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This is the author's manuscript

Original Citation:

Availability:

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2 **Photocatalytic degradation of Bentazone in soil washing wastes containing**
3 **alkylpolyoxyethylene surfactants**

4
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10
11 **Abstract**

12 Three alkylpolyoxyethylene surfactants bearing the same hydrophobic chain and a different
13 number of oxyethylene groups were investigated as suitable candidates for the soil washing
14 treatment of contaminated soil samples containing bentazone. Comparable good recoveries of the
15 pesticide were obtained working with these surfactants. The photocatalytic treatment of the
16 collected washing wastes, performed in the presence of suspended TiO₂ particles under irradiation
17 with simulated sunlight, leads to the effective degradation of bentazone residues after a time
18 depending on the nature and concentration of the chosen amphiphile. Brij 35 was found to be the
19 best surfactant candidate, giving the faster abatement of the pesticide in the collected wastes. The
20 overall treatment time depends on the bentazone mineralization kinetics, markedly slow in the
21 presence of surfactants. Useful information about the photocatalytic degradation route was obtained
22 from the HPLC-MS analysis of transient intermediates formed in water.

23
24
25 **KEYWORDS**

26 Soil washing, Nonionic surfactants, Photocatalysis, Bentazone degradation.

1. INTRODUCTION

Contamination of soils due to the presence of pesticides is of great environmental concern since these generally toxic compounds can be adsorbed onto soil and the starting molecules and their degradation products can reach surface waters or percolate into ground waters. The remediation of pesticide-contaminated soils is thus necessary.

Among the proposed treatments, soil washing is an effective and diffuse remediation procedure (Castelo-Grande et al., 2010). It is largely based on the use of aqueous surfactant solutions and exploits both the solubilization capabilities of micelles towards the pollutants and the lowering of the interface tension between the washing solution and the soil phase (Gotlieb et al., 1993; Chu and Chan, 2003). The removal of a great variety of organic pollutants was reported using this approach (Desphande et al., 1999). Non-ionic surfactants are often the preferred candidates for soil washing due to their lower critical micellar concentration (CMC), which allows to reduce the amount of surfactant employed (Zheng and Obbard, 2002). Moreover, these amphiphiles exhibit lower interferences with ionic components present in soils, reducing the risks of surfactant precipitation.

An important problem arising from soil washing is that the washing wastes must be further disposed or treated before discharge or reuse. Heterogeneous photocatalysis can be proposed as suitable treatment since it allows the effective degradation of a wide variety of organic pollutants present in water and wastewater (Ollis et al., 1989; Bahnemann et al., 1994; Hoffmann et al., 1995; Fujishima et al., 2000; Malato et al., 2002).

The mechanism of photocatalysis was extensively investigated (Serpone and Pelizzetti, 1989; Ollis and Al-Ekabi, 1993; Hoffmann. et al., 1995; Malato et al., 2002). It is essentially based on the generation of electron-hole pairs at the semiconductors surface upon irradiation of the photocatalyst with light having energy higher than its band gap. The generated holes can oxidize adsorbed water or hydroxide ions originating strong oxidizing agents, in particular $\bullet\text{OH}$, which can attack the organic compounds leading to the formation of final non toxic or less toxic products. The complete mineralization of the starting molecules is in some cases obtained (Legrini et al., 1993). Reduction

54 reactions involving conduction band electrons can also occur during the process (Muneer and
55 Bahnemann, 2002).

56 When photocatalysis is applied to treat aqueous wastes, the presence of surfactants in such
57 wastes leads in most cases to a significant inhibition of pollutants degradation (Bianco Prevot et al.,
58 1999; Fabbri et al., 2004). This effect is not unexpected since the surfactant itself is degraded
59 (Hidaka et.al, 1990; Eng et.al., 2010) and can compete with the substrate for the active sites of the
60 semiconductor.

61 In the present work we investigated the treatment of soil samples containing bentazone (3-
62 isopropyl-1H-2,1,3-benzothiadiazin-4-(3H)-one-2,2-dioxide), a contact herbicide often used for
63 selective control of broadleaf weeds and seeds in beans, corn, peanuts and especially in rice fields.

64 Soil washing experiments were performed using nonionic surfactants pertaining to the same
65 class but having a different hydrophobic/hydrophilic balance in order to investigate the effect of this
66 parameter on the bentazone removal from the soil. The effect of amphiphiles structure on the
67 photocatalytic treatment of the wastes was evaluated by following both the kinetics of the pesticide
68 abatement and the formation and evolution of the degradation end products. In order to exclude the
69 accumulation of harmful products during the treatment, the nature and persistence of transient
70 intermediates arising from bentazone degradation were also investigated.

