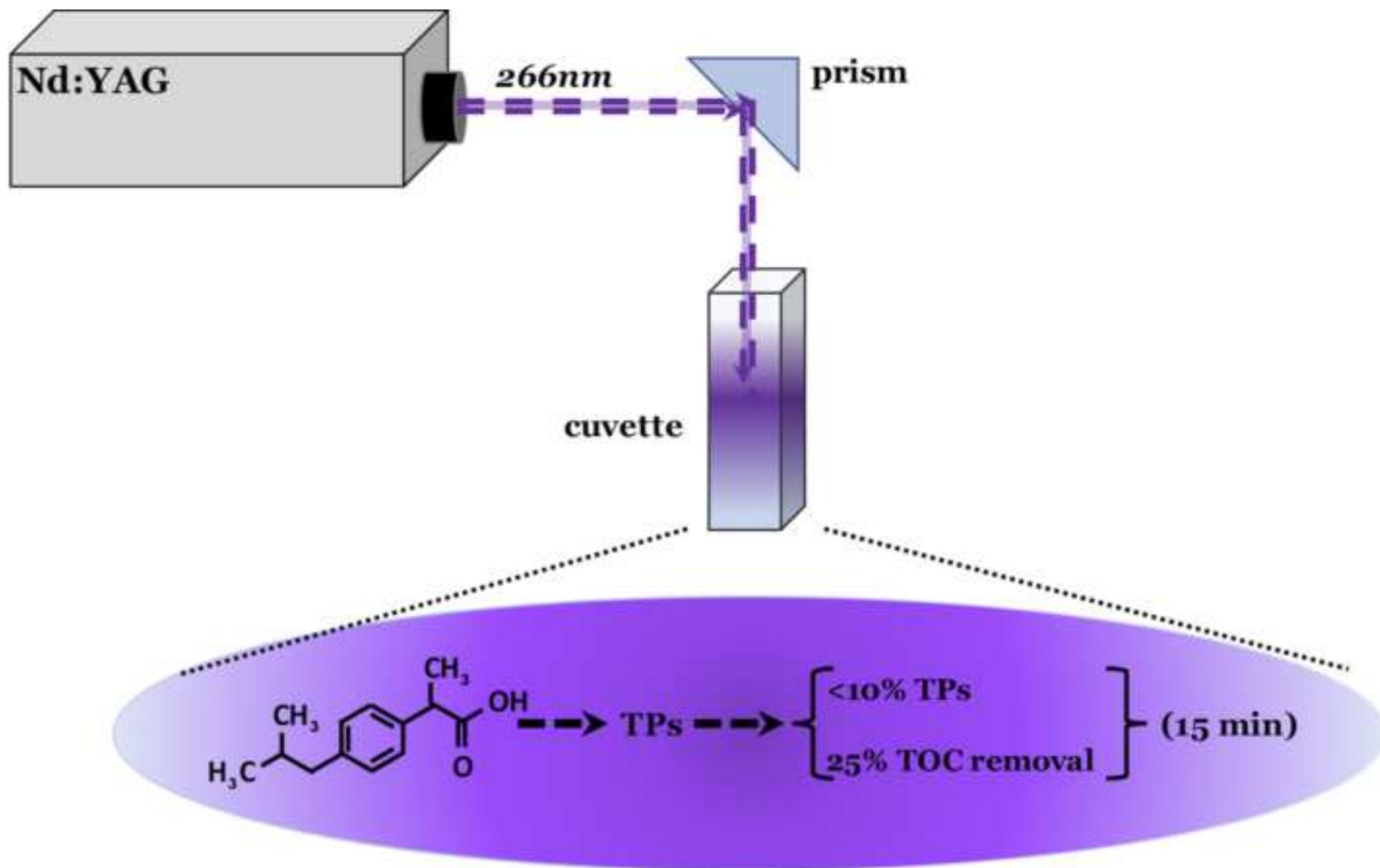***Can UV-C laser pulsed irradiation be used for the removal of organic micropollutants from water? Case study with ibuprofen.***

Francisco Rey-García, Benigno José Sieira, Carmen Bao-Varela, José Ramón Leis, Luis Alberto Angurel, José Benito Quintana, Rosario Rodil, Germán Francisco de la Fuente

Highlights:

-   UV (266 nm) ns-pulsed laser irradiation of tertiary water contaminants is addressed without sensitizers or photocatalysts.

-   Efficient degradation of ibuprofen in distilled water is demonstrated with this direct UV-C laser pulsed irradiation method.

-   25% DOC removal and transformation products (TPs) <10% levels are achieved in 15 min distilled water irradiation.

-   Direct irradiation of wastewater removes 95% of ibuprofen and reduces TPs to <15% within 15 min.

1 ***Can UV-C laser pulsed irradiation be used for the removal of***

2 ***organic micropollutants from water? Case study with ibuprofen***

3

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18 **ABSTRACT**

19 A novel approach based on the direct pulsed irradiation of UV-C light onto

20 ibuprofen (IBP) solutions was evaluated in this work, as proof of concept for the

21 direct removal of micropollutants. The experiments confirmed that laser

22 irradiation is able to completely degrade IBP in 15 min in distilled water, with a

23 DOC depletion of ca. 25% and with transformation products (TPs) remaining in

24 solution and estimated to represent ca. 10% of the initial IBP concentration. In

25   wastewater spiked samples, removal efficiency is slightly lower but still

26   significant (ca. 5% IBP remaining after 15 min). Hence, this work suggests that

27   low power solid state pulsed lasers, emitting at 266 nm wavelength, show

28   promise for the removal of these type of micropollutants from water. These

29   results open new opportunities towards the development of chemical-free water

30   treatment methods based on direct, selective irradiation using state of the art,

31   miniaturized laser devices.

