

An ultrasound-assisted photocatalytic treatment to remove an herbicidal pollutant from wastewaters

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Abstract

Pollutants of emerging concern contaminate surface and ground water. Advanced oxidation processes treat these molecules and degrade them into smaller compounds or mineralization products. However, little information on coupled advanced oxidation techniques and on the degradation pathways of these pollutants is available to identify possible ecotoxic subproducts. In the present work, we investigate the ultrasound assisted photocatalytic degradation pathway of the herbicide Isoproturon. We worked in batch mode in a thermostatic glass reactor. We compared the activity of nanometric TiO₂ P25 with that of Kronos 1077, a micrometric TiO₂. We discuss the individual, additive and synergistic degradation action of photolysis, sonolysis, sonophotolysis, and sonophotocatalysis by varying catalyst loading and/or ultrasound power for the last three techniques. With 0.1 g L⁻¹ catalyst, photocatalysis and sonophotocatalysis completely degrade Isoproturon within 240 min and 60 min, respectively (> 99% conversion). Sonophotocatalysis breaks Isoproturon down into smaller molecules than photocatalysis alone.

Keywords: Isoproturon, sonophotodegradation, wastewater treatment, micrometric catalyst, degradation pathway

1. Introduction

The agricultural industry plays a fundamental role in the development and growth of a country. The huge increase of inhabitants elicited the mass cultivation development. Agriculture has now reached such an extent that the use of pesticides (herbicides, fungicides and insecticides) is essential to guarantee the survival of the humankind. Chemicals are classified by their mode of action (MOA), which describes either functional or anatomical changes within cells resulting from the exposure of an organism to that substance. The mode of action represents the level of complexity between molecular mechanisms and physiological outcomes. Modern pesticides act on a specific nuclear receptor or enzyme with a single MOA with few side effects for humans, animals and plants health [1]. However, the use of pesticides with multiple MOA that act on many cell signaling pathways is still in effect at the present day and they pose a serious threat even when applied in tiny amounts.

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12 The EU Water Framework Directive on Environmental Quality Standards 2008/105/EC an-
13 nounced in Annex X a list of 33 priority substances, which includes metals, pesticides, phthalates,
14 polycyclic aromatic hydrocarbons and endocrine disruptors. Notably, 11 plant protection products
15 are subject to phasing out within an appropriate timetable not exceeding 20 years [2]. While the
16 occurrence and effects of metals, bacteria, hydrocarbons and other ions like nitrates and ammonia
17 in water are extensively described, data on pesticides, pharmaceuticals and phthalates are seldom
18 available. Specifically, herbicides are more water soluble, polar and thermally stable than other
19 contaminants. They have harmful effects on soil, flora and fauna, surface and ground water, which
20 may eventually enter the human being and livestock's food chain [3].

21 Contaminants enter water bodies in a number of ways, including industrial and municipal dis-
22 charge, runoff, spills and deposition of airborne pollutants. Most often, waterways are being polluted
23 by agricultural waste containing toxic compounds that cannot be broken down by natural processes.

24 There is a direct correlation between water pollution and the agricultural practices of the sur-
25 rounding area [4]. Groundwater pollution is rather persistent and the degradation rate in soil is
26 slow. The concentration of organic pollutants in water and soil depends on the presence of microor-
27 ganisms, whose activity, in turn, is affected by pH, temperature, moisture and nutrient content.
28 This creates a spatial variability in the degradation rate of pollutants.

29 The lack of knowledge of the impact on both human health and environment upon long and
30 short-term exposure is one of the main issues of emerging pollutants [5]. Emerging pollutants are
31 new products or chemicals without a regulatory status and whose long-term effects on environment
32 and human health are unknown.

33 It is of utmost importance to dispose off wastewaters in a proper manner as well as to keep the
34 concentration of chemicals in the effluent stream to a certain minimum level in order to comply with
35 the environmental laws, which are becoming more stringent nowadays. The limit concentration of
36 chemicals allowed by law in drinking water is generally $10 \mu\text{g L}^{-1}$ and, for most of pesticides and
37 pharmaceuticals, lower than $0.5 \mu\text{g L}^{-1}$ [2].

38 Isoproturon (IPU) is a phenylurea herbicide widely used for crop protection because of its
39 moderate persistence and relatively low adsorption. On average, the environmental half life of
40 IPU (DT_{50}) is 30 days [6]. However, it has become an occasional water contaminant with proven
41 sub-acute toxicity on rats [7] as well as endocrine disruptor capability on humans [8]. It promotes
42 tumor growth and accounts for other ailments related to the reproductive system [9]. Actually, the
43 20 % to 40 % by weight of the herbicide drizzled on field remains unaffected and the permitted IPU
44 guideline value in water is not respected [10].

45 TiO_2 photocatalysis has recently emerged as a green approach to degrade water pollutants.
46 Because of characteristics such as stability, availability, and cost, titanium dioxide (TiO_2) is the
47 foremost exploited photocatalytic material in every field of application [11]. Degussa P25 (TiO_2)
48 catalyst features great performance in aqueous [12, 13] and air environment [14]. However, its
49 applications are limited due to its nanometric particle size, which poses serious threats when it comes
50 to dermal and pulmonary exposure [15]. Micrometric TiO_2 is a valid alternative to P25 as it presents
51 less health concerns. Notwithstanding TiO_2 based catalysts are efficient in terms of wastewater
52 organic pollutants removal, the formation of toxic by-products is to be taken into account [16].
53 Moreover, the efficacy of photocatalytic processes depends on the nature and composition of the
54 wastewater to be treated.

55 Research into more efficient wastewater treatment technologies for the degradation of complex
56 refractory molecules into simpler ones is key to improve water quality [17, 18]. Going towards this
57 direction, coupling ultrasound with photocatalysis creates an Advanced Oxidation Process (AOP)

58 whereby two combined methods contribute to produce OH radicals. Indeed, acoustic cavitation
59 proved to intensify both physical and chemical processes [19, 20, 21, 22].

