

AperTO - Archivio Istituzionale Open Access dell'Università di Torino

## Micro-TiO<sub>2</sub> coated glass surfaces safely abate drugs in surface water

### **This is the author's manuscript**

*Original Citation:*

*Availability:*

This version is available <http://hdl.handle.net/2318/1682088> since 2019-01-09T18:31:31Z

*Published version:*

DOI:10.1016/j.jhazmat.2018.09.057

*Terms of use:*

Open Access

Anyone can freely access the full text of works made available as "Open Access". Works made available under a Creative Commons license can be used according to the terms and conditions of said license. Use of all other works requires consent of the right holder (author or publisher) if not exempted from copyright protection by the applicable law.

(Article begins on next page)

# Micro-TiO<sub>2</sub> coated glass surfaces safely abate drugs in surface water

Cerrato, G.<sup>1,4</sup>, Bianchi, C. L.<sup>2,4</sup>, Galli, F.<sup>2,4</sup>, Pirola, C.<sup>2,4</sup>, Morandi, S.<sup>1,4</sup>, Capucci, V.<sup>3</sup>

<sup>1</sup>Università di Torino, Dip. Chimica & NIS Interdept. Centre, via P. Giuria 7, 10125 Torino, Italy

<sup>2</sup>Università degli Studi di Milano, Dipartimento di Chimica, via Golgi 19, 20133 Milano, Italy

<sup>3</sup>GranitiFiandre SpA, 41042 Fiorano M.se, Italy

<sup>4</sup>INSTM – Consorzio Interuniversitario per la scienza e tecnologia dei Materiali, via G. Giusti 9, 50121 Firenze

## Abstract

The ingredients of Pharmaceuticals and Personal Care Products (PPCPs) persist in water and conventional treatment plants are not able to remove them efficiently. Sonochemical treatment is insufficient to mineralize organics such as ibuprofen into CO<sub>2</sub> and H<sub>2</sub>O. TiO<sub>2</sub> degrades ibuprofen (IBP) under UV light; however, it does not reach a high grade of conversion. Here, we investigated the mineralization of ibuprofen to CO<sub>2</sub> by TiO<sub>2</sub> UV-C photocatalysis. We replaced nano-sized P25 (the standard catalyst) with a micro-sized commercial sample of TiO<sub>2</sub> to preclude the use of nanoparticles which are dangerous for human health and because typical filtration systems are expensive and inefficient. We deposited micro-TiO<sub>2</sub> on glass Raschig rings to ensure an easy recovery and reuse of the photocatalyst and we studied its performance both with a batch and a continuous reactor. Micro-TiO<sub>2</sub> mineralized 100 % of IBP in 24 h. TiO<sub>2</sub>-coated glass Raschig rings degraded 87 % of IBP in 6 h of UV-C irradiation in a continuous reactor, with a mineralization of 25 %. Electrospray ionization mass spectrometer (ESI-MS, positive mode) analyses identified 13 different byproducts and we hypothesised a degradation pathway for IBP degradation.

Keywords: Ibuprofen degradation; wastewaters; continuous reactor; supported catalyst; Kronos 1077; micrometric sample

## 1. Introduction

Industries at large produce waste that pollutes bodies of water [1,2]. These emerging contaminants are persistent [3] and untreatable with conventional water treatment plants (WTPs) [4]. Pharmaceuticals and Personal Care Products (PPCPs) account for the majority of these contaminants. They retain their concentration and structure or are converted into other compounds in aquatic matrices [5]. PPCPs concentrations' range from ng L<sup>-1</sup> to µg L<sup>-1</sup> in surface water [6,7], which is enough to affect human and wildlife physiology [8,9]. Conventional treatment plants inefficiently remove PPCPs [10]. Behera et al. detected 17 of 20 target compounds in the effluents of an advanced Korean WTP [11]. Koplín et al. found a median of 7 organic wastewater

contaminants in 139 American streams between 1999 and 2000 [12]; in 2017, Glassmayer et al. analyzed drinking water with a GC-MS. It revealed several classes of chemical compounds, including pharmaceuticals [13]. Feng et al. reviewed Electrochemical Advanced Oxidation Processes (EAOPs) to remove anti-inflammatory and analgesic pharmaceuticals, including aspirin, ibuprofen and ketoprofen [14], however this process is unfeasible due to electrical costs. Ibuprofen (IBP), i.e. (RS)-2-(4-(2-methylpropyl)phenyl)propanoic acid, is an anti-inflammatory and has detrimental effects on wastewater active sludge [15]. Davids et al. demonstrated that IBP shifts the structure and population of active sludge bacteria and significantly decreases their activity, especially for nitrification/denitrification bacteria [16]. Ultrasound (355 kHz, 30 W) degrades organic pollutants (initial concentration of pollutant = 23-230 ppm), but it does not mineralize them [17]. Sonolysis (45 kHz, 125 W) and photocatalysis (P25, 1 g L<sup>-1</sup>) degraded chlorinated organic compounds and mineralized them in 200 min [18]. However, in the case of IBP, sono- and photo-degradation produce long-living intermediates that need a post-biological treatment, as reported by Arriaga et al. [19].

Fe<sup>3+</sup> and P25-TiO<sub>2</sub> (concentration of 1 g L<sup>-1</sup>) sonophotocatalytically degraded IBP; photocatalysis mineralized 74 % of the IBP and sono-photocatalysis mineralized 92 % [19] (Xe-OP lamp emitting a photon flux power of 6.9 μE s<sup>-1</sup>, initial concentration of IBP was between 25-200 ppm). Choina et al. doped TiO<sub>2</sub>-P25 by Zr species, improving catalyst activity under UV light, but without completely mineralize it [20], in particular they degraded IBP (20-60 ppm) at room temperature using a Philips UV-vis solar lamp (power of 60 W) and a catalyst concentration of 10 mg L<sup>-1</sup>. Yuan et al. [21] and El-Sheikh et al. [22] focused on visible light photodegradation of IBP. They reached 100 % photodegradation of IBP without complete mineralization. LED lamps, emitting at 410 nm, degraded IBP (initial concentration of 5 ppm) with a power of 40 mW cm<sup>-2</sup> and a photocatalyst concentration of 400 mg L<sup>-1</sup> [21]. On the other hand, El-Sheikh et al. [22] employed a LED lamp with a power of 1 mW cm<sup>-2</sup> emitting at 420 nm. The initial IBP concentration they chose was 20 ppm and a catalyst concentration of 0.5 g L<sup>-1</sup>.

Even though the results reported in literature are encouraging, most of the papers lack a description catalyst recovery. P25-TiO<sub>2</sub> is the standard photocatalyst. However, its nanometric size makes it difficult to filter, considering the high water mass treated in a common wastewater plant (50-100 m<sup>3</sup> y<sup>-1</sup> person<sup>-1</sup> [23]). Moreover, P25 have adverse effects on human health [24].

