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# Investigation of factors that influence $TiO_2$ photoassisted degradations under simultaneous illumination by UV and microwave radiation fields

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## Abstract

Characteristic microwave effects on the $TiO_2$ behavior in photoassisted processes have been examined for surface affinity, electric surface charge, size of aggregated $TiO_2$ particles, and not least the number of $^{\bullet}OH$ radicals formed using *in situ* observation techniques. Novel microwave and UV radiation components were assembled to investigate the microwave effects. Microwave radiation can influence analytical instruments. Hence, the assembled components were designed so as to microwave irradiate only the sample solution containing the $TiO_2$ photomediator particles. Peculiar microwave effects implicated in photoassisted reactions involve both thermal and non-thermal factors.

*Keywords:* $TiO_2$ photocatalysis; *In situ* observation; $^{\bullet}OH$ radical; Surface reaction; Microwave effect

## 1. Introduction

The photoassisted decomposition of pollutants involving $TiO_2$ semiconductor particles has been shown to be an effective and attractive oxidative methodology in the general area of Advanced Oxidation Technologies. Illuminated anatase $TiO_2$ particles with ultraviolet radiation at wavelengths below 387 nm (or below 400 nm for rutile) exhibit strong oxidative power through the valence band holes, which have been instrumental in degrading organic substances through the intermediacy of $^{\bullet}OH$ radicals and similar reactive oxygen species.

Several studies have been reviewed on environmental remediation using $TiO_2$ materials as the photomediators [1–4]. Applications of photoassisted treatments to air pollution have been developed by $TiO_2$ fixation on suitable substrate supports such as air-conditioner filters, among others [5]. However, this photoassisted degradation is not suitable for large-scale wastewater treatment systems because of slow degradation rates of organic compounds dissolved in the wastewater. Among the various factors that affect the degradative process, the following three are significant in the construction of a practical water treatment plant: (i) the extent of adsorption of the organic contaminants on the $TiO_2$ surface at the high concentrations typically encountered in highly loaded waste streams; (ii) the relatively slow permeation of the pollutants in the stream; and (iii) the limitation of the UV light to penetrate and irradiate the photomediator owing to other extraneous components inherently present in a muddy stream, along with its effect on the $TiO_2$ particle surface in the bulk water as the degradative process takes place without significant movement of the organic contaminants. The disposal of polluted wastewaters and the need for drainage are also important considerations in environmental remediation.

In earlier studies we noted that photodegradation can be enhanced with the assistance of microwave radiation to degrade wastewater and soil pollutants (for example, dyes, polymers and surfactants [6a,6b], 2,4-dichlorophenoxyacetic acid [6c], and bisphenol-A [6d]) even under inferior photodecomposition conditions such as small quantities of $TiO_2$ used, low concentration of dissolved oxygen and low light irradiance [6a]. Most of the problems encountered in wastewater treatment by the $TiO_2$-photoassisted process have been resolved by an integrated microwave-/photo-assisted degradation tech-

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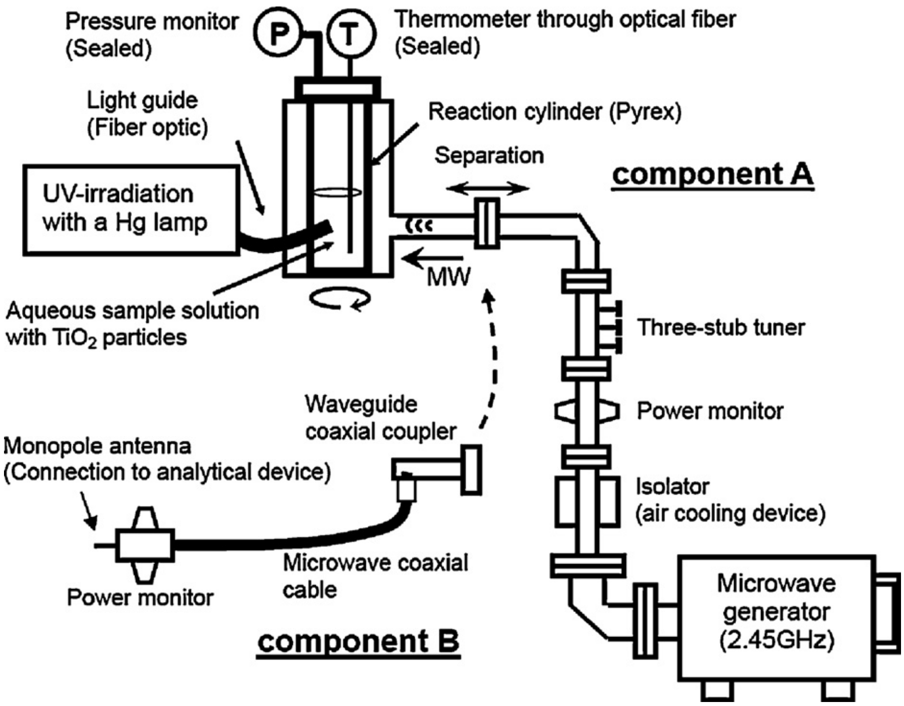