60 When applied to a liquid, ultrasonic waves generate vapour-filled voids via a cyclic succession
61 of expansion and compression phases. Upon collapsing, each cavitation bubble acts as a hotspot
62 by generating micro-jets whose energy increases the temperature and pressure up to 5000 K and
63 500 atm, respectively [23]. These conditions cause water to split and hydroxyl radicals to form. In
64 this sense, ultrasonic cavitation may intensify the photocatalytic wastewater treatment [24]. Mosleh
65 and Rahimi combined ultrasound (25 kHz) and a copper metal organic framework photocatalyst to
66 degrade abamectin [25] and found that there is a synergistic effect between the two AOPs. Some of
67 the same authors degraded trypan blue and vesuvine with a silver metal organic framework (LED
68 light and 25 kHz ultrasound) [26]. Similarly, Vinoth et al. [27] prepared a TiO₂-NiO nanocomposite
69 active under solar light and coupled it with ultrasound (40 kHz) to degrade methyl orange, obtaining
70 a synergy of 4.8 fold. However, only few works focus on IPU degradation pathway. Identifying the
71 subproducts and intermediates yielded in the degradation pathway is of paramount importance to
72 assess their eco and microtoxicity, and select the safest method of degradation as a consequence.
73 Barbeidou et al. studied the sonophotodegradation of malachite green (9 W UVA and 80 kHz
74 ultrasound) and determined the molecule degradation pathway by GC-MS [28]. As far as we know,
75 no one attempted to understand the synergistic effect of ultrasound and photocatalysis on the
76 degradation pathway of water pollutants.

77 Here, we investigated the ultrasound assisted photocatalytic degradation pathway of the her-
78 bicide Isoproturon (IPU) by means of a 100 % anatase micrometric TiO₂ catalyst, Kronos 1077.
79 Our work is original for several reasons: i) we studied the sonophotodegradation of IPU for the
80 first time with Kronos 1077, ii) we optimized catalyst concentration and varied ultrasound power
81 and we demonstrated that micrometric Kronos 1077 is a valid alternative to nano-sized P25, iii)
82 we employed a less harmful material than P25 iv) we propose the IPU degradation pathway using
83 both ultrasound and photocatalysis coupled with ultrasound.

84 **2. Materials and methods**

85 *2.1. Materials*

86 We purchased Isoproturon PESTANALTM analytical standard from Sigma Aldrich. We em-
87 ployed Kronos 1077 as micrometric TiO₂ catalyst and we compared its performance with Degussa
88 P25 nanometric TiO₂ catalyst. The former is 100 % anatase phase and features an average crys-
89 tallite size of 110 nm whereas the latter has an anatase/rutile phase composition of 80 % and 20 %,
90 respectively [29]. Both catalysts were in powder form. We purchased water and acetonitrile from
91 Fischer Scientific, HPLC grade, submicron filtered. We assessed the influence of dissolved salts by
92 using tap water from Milan water supply network (from June to July 2018).

93 *2.2. Experimental*

94 We ran photocatalytic and sonolytic tests separately at first and we successively combined
95 the two methods in a single sono-photocatalytic process (Table 1). For all tests we employed a
96 thermostatic glass reactor where tap water flew in the cooling jacket that kept the temperature
97 inside the reactor at 15 °C. We dispersed the catalyst in the reaction medium under mild magnetic
98 stirring, which was maintained for the entire duration of the tests. The duration of photocatalytic
99 tests was 6 h and we sampled 2 mL every 60 min, whereas ultrasound-assisted experiments lasted
100 3 h and we sampled 2 mL every 30 min.

101 For photocatalytic tests, we filled the reactor with 100 mL of a 20 ppm IPU solution. We selected
 102 the initial concentration of IPU to 20 ppm because of the detection limit of the instrumentation.
 103 A UVA HG 500 W quartz with halides lamp from Jelosil irradiated the IPU working solution. We
 104 arranged the UVA lamp sideways to the reactor at a distance so that the intensity of the UV
 105 radiation was equal to 160 W m^{-2} . We tested distilled and tap water IPU solutions to assess how
 106 the matrix affects the degradation rate of the molecule. We also varied the concentration of the
 107 catalysts (0.05 g L^{-1} , 0.1 g L^{-1} , and 0.2 g L^{-1}) to evaluate the optimal working concentration for
 108 both nanometric and micrometric catalysts. Despite photocatalysis and ultrasonic cavitation follow
 109 different reaction mechanisms, we ran tests with a catalyst concentration of 0.1 g L^{-1} as it proved
 110 to be the optimal one in the first part of the work.

111 For ultrasonic tests, we filled the reactor with 100 mL of a 20 ppm distilled water IPU synthetic
 112 solution. We positioned the ultrasonic processor on top of the reactor and we plunged the US probe
 113 1 cm into the reaction liquid so that it did not touch the glass wall of the reactor. The ultrasonic
 114 processor was a VibraCell VCX 500 (Sonics and Materials) working at a nominal power of 50 W
 115 and a fixed frequency of 20 kHz. The tip is made of a titanium alloy (Ti-6Al-4V) and its diameter
 116 is 13 mm. The probe length is 136 mm. We ran tests at 15 W cm^{-2} , 25 W cm^{-2} , and 50 W cm^{-2} .

Table 1: Summary of the experimental tests

Water type	UV power (W m^{-2})	US power (W cm^{-2})	Catalyst	Catalyst concentration (g L^{-1})
Distilled	160	-	-	-
Tap	160	-	-	-
Distilled	160	-	Kronos 1077	0.05
Distilled	160	-	Kronos 1077	0.1
Distilled	160	-	Kronos 1077	0.2
Tap	160	-	Kronos 1077	0.05
Tap	160	-	Kronos 1077	0.1
Tap	160	-	Kronos 1077	0.2
Distilled	160	-	P25	0.05
Distilled	160	-	P25	0.1
Distilled	160	-	P25	0.2
Tap	160	-	P25	0.05
Tap	160	-	P25	0.1
Tap	160	-	P25	0.2
Distilled	-	15	-	-
Distilled	-	50	-	-
Distilled	160	50	-	-
Distilled	160	25	Kronos 1077	0.1
Distilled	160	25	P25	0.1
Distilled	160	50	Kronos 1077	0.1
Distilled	160	50	P25	0.1

117 *2.3. Analytical Methods*

118 We monitored the degradation of IPU via HPLC-UV and a HPLC-MS identified by-products.
119 The HPLC-UV apparatus uses a Microsorb MV 100-5 C18 250 mm x 4.6 mm column from Agilent
120 Technologies and UV detector. We injected 20 μL of sample and we worked in isocratic mode at
121 0.5 mL min^{-1} with a mobile phase composition of $\text{H}_2\text{O}:\text{ACN}$ 1:1. We kept the column at 30°C .
122 The detection wavelength for IPU was 240 nm. We repeated each analysis twice. HPLC-UV
123 provided with Varian ProStar 6.41 workstation quantitatively monitored only the conversion of
124 IPU, as no by-product appeared nearby its peak, which remained sharp and well outlined. We
125 analyzed IPU and its degradation products by liquid chromatography at atmospheric pressure and
126 heated electrospray ionization (ESI) tandem mass spectrometry. The system consists of an Accela
127 600 HPLC coupled to an Orbitrap LTQ XL mass spectrometer from Thermo Scientific. For the
128 chromatographic separation we used a HPLC Zorbax Eclipse Plus C18 guard column (5 mm x
129 4.6 mm ID; 5 μm) followed by an analytical column Zorbax Eclipse Plus C18 (250 mm x 4.6 mm
130 ID; 5 μm), both from Agilent Technologies. We injected 20 μL of sample upon prior dilution 1:5 in
131 LC-MS grade water and we followed the same chromatographic separation conditions and analysis
132 repetitions indicated for the HPLC-UV method.

