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

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ABSTRACT

A novel approach based on the direct pulsed irradiation of UV-C light onto ibuprofen (IBP) solutions was evaluated in this work, as proof of concept for the direct removal of micropollutants. The experiments confirmed that laser irradiation is able to completely degrade IBP in 15 min in distilled water, with a DOC depletion of ca. 25% and with transformation products (TPs) remaining in solution and estimated to represent ca. 10% of the initial IBP concentration. In
wastewater spiked samples, removal efficiency is slightly lower but still significant (ca. 5% IBP remaining after 15 min). Hence, this work suggests that low power solid state pulsed lasers, emitting at 266 nm wavelength, show promise for the removal of these type of micropollutants from water. These results open new opportunities towards the development of chemical-free water treatment methods based on direct, selective irradiation using state of the art, miniaturized laser devices.

KEYWORDS
UV Laser Chemistry, Ibuprofen, nanosecond pulses, 266nm, transformation products, wastewater

1. INTRODUCTION
The presence of pharmaceuticals in water is one of the topics of major concern in the two latest decades (Wilkinson et al., 2017). Among the different classes of pharmaceuticals, non-steroidal anti-inflammatory drugs (NSAIDs) are one of the most relevant and commonly investigated classes, due to their application over the counter in high dosages and demonstrated presence in the water environment. Ibuprofen (IBP) is one the pharmaceuticals detected at higher concentrations (Rodil et al., 2012; Wilkinson et al., 2017). For these reasons, classical removal technologies, such as biodegradation during wastewater treatment (Quintana et al., 2005) or reactivity with well-established disinfectant systems, both used at wastewater treatment plants (WWTPs) and drinking water facilities, have been investigated. In addition, increased interest has been
recently shown for UV disinfection (Iovino et al., 2016). Several Advanced Oxidation Processes (AOPs), including those which make use of UV radiation, have also been tested with IBP and other NSAIDs, with the objective of improving their removal efficiency during wastewater treatment (Ameta and Ameta, 2018; Miklos et al., 2018; Mlungunza et al., 2019; Romeiro et al., 2018).

The use of UV lamps for degrading pharmaceuticals and other organic micropollutants, such as IBP, is based on the fact that their emission is within the same range (190-380 nm, ultraviolet) as the absorbance bands of the aromatic rings and poly-unsaturated groups present in their structure (Adityosulindro, 2017; da Silva et al., 2014; Iovino et al., 2016; Miklos et al., 2018; Peuravuori and Pihlaja, 2009). These UV sources are characterized by a continuous emission mode, with the most common ones including mono- and polychromatic low- (LP) or medium pressure (MP) mercury lamps (Miklos et al., 2018). Moreover, UV laser emitting diodes (UV-LED) are also employed for the microorganism disinfection of water, specially when utilized for human consumption (Jarvis et al., 2019). Concerning the photocatalytic treatment with conventional UV light sources, Mendez-Arriaga et al. (2010) employed a 1 kW Xe lamp for the photo-Fenton treatment of IBP aqueous solutions within a photoreactor, assessing the irradiation available to be absorbed by H₂O₂ within the 290 to 350 nm spectral range. Furthermore, Georgaki et al. (2014) treated aqueous matrices of IBP by means of photocatalysis. They used TiO₂ and ZnO inside a photoreactor provided with a medium pressure, a 150 W constant power Hg lamp emitting within the 200-600nm range and with λ_max at 365 nm. Later, Chianese et al. (2016) employed a UV crosslinker apparatus, provided
with five UV lamps emitting at 254nm (UV-C range) for irradiating IBP aqueous solutions. Most recently, Lin et al. (2019) employed a 160 W UV-Vis lamp with emission maxima within the 290-545 nm wavelength range in order to establish differences between direct UV photolysis and UV-Vis promoted photocatalysis of IBP in clean water. The latter almost completely degrades IBP, although the photocatalyst is found to significantly decrease its activity as a function of progressive irradiation cycles. A promising new approach reported by Baranda et al. (2017) employed new Pulsed Lamp (PL) technology for pesticide decontamination in water, based on Xe lamp emission with fluence values in the 0.5-10 J cm\(^{-2}\) range and pulse widths in the order of 300-325 µs.