32

33   **KEYWORDS**

34   UV Laser Chemistry, Ibuprofen, nanosecond pulses, 266nm, transformation

35   products, wastewater

36

37   **1. INTRODUCTION**

38   The presence of pharmaceuticals in water is one of the topics of major concern

39   in the two latest decades (**Wilkinson et al., 2017**). Among the different classes

40   of pharmaceuticals, non-steroidal anti-inflammatory drugs (NSAIDs) are one of

41   the most relevant and commonly investigated classes, due to their application

42   over the counter in high dosages and demonstrated presence in the water

43   environment. Ibuprofen (IBP) is one the pharmaceuticals detected at higher

44   concentrations (**Rodil et al., 2012**; **Wilkinson et al., 2017**). For these reasons,

45   classical removal technologies, such as biodegradation during wastewater

46   treatment (**Quintana et al., 2005**) or reactivity with well-established disinfectant

47   systems, both used at wastewater treatment plants (WWTPs) and drinking

48   water facilities, have been investigated. In addition, increased interest has been

49 recently shown for UV disinfection (**Iovino et al., 2016**). Several Advanced

50 Oxidation Processes (AOPs), including those which make use of UV radiation,

51 have also been tested with IBP and other NSAIDs, with the objective of

52 improving their removal efficiency during wastewater treatment (**Ameta and**

53 **Ameta, 2018**; **Miklos et al., 2018**; **Mlungunza et al., 2019**; **Romeiro et al.,**

54 **2018**).

55 The use of UV lamps for degrading pharmaceuticals and other organic

56 micropollutants, such as IBP, is based on the fact that their emission is within

57 the same range (190-380 nm, ultraviolet) as the absorbance bands of the

58 aromatic rings and poly-unsaturated groups present in their structure

59 (**Adityosulindro, 2017**; **da Silva et al., 2014**; **Iovino et al., 2016**; **Miklos et al.,**

60 **2018**; **Peuravuori and Pihlaja, 2009**). These UV sources are characterized by

61 a continuous emission mode, with the most common ones including mono- and

62 polychromatic low- (LP) or medium pressure (MP) mercury lamps (**Miklos et**

63 **al., 2018**). Moreover, UV laser emitting diodes (UV-LED) are also employed for

64 the microorganism disinfection of water, specially when utilized for human

65 consumption (**Jarvis et al., 2019**). Concerning the photocatalytic treatment with

66 conventional UV light sources, **Mendez-Arriaga et al. (2010)** employed a 1 kW

67 Xe lamp for the photo-Fenton treatment of IBP aqueous solutions within a

68 photoreactor, assessing the irradiation available to be absorbed by H_2O_2 within

69 the 290 to 350 nm spectral range. Furthermore, **Georgaki et al. (2014)** treated

70 aqueous matrices of IBP by means of photocatalysis. They used TiO_2 and ZnO

71 inside a photoreactor provided with a medium pressure, a 150 W constant

72 power Hg lamp emitting within the 200-600nm range and with λ_{max} at 365 nm.

73 Later, **Chianese et al. (2016)** employed a UV crosslinker apparatus, provided

74 with five UV lamps emitting at 254nm (UV-C range) for irradiating IBP aqueous

75 solutions. Most recently, **Lin et al. (2019)** employed a 160 W UV-Vis lamp with

76 emission maxima within the 290-545 nm wavelength range in order to establish

77 differences between direct UV photolysis and UV-Vis promoted photocatalysis

78 of IBP in clean water. The latter almost completely degrades IBP, although the

79 photocatalyst is found to significantly decrease its activity as a function of

80 progressive irradiation cycles. A promising new approach reported by **Baranda**

81 **et al. (2017)** employed new Pulsed Lamp (PL) technology for pesticide

82 decontamination in water, based on Xe lamp emission with fluence values in

83 the 0.5-10 J cm^{-2} range and pulse widths in the order of 300-325 µs.

84 In contrast, the use of lasers has not yet been sufficiently explored for the

85 treatment of water containing microcontaminants, and only a limited number of

86 papers have appeared in the literature during the last three decades (**Unkroth**

87 **et al., 1997; Pascu et al., 2011; Smarandache et al., 2012**). The pioneering

88 report by **Unkroth et al. (1997)** made use of ArF and KrF Excimer lasers

89 emitting at 193 and 248 nm, respectively, and described treatment of textile

90 dyes and dyehouse wastewaters both, under direct irradiation and in

91 combination with oxidizers. More than a decade later, **Pascu et al. (2011)**

92 reported on the direct modification of phenothiazines using pulsed solid state

93 Nd:YAG lasers emitting on their second (532 nm), third (355 nm) and forth (266

94 nm) harmonics, as well as a pulsed nitrogen gas laser emitting at 337 nm.

95 Similar work published by **Smarandache et al. (2012)** reported on the

96 degradation of thioridazine and BG1188 pharmaceutical compounds using

97 direct laser irradiation emitted from a pulsed solid state Nd:YAG laser in its third

98 harmonic at 355 nm. A significant amount of published related work, based on

99   the use of lasers, pertains to reactivity and stability studies, however (**Moore**

100   **and Chappuis, 1988**; **Packer et al., 2003**; **Rodríguez-Muñiz et al., 2014**,

101   **Liang et al., 2019**). A good number of these reports deal, in fact, with Laser

102   Flash Photolysis (LFP). They employ a diversity of laser sources to investigate

103   mechanistic aspects of photocatalyst mediated processes (**Moore and**

104   **Chappuis, 1988**; **Packer t al., 2003**; **Rodríguez-Muñiz et al., 2014; Liang et**

105   **al., 2019**). Moreover, in LFP, lasers have often been employed to start chemical

106   reactions by means of singlet oxygen, or even hydroxyl radical generation, from

107   a sensitizer in a pH-controlled medium.

108   The use of pulsed laser sources may be expected to yield promising results

109   towards pollutant removal, considering the previously mentioned work of

110   **Baranda et al. (2017).** These authors registered pesticide removal yields

111   ranging between 60 and 93%, apparently as a consequence of using pulsed UV

112   lamps with higher irradiance levels than those achieved with continuous

113   sources. In this sense, lasers provide a particularly attractive alternative, in view

114   of the fact that they provide irradiance values (W/cm^2) that are orders of

115   magnitude above those achieved with lamps **(Pascu et al. 2011)**.

116   The objective of this work is thus to explore the potential of ns pulsed UV lasers,

117   for direct photochemical removal of micropollutants present in water. For this

118   purpose, IBP was selected as a proof of principle, model compound, and 266

119   nm as the emission wavelength of the laser. The latter is in the same spectral

120   range as the absorbance bands found in aromatic rings and poly-unsaturated

121   groups, present in most NSAIDs compounds. Particular consideration was

122   given to the presence of reported photochemical transformation products (TPs),

123 since they can be in some cases more toxic than the original organic

124 contaminant compounds themselves (**Quintana et al., 2014**).

