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Biodegradation, ecotoxicity and UV254/H₂O₂ treatment of imidazole, 1-methyl-imidazole and N,N'-alkyl-imidazolium chlorides in water

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Abstract: Imidazole-based compounds are used as reagents for the manufacturing of other compounds including imidazolium-based ionic liquids, which have been recently proposed as a green alternative to conventional solvents. Since some imidazole-based compounds have been demonstrated to be harmful to aquatic organisms, the removal of imidazole, 1-methylimidazole, 1-ethyl-3-methyl-imidazolium chloride and 1-butyl-3-methyl-imidazolium chloride from aqueous solutions was attempted by biological oxidation, direct UV254 photolysis, and UV254/H2O2 process at pH 5.5 and 8.5. Results showed that UV254/H2O2 treatment is an effective tool for the removal of the selected compounds at both pHs. In fact, the kinetic constants of the reaction between the photogenerated HO radicals and the four target compounds, estimated by means of both numerical and competition kinetic method, range between $2.32 \cdot 10^9 \text{ M}^{-1} \cdot \text{s}^{-1}$ and $5.52 \cdot 10^9 \text{ M}^{-1} \cdot \text{s}^{-1}$. Moreover, an ecotoxicity assessment of the contaminated water before and after initial treatment without further processing was assessed by using two living aquatic organisms: *Raphidocelis subcapitata* and *Daphnia magna*. The results of this assessment not only corresponded closely to previous findings (in terms of EC50 values) reported in the literature, but also indicated that, in some cases, UV254/H2O2 oxidation by-products could be even more toxic than parent compounds.

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To Editor of
Water Research

Dear Editor,

please find enclosed a copy of the original manuscript: “Biodegradation, ecotoxicity and UV₂₅₄/H₂O₂ treatment of imidazole, 1-methyl-imidazole and N,N'-alkyl- imidazolium chlorides in water” by D. Spasiano, A. Siciliano, M. Race, R. Marotta, M. Guida, R. Andreozzi, F. Pirozzi, which we submit to Water Research. We believe that the findings of the proposed manuscript are relevant to the scope of Water Research and will be of interest to its readership.

Since their industrial use is increasing, imidazole-containing compounds and, in particular, imidazolium-based ionic liquids were recently added to the class of new emerging xenobiotics described as “Contaminant on Horizon”. At the best of our knowledge, this is the first investigation regarding the degradation of imidazole, 1-methylimidazole, 1-ethyl-3-methyl-imidazolium chloride and 1-butyl-3-methyl-imidazolium chloride from aqueous solutions using the UV₂₅₄/H₂O₂ advanced oxidative process. Moreover, for the first time the kinetic constants for HO radical attack on 1-ethyl-3-methyl-imidazolium chloride and 1-butyl-3-methyl-imidazolium chloride were estimated. Finally, ecotoxicity assessments were carried out not only on the contaminated solutions, but also on the effluents at different treatment times.

The proposed manuscript has not been published or presented elsewhere in part or in entirety, and is not under consideration by another Journal. All the Authors have approved the proposal and agree with submission of the manuscript to Water Research. There are no conflicts of interest to declare.

Moreover,

- Six keywords and four highlights are provided in the text;
- Highlights and References are in the correct format;

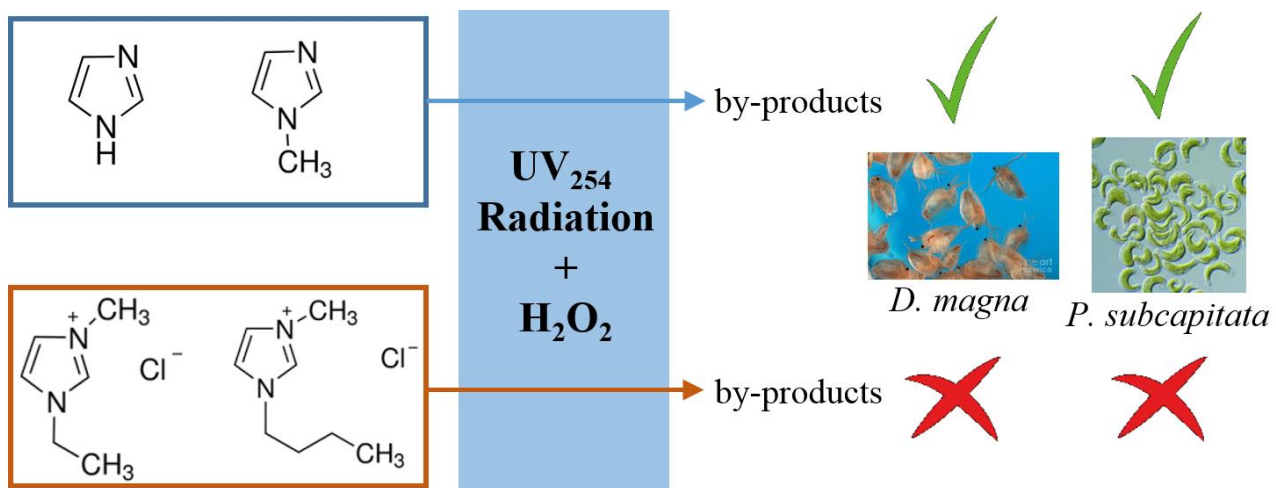
Thank you for your consideration. We look forward to hearing from you.

Sincerely

The Authors

Highlights

- UV/H₂O₂ process was used to remove imidazole-based compounds in aqueous solutions
- The kinetic constants for HO attack on imidazole and its derivatives were estimated
- The ecotoxicity evolution was monitored during the chemical process
- An ecotoxicity increase was observed during the treatment of alkylimidazolium salts



1 **Biodegradation, ecotoxicity and UV₂₅₄/H₂O₂ treatment of imidazole, 1-methyl-**
2 **imidazole and N,N'-alkyl-imidazolium chlorides in water**

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16 *Keywords:* ionic liquids, imidazole, biodegradation, ecotoxicity, H₂O₂ photolysis, kinetic modeling.

17

18 **Abstract**

19 Imidazole-based compounds are used as reagents for the manufacturing of other compounds
20 including imidazolium-based ionic liquids, which have been recently proposed as a green
21 alternative to conventional solvents. Since some imidazole-based compounds have been
22 demonstrated to be harmful to aquatic organisms, the removal of imidazole, 1-methylimidazole, 1-
23 ethyl-3-methyl-imidazolium chloride and 1-butyl-3-methyl-imidazolium chloride from aqueous
24 solutions was attempted by biological oxidation, direct UV₂₅₄ photolysis, and UV₂₅₄/H₂O₂ process
25 at pH 5.5 and 8.5. Results showed that UV₂₅₄/H₂O₂ treatment is an effective tool for the removal of

26 the selected compounds at both pHs. In fact, the kinetic constants of the reaction between the
27 photogenerated HO radicals and the four target compounds, estimated by means of both numerical
28 and competition kinetic method, range between $2.32 \cdot 10^9 \text{ M}^{-1} \cdot \text{s}^{-1}$ and $5.52 \cdot 10^9 \text{ M}^{-1} \cdot \text{s}^{-1}$. Moreover, an
29 ecotoxicity assessment of the contaminated water before and after initial treatment without further
30 processing was assessed by using two living aquatic organisms: *Raphidocelis subcapitata* and
31 *Daphnia magna*. The results of this assessment not only corresponded closely to previous findings
32 (in terms of EC_{50} values) reported in the literature, but also indicated that, in some cases,
33 $\text{UV}_{254}/\text{H}_2\text{O}_2$ oxidation by-products could be even more toxic than parent compounds.

34

35 **1. Introduction**

36 Numerous imidazole-containing compounds have received in the past considerable attention
37 because of their availability and wide range of practical applications. For example, different
38 molecules containing an imidazolinic ring in their structure, such as metronidazole,
39 nitrosoimidazole, megalol, clonidine, guanfacine, and lofexidine hydrochloride exhibit
40 pharmacological and biological activities (Kumar, 2010). Imidazole and its methyl-derivatives are
41 extensively used as corrosion inhibitors of iron and copper (Zhang et al., 2009). Moreover, 1-
42 methylimidazole is used for manufacturing of pharmaceuticals, pesticides, ion-exchange resins,
43 dyeing auxiliaries, photographic chemicals, polyurethanes, curing agent for epoxy resins and ionic
44 liquids (*Ullmann's Encyclopedia of Industrial Chemistry*).

45 Imidazolium-based ionic liquids (IMI-ILs) due to their low vapor pressure and flammability and
46 high solvent properties for organic molecules, are frequently used in a wide range of biological
47 applications and for the preparation of surfactants, plasticizers, antimicrobial and anti-inflammatory
48 agents, scaffolds for biomimetic applications and membranes for oxygen transport (Dupont and
49 Suarez, 2006; Anderson and Long, 2010). They are viewed as potential alternatives to conventional
50 industrial solvents due to their marked chemical and thermal inertness, and could be used as

51 catalysts for many reactions. Therefore, it is likely that IMI-ILs will continue to be manufactured
52 and used on an industrial scale in future.