Fig. 1. Experimental equipment designed for single-mode operation having both UV- and MW-irradiation systems.

nique. A characteristic feature of the reaction on the $TiO_2$ surface involves thermal and non-thermal effects originating from absorption of microwave radiation [6a–6e]. The technology combining the photomediator with the microwave radiation has also been reported by others [7–18]. Examination of the effects of microwave radiation in $TiO_2$ photoassisted degradations has met with some difficulties because of the complex nature of the mechanism by which organic pollutants are decomposed.

Earlier we observed by electron spin resonance (ESR) techniques that the generation of $^{\bullet}OH$ radicals from the photooxidation of water or surface-bound OH groups in UV irradiated $TiO_2$ aqueous dispersion increased by the concomitant use of microwave radiation [19].

In the present article we re-visit the peculiar effect(s) of microwave radiation in photocatalytic surface reactions using some novel manufactured analytical equipment that is expected to contribute to advanced treatments of waste waters. In particular, we examine (i) the surface affinity of the hydrophilic/hydrophobic $TiO_2$ particles, (ii) the particle surface electric charge, and (iii) the particle surface area. Peculiar changes occur to the photocatalyst surface on irradiating the metal oxide with microwaves.

## 2. Experimental

### 2.1. Microwave/UV irradiation systems

Continuous microwave (MW) irradiation was carried out with a Shikoku Keisoku ZMW-003 apparatus containing a microwave generator (2.45 GHz; maximal power, 1.5 kW), a three-stub tuner, a power monitor and an isolator (Shibaura Mechatronics Co. Ltd.) that is illustrated in Fig. 1. Optimal low reflection of the MW radiation was achieved using the three-stub tuner. The UV irradiation source was either a Toshiba high-pressure Hg arc lamp or an Ushio super-high-pressure Hg lamp whose emitted UV radiation was fed to a 250-mL Pyrex cylindrical reactor ($\phi = 45 \times 290$ mm; Taiatsu Techno® Co.; maximal pressure, 1 MPa; temperature, 150 °C) through a fiber optic light-guide. The stirred dispersion was irradiated by microwave and/or UV light radiation.

### 2.2. Material and experimental procedures

The $TiO_2$ was Degussa P-25 (specific surface area, 53 $m^2/g$ by the BET method; particle size, 20–30 nm by TEM; composition, 83% anatase and 17% rutile by X-ray diffraction). Rhodamine-B (RhB; high-purity grade) was supplied by Tokyo Kasei Co. Ltd.

The $TiO_2$-assisted photo-oxidation of substrates was carried out using four different protocols: (i) $TiO_2$ photoassisted degradation with coupled UV light and microwave radiations (PD/MW), (ii) $TiO_2$ photoassisted degradation with UV light only (PD), (iii) microwave irradiation in the absence of $TiO_2$ (MW), and (iv) $TiO_2$ photoassisted degradation with UV light and conventional external heating (PD/TH). For the thermal and the $TiO_2$ photoassisted reactions, the cylindrical reactor was coated with a metal thin film (contained two electrodes) on one side at the bottom of the reactor to provide conventional heating (applied voltage <100 V). The other side of the reactor was uncoated so that UV radiation could be used to irradiate the $TiO_2$ dispersion. Temperature and pressure were controlled in a manner otherwise identical to those used for the PD/MW protocol.

