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On the influence of the microwaves' thermal and non-thermal effects in titania photoassisted reactions

S. Horikoshi [a,*], N. Serpone [b]

[a] Department of Materials and Life Sciences, Faculty of Science and Technology, 7-1 Kioicho, Chiyodaku, Tokyo 102-8554, Japan
[b] Gruppo Fotochimico, Dipartimento di Chimica, Università di Pavia, via Taramelli 10, Pavia 27100, Italy

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ABSTRACT

In this paper we contend that the microwaves' non-thermal effect(s) is an important factor in the enhancement of TiO_2 photoassisted reactions involving the decomposition of organic pollutants in model wastewaters by an integrated microwave-/UV-illumination method (UV/MW). This method proved far superior in degrading organic pollutants than the more traditional TiO_2-assisted photodegradations under UV irradiation alone (UV method). For instance, all the functions in the rhodamine-B (RhB) dye structure decompose competitively by the UV method for which the transformation of the nitrogen atoms was not an insignificant part of the process; however, their transformation to NH_4^+ ions (and some NO_3^- ions) was significantly enhanced by the UV/MW method. The latter also proved far superior to the UV method in the degradation of 1,4-dioxane under identical temperature conditions as for the UV/MW method but with conventional heating (UV/CH). In addition, the microwave-assisted photodegradation of bisphenol-A (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 when MW irradiated leading to enhanced photodegradation at near-ambient temperatures. Such enhancements in process dynamics may be due to enhanced formation of $^\bullet OH$ radicals under UV/MW irradiation, at least for the Evonik P25 titania system. The response of this metal oxide specimen to the microwave non-thermal effect(s) has been correlated to changes in lattice distortions in the TiO_2 crystalline structure.

1. Introduction

Research into the degradation of organic pollutants in aqueous media (or in air) by irradiated TiO_2 has been a topic of much interest for nearly three decades. The utilization of supports in carrying out TiO_2-assisted photocatalysis is not novel. For instance, applications of photoassisted treatments of air pollution have been documented for TiO_2 supported on a suitable substrate such as on a filter in air conditioners and on self-cleaning windows, walls, and tents (among others). Several excellent reviews (see e.g. [1]) have been reported for the photoassisted degradation of organic pollutants in wastewaters. However, there has been relative little research done in this area in the last decade as large-scale treatments of organic pollutants in aquatic environments have not been without some problems, not least of which is the low photodegradation efficiency, a result of several factors: (i) the poor adsorption of wastewater organic pollutants on the TiO_2 surface; (ii) the penetration of UV light tends to be shallow in turbid wastewaters; (iii) the need for dissolved oxygen in photoassisted degradations; and (iv) the need to immobilize TiO_2 nanoparticles in their use in aquatic ecosystems. Moreover, the processing time has been the biggest problem in actual wastewater treatments that have used TiO_2 nanomaterials. The latter issue has been resolved by improving the photoactivity of TiO_2 samples through the simultaneous use of both UV light and microwave (2.45 GHz) radiation [2].

Microwaves have found a particular niche as a heat source in chemical syntheses, mostly organic. The principal feature in the use of microwaves as a heat source for a chemical reaction is the considerable enhancement of the reaction dynamics (i.e. enhanced reaction rates). For example, when microwaves are used, the reaction rates in organic syntheses are significantly faster by (at least) an order of magnitude [3]. Moreover, when microwaves are used in the syntheses of nanoparticles, high-quality nanoparticles are formed in relatively short time [4]. These enhancements occur as a result of the microwaves' thermal and non-thermal effects. Unfortunately, these two aspects of the microwaves are frequently confused. Not least, microwave dielectric heating displays a different temperature distribution from that observed under conventional heating [5].

In many of our studies, we employed equipment assembled and/or manufactured in the laboratory, for which strict control of the microwaves' electromagnetic field could be attained. The temperature of the solutions could be measured rigorously with this equipment. Accordingly, the thermal and non-thermal factors

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[*] Corresponding author. Tel.: +81 3 3238 4662.
E-mail address: horikosi@sophia.ac.jp (S. Horikoshi).

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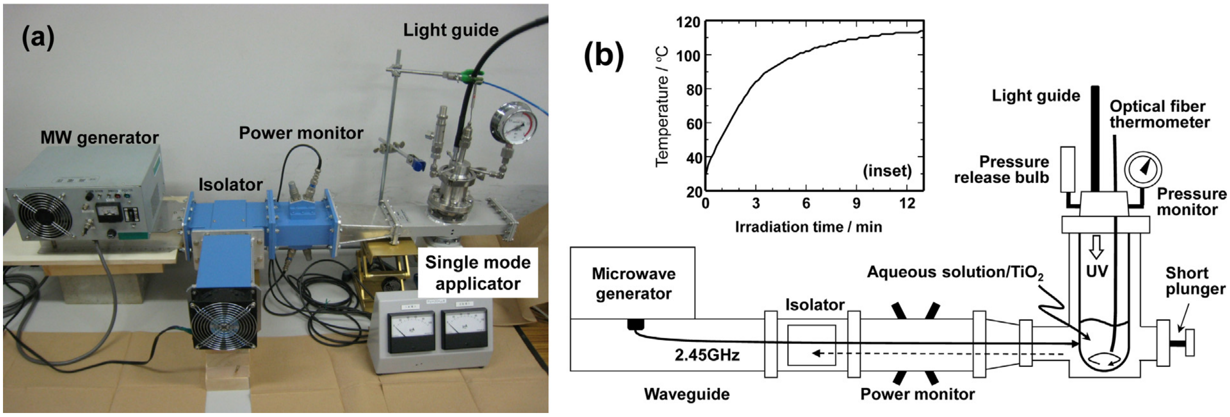