53 This fact raises several concerns about their environmental impact, particularly since IMI-ILs are
54 poorly or negligibly biodegradable (Jordan and Gathergood, 2015; Stolte et al., 2008; Romero et al.,
55 2008; Garcia et al., 2005). It has been demonstrated that imidazolium-based ILs exhibit moderate to
56 high toxicity towards aquatic organisms. In some cases this can be of the same order as traditional
57 organic solvents but can reach two to four orders of magnitude higher. (Bubalo et al., 2014; Cho et
58 al., 2008; Bernot et al., 2005). This clearly may raise questions about their “green” character.

59 Toxicity of IMI-ILs has previously been investigated using both aquatic and non-aquatic organisms
60 to assess their ability to induce cellular and sub-cellular damage (e.g. viability, inhibition of the
61 activity of specific enzymes, genotoxicity) (Peric et al., 2014; Biczak et al., 2014; Wu et al., 2013).

62 Until now, the results have generally indicated that the effect of ionic liquids on biological systems
63 increases with increasing lipophilicity and, in particular, lengthening alkyl chains (Pham et al.,
64 2008; Jastorff et al., 2005; Matzke et al., 2007). I IMI-ILs with longer alkyl chains are more
65 lipophilic than those with shorter ones and are able to pass through cell membranes. Additionally,
66 imidazole and pyridine-based ILs generally display higher toxicity than aliphatic chain-based ILs
67 (Petkovic et al, 2011). It has also been shown that the anionic form had little influence on the
68 toxicity of ILs (Matzke et al., 2008).

69 Although to date there are no studies that demonstrate the presence of ILs as pollutants in sewage,
70 industrial or civil treatment plant effluents, or in surface waters, their presence in water bodies
71 cannot be totally ruled out now or in future. It is worthy to observe that Richardson et al.
72 (Richardson and Ternes, 2014) recently added these compounds to the class of new emerging
73 xenobiotics described as “Contaminant on Horizon”. Since the industrial use of ILs is increasing,
74 many risk scenarios exist for IMI-ILs as contaminants in industrial effluents. Thus, the risk of
75 damage to the aquatic environment deserves consideration and means for decontamination should
76 be assessed.

77 Advanced Oxidation Processes (AOPs) are based on the production of very high reactive oxidant
78 species, such as hydroxyl radicals (Rosenfeldt et al., 2006; Haag and Yao, 1992) and may provide
79 feasible solutions for the removal of non-biodegradable IMI-ILs from wastewater. Recent studies
80 demonstrated the possibility of reaching a complete removal of selected imidazolium-based species
81 at ambient conditions through the adoption of Fenton ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) and Fenton-like ($\text{Fe}^{3+}/\text{H}_2\text{O}_2$)
82 processes (Bocos et al., 2016; Munoz et al., 2015; Domínguez et al., 2014; Siedlecka et al., 2009;
83 Siedlecka et al., 2008). Unfortunately, high H_2O_2 doses are required and iron precipitates are
84 formed, reducing the oxidation activity. Furthermore, some investigations focused on the use of
85 ultraviolet photolysis of hydrogen peroxide ($\text{UV}_{254}/\text{H}_2\text{O}_2$) for oxidation of alkyl-imidazolium-based
86 ILs in water (Czerwicka et al., 2009; Stepnowski and Zaleska, 2005). These demonstrated that the
87 removal efficiency was affected by the length of the n-alkyl chain substituted at position 1 of the 1-
88 alkyl-3-methyl-imidazolium ring. The main oxidation intermediates and by-products formed during
89 the $\text{UV}_{254}/\text{H}_2\text{O}_2$ process were also identified. Currently, a lack of information remains about the
90 kinetic constant values of the reactions between these substances and the photogenerated HO
91 radicals, which are necessary for a $\text{UV}_{254}/\text{H}_2\text{O}_2$ treatment-unit design, and little is known about the
92 ecotoxicity of the by-products that could arise from this treatment.

93 Consequently, the aims of the present investigation are: i) to evaluate the biodegradability and
94 UV_{254} photolysis of imidazole (Imid), 1-methyl-imidazole (1MI) and some water soluble 1-alkyl-3-
95 methyl-imidazolium chlorides (1E3MI and 1B3MI) (Figure 1); ii) to estimate the kinetic constants
96 of the reaction between the target compounds and HO radicals formed by $\text{UV}_{254}/\text{H}_2\text{O}_2$ system; iii)
97 to evaluate the ecotoxicity of the contaminated solutions before and after exposure to the $\text{UV}_{254}/\text{H}_2\text{O}_2$
98 process. For this purpose, two freshwater living organisms, algae *Raphidocelis Subcapitata* and
99 water flea *Daphnia Magna*, were used as bio-indicators for toxicity.

100 The investigation on the acute toxicities of the selected imidazolium based compounds and their by-
101 products is relevant to future discussions regarding the chronic toxicities, treatment, control and fate
102 of these substances and their derivatives in the environment.

103 **2. Materials and methods**

104 **2.1. Materials**

105 Hydrogen peroxide (30% v/v), Imid ($\geq 99\%$ w/w), 1MI (99% v/v), 1E3MI (98% w/w), 1B3MI (\geq
106 98.0% w/w), acetonitrile ($\geq 99.9\%$ v/v), ammonium acetate ($\geq 98\%$ w/w), ammonium chloride
107 (99.99% w/w), calcium chloride ($> 99.9\%$ w/w), benzoic acid ($\geq 99.5\%$ w/w), boric acid ($> 99.5\%$
108 w/w), catalase from *Micrococcus lysodeikticus* (200191 U·ml⁻¹), cobalt(II) chloride hexahydrate
109 (97% w/w), copper(II) chloride dehydrate (99.99% w/w), hydrochloric acid (37% v/v), iron(III)
110 chloride (97% w/w), magnesium sulfate heptahydrate ($\geq 98\%$ w/w), manganese(II) chloride ($\geq 99\%$
111 w/w), magnesium chloride hexahydrate ($> 99.9\%$ w/w), mercury(II) chloride (99% w/w), potassium
112 chloride (99% w/w), potassium dichromate ($\geq 99\%$ w/w), potassium phosphate dibasic ($> 98\%$ w/w)
113 and monobasic (99% w/w), sodium bicarbonate ($\geq 99\%$ w/w), sodium chloride ($> 99.9\%$ w/w),
114 sodium dihydrogen phosphate dodecahydrate ($\geq 99\%$ w/w), sodium hydroxide ($\geq 98\%$ w/w), sodium
115 molybdate dihydrate ($\geq 99\%$ w/w), sodium nitrate ($\geq 99\%$ w/w), disodium ethylenediamine-
116 tetraacetate dihydrate ($\geq 99\%$ w/w), zinc chloride ($\geq 98\%$ w/w), and sulfuric acid were purchased
117 from Sigma-Aldrich. All the solution were prepared using bi-distilled water.

118 Activated sludge, taken from a Wastewater Treatment Plant at Nola (Naples, Italy), was used as our
119 biomass to be spiked with the selected imidazole-containing compounds to study their
120 biodegradability.

121

122 **2.2. Analytical methods**

123 Concentrations of hydrogen peroxide, Imid, 1MI, 1E3MI, 1B3MI, and benzoic acid (BA) were
124 evaluated through HPLC analysis. Specifically, an HPLC (1100 Agilent) apparatus was equipped
125 with a Synergy 4u Polar-RP 80A. A mobile phase, flowing at 1.0 ml min⁻¹, of acetonitrile (A) and a
126 buffer solution (B) of 20.0 mM of ammonium acetate dissolved in water for HPLC was used. A
127 linear gradient was adopted starting with 10% A to 30% A, from the 10th to the 30th minute of each
128 analysis, with a subsequent re-equilibrium time of 4 min.

129 Total organic carbon (TOC) and chemical oxygen demand (COD) were monitored by a TOC
130 analyzer (Shimadzu 5000 A) and Hack[®] cuvette test respectively. Measurements at 620 nm were
131 carried out with a UV–vis spectrophotometer (Agilent).

132 The pH of the solutions was measured and tracked with an Orion 420A+ pH-meter (Thermo).

133 *D. magna* viability and mobility were observed with a stereomicroscope (LEICA EZ4-HD) and
134 visualized on a computer. *R. subcapitata* density was determined by an indirect procedure using a
135 spectrophotometer (Hach Lange DR5000) and a 5 cm cuvette.

136

137 **2.3. Experimental apparatus and procedures**

138 **2.3.1. Biodegradability assessment apparatus and procedures**

139 The composition of the inorganic medium used for the biodegradability test was carried out in
140 accordance with Urano and Kato (Urano and Kato, 1986). Five ml of a mixture of K₂HPO₄
141 ($25.75 \cdot 10^{-3}$ mg·l⁻¹), KH₂PO₄ ($8.5 \cdot 10^{-3}$ mg·l⁻¹), Na₂HPO₄·12H₂O ($44.6 \cdot 10^{-3}$ mg·l⁻¹) and NH₄Cl
142 ($1.7 \cdot 10^{-3}$ mg·l⁻¹), 0.5 ml of an aqueous solution of MgSO₄·7H₂O ($22.5 \cdot 10^{-3}$ mg·l⁻¹), 0.5 ml of CaCl₂
143 ($27.5 \cdot 10^{-3}$ mg·l⁻¹) and 1 ml of FeCl₃·6H₂O ($0.25 \cdot 10^{-3}$ mg·l⁻¹) were added to the bio-reactor. The
144 biodegradation tests were conducted as previously described (Andreozzi et al., 2006) and each
145 sample solution was prepared in a 250 ml reactor with fixed concentration of dry matter. For this
146 purpose, the activated sludge was diluted with the bi-distilled water to a concentration of 3.0 g·l⁻¹.
147 The tests were carried out at constant temperature (25° C), the sample solutions were stirred,
148 aerated (by air bubbling), and the pH was regulated at 7.0 with HCl or NaOH.

