

1 **Influence of structural properties on the activity of WO<sub>3</sub> catalysts for**  
2 **visible light photocatalytic ozonation**

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10  
11 **Abstract**

12 This work is focused on the use of WO<sub>3</sub> catalysts with different structural properties for  
13 photocatalytic ozonation using visible light as radiation source. WO<sub>3</sub> catalysts were  
14 prepared by thermodecomposition of tungstite (H<sub>2</sub>O·WO<sub>3</sub>) at 300-450°C and different  
15 calcination time. Photocatalysts were characterized by means of TGA-DTA, XRD, N<sub>2</sub>  
16 adsorption-desorption isotherms, pH<sub>PZC</sub>, XPS and DR-UV-Vis spectroscopy.  
17 Photocatalytic ozonation under visible light radiation with the catalyst calcined 5 min at  
18 450°C gave place to complete removal of ibuprofen in less than 20 min with 87% TOC  
19 removal at 120 min. This catalyst gave place to a complete removal of a mixture of ten  
20 emerging contaminants in a municipal wastewater in less than 60 min with 40%  
21 mineralization at 120 min. The highest catalytic activity of this material is due to the  
22 formation of monoclinic structure of WO<sub>3</sub>.

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24  
25 **Keywords**

26 Photocatalytic ozonation, tungsten trioxide, crystalline structure, ozone, visible light  
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## 1 1. Introduction

2 The development of efficient water treatment technologies to remove organic pollutants  
3 such as solvents, dyes, pesticides, phenolic compounds or pharmaceuticals and  
4 personal care products, among others, is an important issue worldwide. In general,  
5 these pollutants are persistent, toxic and/or recalcitrant to conventional wastewater  
6 treatments and have shown to be a potential risk to human health and to the  
7 environment. Therefore, they must be removed in order to prevent their discharge and,  
8 of course, to fulfil the required limits of an increasingly stringent legislation.

9 Among the alternative technologies, the combination of ozone and heterogeneous  
10 photocatalysis with a semiconductor, i.e. photocatalytic ozonation, has demonstrated to  
11 efficiently remove organic compounds that are degraded little or slowly by  
12 photocatalysis or ozonation alone. The improvement of the combined process is mainly  
13 related to the formation of higher concentration of oxidizing species such as hydroxyl  
14 radicals compared to the single treatments (Agustina et al., 2005; Augugliaro et al.,  
15 2006). Usually, this treatment has been applied by using  $\text{TiO}_2$  as photocatalyst and UV  
16 irradiation. However, from an environmental and economic point of view, the use of  
17 solar light is a need for the practical deployment of photocatalytic technologies. In this  
18 sense,  $\text{TiO}_2$  presents some limitations since it only uses around 5% of solar radiation in  
19 the UV range in spite of being the archetypical photocatalyst due to its relatively high  
20 efficiency, low cost and availability (Hernández-Alonso et al., 2009).

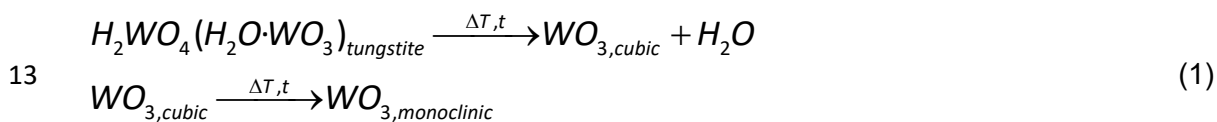
21 Different research efforts have been carried out to overcome this limitation mainly  
22 focusing on the development of doped or modified  $\text{TiO}_2$  or on the use of different  
23 semiconductors such as  $\text{CdS}$ ,  $\text{WO}_3$ ,  $\text{SnO}_2$  or  $\text{ZnO}$  (Hernández-Alonso et al., 2009;  
24 Malato et al., 2009). Among them, bare tungsten trioxide  $\text{WO}_3$  has been considered  
25 unsuitable for efficient photocatalytic oxidation due to its conduction band level respect  
26 to the reduction band level of  $\text{O}_2$ , whereas it has demonstrated an efficient behavior in  
27 the presence of  $\text{O}_3$  (Nishimoto et al., 2010).  $\text{WO}_3$  is a wide-band-gap semiconductor  
28 (2.6-3.0 eV) that can be excited with radiation corresponding to the visible region of the  
29 electromagnetic spectrum (Abe et al., 2008; González-Borrero et al., 2010). This fact  
30 together with its relatively low cost, no toxicity and availability make  $\text{WO}_3$  an attractive  
31 alternative to  $\text{TiO}_2$  for the photocatalytic ozonation processes under visible or solar light  
32 radiation.

33 The use of  $\text{WO}_3$  in the photocatalytic ozonation process has been limited to commercial  
34 monoclinic  $\text{WO}_3$  and phenol as target compound (Nishimoto et al., 2010; Mano et al.,  
35 2011). Thus, this work focuses on the study of  $\text{WO}_3$  photocatalysts with different  
36 structural properties for the photocatalytic ozonation of a model compound using visible  
37 light radiation. Ibuprofen (IBP), a nonsteroidal anti-inflammatory drug, has been  
38 selected as target contaminant which is included in the family of emerging  
39 contaminants (ECs) frequently detected in wastewater and different aquatic  
40 environments (Barceló and Petrovic, 2008; Santos et al., 2009). In addition, a more  
41 realistic application of photocatalytic ozonation with  $\text{WO}_3$  catalysts has been studied in  
42 a mixture of 10 ECs spiked municipal wastewater treatment plant (MWWTP) effluent  
43 using the entire simulated solar radiation spectrum.

## 1 2. Experimental section

### 2 2.1. Catalysts preparation

3 Photocatalysts were prepared by thermodecomposition of commercial H<sub>2</sub>WO<sub>4</sub> (99%,  
4 Sigma-Aldrich) yellow powder precursor. The sample was calcined in air atmosphere in  
5 a muffle furnace at different temperatures (300 and 450°C) for 1 to 30 min in order to  
6 obtain different H<sub>2</sub>WO<sub>4</sub>/WO<sub>3</sub> crystalline structures according to method reported by Cao  
7 et al. (Cao et al., 2012). The thermodecomposition reaction proceeds through water  
8 loss of the tungstite structure of H<sub>2</sub>WO<sub>4</sub> (H<sub>2</sub>O·WO<sub>3</sub>) and subsequent crystallization as  
9 cubic WO<sub>3</sub>. Then, at higher temperature cubic WO<sub>3</sub> can be transformed into the  
10 monoclinic WO<sub>3</sub> crystalline phase (Guery et al., 1997). This process is summarized in  
11 eq. (1). **Table 1** shows the nomenclature of the catalysts and heat-treatment conditions  
12 together with some characterization results.



### 14 2.2. Characterization

16 Thermal gravimetry and differential temperature analysis (TG-DTA) was performed with  
17 a SETSYS Evolution-16 apparatus (Setaram) using the following conditions: sample  
18 loading 20 mg, air flow 50 cm<sup>3</sup> min<sup>-1</sup> at a heating rate of 5 °C min<sup>-1</sup> from room  
19 temperature to 600 °C.

20 The crystalline phases present in the photocatalysts were inferred from their X-ray  
21 diffraction (XRD) patterns recorded using a powder Bruker D8 Advance XRD  
22 diffractometer with a Cu K $\alpha$  radiation ( $\lambda=0.1541$  nm). The data were collected from  
23  $2\theta=10^\circ$  to  $70^\circ$  at a scan rate of 0.02 s<sup>-1</sup> and 1 s per point. Crystalline composition semi-  
24 quantitative analysis of the samples was performed on multi-phase patterns by the  
25 Reference Intensity Ratio (RIR) method using reference diffraction patterns by means  
26 of EVA v.14 software (Bruker-AXS). Due to the overlapping of the main characteristic  
27 peaks of the cubic and monoclinic WO<sub>3</sub> patterns, the analyses for the catalysts with  
28 monoclinic contribution were performed using a calculated value of RIR for the  
29  $2\theta=28.6^\circ$  diffraction peak corresponding to the (112) reflection plane.

30 BET surface area and pore volume of the photocatalysts were determined from their  
31 nitrogen adsorption–desorption isotherms obtained at -196°C using an Autosorb 1  
32 apparatus (Quantachrome). Prior to analysis the samples were outgassed at 150°C for  
33 24 h under high vacuum ( $<10^{-4}$  Pa).

34 The point of zero charge (pH<sub>PZC</sub>) of each sample was estimated using the mass titration  
35 method proposed by Subramanian et al. (Subramanian et al., 1988). Suspensions of  
36 the solid in deionized water at 5% (w/w) were prepared and the pH measured after 24  
37 h of stirring.

1 X-ray photoelectron spectra (XPS) were obtained with a K $\alpha$  Thermo Scientific  
2 apparatus with an Al K $\alpha$  ( $h\nu=1486.68$  eV) X-ray source using a voltage of 12 kV under  
3 vacuum ( $2\times 10^{-7}$  mbar). Due to the lack of C 1s signal, binding energies were calibrated  
4 relative to the O1s peak of stoichiometric WO $_3$  at 530.2 eV (Senthil and Yong, 2007;  
5 Pang et al., 2013).

6 Diffuse reflectance UV-Vis spectroscopy (DR-UV-Vis) measurements, useful in the  
7 determination of the semiconductor band gap, were performed with an UV-Vis-NIR  
8 Cary 5000 spectrophotometer (Varian-Agilent Technologies) equipped with an  
9 integrating sphere device.

10

### 11 **2.3. Catalytic activity measurements**

12 Ibuprofen sodium salt (IBP), was used as target compound to test the catalytic activity  
13 of the synthesized materials. Photocatalytic experiments were carried out in semi-batch  
14 mode in a laboratory-scale system consisting of a 0.5 L glass-made spherical reactor,  
15 provided with a gas inlet, a gas outlet and a liquid sampling port. The reactor was  
16 placed in the chamber of a commercial solar simulator (Suntest CPS, Atlas) provided  
17 with a 1500 W air-cooled Xe arc lamp with emission restricted to visible light of  
18 wavelengths over 390 nm because of the presence of quartz, glass and polyester cut-  
19 off filters. The irradiation intensity was kept at  $550\text{ W m}^{-2}$  and the temperature of the  
20 system was maintained between 25 and 35°C throughout the experiments. If required,  
21 a laboratory ozone generator (Anseros Ozomat Com AD-02) was used to produce a  
22 gaseous ozone-oxygen stream that was fed to the reactor. In that case, the ozone  
23 concentration was recorded on an Anseros Ozomat GM-6000Pro gas analyzer.