71

72 **2. MATERIALS AND METHODS**

73 **2.1 Reagents**

74 Polycrystalline TiO₂ P25 (from Degussa) was employed to perform all the photodegradation
75 tests. In order to remove organic impurities the semiconductor was washed with water and
76 irradiated in solarbox with simulated solar light for ca 12 h. The washed catalyst was then dried in
77 the oven at 80 °C. The TiO₂ dispersions were sonicated in water immediately before use.
78 Acetonitrile (Lichrosolv, Merck) was used as eluent.

79 Laboratory grade monodisperse poly(oxyethylene)₅dodecyl ether (C₁₂E₅) and
80 poly(oxyethylene)₈dodecyl ether (C₁₂E₈) were obtained from Nikkol; poly(oxyethylene)₂₃dodecyl
81 ether (Brij35), purity > 97%, was from Aldrich.

82 Acetone and n-hexane (from Aldrich) were used for the microwave-assisted exhaustive
83 extraction of the soil samples. Pure water was produced using a Milli-Q system (Millipore).
84 Bentazone (Pestanal, Sigma-Aldrich) was used throughout the work.

85 **2.2 Instruments**

86 The following instruments were used: HPLC Merck-Hitachi, equipped with L-6000 and L-6200
87 pumps and a UV-Vis L-4200 detector; microwave digestion system MARSX (from CEM
88 Corporation); double beam spectrophotometer CARY 100 SCAN (Varian); digital tensiometer
89 (K10, from Krüss); HPLC-MS ThermoFinnigan Surveyor MSQ, equipped with a photodiode array
90 detector, an electrospray ionization interface and a single quadrupole analyzer.

91 The irradiation experiments were carried out in Solarbox (CO.FO. MEGRA, Milan), where
92 stirred cylindrical closed cells (40 mm id; 25 mm high, made of Pyrex glass) were placed. A 1500
93 W Xenon lamp source, equipped with a 340 nm cut-off filter was used to simulate the AM1 solar
94 irradiation. The temperature within the solarbox was ca 55 °C.

95 **2.3 Experimental procedures**

96 **2.4 Preparation of the spiked soil samples**

97 A clean soil (sandy clay loam) with an organic carbon content of ca 2.5% and a water content of
98 ca 2.6% was used. Samples of the soil were dried at room temperature, grinded in a mortar and
99 sieved to < 2 mm to remove the bigger particles.

100 The soil was spiked according with the following procedure: 50 g of soil samples were treated
101 with 50 mL of an acetone solution containing the proper amount of dissolved bentazone. The slurry
102 was stirred for about 1 h and then allowed to stand at room temperature under hood with forced

103 ventilation, for ca 24 h. During this step the spiked soil was homogenized several times in order to
104 facilitate the complete evaporation of the organic solvent. The concentration of bentazone in soil
105 samples was selected in order to have a final pesticide concentration of ca 40 mg L⁻¹ in the washing
106 wastes. All the homogenized (clean and spiked) soil samples were kept in refrigerator.

107 **2.5 Microwave-assisted extraction of spiked soil samples**

108 Exhaustive extraction runs with organic solvents were performed prior to the soil washing
109 experiments for comparison purposes. The soil samples were treated following a standard EPA
110 procedure (method N.3546): ca 10 g of soil were weighed in the teflon microwave vessel and 25
111 mL of acetone/hexane (50:50, v/v) were added. The sample was then micro-waved at 110 °C and
112 689.4 kPa for 20 min. The liners were cooled to 25 °C and the suspensions were filtered through
113 0.45 µm Millex–LCR filters (Millipore). Acetone was finally replaced by acetonitrile before the
114 HPLC analysis.

115 **2.6 Soil washing runs**

116 Aqueous washing solutions containing C₁₂E₅, C₁₂E₈ and Brij 35 were prepared. The surfactant
117 concentrations were 5 and 10 mM. Soil washing experiments were typically performed on 2 g of
118 spiked soil to which were added 12.5 mL of the investigated surfactant solutions, placed in stopped
119 tubes in a rotatory mixer (rotation speed: ca 10 rpm, standard contact time: 5 h). The obtained soil
120 dispersions were centrifuged at 5000 rpm for 10 min, then aliquots of the supernatant solutions were
121 filtered through a 0.45 µm Millex–LCR hydrophilic PTFE membrane (Millipore). All the washing
122 tests were performed on relatively fresh (1 wk) spiked soil samples. The effect of ageing was not
123 investigated.