125

126 **2. MATERIALS AND METHODS**

127 *2.1. Chemicals and samples*

128 Aqueous stock solutions of 10 mg L^{-1} were prepared using ibuprofen (IBP) of

129 pharmaceutical grade from Sigma-Aldrich (Merck KGaA, Darmstadt, Germany),

130 double distilled water (DDW) and effluent (EFF) water (pH: 7.1, DOC: 3.5 mg L^{-}

131 ^{1}, total suspended solids: 6 mg L^{-1}, nitrate: 26 mg L^{-1}, nitrite: 0.25 mg L^{-1},

132 chloride: 20 mg L^{-1}, bromide: 0.14 mg L^{-1}, sulfate: 22 mg L^{-1}, fluoride < 0.05 mg

133 L^{-1}, phosphate < 0.04 mg L^{-1}) collected from a wastewater treatment plant

134 located in the NW of Spain, which processes the sewage of ca. 100,000

135 inhabitants and is equipped with primary and conventional activated sludge

136 treatments. This concentration (10 mg L^{-1}) was employed in order to be able to

137 follow DOC and UV changes and detect TPs.

138

139 *2.2. Laser irradiation experiments*

140 Laser experiments were performed on 4 ml aliquots of IBP spiked (10 mg L^{-1}),

141 double distilled water or filtered effluent wastewater. Samples were placed

142 inside 1 cm^{2} base UV fused quartz cuvettes (CV10Q3500S, Thorlabs Inc.,

143 Newton, NJ, USA) and irradiated with a pulsed solid-state laser (Quanta Ray,

144 Spectra-Physics, Newport Corp., Irvine, CA, USA). The laser emission was set

145 at its fourth harmonic (λ=266 nm) with a pulse width of 4-5 ns and a pulse

146 repetition frequency of 50 Hz. The nominal laser emission power was set at 0.9

147   W and the area covered by the beam was set at ca. 1 cm^2. In consequence, the

148   pulse fluence is ca. 18 mJ cm^{-2} and the pulse irradiance ca. 4 MW cm^{-2}. The

149   laser beam was reflected on a narrowband laser line mirror (Y4-1025-45-UNP,

150   CVI Laser Optics, Albuquerque, NM, USA) mounted onto a 45⁰ round mount

151   (Thorlabs Inc.), in order to vertically irradiate the cuvette contents from its top

152   entry (Fig. 1). The laser power was measured employing a FieldMax II TO

153   (Coherent Inc., Santa Clara, CA, USA) power meter equipped with a PowerMax

154   PM150 sensor and placed at the same geometrical point as the quartz cuvettes.

155   It was observed during the treatment that the laser beam irradiated a complete,

156   vertical liquid column, from the upper liquid meniscus to the bottom, inner base

157   surface of the cuvette.

158

159   *2.3. Analytical methods*

160   A Perkin-Elmer UV-vis Lambda Spectrometer (PerkinElmer Inc., Waltham, MA,

161   USA) was employed for spectroscopic studies. In addition, the amount of IBP

162   remaining on several experiments and the formation of TPs was determined by

163   liquid chromatography–high-resolution mass spectrometry (LC-HRMS). To this

164   end, aliquots of the treated solutions at different irradiation times were analyzed

165   employing a quadrupole-time-of-flight mass spectrometer (Agilent 6550 iFunnel

166   QTOF, Agilent, Santa Clara, CA, USA) linked to an Agilent 1290 Infinity II

167   (Agilent) liquid chromatography system. Chromatographic separation was

168   achieved using a 150x2mm, 3µm Luna C18 column (Phenomenex, Torrance,

169   CA, USA) using Milli-Q water and acetonitrile, both containing 0.1% formic acid,

170   as eluents A and B, respectively. The LC gradient was as follows: initially 5% B,

171   ramped to 100%B in 10 min (held for 2 min), then back-conditioned for 9 min.

172 Injection volume was 5 µL. The LC-HRMS system operated in negative

173 ionization mode, with nitrogen being used as nebulizing gas. Spectra

174 registration was performed in the 2 GHz extended dynamic range mode which

175 provides a resolution of ca. 10,000 at *m/z* 121 in the 40-1000 *m/z* range. The

176 mass accuracy was maintained by infusing a reference solution with a

177 secondary electrospray according to manufacturer's specifications. IBP was

178 determined by integration of the 205.1234 *m/z* (± 20 ppm) extracted ion

179 chromatogram. TPs were screened for by extracting the *m/z* value of TPs

180 described in the literature (**Illés et al., 2013**; **Méndez-Arriaga et al., 2010**) at

181 different irradiation times.

182 Dissolved Organic Carbon (DOC) was determined on a Shimadzu TOC-L

183 instrument (Shimadzu Corp., Kyoto, Japan) provided with a 2-channel non-

184 dispersive infrared (NDIR) detector, according to the 5310-B Std. Meth. Ed.20

185 (APHA-AWWA-WPCF) method for water and wastewater examination

186 (**Clesceri et al., 1998**). DOC was calculated from the difference between the

187 total carbon (TC) and inorganic carbon measurements.

188 In addition, pH and temperature were measured before and after each

189 irradiation experiment employing a pH Checker PLUS tester (Hi98100, HANNA

190 Instruments, Woonsocket, RI, USA) and a Checktemp® 1 digital thermometer

191 (Hi98509, HANNA), respectively.

192

193 **3. RESULTS AND DISCUSSION**

194 *3.1. Laser irradiation of double distilled water samples*

195   Initial irradiation experiments were performed with double distilled water spiked

196   with IBP, for maximum periods of 15 min. The UV-vis spectrum of IBP in double

197   distilled water presents two maxima around 221 and 193 nm, with the latter

198   contributed by two bands at 191.7 and 193.4 nm. These maxima can be

199   ascribed to conjugated pi-electrons of the aromatic ring. Additionally, the C=O

200   double bond also promotes signals between 170-200 and, moreover, around

201   270 nm due to n$\rightarrow$π* and π$\rightarrow$π* transitions. When the sample is irradiated, a

202   weak broad band centered at 260 nm is observed in the spectra (Fig. 2). This

203   band's intensity increases up until 2 min of irradiation time, while those with

204   maxima at 221 and 193 nm decrease as the solution is irradiated, suggesting

205   that IBP has been transformed by pulsed laser irradiation. This transformation

206   takes place during the first 12 min of irradiation; the spectrum remains

207   unchanged thereafter (Fig. 2).