24

25 In a typical photocatalytic ozonation experiment, the reactor was first loaded with 0.5 L  
26 of an aqueous solution containing  $10\text{ mg L}^{-1}$  of IBP initial concentration at  $\text{pH}_0=6.5$  (not  
27 buffered). Then, 0.125 g of the catalyst were added and the suspension was stirred in  
28 the darkness for 30 min. After this dark stage, the lamp was switched on and,  
29 simultaneously, a mixture of ozone-oxygen ( $10\text{ mg L}^{-1}$  ozone concentration) was fed to  
30 the reactor at a flow rate of  $20\text{ L h}^{-1}$ . The irradiation time for each experiment was 2 h.  
31 Samples were withdrawn from the reactor at intervals and filtered through a  $0.2\ \mu\text{m}$   
32 PET membrane to remove the photocatalyst particles except for dissolved ozone  
33 analysis.

34

35 Experiments of adsorption (i.e., absence of radiation and ozone), photolysis (i.e.,  
36 radiation in absence of catalysts and ozone), photocatalytic oxidation (i.e., radiation  
37 and catalyst in absence of ozone), ozonation (i.e., absence of radiation and catalyst),  
38 catalytic ozonation (i.e., absence of radiation) were also carried out for comparative  
39 analysis.

40

41 In addition, the effectiveness of the best photocatalytic system was tested in a more  
42 realistic application under complete simulated solar light radiation (wavelength from  
43 300 nm). Ten emerging contaminants: acetaminophen (AAP), metoprolol (MTP),

1 caffeine (CAF), hydrochlorothiazide (HCT), antipyrine (ANT), sulfamethoxazole (SFM),  
2 carbamazepine (CAR), ketorolac (KET), diclofenac (DCF) and ibuprofen (IBP);  
3 frequently found in municipal wastewater effluents (MWW), were selected. They were  
4 added at initial concentration of 0.5 mgL<sup>-1</sup> to a MWW taken from Badajoz MWWTP  
5 (Badajoz, Spain) designed for 225,000 inhabitants with an average inlet flow of 37,500  
6 m<sup>3</sup> day<sup>-1</sup>. Effluents were collected downstream of the MWWTP secondary biological  
7 treatment and filtered. The carbonate-bicarbonate content was eliminated by air  
8 stripping after acidifying the MWW. Then pH was restored and MWW was stored at -  
9 20°C until use.

10  
11 IBP concentration was analyzed by high-performance liquid chromatography HPLC-  
12 DAD (Hitachi, Elite LaChrom) using a Phenomenex C-18 column (5 µm, 150 mm long,  
13 3 mm diameter) as stationary phase and 0.7 mL min<sup>-1</sup> of acetonitrile-acidified water  
14 (0.1% H<sub>3</sub>PO<sub>4</sub>) as mobile phase (60-40 v/v, isocratic). Identification and quantification  
15 was carried out at 220 nm. ECs concentration in MWW matrix were analyzed by the  
16 same HPLC system with 0.2 mL min<sup>-1</sup> of acetonitrile-acidified water (0.1% formic acid)  
17 as mobile phase with a gradient from 10% to 100% in acetonitrile in 40 min and 20 min  
18 re-equilibration time. Identification and quantification was carried out at the maximum  
19 wavelength of each compound. Total organic carbon (TOC) was measured using a  
20 Shimadzu TOC-V<sub>SCH</sub> analyzer. Aqueous ozone was measured by following the indigo  
21 method using an UV-Visible spectrophotometer (Evolution 201, Thermospectronic) set  
22 at 600 nm (Bader and Hoigné, 1981). Ozone in the gas phase was continuously  
23 monitored by means of an Anseros Ozomat GM-6000Pro analyzer. Hydrogen peroxide  
24 concentration was determined photometrically by the cobalt/bicarbonate method, at  
25 260 nm using a UV-Visible spectrophotometer (Evolution 201, Thermospectronic)  
26 (Masschelein et al., 1977).

### 28 3. Results and discussion

#### 29 3.1. Characterization of the photocatalysts

30 Tungstite is a hydrous tungsten oxide, H<sub>2</sub>O·WO<sub>3</sub> that crystallizes in the orthorhombic  
31 system and can be thermally decomposed into different WO<sub>3</sub> structures. WO<sub>3</sub> consists  
32 of a three-dimensional array of corner sharing metal-oxygen octahedral in a chess-  
33 board type of array. The ideal structure is a ReO<sub>3</sub>-type cubic form but this is easily  
34 distorted away since the relatively small tungsten atoms tend to be displaced from the  
35 centres of the octahedral. These displacements are temperature dependent and also  
36 influenced by the presence of impurities that make WO<sub>3</sub> adopts a variety of symmetry  
37 types: monoclinic, triclinic, orthorhombic and tetragonal. In addition, another two  
38 metastable structures of WO<sub>3</sub> have been obtained at low temperatures: hexagonal and  
39 pyrochlore (Tilley, 1995).

40 Thus, the thermal behaviour of the commercial tungstite precursor is mandatory to  
41 understand the crystallization of the different WO<sub>3</sub> structures. **Fig.1** shows the ATG-  
42 DTA profiles for the H<sub>2</sub>WO<sub>4</sub> precursor. The evolution can be divided in 4 different  
43 regions. First of all, from ambient temperature to 150°C, a small weight loss around 1%

1 is observed accompanied by an endothermic contribution which can be assigned to the  
2 evaporation of adsorbed H<sub>2</sub>O. In region II, from 150 to 325°C, a noticeable weight loss  
3 is obtained together with an endothermic peak at 225°C which corresponds with the  
4 loss of coordinated H<sub>2</sub>O from the tungstite structure to form cubic WO<sub>3</sub> (Guery et al.,  
5 1997; Cao et al., 2012). The cubic WO<sub>3</sub> structure is metastable and it can be stabilized  
6 by the presence of Na<sup>+</sup> impurities (Szilágyi et al., 2012). However, at this temperature,  
7 formation of different structures such as monoclinic WO<sub>3</sub> cannot be disregarded as it is  
8 expected from the absence of impurities in the commercial precursor used here. On the  
9 other hand, in the range 325-500°C (region III), it can be observed a slight endothermic  
10 contribution around 371°C followed by an exothermic peak with a maximum centred at  
11 447°C together with a slight weight loss around 0.2%. In this region, the complete  
12 transformation of cubic WO<sub>3</sub> into monoclinic WO<sub>3</sub> occurs (Guery et al., 1997; Cao et al.,  
13 2012). No significant changes are observed in region IV in the range 500-600°C. From  
14 these results, the heat-treatment temperature of the precursor was set at 300 and  
15 450°C to obtain different crystalline phases composition of the catalysts. The time of  
16 the heat-treatment was relatively short (1-30 min) following the work of Cao et al.,  
17 2012. One catalyst was also heat-treated during 60 min for comparative purposes.

18 The structural characterization of the catalysts was performed by XRD as shown in  
19 **Fig.2** where XRD patterns of the tungstite H<sub>2</sub>O·WO<sub>3</sub> orthorhombic phase (JCPDS 018-  
20 1418), cubic WO<sub>3</sub> (JCPDS 41-0905) and monoclinic WO<sub>3</sub> (JCPDS 043-1035) have  
21 been plotted for comparison. It can be noticed that the main peaks in the diffraction  
22 pattern of the precursor, W-0, are attributable to the orthorhombic phase of tungstite,  
23 although a small shoulder around 24.2° can also indicate a low contribution of the cubic  
24 WO<sub>3</sub> phase. When the precursor is heat-treated at 300°C the cubic structure of WO<sub>3</sub> is  
25 progressively formed as the time of calcination increases. Thus, for 1 min at 300°C  
26 (W<sub>300-1</sub>) it can be observed the coexistence of tungstite orthorhombic phase together  
27 with cubic WO<sub>3</sub>, as the main peaks of tungstite at 16.5 and 25.6° decreased in favour of  
28 the increasing cubic diffraction peaks. The transformation of tungstite into cubic WO<sub>3</sub>  
29 has been completed in the W<sub>300-3</sub> catalyst, where the main tungstite diffraction peaks  
30 have completely disappeared and all the diffraction peaks are attributable to cubic  
31 crystalline structure. After that, an increase in the time of calcination at 300°C provokes  
32 the formation of monoclinic WO<sub>3</sub> to some extent. This can be noticed by the presence  
33 of the contributions centred at 26.5 and 28.6°. These are characteristics of the  
34 monoclinic crystalline structure, together with the widening of the peaks at 23.9 and  
35 34.0° that are affected by the overlapped cubic-monoclinic contributions with the  
36 formation of the triple peaks in monoclinic phase at these 2θ values corresponding to  
37 reflections from (001), (020) and (200) planes (Senthil and Yong, 2007). It is also  
38 noticeable that an increase of the calcination time from 5 to 60 min did not produce any  
39 significant change in the XRD patterns (W<sub>300-5</sub> and W<sub>300-60</sub>) which is indicative of the  
40 stabilization of the cubic structure at this temperature. Finally, the temperature increase  
41 from 300 to 450°C provoked the transformation of the cubic phase of WO<sub>3</sub> into  
42 monoclinic one to a greater extent according to previous TGA-DTA results. **Table 1**  
43 shows the semiquantitative analysis of crystalline phases in the catalysts.

1 **Table 1** also summarizes the BET surface area values of the catalysts from N<sub>2</sub>  
2 adsorption-desorption isotherms. In general, small surface areas are obtained in this  
3 type of materials unless different strategies were used to this purpose. As can be  
4 observed, the surface areas undergo a slight increase (from c.a. 30 to 40 m<sup>2</sup>g<sup>-1</sup>) when  
5 the dehydration of tungstite occurs and cubic crystalline structure is formed. On the  
6 other hand, at higher calcination temperature, a decrease of the surface area is  
7 observed in the 450°C catalysts, being higher as the time of the heat treatment  
8 increases.

9 The pH of the point of zero charge was also determined for the catalysts studied and  
10 these results are summarized in **Table 1**. The acidity of the surface can play a  
11 significant role in the behaviour of WO<sub>3</sub> based materials in wastewater treatments in  
12 adsorption processes of organic compounds and species with unpaired electrons  
13 (Tomova et al., 2012). It can be noticed a slight decrease in the value of pH<sub>PZC</sub> together  
14 with the transformation of tungstite into WO<sub>3</sub> cubic structure so that the catalysts with  
15 this majority crystalline phase have a pH<sub>PZC</sub> value around 4. On the other hand, an  
16 increase in the calcination temperature to up to 450°C led to values of pH<sub>PZC</sub> around 5  
17 for W<sub>450-5</sub> and W<sub>450-30</sub> catalysts. The decrease of the surface acidity with increasing  
18 calcination temperature has been previously reported in monoclinic WO<sub>3</sub> (Kanan et al.,  
19 2002) and WO<sub>3</sub>-ZrO<sub>2</sub> catalysts (Sun et al., 2000), and has been attributed to the  
20 creation of vacancies in the WO<sub>3</sub> structure from the extraction of lattice oxygen, which  
21 leads to a decrease in the number of Lewis acid sites (Kanan et al., 2002). In addition,  
22 a higher calcination temperature could also produce the dehydration/dehydroxilation of  
23 the WO<sub>3</sub> surface to some extent lowering the number of Brönsted acid sites (Kanan et  
24 al., 2002).