149 Abiotic control tests (using HgCl₂ to inactivate the sludge) were performed in order to check an
150 eventual adsorption of the tested compounds. The samples were taken at fixed times and filtered
151 through regenerated Merck Millipore cellulose filters (0.45 μm) before analysis.

152 The total suspended solids (TSS) and volatile suspended solids (VSS) of the activated sludge were
153 evaluated according to the standard procedures (APHA, AWWA, WEF, 2005).

154 The substrate concentration was monitored until complete degradation or up to 28 days. When
155 necessary, in order to acclimate the biomass, the recharges with mineral medium and substrate
156 were made until reaching the initial volume and recovering the starting conditions (substrate
157 concentration equal to 10 mg·l⁻¹).

158 The biodegradation investigations were performed in triplicate and in batch conditions for each
159 tested compound.

160

161 **2.3.2. Cylindrical batch photoreactor and procedures**

162 In order to evaluate the kinetics of Imid, 1MI, 1E3MI, and 1B3MI oxidation with the UV₂₅₄/H₂O₂
163 process, a traditional cylindrical batch photoreactor was used as shown in Figure 2. The
164 contaminated solutions were exposed to the radiation emitted by a low-pressure mercury lamp (17
165 W) mainly emitting at 254 nm (Helios Italquartz) in the 0.480 l (V) batch photoreactor with a path
166 length (z) equal to 2.20 cm. The reactor, thermostated at 25 °C, was covered with aluminum foil.
167 The reactor had two inlets for supplying reactants and for withdrawing samples. The photon flux
168 emitted by the UV lamp at 254 nm (I₀), equal to 2.86·10⁻⁶ ein·s⁻¹, was estimated through hydrogen
169 peroxide actinometry (Goldstein et al., 2007).

170 The reacting solutions were prepared by adding one of the target compounds (Imid, 1MI, 1E3MI
171 and 1B3MI) and H₂O₂ to bi-distilled water. The initial concentration of the target compounds used
172 in the experimental runs was equal to almost 10 mg·l⁻¹, for the experimental runs for kinetic
173 modeling, and 150 mg·l⁻¹, for the experimental runs to assess the eco-toxicity of the UV₂₅₄/H₂O₂
174 process by-products. The initial imidazolium based compounds concentrations were chosen in order
175 to simplify the analytical procedures for monitoring substrate consumption. For those experimental
176 runs devoted to the comparison kinetics method, BA was added to the reacting solution as reference
177 compound (Buxton et al., 1988; Onstein et al., 1999).

178 To evaluate the effect of pH on the process kinetics, the reacting solution pH was adjusted to 5.5 or
179 8.5 by the addition of NaOH and H₂SO₄ diluted solutions. All the experimental runs estimating
180 kinetic parameters were carried out in triplicate.

181

182 2.3.3. Eco-toxicity assessment apparatus and procedures

183 For toxicity assessment, K₂Cr₂O₇ was used as the toxicity reference. The following salts were used
184 for the preparation of artificial freshwater: CaCl₂ · 2H₂O, MgSO₄ · 7H₂O, KCl, NaHCO₃, NaNO₃,
185 NH₄Cl, MgCl₂ · 6H₂O, K₂HPO₄, KH₂PO₄, FeCl₃ · 6H₂O, Na₂EDTA · 2H₂O, H₃BO₃, MnCl₂ · 4H₂O,
186 ZnCl₂, CoCl₂ · 6H₂O, Na₂MoO₄ · 2H₂O, CuCl₂ · 2H₂O, NaCl.

187 The algal growth inhibition test with *R. subcapitata*, formerly known as *Selenastrum capricornutum*
188 or *Pseudokirchneriella subcapitata*, was carried out as described in the ISO 8692 protocol (ISO,
189 2012). The growth of the algae exposed to the sample was compared with the growth of the algae in
190 a negative control. For each sample, six replicates were inoculated with 10⁷ algal cells · l⁻¹ in well
191 plates and incubated for 72 hrs at 23 ± 2 °C under continuous illumination (in an irradiance range of
192 120-60 µein · m⁻² · s⁻¹). The specific growth rate (µ) of *R. subcapitata* in each replicate was calculated
193 from the logarithmic increase in cell density in the interval 0-72 h as follows:

$$194 \mu = \frac{\ln N_i - \ln N_0}{t_i - t_0} \quad (1)$$

195 where N₀ and N_i represent the cell concentration at times t₀ and t_i respectively. Results were
196 expressed as the mean (± standard deviation) of the percentage inhibition of the cell growth
197 compared to the negative control.

198 The acute toxicity bioassay at 24 hours with *Daphnia magna* was conducted according to ISO 6341
199 (ISO, 2012). *D. magna* were selected from laboratory stock cultures, were moved in 2.0 l glass
200 beaker maintained at 24 ± 10 °C and were fed on *R. subcapitata*.

201 Twenty four hours before the test, adult daphnia were isolated and neonates produced from these
202 adults were used. For each test, four replicates each using 20 daphnids (<24 h old) were made. The

203 proportion of immobilised daphnids were recorded after 24 h. The test was considered valid if the
204 immobilization in the control did not exceed 10%.

205 Negative and positive controls were included in each testing run. Negative tests were carried out on
206 aqueous solutions containing 36 mM of hydrogen peroxide along with 90 μ l of catalase (used with
207 the aim of destroying residual hydrogen peroxide) per liter of solution.

208 Eco-toxicity data were expressed as the EC₅₀ (median effect concentration) values and its 95%
209 confidence intervals calculated by non-linear regression.

210 The significance of differences between mean values of experimental treatments and controls was
211 assessed by Student's t-test and analysis of variance (ANOVA) with a 0.05 significance level.

212 When ANOVA revealed significant differences among treatments, post-hoc analysis were carried
213 on with Dunnett's method (Dunnett, 1955) and Tukey's test (Tukey, 1949). Statistical analyses
214 were performed using Graphpad Prism software.

215

216 **3. Results and discussions**

217 **3.1 Biodegradability assessment**

218 In the tests with the inactivated sludge, it was firstly verified that the adsorption on them of the
219 substrates investigated does not assume a significant role in their removal, according to Stolte *et al.*
220 (Stolte, 2008).

221 For each tested compound, ten recharges were carried out until a constant biodegradation rate was
222 observed. Among all the IM species studied, biodegradation was only seen for IMID.

223 In order to evaluate the first pseudo-order kinetic constant of biodegradation of Imid ($k_{\text{bio/Imid}}$), the
224 $\ln(C/C_0)$ vs time was plotted (Figure 3), reaching a k_{bio} value equal to 0.24 h⁻¹. These results were in
225 agreement to previous studies (Liwarska-Bizukojc *et al.*, 2015; Liwarska-Bizukojc *et al.*, 2014) in
226 which it was found that the ILs with short alkyl side chains, such as 1E3MI and 1B3MI, are not
227 biodegradable. Therefore, it is possible to assume that these compounds cannot be treated by
228 conventional biological processes.

229

230 **3.2 Direct UV₂₅₄ photolysis**

231 To evaluate the extent of direct photolysis of the four target compounds, they were individually
232 submitted to the UV₂₅₄ lamp photon flux in absence of hydrogen peroxide and at pH equal to 5.5
233 and 8.5.

234 After 2.0 h of irradiation, a 10-15% decrease of the initial substrates concentration ($[S]_0 = 10 \text{ mg}\cdot\text{l}^{-1}$)
235 ¹) was observed at both selected pHs (data not shown). The resistance of Imid, 1MI, 1E3MI, and
236 1B3MI to undergo UV₂₅₄ photolysis can be mainly ascribed to the negligible molar absorption
237 coefficient ($\epsilon_{254}^{S_i}$) (Table 1).

238 On the basis of these results, and as reported previously (Stepnowski et al., 2005), it can be
239 concluded that it is impossible to remove ionic liquids from wastewater in a municipal treatment
240 plant equipped with a UV₂₅₄ disinfection treatment unit alone. However, it is interesting to evaluate
241 if the addition of small amounts of H₂O₂ during UV₂₅₄ disinfection treatment may solve the
242 problem, since it can promote the production of HO radicals, which are known to attack
243 unselectively and rapidly the organic substances.

244

245 **3.2. UV₂₅₄/H₂O₂ process**

246 The UV₂₅₄/H₂O₂ process is frequently used as an AOP method for reducing contamination with
247 biorefractory xenobiotics such as pharmaceuticals (Vogna et al., 2004; Andreozzi et al., 1999;
248 Lopez et al., 2003), illicit drugs (Russo et al., 2016), dyes (Aleboyeh et al., 2012; Guimarães et al.,
249 2012), pesticides (Semitsoglou-Tsiapou et al., 2016; Autin et al., 2013), chlorinated compounds
250 (Kan et al., 2015; Pera-Titus et al., 2004), and so on. However, information is lacking on the kinetic
251 constant values of the HO radical attack on the selected compounds (k_{OH/S_i}).

