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Photocatalytic degradation of Bentazone in soil washing wastes containing alkylpolyoxyethylene surfactants

M. Davezza, D. Fabbri, E. Pramauro*, A. Bianco Prevot
Dipartimento di Chimica Analitica – Università di Torino - 10125 – Torino, Italy
Tel +39 0116707631 Fax +39 0116707615
edmondo.pramauro@unito.it

Abstract

Three alkylpolyoxyethylene surfactants bearing the same hydrophobic chain and a different number of oxyethylene groups were investigated as suitable candidates for the soil washing treatment of contaminated soil samples containing bentazone. Comparable good recoveries of the pesticide were obtained working with these surfactants. The photocatalytic treatment of the collected washing wastes, performed in the presence of suspended TiO_2 particles under irradiation with simulated sunlight, leads to the effective degradation of bentazone residues after a time depending on the nature and concentration of the chosen amphiphile. Brij 35 was found to be the best surfactant candidate, giving the faster abatement of the pesticide in the collected wastes. The overall treatment time depends on the bentazone mineralization kinetics, markedly slow in the presence of surfactants. Useful information about the photocatalytic degradation route was obtained from the HPLC-MS analysis of transient intermediates formed in water.

KEYWORDS

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 $^{\bullet}OH$, 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 reactions involving conduction band electrons can also occur during the process (Muneer and Bahnemann, 2002).

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

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

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

2. MATERIALS AND METHODS

2.1 Reagents

Polycrystalline TiO_2 P25 (from Degussa) was employed to perform all the photodegradation tests. In order to remove organic impurities the semiconductor was washed with water and irradiated in solarbox with simulated solar light for ca 12 h. The washed catalyst was then dried in the oven at 80 °C. The TiO_2 dispersions were sonicated in water immediately before use. Acetonitrile (Lichrosolv, Merck) was used as eluent.

Laboratory grade monodisperse poly(oxyethylene)$_5$dodecyl ether ($C_{12}E_5$) and poly(oxyethylene)$_8$dodecyl ether ($C_{12}E_8$) were obtained from Nikkol; poly(oxyethylene)$_{23}$dodecyl ether (Brij35), purity > 97%, was from Aldrich.

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

2.2 Instruments

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

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

2.3 Experimental procedures

2.4 Preparation of the spiked soil samples

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

The soil was spiked according with the following procedure: 50 g of soil samples were treated with 50 mL of an acetone solution containing the proper amount of dissolved bentazone. The slurry was stirred for about 1 h and then allowed to stand at room temperature under hood with forced ventilation, for ca 24 h. During this step the spiked soil was homogeinized several times in order to facilitate the complete evaporation of the organic solvent. The concentration of bentazone in soil samples was selected in order to have a final pesticide concentration of ca 40 mg L^{-1} in the washing wastes. All the homogenized (clean and spiked) soil samples were kept in refrigerator.

2.5 Microwave-assisted extraction of spiked soil samples

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

2.6 Soil washing runs

Aqueous washing solutions containing $C_{12}E_5$, $C_{12}E_8$ and Brij 35 were prepared. The surfactant concentrations were 5 and 10 mM. Soil washing experiments were typically performed on 2 g of spiked soil to which were added 12.5 mL of the investigated surfactant solutions, placed in stopped tubes in a rotatory mixer (rotation speed: ca 10 rpm, standard contact time: 5 h). The obtained soil dispersions were centrifuged at 5000 rpm for 10 min, then aliquots of the supernatant solutions were filtered through a 0.45 μm Millex–LCR hydrophilic PTFE membrane (Millipore). All the washing tests were performed on relatively fresh (1 wk) spiked soil samples. The effect of ageing was not investigated.

2.7 Bentazone determination

The bentazone determination was performed by HPLC on the filtered solutions, using a mobile phase composed of a mixture of acetonitrile/water 50:50 (v/v), to which 0.3 mL L^{-1} of phosphoric acid (85%) were added. In order to avoid bentazone losses due to the pesticide adsorption onto the semiconductor, an equal volume of acetonitrile was added to the aliquots of irradiated solutions sampled, then the mixtures were filtered through a 0.45 μm Anotop 25 Plus membrane (Whatman) and injected in the column.