25 Surface characterization of the catalysts was performed by XPS to analyse the  
26 stoichiometry and chemical binding states of W. XPS spectra of W 4f region are  
27 depicted in **Fig.S1** of the supplementary information. In all cases, the spectra obtained  
28 showed a doublet with binding energies around 35.5 and 37.6 eV for W 4f<sub>7/2</sub> and W  
29 4f<sub>5/2</sub>, respectively, with the W 4f<sub>7/2</sub>-W4f<sub>5/2</sub> binding energy separation being 2.1 eV. The  
30 energy position of this doublet corresponds to the W<sup>6+</sup> oxidation state in WO<sub>3</sub> (Senthil  
31 and Yong, 2007; Lee et al., 2012; Pang et al., 2013). On the other hand, XPS spectra  
32 of O 1s spectral region for all the catalysts are shown in **Fig.S2**. The main contribution  
33 at 530.2 eV has been assigned to oxygen in the WO<sub>3</sub> lattice (Azimirad et al., 2007;  
34 Senthil and Yong, 2007; Pang et al., 2013). Moreover, an additional contribution  
35 centred at 532.5 eV has been observed for W-0 and W<sub>300-1</sub> catalysts, which has been  
36 assigned to oxygen in water molecules bound in the tungstite structure (H<sub>2</sub>O·WO<sub>3</sub>) or  
37 absorbed in the catalyst surface (Senthil and Yong, 2007). This is consistent with TGA-  
38 DTA and XRD results having these two catalysts more than 80% of tungstite in their  
39 structure.

40 The diffuse reflectance UV-Vis spectra of the photocatalysts (**Fig.3**) showed a higher  
41 optical absorbance in the visible region up to ca. 530 nm for tungstite composed  
42 catalysts (W-0 and W<sub>300-1</sub>) whereas decreased to ca. 480 nm for cubic and monoclinic  
43 WO<sub>3</sub> composed catalysts (W<sub>300-3</sub>, W<sub>300-5</sub>, W<sub>450-5</sub>, W<sub>450-30</sub>). The optical energy band  
44 gap (E<sub>g</sub>) was calculated by means of Tauc's expression in **Fig.S3** (supplementary

1 information), and results are summarized in **Table 1**. These values are approximate  
2 due to the need of extrapolation of the resulting curve as can be observed in **Fig.S3** for  
3 all the catalysts. The  $E_g$  value for tungstite  $H_2WO_4$  (major component of W-0 and W<sub>300-1</sub>)  
4 was found to be 2.42 eV which is increased up to 2.64 when the precursor is  
5 completely transformed into cubic  $WO_3$  structure (in W<sub>300-3</sub> catalyst). Then, the  $E_g$   
6 value was progressively increased up to 2.67 eV as monoclinic  $WO_3$  was formed.  
7 These results are quite similar to previously reported values (González-Borrero et al.,  
8 2010; Cao et al., 2012).

### 9 10 **3.2. Comparison of processes**

11 The effectiveness of the photocatalysts in the use of visible light radiation combined  
12 with ozone was tested using IBP as target compound by cutting off all the wavelengths  
13 lower than 390 nm of the Xe lamp in the solar simulator. First, the performance of the  
14 combined process (photocatalytic ozonation) respect to the single treatments has been  
15 checked with all the catalysts. Results obtained with W<sub>450-5</sub> catalyst are depicted in  
16 **Fig.4** and **Fig.5**, being this catalyst representative of the behaviour of the most active  
17 ones. **Fig.4(A)** shows the time evolution of IBP dimensionless concentration upon the  
18 different treatments applied. First of all, the absence of IBP depletion due to direct  
19 photolysis with visible light radiation was confirmed which is consistent with the UV-Vis  
20 absorption spectrum of this compound (**Fig.S4** of supplementary information). On the  
21 other hand, IBP adsorption capacity of the W<sub>450-5</sub> catalyst at the conditions studied  
22 here was somewhat noticeable, reaching around 10% of IBP removal after 2 h contact  
23 time. The depletion rate of IBP is increased in photocatalytic oxidation reaching 25% of  
24 IBP removal after 2 h of treatment although it can be noticed the low efficiency of the  
25 process as a consequence of the high recombination rate in  $WO_3$  materials used in the  
26 presence of oxygen (Nishimoto et al., 2010). When  $O_3$  is present, all the treatments led  
27 to complete IBP removal in less than 1 h of reaction time (with conversion higher than  
28 99%) regardless of the presence/absence of catalyst and/or radiation in contrast to  $O_3$ -  
29 free treatments. Although the evolution of IBP is quite similar for all the  $O_3$ -treatments,  
30 some slight differences can be observed in the depletion rate. Single ozonation and  
31 photolytic ozonation presented quite similar IBP depletion rate. On the other hand, the  
32 presence of the W<sub>450-5</sub> catalysts and ozone in dark conditions (catalytic ozonation) did  
33 not improve the degradation of IBP thus indicating that this catalyst does not possess  
34 any catalytic effect in ozone decomposition into reactive species such as hydroxyl  
35 radicals or even could produce an inefficient decomposition for IBP degradation.  
36 Photocatalytic ozonation gave place to the highest IBP depletion rate reaching  
37 complete IBP removal in 20 min compared to 40-50 min necessary for the other  $O_3$   
38 treatments.

39 On the other hand, it is known that the oxidation of IBP proceeds through different  
40 steps giving place to different intermediate compounds which are eventually  
41 transformed into  $CO_2$  and  $H_2O$  (complete mineralization). Thus, the mineralization of  
42 IBP has been followed and presented in **Fig.4(B)** as normalized TOC concentration. As  
43 expected from previous IBP results, neither adsorption nor direct photolysis led to  
44 significant mineralization percentages. Photocatalytic oxidation also gave place to



1 negligible mineralization according to the IBP conversion reached, lower than 25%.  
2 Regarding the O<sub>3</sub>-treatments, noticeable differences have been found depending on  
3 the presence/absence of O<sub>3</sub>, radiation and/or photocatalyst. Single ozonation led to  
4 25% of mineralization reached at 60 min and then stopped both as a consequence of  
5 the formation of some intermediate compounds that are refractory to ozone direct  
6 reaction (mainly short-chain organic acids) (Beltrán, 2004), and/or due to the absence  
7 of IBP in the reaction medium which eventually produces hydroxyl radicals through  
8 IBP-O<sub>3</sub> direct reaction as discussed below. Fairly similar results were observed during  
9 photolytic ozonation with visible light radiation. On the other hand, the presence of the  
10 catalyst combined with ozone in dark conditions (catalytic ozonation) did not improve  
11 the previous results. This process showed the poorest behavior of the O<sub>3</sub>-treatments in  
12 terms of mineralization, with negligible TOC conversion during the reaction time,  
13 confirming the absence of any positive catalytic effect in the reaction. In fact, the low  
14 mineralization reached compared to ozone alone treatment is likely indicative of an  
15 inefficient consumption of O<sub>3</sub> in the catalyst surface in the darkness. These results are  
16 contrary to those found for the mineralization of phenol with a commercial WO<sub>3</sub>  
17 (monoclinic) catalyst (Nishimoto et al., 2010), which points out the importance of the  
18 target compound nature to play a key role in the interactions compound-catalyst  
19 surface during catalytic ozonation. On the contrary, photocatalytic ozonation showed  
20 the highest mineralization rate, leading to 87% mineralization in 120 min reaction time.  
21 These results also point out the synergism produced between ozone and visible light  
22 irradiated WO<sub>3</sub> since final TOC removal of the combined process is much higher than  
23 the sum of these values for the individual processes (87% in O<sub>3</sub>/WO<sub>3</sub>/Vis vs. 5% in  
24 O<sub>2</sub>/WO<sub>3</sub>/Vis and 25% in O<sub>3</sub>), confirming also the ability of O<sub>3</sub> to capture the electrons on  
25 the WO<sub>3</sub> surface compared to O<sub>2</sub> (Nishimoto et al., 2010).

26 In addition, time profiles of dissolved ozone and hydrogen peroxide concentration  
27 during the treatments have been plotted in **Fig.5**. Regarding dissolved ozone, in  
28 **Fig.5(A)** it is seen that ozone accumulated in solution during the single ozonation  
29 experiment reaching a maximum concentration at about 60 min reaction time. Different  
30 profiles were observed in the other O<sub>3</sub>-treatments in which ozone concentration  
31 increased in the first minutes of the experiment and then remained almost constant.  
32 The ozone concentration was always lower in catalytic ozonation than during single  
33 ozonation. This observation together with the low mineralization reached, is an  
34 additional evidence of an inefficient decomposition of O<sub>3</sub> on the catalyst surface in the  
35 darkness. On the other hand, in the photocatalytic ozonation process, the maximum  
36 concentration of dissolved ozone was noticeably lower, leading to a nearly steady  
37 concentration of about 1x10<sup>-5</sup> M in contrast to 5x10<sup>-5</sup> M during single ozonation. The  
38 lowest values of dissolved ozone together with the highest mineralization rate observed  
39 in this treatment suggest that O<sub>3</sub> has been consumed on the WO<sub>3</sub> catalyst surface  
40 through its reaction with electrons generated in the photocatalytic process, thus  
41 enhancing the production of oxidizing species such as hydroxyl radicals, as with TiO<sub>2</sub>  
42 catalysts (Agustina et al., 2005; Augugliaro et al., 2006; Mena et al., 2012).