252 To test the efficiency of the UV₂₅₄/H₂O₂ process on the removal of the imidazole-based compounds
253 and, consequently, of estimating the unknown kinetic parameters, some experimental runs were
254 carried out using combinations of different pH, substrate and H₂O₂ initial concentrations.

255 The k_{OH/S_i} values were estimated using a modified quantitative approach, which was successfully
 256 proposed for modelling the removal of phenolic compounds using the UV₂₅₄/H₂O₂ process (Alnaizy
 257 and Akergman, 2000). Particularly, UV₂₅₄/H₂O₂ process for the removal of the target compounds
 258 dissolved in bi-distilled water can be represented with a simplified kinetic scheme constituted by the
 259 reaction r_{1-6} (Table 2). The process starts with the UV₂₅₄ radiation absorption by H₂O₂ molecules,
 260 which undergo direct photolysis, leading to the formation of HO radicals (r_1). The latter can attack
 261 both the H₂O₂ molecules (r_2), generating the less reactive hydroperoxyl radicals, and the organic
 262 substrate (S_i) present into the solution (r_3). The chemical intermediates (BP), considered as pseudo-
 263 component and generated during the reaction r_3 , can be further oxidized producing different BPs
 264 (r_4). Since 1B3MI and 1E3MI were dissolved as chloride salts, it is necessary to take into account
 265 also the consumption of HO radicals for the reaction with Cl⁻ ions deriving from ILs adding (r_5).
 266 Finally, the hydroperoxyl radicals produced through the reaction r_1 undergo a radical termination
 267 reaction to generate hydrogen peroxide (r_6).
 268 Neglecting the direct UV₂₅₄ photolysis of all the organic substrates and taking the steady-state
 269 hypothesis for the hydroxy and hydroperoxyl radicals, the consumption rates of the considered
 270 substrate, H₂O₂, and Cl⁻ ions can be expressed as follows (eq_{1-3}):

$$271 \quad eq_1) \frac{d[S_i]}{dt} = - \frac{2 \cdot k_{HO/S} \cdot [S_i] \cdot F_{H_2O_2}}{k_h \cdot [H_2O_2] + k_{HO/S} \cdot ([S_i] + [BP]) + k_{HO/Cl} \cdot [Cl^-]}$$

$$272 \quad eq_2) \frac{d[H_2O_2]}{dt} = - F_{H_2O_2} - \frac{k_h \cdot [H_2O_2] \cdot F_{H_2O_2}}{k_h \cdot [H_2O_2] + k_{HO/S} \cdot ([S_i] + [BP]) + k_{HO/Cl} \cdot [Cl^-]}$$

$$273 \quad eq_3) \frac{d[Cl^-]}{dt} = - \frac{2 \cdot k_{HO/Cl} \cdot [Cl^-] \cdot F_{H_2O_2}}{k_h \cdot [H_2O_2] + k_{HO/S} \cdot ([S_i] + [BP]) + k_{HO/Cl} \cdot [Cl^-]}$$

274 where the term $F_{H_2O_2}$ represents the direct hydrogen peroxide photolysis rate. $F_{H_2O_2}$:

$$275 \quad eq_4) F_{H_2O_2} = \frac{\Phi_{254}^{H_2O_2} \cdot I_0}{V} \cdot \left(1 - \exp(-2.3 \cdot z \cdot \varepsilon_{254}^{H_2O_2} \cdot [H_2O_2]) \right)$$

276 where $\Phi_{254}^{H_2O_2}$ and $\varepsilon_{254}^{H_2O_2}$ are the quantum yield of direct photolysis and the molar absorption
 277 coefficient for hydrogen peroxide at 254 nm (Table 2). In particular, in eq_4 the radiation absorption
 278 at 254 nm of the selected compounds was neglected due to the low $\varepsilon_{254}^{S_i}$ values (Table 1)
 279 The set of three ODEs constituted by the eq_1 - eq_3 , once integrated by means of the ode45 MATLAB
 280 routine, made it possible to predict the substrate and H₂O₂ concentration trends. The k_{HO/S_i}
 281 parameters were estimated minimizing the square of the differences between the calculated (y) and
 282 experimental (c) concentration of each species through an iterative optimization procedure
 283 (Reklaitis et al., 1983). Specifically, the objective function (Ω) was expressed as:

$$eq_5) \quad \Omega = \sum_{g=1}^h \sum_{i=1}^l \sum_{m=1}^n (y_{g,i,m} - c_{g,i,m})^2$$

284 where h , l and n respectively represent the number of experimental data taken in each experiment,
 285 the number of the followed species in each experiment, and the number of the experiments
 286 considered in the optimization procedure.

287 The k_{OH/S_i} values, not previously reported in literature, estimated in this investigation by the
 288 numerical procedure were further validated by a competition kinetic procedure using BA as
 289 reference compound (Arouma et al., 1989; Buxton et al., 1988).

290 The mass balances necessary for the competition method implementation are those on S_i and BA:

$$291 \quad eq_6) \quad \frac{d[S_i]}{dt} = -k_{HO/S_i} \cdot [S_i] \cdot [HO^\bullet]$$

$$292 \quad eq_7) \quad \frac{d[BA]}{dt} = -k_{HO/BA} \cdot [BA] \cdot [HO^\bullet]$$

293 where $k_{HO/BA}$ represents the kinetic rate constant of the reaction between the HO radicals and BA
 294 and is equal to $5.9 \cdot 10^9 \text{ M}^{-1} \cdot \text{s}^{-1}$ (Buxton et al, 1988; Onstein et al., 1999),.

295 When eq_6 and eq_7 are integrated, it is possible to obtain the following linear relation between the
 296 logarithms of the normalized target compound and BA concentrations:

$$297 \quad eq_8) \quad \ln\left(\frac{[S_i]}{[S_i]_0}\right) = \frac{k_{HO/S_i}}{k_{HO/BA}} \cdot \ln\left(\frac{[BA]}{[BA]_0}\right)$$

298

299 3.2.1. $k_{OH/Si}$ estimation

300 The initial experimental conditions of the experimental runs adopted during the optimization
301 procedures, along with the percentage standard deviation (σ_i) on the imidazole-based compounds
302 and H_2O_2 , are shown in Table 3. In this regard, the percentage standard deviation on the i^{th} -species
303 was evaluated as follows:

$$eq9) \quad \sigma_i(\%) = \frac{1}{\bar{c}_i} \sqrt{\sum_{g=1}^h \frac{(y_{i,g} - c_{i,g})^2}{h - p}} \cdot 100$$

304 where \bar{c}_i represents the average measured concentration of the i^{th} -species and p is the number of the
305 unknown parameters that have to be estimated. In this case, p was set equal to one, since $k_{HO/Si}$
306 represents the sole unknown parameter. As shown in Table 3, the model had good predictive power,
307 since the percentage standard deviations on the investigated compounds and H_2O_2 were slightly
308 lower than those associated with the experimental determination of these species (3-4%).

309 Since the kinetic constant of the reaction between HO^\bullet and Imid ($k_{OH/Imid}$) was already reported in
310 the literature at varying pH of the reacting solution, $k_{OH/Imid}$ was evaluated only through the
311 numerical method. In fact, at pH = 7.4, two different $k_{OH/Imid}$ values were reported: $4.8 \cdot 10^9 M^{-1} \cdot s^{-1}$
312 (Arouma et al., 1989) and $6.4 \cdot 10^9 M^{-1} \cdot s^{-1}$ (Ching et al., 1993) both measured using the competition
313 kinetic method with deoxyribose and HO radicals generated by a Fe(II)/EDTA/ H_2O_2 reaction.
314 Additionally, in a previous paper, two other $k_{OH/Imid}$ values were measured, by means of pulse
315 radiolysis, at pH's of 6.8 and 10.9 and were shown to be $8.7 \cdot 10^9 M^{-1} \cdot s^{-1}$ and $1.2 \cdot 10^{10} M^{-1} \cdot s^{-1}$
316 respectively (Rao et al, 1975). As reported in Table 4, the $k_{HO/Imid}$ values estimated in this
317 investigation seem to agree with some of the previous findings. In particular the $k_{HO/Imid}$ value at pH
318 equal to 8.5 ($4.42 \cdot 10^9 M^{-1} \cdot s^{-1}$) is very close to the value estimated at pH = 7.4 by Arouma et al.
319 (1989). At the same time, the $k_{HO/Imid}$ value at pH equal to 5.5 ($2.33 \cdot 10^9 M^{-1} \cdot s^{-1}$) confirms that this
320 kinetic constant increases with pH.