Here, we report for the first time the complete mineralization of IBP by TiO<sub>2</sub> UV photocatalysis. We replaced nano-sized P25 with a micro-size commercial sample of TiO<sub>2</sub> (Kronos K1077) to avoid the use of nanoparticles, considering their harmful health effects [25] and their difficult

management in WTPs [26]. K1077 degrades NO<sub>x</sub> (see sample A in reference [27]) and ethanol [28].

Moreover, we deposited K1077 on glass Raschig rings to avoid filtration. We therefore aim at studying a process that may be applied in large-scale WTPs.

## 2. Materials and methods

### 2.1 Materials

Ibuprofen (Sigma Aldrich, 99 %) was used without any further purification. We prepared TiO<sub>2</sub> coated Raschig rings with dimensions of 6x6 mm and 8x8 mm (Fig. 1). The thickness of both rings was 1 mm.



Figure 1: Glass Raschig rings without catalyst (on the left) and coated with a thin film of TiO<sub>2</sub> (on the right).

We coated the glass Raschig rings with a tailored ink containing a TiO<sub>2</sub> by Kronos (K1077). K1077 particle size and crystallographic phase composition was reported in a previous work (see Table 1 of reference [27], sample A). This catalyst consists of anatase, its particle dimension ranges from 110 nm to 130 nm and its specific surface area is 10-15 m<sup>2</sup> g<sup>-1</sup>.

The ink was designed and developed for digital ceramic printers [29]. It contains a weight percentage of TiO<sub>2</sub> of 12 % and silica-based compounds that vitrifies at the calcination temperatures and stabilizes the photocatalyst particles. The ink is employed for the production of photocatalytic industrial slabs [30] that were tested for aspirin and paracetamol abatement in water [31].

Both glass rings were immersed in the ink solution for 5 min and then heated at 650 °C for 30 minutes (ramp of 15 °C min<sup>-1</sup>) to favour the inks adhesion onto the glass surface. We characterized the powders before and after the calcination in a previous work by laser Raman microspectroscopy. Calcination does not affect the crystal structure of TiO<sub>2</sub> [30].

## 2.2 Reactors and photocatalytic setup

To assess the performance of the new supported catalyst, we compared a typical test in a batch slurry reactor (Figure 2a) to a continuous reactor filled with K1077-coated Raschig rings (Figure 2b).

For both reactor configurations, a UV-C germicide immersion lamp (Jelosil, model GL8, 220 V, 9 W, emission wavelength: 215 nm) provided UV light and irradiated the solution at a power of 55 W m<sup>-2</sup>. The volume of the reactor is 600 mL, 380 mm height and with an internal diameter of 50 mm. We prepared IBP solution using tap water with a concentration of 20 ppm. We chose the initial concentration of IBP of 20 ppm to work far from the detection limit of the instrumentation. Moreover, even though pollutants' concentration in real wastewaters is lower, the typical initial lab test concentration is of the order of ppm [19,20]. In the batch reactor, K1077 concentration was 0.1 g L<sup>-1</sup>.

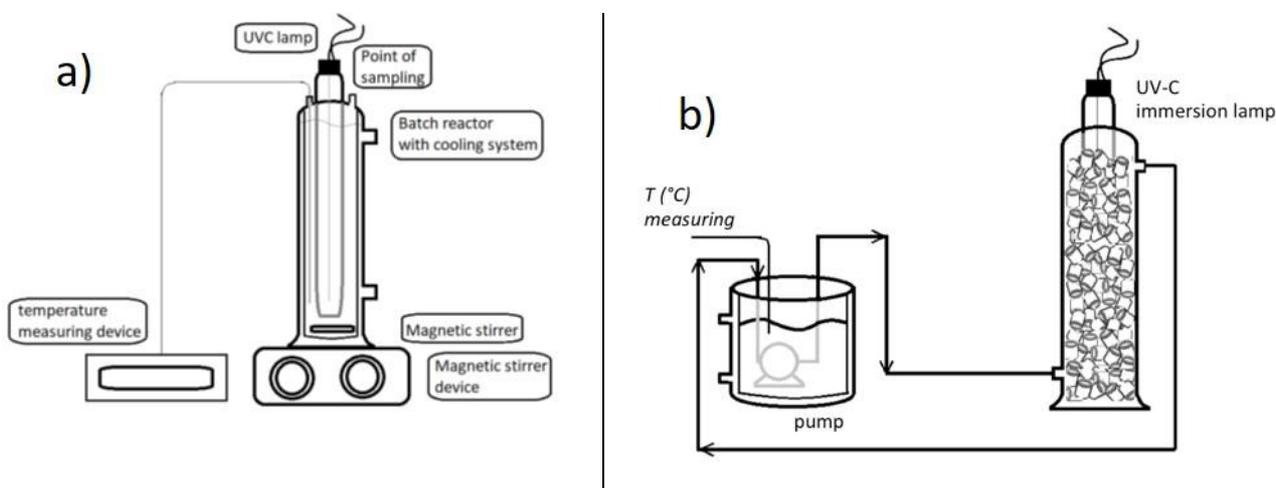


Figure 2: Batch (a) and continuous (b) reactor setup. The catalyst was K1077 powder (a) or K1077 coated Raschig rings (b).

In the continuous configuration (Figure 2b), a pump recirculated the solution through the reactor (from bottom to top), with a flowrate of 100 mL min<sup>-1</sup>. The pump was immersed in a reservoir (with a 2 L volume). The reactor was filled with the Raschig rings. We charged 1030 ± 25 6 x 6 Rings and 625 ± 25 8 x 8 rings respectively. Even though the number is different, the total surface area of these two catalysts were similar (0.22 m<sup>2</sup> and 0.24 m<sup>2</sup>, respectively, see Table S1 in the

Supplementary Material file). We took samples at 60 min intervals for 6 h and kept the temperature constant at  $25 \pm 2$  °C for both setups. Due to safety reasons, we could not run experiments in continuous mode overnight. Prior to photocatalytic tests, we evaluated the photolysis of IBP, i.e we run a test without the catalyst. All the tests were run in duplicate and here we report the average values.

### 2.3 Analytical

An HPLC (1100 Series Instrument, Agilent) with a diode array detector, monitored IBP concentration. It was equipped with a 125 mm  $\times$  4 mm C18 reverse phase column. The mobile phase composition was 72:28 v/v of  $K_2HPO_4 \cdot 3H_2O$  buffer and acetonitrile (HPLC grade), respectively. The buffer contained 2.3 g of  $K_2HPO_4 \cdot 3H_2O$  dissolved in 1000 mL of HPLC grade water. Its pH was adjusted to  $6.8 \pm 0.1$  with NaOH.

IBP peak was detected at 222 nm and peaks of intermediate products were recorded at 210 nm. We selected these two wavelengths according to preliminary tests followed by recording the full UV-vis spectrum (PG Instruments, model T60 U, from 190 nm to 400 nm, see Supplementary Material file, Figure 1S).