208   Moreover, the formation of a clear isosbestic point (i.e. wavelength at which the

209   absorbance of a sample does not change) at 233.5 nm is observed in early

210   stages of the reaction, disappearing after 3 min irradiation. This behavior is

211   consistent with the occurrence of a typical consecutive transformation process

212   (such as A$\rightarrow$B$\rightarrow$C; where A represents IBP, B intermediate TPs, and C the final

213   products).

214   Aiming to corroborate and quantify the above results, i.e. measure the

215   dissipation of IBP and screen for possible TPs being produced, samples were

216   measured by LC-HRMS (see 2.3) at different irradiation times. As presented in

217   Table 1, 5 TPs (out of the 19 TPs screened) could be tentatively identified. The

218   tentatively identified TPs arose from hydroxylation and decarboxylation routes,

219   suggesting a free-radical transformation mechanism, as observed by

220   **Adityosulindro et al. (2018)**.

221   Fig. 3 represents the amount of IBP and TPs in DDW at different irradiation

222   times (Table S1), and, also confirms the observations by direct UV-Vis

223   spectroscopy (Fig. 2), as IBP decreases rapidly until its complete elimination

224   with an irradiation treatment of 15 min. On the other hand, the TPs intensity is

225   higher during the first few minutes of irradiation, thus only the

226   monohydroxylated and dihydroxylated TPs (TP-177, TP-221 and TP-237)

227   remain at the end of the experiment, summing an apparent yield (calculated

228   assuming an LC-HRMS response equivalent to IBP) <10%. Since no pure

229   standards are available for the TPs identified, their yield was calculated

230   considering that their response is the same as that of IBP.

231   Initial and final (15 min) samples were also analyzed for DOC and a DOC

232   removal of 25% (from 8.5 to 6.4 mg L^{-1}) was measured. This, together with that

233   observed in Fig. 3 (Table S1), would indicate that IBP is mostly transformed to

234   low molecular weight chemicals and volatile compounds.

235   Table 2 compares the results obtained in this work with the literature on IBP

236   photochemical studies, including photocatalysis and AOPs. As can be

237   appreciated, direct laser pulsed irradiation can provide removal efficiencies

238   similar to those obtained by methods which include a catalyst, and H_2O_2 in

239   some cases, without requiring additional reagents. Indeed, this data was

240   obtained from a batch scale and would need to be confirmed at a larger scale.

241   In addition, the efficiency of the laser source is higher than that of conventional

242   lamps, as demonstrated comparing the power density of the different sources

243   included in Table 2.

244

245

3.2. Mechanistic considerations

No changes were detected in the temperature of the solutions during the

irradiation experiments. However, a local significant temperature increase could

have taken place since the laser pulse duration (nanoseconds) is faster than

the molecule or solvent thermal relaxation time. On the other hand, remarkable

changes in the pH of the solution were observed along the time length of the

experiment. The pH decreases from 5.25 to 4.52 when IBP has been

completely degraded, as observed in Fig. 2 and corroborated in Fig. 3 (Table

S1). This effect was attributed to the extraction of hydroxyl groups associated to

the formation of hydroxylated TPs (Table 1).

Thermal pulsed laser cumulative effect (also known as incubation) was also

tested as a first assay on the possible production of radicals. Thus, Fig. 4

represents the spectra of a solution irradiated consecutively in sets of 1 min

intervals (with 2 min rest periods between each irradiation), up to a total

cumulative irradiation time of 12 min. Intervals of 1 min were selected here

considering the results presented in Figure 2. These suggest that, within the 1-2

min interval, there is a significant change in the effect of laser irradiation. During

the first minute a low amount of IBP has been removed while, after 2 min

irradiation, peak intensity maxima decrease considerably, evidencing an

important IBP loss. Following this methodology, the degradation process of IBP

takes place slowly since the peak maxima slightly decrease in their intensity

and the isosbestic point is observed even after 12 min of consecutive

irradiation. This fact suggested that the process is stopped in reaction A→B,

269   evidencing that the following consecutive step, namely B➔C, has not taken

270   place and supposing that radicals are not formed, or that their concentration

271   after 1 min irradiation is not sufficient to promote the consecutive reaction.

272   Considering that in previous experiments ~96% IBP is degraded (Table S1)

273   and, concomitantly, achieving a maximum amount of 28.6% for TP-221 after 3

274   min irradiation, it is reasonable to ascertain that a minimum threshold irradiation

275   time above 1 min is needed to achieve the consecutive process A➔B➔C.

276   Thus, a minimum of incubation energy in the form of light quanta, would be

277   needed to ensure complete degradation of IBP and, therefore, to ensure a

278   consecutive process. Likewise, it was verified that the spectra of the 3 and 6

279   min irradiated solutions were maintained after 4 days, demonstrating altogether

280   the irreversibility of the reaction.

281   The probed stability, together with that observed in cumulative studies suggest

282   that a radical reaction mechanism should not be contemplated here. Indeed,

283   standard analysis (**Slanina et al., 2018**) with Rhodamine-6G (Rho6G, Sigma-

284   Aldrich) was also performed by mixing the radical trap with IBP in stoichiometric

285   ratio (1:1), followed by irradiating this solution during 3 min while monitoring

286   absorbance. Since no color change in the solution associated to variation of the

287   spectrum profile was observed, the is no evidence for the presence of radicals.

288   It could be, nevertheless, a competitive process between IBP and Rho6G in

289   which the pharmaceutical degradation is preferent.

290

291   *3.3. LASER irradiation of effluent wastewater samples*

292   In order to test the reaction in real wastewater, a secondary effluent was

293   considered, spiked with IBP (*10* mg L^{-1}) and irradiated at 3, 6 and 15 min. This

294   IBP spiked effluent was analyzed by LC-HRMS for IBP itself and the TPs

295   previously identified in pure water. As presented in Fig. 3 (Table S2), IBP was

296   not completely degraded since still a 5.7% of IBP remained at 15 min and ca.