A 100 RP-C18 column (Lichrospher, 4 mm idx125 mm long, 5 μm particle size) was used. Isocratic elutions were performed at a flow rate of 1 mL min^{-1}. The detector wavelength was 225 nm.

2.8 Analysis of the ionic end products

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

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

The MS operational parameters were: spray voltage 3 kV, temperature of the heated capillary 300 °C and cone voltage 90 kV. Mass spectra were collected in full scan negative mode in the range 50–900 *m/z*.

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

3. RESULTS AND DISCUSSION

3.1 Soil washing experiments

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

It can be seen that Brij 35 and $C_{12}E_5$ show comparable extraction efficiencies, whereas $C_{12}E_8$ gives the best results. Lower recoveries were obtained, as expected, by decreasing the surfactant concentration, although there is not a strictly proportional relationship.

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

The CMCs were determined in the washing wastes obtained using 10 mM surfactant solutions, filtered through 0.45 μm cellulosic filters, by measuring the surface tension as a function of the washing waste dilution. The measured CMC values were 0.4 mM for Brij 35, 1.1 mM for $C_{12}E_8$ and 1.2 mM for $C_{12}E_5$. Since the dilutions of the washing wastes necessary to reach the corresponding CMCs were 1:25 for Brij 35, 1:9 for $C_{12}E_8$ and 1:8 for $C_{12}E_5$, respectively, this confirms that in all the cases the washing solutions were well above the CMC.

3.2 Photocatalytic degradation of bentazone

Preliminary photocatalytic runs were performed in order to evaluate the surfactant influence on the kinetics of the primary process. The pollutant abatement in micellar aqueous solutions containing 10 mg L^{-1} of bentazone and 100 mg L^{-1} of TiO_2 was typically monitored in these experiments. Successive degradation experiments were performed on the soil washing extracts containing ca 40 mg L^{-1} of bentazone and 500-1500 mg L^{-1} of suspended TiO_2. For comparison purposes the pesticide degradation was also investigated in pure water, under the same experimental conditions.

Figure 1 shows the kinetic profiles concerning both series of experiments, obtained by plotting the relative decrease of bentazone concentration as a function of irradiation time; C_0 indicates the initial pesticide concentration before to start the irradiation. Although the pesticide abatement obeys to a saturation-type kinetics and the fit of experimental data follows well a pseudo-first order kinetic trend, the validity of a single kinetic model cannot be generally invoked (Emeline et al., 2005).

Table 2 reports the observed degradation rate constants, k_{obs}, calculated from the plots of $\ln(C/C_0)$ vs. time, which were found to be linear up to ca 70% of bentazone degradation. Each k_{obs} value represents the mean of three independent measurements.

As expected, the presence of surfactants leads to a significant inhibition of the pesticide degradation in respect to that observed in pure water. The more hydrophilic surfactant Brij 35 shows the lower inhibition effect, which could be explained considering that the bigger dimensions of its hydrated polar head reduce the surfactant adsorption on the TiO_2 surface and strongly limit the formation of admicellar structures. In fact, the interactions between the adjacent surfactant tails are hindered (Koopal, 2003) and the competition between surfactant and substrate molecules for the occupation of the active sites on the catalyst surface is strongly reduced. A contribution to the inhibition effects arising from the organic soil components, in particular from humic matter, was observed in previous studies (Minero et al., 1999, Davezza et al., 2011) and must be also considered.

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

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

3.3 Formation and evolution of degradation end products

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

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

In the absence of surfactants the complete disappearance of bentazone was followed by the later stoichiometric formation of sulphate ions, completed after ca 3 h. In the presence of Brij 35 the stoichiometric formation of sulphate was not observed even after 4 h irradiation (formation of ca 60% of $SO_4^{=}$). Only after longer irradiation times (> 6 h) the sulphate recovery becomes complete.

