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## UNIVERSITÀ DEGLI STUDI DI TORINO

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2 **Surfactant-assisted removal of Swep residues from soil and photocatalytic**  
3 **treatment of the washing wastes.**

4

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9

10 **ABSTRACT:**

11 The photocatalytic treatment of soil washing wastes containing the pesticide swep and three  
12 different surfactants: sodium dodecylsulfate (SDS), hexadecyltrimethylammonium bromide  
13 (HTAB) and polyoxyethylene(8) dodecyl ether (C<sub>12</sub>E<sub>8</sub>), has been investigated. Better extraction  
14 performances of swep (methyl-N-(3,4-dichlorophenyl)carbamate) from contaminated soil samples  
15 have been obtained using aqueous SDS solutions. The pesticide abatement in the wastes, performed  
16 by photocatalysis in the presence of irradiated TiO<sub>2</sub> dispersions, was faster in the presence of SDS  
17 and slower in the presence of HTAB, whereas a marked degradation inhibition was observed when  
18 C<sub>12</sub>E<sub>8</sub> solutions were used. The monitoring of end products formation in water, together with a  
19 detailed MS examination of the transient intermediates formed during the earlier steps of the  
20 pesticide degradation, allowed to give insight into the process mechanism operating in aqueous  
21 media.

22

23 **KEYWORDS:** swep, photocatalysis, soil washing, soil remediation.

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28        **Introduction**

29        The intensive use of pesticides in agriculture practice frequently gives rise to the contamination  
30 of soil and water resources, thus suitable remediation techniques are applied in order to overcome or  
31 minimize the risks arising from the use of such products.

32        Among the pest control agents various N-aryl and N-methyl carbamates are widely applied as  
33 herbicides for the treatment of rice and various field crops, such as cotton and soybean. Generally  
34 these compounds, which act as inhibitors of photosynthesis and cell mitosis, exhibit a more or less  
35 relevant persistency in soils depending on their tendency to adsorb, in turn related to the pesticide  
36 structure. Persistencies up to ca. 3 months have been reported for the more hydrophobic carbamates  
37 [1]. Thus, in certain cases, the removal of pesticide residues from soils could be necessary.

38        Soil washing, a well known ex-situ remediation technology, can be applied to remove organic  
39 pollutants from contaminated soils having a relatively small percent (< 30-40%) of silt and clay  
40 fractions. The treatment is usually based on the use of aqueous surfactant solutions, exploiting both  
41 the lowering of the interface tension of the washing liquid and the solubilization capabilities of  
42 micellar aggregates [2-4].

43        Among the surfactants used for soil washing, nonionics are usually preferred on the basis of their  
44 very low critical micellar concentration (c.m.c.), which reduces the presence of residual surfactant  
45 on the washed solid [5]. On the other hand, anionic surfactants exhibit a lower tendency to adsorb  
46 onto the soil particles, but have higher c.m.c. values. In some cases the use of mixtures of these two  
47 types of surfactants has been proposed [6-8]. Cationic surfactants are generally less used since they  
48 tend to adsorb strongly onto the soil.

49        In all the cases, soil washing gives rise to the production of significant amounts of washing  
50 wastes, which must be successively disposed and/or treated.

51        In the past years increased attention has been devoted to the application of advanced oxidation  
52 processes (AOPs), in particular photocatalysis, to treat complex aqueous wastes [9-12]. This  
53 approach is interesting since it allows to convert most organic pollutants into harmless chemicals.

54 However, the feasibility of photocatalytic treatments of surfactant-containing aqueous wastes has  
55 to be carefully examined, since surfactants are themselves degraded [13] and their aggregation  
56 structures can largely influence the degradation of the target pollutants [14-16].

57 In this work we investigated the performances of different aqueous surfactant solutions, used as  
58 soil washing agents, to extract swep residues from contaminated soil samples. Successively, the  
59 possible application of heterogeneous photocatalysis to effectively remove the pesticide from the  
60 washing wastes was investigated by using TiO<sub>2</sub> dispersions under simulated sunlight irradiation.

61 The analysis of swep degradation in water, with particular attention devoted to the isolation and  
62 identification of the transient products formed during the initial reaction steps, has also been  
63 performed in order to give insight into the process mechanism, which until now has not been  
64 examined in detail.

65

## 66 **EXPERIMENTAL SECTION**

### 67 **Materials and methods**

#### 68 **Soil samples**

69 Clean soil samples, taken from a hill zone near Alba (Piedmont region, Italy), were sieved to < 2  
70 mm to remove the bigger particles and vegetable remnants and successively homogenized. The  
71 mean organic fraction content in such soils is typically around 2 %.

72 The percent of water in these samples (2.6%) was determined using the EPA Method 345466:  
73 weighed amounts of soil and Na<sub>2</sub>SO<sub>4</sub> (dried at 400 °C for 4 hours) have been mixed and heated at  
74 105 °C overnight; the loss weight after this treatment allows to estimate the percentage of humidity.

#### 75 **Reagents**

76 Swep (purity 99.9%, Sigma Aldrich) was used as received.

77 Polycrystalline TiO<sub>2</sub> Degussa P25 (composed of c.a. 80% anatase and 20% rutile) was employed  
78 in all the photodegradation experiments. In order to remove any organic impurity this oxide was  
79 washed with water and irradiated under stirring with simulated solar light for about 12 h. The

80 washed semiconductor was then dried in the oven at 80 °C. The resulting powder was resuspended  
81 in water by sonication immediately before use.

82 Methanol (Fluka)/ water mixtures were used as LC eluents. Na<sub>2</sub>CO<sub>3</sub>, NaHCO<sub>3</sub> solutions (Merck)  
83 and metansulfonic acid (Merck) were used as eluents for the IC measurements.

84 NaOH and H<sub>2</sub>SO<sub>4</sub> (Merck) were used to adjust the pH. The analytical-grade surfactants N-  
85 hexadecyl-N,N,N-trimethylammonium bromide (HTAB, Merck), sodium dodecyl sulphate (SDS,  
86 Merck) and polyoxyethylene(8) lauryl ether (C<sub>12</sub>E<sub>8</sub>, Nikkol) were used in soil washing experiments.  
87 Acetone and n-hexane (both from Aldrich) were employed for the exhaustive extraction of the soil  
88 samples. Pure water was produced using a Milli-QTM system (Millipore).

### 89 **Instruments and methods**

90 The substrate degradation was followed by HPLC, employing a Merck-Hitachi instrument,  
91 equipped with a L-6200 pump and UV-vis L-4200 detector. A column RP-C18 (Lichrospher, 4mm  
92 i.d.×125 mm long, from Merck) was used. The eluent was methanol /water 60/40% (v/v), flow rate  
93 1.0 mL min<sup>-1</sup>. The detector wavelength was 220 nm.

94 The formation of ionic degradation products was followed by a suppressed ion chromatography,  
95 employing a Dionex DX 500 instrument equipped with a conductimeter detector (ED 40, Dionex).  
96 The anions (nitrate and nitrite) have been analysed by using an AS9HC anionic column (Dionex)  
97 200 mm long x 4mm i.d. The elutions were performed at 30°C, at a flow rate of 1mL min<sup>-1</sup> using an  
98 aqueous solution of K<sub>2</sub>CO<sub>3</sub> (10 mM) and NaHCO<sub>3</sub> (4 mM).

