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Environmental remediation by an integrated microwave/UV illumination method

VII. Thermal/non-thermal effects in the microwave-assisted photocatalyzed mineralization of bisphenol-A

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Abstract

The photodegradation of the endocrine disruptor 4,4′-isopropyldiphenol (bisphenol-A, BPA; 0.1 mM) was examined in aqueous TiO_2 dispersions to assess thermal versus non-thermal effects of the microwave radiation assisted photocatalytic process driven by UV radiation. The effects were examined by comparing the results of the photodegradative process from the hybrid UV/microwave irradiation (PD/MW) with a UV/conventional heating method (PD/TH) and with UV illumination alone (PD). Mechanistic considerations followed from monitoring the process by UV/Vis absorption spectroscopy (cleavage of benzene rings), total organic carbon (TOC) assays, identification of intermediates by electrospray mass spectral techniques, and from calculations of frontier electron densities and partial charges of all non-hydrogen atoms in the BPA skeleton. Near-quantitative mineralization of BPA occurred after only 90 min of irradiation by the PD/MW and PD/TH routes, contrary to the PD route, which accounts for only 67% mineralization under identical conditions. Microwave radiation alone on a solution of BPA (no TiO_2) had no effect on the TOC, except for an increase of the pH of the solution (6.7–7.2) and formation of a small quantity of formic acid (ca. 0.005 mM) originating from oxidation of the isopropyl methyl groups after a 30 min irradiation period. For the other three routes, other intermediates were identified in addition to acetic acid and formic acids: 4-hydroxyacetophenone (PD/MW, PD/TH, PD), 4-hydroxybenzaldehyde (PD/MW, PD/TH), 4-hydroxyphenylisopropanol (PD/TH, PD), phenol and hydroquinone (PD/TH), and 3-hydroxy-1,3,5-hexatriene (PD/MW). Mechanistic differences are attributed to adsorption mode variations of the BPA substrate on the TiO_2 particle surface.

Keywords: Microwave; Photooxidation; Photodegradation; Bisphenol-A; Titanium dioxide; Endocrine disruptors

1. Introduction

There is growing interest in the synthesis of organic and inorganic substances through microwave-assisted processes [1,2]. Mostly effects generated by the microwave radiation have assisted these processes. In previous articles [3–6] we reported that mineralization of wastewater substances could be achieved with reasonably good efficiency under simultaneous irradiation by UV light and microwaves. The UV radiation was provided by a microwave-powered plasma light source [7–9]. The consequence of the microwave radiation on the aqueous TiO_2 dispersion was described as originating from either a thermal and/or a non-thermal effect [10,11]. The thermal effect was a major contributor to the cleavage of the phenyl group in the photocatalytic degradation of 2,4-dichlorophenoxyacetic acid (2,4-D) [11].

Bisphenol-A (BPA) was used in the present study as a model substrate (contains two phenyl rings) representative of a wide class of endocrine disruptors. It is widely used as a raw material for plasticizers in the manufacturing of polycarbonate and epoxy resins; the worldwide annual use is ca. 1700 metric tons. It accumulates in nature without decomposition causing reproductive damages to a variety of animal species [12]. Earlier, Ohko et al. [13] reported the photocatalyzed degradation of BPA and noted that the transcriptional estrogenic activity in response to human estrogen receptor in a yeast hybrid assay decreased dramatically to less than 1% of the initial BPA activity after 4 h of UV

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illumination. The present study was initiated (see also [14]) to elucidate whether thermal and/or non-thermal microwave effects, if any, impacted on the photodegradative process, and whether the microwave-assisted photocatalytic process (PD/MW) was more efficient relative to the photocatalytic route (PD) alone. The former route was twofold more efficient, with the latter PD route necessitating ca. 20 h to achieve mineralization of 0.175 mM BPA in aqueous media in the presence of TiO_2 particles (loading, 1 g l^{-1}; UV light irradiance, 10 mW cm^{-2}) [13]. Although experimental details used herein are somewhat different from those used earlier [13,14], it is nonetheless relevant that the PD/MW route can achieve the same extent of mineralization of BPA in much shorter time (only 1.5 h).

2. Experimental section

Titanium dioxide was Degussa P-25 (particle size, 20–30 nm; surface area, 53 m^2 g^{-1}; 83% anatase, 17% rutile). BPA (4,4’-isopropyldiphenol) was supplied by Tokyo Kasei Co. Ltd. as a highly pure reagent grade substance.