In the microwave-assisted degradation of rhodamine-B dye used as a model substrate in aqueous $TiO_2$ dispersions, the microwave power radiated from the magnetron was ca. 220 W as monitored by a power monitor (see Fig. 1). Microwave radiation (single mode operation; *component A*) used to irradiate the aqueous RhB solution containing $TiO_2$ particles (30 mL) was delivered through a wave-guide. The UV irradiation source was a Toshiba 75-W Hg lamp; irradiance ca. 0.3 mW $cm^{-2}$ in the wavelength range 310–400 nm (maximal emission at 360 nm).

### *2.3. Surface characterization of $TiO_2$ particles (in situ contact angles and zeta-potentials)*

#### *2.3.1. Contact angles*

$TiO_2$ P-25 particles were fixed onto a Pyrex glass plate (10 mm × 20 mm) placed in the wave-guide of the microwave radiation, following which the ion-exchanged water was allowed to drip on the $TiO_2$ surface under irradiation by microwaves (power, 220 W) and UV/vis light (irradiance, ca. 10 mW $cm^{-2}$). The contact angle was measured using the window on the side of the microwave wave-guide.

#### *2.3.2. Zeta-potentials*

Changes in zeta-potentials for several aqueous dispersions of different pHs (controlled with HCl and NaOH) were monitored with a Microtec ZEECOM ZC2000 apparatus under UV irradiation alone and under MW/UV irradiation. Dispersions containing air-equilibrated ion-exchanged water (5 mL) and P-25 $TiO_2$ particles (loading, 10 mg) were sonicated for ca. 30 s in the dark and then introduced into the sample cell, also under dark conditions. The supply component of the microwave and UV radiations to the suspension in the sample cell was assembled as depicted in Fig. 1 (*component B*). The anode and cathode electrodes of the zeta-potential equipment were connected to both ends of the sample cell. We confirmed that the MW radiation had no influence on the electrodes through possible leakage of the microwaves. UV light radiation impinged on the front side of the sample cell through the optical fiber. By contrast, the microwaves were fed with a monopole antenna from the top side of the sample cell through the coaxial cable. Both the microwaves and the UV light were fed into the aluminum box that enclosed part of the sample cell. The microwaves were supplied from the magnetron through the microwave coaxial cable (N-cable). The irradiance of the UV light and the microwave radiation power were 0.1 mW $cm^{-2}$ (at ∼360 nm) and ca. 1 W, respectively.

### *2.4. Changes in the size of $TiO_2$ particle aggregates (in situ light scattering technique)*

Changes in the size distributions of $TiO_2$ particle aggregates were analyzed by dynamic light scattering (DLS) with an Otsuka Electrophoretic Co. Ltd. FPAR100 light scattering equipment under UV irradiation alone and under simultaneous MW/UV irradiation. The sample reactor was located at a distance of 1 mm from the inside sidewall of the wave-guide (see Fig. 2). The light scattering probe was positioned so as to use the reflection from the fiber optic type system. Light irradiation and detection of the scattered light by the probe were carried out through the two holes of the wave-guide. The focus of the light from the probe was adjusted from the point of the probe to 18 mm by a comparison table of the *x*,*y*,*z* axes stages to the aqueous $TiO_2$ dispersion (loading, 60 mg of $TiO_2$ in 30 mL of ion-exchanged water) close to the inner wall of the container. The optimal position was found by noting the maximum scattered intensity.