99 The determination of ammonium ions was performed by employing a CS12A column (Dionex)  
100 200 mm long x 4mm i.d., using metansulphonic acid 25mM as eluent, at a flow rate of 1mL min<sup>-1</sup>.

101 The evolution of the dissolved organic carbon (DOC) during the photocatalytic runs was  
102 followed using a Shimadzu 5000 TOC analyzer (catalytic oxidation on Pt at 680 °C). Calibration  
103 runs were performed injecting known amounts of potassium phthalate.

104 The analysis of organic intermediates, arising from the initial steps of swep degradation, was  
105 performed by HPLC-MS. A Dionex Ultimate 3000 HPLC coupled with a Surveyor PDA UV

106 detector and a LTQ Orbitrap mass spectrometer (Thermo Scientific) equipped with an atmospheric  
107 pressure interface and an ESI ion source was used. The LC column effluent was delivered into the  
108 ion source using nitrogen as sheath and auxiliary gas. The source voltage was set to 3.1 kV. The  
109 heated capillary temperature was maintained at 275°C. The main tuning parameters adopted for ESI  
110 source were: capillary voltage -34.00 V, tube lens offset -68.57 V. Mass accuracy of recorded ions  
111 (vs calculated) was  $\pm 15$  ppm (without internal calibration). The chromatographic separations were  
112 performed on a Phenomenex Luna 3  $\mu$  C18 (2) column, 150  $\times$  2.0 mm, 3  $\mu$ m particle size,  
113 thermostated at 30°C. Injection volume was 20  $\mu$ L and flow rate 200  $\mu$ L min<sup>-1</sup>. The following  
114 gradient mobile phase composition was adopted: acetonitrile /ammonium acetate 0.1 mM 20/80 to  
115 100/0 in 40 min. MS and MS<sup>n</sup> analyses were performed in the negative ions mode; the mass range  
116 was 50–350 Da.

117

## 118 **Analytical procedures**

### 119 **Soil spiking**

120 100 g of soil was treated with 100 mL of an acetone solution containing the pesticide. The  
121 concentration of swep was chosen in order to obtain a final concentration of ca. 20 mg L<sup>-1</sup> in the  
122 washing solutions, near to its solubility limit in water (ca. 50 mg L<sup>-1</sup>)[17].

123 The soil was mixed thoroughly with a magnetic stirrer for 1 h and then left unsealed overnight  
124 under hood to allow the solvent evaporation.

### 125 **Soil washing experiments.**

126 All the washing runs were performed on 3.75 g of soil to which 25 mL of aqueous surfactant  
127 solution was added. The samples were placed in stopped tubes in a rotatory mixer (rotation speed:  
128 ca. 10 rpm). The standard contact time was 5 h.

129 The obtained soil dispersions were centrifuged at 5000 rpm for 10 min and aliquots of the  
130 supernatant clear solutions were filtered through 0.45  $\mu$ m Millex LCR hydrophilic PTFE

131 membranes (Millipore). The quantification of substrate has been performed by HPLC, as previously  
132 detailed.

### 133 **Degradation experiments**

134 The degradation experiments were carried out in a photochemical stirred batch reactor from  
135 Helios-Italquarz (Milan), equipped with a medium pressure mercury lamp (125 W). The Pyrex glass  
136 jacket surrounding the lamp acted as a cut-off filter for wavelengths shorter than 300 nm.

137 A series of preliminary photocatalytic runs were performed on 500 mL of solution containing ca  
138  $17 \text{ mg L}^{-1}$  of swep,  $200 \text{ mg L}^{-1}$  of dispersed  $\text{TiO}_2$  and other additives, if necessary. The soil washing  
139 solutions were degraded in the presence of different amounts of semiconductor ( $200\text{-}1000 \text{ mg L}^{-1}$ )  
140 and were kept saturated with bubbling air during the treatment. The temperature was  $25 \text{ }^\circ\text{C}$ .  
141 Samples ( $5 \text{ mL}$ ) of irradiated dispersion were taken from the reactor at different times; all the  
142 analytical determinations were performed after filtration.

143 In order to ensure the quantitative recovery of the substrate,  $5 \text{ ml}$  of methanol were added to the  
144 samples taken during the degradation runs before the filtration.

145

## 146 **RESULTS AND DISCUSSION**

### 147 **Soil washing performances**

148 The extraction performances of three surfactants (HTAB, SDS and  $\text{C}_{12}\text{E}_8$ ) were investigated.  
149 These surfactants were chosen on the basis of their non-aromatic nature, in order to reduce the  
150 possible competition between the amphiphiles and the investigated soil pollutant during the  
151 photocatalytic treatment step.

152 Taking into account the c.m.c. and aggregation number data, surfactant concentrations were  
153 chosen in order to have initially nearly the same concentration (c.a.  $8.3 \times 10^{-6} \text{ M}$ ) of micelles,  
154 assumed as macromolecules. The working concentrations of HTAB, SDS and  $\text{C}_{12}\text{E}_8$  were  $1.0 \times 10^{-3}$   
155  $\text{M}$ ,  $8.6 \times 10^{-3} \text{ M}$  and  $1.1 \times 10^{-3} \text{ M}$ , respectively. Measurements of surface tension of these surfactant

156 solutions after contact with soil samples (and filtration through 0.45  $\mu\text{m}$  filters) clearly indicated  
157 that the surfactant concentrations are still above the c.m.c. in all the cases.

158 After the established contact period (5 h) all the soil extracts showed a yellowish colour. The  
159 recovery yields are reported in Figure 1. The percentages were calculated with respect to the  
160 recoveries obtained using the mixture acetone/hexane 50:50 v/v, in the same experimental  
161 conditions. The standard deviations, estimated from five replicated measurements, were in the range  
162 5-8%.

163 It can be seen that SDS allows to obtain the higher recovery. The extraction results can be  
164 explained taking into account two mechanisms occurring in surfactant soil washing: the first one  
165 prevails below the critical micelle concentration (soil rollup mechanism), whereas the second one  
166 takes place above this concentration limit (solubilization) [18].

167 Anionic and nonionic surfactant are less likely to be absorbed onto the soil and this leads to  
168 enhanced micelle formation in the washing solution, thus favouring a higher recovery of  
169 hydrophobic substrates. For cationic surfactants their adsorption onto soils takes place in two  
170 phases: initially via cation exchange and after by formation of double-layer and admicelles on the  
171 soil surfaces. The contaminant partition between these structures tends to reduce the remediation  
172 efficiency [19].

173

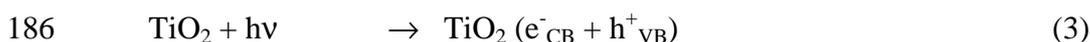
#### 174 **Photocatalytic degradation experiments**

175 Before to start with the photocatalytic runs some blank experiments were performed in the dark,  
176 in the absence of  $\text{TiO}_2$ . No appreciable degradation of swep was observed after 2 hours irradiation,  
177 thus confirming its photostability under the described working conditions.