321 The kinetic constant of the reaction between HO radicals and 1MI ($k_{OH/1MI}$) measured by pulse
322 radiolysis at pH's of 9.4 and 4.5 were shown to be $8.1 \cdot 10^9 \text{ M}^{-1} \cdot \text{s}^{-1}$ and $5.0 \cdot 10^9 \text{ M}^{-1} \cdot \text{s}^{-1}$ (Rao et al,
323 1975). Since these two values are the only ones reported in literature, both the direct and the
324 competition kinetic methods were used for evaluating $k_{OH/1MI}$ values which are reported in Table 4
325 along with 95% confidence interval (CI) and the coefficients of determination (R^2). The results
326 obtained with the competition kinetic method are close to those previously obtained at similar pH.
327 As in the case of $k_{HO/Imid}$, and as previously reported for 1MI (Rao et al, 1975), the trend for $k_{HO/1MI}$
328 to increase at increasing pH is confirmed.

329 The differences of k_{OH/S_i} values for Imid and 1MI at two pHs could be tentatively ascribed to the
330 higher reactivity of the un-protonated forms with respect to protonated forms with pK_a values 6.99
331 for Imid (Catalan and Elguero, 1984) and 7.33 for 1MI (Charton, 1965).

332 The comparison of $k_{OH/1B3MI}$ and $k_{OH/1E3MI}$ values at the two selected pH shows that the reaction rate
333 between the HO radicals and the imidazolium-based ILs increase with increasing alkyl chain length,
334 as recently reported for the same ILs (Domínguez et al., 2014). The increase in reactivity of the HO
335 radical with the lengthening of the substituent of the imidazolium ionic liquid at position 1-N could
336 be due to the presence of a higher number of oxidizable centers at greater lengths.

337

338 **3.2.2. Validation of the proposed model and the values of kinetic parameter estimated**

339 With the aim of validating the mathematical model, the results of fourteen additional photocatalytic
340 runs, carried out using different S_i and H_2O_2 initial concentrations (Table 5), were compared with
341 the model predictions without any further adjustment of the previously estimated parameters
342 (k_{HO/S_i}). The model was predictive for the observed behavior of the system as shown by the
343 percentage standard deviation values on the investigated species and H_2O_2 . This conclusion can
344 also be confirmed, on a qualitative basis, by a visual comparison of the calculated and experimental
345 concentration data for all the measured species involved in the process. For this purpose, the S_i and

346 H₂O₂ theoretical and experimental concentrations of some experimental runs used for the validation
347 procedure were reported in Figure 4.

348

349 **3.3. Eco-toxicity assessment**

350 The “effect-driven approach” (Escher and Fenner, 2011), in which a compound is degraded and is
351 analyzed with eco-bioassays, was used to follow the eco-toxicity evolution of the selected
352 imidazolium based compounds during the UV₂₅₄/H₂O₂ process.

353 Ecotoxicological tests were performed on samples collected from UV₂₅₄/H₂O₂ experiments
354 performed in the cylindrical batch reactor with an aqueous solution containing one of the substrates
355 and H₂O₂ at initial concentrations of 150 mg·l⁻¹ and 1224 mg·l⁻¹ (36·10⁻³ M) respectively. The
356 1E3MI and 1B3MI initial concentration of 150 mg·l⁻¹ were calculated for the ionic species (1E3MI⁺
357 and 1B3MI⁺) without taking into consideration the contribution of chloride ions. As reported in
358 previous studies (Postigo et al., 2011; An et al., 2015; Xu et al., 2014), such high initial substrate
359 concentrations were chosen to better assess ecotoxicological effects of photogenerated by-products
360 and to determine the median effective concentration (EC₅₀) of the selected substrates.

361 In addition to the sample collected at baseline (t_0), two further samples were collected at a reaction
362 time (t_f) corresponding to almost complete substrate conversion and at double that time ($2t_f$) The
363 samples taken at $2t_f$ were deemed to be representative of a solution expected to contain secondary
364 oxidation by-products. Within the reaction range chosen, TOC and COD analysis evidenced a
365 noticeable mineralization phenomenon, as reported in Table 6.

366 The results of ecotoxicological tests with *D. magna* and *R. subcapitata* in the presence of imidazole,
367 1-methyl-imidazole, 1-ethyl-3-methyl-imidazolium, and 1-butyl-3-methyl-imidazolium chlorides
368 contaminated solutions are shown in Table 7.

369 Results with *D. magna* and *R. subcapitata* showed that the relative toxicity order was 1B3MI⁺ >
370 1MI ≈ 1E3MI⁺ > Imid. In particular, the EC₅₀ of 1B3MI⁺ was estimated as 70.4 μM and 249 μM for
371 *D. magna* and *R. subcapitata* respectively. The EC₅₀ values of 1MI and 1E3MI⁺, measured with the

372 same organisms, are one order of magnitude higher than those evaluated for 1B3MI⁺. Finally, the
373 EC₅₀ values of Imid measured with *D. magna* and *R. subcapitata* are even greater than those of 1MI
374 and 1E3MI⁺. These results agree with published findings that the negative effect of ionic liquids on
375 biological systems increases with lengthening alkyl chains (Petkovic et al., 2011; D.
376 Demberelnyamba et al., 2004). Additionally, the EC₅₀ values, measured here with 1E3MI⁺ and
377 1B3MI⁺ are very close to those previously evaluated (Table 7).

378 In general, when compared to *R. subcapitata*, *D.magna* was more sensitive to Imid, 1MI, 1E3MI
379 and 1B3MI solutions, as shown in Table 7. The mechanism of toxicity of IMI-ILs towards *D.magna*
380 remains unknown but several studies have suggested destabilization of membrane permeability,
381 defense enzyme activity and structural damage to the DNA, as possible contributors to IMI-ILs
382 toxicity to *D.magna* (Samorì et al., 2010; Luo et al., 2008).

383 On the basis of the EU-Directives 93/67/ECC (EC 1996), the hazard rankings of the four selected
384 substances were also reported in Table 7 by their EC₅₀ values (whereby EC₅₀ < 1.0 mg·l⁻¹ is deemed
385 ‘very toxic to aquatic organisms’; 1.0–10 mg·l⁻¹ are ‘toxic to aquatic organisms’ and 10–100 mg·l⁻¹
386 are classified as ‘harmful to aquatic organisms’ and chemicals with an EC₅₀ above 100 mg·l⁻¹ are
387 not classified).

388 The results of 24 h immobilization tests with *D. magna* in contact with *t*₀, *t*_f and 2*t*_f samples at
389 varying the dilution factor are displayed in Figure 5. We observed that the *t*_f treated samples notably
390 showed almost the same toxicity as the *t*₀ sample (untreated) on *D. magna*, except for the
391 UV₂₅₄/H₂O₂ treated 1E3MI containing solution. In fact, when the solution containing 1E3MI⁺, at the
392 initial concentration of 150 mg·l⁻¹, undergoes the proposed treatment duration equal to *t*_f, a dilution
393 factor of the treated solution equal to 6.2·10⁻², allows for a 50% immobilization frequency. By
394 contrast, the EC₅₀ of 1E3MI⁺ on *D. magna*, the *t*₀ untreated solution needs a dilution factor equal to
395 only 4.2·10⁻¹ to generate the same immobilization frequency. Nevertheless, toxicity was
396 significantly reduced when daphnids were exposed to 2*t*_f samples of all tested compounds, thus
397 demonstrating that the secondary oxidation by-products did not affect the mobility of *D. magna*.

398 When the toxicity on *R. subcapitata* of t_f and $2t_f$ samples at varying dilution factor was studied,
399 somewhat different results from those achieved with *D. magna* were obtained. As shown in Figure
400 6, both t_f and $2t_f$ diluted samples, deriving from UV₂₅₄/H₂O₂ treatment of 1E3MI⁺ and 1B3MI⁺
401 solutions had a toxicity higher than t_0 diluted sample. In particular, for t_f and $2t_f$ samples collected
402 from treated 1B3MI⁺ solutions, the dilution factors needed to produce a 50% inhibition of algal
403 grow rate are close to $1.4 \cdot 10^{-1}$. This dilution factor is almost half of that necessary to obtain the
404 same inhibition of growth rate by diluting the t_0 sample ($2.3 \cdot 10^{-1}$). For t_f and $2t_f$ samples of treated
405 1E3MI⁺ solutions, the dilution factors that lead to a 50% inhibition of algal growth rate are equal to
406 $2.4 \cdot 10^{-1}$ and $4.9 \cdot 10^{-1}$ respectively. In this case, the increasing in toxicity, due to the UV₂₅₄/H₂O₂
407 treatment, is even more pronounced since the untreated t_0 solution should be concentrated 2.4 times
408 to inhibit the algal growth of 50%.

409 An increase in toxicity of the UV₂₅₄/H₂O₂ treated solutions has already been reported. In fact, in
410 recent papers it was noted that some by-products are even more toxic than their parent drugs as in
411 the case of the direct UV₂₅₄ photolysis and UV₂₅₄/H₂O₂ treatment of oxytetracycline, doxycycline,
412 ciprofloxacin, and fenofibric acid (Yuan et al., 2011; Santiago et al., 2011). This means that a
413 decrease of COD and TOC (Table 7) does not always correspond to a consequent decrease in
414 toxicity of the compounds.