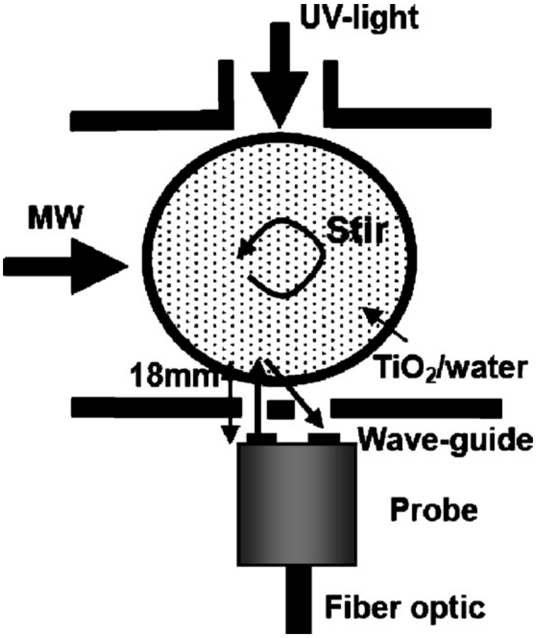


Fig. 2. Illustration of the experimental setup of the dynamic light scattering assembly with a refracted probe system.

## 3. Results and discussion

### *3.1. Degradation of a model wastewater substrate using the MW/$TiO_2$ photomediator system*

The photoassisted degradation of the dye rhodamine-B (RhB) was selected to probe the effects that microwaves have on the process. Typically, the photodegradation rate of cationic RhB dye is slow in acidic media because of the positive $TiO_2$ surface charge ($Ti–OH_2^+$) which repels the cationic RhB dye by Coulombic forces. The degradation of an aqueous solution of RhB with and without $TiO_2$ is reported in Fig. 3. From the intensity of the color fading it is evident that the rate of degradation of this cationic dye is significantly enhanced when the aqueous $TiO_2$ dispersion is exposed to both microwave and UV light irradiation (compare the PD/MW with the others in Fig. 3). Accordingly, a treatment method that can treat larger quantities of pollutants in wastewaters is conceivable by a hybrid combination of the microwave technology and the $TiO_2$ photoassisted technology. It is interesting that this metal–oxide photoassisted degradation is unaffected by conventional heating (compare the PD with the PD/TH protocol in Fig. 3).

The effects of the microwave radiation are best displayed in the photodegradation of some model compounds [6e]. For

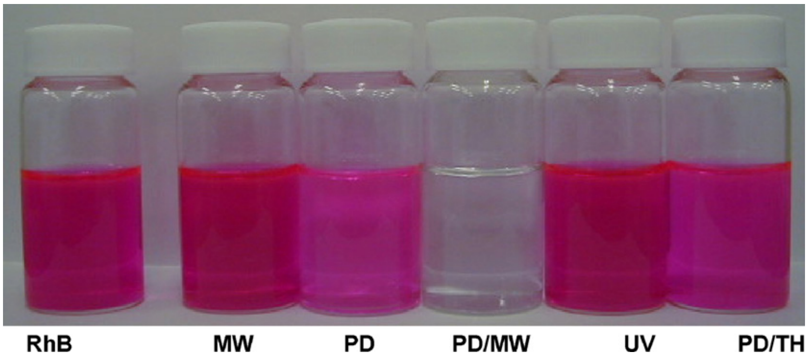


Fig. 3. Visual comparison of the color fading (degradation) in RhB solutions (0.05 mM) subsequent to being subjected to various degradation methods for 150 min. From left to right: initial RhB solution; MW, solution irradiated by microwave radiation; PD, photoassisted degradation with $TiO_2$; PD/MW, integrated microwave-/photo-assisted degradation; UV, RhB solution illuminated with UV light alone; PD/TH, thermal-/photo-assisted degradation. Light irradiance was 0.3 mW cm$^{-2}$; microwave power output was ca. 220 W. $TiO_2$ particles were removed by filtration.

instance, no differences were noted in the $TiO_2$ photoassisted degradation of bisphenol-A between conventional heating and caloric (thermal factor) heating by microwave irradiation [6d]. By contrast, the photoassisted degradation of bisphenol-A was significantly faster when simultaneously MW/UV irradiated under cooling conditions (i.e. at near-ambient temperatures). This unusual observation was attributed to non-thermal effects of the microwave radiation [20].