An aqueous dispersion of BPA (0.1 mM, 30 ml; initial $pH = 6.7$) and TiO_2 particles (loading, 60 mg) was placed in a 250 ml Pyrex cylindrical reactor ($\phi = 45\,mm \times 290\,mm$; Taiatsu Techno® Co.; maximal pressure, 1 MPa; maximal temperature, 150 °C), through a wave-guide. Microwave radiation was supplied by a Shikoku Keisoku system (Fig. 1) and consisted of a microwave generator (2.45 GHz; maximal power, 1.5 kW), a three-stub tuner, a power monitor, and an isolator manufactured by Shibaura Mechatronics Co. Ltd. Microwave power was 300 W, and the system was used in a single mode operation. Other properties and details of the microwave system have been reported previously [4,7–11].

The UV light source was an Ushio 250 W Hg lamp whose radiation was incident on the 250 ml Pyrex cylindrical reactor through a fiber optic light guide (light irradiance, ca. 0.9 mW cm^{-2}). The dispersion was continually stirred during irradiation. The reactor was sealed with two Teflon rings and a stainless steel cap. The UV source and the microwave generator were located on the front and right side of the device, respectively. Both radiation sources were set at 90° to each other as illustrated in the inset of Fig. 1.

The photodegradation of BPA was achieved following four different routes: (a) the UV-driven and microwave-assisted photocatalytic degradation of air-equilibrated BPA/TiO_2 dispersions (PD/MW); (b) the UV-driven photocatalytic route under identical conditions (PD); (c) the microwave irradiation of the BPA solution in the absence of TiO_2 (MW); (d) the UV-driven photocatalytic degradation of externally heated BPA/TiO_2 dispersions (PD/TH). In the latter case, a segment of the cylindrical Pyrex photoreactor was coated with a metallic film (MOCVD technique) on one side at the bottom of the reactor to provide the external heat source; the applied voltage was ≤100 V. The

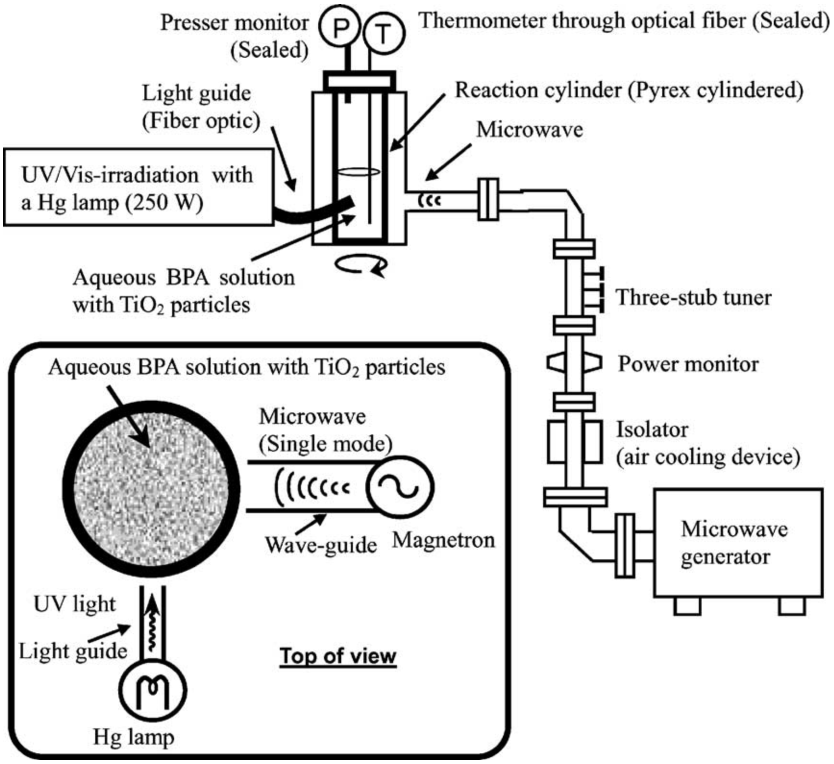


Fig. 1. Experimental setup used in the photocatalytic decomposition of BPA in aqueous TiO_2 dispersions using an integrated UV/Vis source (250 W Hg lamp) and a source of microwave radiation.

other side of the reactor was left transparent (uncoated) to UV radiation to drive the photomineralization of the BPA plasticizer. The rate of increase of the solution temperature in the PD/MW route was continually monitored during the irradiation period, and was equivalent to the heating rate used for the PD/TH route. That is, the quantity of thermal energy supplied to the photoreactor at each irradiation time was the same for both the PD/MW and PD/TH routes. For the latter, temperature (error was less than 1 °C) and pressure were both controlled in a manner identical to those used for the PD/MW method.