A total organic carbon analyzer (TOC 5000A, Shimadzu Instrument) calculated the IBP mineralization.

A field emission scanning electron microscope LEO1525 (SEM) imaged the K1077 Raschig rings after a sputtering coating with chromium.

An electrospray ionization mass spectrometer (LCQ Advantage System ESI-MS, Thermo Finnigan) individuated some of the degradation byproducts. The MS spectra were obtained by direct infusion of the samples' solutions under ionization. The instrument applied a voltage of +3.0 kV to the ESI. We operated in positive mode, even though IBP was better detected in negative mode since it is an acid, because of the lower signal to noise ratio, which permitted to individuate photodegradation by-products (compare Figure 2S and 3S in Supplementary material). Full-scan mass spectra were recorded in the mass/charge (m/z) range of 50 to 2000.

## 3. Results and discussion

### 3.1 Batch photodegradation of IBP

UV-C light degrades IBP in 5 h (Figure 3, conversion of 99.0 %). Da Silva et al. obtained the same conversion [32]. We calculated a half-life time of 28.7 min for the photolysis of IBP, assuming pseudo-first order kinetics. Da Silva et al. obtained a value of 18.4 min; this is ascribable to the different power emitted by the UV-C lamps (they employed three UV-C lamps with a nominal

power of 9 W each, therefore applying a total power of 27 W [32]). K1077 improves the degradation of IBP, with a conversion of 99.0 % in 4 h. However, UV-C mineralizes 18 % in 6 h while with K1077 32 % is mineralized.

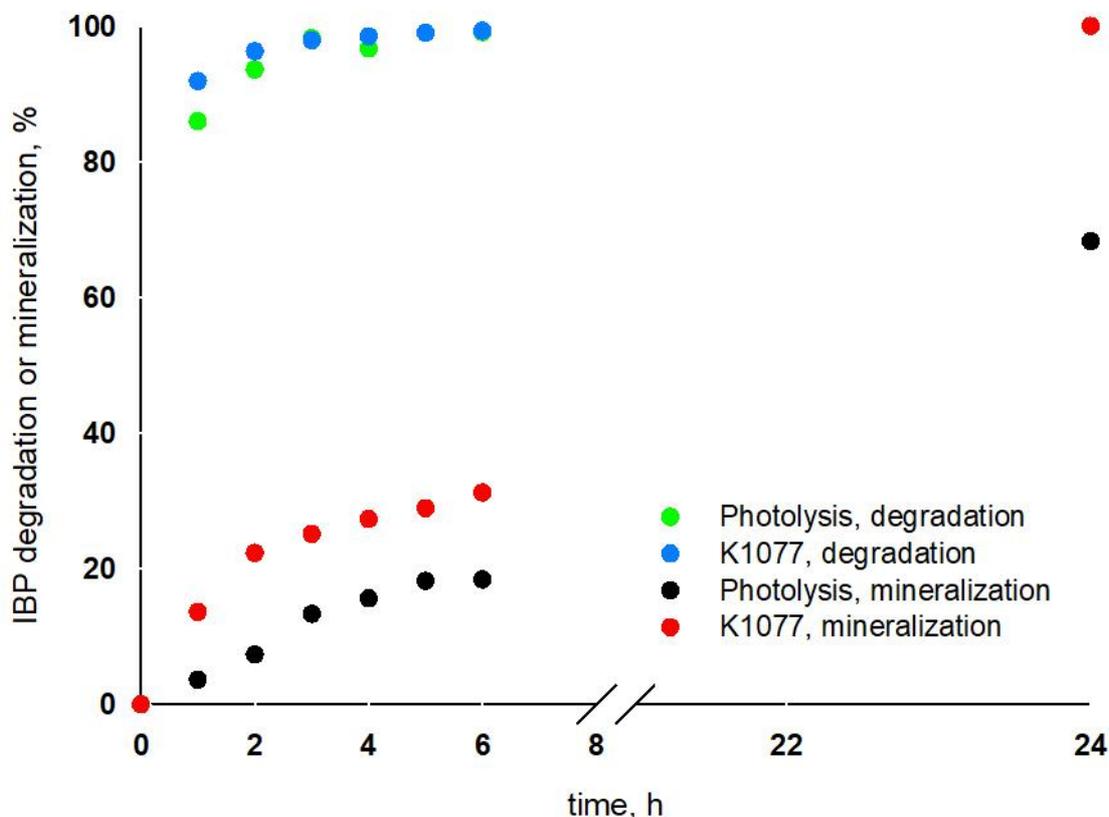


Figure 3: Batch degradation and mineralization of IBP with and without (photolysis) K1077 powder.

After 24 h, K1077 mineralizes all IBP.

Braz et al. studied the ecotoxicity of IBP byproducts against *Daphnia Similis* [33]. The generated hydroxylated byproducts led to a microorganism mortality rate of 80 % after 6 h. Méndez-Arriaga reached the same conclusion with *Vibro Fischeri* bacteria as a reference [19]. Since byproducts are more toxic than IBP itself, it is necessary to reach a high grade of mineralization. We therefore conclude that the use of a photocatalyst is necessary to mineralize all chemicals formed during IBP degradation and photolysis is not a viable technique for water treatment plants.

### 3.2 Photodegradation of IBP using glass Raschig rings

A balance weighted the Raschig rings before and after the coating. TiO<sub>2</sub> loading was 0.005 g ± 0.001 g per ring ( $\alpha = 0.05$ ). We obtained this value subtracting the average weight of 25 Raschig rings coated by the average weight of 25 rings uncoated on a precision balance (0.1 mg precision).

Therefore, the mass of catalyst in the two reactors is different. The slurry reactor contains 0.06 g of K1077 while we charged in the continuous reactor  $3.13 \pm 0.20$  g and  $5.15 \pm 0.20$  g of K1077 coated on 8x8 and 6x6 rings, respectively. We believe that running a test with a constant mass of catalyst, i.e. without filling all the reactor with rings, is not coherent since we aim at using our new catalyst in a real application, and thus we studied the performance of the reactor filled with coated Raschig rings, without considering the different amount of catalyst charged.

8 x 8 mm glass Raschig rings achieved higher degradation and mineralization compared to the 6 x 6 mm (Figure 4). Ibuprofen final degradation was 87% and 66 % using 8 x 8 mm and 6 x 6 mm Raschig rings, respectively; mineralization was 25 % and 13 %, respectively (Figure 5).