### 3.2. *Specific surface features of the $TiO_2$ particle under MW/UV irradiation*

#### 3.2.1. *Contact angles*

Generally, UV/vis light radiation can alter the hydrophilic/hydrophobic nature of the $TiO_2$ particle surface [21,22]. The hydrophilic/hydrophobic nature of the $TiO_2$ particle surface is an important factor in wastewater treatment because the photoassisted degradation of organic substrates is heavily dependent on surface events. Such hydrophilic/hydrophobic changes that might occur on the $TiO_2$ surface were therefore examined by contact angle measurements with water under MW/UV irradiation [6b]. After no less than five repeated measurements, the average contact angles were less than $\sim 4^\circ$ under UV/vis illumination alone (the PD protocol) but were ca. $18^\circ$ when microwave radiation was coupled to UV light (the PD/MW protocol). This increase in contact angles on the $TiO_2$ particles indicates that microwave radiation increased the hydrophobic character of the $TiO_2$ particle surface, which has consequences on the adsorption mode of the organic substrate, and thus on the overall mechanism of degradation. Changes in the morphology of the $TiO_2$ surface involve changes in the population of surface hydroxyl groups as a result of the microwave irradiation [6b,17]. It is tempting to speculate that the cause for the increase of hydrophobicity is partially due to formation of micro-/nano-scale hot spots on the $TiO_2$ surface, although we were unable to measure such spots by thermographic and by IR thermometric methods. Note that the contact angles measured when the $TiO_2$ particles were exposed to the PD/MW protocol were never smaller than the angles measured when the PD method was used.

#### 3.2.2. *Zeta-potentials*

The surface electric charge of $TiO_2$ particles under simultaneous MW/UV irradiation was measured *in situ* using the zeta-potential technique. The surface charge on the $TiO_2$ particles caused by UV irradiation was perturbed further when the particles were also exposed to MW irradiation. The surface electric charge of $TiO_2$ particles is another important factor that impinges on the rate of adsorption of substrates on the $TiO_2$ surface. In acidic media, the photoassisted degradation rate of anionic substances is expectedly faster than for cationic substrates owing to differences in the dynamics of adsorption on the positively charged $TiO_2$ surface ($Ti–OH_2^+$) [23,24].

Changes of the zeta-potential on the $TiO_2$ particle surface with pH changes in several aqueous dispersions are illustrated in

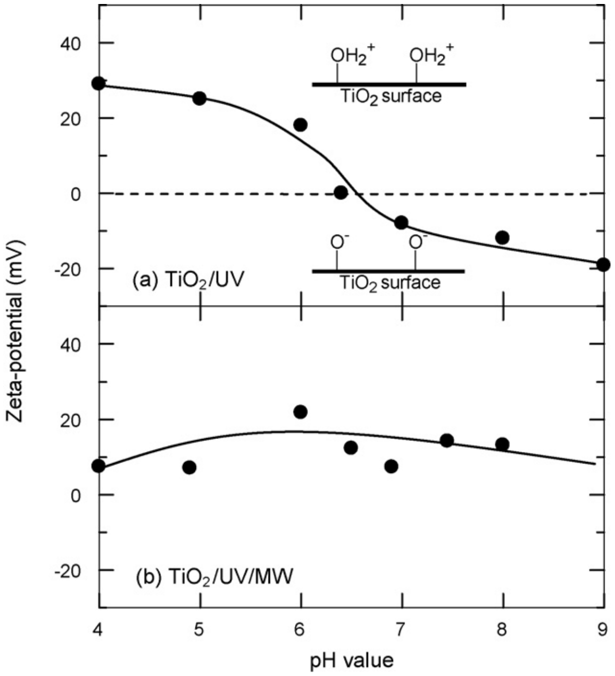


Fig. 4. The *in situ* observation of the pH dependence of the zeta-potential on the $TiO_2$ particle surface (P-25) under (a) UV irradiation alone and (b) under simultaneous MW/UV irradiation.