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

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

3.4 Identification of the main transient intermediates formed in water

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

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

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

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

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

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

The second intermediate with *m/z* 255 (compound B, t_R = 7.3 min) has a fragmentation pattern consisting of fragments at *m/z* 191, 148 and 108. The fragment at *m/z* 191 corresponds to a loss of SO_2, like to the previous isomer. The fragments at *m/z* 148 and 108 are peculiar of the ring moiety hydroxylation: the first fragment derives from the loss of the isopropyl and sulphur dioxide groups and a further fragmentation of the heteroatomic ring gives a signal at *m/z* 108. These hypotheses are sustained by the literature data concerning photolytic experiments (Laganà et al., 2002; Peschka et al., 2007; Eyheraguibel et al., 2009) where the similar fragmentation routes were described and attributed to the same compounds. The third intermediate found (compound C, t_R = 4.3 min) having *m/z* 253 is probably originated from the rapid oxidation of compound B, having the OH group on the alkylic chain.

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

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

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

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

4. CONCLUSIONS

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

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

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

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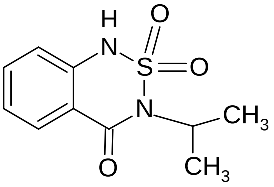
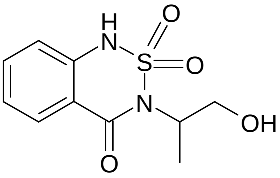
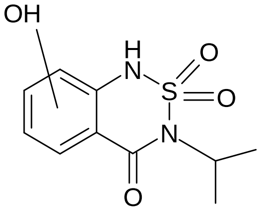
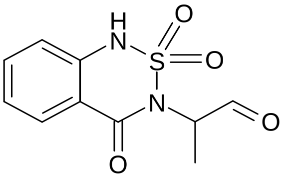
Table 1. Extraction yields obtained in the soil washing experiments.

SOIL WASHING SOLUTIONS	% Recovery	Standard Deviation
Acetone/n-Hexane	**97**	**4**
H_2O	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

Table 2. Observed reaction rates measured in the photocatalytic experiments

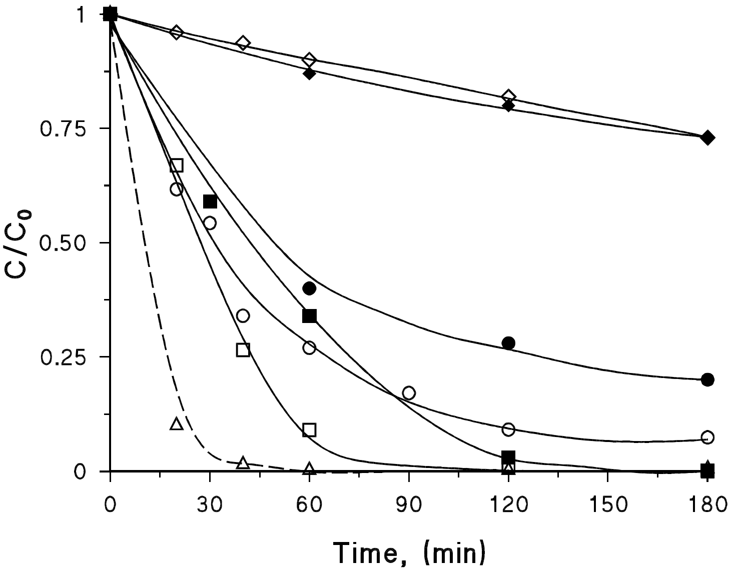
Aqueous surfactant solutions (10 mg L^{-1} bentazone, TiO_2 100 mg L^{-1})	**k_{obs} (min^{-1})**
H_2O	1.1 x 10^{-1}
Brij 35 10 mM	4.1 x 10^{-2}
$C_{12}E_5$ 10 mM	1.4 x 10^{-3}
$C_{12}E_8$ 10 mM	2.3 x 10^{-2}
Soil washing extracts (40 mg L^{-1} bentazone)	**k_{obs} (min^{-1})**
H_2O , TiO_2 500 mg L^{-1}	5.4 x 10^{-2}
H_2O , 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}

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

(*m/z*)	**Possible structures of the transient intermediates**	**t_R (min)**	**Product ions**
239		10.1	239 (100), 197(21), 175(17), 132 (22)
255 A		4.8	255 (100), 197 (17), 191 (27), 132 (16)
255 B		7.3	255 (100), 191 (45), 148 (15), 108 (7)
253 C		4.3	253 (100)