124 **2.7 Bentazone determination**

125 The bentazone determination was performed by HPLC on the filtered solutions, using a mobile
126 phase composed of a mixture of acetonitrile/water 50:50 (v/v), to which 0.3 mL L⁻¹ of phosphoric

127 acid (85%) were added. In order to avoid bentazone losses due to the pesticide adsorption onto the
128 semiconductor, an equal volume of acetonitrile was added to the aliquots of irradiated solutions
129 sampled, then the mixtures were filtered through a 0.45 μm Anotop 25 Plus membrane (Whatman)
130 and injected in the column.

131 A 100 RP-C18 column (Lichrospher, 4 mm id x 125 mm long, 5 μm particle size) was used.
132 Isocratic elutions were performed at a flow rate of 1 mL min^{-1} . The detector wavelength was 225
133 nm.

134 **2.8 Analysis of the ionic end products**

135 The ionic end products were analysed using suppressed IC, employing a Dionex DX instrument
136 equipped with an ED 40 conductimeter detector (Dionex). Nitrate was determined using an AS9HC
137 column (4 mm id x 200 mm long) from Dionex. Elution with a solution of K_2CO_3 12 mM and
138 NaHCO_3 5 mM (50:50 v/v) was performed with a flow rate of 1 mL min^{-1} . The determination of
139 ammonium was performed using a CS12A column (4 mm id x 200 mm long), from Dionex.
140 Methanesulphonic acid 25 mM was used as eluent at flow rate of 1 mL min^{-1} .

141 **2.9 LC-MS analysis of transient organic intermediates formed in water**

142 The MS operational parameters were: spray voltage 3 kV, temperature of the heated capillary
143 300 $^\circ\text{C}$ and cone voltage 90 kV. Mass spectra were collected in full scan negative mode in the range
144 50–900 m/z .

145 The chromatographic separations were conducted using a Lichrosphere 100 RP-18e (250 mm x 4
146 mm, particle size 10 μm). An aqueous solution of acetic acid 0.5% (v/v) and acetonitrile (50:50 v/v)
147 was used as eluent under isocratic condition, at a flow rate of 0.5 mL min^{-1} .

148 **3. RESULTS AND DISCUSSION**

149 **3.1 Soil washing experiments**

150 The pesticide recoveries obtained after washing the spiked soil samples with 5 and 10 mM
151 surfactant solutions were evaluated and compared with those obtained using the microwave-assisted
152 extraction. Table 1 reports the obtained recoveries and the corresponding standard deviation values
153 (from five replicated extractions). The reported percent extractions of the washing solutions were
154 calculated with respect to the recovery obtained using the exhaustive extraction with acetone/n-
155 hexane.

156 It can be seen that Brij 35 and C₁₂E₅ show comparable extraction efficiencies, whereas C₁₂E₈
157 gives the best results. Lower recoveries were obtained, as expected, by decreasing the surfactant
158 concentration, although there is not a strictly proportional relationship.

159 Taking into account that a more or less significant surfactant adsorption onto soil usually occurs
160 (Shen, 2000) and that the solubilization power of the washing solutions is strictly related to the
161 presence of micelles, the existence of these aggregates after the washing must be confirmed. The
162 determination of the surface tension of the soil washing extracts (Chu and Chan, 2003) allows to
163 verify this condition.

164 The CMCs were determined in the washing wastes obtained using 10 mM surfactant solutions,
165 filtered through 0.45 µm cellulosic filters, by measuring the surface tension as a function of the
166 washing waste dilution. The measured CMC values were 0.4 mM for Brij 35, 1.1 mM for C₁₂E₈
167 and 1.2 mM for C₁₂E₅. Since the dilutions of the washing wastes necessary to reach the
168 corresponding CMCs were 1:25 for Brij 35, 1:9 for C₁₂E₈ and 1:8 for C₁₂E₅, respectively, this
169 confirms that in all the cases the washing solutions were well above the CMC.

170

171 3.2 Photocatalytic degradation of bentazone

172 Preliminary photocatalytic runs were performed in order to evaluate the surfactant influence on
173 the kinetics of the primary process. The pollutant abatement in micellar aqueous solutions
174 containing 10 mg L⁻¹ of bentazone and 100 mg L⁻¹ of TiO₂ was typically monitored in these
175 experiments. Successive degradation experiments were performed on the soil washing extracts
176 containing ca 40 mg L⁻¹ of bentazone and 500-1500 mg L⁻¹ of suspended TiO₂. For comparison
177 purposes the pesticide degradation was also investigated in pure water, under the same experimental
178 conditions.