178 The mechanism of photocatalysis, extensively investigated and reported in the literature [9-12],  
179 will be not examined here. Basically, the degradation of a wide number of organic substrates occurs  
180 through a multistep process involving the attack of organic molecules by reactive oxidizing species,

181 in particular  $\bullet\text{OH}$ , formed upon irradiation of the semiconductor particles. Protonation or  
182 deprotonation of surface hydroxy groups can occur depending on the solution pH.

183



189 In addition to the oxidation paths, reduction processes involving the electrons in the conduction  
190 band could be also present in some cases [20].

191 Taking into account the nature of the examined pesticide and the properties of the employed  
192 semiconductor, the photocatalytic degradation was investigated at different initial pH values of the  
193 aqueous dispersions: 3.0, 5.6 and 8.0, which are below, in the range and above the isoelectric point  
194 of anatase [21], respectively.

195 Figure 2 shows the evolution of the primary process as a function of the initial pH. As previously  
196 reported for most organic compounds, the swep degradation follows a pseudo-first order kinetic  
197 law, according to the equation:

198

$$199 \quad -dC_{\text{sub}}/dt = k_{\text{obs}} C_{\text{sub}} \quad (6)$$

200

201 where  $C_{\text{sub}}$  is the substrate concentration and  $k_{\text{obs}}$  is the observed first-order rate constant. According  
202 to Eq. (6), linear plots of  $\ln(C/C_0)$  versus time have been obtained up to ca. 70–80% swep  
203 degradation (see inset in Figure 2).

204 The analysis of the primary process reveals a modest increase of the degradation rate with  
205 increasing initial pH. Taking into account that the protonation of the amido groups occurs in strong  
206 acidic media [22, 23] and that deprotonation of swep is expected only at high pH values (a  $\text{p}K_a$  value

207 around 14 is reported [24]), negligible repulsive effects between sweep and semiconductor particles  
208 are expected within the investigated pH range. Thus, the observed modest increase in the reaction  
209 rate with increasing pH could be mainly attributed to the increased formation of OH radicals due to  
210 the improved transfer of holes to the adsorbed water and hydroxyls, according to eqns. 4 and 5.

211 Although the photocatalytic degradation of various carbamic pesticides in water under different  
212 experimental conditions has been previously investigated, only one report [25] concerned sweep and  
213 a lack of information still exists about the degradation mechanism of this pesticide in aqueous  
214 media. Our attention was thus focused on this point, with particular interest devoted to the MS  
215 characterization of organic transient intermediates formed during the initial degradation steps.

216

#### 217 **Analysis of the end products.**

218 The formation of the mineralization end products has been investigated at pH 5.6. Figure 3  
219 shows the decrease of dissolved organic carbon during the irradiation of aqueous solutions of  
220 pesticide in the presence of 200 mg L<sup>-1</sup> of TiO<sub>2</sub>.

221 A residual concentration of DOC (ca 13 % of the initial content) was found even after 120 min  
222 irradiation, indicating a slow mineralization process. Taking into account that the complete  
223 disappearance of the pesticide occurs in a shorter time (ca 60 min), the residual DOC can be  
224 attributed to the presence of organic intermediates [26-28, 25]. Since the presence of aromatic  
225 derivatives was not detected by HPLC after 60 min irradiation, it can be reasonably attributed to  
226 compounds originated from the ring opening the organic carbon found in the solution at that time.

227 The evolution of chloride, nitrate and ammonium was reported in Figure 3. It can be noted that  
228 the stoichiometric formation of Cl<sup>-</sup> is obtained after ca. 60 min irradiation, thus indicating that the  
229 pesticide dechlorination is much faster than its mineralization to CO<sub>2</sub>.

230 No nitrite traces were detected under the employed experimental conditions, in agreement with  
231 previous results reported for other carbamates [27].

232 As far as the formation of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  is concerned, we observed a continuous increase of  
233 their concentrations with increasing irradiation time. Ammonium was found to be the main  
234 nitrogen-containing end product and accounts for ca. 53% of the total nitrogen, after 120 min  
235 irradiation. At this time the nitrogen mass balance is lower than the stoichiometric value, thus  
236 indicating that organic nitrogen could be still present, probably in organic intermediates. However,  
237 the possible formation of hydroxylamine during the ammonia photooxydation over  $\text{TiO}_2$  has also  
238 been hypothesized and further degradation of this product leads to the formation of gaseous  $\text{N}_2$  and  
239 nitrogen oxides [29], which can be more easily lost.

#### 240 **Identification of transient intermediates formed in the earlier reaction steps**

241 The investigation of the nature of organic intermediates was performed via HPLC–DAD–MS  
242 analysis on the irradiated solutions, previously concentrated up to 50 times. The samples were taken  
243 after 10 and 15 min irradiation, times at which the aromatic intermediates are still present at  
244 significant concentrations and can be better evidenced.

245 Figure 4 shows different digital reconstructions, at various significant  $m/z$  values, of the  
246 chromatographic pattern of the sample, degraded at pH 5.6. Also the solutions irradiated at pH 3  
247 and 8 showed similar profiles, thus supporting the hypothesis that pH mainly affects the swep  
248 abatement kinetics, whereas the degradation mechanism seems to remain essentially the same.

249 The intermediates structures, reported in Table 1, have been proposed on the basis of the  
250 evidenced  $m/z$  values and considering the corresponding  $\text{MS}^n$  spectra fragmentation.

251 Three peaks with retention times shorter than swep have been found when extracting from the  
252 total ionic current the  $m/z$  234; this value, higher than that of the parent molecule, and the  
253 chromatographic behaviour are consistent with the hypothesis of the formation of mono  
254 hydroxylated products. The  $\text{MS}^2$  spectra of these compounds present only a product ion at 202  $m/z$   
255 deriving from the neutral loss of the  $\text{CH}_3\text{OH}$  molecule. Taking into account that the fragmentation  
256 pathway of swep also showed this loss as main fragmentation, we can hypothesize the introduction  
257 of OH on one of the available positions of the aromatic ring.

258 In the MS<sup>3</sup> spectrum of *m/z* 202, the *m/z* 166 ion (-36 Da, assigned to HCl loss) is the most  
259 abundant fragment present for the three signals. Nevertheless the analysis of the spectrum did not  
260 provide useful information to discriminate between the three possible isomers.

261 For the intermediate with *m/z* 200, two peaks were detected. The isotopic profile shows the  
262 presence of only one chlorine atom in the structure, thus suggesting that the degradation path can  
263 lead to the simultaneous hydroxylation and dechlorination of the molecule, in agreement with the  
264 observed chloride evolution. The number of detected peaks is consistent with the two possible  
265 positions of substitution of Cl with OH group. However the more abundant formation or  
266 accumulation of only one of isomers (peak at *t<sub>R</sub>*=13.23 min) was observed. By an accurate MS<sup>3</sup>  
267 analysis, both signals show the formation of two fragment ions having *m/z* 168 and 141, due  
268 respectively to the neutral group loss of 32 (CH<sub>3</sub>OH) and to a radical loss of 59 Da (•C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>). The  
269 MS<sup>4</sup> fragmentation has been performed on both ions, but the observed loss of 36 (HCl) didn't  
270 supply further information.

271 The formation of the above mentioned transient derivatives suggests that the ring hydroxylation,  
272 with or without the elimination of halogen atoms, is the main initial reaction step of the  
273 photocatalytic degradation of swep.