297   another 15% was simply transformed into TP-237, TP-177 and TP-221.

298   **Quintana et al. (2005)** achieved, after microbial biodegradation, IBP

299   degradation values above 90% in 22 days on effluent waters from the same

300   wastewater treatment plant, also identifying the TPs just mentioned above. As a

301   recent comparison, **de Wilt et al. (2018)** achieved complete IBP removal from

302   effluent water by a recent optimized AOPs within a short time. They combined

303   ozonation and biological reactors, however, while the approach presented here

304   makes use of direct pulsed laser light. On the other hand, although a significant

305   depletion of IBP and TPs was, nevertheless, achieved in 15 min, the remaining

306   quantities probably appear due to the competition of other chemicals (**Rodil et**

307   **al., 2012; Wilkinson et al., 2017**) present in the wastewater effluent. Indeed,

308   the reaction mechanism in effluent samples may differ from that in pure water,

309   due to the presence of nitrates, nitrites, dissolved organic matter and other

310   water constituents, and to indirect photolytic mechanisms. Such processes are

311   normally associated to accelerated kinetics (**Chiron et al., 2009**; **McNeill and**

312   **Canonica, 2016**; **Castro et al., 2017**), but decelerative effects can also occur

313   (**Russo et al., 2016**). However, they were not observed in this case, and only

314   the same 5 TPs identified in pure water could be detected (from the 19 TPs that

315   were screened). Such accelerated kinetics could, however, be more relevant at

316   lower (closer to environmentally expected) concentrations.

317   Considering that **Baranda et al. (2017)** employed low fluences of pulsed light

318   from a Xe lamp to remove some pesticides containing aromatic rings, C=O

319   double bonds and hydroxyl groups like ibuprofen, it must be assumed that other

320   NSAIDs present could be degraded reducing the IBP removal rate. In addition,

321   their influence would be masked in the UV spectra due to variations that are

322   also associated to bands around 170-200 nm (assigned to C=O double bond)

323   and/or 270 nm (assigned to the n$\rightarrow$π* and π$\rightarrow$π* transitions). On the other

324   hand, N.B. that in Table S2, TPs formation yields are calculated assuming the

325   IBP response, as pure standards were not available, as commented before.

326   Thus, such yield is just a qualitative estimation (that is why the sum of IBP and

327   TPs is over 100% after 3 min irradiation).

328   Finally, a discrete DOC removal of 3.5% was measured for initial (3 min) and

329   final (15 min) samples. This value is close to that registered by **Adityosulindro**

330   **et al. (2018)** using a heterogeneous Fenton process with Fe-catalyst for effluent

331   solutions spiked with IBP (20 mg L^{-1}) and treated during 3 hours. Removals of

332   23% and 3% for IBP and DOC, respectively, were achieved without pH

333   modification. In addition, their effluent comes from a small village wastewater

334   treatment plant, while our work concerns wastewater from a plant treating the

335   sewage of ca. 100,000 inhabitants.

336   Concerning the energy efficiency for contaminant removal from water for this

337   pulsed laser technique, the Electrical Energy per Order (E_{EO}) was estimated

338   using the method published by **Bolton et al. (2001)** and an equivalent,

339   commercially available pulsed laser with emission at 266 nm and 1 kHz pulse

340   repetition rate. Considering the IBP degradation (Table S2), E_{EO} values

341   approaching 23.3 kWh m^{-3} per order would be achieved in waste water.

342   Although these values are not yet competitive, recent advances on 266 nm

343   solid state laser technology (**Zhai et al., 2013**; **Fang et al., 2017**) suggest that

344 these efficiency levels may be increased significantly with state-of-the-art

345 lasers. In addition, new industrial laser integration devices enable the use of

346 fast large area beam scanning, which opens the way to use recent advances in

347 high efficiency continuous processing, as demonstrated in other areas of

348 technology (**Lennikov et al., 2013**; **Cubero et al., 2020**).

349

350 **CONCLUSIONS**

351 This work demonstrates that a 0.9 W nominal power, ns pulsed laser emitting at

352 a wavelength of 266 nm is able to efficiently degrade, or significantly reduce the

353 presence of a relevant microcontaminant (IBP) in water. It does so to almost a

354 complete extent in ultrapure water, in less than 6 min, and to a significant extent

355 in real waste water matrices, in less than 15 min and without the need for a

356 catalyst or auxiliary oxidants. Further research is warranted with additional

357 microcontaminants, at concentrations closer to environmental levels and

358 considering ecotoxicological aspects, since TPs may be more toxic than the

359 original microcontaminants themselves (**Fan et al., 2020**; **Russo et al., 2018**).

360 Yet, the results presented here may open new opportunities for simple and

361 efficient water treatment methods based on the use of new generation lasers.

362 Since lasers enable miniaturization and achievement of directional beam

363 delivery, they bring about new opportunities for scale up geometries which are

364 not reasonably achievable with more conventional sources.

365

366 **ACKNOWLEDGEMENTS**

15

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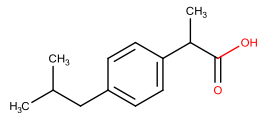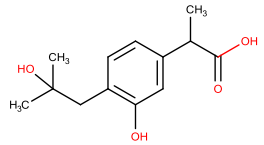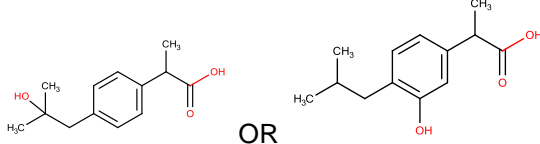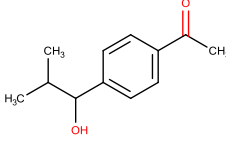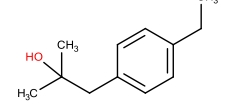
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Table 1: LC-HRMS data on IBP and the detected TPs. Previously TPs were screened for as detailed on 2.3.