133 A Thermo Scientific LTQ XL mass spectrometer scanned IPU samples by Fourier-Transform
134 (FT) and ion trap (IT-MS) in positive mode. The spectrometer accommodates a high resolution
135 Orbitrap detector (MS), which is in tandem with the HPLC system. The spectrometer also lodges
136 a pneumatic assisted heated ESI source. We set the heater at 300°C and the temperature of the
137 capillary was 375°C .

138 We optimized the instrument detection parameters by direct infusion of 2 ppm IPU analytical
139 standard at $10 \mu\text{L min}^{-1}$. For source optimization we used helium as collision gas and nitrogen
140 as auxiliary, sweep and sheath gas for focusing gases in the source. The FT detector acquired
141 information in full scan mode from 50 m/z to 600 m/z at 60 000 high resolution with a mass
142 accuracy tolerance of 5 ppm. We set the ion trap with 22 specific transitions by using a collision
143 induced dissociation (CID) of 45 % normalized collision energy (NCE) to ensure the generation of
144 product ions on the MS2 spectra for the identification of the selected precursor ions. A Thermo
145 Xcalibur software (Thermo Scientific, Waltham, MA, USA) and the open-source software MZmine
146 2 processed, visualized, and profiled data analysis.

147 **3. Results and discussion**

148 *3.1. Photolysis and photocatalysis*

149 Photolysis converted 18 % and 10 % of IPU in 6 h in distilled and tap water, respectively (Fig-
150 ure 1).

151 We obtained a half-life time of 23 h in distilled water, assuming a first order kinetic (kinetic
152 constant of 0.0005 min^{-1} , $R^2 = 0.98$). Dureja et al. [30], report a IPU half-life time of 5 h and
153 30 h under UV and visible irradiation, respectively. (wavelength from 254 nm to 300 nm, 125 W).
154 However, Sanches et al. [31] photolyzed IPU with a low pressure Hg lamp emitting at 254 nm and
155 observed an IPU first order degradation kinetic constant of 0.0006 min^{-1} , which agrees with our
156 results. Photolysis of organic compounds is generally less active in deionized water [32] than in
157 aqueous solution containing salts. For instance, 1 mg L^{-1} of 2,4-Dinitrotoluene photolyzes with an
158 half-life of 1 h in seawater and in 4 h in distilled water [33]. We hypothesize that the complex matrix
159 of Milano tap water contains molecules (such as other pharmaceuticals or small amount of organics)
160 that absorb UV radiation and compete to IPU degradation, leading to lower IPU photoconversion.

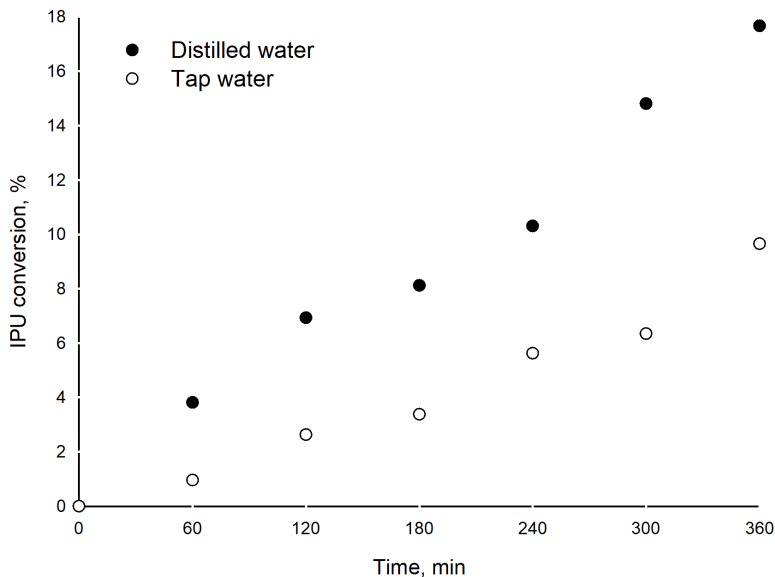


Figure 1: Photolytic degradation of IPU in Milan tap and distilled water. Maximum error is $\pm 3\%$ considering two repetitions and instrument resolution.

161 In fact, Azzelino et al. [34] report an average chemical oxygen demand and biological oxygen
 162 demand in Lombardy waters of 7.94 mg L^{-1} and 2.54 mg L^{-1} , respectively. Therefore, scientists
 163 should tune the experimental parameters for each water matrix and pollutants. We then evaluated
 164 how the concentration of the catalyst charged into the reactor affects the final conversion of IPU,
 165 either in distilled or tap water (Figure 2).

166 With a catalyst concentration of 0.1 g L^{-1} and 0.2 g L^{-1} we achieved complete IPU conversion
 167 in 6 h. We chose 0.1 g L^{-1} as optimal concentration to pursue further tests as it provides the same
 168 results as a concentration of 0.2 g L^{-1} . Moreover, 0.1 g L^{-1} is the standard catalyst concentration
 169 loaded within the reactor for most photochemical reactions as it does not screen the UV radiation
 170 excessively [35].

171 In distilled water, Kronos and P25 behave similarly (Figure 2a and Figure 2b). In fact, they
 172 reach the same final conversion in 6 h at any catalyst concentration. In tap water, experiments show
 173 comparable kinetic rates for both Kronos (0.0049 min^{-1} at 0.05 g L^{-1} and 0.0088 min^{-1} at 0.1 g L^{-1})
 174 and P25 (0.0058 min^{-1} at 0.05 g L^{-1} and 0.0176 min^{-1} at 0.1 g L^{-1}) at all catalyst concentrations
 175 but 0.2 g L^{-1} . In this case, P25 (kinetic constant of 0.025 min^{-1}) exhibits a better performance
 176 than Kronos (kinetic constant of 0.015 min^{-1}) (Figure 2c and Figure 2d).