Fig. 1. (a) Photograph of an integrated microwave/photoreactor (MPR) system having a single-mode applicator, and (b) display of the MPR and a typical plot (inset) of change of temperature with irradiation time for an aqueous TiO_2 dispersion under microwave irradiation.

could be delineated in terms of which one might cause or predominate in the enhancement of chemical reactions. Our interest, therefore, rested in finding out aspects that these two factors have on chemical reactions when subjected to microwave irradiation. In this paper we summarize some of our recent findings focused on the possible role of the non-thermal effect(s) on the microwaved metal oxide and, by extrapolation, on the reactions.

2. Experimental setup of an integrated microwave/photoreactor system

Continuous microwave irradiation of a wastewater sample can typically be achieved in a single-mode applicator using a 2.45 GHz microwave generator, a power monitor (to assess incident and reflected microwave power), a three stub tuner and an isolator (an air cooling device) such as the one fabricated by the Hitachi Kyowa Engineering Co. Ltd. (Fig. 1a). A typical reactor setup would contain a model wastewater sample (30 mL) containing TiO_2 particles (Evonik P25; loading, 60 mg) introduced into a closed high-pressure 150 mL Pyrex glass cylindrical reactor. The reactor was subsequently UV-irradiated with a super high-pressure Hg lamp through a light guide. The solution temperature was measured with an optical fiber thermometer. A pressure gauge and a release bulb were connected to the cover of the reactor. The reaction mixture was stirred continually using a magnetic bar during UV and/or microwave (MW) irradiation. In some of our studies, other microwave frequencies were also used to effect the reaction: for example, 5.8 GHz microwaves from a single-mode applicator [6].

Three different methodologies have been used to examine the photodecomposition of aqueous samples of pollutants in aqueous TiO_2 dispersions. The first is the photo-/microwave- assisted method using UV light and microwave irradiation in the presence of TiO_2 (UV/MW). The second method entailed UV irradiation alone (UV), whereas the third method involved a thermally-assisted photodegradation of the TiO_2 dispersions using UV light and externally applied conventional heat (UV). In the present context, the external heat was supplied by coating one part of the cylindrical photoreactor with a thin metallic film on one side at the bottom of the reactor, whereas the uncoated side permitted the UV radiation to reach the dispersion. The pressure and the rate of increase of temperature (error typically $\leq \pm 1\,^{\circ}C$) in the UV/CH method were maintained at levels otherwise identical to those used in the UV/MW methodology. As such, no differences in temperature profiles were observed when using either microwave dielectric heating or conventional heating.

3. Results and discussion

3.1. *Degradation of the rhodamine-B (RhB) dye*

In earlier studies [7,8], we explored the photoassisted degradation of the cationic dye rhodamine-B (RhB) to probe the effects of microwaves on the process. The photodegradation rate of RhB was slow in acidic media because of the positive TiO_2 surface charge ($Ti{-}OH_2{}^+$) under slightly acidic aqueous conditions (TiO_2: pH = 6.3). Changes in color intensity of the RhB dye solutions occurring under various conditions are illustrated in Fig. 2. The photodegradation of RhB is clearly evident on using the TiO_2-assisted UV/MW method. These observations demonstrated that a method that could treat large quantities of pollutants in wastewaters by a hybrid combination of microwaves and TiO_2 photoassisted technologies was certainly conceivable. The photodegradation by this metal oxide was unaffected by conventional heating (CH) – compare, for example, the results from the UV and the UV/CH methods in the presence of TiO_2 (Fig. 2).

The microwave effects were examined by the temporal decay of total organic carbon (TOC) in the degradation of aqueous RhB solutions under four different methodologies. Results displayed in Fig. 3a show that for a TiO_2 loading of 60 mg (volume, 30 mL) there is no distinction between the efficacy of the UV and UV/CH methods. In the absence of the metal oxide TiO_2, no changes in TOC occurred

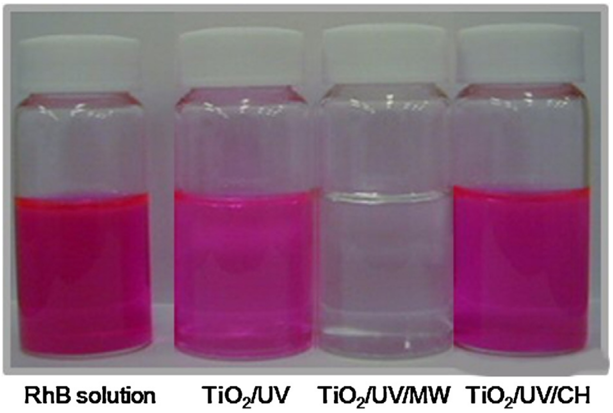

Fig. 2. Visual comparison of color fading in the degradation of RhB solutions (0.05 mM) subsequent to being subjected to various degradation methods for 150 min. From left to right: initial RhB solution; TiO_2/UV, photoassisted degradation; TiO_2/UV/MW, integrated microwave-/photo-assisted degradation; TiO_2/UV/CH, thermal- and photo-assisted degradation.

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