179 Figure 1 shows the kinetic profiles concerning both series of experiments, obtained by plotting
180 the relative decrease of bentazone concentration as a function of irradiation time; C₀ indicates the
181 initial pesticide concentration before to start the irradiation. Although the pesticide abatement obeys
182 to a saturation-type kinetics and the fit of experimental data follows well a pseudo-first order kinetic
183 trend, the validity of a single kinetic model cannot be generally invoked (Emeline et al., 2005).

184 Table 2 reports the observed degradation rate constants, k_{obs}, calculated from the plots of
185 ln(C/C₀) vs. time, which were found to be linear up to ca 70% of bentazone degradation. Each k_{obs}
186 value represents the mean of three independent measurements.

187 As expected, the presence of surfactants leads to a significant inhibition of the pesticide degradation
188 in respect to that observed in pure water. The more hydrophilic surfactant Brij 35 shows the lower
189 inhibition effect, which could be explained considering that the bigger dimensions of its hydrated
190 polar head reduce the surfactant adsorption on the TiO₂ surface and strongly limit the formation of
191 admicellar structures. In fact, the interactions between the adjacent surfactant tails are hindered
192 (Koopal, 2003) and the competition between surfactant and substrate molecules for the occupation
193 of the active sites on the catalyst surface is strongly reduced. A contribution to the inhibition effects
194 arising from the organic soil components, in particular from humic matter, was observed in previous
195 studies (Minero et al., 1999, Davezza et al., 2011) and must be also considered.

196 Since the measured pH of the washing solutions was in the range 6.5-6.8, around the isoelectric
197 point of the employed semiconductor (Lee et al., 2003) and the reported pK_a of bentazone is 3.2
198 (Abernathy and Wax, 1973), the contribution of repulsive effects between the pesticide and TiO_2 to
199 the observed degradation inhibition can be neglected.

200 The observation of the HPLC pattern of the irradiated solutions at low irradiation time (10 min)
201 reveals that the number of peaks and their corresponding retention times (t_R) are the same in pure
202 water and in surfactant-containing solutions. This indicates that the same transient intermediates are
203 formed in both systems, suggesting that the presence of amphiphiles alters the kinetics but not the
204 degradation mechanism.

205 **3.3 Formation and evolution of degradation end products**

206 Taking into account the favourable performances of Brij 35 10 mM, the kinetics of end products
207 formation was investigated in water and in the presence of this surfactant. Since the TOC analysis is
208 precluded due to the presence of an excess of degradable surfactant, the determination of the
209 mineralization end-products concerned ammonium, nitrate and sulphate. The analysis was
210 performed on aqueous solutions containing 40 mg L^{-1} of bentazone and different concentrations
211 (500 and 1500 mg L^{-1}) of TiO_2 . The obtained results confirm that the presence of Brij 35 also
212 inhibits significantly the formation of these ionic species.

213 The kinetic profiles depicted in Fig. 2a were obtained working in water with the higher
214 semiconductor concentration. The evolution of bentazone abatement, followed under the same
215 experimental conditions, is also shown. In Fig. 2b the inhibitory effect due to the presence of Brij
216 35 10 mM on the kinetics of end-products formation is evidenced. Lower degradation rates, but
217 similar kinetic profiles, were obtained working with 500 mg L^{-1} of TiO_2 .

218 In the absence of surfactants the complete disappearance of bentazone was followed by the later
219 stoichiometric formation of sulphate ions, completed after ca 3 h. In the presence of Brij 35 the

220 stoichiometric formation of sulphate was not observed even after 4 h irradiation (formation of ca
221 60% of SO_4^-). Only after longer irradiation times (> 6 h) the sulphate recovery becomes complete.

222 The mineralization of the organic nitrogen generally leads to the formation of nitrate, nitrite
223 (only in certain cases) and ammonium ions (or ammonia) in different ratios (Low et al., 1991;
224 Maillard-Dupuy et al., 1994). When nitrate and ammonium are the end products found, their
225 relative concentrations in turn depend on experimental parameters, such as the irradiation time and
226 the oxygen concentration (Pramauro et al., 1997). In the present work the stoichiometric
227 mineralization of organic nitrogen into NO_3^- and NH_4^+ was observed after ca 2 h in experiments
228 performed in water, whereas the sum of both species becomes nearly stoichiometric ($> \text{ca } 95\%$)
229 after 4 h irradiation in the presence of Brij 35. The nitrate concentration remains practically constant
230 after 1 h irradiation and represents ca 10% of the stoichiometric nitrogen, whereas the increase of
231 ammonium concentration stops after ca 3 h irradiation.