416 **FIGURE 1**

417



418

419

FIGURE 2

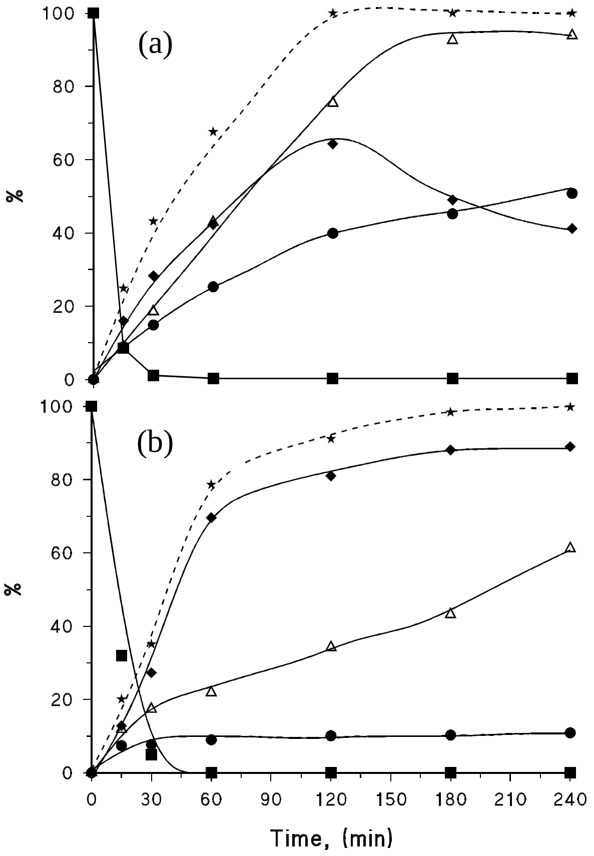


FIGURE 3

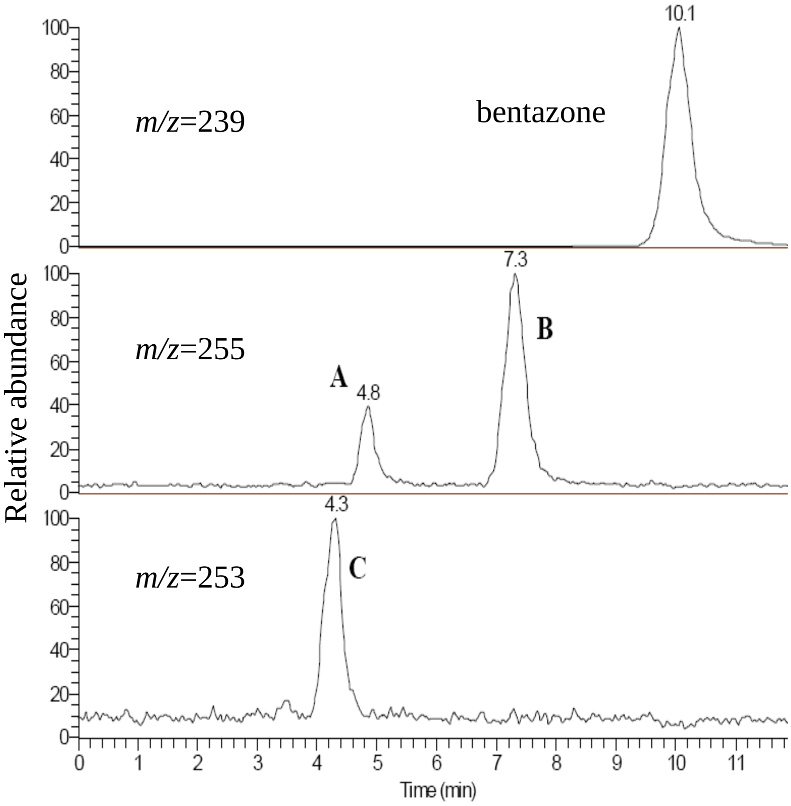

10.1
bentazone
m/z=239
7.3
B
m/z=255
A
4.8
4.3
C
m/z=253
Relative abundance
100
80
60
40
20
0
0
1
2
3
4
5
6
7
8
9
10
11
Time (min)

FIGURE 4