274 For the most abundant compounds having *m/z* 200 (*t<sub>R</sub>* =13.2 min) and *m/z* 234 (*t<sub>R</sub>* = 21.4 min and  
275 *t<sub>R</sub>* = 22.6 min), their formation and disappearance during the degradation treatment was followed by  
276 HPLC-UV at the three investigated initial pH values (see Figure 5A, B, C). The analysis was  
277 directly performed on the irradiated solution, without preconcentration.

278 It can be seen that the evolution of the different peaks shows a typical bell-shaped profile. At pH  
279 5.6 the intermediates formation is faster, reaching a maximum amount of intermediates formed after  
280 ca. 20 min irradiation. The complete degradation of the intermediates at this pH occurs after 50-60  
281 min irradiation, whereas working at the other reported pH values, in particular at pH 3, a slower  
282 degradation rate of the transient intermediates is observed.

283 Concerning the other degradation products reported in Table 1, the key role of the HRMS was  
284 essential for the structure assignment of intermediates having  $m/z = 250$ ; in fact among the three  
285 signals obtained, compound A has an accurate  $m/z$  value of 249.9274, whereas this value is equal to  
286 249.9636 for compounds B and C.

287 Compounds B and C were identified as the substrate dihydroxyderivatives; their MS<sup>2</sup> spectra  
288 analysis show for both isomers the formation of a product ion at  $m/z$  217.9287, due to the loss of  
289 CH<sub>3</sub>OH. On the basis of the previous considerations, it is possible to propose the introduction of  
290 both OH groups on the ring.

291 For compound A, the high resolution mass spectrum suggests the empirical formula: C<sub>7</sub>H<sub>2</sub>O<sub>5</sub>NCl<sub>2</sub>,  
292 which is compatible with the proposed structure reported in Table 1.

293 The MS<sup>n</sup> analysis suggests a different fragmentation pattern in respect with the compounds B  
294 and C. The absence of CH<sub>3</sub>OH loss and the presence of product ions at  $m/z$  214 (-36 HCl) and 145  
295 (radical loss of 105 Da •C<sub>3</sub>H<sub>2</sub>ClO<sub>2</sub>) are in agreement with the proposed structure.

296 Three species at  $m/z$  216 were detected and labelled D, E, F. The mass difference (16 Da) in  
297 respect to the intermediate having  $m/z$  200 allows us to hypothesize the introduction of a second OH  
298 group on the ring. The corresponding MS/MS spectra still exhibit the loss of 32 Da (signal at  $m/z$   
299 184), thus confirming the preferential OH attack on the aromatic moiety.

300 The formation of product ions having  $m/z$  148 (-36 Da, HCl loss) and  $m/z$  120 (- 28 Da, CO loss)  
301 was observed in the MS<sup>3</sup> spectra performed on the ion at  $m/z$  184; in all cases we can hypothesize  
302 the formation of three isomers coming from the introduction of a second OH group in each one of  
303 the three available positions on the ring.

304 In addition to intermediate A, a structure deriving from the partial degradation of the carbamic  
305 group was assumed for the compound with  $m/z$  156.

306 Two signals were detected for  $m/z$  232 value, although the first at  $t_R = 3.5$  min is more abundant  
307 than the second,  $t_R = 5$  min . The accurate mass value suggests an empirical formula of C<sub>7</sub>H<sub>3</sub>O<sub>6</sub>NCl,  
308 which allows to hypothesize the structure shown in Table 1.

309 As reported for compound A with  $m/z$  250, the corresponding MS<sup>2</sup> spectra didn't show the  
310 typical loss of 32 Da observed for swep and its hydroxyderivatives; in particular for compound G a  
311 loss of 105 Da, corresponding to a loss of C<sub>3</sub>H<sub>2</sub>ClO<sub>2</sub> radical, was shown, whereas the formation of a  
312 product ion with  $m/z$  188 was found for compound J, suggesting the loss of one CO<sub>2</sub> molecule.

313 Taking into account that only three intermediates are largely abundant, they can be considered as  
314 the initial products formed starting from the swep molecule. The sequence of events leading to the  
315 formation of the other detected compounds is more difficult to ascertain since these compounds are  
316 less abundant and, moreover, they can originate from different intermediates. On the basis of the  
317 above considerations it becomes difficult to propose a possible unique reaction mechanism.

318 It is well known that the formation of simpler organic products, originated at much longer  
319 irradiation times after the aromatic ring opening, occurs during the photocatalytic treatments.  
320 However, their identification was not examined since it was out of the scope of this reported  
321 preliminary study.

322

### 323 **Effect of surfactants on the primary process kinetics**

324 In order to investigate the effect of amphiphiles on the kinetics of swep degradation,  
325 photocatalytic runs were successively carried out in the presence of the investigated surfactants, at  
326 pH 5.6. The surfactant concentrations were the same employed during the soil washing  
327 experiments. The main scope of these experiments was the monitoring of the pesticide abatement  
328 and the corresponding results are shown in Figure 6, where the swep degradation profile in water at  
329 pH 5.6 was included for comparison purposes.

330 A comparison of kinetic data obtained in water with that obtained in the presence of the three  
331 examined surfactants clearly indicates a more or less relevant inhibition of the photocatalytic  
332 process when performed in the presence of surfactants. The non ionic surfactant C<sub>12</sub>E<sub>8</sub> shows the  
333 highest inhibiting effect since only ca. 3.0 % of initial substrate was degraded after 2 hours  
334 irradiation at pH 5.6. For this surfactant, experiments at pH 3 and 8 were not further performed.

335 If the ionic surfactants are considered, the degradation was slower in the presence of HTAB. For  
336 both SDS and HTAB the degradation still fits a pseudo-first order kinetic law, but only up to  
337 approximately 25-30 % of substrate conversion. From the examination of Figure 6 it can be seen  
338 that the percent of swep abatement after 30 min irradiation, at pH 5.6, is around 22% in the  
339 presence of SDS and less than 8% in the presence of HTAB, whereas it reaches a value near 85% in  
340 pure water under the same conditions. After 120 min irradiation the degradation is still uncomplete;  
341 for example, at pH = 8, less than 29% of swep was degraded in the presence of HTAB, whereas  
342 more than 60% of the initial pesticide was degraded in the presence of SDS.

343 Some experiments have been also performed at surfactant concentrations below the  
344 corresponding c.m.c. values. The results (not shown here) are in agreement with previous findings  
345 reported in literature for other substrates. The observed inhibition effects are, as expected, lower  
346 under these conditions.

347 In order to further optimize the photocatalytic treatment, the effect of  $\text{TiO}_2$  concentration and of  
348 air saturation on the process were investigated at a fixed initial pH (5.6) in the presence of SDS and  
349 HTAB. As reported in Table 2, an increase of the catalyst concentration until  $1000 \text{ mg L}^{-1}$  raises the  
350 degradation rate, particularly in the case of SDS.

351 Moreover, a significant improvement of the degradation performances was also achieved by  
352 operating the saturation of the irradiated suspension with a bubbled air (flow rate  $\text{ca. } 12 \text{ mL min}^{-1}$ )  
353 through the reaction vessel. For SDS, in the presence of  $1000 \text{ mg L}^{-1}$  of  $\text{TiO}_2$ , the observed swep  
354 abatement passes from ca. 80% to ca. 98% after 2 hours irradiation.