43 On the other hand, hydrogen peroxide is commonly formed through direct ozone  
44 reactions (Rakowski and Cherneva, 1990; Mvula and von Sonntag, 2003; Leitzke and

1 von Sonntag, 2009). This has been experimentally confirmed in this work for IBP, as  
 2 shown in **Fig.5(B)**. Thus, during single ozonation an increase in H<sub>2</sub>O<sub>2</sub> concentration up  
 3 to 45 min, when IBP was completely removed, can be observed. Then, H<sub>2</sub>O<sub>2</sub>  
 4 concentration remained almost constant until the end of the experiment. The  
 5 concentration of H<sub>2</sub>O<sub>2</sub> formed during catalytic and photolytic ozonation was somewhat  
 6 lower. On the other hand, during photocatalytic ozonation the formation of H<sub>2</sub>O<sub>2</sub> takes  
 7 place at higher rate reaching a maximum concentration at about 20-30 min when IBP  
 8 was completely removed. Then the consumption of H<sub>2</sub>O<sub>2</sub> was faster and the  
 9 concentration negligible at the end of the treatment. These results point out that H<sub>2</sub>O<sub>2</sub> is  
 10 being consumed through photocatalytic reactions probably acting as an electron  
 11 acceptor in the WO<sub>3</sub> surface thus increasing the production of hydroxyl radicals and  
 12 avoiding recombination to some extent, as also occurs with TiO<sub>2</sub> (Mena et al., 2012).  
 13 Finally, the formation of H<sub>2</sub>O<sub>2</sub> during photocatalytic oxidation was much lower than in  
 14 ozone processes confirming the production of H<sub>2</sub>O<sub>2</sub> mainly through direct IBP-O<sub>3</sub>  
 15 reaction.

16 Therefore, compared to individual processes, photocatalytic ozonation treatment with  
 17 WO<sub>3</sub> and visible-light radiation led to a faster IBP depletion with the highest  
 18 mineralization rate due to the synergistic effect between O<sub>3</sub> and irradiated WO<sub>3</sub>.

### 19 **3.2.1. Simplified mechanistic approach of IBP photocatalytic ozonation**

20 Direct ozone reactions in water follow second order kinetics and the kinetic regime can  
 21 be established through the determination of the Hatta number according to (Beltran,  
 22 2004):

$$23 \quad Ha = \frac{\sqrt{k_{IBP-O_3} D_{O_3} C_{IBP}}}{k_L} \quad (2)$$

24 Where D<sub>O<sub>3</sub></sub>=1.3x10<sup>-9</sup> m<sup>2</sup>s<sup>-1</sup> is the ozone diffusivity in water (Johnson and Davis, 1996),  
 25 and k<sub>L</sub>=5x10<sup>-5</sup> ms<sup>-1</sup> is the individual liquid phase mass transfer coefficient for a bubbled  
 26 stirred tank (Froment and Bishoff, 1979), being C<sub>IBP</sub> the molar IBP concentration and  
 27 k<sub>IBP-O<sub>3</sub></sub>=9.1 M<sup>-1</sup>s<sup>-1</sup> the direct reaction rate constant (Huber et al., 2005). The highest  
 28 calculated value was 0.023 for the initial conditions thus confirming slow kinetic regime  
 29 of ozone absorption. Thus the depletion rate of IBP through direct O<sub>3</sub> reaction is  
 30 described as follows:

$$31 \quad \left. -\frac{dC_{IBP}}{dt} \right)_{O_3} = \frac{1}{z} k_{IBP-O_3} C_{O_3} C_{IBP} \quad (3)$$

32 Where z=1 is the stoichiometric coefficient of the reaction in mol O<sub>3</sub>/mol IBP and C<sub>O<sub>3</sub></sub> is  
 33 the dissolved ozone concentration. The differential equation (3) was solved using the  
 34 value of the kinetic constant and the experimental values of C<sub>O<sub>3</sub></sub> by means of 4<sup>th</sup> order  
 35 Runge-Kutta. The results of simulated dimensionless C<sub>IBP</sub> together with the

1 experimental values during single ozonation are depicted in **Fig.6**. It can be clearly  
 2 noticed that the experimental rate of IBP depletion is higher than the expected results  
 3 (simulated), thus indicating that additional reactions may develop and contribute to IBP  
 4 removal. Indirect reactions due to O<sub>3</sub> decomposition are initiated through the following  
 5 steps:



12 These reactions lead to the formation of hydroxyl radicals (HO<sup>•</sup>) capable of oxidizing  
 13 IBP in water. However, the pH of the reaction was from 6.5 to 4.5 and therefore,  
 14 reaction (4) between O<sub>3</sub>/OH<sup>-</sup> seems not to play an important role on the IBP  
 15 disappearance. In addition, the accumulation of H<sub>2</sub>O<sub>2</sub> was observed during the single  
 16 ozonation experiment at these pH (**Fig.5(B)**), thus indicating that the reaction (6)  
 17 between O<sub>3</sub>/ HO<sub>2</sub><sup>-</sup> can be also disregarded. These evidences together with the  
 18 evolution of mineralization whereas IBP is still present in the reaction medium during  
 19 single ozonation lead to hypothesize the formation of ozonide radical through IBP-O<sub>3</sub>  
 20 direct reaction, as it has been previously reported for phenol or diclofenac (Mvula and  
 21 Sonntag, 2003; Buffle and von Gunten, 2006; Sein et al., 2008):



23 which immediately results in the formation of HO<sup>•</sup> through reaction (9), being INT any  
 24 intermediate organic compound.

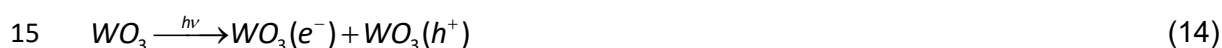
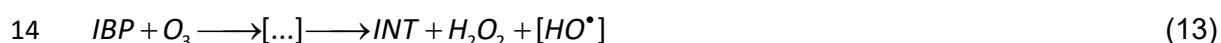
25 With these considerations, the depletion rate of IBP through direct O<sub>3</sub> reaction taking  
 26 into account the formation of HO<sup>•</sup> during this reaction is described as follows:

$$27 \quad \left. -\frac{dC_{IBP}}{dt} \right)_{O_3-HO^{\bullet}} = k_{IBP-O_3} C_{O_3} C_{IBP} + k_{IBP-HO^{\bullet}} C_{HO^{\bullet}} C_{IBP} \quad (11)$$

$$28 \quad \left. \frac{dC_{HO^{\bullet}}}{dt} \right)_{IBP-O_3} = k_{IBP-O_3} C_{O_3} C_{IBP} - k_{IBP-HO^{\bullet}} C_{HO^{\bullet}} C_{IBP} \quad (12)$$

1 Where  $k_{IBP-HO\cdot}$  is the rate constant between hydroxyl radical and IBP and  $C_{HO\cdot}$  is the  
 2 hydroxyl radical concentration. The differential equations (11) and (12) were  
 3 simultaneously solved using the value of the kinetic constants and the experimental  
 4 values of  $C_{O_3}$  by means of 4<sup>th</sup> order Runge-Kutta ( $k_{IBP-HO\cdot}=7.4 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ , Huber et al.  
 5 (2005)). These results are also depicted in **Fig.6**, where it can be observed that the  
 6 experimental IBP depletion rate is still higher than the simulated values. This could be  
 7 related to the accuracy of the rate constants used for the simulation and/or the  
 8 development of additional IBP degradation routes. The confirmation of the different  
 9 degradation ways needs extra experiments out of the scope of this work.

10 According to this and the previous findings, it can be postulated that photocatalytic  
 11 ozonation of IBP with  $WO_3$  catalyst takes place through reactions (13)-(20), where both  
 12  $O_3$  and  $HO\cdot$  are responsible for IBP disappearance and photogenerated oxidizing  
 13 species ( $HO\cdot$  and/or positive holes) are the main responsible for mineralization.



22 Reaction (13) summarizes the direct IBP- $O_3$  steps that would lead to some large  
 23 organic intermediates together with  $H_2O_2$  detected and accumulated during single  
 24 ozonation experiment, and eventually with the formation of  $HO\cdot$ . On the other hand,  
 25 visible light radiation provokes the creation of electron-hole pairs (reaction (14)) and  
 26 electrons are proposed to react with dissolved  $O_3$  and  $H_2O_2$  through reactions (15) and  
 27 (16), according to the profiles of these species during photocatalytic ozonation versus  
 28 single ozonation. Finally, photogenerated holes and hydroxyl radicals can oxidize both  
 29 IBP and any  $INT$  to achieve the complete mineralization into  $CO_2$  and  $H_2O$  according to  
 30 reactions (17)-(20).

31 The relative contribution of each step to the overall process would depend on the  
 32 experimental conditions (e.g. pH, ozone dose or catalyst loading), and the confirmation  
 33 of the intermediate species formed requires additional experimental work that will be  
 34 the subject of a future work.

### 3.3. Catalysts screening for photocatalytic ozonation under visible-light radiation

All the catalysts prepared were tested in the photocatalytic ozonation of IBP under visible-light radiation. The results are depicted in **Fig.7** and **Fig.8** together with single ozonation results for the sake of comparison. Regarding the evolution of IBP (**Fig.7(A)**) results are quite similar although some trends can be extracted. First of all, slight differences were observed in the IBP adsorption capacity of the catalysts during the dark stage that is generally consistent with the values of  $pH_{PZC}$  obtained where a higher surface acid character led to a higher amount of initial IBP adsorbed. However, these differences seem not to play a crucial role in the behavior of the catalysts. On the other hand, it can be noticed that W-0 and W<sub>300-1</sub> catalysts gave place to similar IBP depletion rate than ozone alone whereas the rest of the catalysts gave place to a slight higher depletion rate. In general, the catalytic activity is increased as the heat-treatment (both in time and/or temperature) was increased. Main differences between ozone and O<sub>3</sub>-photocatalytic processes were found in terms of mineralization (see **Fig.7(B)**). Ozone alone gave place to a 25% mineralization reached at about 60 min reaction time. On the other hand, the tungstite precursor, W-0, and the subsequent catalysts W<sub>300-1</sub> and W<sub>300-3</sub> showed a very different normalized TOC profile. It can be noticed a first step in which mineralization is slow, with a TOC removal rate fairly lower than during ozone alone reaction up to 60 min. After this time, the mineralization rate increased achieving around 35-40% of mineralization at 120 min with the three catalysts. It can be noticed that besides the differences in the properties of these three catalysts ( $E_g$ ,  $S_{BET}$ ,  $pH_{PZC}$ , etc.), they have in common that no monoclinic WO<sub>3</sub> crystallization has occurred during the heat-treatment applied. A significant increase of the catalytic activity is observed with the W<sub>300-5</sub> catalyst in terms of mineralization, reaching around 70% TOC removal at 120 min. The main differences of this and the previous catalysts are the presence of monoclinic crystalline phase to some extent in its structure according to XRD results. The best results were obtained with the 450°C heat-treated catalysts reaching around 85-87% mineralization at 120 min reaction time. In these catalysts, an important contribution of monoclinic WO<sub>3</sub> higher than 75% was observed together with a higher  $pH_{PZC}$  which could indicate the presence of oxygen vacancies to some extent, although this could not be confirmed by XPS. The differences found in the mineralization profile of W<sub>450-5</sub> and W<sub>450-30</sub> catalysts, the first one leading to the highest mineralization rate, could be related to the higher  $S_{BET}$  found in this catalyst.