Loss of UV absorption features of BPA was monitored with a JASCO V-570 UV spectrophotometer. Total organic carbon (TOC) remaining in solution was assayed with a Shimadzu TOC-5000A instrument. Carboxylate intermediates, such as acetic acid and formic acid, were analyzed with a JASCO HPLC chromatograph using a Shodex OA System comprising an RSpak KC-811 column and a Shodex OA kit for analyses of organic acids. The methodology incorporated a post-column procedure and spectroscopic detection at 445 nm. Other organic intermediates were identified by direct injection into the mass spectral detector of an Agilent Technologies 1100 LC-MSD system (electrospray ionization: API-ESI; the LC column was not used) operated in the negative ion mode; the capillary voltage was 2.80 kV. The eluent was a 1:1 solution of acetonitrile:water. The flow rate of heated dry nitrogen gas (heater temperature, 300 °C) was maintained at $10\,\mathrm{l\,min^{-1}}$ and the gas pressure was $2.81 \times 10^4\,\mathrm{Kg\,m^{-2}}$. The mass spectrometer was scanned from *m*/*z* 50–300 at a flow rate of $0.3\,\mathrm{ml\,min^{-1}}$ for recording mass spectra. Injection of the 10 μl volume of the sample solution was achieved using an Agilent Technologies 1100 auto-sampling device.

Molecular orbital calculations were carried out at the single determinant (Hartree-Fock) level for optimization of the minimum energy obtained at the AM1 level. All semi-empirical calculations were performed in MOPAC Version 6 with a CAChe package (Fujitsu Co. Ltd.). An initial position for a possible $^\bullet$OH radical attack was estimated from calculations of frontier electron densities of all non-hydrogen atoms in the BPA structure (see below). The mode by which BPA might adsorb onto the TiO_2 surface was estimated from calculated partial charges of all non-hydrogen atoms of BPA [15–18].

3. Results and discussion

The temporal decreases of UV absorption features of the two aromatic rings of BPA during its photodegradation are depicted in Fig. 2. The relevant dynamics of the break-up of the BPA phenyl rings by the PD/MW and PD/TH routes show that cleavage of the rings was ca. twofold faster than for the PD route. In fact, for these two routes, the UV absorption features of BPA in the 195–300 nm spectral range vanished completely after irradiating (UV/MW or UV/TH) the dispersions for 1.5 h. Differences between the PD/MW and PD/TH routes were negligible. Accordingly, we infer that any variation in the degradation of BPA by the PD and PD/MW routes may not be the microwave radiation per se, but the thermal effect(s) originating from absorption of the microwave radiation by the dispersion (however, see also below).

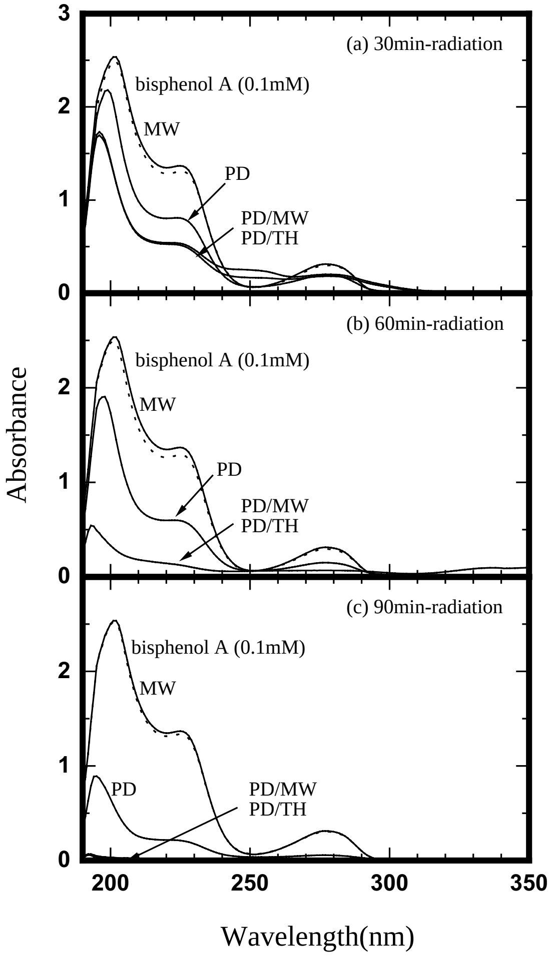


Fig. 2. Time-profiles of the disappearance of UV spectral patterns of BPA reflecting the cleavage of the aromatic ring(s) of BPA by the MW, PD, PD/MW and PD/TH routes.

The time-profiles of the decrease in TOC remaining in the BPA solution during the degradation of BPA are depicted in Fig. 3. Interestingly, the TOC profiles for the PD/MW and PD/TH routes exhibited nearly identical parallel behavior with irradiation time. Evidently, the TOC data infer that any non-thermal microwave effect has little influence in the loss of TOC. However, the temporal changes in pH appear to indicate otherwise (see below), as do the results from the time-profiles of formation of carboxylic acid and other intermediates. The PD route alone was relatively ineffective, achieving only ca. 67% mineralization of BPA under identical conditions. Microwave irradiation of the BPA solution alone was totally ineffective during the 1.5 h period.

