) range of 50 - 1000.

The mineralization degree of the pollutants was determined by Total Organic Carbon (TOC) measurements (Shimadzu TOC-V CPN Analyzer).

	simulated drinking	bottled mineral
	water	water
Ca <sup>2+</sup> (mg L <sup>-1</sup> )	45	49
Na⁺ (mg L¹)	46	6
Mg <sup>2+</sup> (mg L <sup>-1</sup> )	9	29
Cl <sup>-</sup> (mg L <sup>-1</sup> )	79	2
SO <sub>4</sub> <sup>2-</sup> (mg L <sup>-1</sup> )	37	4
HCO <sub>3</sub> <sup>-</sup> (mg L <sup>-1</sup> )	122	301
conductivity (µS cm <sup>-1</sup> )	478	415
pН	7.0	7.5

Table S2 - Electrolyte concentrations and physicochemical parameters of simulated and commercial bottled drinking water.



Figure S1 - XRPD pattern of the synthesized photocatalyst.



Figure S2 – a)  $N_2$  adsorption-desorption isotherm recorded in subcritical conditions and b) pore size distribution of the photocatalyst.



Figure S3 - Degradation and final mineralization degree (inset) of the four pollutants by photolysis ( $C_0 = 35$  mg L<sup>-1</sup>; 0.5 g L<sup>-1</sup> TiO<sub>2</sub>; ultrapure water matrix).

Molecule	<i>k</i> (50 min) / 10 <sup>3</sup> min <sup>-1</sup>	Mineralization (360 min) / %
тс	65 ± 3	94 ± 1
CF	8 ± 1	41 ± 1
PC	$7.2 \pm 0.1$	77 ± 1
AT	6 ± 1	61 ± 1

Table S3 - Pseudo-first order constants, k, in the first 50 min and final mineralization degree of the different molecules, in single pollutant photocatalytic tests ( $C_0 = 35 \text{ mg } \text{L}^{-1}$ ; 0.5 g  $\text{L}^{-1}$  TiO<sub>2</sub>; ultrapure water matrix).



Figure S4 - Comparison between the pollutant disappearance curves of caffeine in the single pollutant test and in the mixture.



Figure S5 – Mineralization curves of the pollutants mixture for the synthesized (T) and the commercial photocatalysts (P25).

	ads (%)	<i>k</i> (min⁻¹)
ultrapure	30	65 ± 3
simulated	28	64 ± 6
ultrapure	5	7.2 ± 0.1
simulated	2	$3.8 \pm 0.1$
ultrapure	2	7.5 ± 0.8
simulated	1	7.6 ± 0.1
ultrapure	1	6.3 ± 0.5
simulated	2	4.2 ± 0.2
	ultrapure simulated ultrapure simulated ultrapure simulated ultrapure simulated	ads (%)   ultrapure 30   simulated 28   ultrapure 5   simulated 2   ultrapure 2   ultrapure 1   ultrapure 1   simulated 2   simulated 2   simulated 2   simulated 1   ultrapure 1   simulated 2

Table S4 – Dark adsorption and kinetic constants, k, of the single pollutant degradation reactions in ultrapure and simulated drinking water matrices (C<sub>0</sub> = 35 mg L<sup>-1</sup>; 0.5 g L<sup>-1</sup> TiO<sub>2</sub>).



Figure S6 - Comparison of the mineralization degree of the tests in mixture (left histogram) and that of single pollutant tests (right histogram) after 6 h irradiation, in ultrapure and simulated drinking water.



Figure S7 – SEM images of the  $TiO_2$ -coated titanium mesh.