355 The observed degradation enhancement was less neat for HTAB, for which a modest increase  
356 (from ca. 30% to ca. 34%) was, for example, observed when working in the presence of  $600 \text{ mg L}^{-1}$   
357 of  $\text{TiO}_2$ .

358

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360

361 **Degradation of soil washing wastes**

362 On the basis of the above reported results, a set of experiments were performed on simulated soil  
363 washing wastes obtained by treating spiked soil samples with SDS. This surfactant was chosen on  
364 the basis of both extraction yield and kinetic degradation performances.

365 Therefore soil samples (94 g) were spiked with swep (24 mg) dissolved in acetone. After drying,  
366 the soil was extracted for 5 hours with 625 mL of SDS 8.6 mM and 500 mL of soil washing extract  
367 were collected. The measured swep concentration in the extract was ca. 17 mg L<sup>-1</sup>.

368 After centrifugation the supernatant waste was degraded in the reactor, in the presence of 1000  
369 mg L<sup>-1</sup> of TiO<sub>2</sub>, at pH 5.6, under continuous air flow. Samples of irradiated dispersion were taken at  
370 different irradiation times and analysed after filtration, as previously described. The complete  
371 disappearance of swep was achieved after ca 6 h (see Figure 7). The results are the mean of two  
372 replicated set of measurements.

373 The presence in the waste of other organic components coming from the soil leads to a slower  
374 degradation of the pesticide, if compared with previous findings obtained working with SDS in the  
375 absence of soil. However, even under these conditions, the photocatalytic treatment of the washing  
376 waste appears viable.

377

378 **CONCLUSIONS**

379 The photocatalytic degradation of swep is relatively fast (within 50-60 min) in aqueous media  
380 under the examined experimental conditions. The HPLC-MS analysis of the organic compounds  
381 formed in water during the earlier degradation steps suggests that the simultaneous dechlorination  
382 and hydroxylation of the swep aromatic ring are the major initial routes of the process.

383 The presence of surfactants largely affects the degradation kinetics, however the treatment of  
384 surfactant-containing wastes arising from soil washing appears possible after a proper selection of  
385 the amphiphile. In particular SDS showed, among the surfactants investigated in this study, the best  
386 extraction efficiency of swep from contaminated soil samples. This surfactant also exhibited lower

387 inhibiting effects on the pesticide photocatalytic degradation, thus suggesting its possible use for  
388 environmental remediation purposes.

389

390

391 **Acknowledgements**

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393 acknowledged.

394

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- 434

435 **Captions**

436 **Figure 1** Recoveries of swep using the investigated surfactants.

437 **Figure 2** Effect of initial pH on swep degradation, pH= 5.6 (●), 8 (□), 3 (★).

438 **Figure 3** Evolution of end products and DOC during the photocatalytic degradation of swep in the  
439 presence of 200 mg L<sup>-1</sup> of TiO<sub>2</sub> (○ chloride, ∇ DOC, ◆ nitrate, ★ ammonium, dashed line:  
440 primary process).

441 **Figure 4** LC–MS pattern of the swep sample after 10 min irradiation displayed at different *m/z*  
442 values. Initial pH = 5.6.

443 **Figure 5** Evolution of main intermediates formed from swep degradation as a function of the  
444 irradiation time. A: *m/z* 200 ( *t<sub>R</sub>* = 13.2 min), B: *m/z* 234 (*t<sub>R</sub>* = 21.4 min), C *m/z* 234 (*t<sub>R</sub>* = 22.6 min).  
445 pH= 5.6 (●), 8 (□), 3 (★).

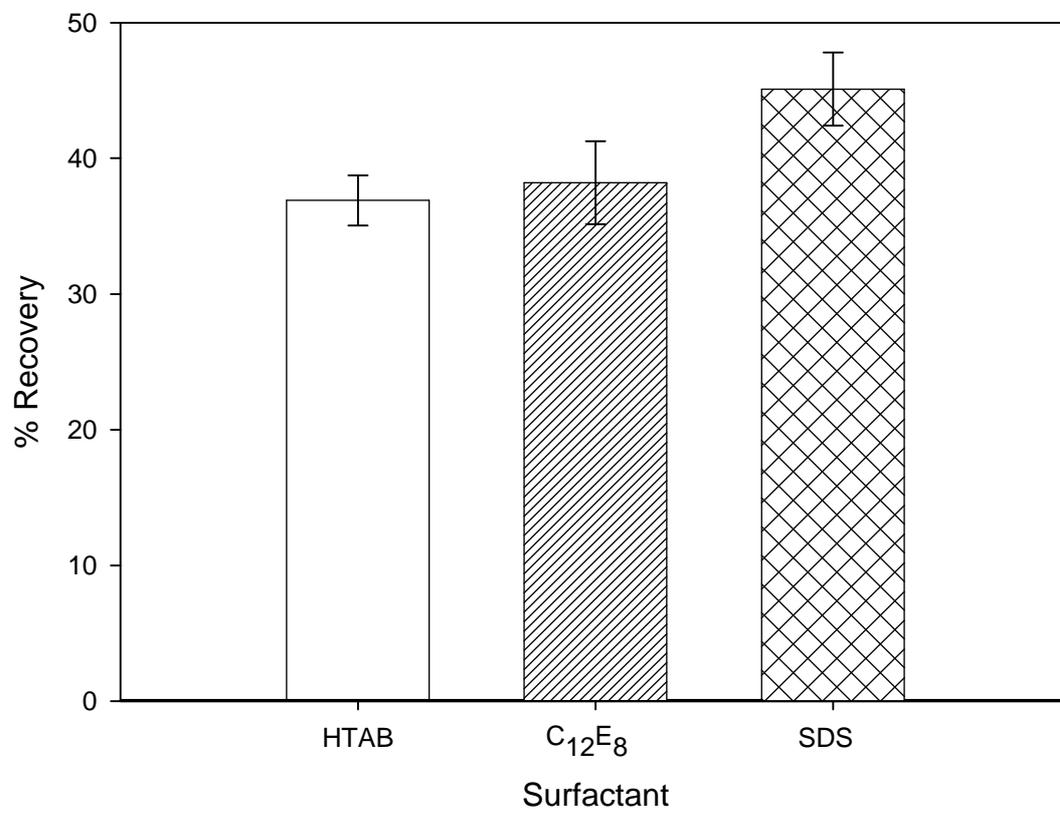
446 **Figure 6** Effect of surfactants on the evolution of the primary process during the photocatalytic  
447 abatement of swep. Dashed line: swep degradation profile in water at pH 5.6

448 **Figure 7** Photocatalytic degradation of swep in the soil washing waste.