In addition, the evolution of dissolved ozone and hydrogen peroxide concentration formed during the reaction has been plotted in **Fig.8**. Regarding dissolved ozone (**Fig.8(A)**), it is noticeable the lower values of steady concentration with the most active catalysts, W<sub>450-5</sub> and W<sub>450-30</sub>, compared to the single ozonation reaction. These results suggest an efficient O<sub>3</sub> consumption on the catalysts surface through its reaction with electrons generated in the photocatalytic process. **Fig.8(B)** shows the hydrogen peroxide concentration evolution with all the catalysts where the faster decomposition rate is also observed for the most active catalysts (W<sub>450-5</sub> and W<sub>450-30</sub>), thus being likely indicative of a higher consumption of H<sub>2</sub>O<sub>2</sub> in surface reactions as electron acceptor.

1 Therefore, at similar textural and optical properties, the monoclinic structure in  $\text{WO}_3$   
2 catalysts seems to be beneficial for the photocatalytic ozonation process with visible  
3 light.

#### 4 **3.4. Simulated solar light photocatalytic ozonation of ECs in MWW**

5 The selected catalyst  $\text{W}_{450-5}$  which presented the highest catalytic activity in the  
6 photocatalytic ozonation of IBP with visible light was tested in the photocatalytic  
7 ozonation of a mixture of ten ECs (AAP, MTP, CAF, HCT, ANT, SFM, CAR, KET, DCF  
8 and IBP) in a real municipal wastewater effluent. The characterization of the main  
9 parameters of the MWW effluent is summarized in **Table 2**. The photocatalytic  
10 ozonation treatment was carried out under the entire simulated solar light radiation  
11 from 300 nm. For comparative purposes also single ozonation treatment was carried  
12 out. The evolution of the ECs is depicted in **Fig.9**. It can be noticed that much of these  
13 compounds (AAP, ANT, SFM, CAR, KET and DCF) presented similar depletion rate  
14 both in single ozonation and photocatalytic ozonation treatments as a consequence of  
15 their high reactivity in  $\text{O}_3$  direct reaction. Thus, the  $\text{O}_3$  itself is highly effective to remove  
16 these compounds. Direct rate constants of ECs with  $\text{O}_3$  are summarized in **Table S1**.  
17 On the other hand, the ECs whose rate constant is lower such as MTP, CAF, HCT and  
18 IBP, were faster eliminated through photocatalytic ozonation (in less than 60 min),  
19 being the differences found between ozone alone and the combined process higher as  
20 lower was the direct rate constant of  $\text{O}_3$ -EC reaction. Again in the MWW matrix main  
21 differences between ozone and photocatalytic ozonation were found in terms of TOC  
22 removal as shown in **Fig.10**. As it can be seen, ozone alone gave place to a lower  
23 degree of mineralization reaching less than 10% TOC removal after 120 min in contrast  
24 to a mineralization higher than 40% during photocatalytic ozonation. In addition, **Table**  
25 **2** also shows the characterization of other important parameters in wastewater after the  
26 treatments being noticeable the decrease in COD and aromaticity when the combined  
27 treatment is applied. Finally, **Fig.11** shows the evolution of dissolved  $\text{O}_3$  concentration  
28 together with the formation of  $\text{H}_2\text{O}_2$  during the treatments. The obtained profiles are  
29 consistent with previous results thus indicating the consumption of both  $\text{O}_3$  and  $\text{H}_2\text{O}_2$   
30 (formed through  $\text{O}_3$ -ECs direct reaction) at the  $\text{WO}_3$  surface leading to the formation of  
31 additional oxidizing species such as hydroxyl radicals, which improve the mineralization  
32 reached. Thus, intermediate compounds formed from ECs oxidation are expected to be  
33 more easily eliminated through photocatalytic ozonation compared to single ozonation.

34 Therefore, the use of  $\text{WO}_3$  as catalyst for photocatalytic ozonation of ECs containing  
35 MWW is an attractive alternative that improves the use of solar radiation leading to a  
36 fast elimination of organic contaminants (mainly those refractory to ozone reactions)  
37 and achieving an important mineralization degree.

#### 38 **4. Conclusions**

39  $\text{WO}_3$  catalysts with different structural and surface properties were prepared by  
40 thermodecomposition of commercial tungstite ( $\text{H}_2\text{O}\cdot\text{WO}_3$ ) at different temperatures,  
41 300 and 450°C, and short times, from 1 to 30 min. This heat-treatment allows obtaining  
42 tungstite, cubic and monoclinic crystalline phases of tungsten trioxide. In general, as  
43 time or temperature increased, monoclinic structure is formed which is also

1 accompanied by a reduction of specific surface area and an increase in the presence  
2 of oxygen vacancies. These properties, monoclinic structure together with the presence  
3 of oxygen vacancies played a key role in the behaviour of the WO<sub>3</sub> catalysts in the  
4 photocatalytic ozonation of IBP under visible light radiation, favouring the electron  
5 transport in the catalyst surface to some extent, thus improving the efficiency of the  
6 process. Among the treatments tested with the best catalytic system, photocatalytic  
7 ozonation showed a synergistic effect between ozone and irradiated WO<sub>3</sub> leading to a  
8 complete IBP depletion in less than 20 min with a degree of mineralization at about  
9 87% at 120 min. Finally, the use of WO<sub>3</sub> as catalyst for photocatalytic ozonation of ECs  
10 in a MWW effluent with simulated solar radiation led to a fast elimination of the  
11 contaminants in less than 60 min and a mineralization degree higher than 40% at 120  
12 min. The mechanism and kinetics of photocatalytic ozonation with WO<sub>3</sub> catalysts will be  
13 the subject of further work.

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21

#### 22 **Appendix A. Supporting information**

23 Supplementary data associated with this article can be found in the online version at  
24 XXXXXXXXX

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31 **Figure 6.** Experimental and simulated IBP dimensionless concentration evolution  
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35 **Figure 7.** (A) IBP and (B) TOC dimensionless concentration evolution during  
36 photocatalytic ozonation with all the catalysts studied (lines show trends). Conditions:  
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45 **Figure 9.** ECs dimensionless concentration during ozonation and photocatalytic  
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1 **Figure 10.** TOC dimensionless concentration evolution during ozonation and  
2 photocatalytic ozonation with  $W_{450-5}$  catalyst in a MWW effluent (lines show trends).  
3 Conditions:  $pH_0=6.5$ ,  $T=25-35^\circ\text{C}$ ,  $C_{\text{ECs},0}=0.5 \text{ mg L}^{-1}$ ,  $C_{\text{WO}_3}=0.25 \text{ g L}^{-1}$ ,  $C_{\text{O}_3\text{ginlet}}=10 \text{ mg L}^{-1}$ ,  
4  $Q_g=20 \text{ L h}^{-1} (\text{O}_3/\text{O}_2)$ .  
5  
6 **Figure 11.** (A) Dissolved  $\text{O}_3$  concentration and (B)  $\text{H}_2\text{O}_2$  concentration during ozonation  
7 and photocatalytic ozonation with  $W_{450-5}$  catalyst in MWW effluent (lines show trends).  
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9  $Q_g=20 \text{ L h}^{-1} (\text{O}_3/\text{O}_2)$ .  
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**Table 1.** Nomenclature, calcination conditions and some properties of the photocatalysts

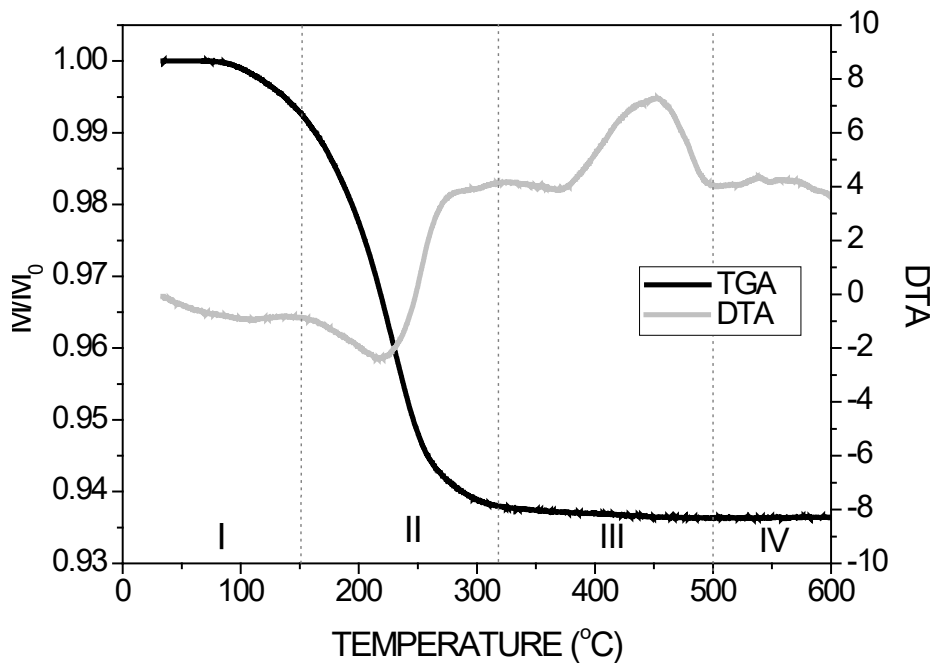
CATALYST	Calcination conditions	Tungstite (%)	Cubic (%)	Monoclinic (%)	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	pH <sub>PZC</sub>	E <sub>g</sub> (eV)
W-0	---	~100	0	0	27.8	4.71	2.42
W <sub>300</sub> -1	300°C, 1 min	82.0	18.0	0	28.7	4.39	2.43
W <sub>300</sub> -3	300°C, 3 min	0	100	0	40.3	4.13	2.64
W <sub>300</sub> -5	300°C, 5 min	0	85.7	14.3	39.0	4.18	2.65
W <sub>300</sub> -60	300°C, 60 min	0	80.3	19.7	n.m	n.m	n.m
W <sub>450</sub> -5	450°C, 5 min	0	23.9	76.1	30.2	5.25	2.65
W <sub>450</sub> -30	450°C, 30 min	0	9.5	90.5	21.1	4.98	2.67

