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The microwave-/photo-assisted degradation of bisphenol-A in aqueous TiO_2 dispersions revisited Re-assessment of the microwave non-thermal effect

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Abstract

The microwave-assisted photodegradation of bisphenol-A (BPA) in the presence of TiO_2 was examined at ambient temperature to unravel some details on the importance of the microwave non-thermal effect. Normally, bisphenol-A photodegrades under microwave irradiation as a result of a thermal effect emanating from the microwave radiation which sees increase in temperature in the aqueous TiO_2 dispersion. However, on cooling the dispersion with circulating silicone oil at −20 °C, the temperature of the dispersion could be maintained constant at 21 °C. Under the latter irradiation conditions, the microwave-assisted photodegradation of BPA was shown to be not only due to a microwave thermal effect, but also to a significant non-thermal effect that might implicate hot-spots on the TiO_2 particle surface leading to enhanced photodegradation under constant ambient temperature. Other origins of the microwave non-thermal effect may include additional formation of charge carriers on the photomediator TiO_2 and formation of additional trap sites that may otherwise prolong the lifetimes of the charge carriers through diminished recombination and ultimately increase process kinetics.

Keywords: Photooxidation; Photodegradation; Microwave radiation; Bisphenol-A; Titanium dioxide; Photocatalysis; Microwave non-thermal effects

1. Introduction

Bisphenol-A (BPA) is one of many listed endocrine disruptors, which accumulates in the natural world with serious consequences causing damage to the reproductive cycle in a variety of animal species [1]. It has been used widely (about 1700 t per year) as a raw precursor of plasticizers in the fabrication of polycarbonate and epoxy resins [2]. Some reports on the photo-assisted degradation of BPA have examined the optimization of conditions toward improved degradation efficiency and pathways [3–8]. Some of our recent studies have shown that the photooxidative degradation of wastewater substances can be achieved with reasonable efficiency in titania dispersions under simultaneous irradiation by UV light and microwave radiation [9–12]. In an earlier study [13], the photo-assisted degradation of bisphenol-A under microwave irradiation was inferred to originate mostly from the microwave thermal effect, with the non-thermal effect having little influence on the photomineralization of this endocrine disruptor.

In the present study we revisited the microwave- assisted photodegradation of BPA to further evaluate the extent to which the non-thermal effect might contribute to its degradation relative to the thermal effect by re-examining the photodegradation of BPA under controlled ambient temperature conditions.

2. Experimental

2.1. Materials and analytical procedures

Reagent grade bisphenol-A (4,4′-isopro-pylidenediphenol) was supplied by Wako Pure Chem. Co. Ltd. The photo-assisted mediator was Degussa P-25 titanium dioxide (TiO_2) whose particle size was 20–30 nm (by transmission electron microscopy);

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its surface area was 53 $m^2\ g^{-1}$ (BET method) and the crystalline structure was 83% anatase and 17% rutile determined by X-ray diffraction analysis [14].

Loss of bisphenol-A in aqueous TiO_2 dispersions was monitored by UV/vis spectroscopy at 275 nm using a Shimadzu UV-1700 spectrophotometer, whereas loss of total organic carbon was assayed using a Shimadzu TOC-Vc apparatus.

2.2. Experimental set-up

The integrated microwave/photoreactor (MPR) was equipped with a cooling system and is illustrated in Fig. 1a. The Pyrex reactor consisted of a double-layer structure with internal and external diameters being, respectively, 75 and 100 mm. The silicone oil refrigerant was circulated through the inner part of this double layer structure using a circulation cooling apparatus. The silicone oil absorbed negligible quantities of microwave radiation (dielectric loss factor: $\varepsilon'' = 0.009$ below 25 °C determined by a network analyzer); ignition point of the oil is 443 °C. The temperature of the silicone oil was maintained at −20 °C by the recirculation apparatus operating at the maximal flow rate possible.