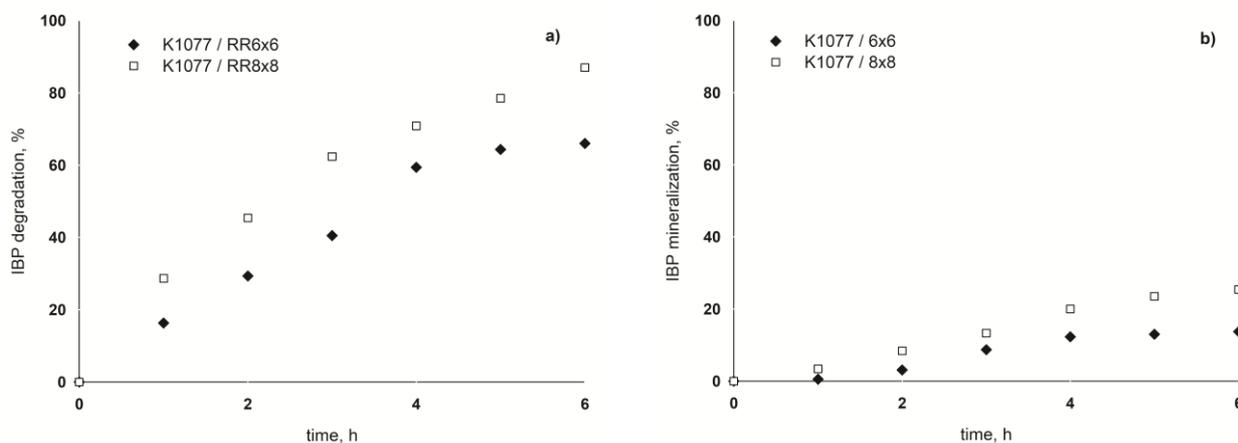


Figure 4: IBP photodegradation (a) and mineralization % (b) over time; comparison between  $\text{TiO}_2$ -functionalized 8x8 mm (empty symbols) and 6x6 mm (full symbol) Raschig rings.

In the batch slurry reactor, IBP is always in contact with the catalyst and the light. In contrast, in the continuous reactor the pump flows IBP through a reservoir and then into the actual reactor.

If we consider the volume of tubes and connections as negligible, the ratio between the volume of the reactor and the volume of the reservoir is  $0.6 \text{ L} / 2 \text{ L} = 0.3$ . This means that 30 % of the test time IBP reacts in the continuous reactor. This calculation holds because we assumed that there is not a residence time distribution of IBP inside the reactor.

Considering the actual reaction time, we can conclude that the continuous reactor is less efficient than the slurry reactor (Figure 5), with an IBP conversion of 96.3 % in 2 h versus 87 % in 1.8 h

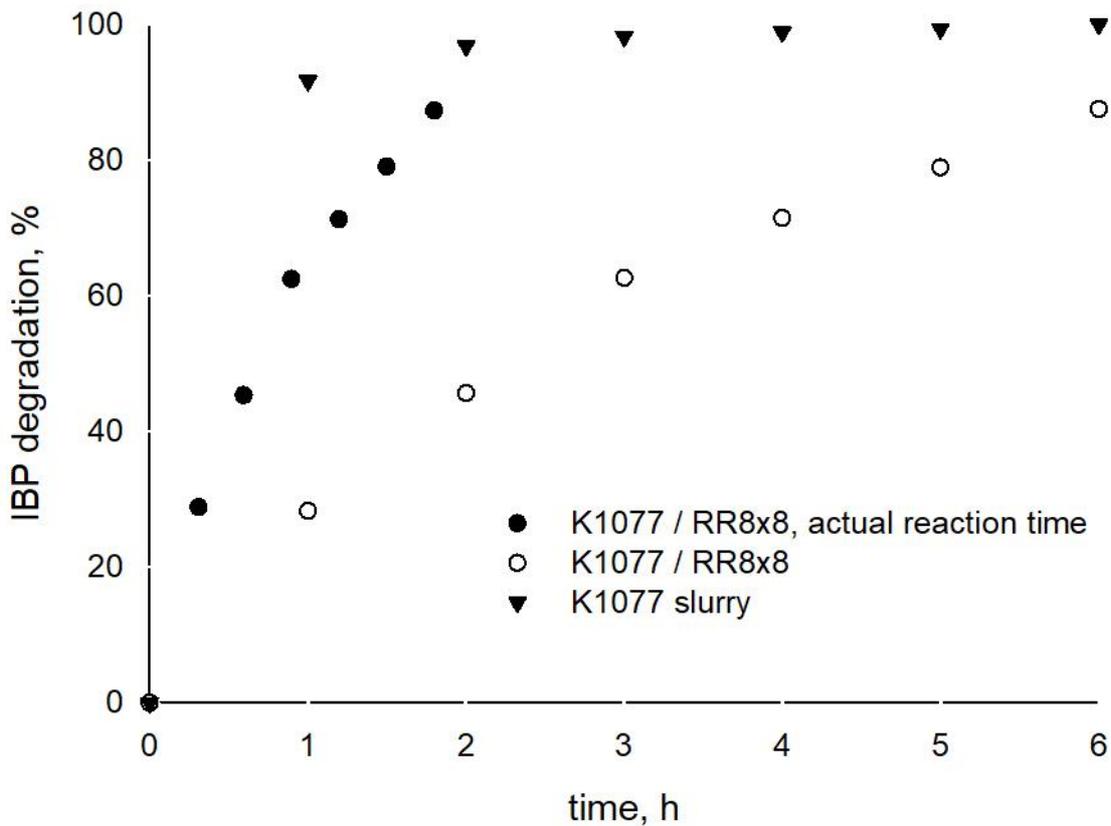


Figure 5: comparison between the performance of the slurry batch reactor (diamonds) with the continuous reactor considering the actual residence time of IBP in contact with the catalyst (full points) or the total test time (empty points).

We explain the difference in activity with a “screening effect” of the TiO<sub>2</sub> layers deposited on the Raschig rings. We studied the contribution of the TiO<sub>2</sub> layers by comparing 8 x 8 mm TiO<sub>2</sub>-coated glass Raschig rings with bare ones. TiO<sub>2</sub> deposition increased the degradation of IBP from 71 % to 87 % in 6 h, and it increased the mineralization by 11 %.

Results are consistent with the limitation of UV-C irradiation due to the increase of glass Raschig ring layers. Quartz rings avoid this problem but we did not run any experiments with this material because of the high cost of quartz, which affects negatively

We ran the continuous reactor filled with uncoated 8x8 mm glass Raschig rings and confirmed our assumptions (Figure 6).