Compound	Molecular formula	[M-H]⁻ (m/z)	Error (ppm)	Score (%)[1]	Structure [2]	Reference
IBP	C13H18O2	205.1234	-1.96	99.23		--
TP-237	C13H18O3	237.1132	3.28	97.36		Illés et al., 2013
TP-221	C13H18O3	221.1183	-2.33	98.80	OR	Illés et al., 2013
TP-191	C12H16O2	191.1078	-1.84	99.38		Méndez-Arriaga et al., 2010
TP-177	C12 H18 O	177.1285	-2.18	99.21		Méndez-Arriaga et al., 2010

Illés et al., 2013

TP-175   C12H16O   175.1128   5.33   95.52
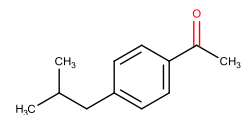
Table 3: Comparison of different approaches published in the literature for IBP removal in pure water.

Process	Conc. (mg/L)	Volume (mL)	Time (min)	Power density (mJ/cm^2)	IBP removal	TOC removal	Reference
UV-vis/H2O2/Fe(II)	179	1500	60	-	100%	~40%	Méndez-Arriaga et al., 2010
UVA/TiO2	5	2000	120	-	98.9	-	da Silva et al., 2014
UVA/TiO2	10	500	18	0.06	100%	-	Georgaki et al., 2014
UVA/ZnO	10	500	18	0.06	100%	-	Georgaki et al., 2014
UVC	46	20	60	0.04	70%	-	Iovino et al., 2016
H2O2/Fe	20	9	120	-	88%	27%	Adityosulindro et al., 2018
UV-vis/TiO2nano	5	50	180	-	100%	-	Lin et al., 2019
UVC (LASER)	10	4	12	18	100%	25%	This work

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Figure Captions:

- Figure 1: Experimental set-up configuration employed to carry out Laser irradiation of Ibuprofen solutions reported in this work. The apparatus consists of a Solid State Laser emitting on its fourth harmonic, a mirror at a 90º angle which reflects the laser beam into a quartz cuvette, containing the ibuprofen solution.

- Figure 2: UV absorption spectra of irradiated IBP 10 mg L^{-1} solutions noting the isosbestic point. Inset: detail of absorption spectra around band at 260 nm.

- Figure 3: Graphics representing percentage of IBP remaining and TPs formed at different irradiation times in a) ultrapure (DDW), and, b) effluent (EFF) water. N.B.: the yield of the TPs formed was calculated (Table S1, Table S2) considering that their response is the same as that of IBP, since no pure standards were available.