177 Photodegradation rates depend on salt concentration, pH, COD of water and size of catalyst
 178 aggregates [36]. Therefore, we executed all the remaining tests in distilled water to assess the
 179 fragmentation pathway in different processes in an ideal case, i.e. with no matrix effect.

180 3.2. Sonolysis

181 We investigated sonolysis at an ultrasound power of 15 W cm^{-2} and 50 W cm^{-2} .

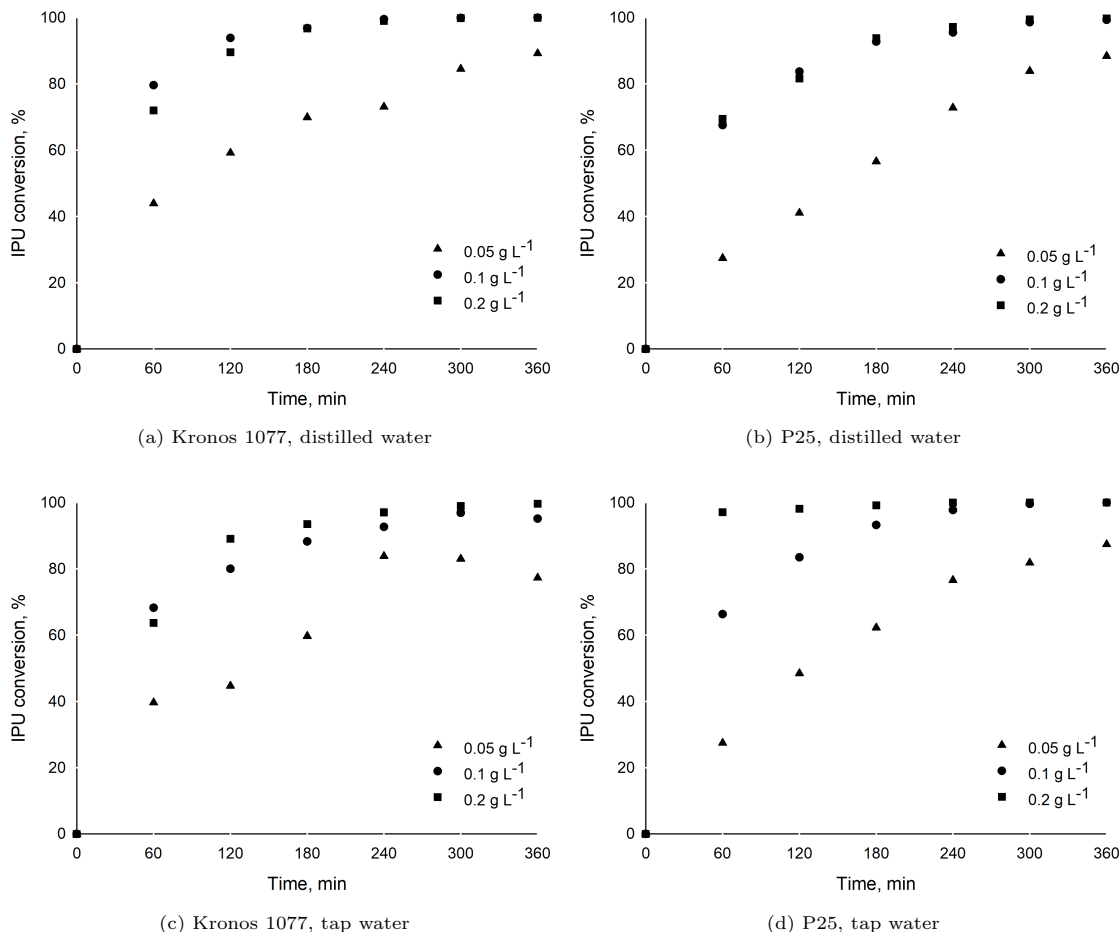


Figure 2: Photocatalytic degradation of IPU with different catalysts concentration. Maximum error is $\pm 3\%$ considering two repetitions and instrument resolution.

182 Sonolysis degrades 75% of IPU in 3 h (Figure 3). It is more effective than UVA photolysis,
 183 which converts 9% of IPU in distilled water in 6 h (Figure 1). However, HPLC-UV revealed several
 184 by-products. Sonication alone is not powerful enough to ensure the complete degradation of IPU,
 185 therefore, we merged UVA radiation and ultrasound to intensify the degradation process.

186 3.3. Sonophotocatalysis

187 We worked at an ultrasound power of 25 W cm^{-2} and 50 W cm^{-2} .

188 Generally, for the sonolytic degradation, the higher the ultrasound power, the greater the IPU
 189 sonodegradation [37], and our results confirm this. Sonophotolysis degrades 36% of IPU
 190 at 50 W cm^{-2} (Figure 3). We observe that the addition of ultrasonic cavitation to photolysis
 191 promotes IPU degradation compared to the photolytic process (Figure 1, and 3). Furthermore, the
 192 final conversion reached with sonolysis (Figure 3) is two times superior than that obtained with

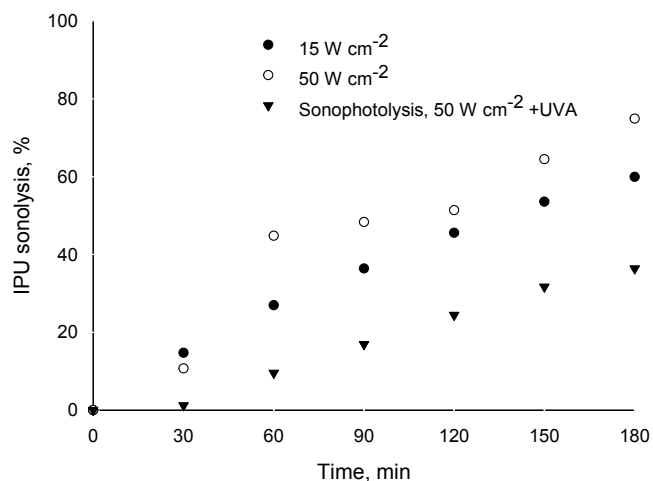


Figure 3: Sonolytic degradation of IPU in distilled water at 15 W cm^{-2} and 50 W cm^{-2} and sonophotolytic degradation of IPU at 50 W cm^{-2} . Maximum error is $\pm 3\%$ considering two repetitions and instrument resolution.