415

416 **Conclusion**

417 The removal of Imid, 1MI, 1E3MI and 1B3MI from contaminated aqueous solutions was
418 effectively carried out by means of the UV₂₅₄/H₂O₂ advanced oxidation process. By contrast, both
419 aerobic biological oxidation and direct UV₂₅₄ photolysis are not able to remove the four target
420 compounds except in the case of Imid biodegradation, which is characterized by a $k_{bio/Imid}$ equal to
421 0.24 h^{-1} .

422 With the aim of providing useful data for the design of a UV₂₅₄/H₂O₂ treatment unit for the removal
423 of the selected compounds, the data we generated were used for the determination of the $k_{OH/Si}$ at

424 both selected pHs (numerical method). The $k_{OH/Si}$ values were shown to be between $2.32 \cdot 10^9 \text{ M}^{-1} \cdot \text{s}^{-1}$
425 and $5.52 \cdot 10^9 \text{ M}^{-1} \cdot \text{s}^{-1}$. Moreover, in accordance with previous findings on Imid and 1MI, the data
426 we obtained confirmed a dependency of $k_{OH/Si}$ with pH and Imid and 1MI pK_a values. Since very
427 little and mainly dated information was found on the $k_{OH/Si}$ of 1MI, 1E3MI, and 1B3MI, these
428 kinetic constants were evaluated using the competition kinetic method with benzoic acid as a
429 reference compound. Reasonable agreement of $k_{OH/Si}$ values estimated with the two methods was
430 found at both pHs. The validation procedure also demonstrated that the model had good predictive
431 ability for the behavior of the system.

432 Ecotoxicity assessments conducted using *R. subcapitata* and *D. magna*, and solutions contaminated
433 with the target compounds before and after the $\text{UV}_{254}/\text{H}_2\text{O}_2$ treatment showed three interesting
434 findings: i) in accordance with previous literature findings, 1E3MI and 1B3MI should be considered
435 harmful and toxic to aquatic organisms; ii) the toxicity of N,N'-alkyl-imidazolium salts increases at
436 increasing alkyl chain length; iii) the 1E3MI and 1B3MI by-products deriving from the $\text{UV}/\text{H}_2\text{O}_2$
437 process are even more toxic than the target compounds.

438

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444

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	Imid	1MI	1E3MI	1B3MI
$\epsilon_{254}^{S_i}$ ($10^{-6} \text{ M}^{-1} \text{ cm}^{-1}$)	2.8	2.3	4.6	2.4

Table 1

r ₁)	$\text{H}_2\text{O}_2 \xrightarrow{h\nu} 2\text{HO}^\bullet$	$\Phi_{254}^{\text{H}_2\text{O}_2} = 0.55 \text{ mol ein}^{-1}$ $\varepsilon_{254}^{\text{H}_2\text{O}_2} = 18.6 \text{ M}^{-1} \text{ cm}^{-1}$	Goldstein et al. (2007)
r ₂)	$\text{HO}^\bullet + \text{H}_2\text{O}_2 \xrightarrow{k_h} \text{H}_2\text{O} + \text{HO}_2^\bullet$	$k_h = 2.7 \cdot 10^7 \text{ M}^{-1}\text{s}^{-1}$	Buxton et al. (1988)
r ₃)	$\text{S}_i + \text{HO}^\bullet \xrightarrow{k_{\text{HO}/\text{S}_i}} \text{BP}$	$k_{\text{HO}/\text{S}_i} = \text{unknown}$	(estimated in this work)
r ₄)	$\text{BP} + \text{HO}^\bullet \xrightarrow{k_{\text{HO}/\text{BP}}} \text{BP}$	$k_{\text{HO}/\text{BP}} \approx k_{\text{HO}/\text{S}_i}$	(assumed in this work)
r ₅)	$\text{Cl}^- + \text{HO}^\bullet \xrightarrow{k_{\text{HO}/\text{Cl}}} \text{ClOH}^-$	$k_{\text{HO}/\text{Cl}} = 4.3 \cdot 10^9 \text{ M}^{-1}\text{s}^{-1}$	Buxton et al. (1988)
r ₆)	$2\text{HO}_2^\bullet \xrightarrow{k_t} \text{H}_2\text{O}_2 + \text{O}_2$	$k_t = 8.3 \cdot 10^5 \text{ M}^{-1}\text{s}^{-1}$	Bielski et al., (1985)

Table 2

		[Si] ₀ (10 ⁻³ M)	[H ₂ O ₂] ₀ (10 ⁻³ M)	pH	σ _{Si} (%)	σ _{H₂O₂} (%)
IMID	run1	0.143	16.5	5.5	0.75	0.20
	run2	0.142	17.7	8.5	0.88	0.28
1MI	run3	0.158	18.7	5.5	0.25	0.12
	run4	0.085	4.3	5.5	0.28	0.56
	run5	0.131	16.0	8.5	1.58	0.19
	run6	0.131	8.9	8.5	0.95	0.97
	run7	0.067	4.5	8.5	0.11	1.72
1E3MI	run8	0.099	16	5.5	1.61	0.19
	run9	0.096	8.4	5.5	1.81	0.06
	run10	0.099	17	8.5	0.73	0.56
	run11	0.085	8.5	8.5	1.46	0.20
1B3MI	run12	0.077	17	5.5	0.46	0.13
	run13	0.120	8.8	5.5	0.91	0.38
	run14	0.081	16	8.5	0.28	0.12
	run15	0.131	8.1	8.5	0.33	0.92

Table 3

	Numerical method		Competition kinetic method*		Literature findings		
	pH=5.5	pH=8.5	pH=5.5	pH=8.5	$k_{OH/Si}$ ($M^{-1}\cdot s^{-1}$)	pH	Ref
$k_{OH/Imid}$ ($M^{-1}\cdot s^{-1}$) CI ($M^{-1}\cdot s^{-1}$)	$2.33\cdot 10^9$ $2.3\cdot 10^8$	$4.42\cdot 10^9$ $3.8\cdot 10^8$	- -	- -	$4.8\cdot 10^9$ $6.4\cdot 10^9$ $8.7\cdot 10^9$ $1.2\cdot 10^{10}$	7.4 7.4 6.8 10.9	§ † ‡ ‡
$k_{OH/IMI}$ ($M^{-1}\cdot s^{-1}$) CI ($M^{-1}\cdot s^{-1}$) R^2	$2.32\cdot 10^9$ $2.3\cdot 10^8$ -	$4.25\cdot 10^9$ $6.3\cdot 10^8$ -	$3.92\cdot 10^9$ - 0.99	$6.32\cdot 10^9$ - 0.98	$5.0\cdot 10^9$ $8.1\cdot 10^9$	4.5 9.4	‡ ‡
$k_{OH/IE3MI}$ ($M^{-1}\cdot s^{-1}$) CI ($M^{-1}\cdot s^{-1}$) R^2	$3.43\cdot 10^9$ $3.3\cdot 10^8$ -	$3.69\cdot 10^9$ $2.3\cdot 10^8$ -	$2.91\cdot 10^9$ - 0.98	$2.72\cdot 10^9$ - 0.99			
$k_{OH/IB3MI}$ ($M^{-1}\cdot s^{-1}$) CI ($M^{-1}\cdot s^{-1}$) R^2	$4.49\cdot 10^9$ $4.7\cdot 10^8$ -	$5.52\cdot 10^9$ $5.8\cdot 10^8$ -	$3.90\cdot 10^9$ - 0.99	$5.11\cdot 10^9$ - 0.98			

Table 4

		$[\text{Si}]_0$ (10^{-3} M)	$[\text{H}_2\text{O}_2]_0$ (10^{-3} M)	pH	σ_{Si} (%)	$\sigma_{\text{H}_2\text{O}_2}$ (%)
IMID	run1s	0.127	8.9	5.5	0.45	0.45
	run2s	0.070	17.6	8.5	1.62	0.14
1MI	run3s	0.155	8.7	5.5	1.67	1.01
	run4s	0.115	4.4	5.5	1.07	1.69
	run5s	0.148	4.1	8.5	0.74	1.55
	run6s	0.118	2.0	8.5	0.18	0.28
1E3MI	run7s	0.091	5.2	5.5	0.17	0.18
	run8s	0.093	2.3	5.5	1.07	0.40
	run9s	0.082	4.5	8.5	0.12	1.00
	run10s	0.081	2.4	8.5	0.10	0.30
1B3MI	run11s	0.050	4.1	5.5	0.11	0.73
	run12s	0.063	1.8	5.5	0.23	0.76
	run13s	0.063	3.9	8.5	1.22	0.36
	run14s	0.057	1.9	8.5	0.71	0.76

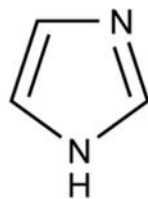
Table 5

	t_f (min)	$2t_f$ (min)	TOC/TOC ₀ (%)		COD/COD ₀ (%)	
			t_f	$2t_f$	t_f	$2t_f$
Imid	41	82	76	58	60	44
1MI	33	66	77	59	66	50
1E3MI	27	54	90	63	69	44
1B3MI	21	42	92	78	78	62