232 The kinetics of formation of the end-products should be carefully considered in order to select
233 the proper irradiation time since residual organic products arising from bentazone degradation are
234 still present after the complete disappearance of the starting pesticide. No traces of aromatic
235 residues have been detected in the wastes after ca 2 h irradiation on the basis of the negligible
236 absorbance of the solutions observed in the wavelength range 220-280 nm, however the presence of
237 organic compounds arising from the aromatic ring breaking cannot be excluded.

238 **3.4 Identification of the main transient intermediates formed in water**

239 Some studies concerning the reaction products generated from the bentazone photolysis in water,
240 soil and plants have been reported (Wagner et al., 1996; Burrows et al., 2002), but a lack of
241 information exists concerning the identification of the transient intermediates originated during the
242 TiO_2 -mediated photocatalytic degradation of this pesticide. In order to obtain information about the
243 mechanism of bentazone degradation, some photocatalytic runs were performed in water on
244 dispersions containing 40 mg L^{-1} of herbicide and 1500 mg L^{-1} of TiO_2 .

245 The analysis of the intermediates formed during the initial steps of the process was performed by
246 HPLC-DAD-MS. Figure 3 shows the digital reconstruction of the chromatographic pattern of the
247 solutions after 10 min irradiation, time at which the intermediates are more abundant and better
248 evidenced.

249 The LC-MS analysis revealed the presence of three intermediates at different t_R : all of them have
250 an aromatic structure, as confirmed by the diode-array analysis of the corresponding peaks. Table 3
251 summarizes the proposed structures: their identification was conducted on the basis of the
252 corresponding m/z values and their mass fragmentation spectra, taking into account the intrinsic
253 limits of the LC-MS technique.

254 The fragmentation pathway of bentazone leads to the formation of fragments with m/z 197 and
255 175; the first ion results from the loss of the isopropyl group and the second from sulphur dioxide
256 with subsequent ring closure. The loss of both groups produces the fragment with m/z 132.

257 Two peaks have been found when extracting from the total ionic current the m/z 255: this value
258 is higher than that of the parent molecule and consistent with the hypothesis of formation of mono-
259 hydroxylated products. However the fragmentation pattern of these two molecules allowed us to
260 pinpoint the different position of the hydroxyl group.

261 The mass spectrum of compound A ($t_R = 4.8$ min) shows the presence of signals at m/z 197, 191,
262 and 132. The fragment with m/z 197 results from the loss of hydroxylated isopropyl group, likewise
263 the fragment with m/z 191 derives from the loss of the sulphur dioxide and the subsequent ring
264 closure. The loss of either groups was hypothesised for the fragment with m/z 132. Since the
265 fragment ions having m/z 197 and 132 are also observed in the case of the bentazone molecule, this
266 product could be attributed to the hydroxylated bentazone on one of the two methyl groups of the
267 isopropyl substituent.

268 The second intermediate with m/z 255 (compound B, $t_R = 7.3$ min) has a fragmentation pattern
269 consisting of fragments at m/z 191, 148 and 108. The fragment at m/z 191 corresponds to a loss of
270 SO_2 , like to the previous isomer. The fragments at m/z 148 and 108 are peculiar of the ring moiety

271 hydroxylation: the first fragment derives from the loss of the isopropyl and sulphur dioxide groups
272 and a further fragmentation of the heteroatomic ring gives a signal at m/z 108. These hypotheses are
273 sustained by the literature data concerning photolytic experiments (Laganà et al., 2002; Peschka et
274 al., 2007; Eyheraguibel et al., 2009) where the similar fragmentation routes were described and
275 attributed to the same compounds. The third intermediate found (compound C, $t_R = 4.3$ min) having
276 m/z 253 is probably originated from the rapid oxidation of compound B, having the OH group on
277 the alkylic chain.

278 No significant information has been obtained from the MS spectrum, only more detailed MS/MS
279 analysis could give structural clarification. Nevertheless, the methyl group oxidation to form
280 alcohol then aldehyde cannot be excluded since analogous observations are present in literature for
281 other aromatic molecules having methyl substituents (Fabbri et al., 2006).