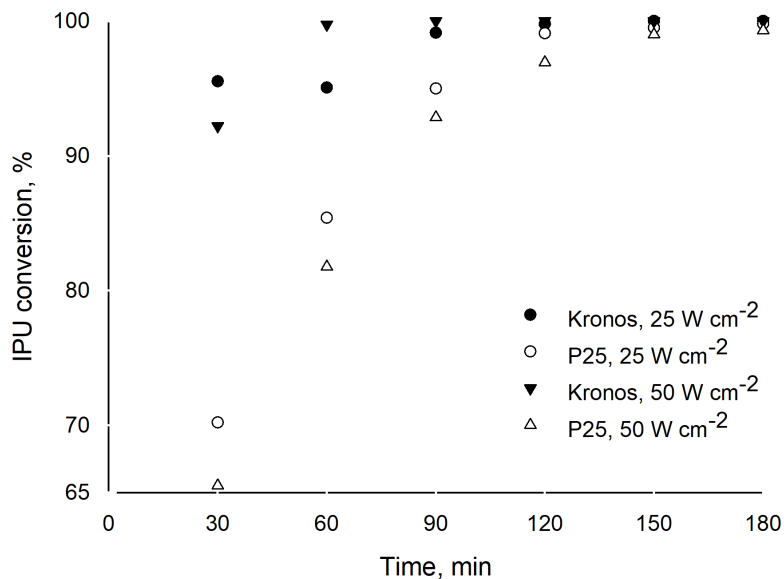


Figure 4: Sonophotocatalytic degradation of IPU in distilled water. Catalyst concentration is 0.1 g L^{-1} . Maximum error is $\pm 3\%$ considering two repetitions and instrument resolution.

193 sonophotolysis (Figure 4). This opposes the accepted idea that photolysis and sonolysis effects are
 194 additive or even synergistic [38]. Indeed, Peller et al. proved that coupling sonolysis and photolysis
 195 does not change the degradation lifetime of 2,4-Dichlorophenol [39]. Park et al. demonstrated

196 that the energy ratio between UV and US should be tuned to maximize sonophotodegradation of
197 trihalomethanes [40]. For these components, the photolysis has a predominant role due to the liable
198 C–Br bonds present in the molecules studied, thus the optimum ratio resulted US : UV = 1 : 3 and
199 US : UV = 0 : 4. We did not aim at optimizing such ratio, but we speculate that IPU, not having
200 liable bonds, may require more energy than the one provided by just UV to be degraded. However,
201 in our case coupling ultrasound and photolysis seems even detrimental. The reasons behind this
202 behavior remains to be explained with further experiments.

203 Sonophotocatalysis in distilled water converted 100 % of IPU in 3 h with both catalysts and at
204 both ultrasound power tested (Figure 4). Photocatalysis with Kronos and P25 at 25 W cm^{-2} and
205 50 W cm^{-2} achieved 100 % conversion of IPU in 3 h.

206 Specifically, Kronos converts more than 99 % of IPU in 60 min at 50 W cm^{-2} and in 90 min at
207 25 W cm^{-2} . P25 converts 100 % of IPU in 120 min at 25 W cm^{-2} and 50 W cm^{-2} .

208 3.4. By-products analysis

209 HPLC-UV by-products' peaks were broad and not sharp. This indicated that by-products
210 featured similar polarity and, as a result, they exited the column with almost the same retention
211 time.

212 LC-MS/MS spectra identified two main types of by-products for both the photocatalytic and
213 sonophotocatalytic degradation processes (see Fig S1 and S2 in the Supporting Information).

214 The first class forms upon the oxidation of IPU by highly reactive hydroxyl radicals, which
215 is ascribable to the general reactivity of TiO_2 in aqueous environment. The substitution by $\cdot\text{OH}$
216 radicals takes place on the benzene ring (structures 221A, 223D, and 239A), the isopropyl group
217 (structures 209 A/B, 221C, and 223A/B), and on the dimethylamine group (structures 221B and
218 223C/E). MS also revealed multiple hydroxylation on the aromatic ring and on the isopropyl
219 group (structures 225B/A, 237, 239A/B/C, 255A/B/C, 268, and 284).

220 The second class makes up derivatives in which entire substituents, like methyl or isopropyl, are
221 replaced by an hydroxyl radical. Such reactions take place at various position on the IPU molecule
222 and on by-products themselves (structures 167 and 181).

223 IPU also undergoes simple N-demethylation or dehydrogenation of the isopropyl group (struc-
224 tures 191, 193, 205, and 221A).

225 As far as photocatalysis and sonophotocatalysis with Kronos are concerned, LC-MS/MS analyses
226 pointed out two different IPU fragmentation patterns.

227 Photocatalysis elicited the formation of higher molecular weight by-products in the first part
228 of the reaction (from 30 min to 90 min), originating from the oxidation and recombination of high
229 molecular weight fragments (from 209 m/z to 296 m/z, Table 2).

230 On the contrary, sonophotocatalysis fragmented the pesticide into molecules with a lower molec-
231 ular weight than that of IPU (from 167 m/z to 205 m/z) in the same range time mentioned herein-
232 above (Table 3).

233 Table 2 summarizes the structures of the by-products identified after the degradation of IPU
234 by UVA light.

235 During photocatalytic treatment, many intermediates form after 1 h of reaction (see Table S1
236 in the Supporting Information material for the raw data). After 2 h, such intermediates undergo
237 oxidation to form heavier by-products (Figure 5). Throughout the reaction, we identified 21 by-
238 products, many of which were already reported [41, 42]. In particular, Amorisco et al. [43] describe
239 how by-product 225 originates from structure 209A. However, according to our analysis, by-product
240 225B might derive also from structure 223A as the concavity of the curve for structure 225B changes

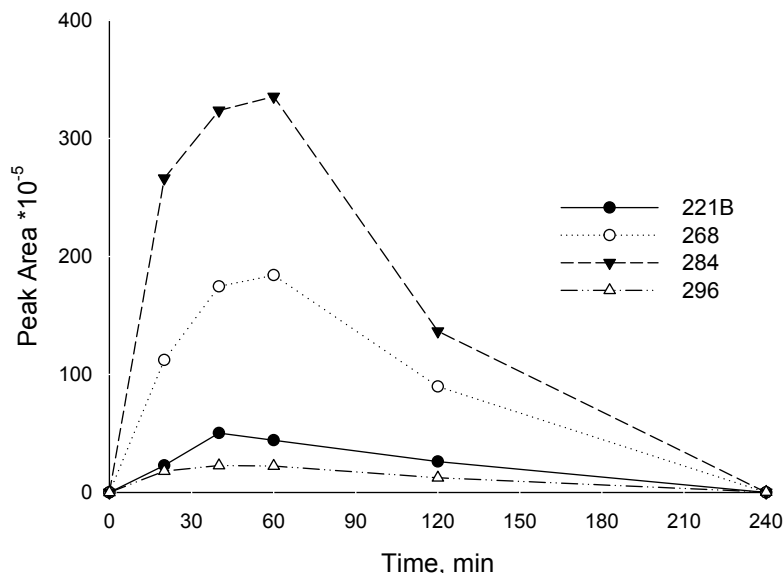


Figure 5: Evolution trend of higher molecular weight structures from intermediate 221B during photocatalytic treatment.