Fig. 4. Under UV light irradiation alone (PD), the zeta-potential decreased with an increase in pH of the $TiO_2$ dispersions (Fig. 4a). The point of zero charge (pzc) of the $TiO_2$ particles under UV irradiation occurs at pH 6.7. On the other hand, the typical zeta-potential curve was not evident under simultaneous MW/UV irradiation conditions (Fig. 4b). In the latter case, the zeta-potential obtained remained positive in the 0–20 mV range for dispersions in the pH range 4–9. We were unable to measure an actual charge on the $TiO_2$ particle surface probably because of unexpected convection currents caused by the microwave heating of only a portion of the dispersion in the sample cell. Evidently, the disorder in the $TiO_2$ surface charge is generated by the electric and/or magnetic fields of the microwave radiation. In all cases the pzc measurements were repeated no less than five times at each pH examined.

### *3.2.3. Size distributions*

In addition to the above, we have also sought other factors that might impact further on the photodegradation of substrates when microwave radiation is also implicated in the process. To this end, we employed the dynamic light scattering technique to measure the size distributions of the $TiO_2$ particles and $TiO_2$ aggregates in aqueous $TiO_2$ dispersions (Fig. 5). Transmission electron microscopy (TEM) images of $TiO_2$ particles show that they possess primitive crystalline sizes of about 20–30 nm (diameter). However, the P-25 $TiO_2$ product consists of aggregate assemblies, which when exposed to UV radiation (PD method; Fig. 5a) for ca. 75 min led the initial aggregate size (363 nm) to decrease to 282 nm that was ascribed to a breakup of the aggregates by the turbulent stirring of the suspension (mechanical factor). Under the PD/MW protocol (Fig. 5b), the size of the $TiO_2$ particle/water aggregates decreased from an initial 361 to 25 nm at 132 °C after 50 min of microwave/UV irradiation, whereas under conventional heating (PD/TH protocol) the initial size (357 nm) dropped to 35 nm at 126 °C after 50 min of irradiation (Fig. 5c). Evidently, the size distributions of the aggregated particles vary with an increase of the temperature of the dispersion for the PD/MW and PD/TH protocols. Deaggregation is therefore the result of a thermal factor because it is observed by both microwave and conventional heating, and causes an increase in the number of reaction sites (increased surface area) at the $TiO_2$ particle surface.

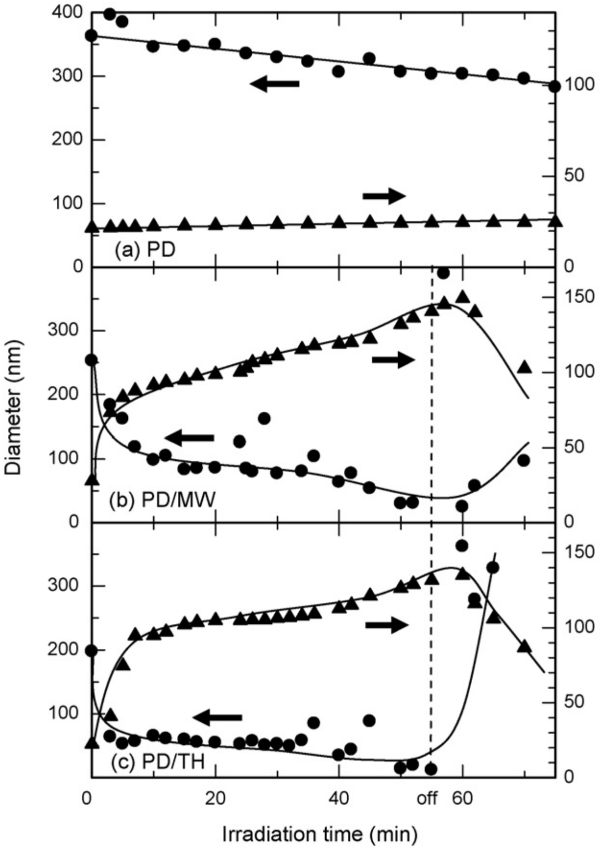
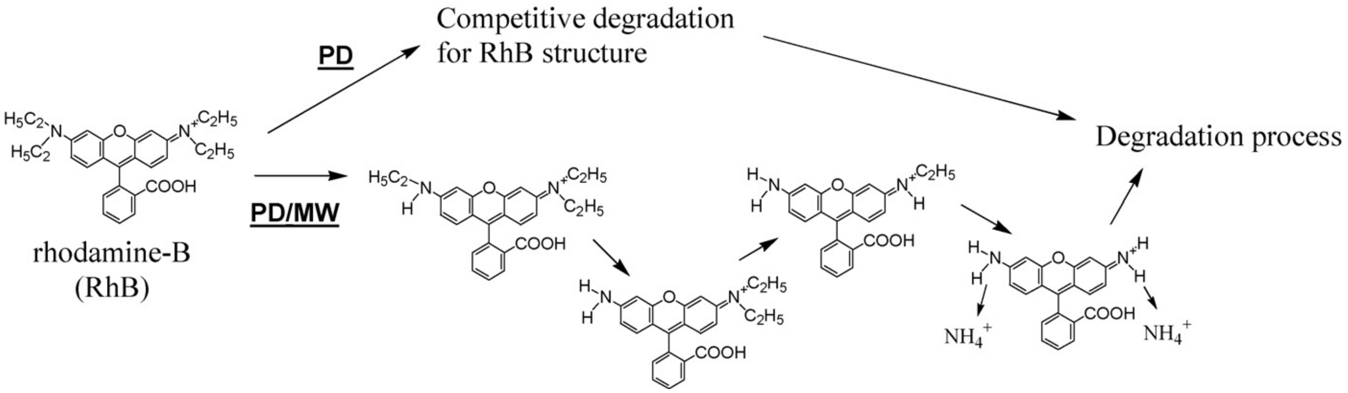