In contrast, the use of lasers has not yet been sufficiently explored for the treatment of water containing microcontaminants, and only a limited number of papers have appeared in the literature during the last three decades (Unkroth et al., 1997; Pascu et al., 2011; Smarandache et al., 2012). The pioneering report by Unkroth et al. (1997) made use of ArF and KrF Excimer lasers emitting at 193 and 248 nm, respectively, and described treatment of textile dyes and dyehouse wastewaters both, under direct irradiation and in combination with oxidizers. More than a decade later, Pascu et al. (2011) reported on the direct modification of phenothiazines using pulsed solid state Nd:YAG lasers emitting on their second (532 nm), third (355 nm) and forth (266 nm) harmonics, as well as a pulsed nitrogen gas laser emitting at 337 nm. Similar work published by Smarandache et al. (2012) reported on the degradation of thioridazine and BG1188 pharmaceutical compounds using direct laser irradiation emitted from a pulsed solid state Nd:YAG laser in its third harmonic at 355 nm. A significant amount of published related work, based on
the use of lasers, pertains to reactivity and stability studies, however (Moore and Chappuis, 1988; Packer et al., 2003; Rodríguez-Muñiz et al., 2014, Liang et al., 2019). A good number of these reports deal, in fact, with Laser Flash Photolysis (LFP). They employ a diversity of laser sources to investigate mechanistic aspects of photocatalyst mediated processes (Moore and Chappuis, 1988; Packer et al., 2003; Rodríguez-Muñiz et al., 2014; Liang et al., 2019). Moreover, in LFP, lasers have often been employed to start chemical reactions by means of singlet oxygen, or even hydroxyl radical generation, from a sensitizer in a pH-controlled medium.

The use of pulsed laser sources may be expected to yield promising results towards pollutant removal, considering the previously mentioned work of Baranda et al. (2017). These authors registered pesticide removal yields ranging between 60 and 93%, apparently as a consequence of using pulsed UV lamps with higher irradiance levels than those achieved with continuous sources. In this sense, lasers provide a particularly attractive alternative, in view of the fact that they provide irradiance values (W/cm²) that are orders of magnitude above those achieved with lamps (Pascu et al. 2011).

The objective of this work is thus to explore the potential of ns pulsed UV lasers, for direct photochemical removal of micropollutants present in water. For this purpose, IBP was selected as a proof of principle, model compound, and 266 nm as the emission wavelength of the laser. The latter is in the same spectral range as the absorbance bands found in aromatic rings and poly-unsaturated groups, present in most NSAIDs compounds. Particular consideration was given to the presence of reported photochemical transformation products (TPs),
since they can be in some cases more toxic than the original organic contaminant compounds themselves (Quintana et al., 2014).

2. MATERIALS AND METHODS

2.1. Chemicals and samples

Aqueous stock solutions of 10 mg L\(^{-1}\) were prepared using ibuprofen (IBP) of pharmaceutical grade from Sigma-Aldrich (Merck KGaA, Darmstadt, Germany), double distilled water (DDW) and effluent (EFF) water (pH: 7.1, DOC: 3.5 mg L\(^{-1}\), total suspended solids: 6 mg L\(^{-1}\), nitrate: 26 mg L\(^{-1}\), nitrite: 0.25 mg L\(^{-1}\), chloride: 20 mg L\(^{-1}\), bromide: 0.14 mg L\(^{-1}\), sulfate: 22 mg L\(^{-1}\), fluoride < 0.05 mg L\(^{-1}\), phosphate < 0.04 mg L\(^{-1}\)) collected from a wastewater treatment plant located in the NW of Spain, which processes the sewage of ca. 100,000 inhabitants and is equipped with primary and conventional activated sludge treatments. This concentration (10 mg L\(^{-1}\)) was employed in order to be able to follow DOC and UV changes and detect TPs.