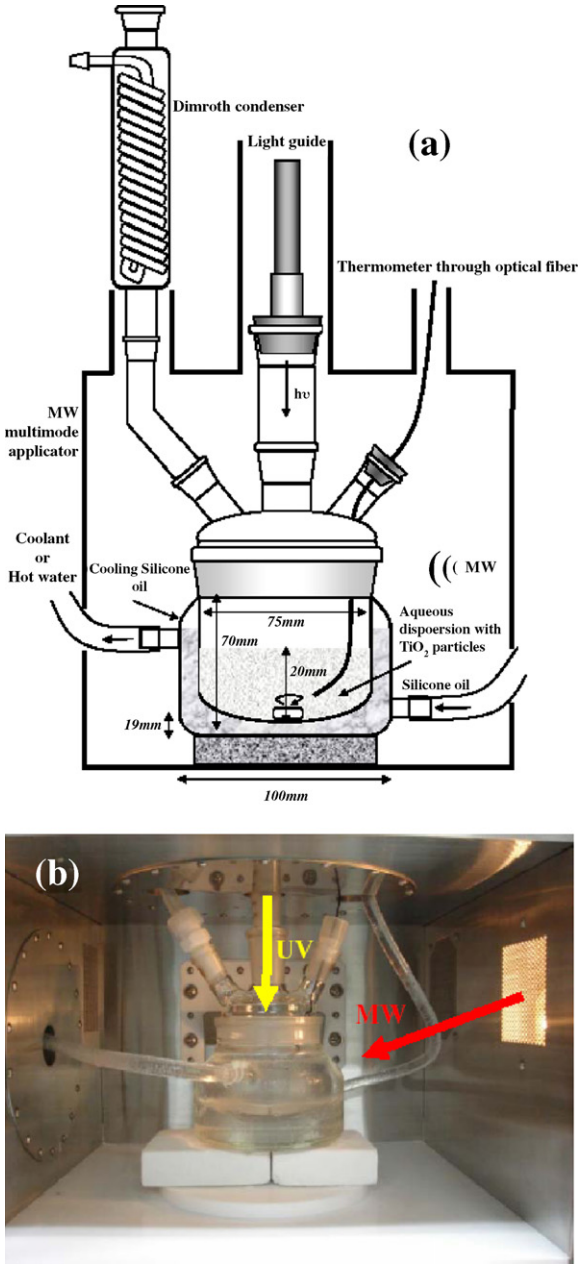

Fig. 1. (a) Schematic illustration of the microwave-assisted photoreactor with a cooling system (MPR) in the microwave multimode applicator; (b) photograph of the MPR apparatus.

The microwave irradiation source was a Shikoku Keisoku μReactor (SMW-087) system (Fig. 1b) consisting of a microwave generator (frequency, 2.45 GHz; maximal power, 200 W) operated in the CW mode and a multimode applicator. The cooling capacity of the cooling system was optimized to correspond to heating by the microwave radiation source of about 20–25 W. Note that preliminary experiments had determined that, at MW powers above and below 45 W, the temperature constancy could not be maintained. Accordingly, the irradiation power of the microwave was set at 45 W from considerations of the absorption of the microwaves by the MPR reactor and by the microwave applicator.

The UV light source was a super high-pressure 150-W mercury lamp which emitted UV light at the following wavelengths: 289, 297, 303, 313, 334 and 365 nm. Irradiation of the vigorously stirred aqueous TiO_2 dispersion at all these wavelengths was achieved from the top of the reactor using a light guide (no window was placed between the irradiation source and the dispersion). Note that the reactor design precluded a precise measurement of the energy balance inside the reactor from all the irradiation sources; however, for the purpose of the present study, all experiments were carried out under otherwise identical conditions except for the obvious modifications in the protocols (see below). The temperature of the aqueous TiO_2 dispersion was measured through a sealed optical fiber thermometer (Amoth FL-2000, Anritsu Meter Co. Ltd.).

2.3. Experimental techniques

Air-equilibrated aqueous bisphenol-A solutions (0.05 mM, 50 mL) containing TiO_2 particles (loading, 150 mg) were sonicated for ca. 20 s in the dark and then introduced into the MPR reactor under dark conditions. The course of the BPA degradation was followed using three experimental protocols: (a) the integrated microwave-/photo-assisted method in the presence of TiO_2 particulates (PD/MW); (b) the PD/MW method under controlled ambient temperature with the cooling system (PD/MW/Cool); and (c) the photo-assisted method alone (PD) mediated by TiO_2.

2.4. Temperature time profiles

The temporal profiles of temperature in aqueous BPA/TiO_2 dispersions are shown in Fig. 2. The initial temperature was 9 °C in the case of the PD/MW/Cool method which then increased to ca. 21 °C by absorption of MW radiation for 6 min.