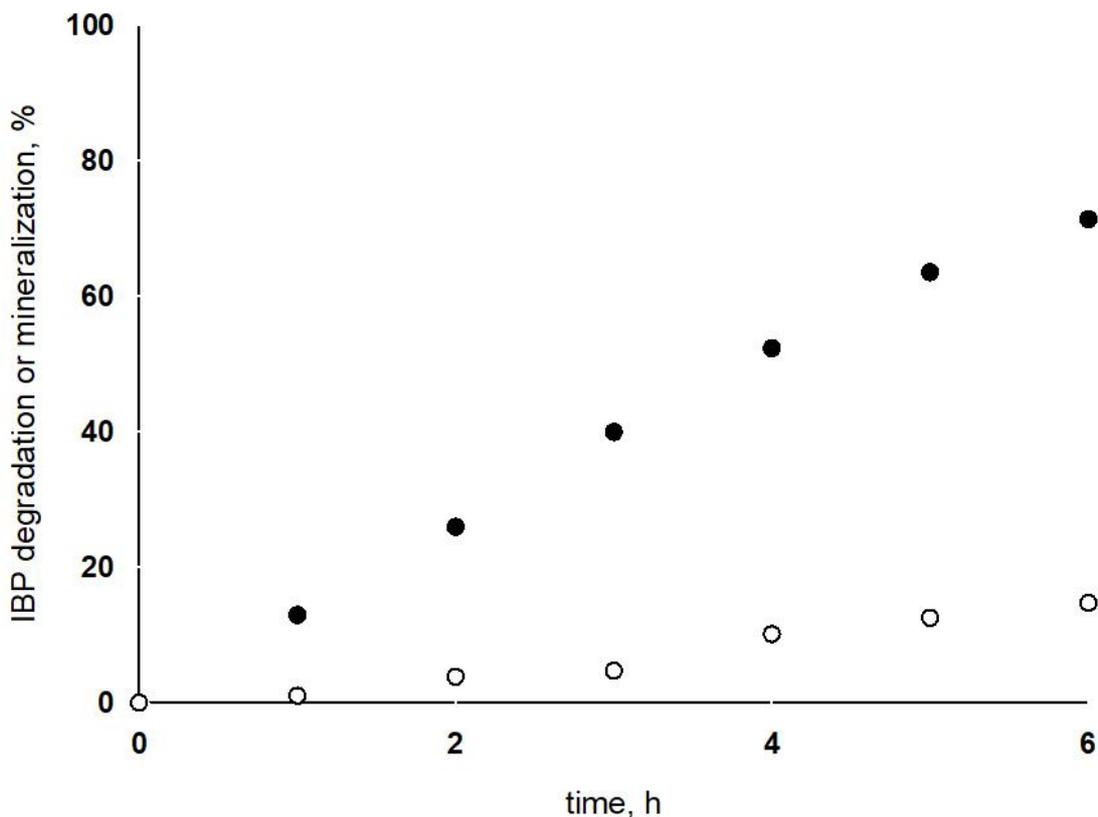


Figure 6: IBP photodegradation (full points) and mineralization (empty points) over time in the continuous reactor filled with uncoated glass 8x8 mm Raschig rings.

Even though the performance of K1077-coated Raschig rings is lower compared to the slurry reactor, the rings are recoverable and we observed no powder leaching (verified by centrifugation of a sample taken from the reservoir at the end of the reaction, i.e. after 6 h). This datum should be confirmed also after running the reactor for sever hours, but it is promising. We propose a reactor configuration that requires no catalyst filtration, an economic advantage in a real application.

### 3.3 Microscopy and coated-rings stability

SEM images revealed that fresh K1077 agglomerates on the Raschig ring surface and creates irregular blocks of 60-75  $\mu\text{m}$  (Figure 7a), whereas after 6 h, K1077 uniformly covers the rings (Figure 7b) unaltering the average dimensions. At greater magnification we detected a change in the catalyst shape: the starting K1077 exhibits mixed morphological features, being constitute of elongated rods and rounder agglomerates (Figure 7c). After the photocatalytic run the material's particles are spherical (Figure 7d). Water flow through the Raschig rings increases turbulence causing the morphological transformation.

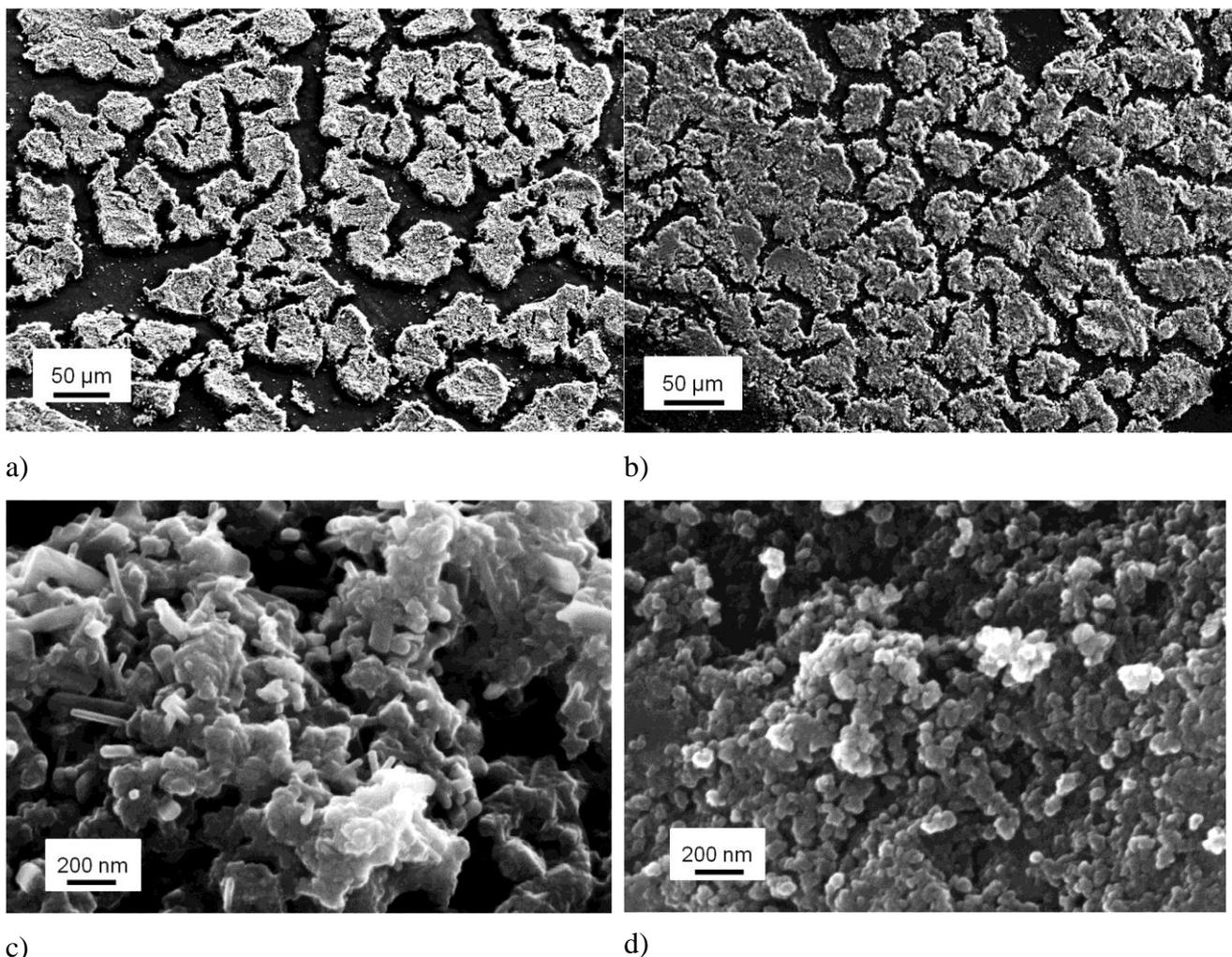


Figure 7: SEM images of the surface of a Raschig ring before (a and c) and after (b and d) the reaction in the continuous reactor.