The pH of the initial BPA solution was 6.7. No large temporal changes of pH (within ±0.2 pH units) were seen

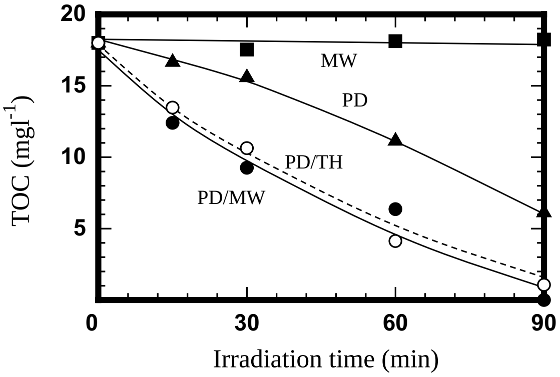
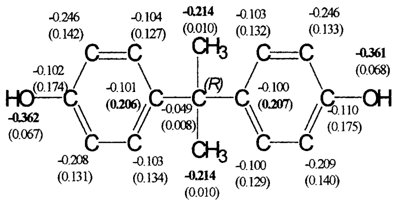


Fig. 3. Temporal loss of TOC in the photocatalyzed degradation of a BPA solution by the MW, PD, PD/MW and PD/TH routes.

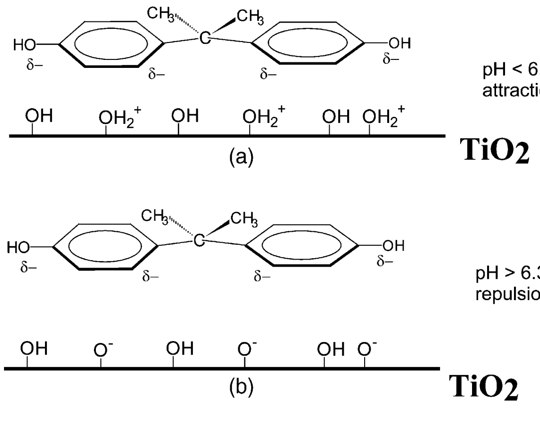
for the PD and PD/MW routes. By contrast, the pH of the microwaved BPA aqueous solution increased linearly from pH 6.7 to ca. 7.2 after the 1.5 h irradiation period. Zeta-potential measurements showed that the isoelectric point of TiO_2 (P-25) was ca. 6.3 under our experimental conditions. Accordingly, at pH 6.7 the surface charge of the TiO_2 particles was slightly negative. More significant was the temporal behavior of the pH of the BPA/TiO_2 dispersion under the PD/TH experimental conditions. The dispersion turned somewhat more acidic (pH ∼ 5.3) after 1 h; after 1.5 h, the pH was 5.7. Evidently, the PD/TH process rendered the surface charge of the TiO_2 particles more positive. Such pH changes can have a non-insignificant result not only on the mode of adsorption of the BPA substrate on the TiO_2 surface, as inferred in Scheme 1, but also on the selectivity of the photodegradative reaction occurring on the particle surface since redox reactions are very sensitive to changes in the surface potential [19].

Possible differences in the extent of adsorption of BPA on the TiO_2 surface were estimated from calculations of partial charges of all the non-hydrogen atoms in BPA. The results are indicated in the chemical structure of BPA below, along



with the relevant frontier electron densities (values in brackets). The most negatively charged atoms in the BPA structure are the two oxygen atoms (−0.362), with the next ones being the carbons *ortho* to the phenolic group (−0.246 and −0.209) and the two methyl carbons (−0.214). The two carbons at position *para* to the phenolic group are the atoms that bear the largest frontier electron density (0.207), followed by the carbons bearing the OH group (0.175). These sites are those expected to be the most likely sites of attack by neutral $^\bullet$OH radicals.

On the basis of the above description, we deduce that for the PD/TH route the BPA substrate is likely adsorbed on the positively charged particle surface (pH < 6.3) through the most negative oxygen and carbon atoms in such a way that the BPA molecule lies relatively flat against the particle surface (Scheme 1). By contrast, for the PD and the PD/MW routes, adsorption (if any) is expected to be rather limited against a somewhat negative particle surface. Consequently, we expect that the degradation of BPA and loss of TOC will be significantly more efficient for the PD/TH route relative to the PD/MW route. Such expectation and results obtained, however, are in contrast to our earlier observations [11] for the mineralization of another herbicide, namely the 2,4-D substrate for which the PD/MW route was more effective



Scheme 1. Diagram showing the adsorption mode of BPA on (a) a positive TiO_2 particle surface at pH <6.3 and on (b) a negative TiO_2 particle surface at pH >6.3. Note that the isoelectric point (pzc) for the TiO_2 used is 6.3 (see text).