No further increase in temperature occurred on continuing microwave irradiation with the temperature remaining constant

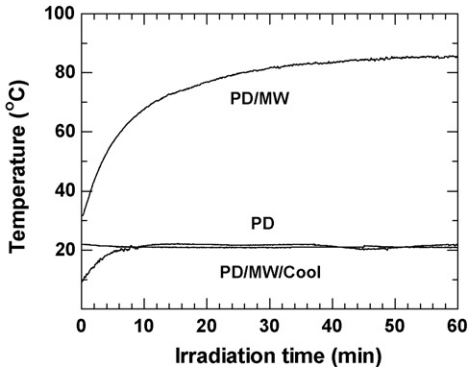

Fig. 2. Temperature time profiles in the aqueous TiO_2 dispersions as a function of irradiation time for the three experimental protocols.

at 21 °C. The temperature equilibrium state was the competitive result of the decrease of temperature in the cooled MPR reactor and the increase in temperature caused by the microwave irradiation. For the PD/MW method the initial temperature was 24 °C increasing rapidly on MW irradiation until it reached a steady state at ca. 85 °C after 60 min. The average temperature of the dispersions in the PD method was 21 °C.

3. Results and discussion

The temporal course of the degradation of bisphenol-A was monitored by UV absorption at 275 nm, which corresponds to the spectral features of the two aromatic rings of BPA [13]; at this wavelength previous work [3,13,15] has shown that intermediates formed contribute little, if any, to the absorbance. Accordingly, the decrease in concentration of BPA is illustrated in Fig. 3a, whereas the temporal loss of total organic carbon (TOC) is displayed in Fig. 3b. The relevant dynamics of the break-up of the BPA phenyl rings by the PD/MW method shows that cleavage of the rings is ca. two-fold faster than for the PD method (3.3×10^{-4} mM min^{-1} versus 1.7×10^{-4} mM min^{-1}, respectively), confirming previous observations [13]. This earlier study found that the kinetics of photomineralization of BPA through loss of total organic carbon were nearly identical for the PD/MW method and for the photo-assisted method under conventional heating (PD/TH) at otherwise identical temperatures. The microwave thermal effect does indeed promote the photo-assisted degradation of BPA. If we now examine the results summarized in Fig. 3a, it is evident that the rate of the microwave-/photo-assisted degradation of BPA under the controlled ambient conditions (PD/MW/Cool), with temperature maintained constant at ca. 21 °C, is two-fold faster than for degradation of BPA by the PD/MW protocol (6.5×10^{-4} mM min^{-1} versus 3.3×10^{-4} mM min^{-1}, respectively) taking place at the higher temperature (see Fig. 2). The extent of degradation of BPA followed the order: PD/MW/Cool (78%) > PD/MW (42%) > PD (21%) after microwave and/or UV irradiation alone for 60 min. The corresponding kinetics of loss of TOC are: PD/MW/Cool, 7.7×10^{-2} mg L^{-1} min^{-1}; PD/MW, 5.7×10^{-2} mg L^{-1} min^{-1}; and PD, 4.1×10^{-2} mg L^{-1} min^{-1}. After 60 min of irradiation, the extent of mineralization of BPA was 52% for the PD/MW/Cool protocol, 41% for the PD/MW method and 28% for the PD protocol. Clearly under the conditions used, the microwave-/photo-assisted degradation of BPA was most efficient when carried out at ambient temperature.