Even though the morphology of the catalyst changed after the test, we did not observe a substantial leaching of K1077 from the glass because after a centrifugation at 10 000 rpm of the solution remained in the reservoir at the end of the test, we did not find any powder. This confirms that the procedure we propose yields a catalyst that is stable and easy to recover.

### 3.4 IBP photodegradation byproducts

The mass spectra revealed a high abundance of ions with molecular masses of 160, 188, and 370 Da (Table 1, 1 h).

IBP's molecular mass is 206 Da; the ions with masses of 160 Da and 188 Da are therefore degradation products. The ion with a mass of 370 Da belongs to higher complexes. The spectra at 1 h and 4 h are reported in Figure S3 in the Supplementary Material file.

Table 1: most abundant molecular masses in each sampling (from top to bottom), continuous reactor, 8x8 mm K1077 coated Raschig rings. Since the voltage of the ESI is positive, the masses reported are reduced by a unity ( $H^+$  mass) , i.e. we reduced by 1 the mass obtained by the MS spectra.

time (h)	1	4	5	6	8	24
	160	188	188	297	115	115
	188	160	160	262	106	86
	370	370	370	149	135	135
Molecular mass (Da)	176	296	176	176	86	77
	206	206	206	188	77	106
	118	176	293	84		
	104	293	290	110		
			104	104		

The most abundant ion masses are 115 Da and 106 Da at 8 h along with 115 Da and 86 Da at 24 h. Photocatalysis degrades aromatic rings whereas sonolysis does not [34].

We identified 13 different molecules and propose a pathway for ibuprofen photodegradation (Figure 8). Initially, K1077 decarboxylizes IBP creating radicals that react to form dimers or an alcohol through the reaction with water. DellaGreca et al. [35] identified the same first step in the photodegradation of Naproxen-Na. Furthermore, they detected dimers in the presence of inorganic salts. Olefin and etoxy derivatives were detected during the degradation in distilled water. Alternatively, Castell et al. [36], instead, studied the photodegradation product of IBP in methanol and identified the presence of dimers in absence of salts. They individuated p-ethylisobutylbenzene, 1-(4-isobutylphenyl)ethanol and 4-isobutylacetophenone. We detected the latter product with K1077 and a UV-C light source.

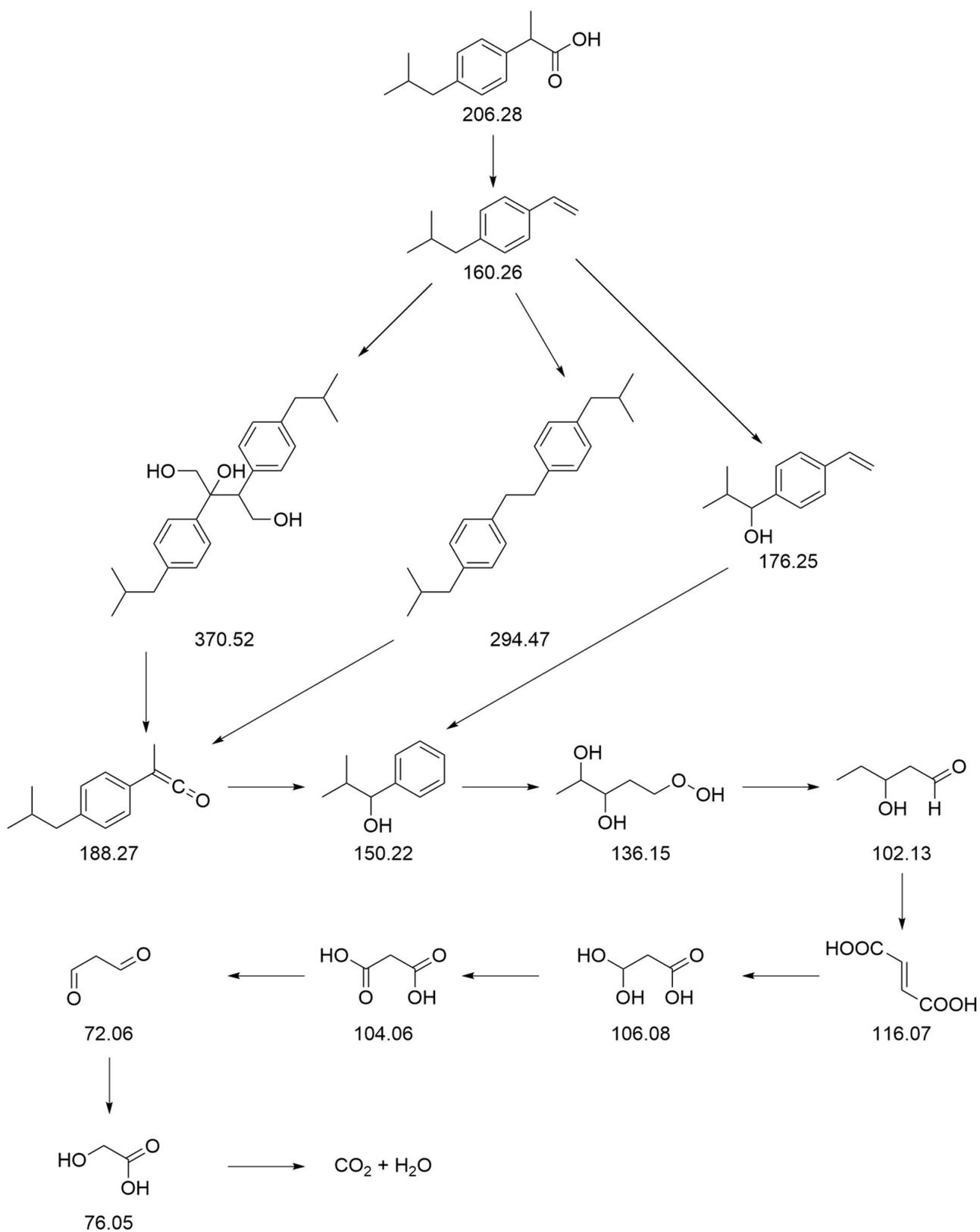


Figure 8: Proposed route for the photodegradation of IBP. All possible isomers are not displayed. The numbers near the molecules correspond to their molecular masses. The molecule whose mass

are not into Table 1 are reported as hypothetical by-products to get to the complete mineralization of IBP

## Conclusion

TiO<sub>2</sub>-coated Raschig rings are an excellent option for photocatalytic water treatment plants because of their safer profile compared to a nanometric catalyst.