282 The HPLC-UV analysis confirmed that the three observed intermediates are present in the initial
283 steps of the photocatalytic degradation process, together with the substrate, but they further
284 disappear after ca 30 min irradiation, time after which bentazone is no more present in the reaction
285 medium (see Fig. 4).

286 Considering the area values of intermediates it is possible to hypothesize the oxidation of the
287 hydroxyl group of compound A, which leads to the formation of the aldehydic structure of
288 compound C, followed by a rapid degradation occurring after ca 10 min irradiation. A comparable
289 persistence of the three intermediates is observed and for all of them the maximum amount is
290 reached after ca 10 min irradiation, then they completely disappear after 30 minutes.

291 The examination of the HPLC patterns confirms that both the formation and degradation of
292 intermediates A, B and C are much slower in the presence of Brij 35, but no traces of such
293 compounds were evidenced in pre-concentrated washing wastes after ca 2 h irradiation.

294

295 **4. CONCLUSIONS**

296 The obtained results suggest that the investigated aqueous surfactant solutions can effectively
297 remove the residues of bentazone from the contaminated soil samples. If the photocatalytic
298 treatment of the washing wastes is examined, Brij 35 shows the lower inhibition effects on the
299 pesticide abatement and can be proposed as a suitable candidate for soil washing. Under the
300 investigated conditions, working with 1500 mg L^{-1} of suspended TiO_2 , bentazone can be completely
301 removed from the wastes after less than 1 h irradiation, whereas no traces of aromatic residues were
302 found after ca 2 h.

303 The complete mineralization of the pesticide is significantly slower, being the quantitative
304 transformation of the organic nitrogen achieved only after ca 4 h. Even longer treatment times
305 (around 6 h) are necessary in order to obtain the stoichiometric formation of sulphate.

306 The HPLC-MS analysis performed on irradiated aqueous dispersions reveals the presence of
307 three main transient intermediates, two of them also found in photolytic experiments reported in the
308 literature. These compounds, in turn completely degraded, are less persistent than the starting
309 pesticide.

310

311 **ACKNOWLEDGEMENT**

312 Finacial support from MIUR (Rome) is gratefully acknowledged.

313

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401

402

403 **Table 1.** Extraction yields obtained in the soil washing experiments.
404
405

SOIL WASHING SOLUTIONS	% Recovery	Standard Deviation
Acetone/n-Hexane	97	4
H ₂ O	60	5
Brij 35 5 mM	86	2
C ₁₂ E ₅ 5 mM	87	5
C ₁₂ E ₈ 5 mM	95	4
Brij 35 10 mM	95	4
C ₁₂ E ₅ 10 mM	95	5
C ₁₂ E ₈ 10 mM	100	3

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407 **Table 2.** Observed reaction rates measured in the photocatalytic experiments

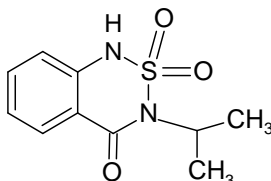
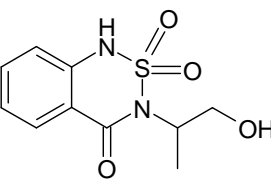
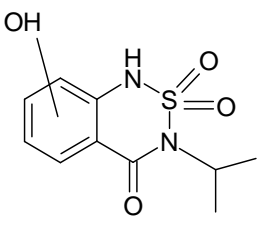
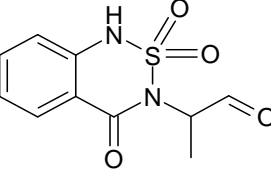
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Aqueous surfactant solutions (10 mg L ⁻¹ bentazone, TiO ₂ 100 mg L ⁻¹)	k_{obs} (min⁻¹)
H ₂ O	1.1 x 10 ⁻¹
Brij 35 10 mM	4.1 x 10 ⁻²
C ₁₂ E ₅ 10 mM	1.4 x 10 ⁻³
C ₁₂ E ₈ 10 mM	2.3 x 10 ⁻²
Soil washing extracts (40 mg L ⁻¹ bentazone)	
H ₂ O , TiO ₂ 500 mg L ⁻¹	5.4 x 10 ⁻²
H ₂ O , TiO ₂ 1500 mg L ⁻¹	1.5 x 10 ⁻¹
Brij 35 10 mM, TiO ₂ 500 mg L ⁻¹	9.4 x 10 ⁻³
C ₁₂ E ₅ 10 mM, TiO ₂ 500 mg L ⁻¹	8.9 x 10 ⁻⁴
C ₁₂ E ₈ 10 mM, TiO ₂ 500 mg L ⁻¹	8.9 x 10 ⁻³
Brij 35 10 mM, TiO ₂ 1500 mg L ⁻¹	1.8 x 10 ⁻²
C ₁₂ E ₅ 10 mM, TiO ₂ 1500 mg L ⁻¹	1.7 x 10 ⁻³
C ₁₂ E ₈ 10 mM, TiO ₂ 1500 mg L ⁻¹	1.1 x 10 ⁻²

409

410 **Table 3** Intermediates found in the earlier steps of bentazone degradation. Intermediate compounds
 411 formed from bentazone transformation and detected by HPLC/MS. In round brackets are shown the
 412 relative ion abundances.