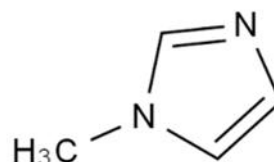
Table 6

	Species	Endpoint measured	EC ₅₀ (CI 95%) (µM)	Reference	Hazard ranking ^a
Imid	<i>R. subcapitata</i>	72h	14700 (13500-16200)	in this study	*
	<i>D.magna</i>	24 h	2140 (1850-2440)	in this study	*
1MI	<i>R. subcapitata</i>	72 h	3480 (2950-4090)	in this study	*
	<i>D.magna</i>	24 h	524 (414-670)	in this study	**
1E3MI⁺	<i>R. subcapitata</i>	72 h	2730 (2520-2990)	in this study	*
	<i>D.magna</i>	24 h	774	Steutde et al. (2012)	**
			567 (441 -639)	in this study	**
1B3MI⁺	<i>R. subcapitata</i>	96 h	277	Wells and Coombe (2006)	**
		72 h	249 (223-287)	in this study	**
	<i>D.magna</i>	48 h	84.8	Bernot et al. (2005) Couling et al. (2006)	**
			46.7	Wells and Coombe (2006)	***
		24 h	70.8	Garcia et al. (2005)	***
			70.4 (50.3-79.0)	in this study	***

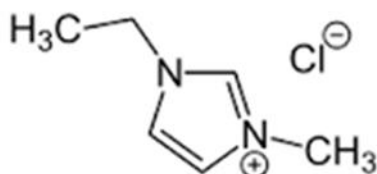
Table 7



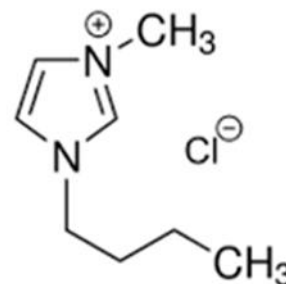
Imidazole (Imid)



1-methylimidazole (1MI)