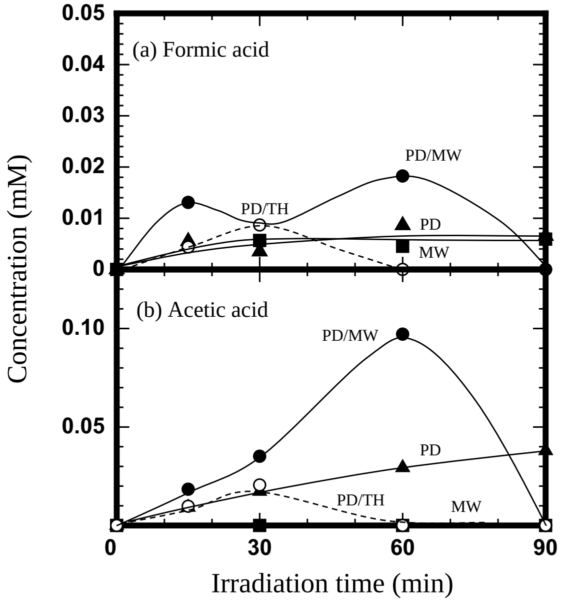


Fig. 4. Temporal formation of formic and acetic acid during the degradation of BPA by the four routes used.

in comparison to the PD/TH route. In the 2,4-D case, the difference was associated with a non-thermal effect(s) [1,2] induced by the microwave radiation on the TiO_2 particles. We postulate that a microwave non-thermal effect also operates in the mineralization of BPA, and that such effect is offset by the extent of differences in the mode of adsorption of BPA between the PD/MW and PD/TH routes.

The temporal formation of acetic acid and formic acid intermediates taking place during the degradation of BPA is shown in Fig. 4. Larger quantities of the two carboxylic acids were produced by the PD/MW route than by the PD and PD/TH routes, and a greater quantity of acetic acid formed by the PD/MW route. Formation of formic acid displayed two maxima, one after 15 min (0.012 mM) and the other after 60 min (0.02 mM) of irradiation by the PD/MW route. The first is assigned to the direct oxidation of the two methyl groups in BPA. Also, the PD and MW routes alone show identical formation dynamics and quantity of formic acid

