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1 **Hydroxyl Radical as an unlikely Key Intermediate in the Photodegradation**  
2 **of Emerging Pollutants**

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## 12 **ABSTRACT**

13 In this work a kinetic model, in combination with time-resolved experiments, is applied to  
14 assess the involvement of  $\bullet\text{OH}$  in the photodegradation of emerging pollutants (EPs) by means  
15 of advanced oxidation processes. By contrast with the general assumption, quenching of the  
16 short-lived  $\bullet\text{OH}$  in the real waters by the (highly diluted) EPs must be very inefficient, so  
17 removal of EPs cannot purely rely on the generation and reaction of  $\bullet\text{OH}$ . This suggests that  
18 more complex pathways have to be considered to explain the photodegradation of EPs actually  
19 achieved under the employed oxidative conditions, possibly involving other reactive species  
20 with longer lifetimes or chain degradation processes.

21

## 22 INTRODUCTION

23 Solar photochemical processes have been considered as the main abiotic pathway determining  
24 the fate of pollutants in the environment and have deserved considerable attention from  
25 researchers in recent years (1). Specifically, advanced oxidation processes (AOPs) for  
26 wastewater treatment, based on photo-Fenton or semiconductor photocatalysis, have been  
27 driven under sunlight (2). In general, it is accepted that these processes are triggered by  
28 generation of hydroxyl radical or other highly reactive species, such as excited states, singlet  
29 oxygen or superoxide anion (3).

30 A wide range of drugs or personal care products (labelled as emerging pollutants, EPs)  
31 are ubiquitously found in aqueous systems at concentrations ranging from  $\mu\text{g/L}$  to  $\text{ng/L}$  (4).  
32 These concentrations are low, yet they could be associated with biological or environmental  
33 risks that remain mostly unknown. Although AOPs have been used for the removal of a  
34 number of EPs, the nature of the key oxidizing species is still a matter of discussion. In this  
35 context, hydroxyl radical ( $\bullet\text{OH}$ ) has been claimed to play an important role in most of these  
36 processes (3). However, the short lifetime of this radical (in the ns- $\mu\text{s}$  range) (5), its low steady  
37 state concentration (between  $10^{-15}$  and  $10^{-18}$  M) (6) and its difficult direct detection have  
38 dissuaded researchers in the field to make a reliable evaluation of the real  $\bullet\text{OH}$  role when  
39 pollutants are at such low concentrations. In fact, literature data are not fully consistent: while

40 some reports point to a substantial •OH involvement others suggest only a marginal  
41 contribution of this species (7-14).

42 Here, this issue has been addressed for the case of homogeneous solutions by  
43 application of a fast kinetics model to the analysis of different situations with a variety of •OH  
44 lifetimes, EPs concentrations and quenching rate constants, in an attempt to cover a wide range  
45 of reported values. The model has been validated by experimental measurements, using  
46 transient absorption spectroscopy to determine the reaction rate constants for quenching of  
47 •OH by three widely used EPs, namely ibuprofen, caffeine and acetaminophen (Figure 1).

48 <Figure 1>

## 49 **MATERIALS AND METHODS**

50 Acetaminophen, ibuprofen, caffeine, *trans*-stilbene (TS) and N-hydroxypyridine-2(1H)-thione  
51 (NPT) were purchased from Sigma-Aldrich Co. and were used without further purification.

52 Acetonitrile was of HPLC quality from Scharlau.

53 *Laser flash photolysis (LFP) measurements:* A pulsed Nd: YAG laser was used for the excitation  
54 at 355 nm. The single pulses were *ca.* 10 ns duration and the energy was 42 mJ/pulse. A pulsed Xe  
55 lamp was employed as detecting light source. The LFP apparatus consisted of the pulsed laser, the  
56 Xe lamp, a monochromator, and a photomultiplier made up of a tube, housing, and power supply.  
57 The output signal from the oscilloscope was transferred to a personal computer.

58 *Kinetic experiments to determine the reactivity of •OH radical (15):* The concentration of N-  
59 hydroxypyridine-2-thione (NPT) and *trans*-stilbene (TS) for the kinetic experiments was  
60 adjusted to 0.29 mM and 7.5 mM in deaerated acetonitrile, respectively. To a set of quartz  
61 cuvettes with this solution, concentrations of the emerging pollutant or standard (naphthalene)  
62 were added in parallel, typically in the range  $10^{-6}$  to  $10^{-2}$  M, and the corresponding traces at  
63 390 and 490 nm were recorded after the laser pulse. Plotting the ratio between the transient  
64 absorbance at 390 nm in the absence ( $\Delta A_0$ ) and in the presence of each EP ( $\Delta A$ ) (see Figure  
65 S1) versus concentration the corresponding Stern-Volmer plots were obtained (see Figure S2).  
66 Determination of the absolute rate constants for the reaction between the emerging pollutants  
67 and •OH (Table S1) was based on the comparison between the obtained slopes and the known  
68 absolute rate constant for naphthalene ( $k_{\bullet OH} = 1.8 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ ) (2). The signal at 490  
69 corresponding to the pyriithyl radical, served as a calibration parameter (see Figure S3).