241 when the curve for structure 223A reaches its maximum at 30 min, as in the case of structure 209A
 242 (Figure 7).

243 Molecules 268, 284, and 296 have never been reported before (Table 2). We successfully identified
 244 268 and 284 by analyzing the MS fragmentations patterns provided by HPLC-MS. For structure
 245 268 we observed fragments corresponding to the loss of the hydroxy group on the aromatic ring
 246 and of the carboxylic oxygen on the isopropyl group in para position to the urea group. The MS
 247 also reported fragmentation corresponding to the carboxylic acid group bonded to the urea. For
 248 structure 284 we observed fragmentation related to the second hydroxy group on the aromatic ring.
 249 Molecule 296 structure remains unknown. Therefore, we propose the IPU degradation pathway
 250 without considering product 296 (Figure 6).

251 The sonophotocatalytic degradation mechanism differs from that observed in the photodegrada-
 252 tion. In fact, almost all by-products identified originate directly from IPU and few reaction
 253 intermediates were observed (see Table S2 in the Supporting Information material for the raw
 254 data).

255 The fact that sonophotocatalysis provokes the generation of lower molecular weight by-products
 256 than photocatalysis alone is likely related to the presence of a higher concentration of hydroxyl
 257 radicals, which accelerates the oxidation process and promotes fragmentation. Moreover, at the
 258 end of the reaction, no byproduct was detected by HPLC-MS (Figure 8). Table 3 reports all the
 259 by-products identified after sonophotocatalytic treatment.

260 Molecules 167, 187, 254, 268, 280, and 296 have never been reported before. We successfully
 261 identified 167, 268, but 187, 254, 280, and 296 structures remain unknown (Figure 9). For molecule
 262 268 we observed the same fragmentation pattern as in the case of photocatalytic treatment. For

Molecule	R ₁	R ₂	R ₃	R ₄	R ₅
181	CH ₃	H	OH	–	–
191	CH ₃	H	CHCH ₂	–	–
193	H	H	CH ₂ (CH ₃) ₂	–	–
205	CH ₃	H	CH(CH ₂)CH ₃	–	–
209 A	CH ₃	H	CH ₂ (CH ₃)OH	–	–
209 B	H	H	C(CH ₃) ₂ OH or CH ₂ (CH ₃)CH ₂ OH	–	–
221 A	CH ₃	H	CH(CH ₂)CH ₃	OH	–
221 B	C(O)H	H	CH ₂ (CH ₃) ₂	–	–
223 A	CH ₃	H	CH ₂ (CH ₃)CH ₂ OH	–	–
223 C	CH ₃ OH	H	CH ₂ (CH ₃) ₂	–	–
223 D	CH ₃	H	CH ₂ (CH ₃) ₂	OH	–
223 E	CH ₃	OH	CH ₂ (CH ₃) ₂	–	–
225 B	CH ₃	H	CH(OH)CH ₂ OH	–	–
239 A	CH ₃	H	C(CH ₃) ₂ OH	OH	–
239 B	CH ₃	H	CH(CH ₂ OH) ₂ or C(CH ₃)(OH)CH ₂ OH	–	–
239 C	CH ₃	H	CH ₂ (CH ₃) ₂	OH	OH
255 A	CH ₃	H	C(CH ₃) ₂ OH or CH ₂ (CH ₃)CH ₂ OH	OH	OH
255 B	CH ₃	OH	C(CH ₃) ₂ OH or CH ₂ (CH ₃)CH ₂ OH	OH	–
255 C	CH ₃	OH	C(CH ₃) ₂ OH or CH ₂ (CH ₃)CH ₂ OH	OH	–
268	C(O)OH	H	CH(CH ₃)C(O)H	OH	–
284	C(O)OH	H	CH(CH ₃)C(O)H	OH	OH

Table 2: By-products identified upon photocatalytic treatment.

263 molecule 167, the HPLC–MS reported fragmentations corresponding to the loss of the isopropyl
 264 group in para position to the urea, and corresponding to the hydroxy group on the urea group
 265 (specifically, on the nitrogen atom directly bonded to the aromatic ring). All the by-products iden-
 266 tified are phenyl ureas, which possess a pharmacological action as anticonvulsant, antimicrobial, an-
 267 tiviral and anti inflammatory agents [44]. Photocatalysis is unable to degrade aryl intermediates in
 268 6 h, yielding a wastewater that may be either as toxic or more toxic than isoproturon-contaminated
 269 water. Instead, the sonophotocatalytic process, completely removes phenyl ureas in 3 h.