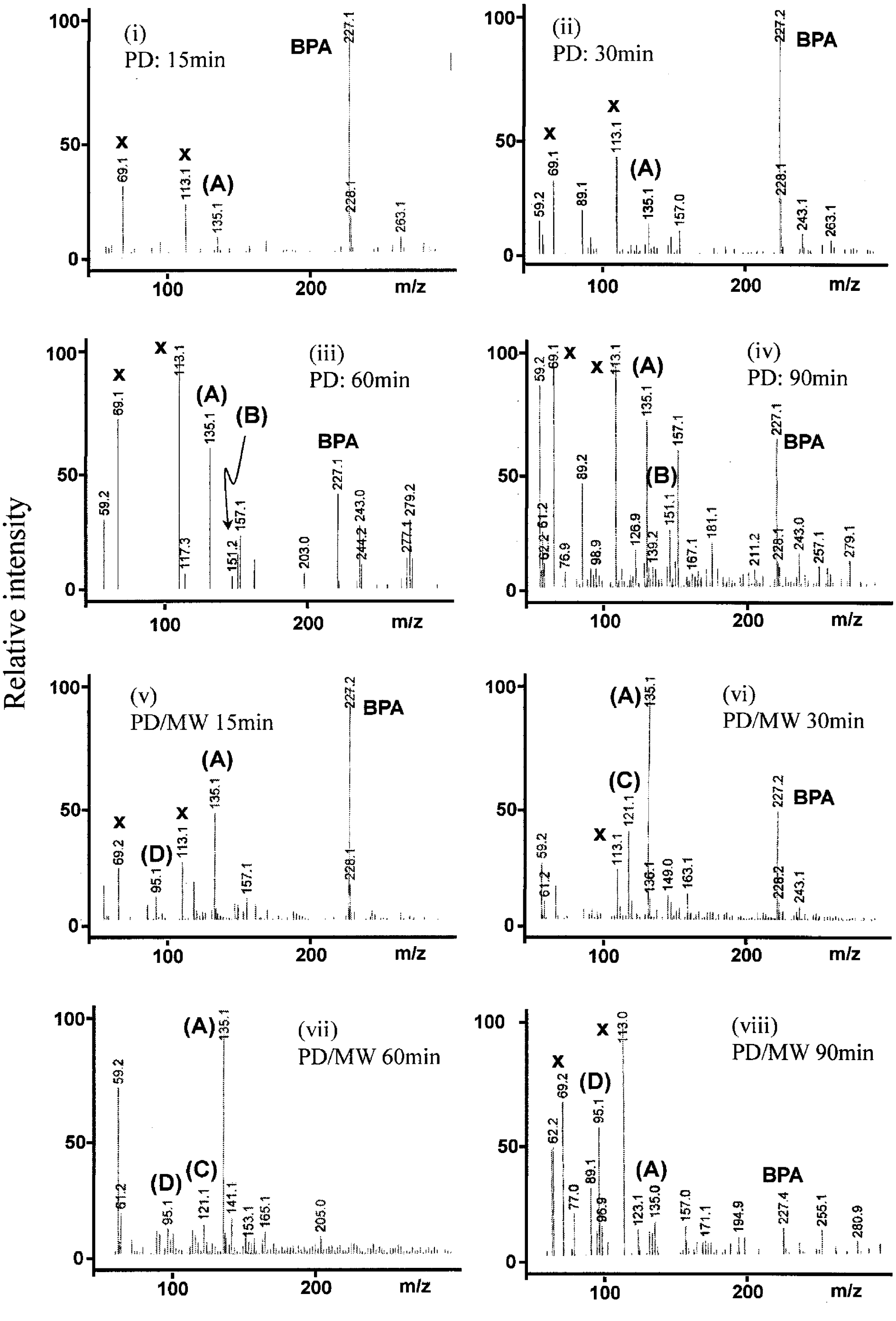


Fig. 5. Electrospray mass spectra in the negative ion mode recorded during the photodegradation of BPA by the PD (i–iv), PD/MW (v–viii), and PD/TH route (ix–xii) for 15, 30, 60 and 90 min of irradiation.