n.m.: not measured

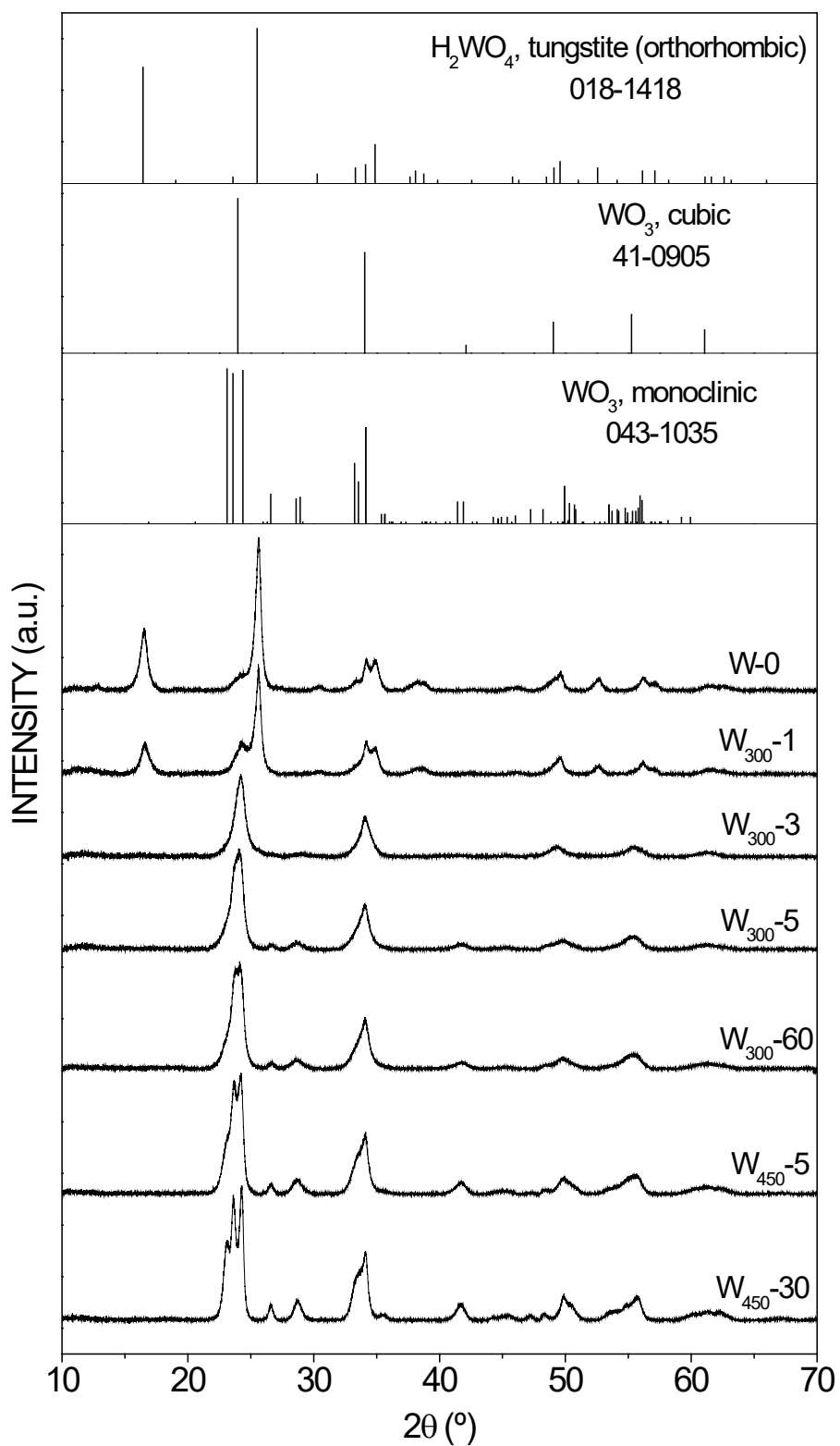
**Table 2.** Characterization of MWW effluent

<b>PARAMETER</b>	<b>Before treatment</b>	<b>Ozonation</b>	<b>Photocatalytic ozonation</b>
TOC (mgC L <sup>-1</sup> )	14.2	13.1	8.2
IC (mgC L <sup>-1</sup> )	0.19	0.15	0.20
Turbidity (NTU)	3.0	n.m.	n.m.
pH	6.5	5.9	5.7
Absorbance 254 nm	0.268	0.102	0.015
COD (mgO <sub>2</sub> L <sup>-1</sup> )	44	33	13
BOD (mgO <sub>2</sub> L <sup>-1</sup> )	28	n.m.	n.m.
Phosphate (mg L <sup>-1</sup> )	5	5	5