270 As reported by Noorimotlagh et al., the wastewater pH affects the degradation process of organic

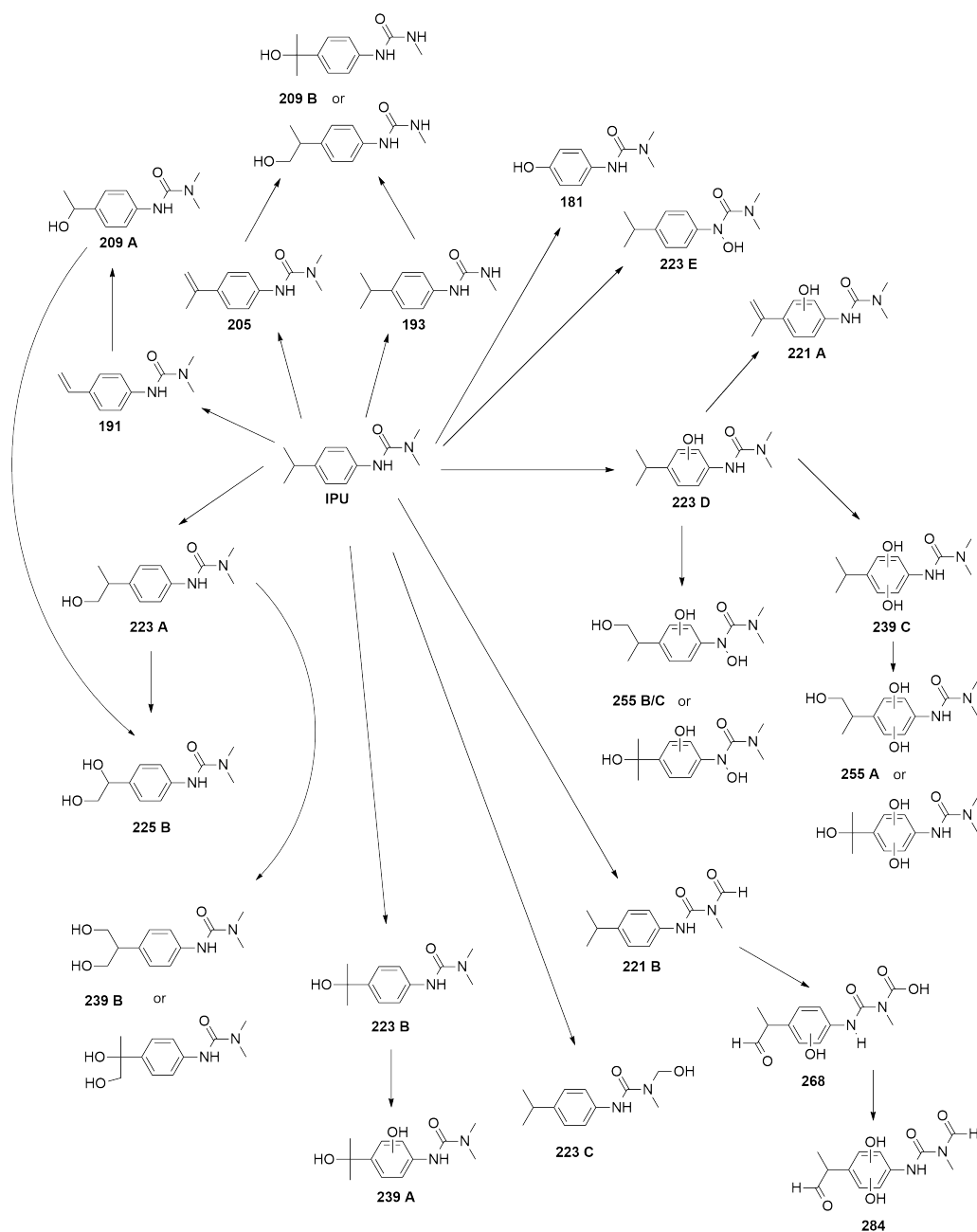


Figure 6: IPU degradation pathway upon photocatalytic treatment.

271 pollutants [45]. In the present work, we did not modify the pH as the addition of an extra chemical
 272 compound would impact on the cost of the treatment in a real industrial plant and would increase

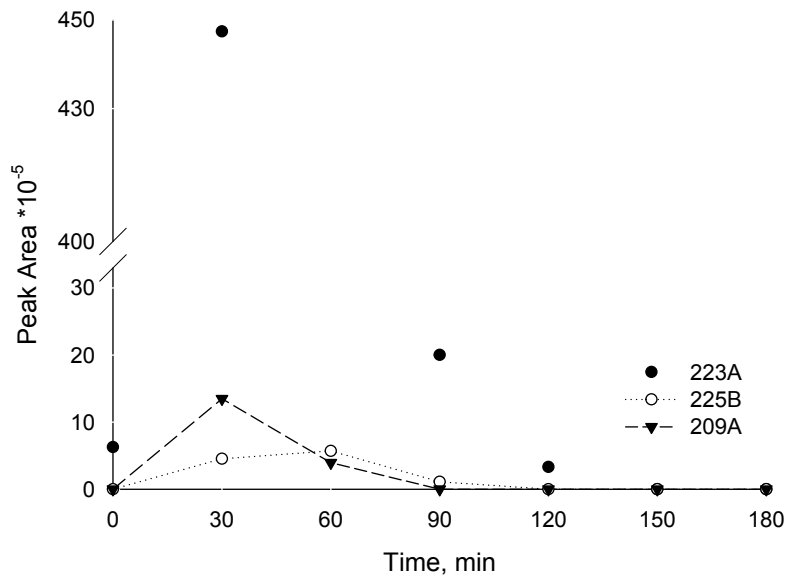


Figure 7: Evolution trend of by-product 225B from 209A and from 223A.

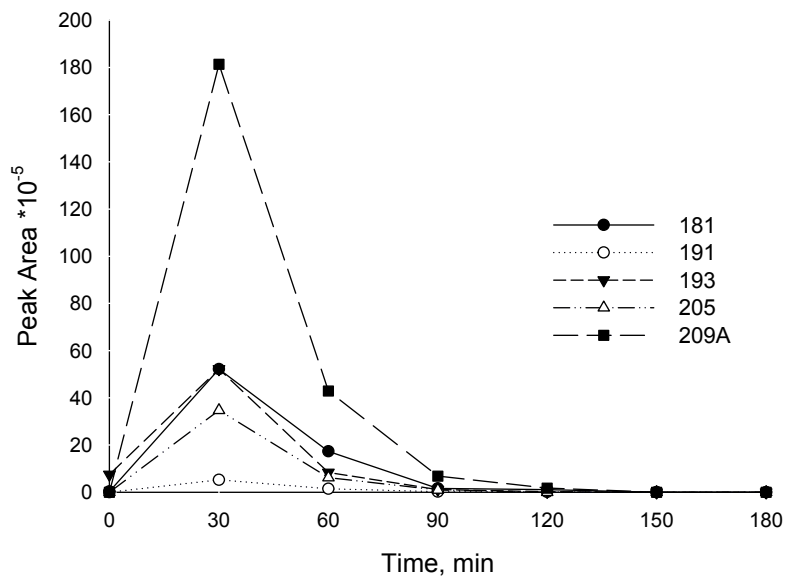
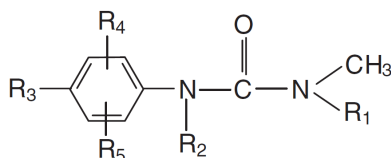


Figure 8: Evolution trend of lower molecular weight structures from IPU during sonophotocatalytic treatment.