2.2. Laser irradiation experiments

Laser experiments were performed on 4 ml aliquots of IBP spiked (10 mg L\(^{-1}\)), double distilled water or filtered effluent wastewater. Samples were placed inside 1 cm\(^2\) base UV fused quartz cuvettes (CV10Q3500S, Thorlabs Inc., Newton, NJ, USA) and irradiated with a pulsed solid-state laser (Quanta Ray, Spectra-Physics, Newport Corp., Irvine, CA, USA). The laser emission was set at its fourth harmonic (\(\lambda = 266\) nm) with a pulse width of 4-5 ns and a pulse repetition frequency of 50 Hz. The nominal laser emission power was set at 0.9
and the area covered by the beam was set at ca. 1 cm². In consequence, the pulse fluence is ca. 18 mJ cm⁻² and the pulse irradiance ca. 4 MW cm⁻². The laser beam was reflected on a narrowband laser line mirror (Y4-1025-45-UNP, CVI Laser Optics, Albuquerque, NM, USA) mounted onto a 45º round mount (Thorlabs Inc.), in order to vertically irradiate the cuvette contents from its top entry (Fig. 1). The laser power was measured employing a FieldMax II TO (Coherent Inc., Santa Clara, CA, USA) power meter equipped with a PowerMax PM150 sensor and placed at the same geometrical point as the quartz cuvettes. It was observed during the treatment that the laser beam irradiated a complete, vertical liquid column, from the upper liquid meniscus to the bottom, inner base surface of the cuvette.

2.3. Analytical methods

A Perkin-Elmer UV-vis Lambda Spectrometer (PerkinElmer Inc., Waltham, MA, USA) was employed for spectroscopic studies. In addition, the amount of IBP remaining on several experiments and the formation of TPs was determined by liquid chromatography–high-resolution mass spectrometry (LC-HRMS). To this end, aliquots of the treated solutions at different irradiation times were analyzed employing a quadrupole-time-of-flight mass spectrometer (Agilent 6550 iFunnel QTOF, Agilent, Santa Clara, CA, USA) linked to an Agilent 1290 Infinity II (Agilent) liquid chromatography system. Chromatographic separation was achieved using a 150x2mm, 3µm Luna C18 column (Phenomenex, Torrance, CA, USA) using Milli-Q water and acetonitrile, both containing 0.1% formic acid, as eluents A and B, respectively. The LC gradient was as follows: initially 5% B, ramped to 100%B in 10 min (held for 2 min), then back-conditioned for 9 min.
Injection volume was 5 µL. The LC-HRMS system operated in negative ionization mode, with nitrogen being used as nebulizing gas. Spectra registration was performed in the 2 GHz extended dynamic range mode which provides a resolution of ca. 10,000 at m/z 121 in the 40-1000 m/z range. The mass accuracy was maintained by infusing a reference solution with a secondary electrospray according to manufacturer’s specifications. IBP was determined by integration of the 205.1234 m/z (± 20 ppm) extracted ion chromatogram. TPs were screened for by extracting the m/z value of TPs described in the literature (Illés et al., 2013; Méndez-Arriaga et al., 2010) at different irradiation times.

Dissolved Organic Carbon (DOC) was determined on a Shimadzu TOC-L instrument (Shimadzu Corp., Kyoto, Japan) provided with a 2-channel non-dispersive infrared (NDIR) detector, according to the 5310-B Std. Meth. Ed.20 (APHA-AWWA-WPCF) method for water and wastewater examination (Clesceri et al., 1998). DOC was calculated from the difference between the total carbon (TC) and inorganic carbon measurements. In addition, pH and temperature were measured before and after each irradiation experiment employing a pH Checker PLUS tester (Hi98100, HANNA Instruments, Woonsocket, RI, USA) and a Checktemp® 1 digital thermometer (Hi98509, HANNA), respectively.

3. RESULTS AND DISCUSSION

3.1. Laser irradiation of double distilled water samples
Initial irradiation experiments were performed with double distilled water spiked with IBP, for maximum periods of 15 min. The UV-vis spectrum of IBP in double distilled water presents two maxima around 221 and 193 nm, with the latter contributed by two bands at 191.7 and 193.4 nm. These maxima can be ascribed to conjugated pi-electrons of the aromatic ring. Additionally, the C=O double bond also promotes signals between 170-200 and, moreover, around 270 nm due to n→π* and π→π* transitions. When the sample is irradiated, a weak broad band centered at 260 nm is observed in the spectra (Fig. 2). This band’s intensity increases up until 2 min of irradiation time, while those with maxima at 221 and 193 nm decrease as the solution is irradiated, suggesting that IBP has been transformed by pulsed laser irradiation. This transformation takes place during the first 12 min of irradiation; the spectrum remains unchanged thereafter (Fig. 2).