449

450 **Figure 1**

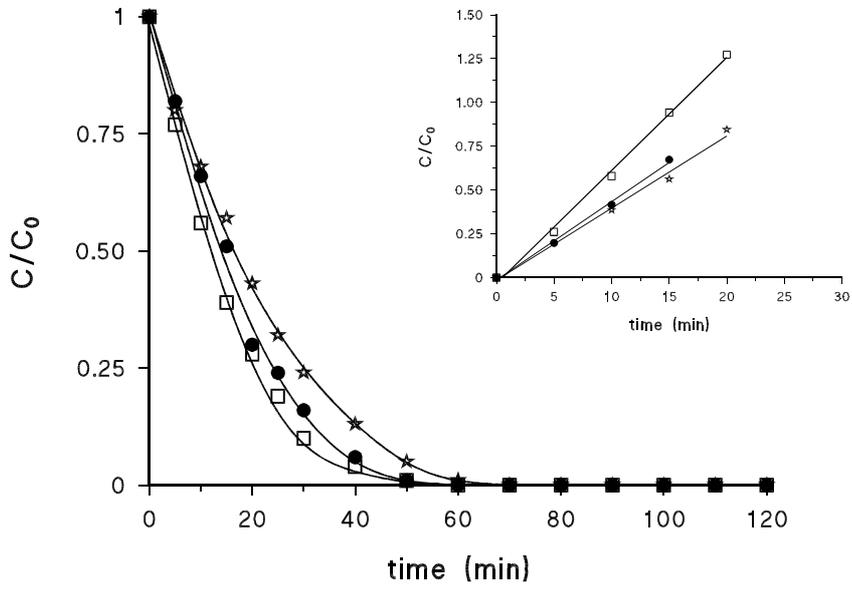
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453 **Figure 2**

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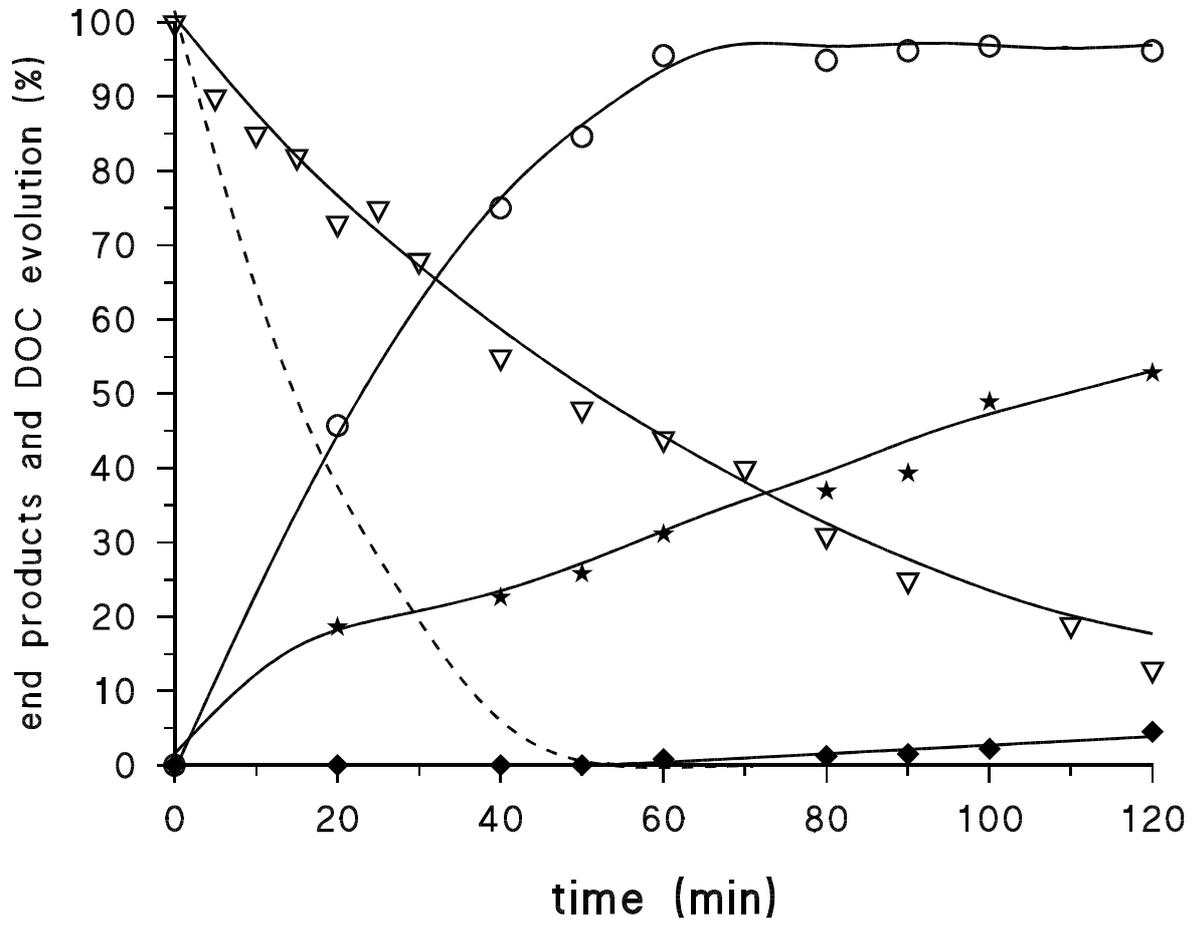


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457 **Figure 3**

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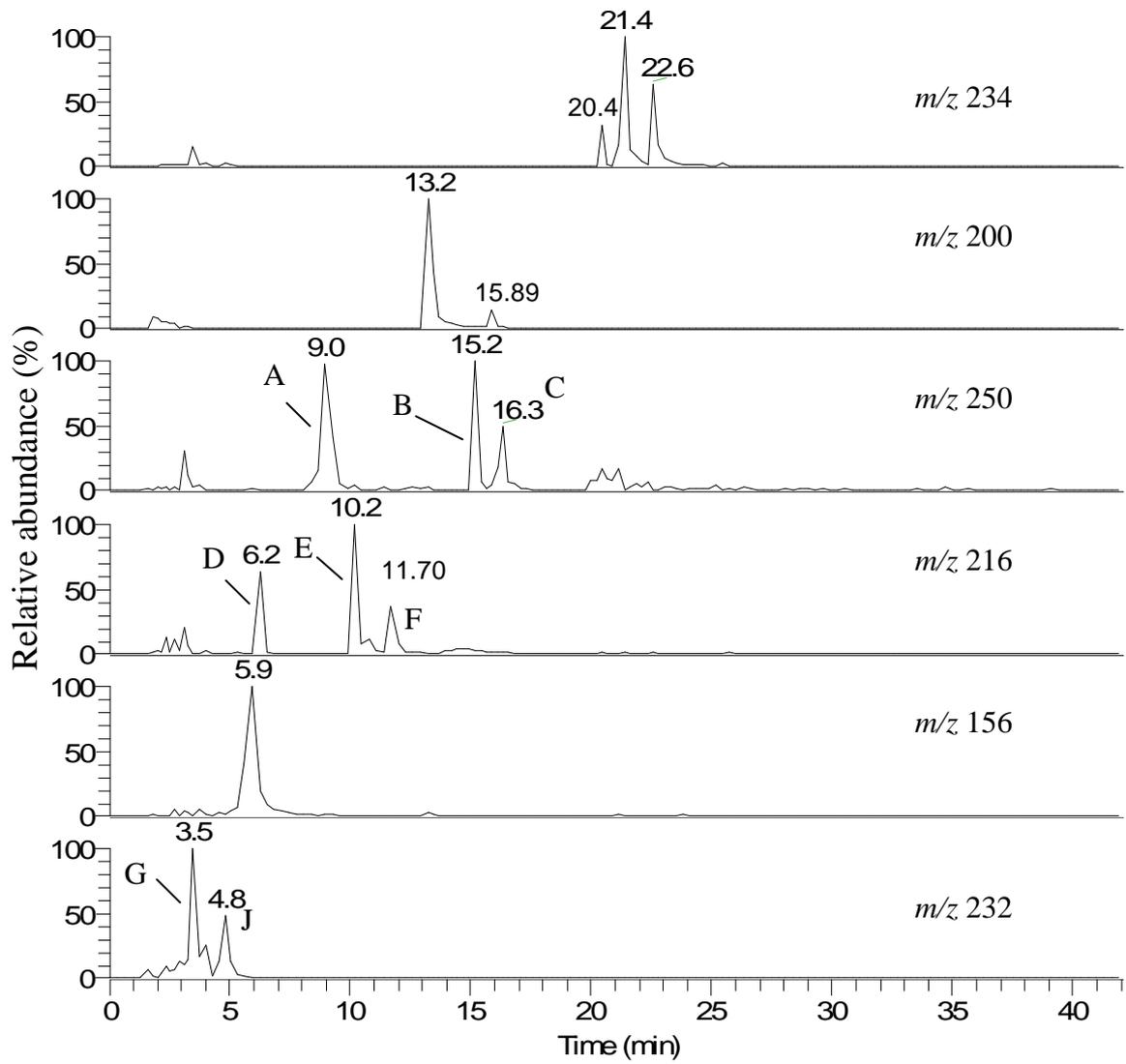
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463 **Figure 4**