- Figure 4: UV-vis absorption spectra of a 10 mg L^{-1} IBP solution irradiated during consecutive 1 min intervals, with 2 min rest in between each irradiation.
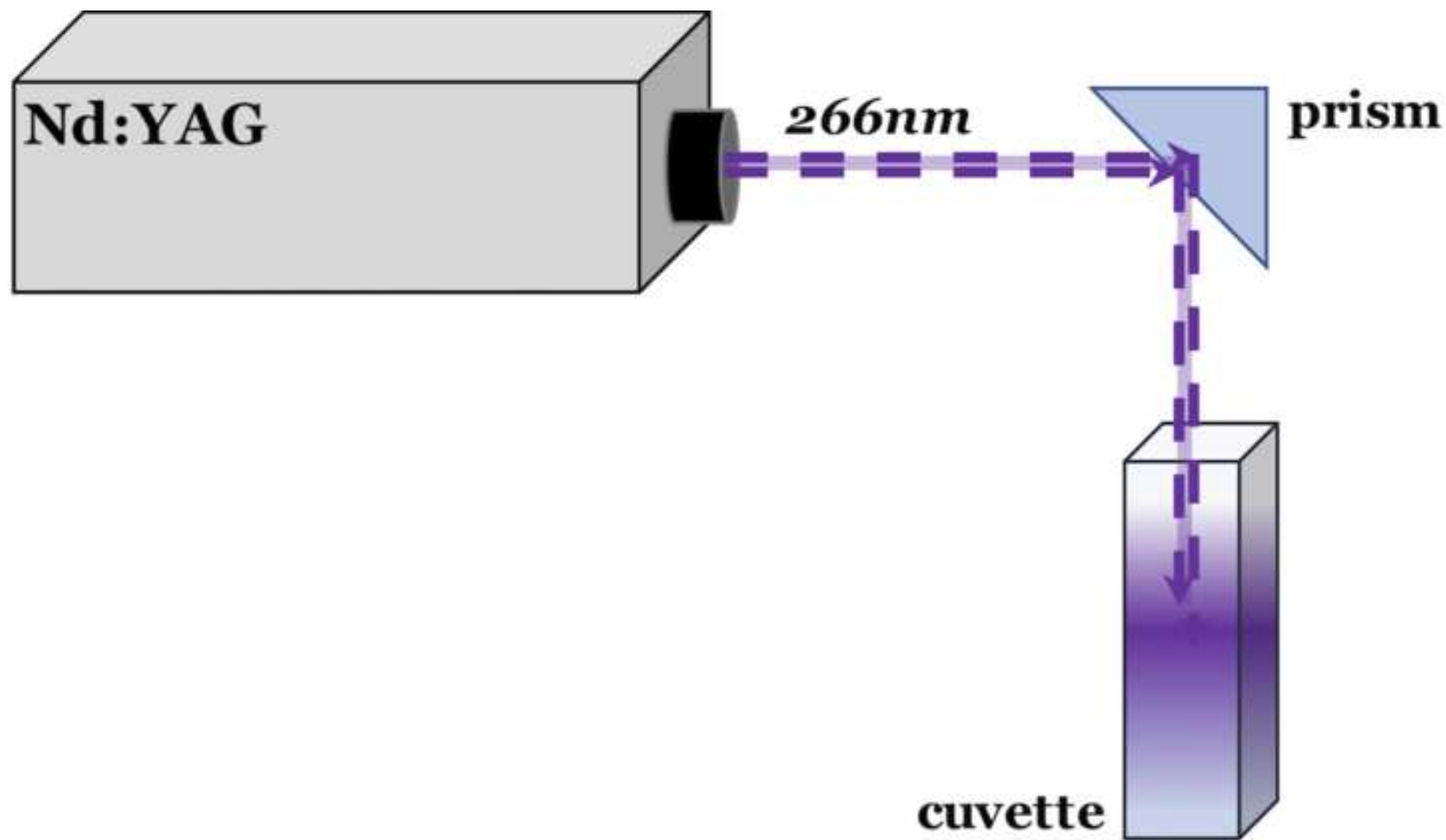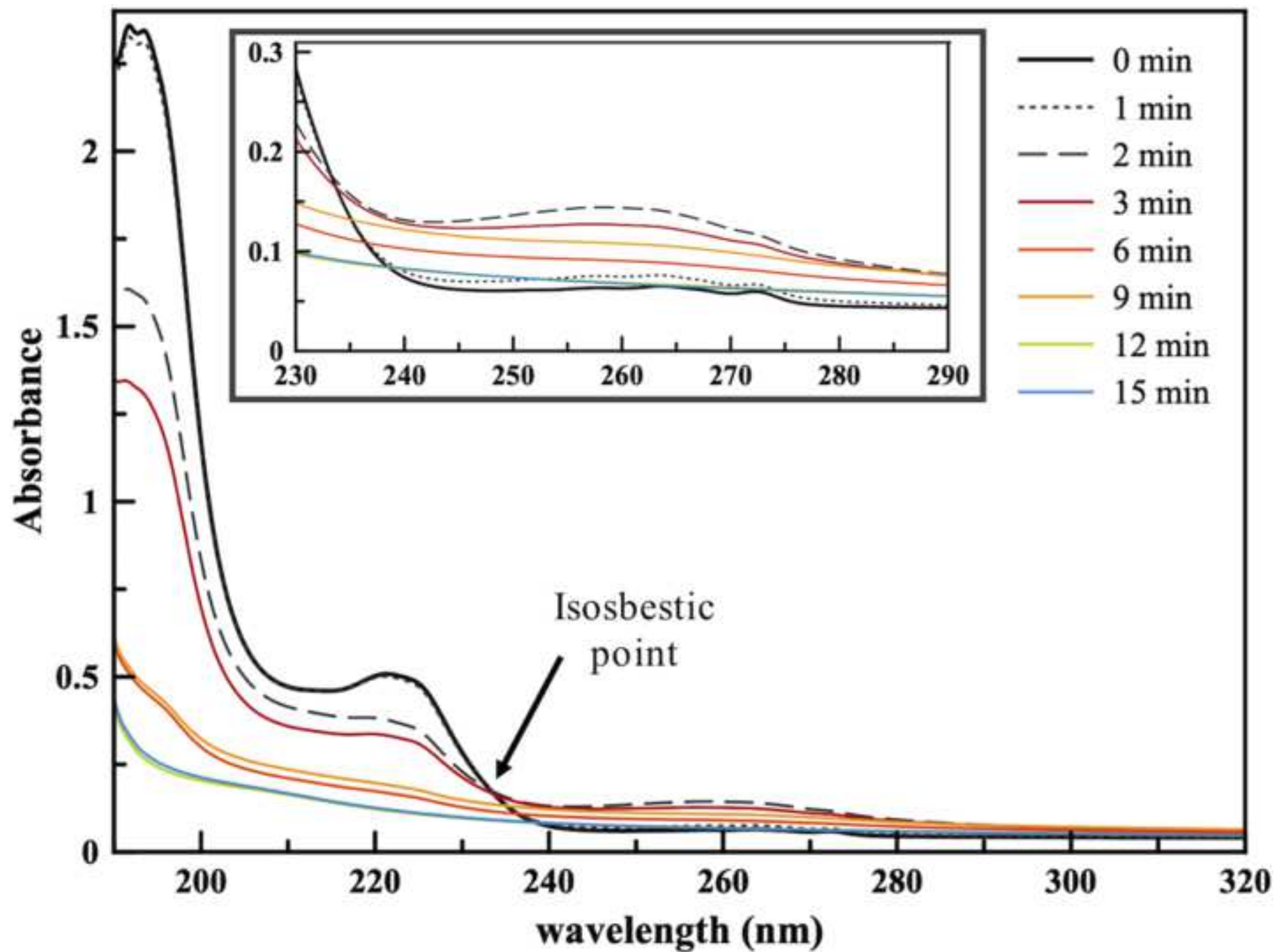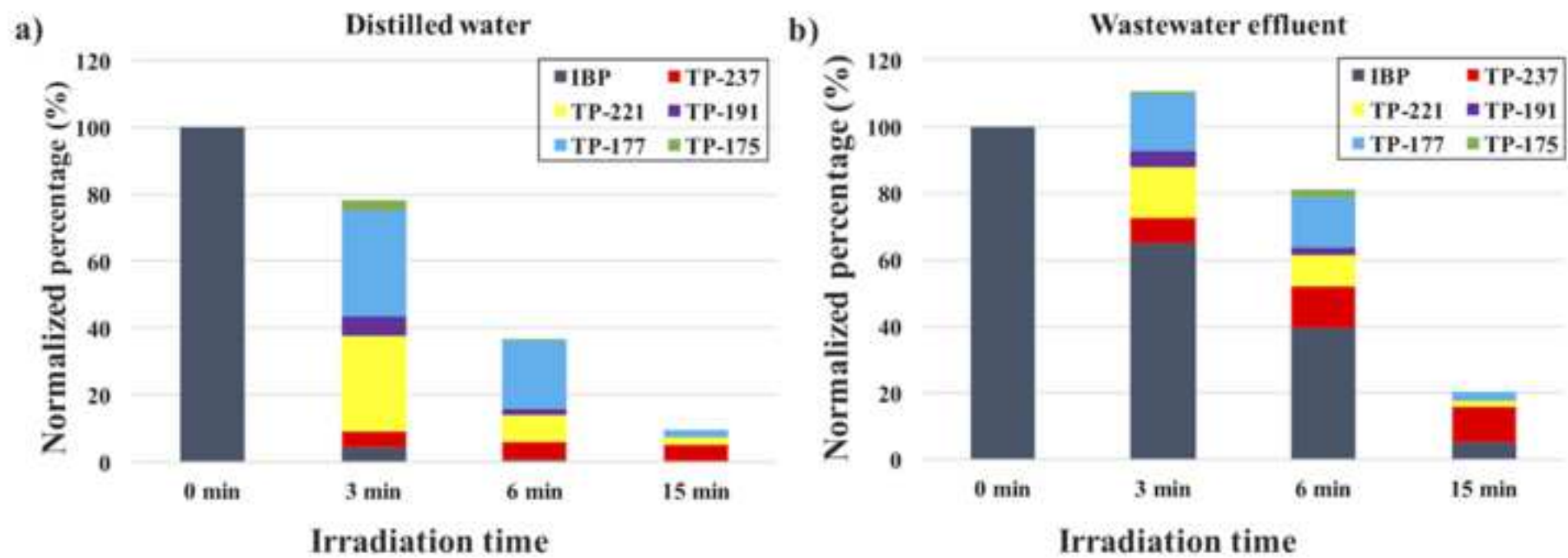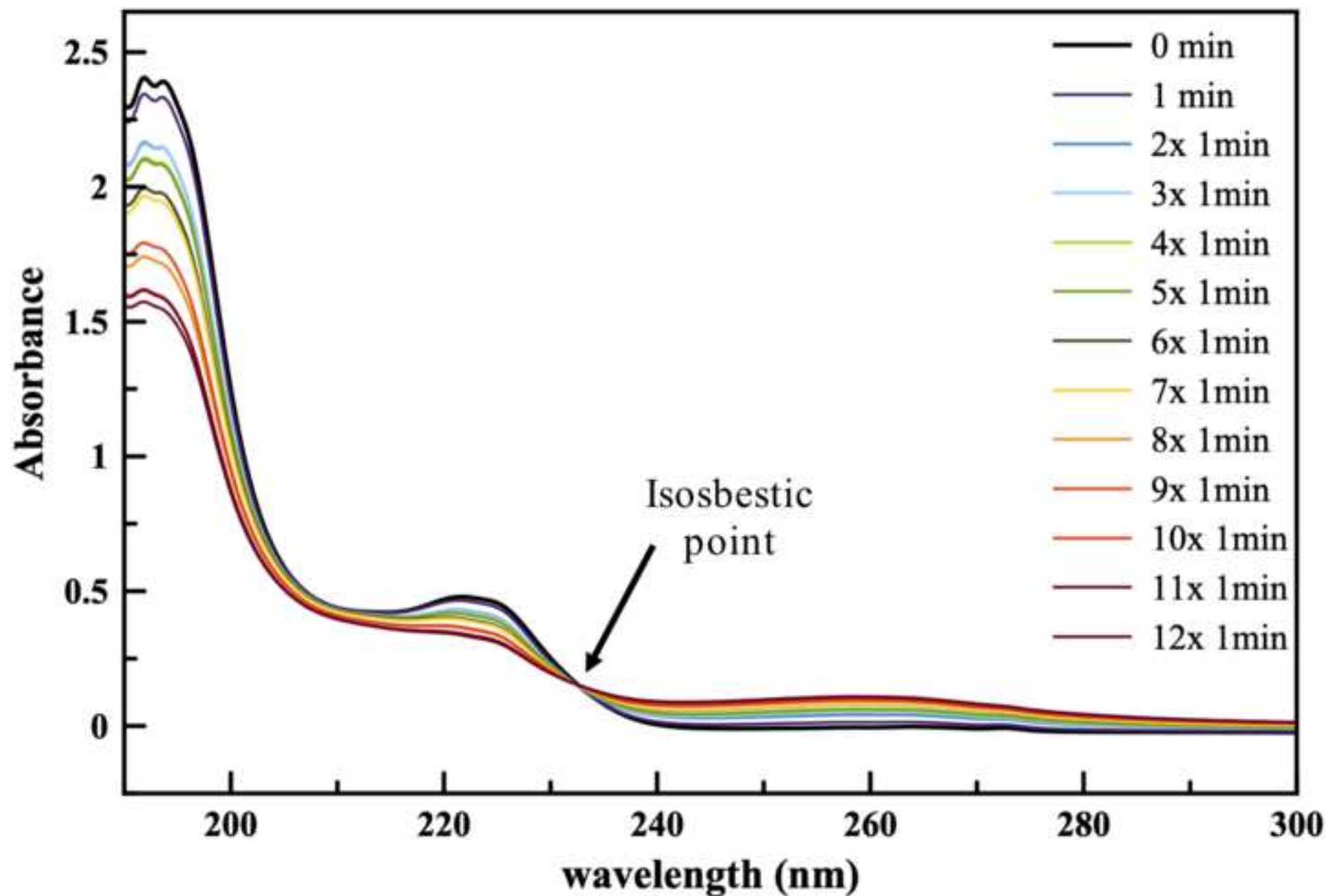
Figure 1