We proved that micro-TiO<sub>2</sub> powders degrade and mineralize ibuprofen with UV-C. Replacing nano-P25 with micrometric K1077 eliminates the need for nanoparticles, which are harmful. We deposited micrometric TiO<sub>2</sub> on glass Raschig rings and found that in a continuous reactor they degraded 87 % of ibuprofen, with a mineralization of 25.4 %. We propose a unit operation that does not need any filtration step to recover the catalyst. We did not optimize the pump flowrate, another variable that influences conversion of ibuprofen. The new coated catalyst does not leach K1077. We also identified degradation by-products and proposed a possible reaction pathway for ibuprofen at our experimental conditions.

## Acknowledgment

We thank Mr. Nicolas A. Patience for helpful scientific discussions and the English revision of the manuscript and Dr. Ermelinda Falletta for the discussion of the ESI-MS spectra.

## References

- [1] A.J. Gushgari, R.U. Halden, A.K. Venkatesan, Occurrence of N -nitrosamines in U.S. freshwater sediments near wastewater treatment plants, *J. Hazard. Mater.* 323 (2017) 109–115. doi:10.1016/j.jhazmat.2016.03.091.
- [2] K.R. Echols, J.C. Meadows, C.E. Orazio, Pollution of Aquatic Ecosystems II: Hydrocarbons, Synthetic Organics, Radionuclides, Heavy Metals, Acids, and Thermal Pollution, in: *Encycl. Inl. Waters*, Elsevier, 2009: pp. 120–128. doi:10.1016/B978-012370626-3.00223-4.
- [3] B. Blair, A. Nikolaus, C. Hedman, R. Klaper, T. Grundl, Evaluating the degradation, sorption, and negative mass balances of pharmaceuticals and personal care products during wastewater treatment, *Chemosphere*. 134 (2015) 395–401. doi:10.1016/j.chemosphere.2015.04.078.
- [4] E.J. Rosi-Marshall, T. V Royer, Pharmaceutical Compounds and Ecosystem Function: An Emerging Research Challenge for Aquatic Ecologists, *Ecosystems*. 15 (2012) 867–880. doi:10.1007/s10021-012-9553-z.
- [5] Y. Yang, Y.S. Ok, K.-H. Kim, E.E. Kwon, Y.F. Tsang, Occurrences and removal of pharmaceuticals and personal care products (PPCPs) in drinking water and water/sewage treatment plants: A review, *Sci. Total Environ.* 596–597 (2017) 303–320. doi:10.1016/j.scitotenv.2017.04.102.
- [6] Y. Cabeza, L. Candela, D. Ronen, G. Teijon, Monitoring the occurrence of emerging contaminants in treated wastewater and groundwater between 2008 and 2010. The Baix Llobregat (Barcelona, Spain), *J. Hazard. Mater.* 239–240 (2012) 32–39. doi:10.1016/j.jhazmat.2012.07.032.
- [7] E. Archer, B. Petrie, B. Kasprzyk-Hordern, G.M. Wolfaardt, The fate of pharmaceuticals and personal care products (PPCPs), endocrine disrupting contaminants (EDCs), metabolites and illicit

drugs in a WWTW and environmental waters, *Chemosphere*. 174 (2017) 437–446.  
doi:10.1016/j.chemosphere.2017.01.101.

- [8] B. Petrie, R. Barden, B. Kasprzyk-Hordern, A review on emerging contaminants in wastewaters and the environment: Current knowledge, understudied areas and recommendations for future monitoring, *Water Res.* 72 (2015) 3–27. doi:10.1016/j.watres.2014.08.053.
- [9] V.S. Thomaidi, A.S. Stasinakis, V.L. Borova, N.S. Thomaidis, Is there a risk for the aquatic environment due to the existence of emerging organic contaminants in treated domestic wastewater? Greece as a case-study, *J. Hazard. Mater.* 283 (2015) 740–747. doi:10.1016/j.jhazmat.2014.10.023.
- [10] Y. Zhang, S.-U. Geißen, C. Gal, Carbamazepine and diclofenac: Removal in wastewater treatment plants and occurrence in water bodies, *Chemosphere*. 73 (2008) 1151–1161.  
doi:10.1016/j.chemosphere.2008.07.086.
- [11] S.K. Behera, H.W. Kim, J.-E. Oh, H.-S. Park, Occurrence and removal of antibiotics, hormones and several other pharmaceuticals in wastewater treatment plants of the largest industrial city of Korea, *Sci. Total Environ.* 409 (2011) 4351–4360. doi:10.1016/j.scitotenv.2011.07.015.
- [12] D.W. Kolpin, E.T. Furlong, M.T. Meyer, E.M. Thurman, S.D. Zaugg, L.B. Barber, H.T. Buxton, Pharmaceuticals, Hormones, and Other Organic Wastewater Contaminants in U.S. Streams, 1999–2000: A National Reconnaissance, *Environ. Sci. Technol.* 36 (2002) 1202–1211.  
doi:10.1021/es011055j.
- [13] S.T. Glassmeyer, E.T. Furlong, D.W. Kolpin, A.L. Batt, R. Benson, J.S. Boone, O. Conerly, M.J. Donohue, D.N. King, M.S. Kostich, H.E. Mash, S.L. Pfaller, K.M. Schenck, J.E. Simmons, E.A. Varughese, S.J. Vesper, E.N. Villegas, V.S. Wilson, Nationwide reconnaissance of contaminants of emerging concern in source and treated drinking waters of the United States, *Sci. Total Environ.* 581–582 (2017) 909–922. doi:10.1016/j.scitotenv.2016.12.004.
- [14] L. Feng, E.D. van Hullebusch, M.A. Rodrigo, G. Esposito, M.A. Oturan, Removal of residual anti-inflammatory and analgesic pharmaceuticals from aqueous systems by electrochemical advanced oxidation processes. A review, *Chem. Eng. J.* 228 (2013) 944–964. doi:10.1016/j.cej.2013.05.061.
- [15] G. Amariei, K. Boltes, R. Rosal, P. Letón, Toxicological interactions of ibuprofen and triclosan on biological activity of activated sludge, *J. Hazard. Mater.* 334 (2017) 193–200.  
doi:10.1016/j.jhazmat.2017.04.018.
- [16] M. Davids, D. Gudra, I. Radovica-Spalvina, D. Fridmanis, V. Bartkevics, O. Muter, The effects of ibuprofen on activated sludge: Shift in bacterial community structure and resistance to ciprofloxacin, *J. Hazard. Mater.* 340 (2017) 291–299. doi:10.1016/j.jhazmat.2017.06.065.
- [17] R. Singla, F. Grieser, M. Ashokkumar, Sonochemical degradation of martius yellow dye in aqueous solution, *Ultrason. Sonochem.* 16 (2009) 28–34. doi:10.1016/j.ultsonch.2008.05.012.
- [18] K. Hirano, H. Nitta, K. Savada, Effect of sonication on the photo-catalytic mineralization of some chlorinated organic compounds, *Ultrason. Sonochem.* 12 (2005) 271–276.  
doi:10.1016/j.ultsonch.2004.01.034.
- [19] F. Méndez-Arriaga, S. Esplugas, J. Giménez, Photocatalytic degradation of non-steroidal anti-inflammatory drugs with TiO<sub>2</sub> and simulated solar irradiation, *Water Res.* 42 (2008) 585–594.  
doi:10.1016/j.watres.2007.08.002.
- [20] J. Choina, C. Fischer, G.-U. Flechsig, H. Kosslick, V.A. Tuan, N.D. Tuyen, N.A. Tuyen, A. Schulz, Photocatalytic properties of Zr-doped titania in the degradation of the pharmaceutical ibuprofen, *J. Photochem. Photobiol. A Chem.* 274 (2014) 108–116. doi:10.1016/j.jphotochem.2013.08.018.
- [21] C. Yuan, C.-H. Hung, H.-W. Li, W.-H. Chang, Photodegradation of ibuprofen by TiO<sub>2</sub> co-doping with urea and functionalized CNT irradiated with visible light – Effect of doping content and pH, *Chemosphere*. 155 (2016) 471–478. doi:10.1016/j.chemosphere.2016.04.055.
- [22] S.M. El-Sheikh, T.M. Khedr, A. Hakki, A.A. Ismail, W.A. Badawy, D.W. Bahnemann, Visible light activated carbon and nitrogen co-doped mesoporous TiO<sub>2</sub> as efficient photocatalyst for degradation of ibuprofen, *Sep. Purif. Technol.* 173 (2017) 258–268. doi:10.1016/j.seppur.2016.09.034.
- [23] M. Henze, P. Harremoës, J. la Cour Jansen, E. Arvin, *Wastewater treatment: biological and chemical processes*, Springer Science & Business Media, 2001.
- [24] R. Zhang, Y. Bai, B. Zhang, L. Chen, B. Yan, The potential health risk of titania nanoparticles, *J. Hazard. Mater.* 211–212 (2012) 404–413. doi:10.1016/j.jhazmat.2011.11.022.
- [25] Y. Ze, L. Zheng, X. Zhao, S. Gui, X. Sang, J. Su, N. Guan, L. Zhu, L. Sheng, R. Hu, J. Cheng, Z. Cheng, Q. Sun, L. Wang, F. Hong, Molecular mechanism of titanium dioxide nanoparticles-induced oxidative injury in the brain of mice, *Chemosphere*. 92 (2013) 1183–1189.