Moreover, the formation of a clear isosbestic point (i.e. wavelength at which the absorbance of a sample does not change) at 233.5 nm is observed in early stages of the reaction, disappearing after 3 min irradiation. This behavior is consistent with the occurrence of a typical consecutive transformation process (such as A→B→C; where A represents IBP, B intermediate TPs, and C the final products).

Aiming to corroborate and quantify the above results, i.e. measure the dissipation of IBP and screen for possible TPs being produced, samples were measured by LC-HRMS (see 2.3) at different irradiation times. As presented in Table 1, 5 TPs (out of the 19 TPs screened) could be tentatively identified. The tentatively identified TPs arose from hydroxylation and decarboxylation routes,
suggesting a free-radical transformation mechanism, as observed by
Adityosulindro et al. (2018).

Fig. 3 represents the amount of IBP and TPs in DDW at different irradiation
times (Table S1), and, also confirms the observations by direct UV-Vis
spectroscopy (Fig. 2), as IBP decreases rapidly until its complete elimination
with an irradiation treatment of 15 min. On the other hand, the TPs intensity is
higher during the first few minutes of irradiation, thus only the
monohydroxylated and dihydroxylated TPs (TP-177, TP-221 and TP-237)
remain at the end of the experiment, summing an apparent yield (calculated
assuming an LC-HRMS response equivalent to IBP) <10%. Since no pure
standards are available for the TPs identified, their yield was calculated
considering that their response is the same as that of IBP.

Initial and final (15 min) samples were also analyzed for DOC and a DOC
removal of 25% (from 8.5 to 6.4 mg L\(^{-1}\)) was measured. This, together with that
observed in Fig. 3 (Table S1), would indicate that IBP is mostly transformed to
low molecular weight chemicals and volatile compounds.

Table 2 compares the results obtained in this work with the literature on IBP
photochemical studies, including photocatalysis and AOPs. As can be
appreciated, direct laser pulsed irradiation can provide removal efficiencies
similar to those obtained by methods which include a catalyst, and H\(_2\)O\(_2\) in
some cases, without requiring additional reagents. Indeed, this data was
obtained from a batch scale and would need to be confirmed at a larger scale.

In addition, the efficiency of the laser source is higher than that of conventional
lamps, as demonstrated comparing the power density of the different sources
included in Table 2.
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 \( A \rightarrow B \),
evidencing that the following consecutive step, namely B→C, has not taken
place and supposing that radicals are not formed, or that their concentration
after 1 min irradiation is not sufficient to promote the consecutive reaction.
Considering that in previous experiments ~96% IBP is degraded (Table S1)
and, concomitantly, achieving a maximum amount of 28.6% for TP-221 after 3
min irradiation, it is reasonable to ascertain that a minimum threshold irradiation
time above 1 min is needed to achieve the consecutive process A→B→C.
Thus, a minimum of incubation energy in the form of light quanta, would be
needed to ensure complete degradation of IBP and, therefore, to ensure a
consecutive process. Likewise, it was verified that the spectra of the 3 and 6
min irradiated solutions were maintained after 4 days, demonstrating altogether
the irreversibility of the reaction.
The probed stability, together with that observed in cumulative studies suggest
that a radical reaction mechanism should not be contemplated here. Indeed,
standard analysis (Slanina et al., 2018) with Rhodamine-6G (Rho6G, Sigma-
Aldrich) was also performed by mixing the radical trap with IBP in stoichiometric
ratio (1:1), followed by irradiating this solution during 3 min while monitoring
absorbance. Since no color change in the solution associated to variation of the
spectrum profile was observed, the is no evidence for the presence of radicals.
It could be, nevertheless, a competitive process between IBP and Rho6G in
which the pharmaceutical degradation is preferent.