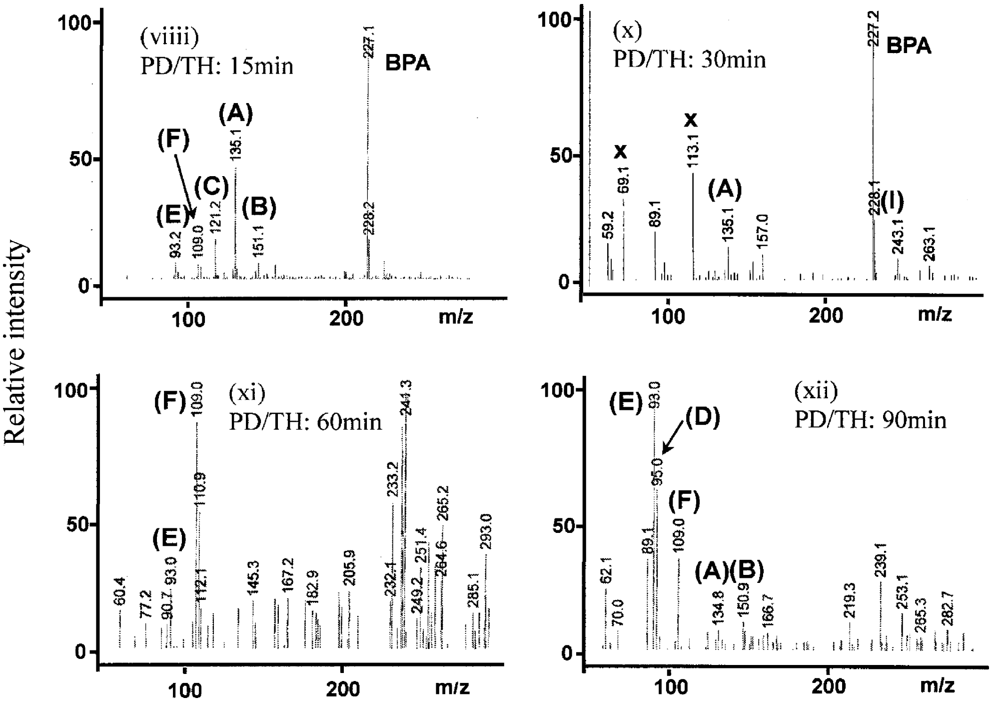


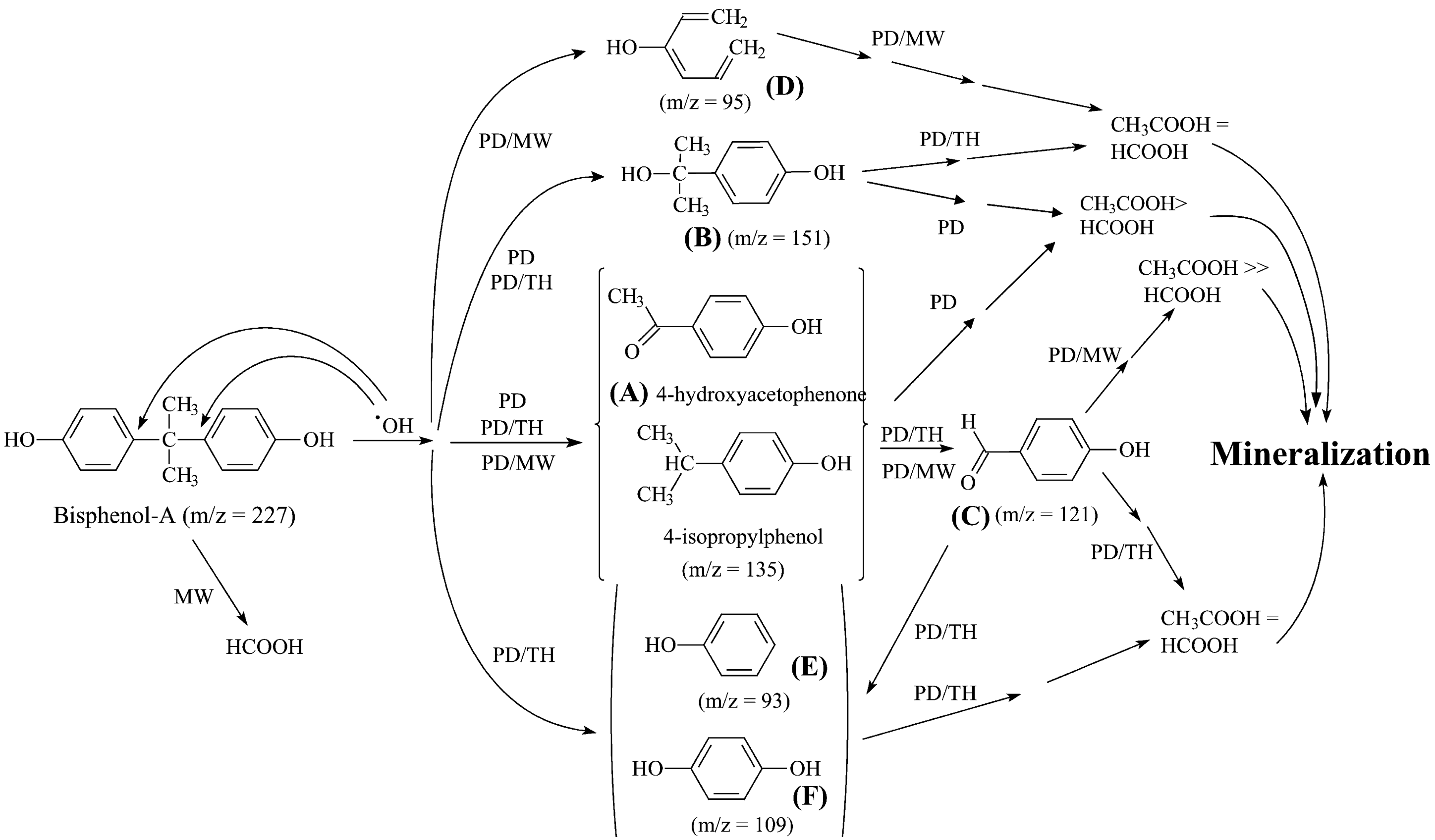
Fig. 5. (*Continued*).

after 1.5 h (0.006 mM). These observations are in keeping with the earlier study [15] on the photocatalyzed degradation of BPA, which showed that the NMR resonance signal of the two methyl groups at 1.62 ppm decreased by ca. 60% after only 10 min of UV irradiation. Microwave irradiation of the BPA solution produced no acetic acid, confirming its effect only on the methyl groups. The PD route also produced acetic acid, but which did not degrade even after 1.5 h of UV irradiation (ca. 0.04 mM). The latter accounts for some of the TOC remaining in solution by the PD method (see Fig. 3). Unlike the PD/MW, which displayed maximal formation of acetic acid after 60 min (0.10 mM), the maximal quantity of acetic acid formed by the PD/TH route (0.002 mM; for formic acid, 0.008 mM) occurred after 0.5 h of irradiation. The overall behavior of formation and decay of acetic acid is consistent with the mass spectral peak at $m/z = 59$ in the negative ion mode for all three routes used (see Fig. 5).

It is relevant to note that although degradation of BPA and loss of TOC correlate identically for the PD/MW and PD/TH routes, such was not the case for the carboxylic acids. The variation(s) observed between formation of acetic acid and formic acid must originate from the differences between these two routes in which the thermal effects were kept equivalent. We ascribe such variations to the non-thermal effect(s) originating from the microwave radiation. How these non-thermal effects might influence the nature of the TiO_2 particles and thus the surface redox chemistry was described elsewhere [11].