413

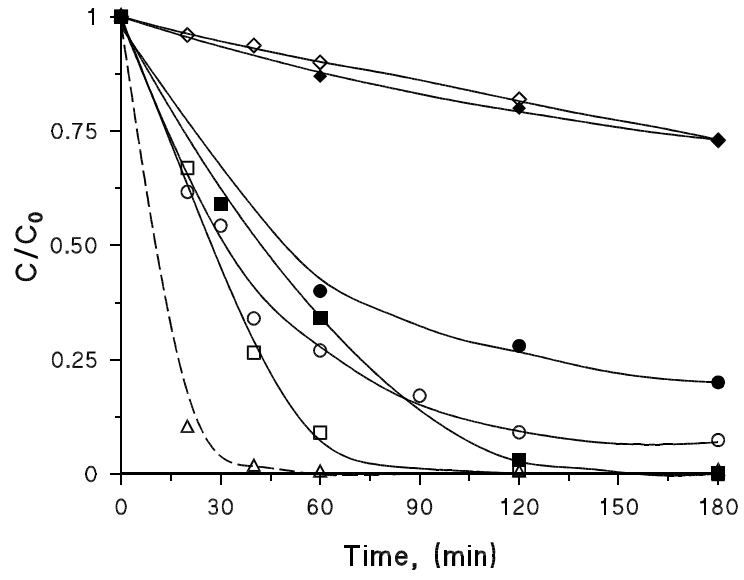
(<i>m/z</i>)	Possible structures of the transient intermediates	<i>t_R</i> (min)	Product ions
239	 <p>The structure shows a benzimidazole ring system with a sulfonamide group (-NH-SO₂-) at the 2-position and a dimethylamino group (-N(CH₃)₂) at the 4-position.</p>	10.1	239 (100), 197(21), 175(17), 132 (22)
255 A	 <p>The structure shows a benzimidazole ring system with a sulfonamide group (-NH-SO₂-) at the 2-position and an isobutyl group (-CH₂-CH(CH₃)-CH₂-OH) at the 4-position.</p>	4.8	255 (100), 197 (17), 191 (27), 132 (16)
255 B	 <p>The structure shows a benzimidazole ring system with a sulfonamide group (-NH-SO₂-) at the 2-position and a hydroxyisobutyl group (-CH₂-CH(CH₃)-CH₂-OH) at the 4-position. A hydroxyl group (-OH) is also attached to the benzimidazole ring at the 5-position.</p>	7.3	255 (100), 191 (45), 148 (15), 108 (7)
253 C	 <p>The structure shows a benzimidazole ring system with a sulfonamide group (-NH-SO₂-) at the 2-position and an isobutyraldehyde group (-CH₂-CH(CH₃)-CHO) at the 4-position.</p>	4.3	253 (100)

414

415

416 **FIGURE 1**

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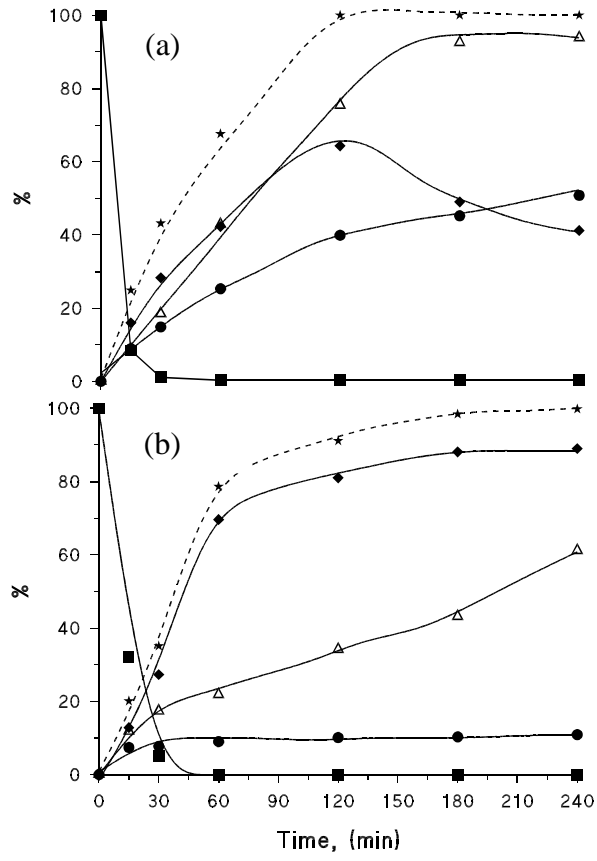