## 70 **RESULTS AND DISCUSSION**

71 A quantitative assessment of the actual involvement of a given reactive intermediate can be  
72 made according to a straightforward kinetic model. Thus, quenching of •OH by EPs is a  
73 bimolecular process that competes with the other decay pathways. In homogeneous solutions,  
74 the rate constants are in general diffusion-controlled for the former ( $k_q$ ), while for the latter an  
75 overall value can be determined from the reciprocal •OH lifetime in the absence of EPs ( $k_d$ ).  
76 Hence, the quenching efficiency (E in percentage) depends on  $k_q$  and  $k_d$ , as well as on the  
77 quencher concentration ([EP]), according to the following equation:

78

$$E(\%) = 100 \frac{k_q[EP]}{k_q[EP] + k_d} \quad \text{eq. 1}$$

79  
80  
81

82 Thus, considering the •OH lifetime in the upper limit of the accepted range (for  
83 instance 1 μs) and diffusion control in water ( $k_q$ , in the order of  $10^9 \text{ M}^{-1}\text{s}^{-1}$ ), application of the  
84 above equation to the case of mM quencher concentration ( $[EP] = 10^{-3} \text{ M}$ ) leads to a quenching  
85 efficiency  $E = 50\%$ . Conversely, if EP is present at μM concentrations (still higher than those  
86 found for EPs), the corresponding E value is only 0.1%.

87 The situation would be even less favorable for •OH involvement as a key species if its  
88 lifetime is taken closer to the lower limit (*ca.* 1 ns). In this case, at unrealistic mM EPs  
89 concentrations the quenching efficiency would only be  $E = 0.1\%$ , while in the μM range the  
90 value would drop down to 0.00001%.

91 To validate the aforementioned kinetic model, a methodology based on fast kinetic  
92 measurements is applied here to determine the reactivity of •OH with three different EPs,  
93 namely ibuprofen, caffeine and acetaminophen (Figure 1). The •OH was generated by  
94 homolytic rupture of *N*-hydroxypyridine-2(1H)-thione (NPT) upon laser flash photolysis at 355  
95 nm. Disclosure of this “invisible” species was achieved by trapping with *t*-stilbene (TS), which  
96 gave rise to a detectable adduct (TS-OH•) displaying a characteristic transient absorption band  
97 with maximum at 390 nm. From the intercept of the linear plot representing the rise time of the  
98 signal *versus* TS concentrations the decay lifetime of 50 ns has been obtained for •OH in the  
99 absence of TS, under the employed experimental conditions.(15) Competitive kinetic  
100 experiments allowed determining the rate constants for the reaction between •OH and the

101 selected EPs (Figure 2) (15-17). Thus, the kinetic traces at 390 nm were recorded in the  
102 absence and in the presence of increasing EPs concentrations in the range  $10^{-6}$ - $10^{-2}$  M (see  
103 Figure 3 for ibuprofen). From the slopes of the linear fittings shown in the Stern-Volmer plots  
104 (see inset of Figure 3), using naphthalene as standard ( $k_q = 1.8 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ )(16), rate constant  
105 values of  $4.0 \times 10^9$ ;  $3.1 \times 10^9$  and  $1.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$  were determined for ibuprofen, caffeine and  
106 acetaminophen, respectively; all of them are close to diffusion control(18).

107 < Figure 2 >

108

109 <Figure 3 >

110

## 111 **CONCLUSION**

112 Overall, the experimental results combined with the kinetic analysis do not support a key direct  
113 role for  $\bullet\text{OH}$  in the removal of EPs by means of AOPs. In the real (diluted) EPs-containing  
114 waters, quenching of this short-lived intermediate must be very inefficient (less than one per  
115 million of the generated  $\bullet\text{OH}$  radicals, according to equation 1). In other words, EPs  
116 photodegradation cannot purely rely on the generation and reaction of  $\bullet\text{OH}$ , since this would  
117 require extremely long sunlight exposure times or unsustainable energy-consuming artificial  
118 illumination.

119 This suggests that more complex alternative pathways have to be considered to explain  
120 the oxidative photodegradation of EPs actually achieved under AOPs conditions, possibly



121 mediated by other radical species with longer lifetimes or chain propagation processes (7). The  
122 nature of such longer-lived radicals remains uncertain, although they could seemingly derive  
123 from reaction of •OH with natural organic matter or dissolved inorganic ions.

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## 131 **SUPPLEMENTARY MATERIALS**

132 Additional Supporting Information may be found in the online version of this article:

133 **Figure S1.** Kinetic traces recorded at 390 nm after laser flash photolysis ( $\lambda_{\text{exc}} = 355$   
134 nm) of NPT (0.29 mM) and TS (7.5 mM) in the presence of increasing concentrations of  
135 ibuprofen, caffeine or acetaminophen in deaerated acetonitrile solutions.

136 **Figure S2.** Stern-Volmer plots obtained as the ratio  $\Delta A_0/\Delta A$  of the traces measured at  
137 390 nm versus concentration of the EP: ibuprofen, caffeine, acetaminophen and naphthalene  
138 (used as reference).

139 **Figure S3.** Plot of the relative transient absorbance versus naphthalene concentration at  
140 390 nm (formation of the •OH adduct of *trans*-stilbene) and at 490 nm (formation of the  
141 pyrithiyl radical, for calibration).

142 **Table S1.** Rate constants for the reaction of •OH with the emerging pollutants.

143 Table Sx and Figure Sx can be found at DOI: 10.1562/2006-xxxxxx.s1.

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205

## 206 **FIGURE CAPTIONS**

207 **Figure 1.** Chemical structures of the selected emerging pollutants.

208 **Figure 2.** Simplified approach for generation and detection of •OH.

209 **Figure 3.** Kinetic traces recorded at 390 nm after laser flash photolysis ( $\lambda_{\text{exc}} = 355 \text{ nm}$ )  
210 of deaerated acetonitrile solutions of NPT (0.29 mM), in the presence of TS (7.5 mM)

211 and ibuprofen ( $10^{-6}$ - $10^{-2}$  M). Inset: Stern-Volmer plot obtained as the ratio  $\Delta A_0/\Delta A$

212 *versus* concentration of ibuprofen.

213