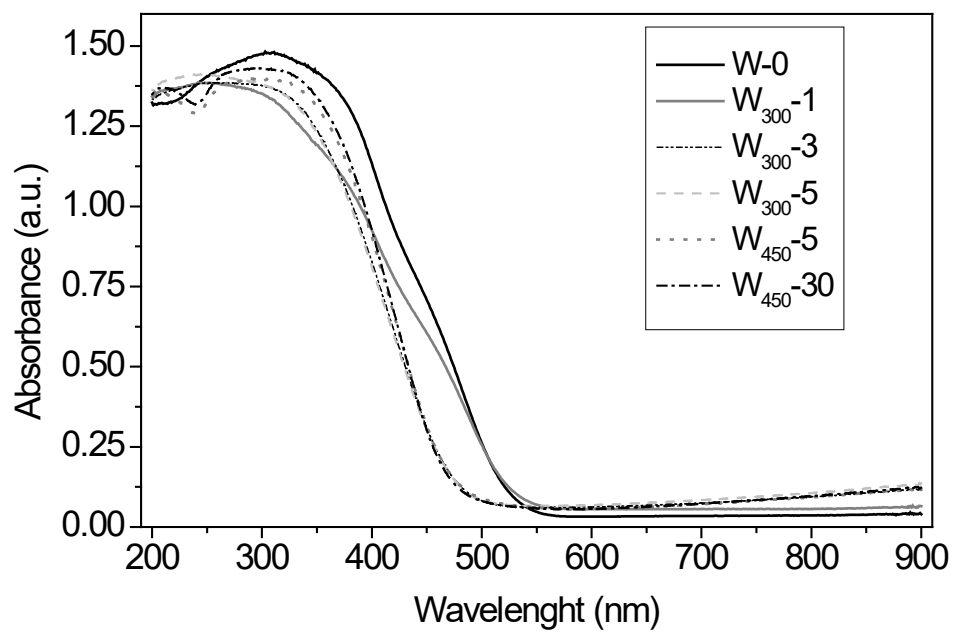
n.m.: not measured



**Figure 1.** ATG-DTA profiles of  $H_2WO_4$  precursor

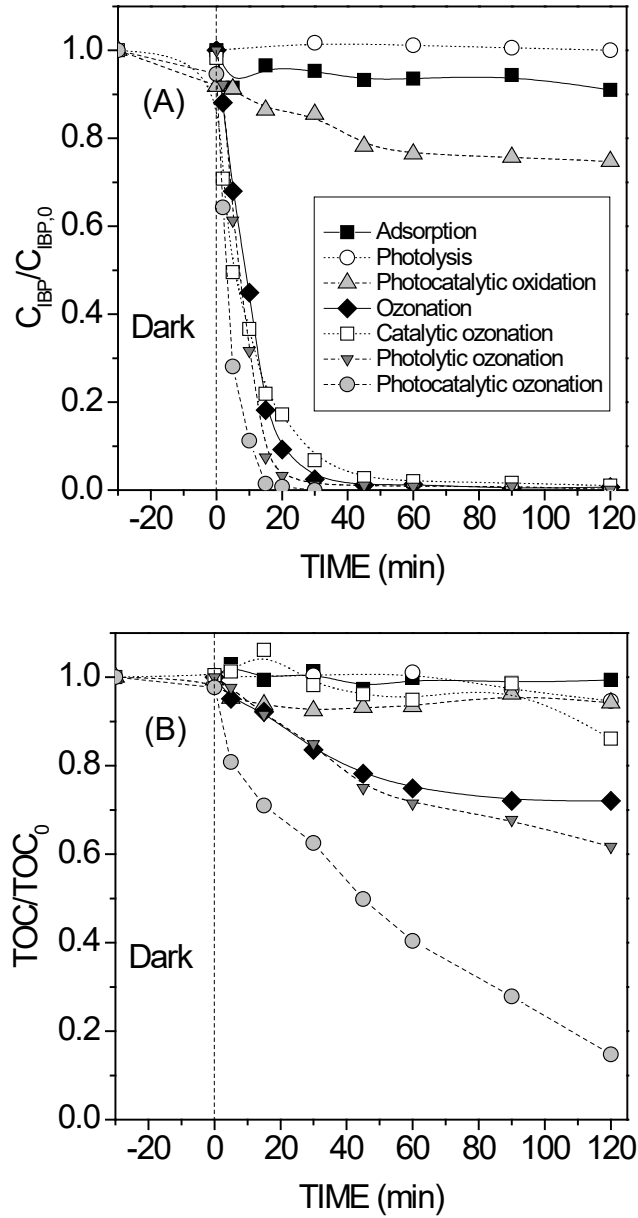


**Figure 2.** XRD patterns of the catalysts

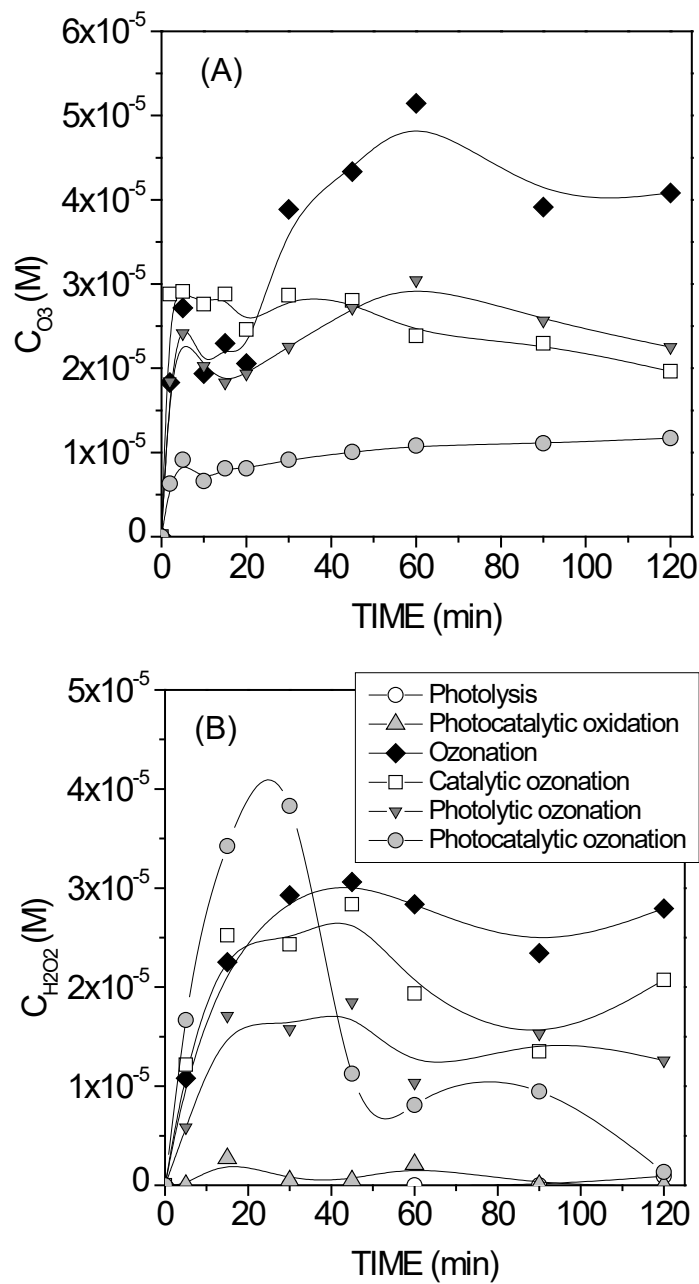


**Figure 3.** DR-UV-Vis spectra of the catalysts

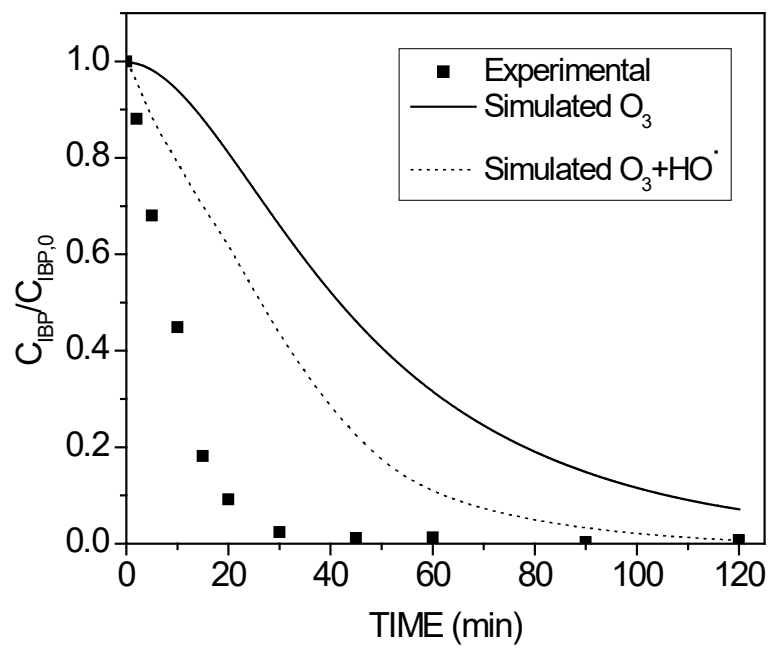




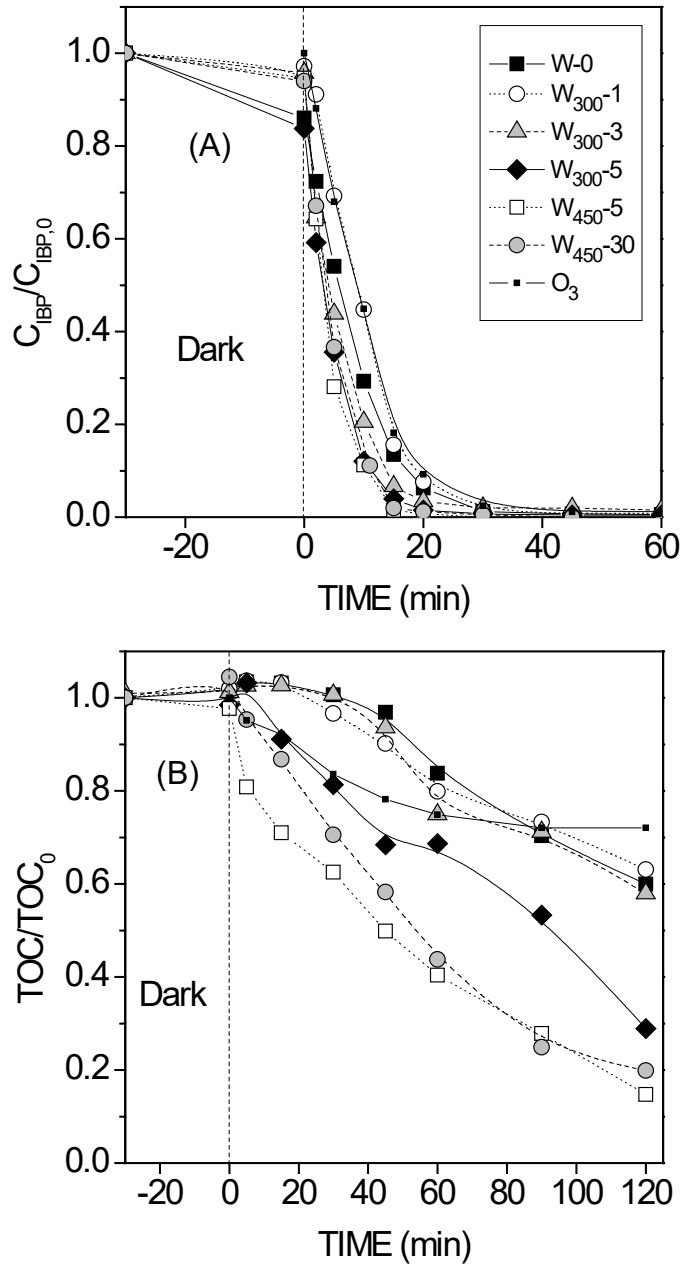
**Figure 4.** (A) IBP and (B) TOC dimensionless concentration evolution during all the treatments applied with  $W_{450-5}$  catalyst (lines show trends). Conditions:  $pH_0=6.5$ ,  $T=25-35^\circ C$ ,  $C_{IBP,0}=10 \text{ mg L}^{-1}$ ,  $C_{WO_3}=0.25 \text{ g L}^{-1}$ ,  $C_{O_3 \text{ inlet}}=10 \text{ mg L}^{-1}$ ,  $Q_g=20 \text{ L h}^{-1}$  ( $O_2$  or  $O_3/O_2$ ).



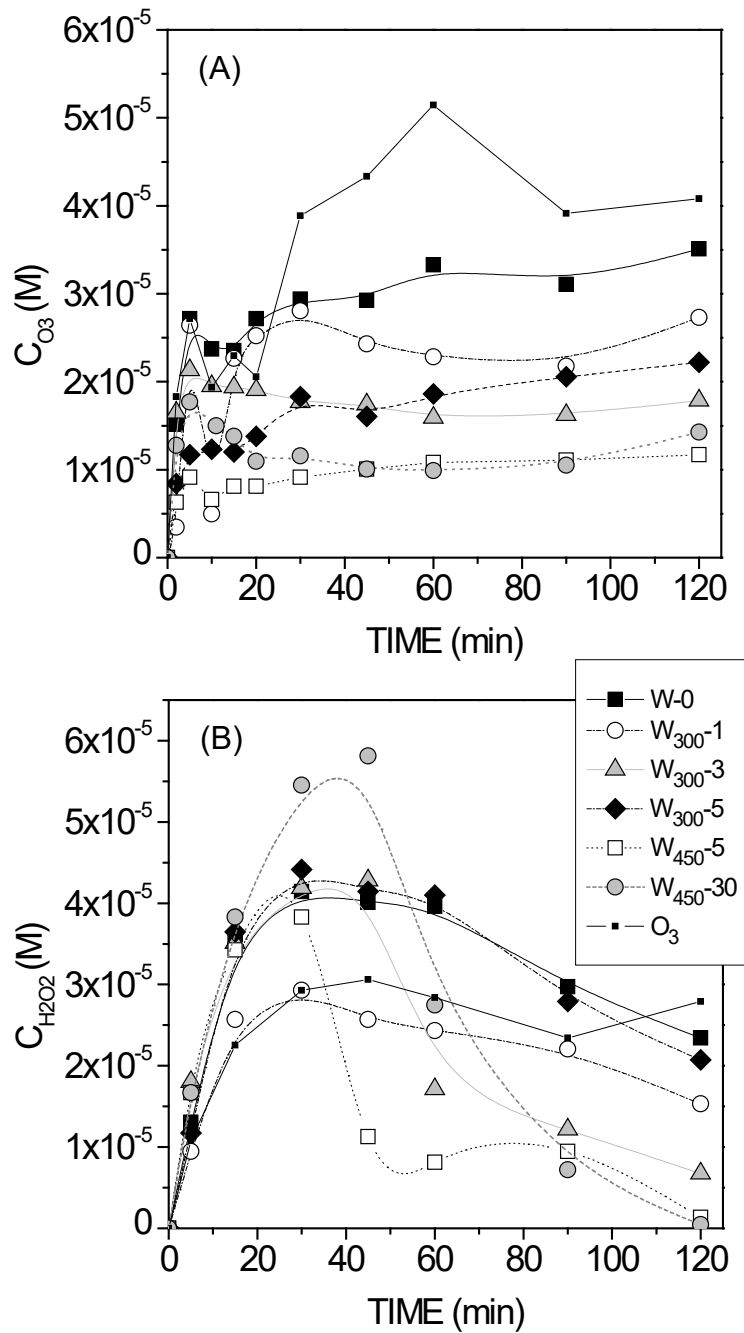
**Figure 5.** (A) Dissolved O<sub>3</sub> concentration and (B) H<sub>2</sub>O<sub>2</sub> concentration during all the treatments applied with W<sub>450-5</sub> catalyst (lines show trends). Conditions: pH<sub>0</sub>=6.5, T=25-35°C, C<sub>IBP,0</sub>=10 mg L<sup>-1</sup>, C<sub>WO<sub>3</sub></sub>=0.25 g L<sup>-1</sup>, C<sub>O<sub>3</sub>ginlet</sub>=10 mg L<sup>-1</sup>, Q<sub>g</sub>=20 L h<sup>-1</sup> (O<sub>2</sub> or O<sub>3</sub>/O<sub>2</sub>).