Fig. 5. *In situ* observations of particle size distributions against temperature in aqueous $TiO_2$ dispersions by the (a) PD, (b) PD/MW and (c) the PD/TH methods. Vertical dotted line represents the termination of conventional heating and microwave irradiation.

### *3.2.4. Photodegradation dynamics*

The photoassisted process in the degradation of a cationic substrate is usually the slow step in aqueous acidic media (pH < 6.7). However, the $TiO_2$ photoassisted degradation of RhB and other such cationic substances is somehow promoted by the existing disorder of the $TiO_2$ particle surface charge under the microwave radiation field. Adsorption of the substrates on the surface of $TiO_2$ particles was a major factor that rationalizes these differences.



Scheme 1. Proposed initial mechanistic steps of the degradation of RhB by the PD and PD/MW methods.

The initially formed intermediates also play a role in the extent of adsorption of organic substances on the $TiO_2$ surface and therefore can impact on the overall dynamics of the photomineralization with significant differences observed whether the dispersion is exposed to UV radiation alone (PD) or to both MW and UV radiations (PD/MW). For instance, in the $TiO_2$ photoassisted degradations of RhB (Scheme 1 and Ref. [6b]) and dimethyl phthalate [6e], UV irradiation alone produced intermediates different from those seen under MW/UV irradiation; the latter PD/MW protocol was more efficient than the PD method. The photodegradation of 4-chlorophenol also displayed formation of different intermediates when the dispersion was treated with either the PD/MW or the PD/TH protocols. Differences are attributed to variations in the mode of adsorption of the substrate on the $TiO_2$ surface [6f]. These observations are evidently due to the characteristic changes occurring on the $TiO_2$ surface as a result of it being exposed to microwave radiation. Thus the decomposition of organic pollutants can be optimized by changes in the physical and chemical properties of the $TiO_2$ surface that accompany microwave irradiation.

## 4. Concluding remarks

The source of the increased efficiency of a $TiO_2$ photoassisted reaction when coupled to a microwave radiation field cannot be due to a microwave thermal effect alone since the same cannot be achieved by the usual conventional heating (caloric) methods. The peculiar effect revealed by this study is that the photoreaction occurring on the photocatalyst surface also contributes to the peculiar effects of microwave radiation other than changes in the electronic charge of the surface, in the affinity of the surface, and in particle aggregation. Formation of $^{\bullet}OH$ radicals, which play an important role in the degradation of substrates, increased nearly twofold under simultaneous irradiation of the $TiO_2$ dispersion by microwaves and UV light [19]. This increase is likely due to some sort of surface restructuring induced by the microwave radiation. Specific effects of the microwave radiation field on the photoassisted process are clearly demonstrated by the increase in the number of surface-active species and by the increased dynamics of surface reactions.

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