**1-ethyl-3-methylimidazolium
chloride (1E3MI)**



**1-butyl-3-methylimidazolium
chloride (1B3MI)**

Figure 1

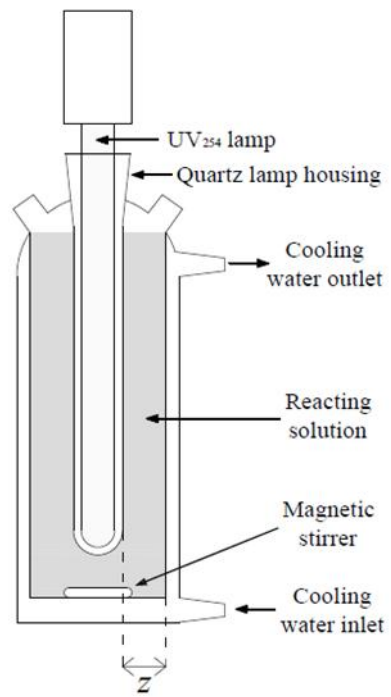


Figure 2

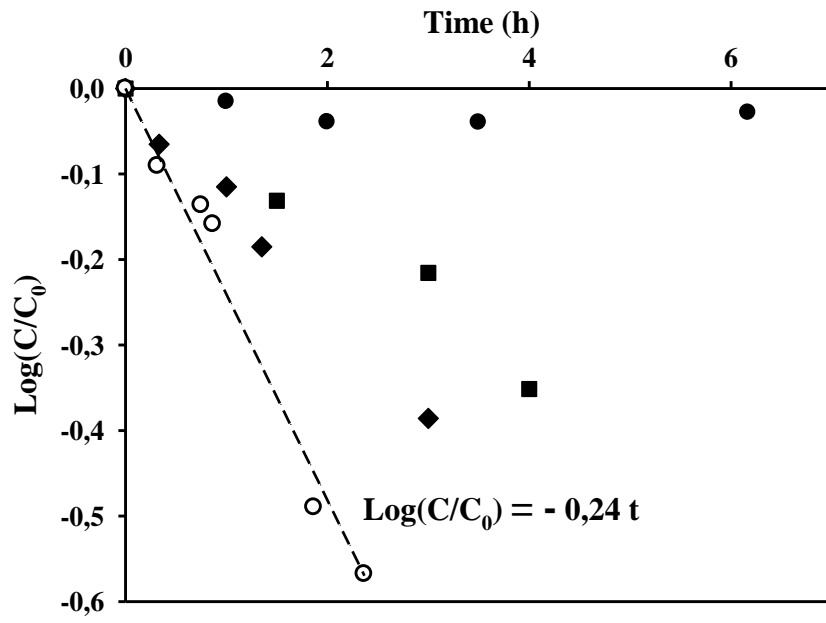


Figure 3

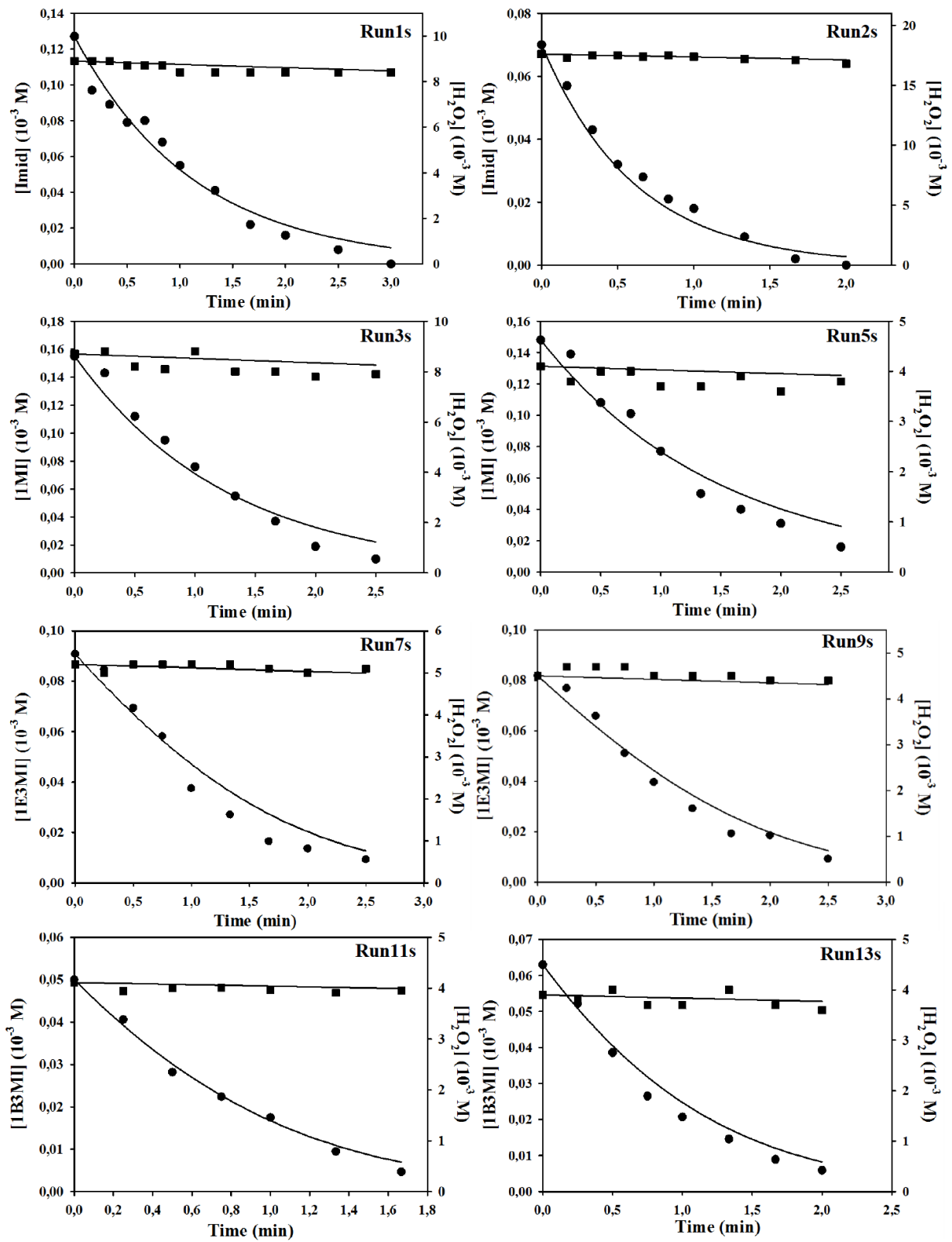


Figure 4

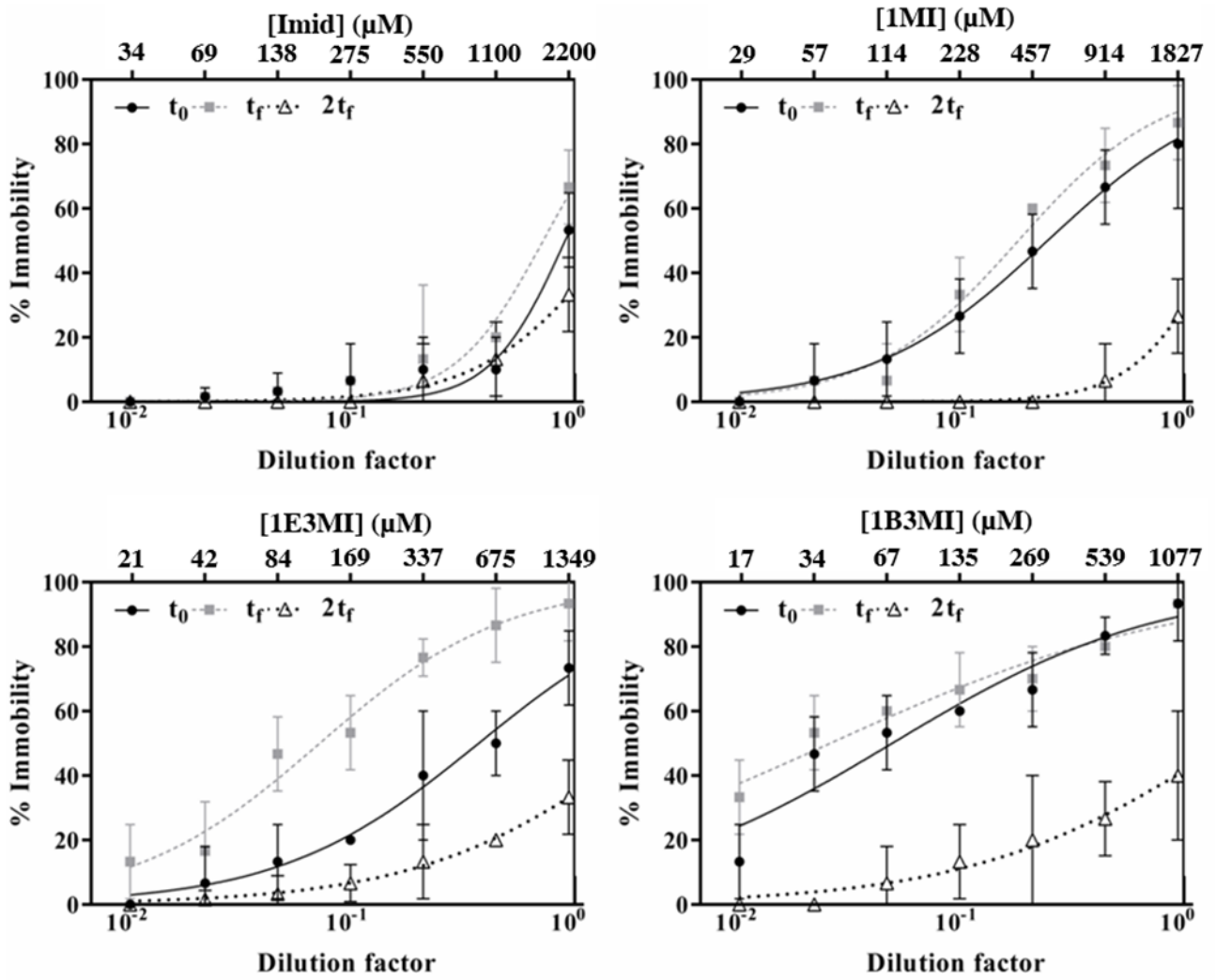


Figure 5

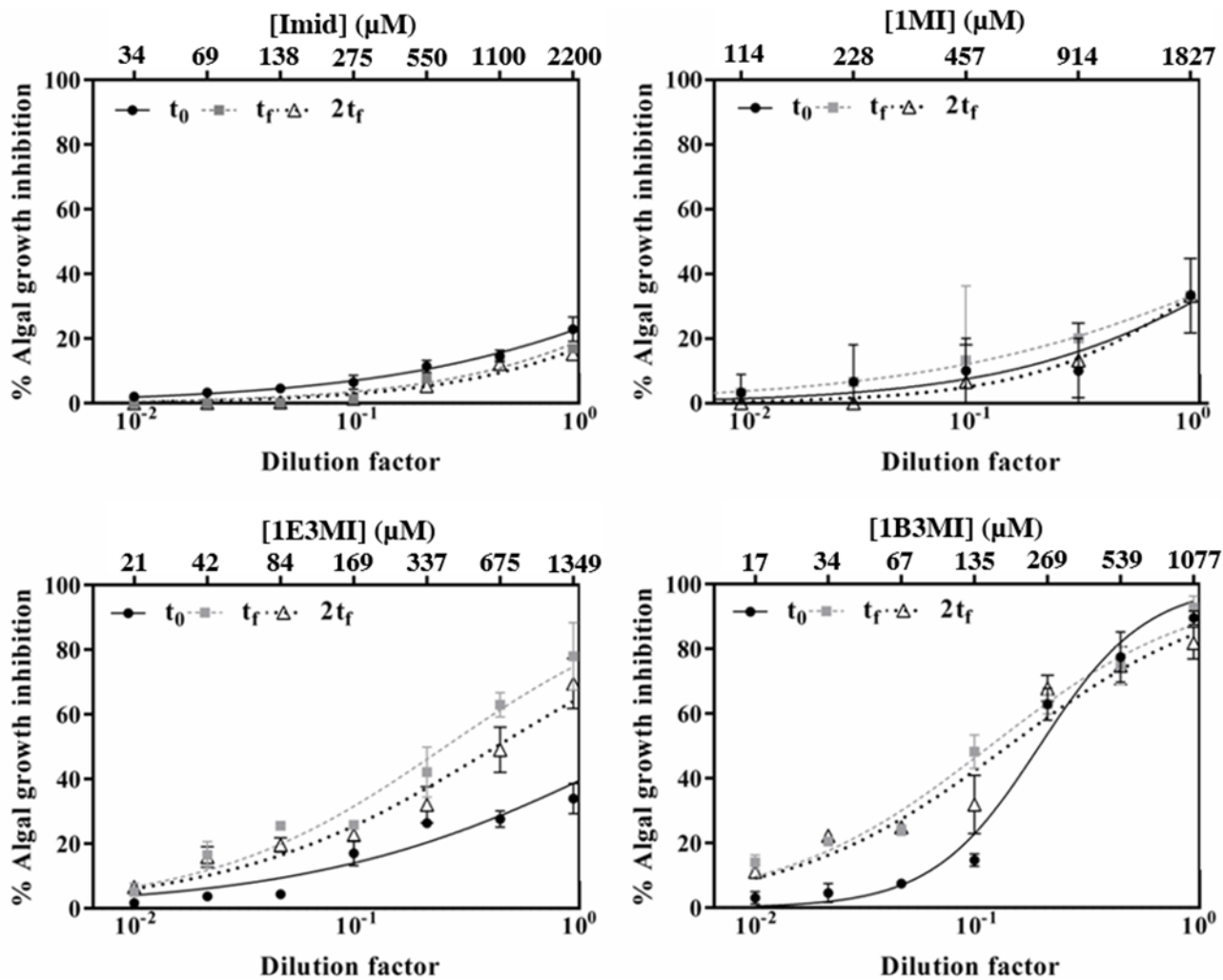


Figure 6

Figure 1. Structural formulas of the investigated compounds.

Figure 2. Cylindrical batch photoreactor scheme.

Figure 3. Biodegradation test of the imidazole. ●: 1th recharge; ■: 4th recharge; ◆: 6th recharge; ○: 10th recharge. T = 25 °C. [VSS]= 3.0 g·l⁻¹.

Figure 4. Results of validation procedure. Predicted (continuous lines) and experimental (symbols) concentration-time profiles for S_i oxidation by means of the UV₂₅₄/H₂O₂ advanced oxidation process. (●) [S_i], (■) [H₂O₂]. T = 25 °C. The initial concentrations of the reagents and the initial pH of the solutions were reported in Table 5.

Figure 5. Dose-response curve describing the effects of Imid, 1MI, 1E3MI⁺, 1B3MI⁺ and its UV₂₅₄/H₂O₂ by-products on mobility of *D. magna*.

Figure 6. Dose-response curve describing the inhibitory effects of Imid, 1MI, 1E3MI⁺, 1B3MI⁺ and its UV₂₅₄/H₂O₂ by-products on growth of *R. subcapitata*.

Table 1. Imid, 1MI, 1E3MI, and 1B3MI molar absorption coefficient at 254 nm and pH=7.0.

Table 2. UV₂₅₄/H₂O₂ kinetic scheme along with the kinetic parameters.

Table 3. Initial conditions of the UV₂₅₄/H₂O₂/S_i runs adopted during the optimization procedure and the calculated percentage standard deviations on the examined species.

Table 4. k_{HO/S_i} values estimated with both numerical and competition kinetic methods. *evaluated through the data of experimental UV₂₅₄/H₂O₂ runs in presence of benzoic acid ([BA]₀ = [S_i]₀ = 1.5·10⁻⁴ M) and [H₂O₂]₀ = 6.5·10⁻³ M. § Arouma et al., (1989). † Ching et al. (1993). ‡ Rao et al. (1975).

Table 5. Initial conditions of the UV₂₅₄/H₂O₂/S_i runs used for validate the model and the calculated percentage standard deviations on the examined species.

Table 6. Normalized TOC and COD concentration at different reaction times.

Table 7. Ecotoxicity of Imid, 1MI, 1B3MI⁺ and 1E3MI⁺ to *R. subcapitata* and *D. magna*. ^a Hazard ranking: * practically harmless; ** harmful to aquatic organisms; *** toxic to aquatic organisms.