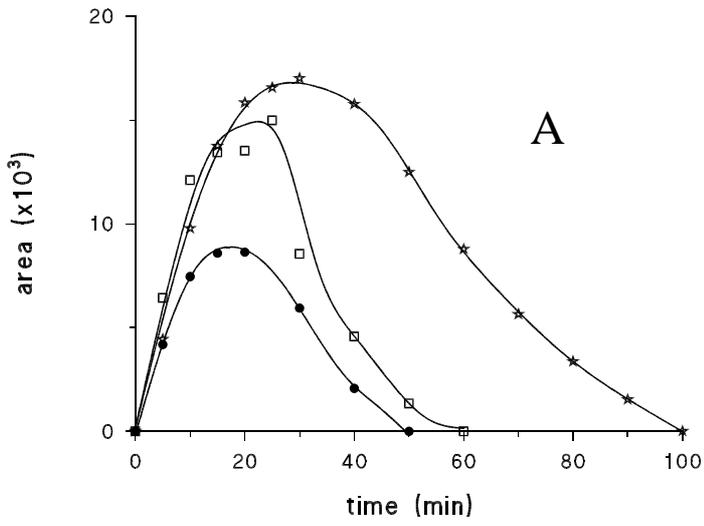
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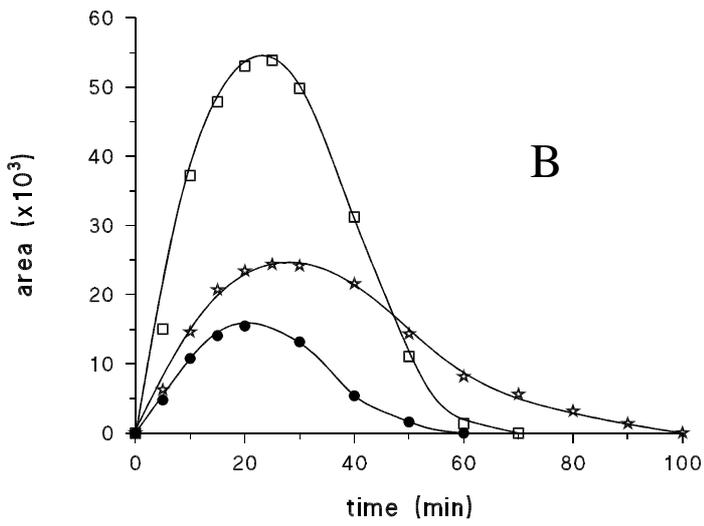
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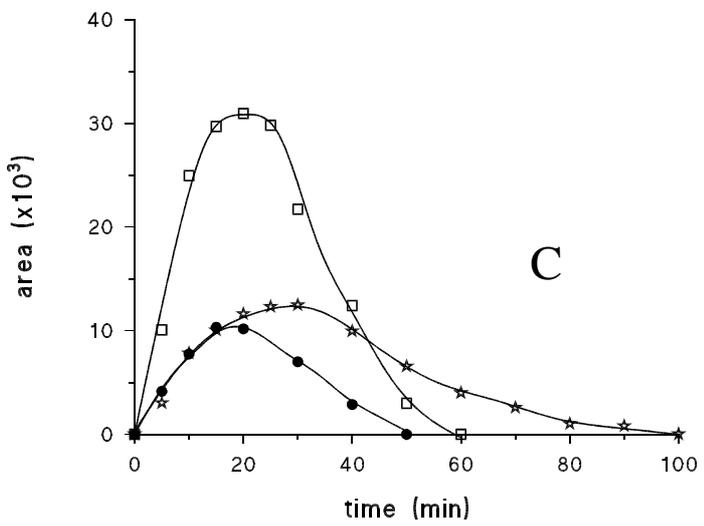
467 **Figure 5**



468



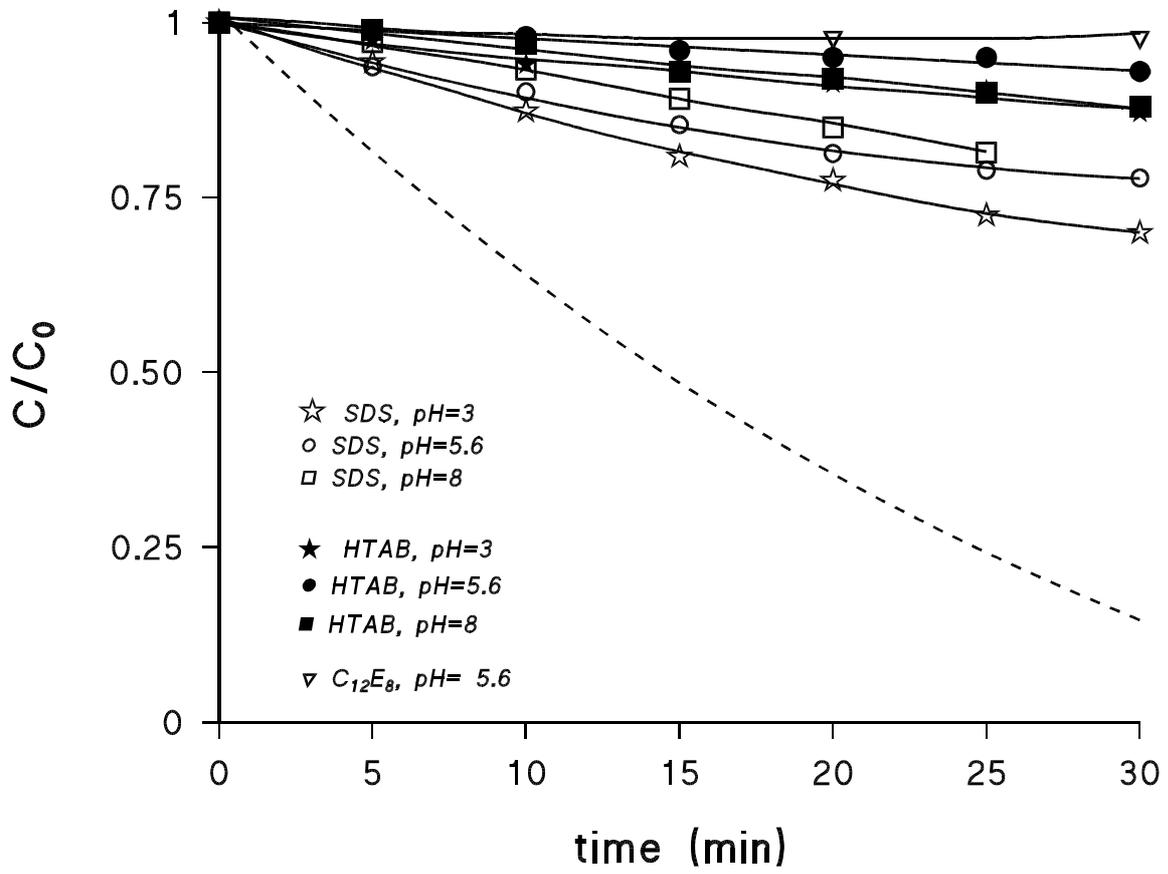
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471 **Figure 6**