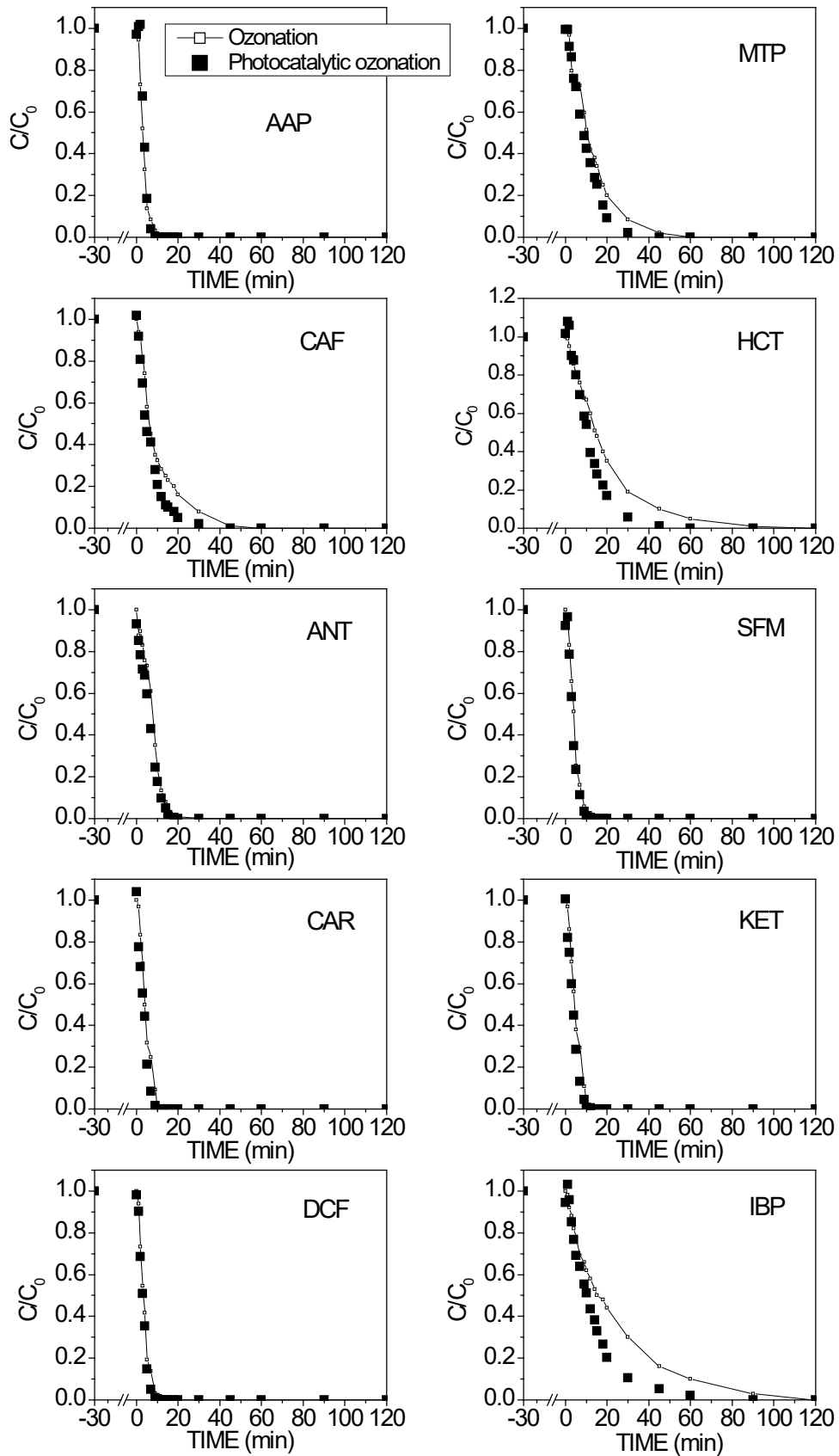
**Figure 6.** Experimental and simulated IBP dimensionless concentration evolution during single ozonation. Conditions:  $\text{pH}_0=6.5$ ,  $T=25\text{-}35^\circ\text{C}$ ,  $C_{\text{IBP},0}=10 \text{ mg L}^{-1}$ ,  $C_{\text{O}_3\text{ginlet}}=10 \text{ mg L}^{-1}$ ,  $Q_g=20 \text{ L h}^{-1}$  ( $\text{O}_3/\text{O}_2$ ).



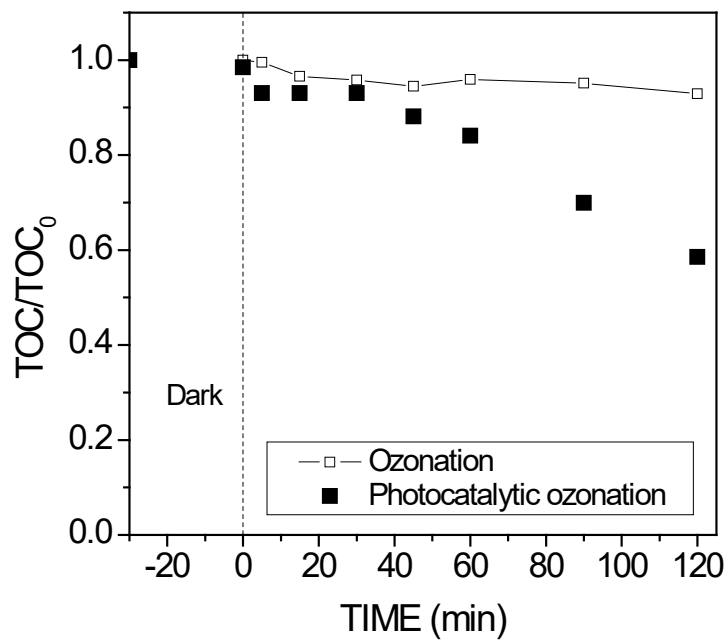
**Figure 7.** (A) IBP and (B) TOC dimensionless concentration evolution during photocatalytic ozonation with all the catalysts studied (lines show trends). Conditions:  $pH_0=6.5$ ,  $T=25-35^\circ\text{C}$ ,  $C_{IBP,0}=10\text{ mg L}^{-1}$ ,  $C_{WO_3}=0.25\text{ g L}^{-1}$ ,  $C_{O_3\text{inlet}}=10\text{ mg L}^{-1}$ ,  $Q_g=20\text{ L h}^{-1}$  ( $O_3/O_2$ ).



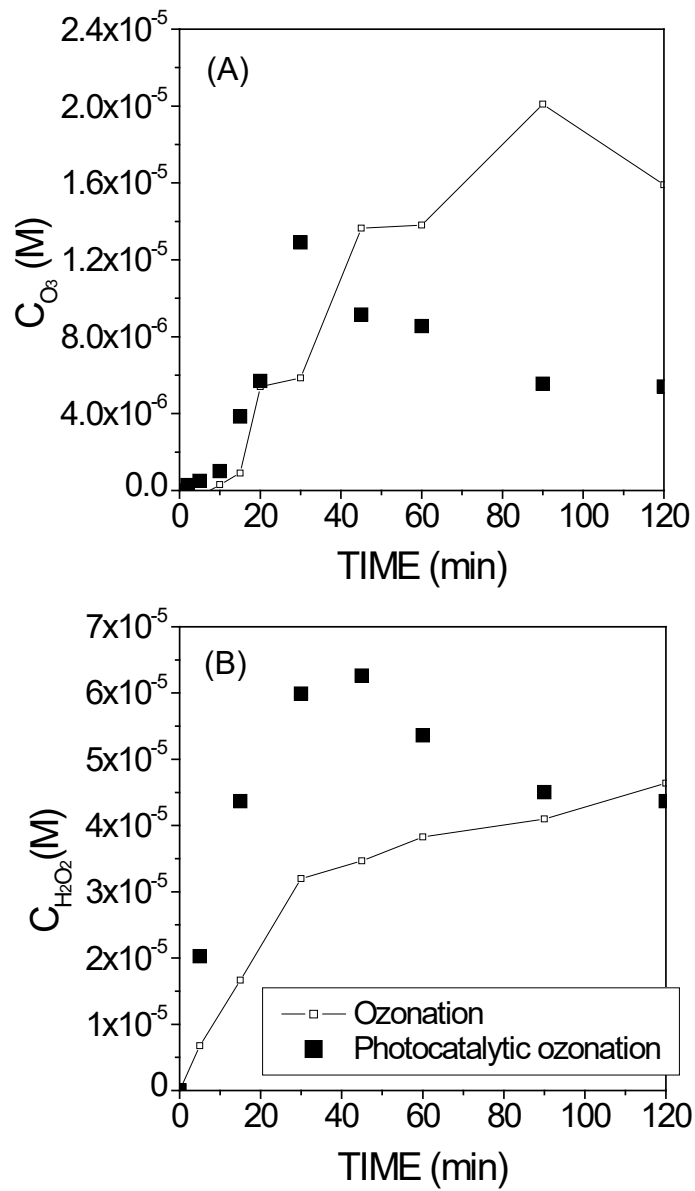
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**Figure 9.** ECs dimensionless concentration during ozonation and photocatalytic ozonation with  $W_{450-5}$  catalyst in a MWW effluent (lines show trends). Conditions:  $pH_0=6.5$ ,  $T=25-35^\circ C$ ,  $C_{ECs,0}=0.5 \text{ mg L}^{-1}$ ,  $C_{W_{O3}}=0.25 \text{ g L}^{-1}$ ,  $C_{O_{3inlet}}=10 \text{ mg L}^{-1}$ ,  $Q_g=20 \text{ L h}^{-1}$  ( $O_3/O_2$ ).



**Figure 10.** TOC dimensionless concentration evolution during ozonation and photocatalytic ozonation with  $W_{450-5}$  catalyst in a MWW effluent (lines show trends). Conditions:  $pH_0=6.5$ ,  $T=25-35^\circ\text{C}$ ,  $C_{ECs,0}=0.5 \text{ mg L}^{-1}$ ,  $C_{WO_3}=0.25 \text{ g L}^{-1}$ ,  $C_{O_3\text{inlet}}=10 \text{ mg L}^{-1}$ ,  $Q_g=20 \text{ L h}^{-1}$  ( $O_3/O_2$ ).



**Figure 11.** (A) Dissolved O<sub>3</sub> concentration and (B) H<sub>2</sub>O<sub>2</sub> concentration during ozonation and photocatalytic ozonation with W<sub>450-5</sub> catalyst in MWW effluent (lines show trends). Conditions: pH<sub>0</sub>=6.5, T=25-35°C, C<sub>ECs,0</sub>=0.5 mg L<sup>-1</sup>, C<sub>WO<sub>3</sub></sub>=0.25 g L<sup>-1</sup>, C<sub>O<sub>3</sub>ginlet</sub>=10 mg L<sup>-1</sup>, Q<sub>g</sub>=20 L h<sup>-1</sup> (O<sub>3</sub>/O<sub>2</sub>).