3.3. LASER irradiation of effluent wastewater samples
In order to test the reaction in real wastewater, a secondary effluent was
considered, spiked with IBP (10 mg L⁻¹) and irradiated at 3, 6 and 15 min. This
IBP spiked effluent was analyzed by LC-HRMS for IBP itself and the TPs previously identified in pure water. As presented in Fig. 3 (Table S2), IBP was not completely degraded since still a 5.7% of IBP remained at 15 min and ca. another 15% was simply transformed into TP-237, TP-177 and TP-221. Quintana et al. (2005) achieved, after microbial biodegradation, IBP degradation values above 90% in 22 days on effluent waters from the same wastewater treatment plant, also identifying the TPs just mentioned above. As a recent comparison, de Wilt et al. (2018) achieved complete IBP removal from effluent water by a recent optimized AOPs within a short time. They combined ozonation and biological reactors, however, while the approach presented here makes use of direct pulsed laser light. On the other hand, although a significant depletion of IBP and TPs was, nevertheless, achieved in 15 min, the remaining quantities probably appear due to the competition of other chemicals (Rodil et al., 2012; Wilkinson et al., 2017) present in the wastewater effluent. Indeed, the reaction mechanism in effluent samples may differ from that in pure water, due to the presence of nitrates, nitrites, dissolved organic matter and other water constituents, and to indirect photolytic mechanisms. Such processes are normally associated to accelerated kinetics (Chiron et al., 2009; McNeill and Canonica, 2016; Castro et al., 2017), but decelerative effects can also occur (Russo et al., 2016). However, they were not observed in this case, and only the same 5 TPs identified in pure water could be detected (from the 19 TPs that were screened). Such accelerated kinetics could, however, be more relevant at lower (closer to environmentally expected) concentrations. Considering that Baranda et al. (2017) employed low fluences of pulsed light from a Xe lamp to remove some pesticides containing aromatic rings, C=O
double bonds and hydroxyl groups like ibuprofen, it must be assumed that other
NSAIDs present could be degraded reducing the IBP removal rate. In addition,
their influence would be masked in the UV spectra due to variations that are
also associated to bands around 170-200 nm (assigned to C=O double bond)
and/or 270 nm (assigned to the n→π* and π→π* transitions). On the other
hand, N.B. that in Table S2, TPs formation yields are calculated assuming the
IBP response, as pure standards were not available, as commented before.
Thus, such yield is just a qualitative estimation (that is why the sum of IBP and
TPs is over 100% after 3 min irradiation).

Finally, a discrete DOC removal of 3.5% was measured for initial (3 min) and
final (15 min) samples. This value is close to that registered by Adityosulindro
et al. (2018) using a heterogeneous Fenton process with Fe-catalyst for effluent
solutions spiked with IBP (20 mg L⁻¹) and treated during 3 hours. Removals of
23% and 3% for IBP and DOC, respectively, were achieved without pH
modification. In addition, their effluent comes from a small village wastewater
treatment plant, while our work concerns wastewater from a plant treating the
sewage of ca. 100,000 inhabitants.

Concerning the energy efficiency for contaminant removal from water for this
pulsed laser technique, the Electrical Energy per Order (E_{EO}) was estimated
using the method published by Bolton et al. (2001) and an equivalent,
commercially available pulsed laser with emission at 266 nm and 1 kHz pulse
repetition rate. Considering the IBP degradation (Table S2), E_{EO} values
approaching 23.3 kWh m⁻³ per order would be achieved in waste water.
Although these values are not yet competitive, recent advances on 266 nm
solid state laser technology (Zhai et al., 2013; Fang et al., 2017) suggest that
these efficiency levels may be increased significantly with state-of-the-art lasers. In addition, new industrial laser integration devices enable the use of fast large area beam scanning, which opens the way to use recent advances in high efficiency continuous processing, as demonstrated in other areas of technology (Lennikov et al., 2013; Cubero et al., 2020).

CONCLUSIONS

This work demonstrates that a 0.9 W nominal power, ns pulsed laser emitting at a wavelength of 266 nm is able to efficiently degrade, or significantly reduce the presence of a relevant microcontaminant (IBP) in water. It does so to almost a complete extent in ultrapure water, in less than 6 min, and to a significant extent in real waste water matrices, in less than 15 min and without the need for a catalyst or auxiliary oxidants. Further research is warranted with additional microcontaminants, at concentrations closer to environmental levels and considering ecotoxicological aspects, since TPs may be more toxic than the original microcontaminants themselves (Fan et al., 2020; Russo et al., 2018).

Yet, the results presented here may open new opportunities for simple and efficient water treatment methods based on the use of new generation lasers. Since lasers enable miniaturization and achievement of directional beam delivery, they bring about new opportunities for scale up geometries which are not reasonably achievable with more conventional sources.