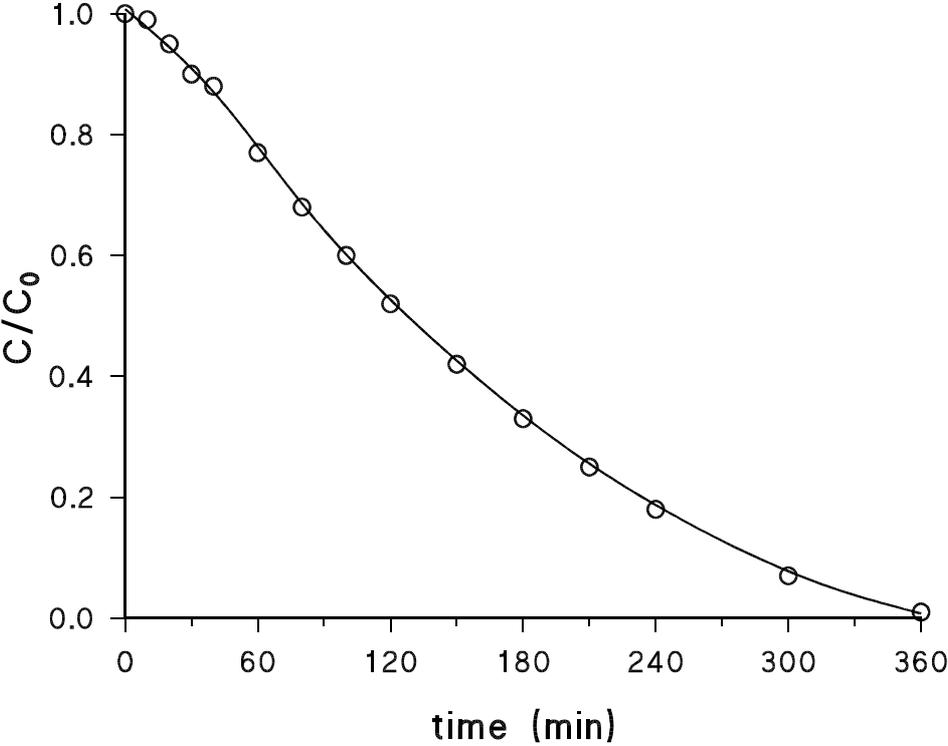
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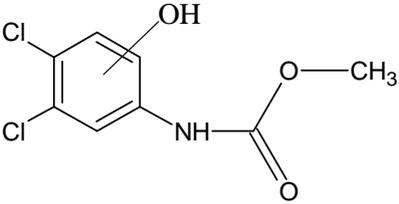
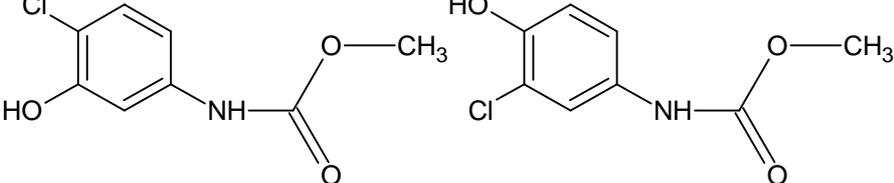
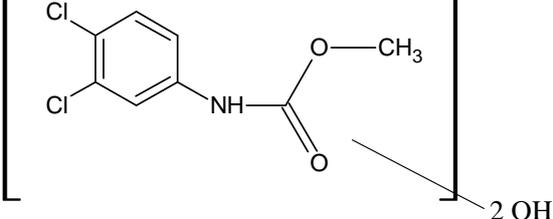
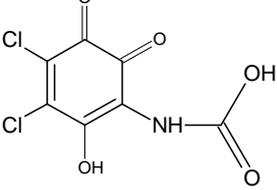
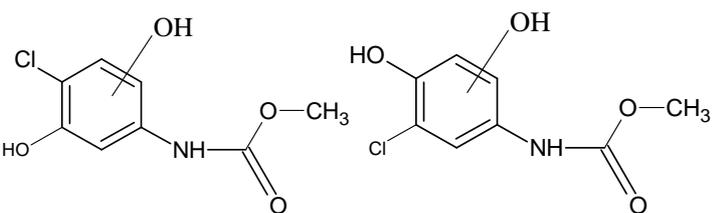
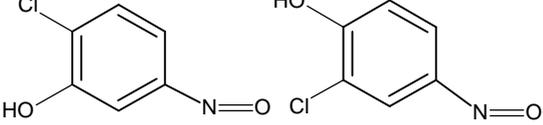
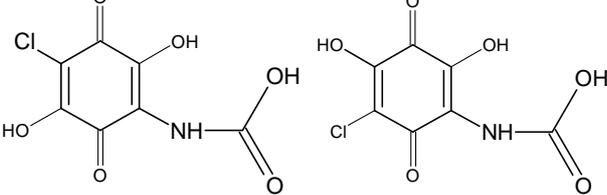
475 **Figure 7**



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477

478 **Table 1**

Precursor ion ( $m/z$ )	Possible structures of the transient intermediates	$t_R$ (min)
234		20.4 21.4 22.6
200		13.2 15.9
250		15.2 16.3
250		8.9
216		6.2 10.2 11.7
156		5.9
232		3.5 5.0

480 **Table 2** Percentage of substrate abatement after 120 min as a function of TiO<sub>2</sub> concentration.

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482

	<b>HTAB</b>			<b>SDS</b>		
TiO <sub>2</sub> conc. (mg L <sup>-1</sup> )	200	600	1000	200	600	1000
% Abatement	19	30	30	35	47	80

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