Differences in the degradation pathway for BPA are likely to depend closely on the route taken to mineralize the BPA substrate. Mass spectra recorded by the electrospray technique in the negative ion mode (anionic species S; $[S–H^+]$) and identification of the various intermediates produced should provide some evidence as to mechanistic details. The mass spectra were recorded after 15, 30, 60 and 90 min of irradiation for the PD (Fig. 5i–iv), PD/MW (Fig. 5v–viii) and PD/TH (Fig. 5ix–xii). The BPA mass peak was observed at $m/z = 227$. The signals at $m/z = 69$ and 113 are likely due to some adventitious impurities as attested by a control experiment using only the solvent water. Note that the mass spectra are rather complex and display several peaks of known and unknown intermediates formed by the three methods employed (PD/MW, PD/TH, and PD). The present study focused mostly on the main intermediates.

For the PD method, one intermediate species appeared at $m/z = 135$ (**A**) after 15 min of irradiation; another appeared at $m/z = 151$ (**B**) after irradiation for 1 h. The new species (**A**) is attributed to 4-hydroxyacetophenone confirming the previous observations by Ohko et al. [13], although we cannot preclude 4-isopropylphenol [11], which would also occur at $m/z = 135$. The other species (**B**) is identified as 4-hydroxyphenyl-2-propanol generated by cleavage of the single bond between the isopropyl carbon and the phenyl group (see structure above). Under our experimental conditions, we were unable to confirm the formation of 3-(4-hydroxyphenyl)-3-methyl-2-oxobutanoic acid ($m/z = 207$) and 4-vinylphenol ($m/z = 133$) [13] in the MS negative ion mode using the photocatalytic PD route. The intermediate species (**A**) was also produced by the PD/MW and PD/TH routes. By contrast, species (**B**) did not form by the PD/MW route yielding instead another intermediate (**C**) at $m/z = 121$ after 30 min of irradiation, which we



Scheme 2. Proposed mechanistic steps in the photodegradation of BPA by the PD, PD/TH, and PD/MW routes (the MW route to irradiate the BPA solution alone is also shown).

identified as 4-hydroxybenzaldehyde. The latter route also produced another intermediate at $m/z = 95$ that we ascribe to 3-hydroxy-1,3,5-hexadiene (**D**).

Contrary to the PD/MW route, the PD/TH route produced all three intermediates (**A**)–(**C**) after only 15 min of irradiation. The two major peaks at $m/z = 93$ (**E**) and 109 (**F**) (Fig. 5xi and xii) seen after 1 and 1.5 h of irradiation by the PD/TH route for those of phenol and hydroquinone, respectively, originated from the complete break-up of the BPA structure. No mass spectral peaks were seen at $m/z = 227$ after these two irradiation times, or from further reactions of intermediates (**A**)–(**C**).

3.1. Proposed degradation mechanisms for BPA

On the basis of the above discussion and data it is possible to deduce an overall pathway for the degradation of BPA by the various routes taken to achieve nearly quantitative or partial mineralization of BPA (see Scheme 2). Microwave irradiation of the BPA solution yielded formic acid as did the PD route by oxidation of the two methyl groups in the BPA structure. Curiously, these two routes did not degrade the formic acid to carbon dioxide, at least for less than 1.5 h of irradiation under the conditions employed. The PD and PD/MW (and likely PD/TH also) routes produce the highly oxidizing $^{\bullet}OH$ radicals when the TiO_2 is UV irradiated [11]. These radicals preferentially attack the two phenyl carbons bearing the highest electron density (see BPA structure above and the results from the MOPAC calculations) to initiate the break-up of BPA yielding the principal intermediates (**A**) and (**B**), along with the hydroxyhexadiene species. Species (**C**) is formed in a secondary step from either or both intermediates (**A**) and (**B**). Further irradiation (Scheme 2) subsequently produces acetic acid and formic acid, and ultimately carbon dioxide as evidenced by the near-quantitative loss of TOC for the PD/MW and PD/TH routes only (see Fig. 3). Phenol (**E**) and hydroquinone (**F**) are formed initially from BPA and/or from the three principal intermediates (**A**)–(**C**) through the PD/TH route.

The major factor that distinguishes the PD/TH and PD/MW routes (temperature of reactions, ca. 140 °C) from the photocatalytic PD route is the thermal factor; the PD route was carried out at ambient temperatures. Any variation(s) observed between the PD/TH and the PD/MW routes are consequently due to some non-thermal effects, the details of which were presented previously [11].

4. Concluding remark

In summary, the present study has demonstrated that a refractory substrate such as the BPA plasticizer can be mineralized efficiently and almost quantitatively in relatively short time by the microwave-assisted photocatalytic route.

Acknowledgements

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