Molecule	R ₁	R ₂	R ₃	R ₄	R ₅
167	OH	H	H	-	-
181	CH ₃	H	OH	-	-
191	CH ₃	H	CHCH ₂	-	-
193	H	H	CH ₂ (CH ₃) ₂	-	-
205	CH ₃	H	CH(CH ₂)CH ₃	-	-
209 A	CH ₃	H	CH ₂ (CH ₃)OH	-	-
209 B	H	H	C(CH ₃) ₂ OH or CH ₂ (CH ₃)CH ₂ OH	-	-
221 A	CH ₃	H	CH(CH ₂)CH ₃	OH	-
221 B	C(O)H	H	CH ₂ (CH ₃) ₂	-	-
221 C	CH ₃	H	CH(CH ₃)C(O)H	-	-
223 A	CH ₃	H	CH ₂ (CH ₃)CH ₂ OH	-	-
223 B	CH ₃	H	C(CH ₃) ₂ OH	-	-
223 C	CH ₃ OH	H	CH ₂ (CH ₃) ₂	-	-
223 D	CH ₃	H	CH ₂ (CH ₃) ₂	OH	-
223 E	CH ₃	OH	CH ₂ (CH ₃) ₂	-	-
225 A	CH ₃	H	CH(OH)CH ₃	OH	-
225 B	CH ₃	H	CH(OH)CH ₂ OH	-	-
237	CH ₃	H	CH(CH ₃)C(O)H	OH	-
239 A	CH ₃	H	C(CH ₃) ₂ OH	OH	-
255 A	CH ₃	H	C(CH ₃) ₂ OH or CH ₂ (CH ₃)CH ₂ OH	OH	OH
255 B	CH ₃	OH	C(CH ₃) ₂ OH or CH ₂ (CH ₃)CH ₂ OH	OH	-
255 C	CH ₃	OH	C(CH ₃) ₂ OH or CH ₂ (CH ₃)CH ₂ OH	OH	-
268	C(O)OH	OH	CH(CH ₃)C(O)H	OH	-

Table 3: By-products identified upon sonophotocatalytic treatment.

273 the complexity of the matrix to treat.

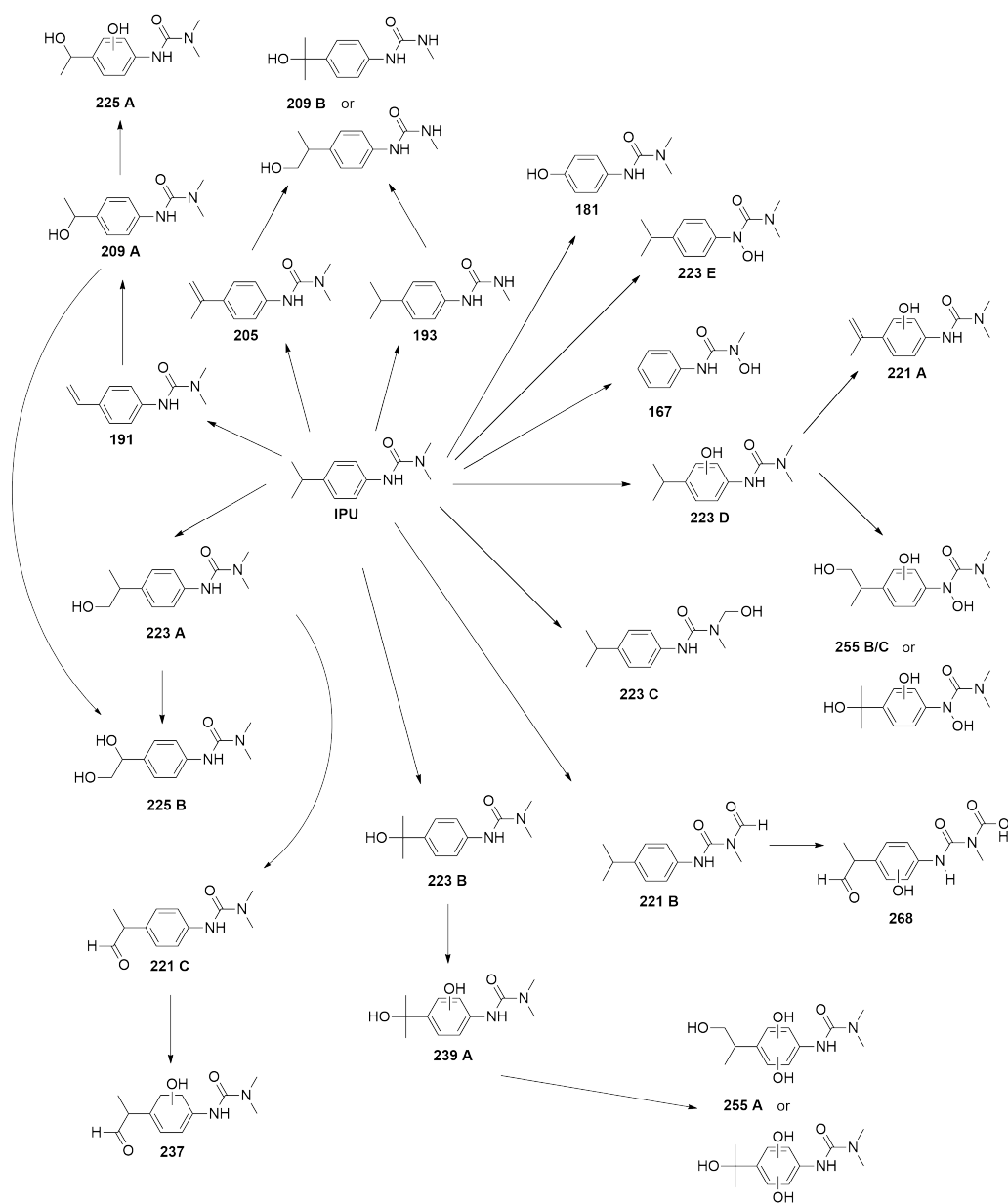


Figure 9: IPU degradation pathway upon sonophotocatalytic treatment.

274 **4. Conclusions**

275 Sonophotocatalysis with an ultrasonic power of 50 W cm^{-2} degrades 100% of Isoproturon (IPU)
 276 in less than 1 h. We demonstrate that Kronos 1077 is a valid photocatalyst to substitute P25,
 277 which is nanometric and poses serious health and environmental concerns. Both catalysts were

278 equally active in the degradation of IPU at a catalyst concentration of 0.1 g L^{-1} , whereby complete
279 conversion was achieved in maximum 150 min at both 50 W cm^{-2} and 25 W cm^{-2} .

280 We proposed the degradation pathway of Isoproturon in photocatalytic and sonophotocatalytic
281 processes. We detected 7 by-products that were never reported before, of which 3 were identified.
282 Ultrasound coupled with photocatalysis leads to lower molecular weight byproducts compared to
283 photocatalysis alone. However, coupling ultrasound with UV irradiation in absence of a photocata-
284 lyst is detrimental for the degradation of IPU. This result remains to be explained. Further studies
285 will also investigate the stability and reusability of the catalyst and disclose the effect of dissolved
286 salts on Isoproturon degradation pathway.

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