doi:10.1016/j.chemosphere.2013.01.094.

- [26] L.K. Limbach, R. Bereiter, E. Müller, R. Krebs, R. Gälli, W.J. Stark, Removal of Oxide Nanoparticles in a Model Wastewater Treatment Plant: Influence of Agglomeration and Surfactants on Clearing Efficiency, *Environ. Sci. Technol.* 42 (2008) 5828–5833. doi:10.1021/es800091f.
- [27] C.L. Bianchi, C. Pirola, F. Galli, G. Cerrato, S. Morandi, V. Capucci, Pigmentary TiO<sub>2</sub>: A challenge for its use as photocatalyst in NO<sub>x</sub> air purification, *Chem. Eng. J.* 261 (2015) 76–82. doi:10.1016/j.cej.2014.03.078.
- [28] C.L. Bianchi, C. Pirola, F. Galli, M. Stucchi, S. Morandi, G. Cerrato, V. Capucci, Nano and micro-TiO<sub>2</sub> for the photodegradation of ethanol: experimental data and kinetic modelling, *RSC Adv.* 5 (2015) 53419–53425. doi:10.1039/C5RA05385D.
- [29] GranitiFiandre S.p.A, DigitalLife, (2017). <http://digitalife.active-ceramic.com/> (accessed April 24, 2018).
- [30] C.L. Bianchi, C. Pirola, M. Stucchi, G. Cerrato, F. Galli, A. Di Michele, S. Biella, W.-F. Chen, P. Koshy, C. Sorrell, V. Capucci, Photocatalytic TiO<sub>2</sub>: From Airless Jet Spray Technology to Digital Inkjet Printing, in: *Titan. Dioxide - Mater. a Sustain. Environ., InTech*, 2018: pp. 261–279. doi:10.5772/intechopen.72790.
- [31] C.L. Bianchi, B. Sacchi, C. Pirola, F. Demartin, G. Cerrato, S. Morandi, V. Capucci, Aspirin and paracetamol removal using a commercial micro-sized TiO<sub>2</sub> catalyst in deionized and tap water, *Environ. Sci. Pollut. Res.* 24 (2017) 12646–12654. doi:10.1007/s11356-016-7781-z.
- [32] J.C.C. da Silva, J.A.R. Teodoro, R.J. de C.F. Afonso, S.F. Aquino, R. Augusti, Photolysis and photocatalysis of ibuprofen in aqueous medium: characterization of by-products via liquid chromatography coupled to high-resolution mass spectrometry and assessment of their toxicities against *Artemia Salina*, *J. Mass Spectrom.* 49 (2014) 145–153. doi:10.1002/jms.3320.
- [33] F.S. Braz, M.R.A. Silva, F.S. Silva, S.J. Andrade, A.L. Fonseca, M.M. Kondo, Photocatalytic Degradation of Ibuprofen Using TiO<sub>2</sub>; and Ecotoxicological Assessment of Degradation Intermediates against *Daphnia similis*, *J. Environ. Prot. (Irvine, Calif.)* 05 (2014) 620–626. doi:10.4236/jep.2014.57063.
- [34] J. Madhavan, F. Grieser, M. Ashokkumar, Combined advanced oxidation processes for the synergistic degradation of ibuprofen in aqueous environments, *J. Hazard. Mater.* 178 (2010) 202–208. doi:10.1016/j.jhazmat.2010.01.064.
- [35] M. DellaGreca, M. Brigante, M. Isidori, A. Nardelli, L. Previtera, M. Rubino, F. Temussi, Phototransformation and ecotoxicity of the drug Naproxen-Na, *Environ. Chem. Lett.* 1 (2003) 237–241. doi:10.1007/s10311-003-0045-4.
- [36] J. V. Castell, M.J. Gomez-L., M.A. Miranda, I.M. Morera, Photolytic degradation of ibuprofen. Toxicity of the isolated photoproducts on fibroblasts and erythrocytes., *Photochem. Photobiol.* 46 (1987) 991–996. doi:10.1111/j.1751-1097.1987.tb04882.x.