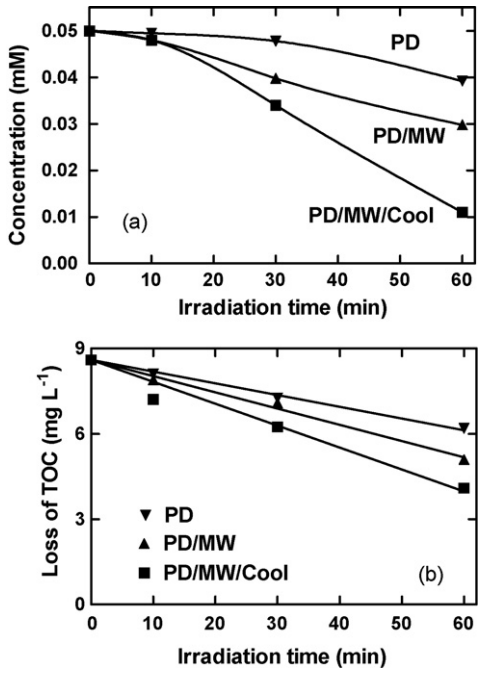

Fig. 3. (a) Temporal decrease of concentration of bisphenol-A (0.05 mM) during its decomposition in aqueous media by the photo-assisted oxidation (PD), by the microwave-/photo-assisted oxidation (PD/MW) method, and by the integrated microwave-/photo-assisted degradation under cooling conditions (PD/MW/Cool). (b) Temporal loss of total organic carbon (ppm) in the degradation of bisphenol-A.

The above notwithstanding, the microwave thermal effect in the photo-assisted degradation of BPA was also re-examined using the conventional heating method (PD/TH) at temperatures of 20, 50 and 80 °C (±2 °C) by circulating hot water in the double-layered photoreactor of Fig. 1. The ratio of the relevant degradation rates were 1.0 (20 °C):1.4 (50 °C):1.8 (80 °C). Note that the degradation rate of BPA at the lower temperature never exceeded the corresponding rate at the higher temperatures, a result in line with the recent findings by Kaneco et al. [4]. Clearly, the photo-assisted decomposition of BPA increases with heating the dispersion, whether by microwave radiation or by conventional methods, in contrast to earlier reports [4,16], which noted that although the extent of degradation of bisphenol-A in aqueous TiO_2 dispersions increased gradually with temperature from ca. 60 to 70%, no appreciable change was observed in the temperature range 10 to 70 °C, and that the photo-assisted degradation of BPA is not very sensitive to temperature. Also evident in Fig. 3 is that the non-thermal effect (i.e. the non-conventional thermal effect) in the degradation of BPA is clearly more significant than the thermal effect.

A unique heating/non-heating effect (in the conventional sense) acting on the TiO_2 particle surface by microwave radiation must be closely associated with and originate from the PD/MW/Cool method. Accordingly, we further examined the generation of microwave-induced heat at the TiO_2 particle to

probe this MW thermal effect by irradiating at full microwave power (200 W) a sample of water (20 mL) alone without TiO_2 particles and an aqueous dispersion (20 mL) of TiO_2 (100 mg). The temperature rise in the aqueous dispersion was slightly slower than in pure water, suggesting that the microwaves were also absorbed (to a slight extent) by the TiO_2 particles first and then by water. However, note that water was not heated as a result of any hot-spots [17] that may have formed on the TiO_2 particles. We deduce that regardless of the nature of the process that occurs on the TiO_2 particles, it is a relatively slow process.

In an earlier study on the picosecond spectroscopy of TiO_2 nanoparticles we reported [18] that about 10% of the photogenerated charge carriers (electrons and holes) escaped recombination in times below 10 ns, in accord with reported quantum yields of such photodegradations (about 10–15% [19]). Time-resolved microwave conductivity studies have also demonstrated that microwave radiation can induce formation of the same types of charge carriers in TiO_2 [20] as by light irradiation. Accordingly, it is not inconceivable that the enhancement of the photo-degradation of BPA by the microwave-induced non-thermal effect involves additional formation of charge carriers other than those produced by UV illumination of the TiO_2 particles. Moreover, microwave radiation may also induce formation of additional charge carrier trap sites that would prolong the lifetimes of the charge carriers [21], thereby slowing down their recombination and increasing process kinetics. Such events would be consistent with our present observations (Fig. 3).

4. Concluding remarks

We have shown that the photodegradation of the endocrine disruptor bisphenol-A is enhanced by the microwave non-thermal effect as evidenced by comparing the process occurring under controlled ambient temperature conditions at 21 °C (PD/MW/Cool) with the process occurring at the higher temperature (PD/MW; Fig. 3). Thus, both thermal [13] and non-thermal microwave effects are responsible for the enhanced photodegradation of bisphenol-A. As well, although we have deduced that the photo-activity of titanium dioxide particles is somehow promoted by the microwave radiation, there is nonetheless further work that needs to be done to ascertain some of the inferred hypotheses presented here.

Acknowledgments

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