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420 **FIGURE 2**

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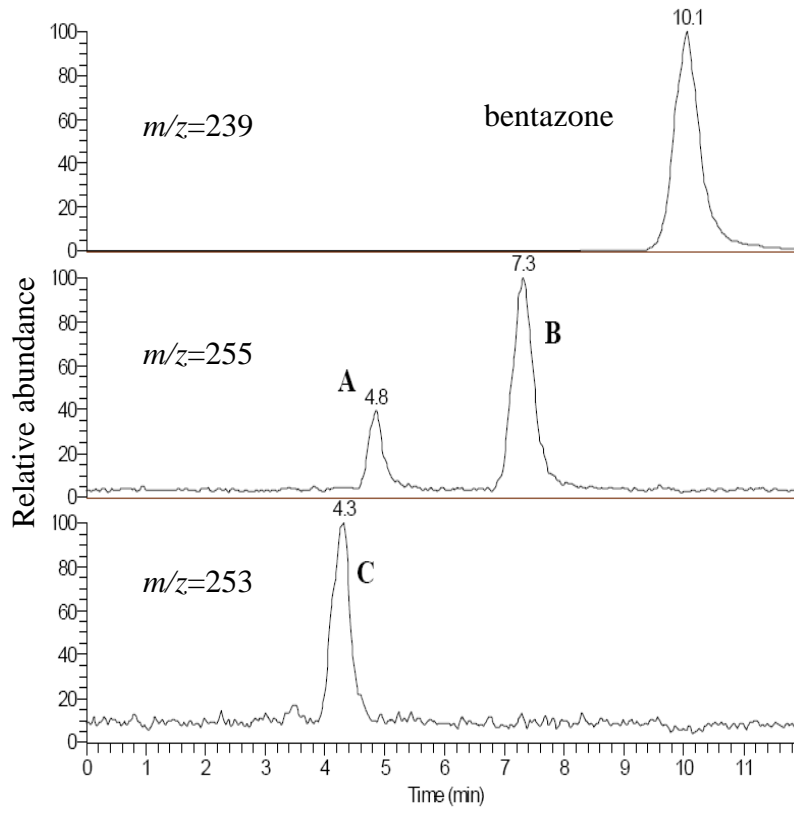
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428 **FIGURE 3**

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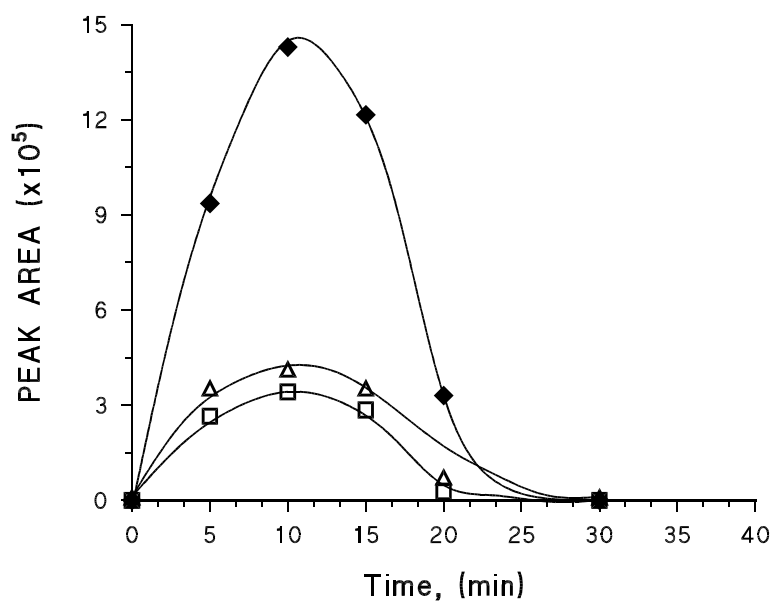
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432 **FIGURE 4**

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