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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.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular formula</th>
<th>[M-H]^- (m/z)</th>
<th>Error (ppm)</th>
<th>Score (%)</th>
<th>Structure</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>IBP</td>
<td>C13H18O2</td>
<td>205.1234</td>
<td>-1.96</td>
<td>99.23</td>
<td><img src="image" alt="IBP Structure" /></td>
<td>--</td>
</tr>
<tr>
<td>TP-237</td>
<td>C13H18O3</td>
<td>237.1132</td>
<td>3.28</td>
<td>97.36</td>
<td><img src="image" alt="TP-237 Structure" /></td>
<td>Illés et al., 2013</td>
</tr>
<tr>
<td>TP-221</td>
<td>C13H18O3</td>
<td>221.1183</td>
<td>-2.33</td>
<td>98.80</td>
<td><img src="image" alt="TP-221 Structure" /></td>
<td>Illés et al., 2013</td>
</tr>
<tr>
<td>TP-191</td>
<td>C12H16O2</td>
<td>191.1078</td>
<td>-1.84</td>
<td>99.38</td>
<td><img src="image" alt="TP-191 Structure" /></td>
<td>Méndez-Arriaga et al., 2010</td>
</tr>
<tr>
<td>TP-177</td>
<td>C12H18O</td>
<td>177.1285</td>
<td>-2.18</td>
<td>99.21</td>
<td><img src="image" alt="TP-177 Structure" /></td>
<td>Méndez-Arriaga et al., 2010</td>
</tr>
</tbody>
</table>
Illés et al., 2013

1 The score (in percentage) represents how well molecular formula and HRMS data match, considering mass error and isotopic profile.

2 Structures proposed on the basis of the referenced published literature.
Table 3: Comparison of different approaches published in the literature for IBP removal in pure water.

<table>
<thead>
<tr>
<th>Process</th>
<th>Conc. (mg/L)</th>
<th>Volume (mL)</th>
<th>Time (min)</th>
<th>Power density (mJ/cm²)</th>
<th>IBP removal</th>
<th>TOC removal</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV-vis/H₂O₂/Fe(II)</td>
<td>179</td>
<td>1500</td>
<td>60</td>
<td>-</td>
<td>100%</td>
<td>~40%</td>
<td>Méndez-Arriaga et al., 2010</td>
</tr>
<tr>
<td>UVA/TiO₂</td>
<td>5</td>
<td>2000</td>
<td>120</td>
<td>-</td>
<td>98.9</td>
<td>-</td>
<td>da Silva et al., 2014</td>
</tr>
<tr>
<td>UVA/TiO₂</td>
<td>10</td>
<td>500</td>
<td>18</td>
<td>0.06</td>
<td>100%</td>
<td>-</td>
<td>Georgaki et al., 2014</td>
</tr>
<tr>
<td>UVA/ZnO</td>
<td>10</td>
<td>500</td>
<td>18</td>
<td>0.06</td>
<td>100%</td>
<td>-</td>
<td>Georgaki et al., 2014</td>
</tr>
<tr>
<td>UVC</td>
<td>46</td>
<td>20</td>
<td>60</td>
<td>0.04</td>
<td>70%</td>
<td>-</td>
<td>Iovino et al., 2016</td>
</tr>
<tr>
<td>H₂O₂/Fe</td>
<td>20</td>
<td>9</td>
<td>120</td>
<td>-</td>
<td>88%</td>
<td>27%</td>
<td>Adityosulindro et al., 2018</td>
</tr>
<tr>
<td>UV-vis/TiO₂ nano</td>
<td>5</td>
<td>50</td>
<td>180</td>
<td>-</td>
<td>100%</td>
<td>-</td>
<td>Lin et al., 2019</td>
</tr>
<tr>
<td>UVC (LASER)</td>
<td>10</td>
<td>4</td>
<td>12</td>
<td>18</td>
<td>100%</td>
<td>25%</td>
<td>This work</td>
</tr>
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</table>
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

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 4

The figure shows a series of absorbance spectra over different wavelengths (nm) for various times (0 min to 12x 1 min). The absorbance values range from 0 to 2.5. The spectra exhibit a characteristic isosbestic point, which is a wavelength at which the absorbance remains constant regardless of the time. This point is marked on the graph.
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:

F. Rey-García: investigation, methodology, formal analysis, writing

B.J. Sieira: formal analysis, writing

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.

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<th>TP-221</th>
<th>TP-191</th>
<th>TP-177</th>
<th>TP-175</th>
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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.

<table>
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<th>TP-221</th>
<th>TP-191</th>
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