Figure 2

Figure 3

Figure 4

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

In representation of all authors: Francisco Rey García
Zaragoza, March 3, 2020

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Author contributions:

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C. Bao-Varela: investigation, formal analysis, writing - review

J.R. Leis: methodology, formal analysis, writing - review

L.A. Angurel: conceptualization, supervision, writing - review

J.B. Quintana: methodology, formal analysis, writing

R. Rodil: methodology, formal analysis, writing - review

G.F. de la Fuente: conceptualization, methodology, writing - review

Table S1: Percentage of IBP remaining and TPs formed at different irradiation times in ultrapure water. N.B.: the yield of the TPs formed was calculated considering that their response is the same as that of IBP, since no pure standards were available.

Time (min)	IBP	TP-237	TP-221	TP-191	TP-177	TP-175
0	100	0.0	0.0	0.0	0.0	0.0
3	4.1	5.1	28.6	5.6	31.9	2.9
6	0.7	5.3	8.2	1.6	20.4	0.4
15	0.0	5.2	2.3	0.0	2.3	0.0

Table S2: Percentage of IBP remaining and TPs formed at different irradiation times in spiked effluent water. N.B.: the yield of the TPs formed was calculated considering that their response is the same as that of IBP, since no pure standards were available.

Time (min)	IBP	TP-237	TP-221	TP-191	TP-177	TP-175
0	100	0.0	0.0	0.0	0.0	0.0
3	64.8	7.6	15.6	4.5	17.	1.2
6	39.5	12.5	9.5	2.2	15.3	2.1
15	5.3	10.4	1.9	0.0	2.9	0.0