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Environmental remediation by an integrated microwave/UV-illumination method II. Characteristics of a novel UV–VIS–microwave integrated irradiation device in photodegradation processes

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Abstract

In this brief article we examined the characteristics of a novel UV–VIS–microwave integrated irradiation device and explore its usefulness using the now well-established photo-degradation of a cationic dye (rhodamine-B; RhB) as a test substrate. The device consisted of a double quartz cylindrical plasma photoreactor (DQCPP) equipped with a microwave (MW) powered electrodeless Hg/Ne irradiation source. The latter is activated only by the MW radiation. The integrated MW–UV–VIS radiations so produced and incident on the DQCPP reactor significantly enhanced the decomposition of the RhB dye through simultaneous photocatalytic and photosensitization processes.

Keywords: Microwave; Photooxidation; Photodegradation; Rhodamine-B; Titanium dioxide; Microwave plasma; Dyes

1. Introduction

Photocatalytic degradative methods are suitable means to decontaminate aquatic organic pollutants [1]. This photocatalytic degradation is made possible, at least in part, by a relatively facile adsorption of simple and diluted gas components (e.g. simple aldehydes and carboxylic acids) on the TiO_2 particle surface. High oxygen concentrations in the aqueous waste solutions and low concentrations of organics are essential conditions in a wastewater treatment plant that involves a UV-lamp. Three factors present significant challenges in the construction of a practical water treatment device: (i) the extent of adsorption of organic contaminants on the TiO_2 particle 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 photocatalyst owing to the nature of the stream, and its effect on the TiO_2 particle surface in bulk water as the process proceeds without significant movement of the organic contaminants. Disposal of polluted wastewaters and the need for drainage are also important considerations. The first two issues can be resolved with devices that employ microwave (MW) radiation or supercritical water oxidation [2] in the presence of some photocatalyst (e.g. TiO_2). Ozone and UV methodologies have also been exploited for environmental remediation [3]. For a cationic dye such as rhodamine-B (RhB), integration of the photocatalytic method with MW radiation enhances the degradation [4].

In this study we examine to resolve the last issue utilizing a new approach that involves a double quartz cylindrical plasma photoreactor (DQCPP). Microwave plasma is commonly employed as a useful etching tool for materials, in chemical vapor deposition (CVD), in surface processing of polymers and semiconductors, light sauce, plasma torch, CO_2 laser, among others (see e.g. Ref. [5,6]). Our device (DQCPP) is equipped with a MW-powered Hg/Ne lamp that produces wavelengths of radiation in both the UV and visible region, with the concomitant advantage that the MW radiation is also involved in enhancing the degradation process. The advantage of this approach rests on the following points. (a) The energy to produce the UV–VIS radiation can be supplied external to the photoreactor (i.e. external to the wall and the plastic board of the DQCPP lamp). (b) The device is simplified because it involves neither electric wires

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nor electrodes in the lamp housing. (c) Both UV–VIS and MW radiations are available simultaneously in situ. (d) To the extent that the lamp is electrodeless, the reactor device might be more practical than a UV lamp/MW integrated system [4].

2. Experimental

Tokyo Kasei Co., Ltd. supplied the cationic RhB dye. The TiO_2 catalyst specimen was a gift from Degussa (P-25; surface area, 53 $m^2\,g^{-1}$ by BET; particle size, about 20–30 nm by TEM; crystallinity, 83% anatase and 17% rutile by X-ray diffraction). The MW irradiation equipment was obtained from the Shikoku Instrumentation Co., Ltd. It was equipped with a Toshiba microwave generator (2.45 GHz; maximum power, 1.5 kW). The internal dimensions of the MW oven were 49 cm (width) / 30 cm (height) / 44 cm (depth). Unless noted otherwise, the oven was operated at a power of 320 W. Microwave irradiation was continuous and the MW intensity was adjusted by connection to a power monitor and a three-stub tuner as illustrated in Fig. 1.

The double quartz cylindrical photoreactor (dimensions: 19 cm (length) × 7 cm (external diameter) × 1.5 cm (internal diameter)) contained mercury gas plus a very small quantity of neon gas introduced as a purge gas in the DQCPP lamp device after bringing the system to vacuum (ca. 10^{-7} Torr). It was connected to a teflon tube (2 m long and $\varnothing = 9$ mm) through which a RhB/TiO_2 aqueous dispersion was circulated using a peristaltic pump (116 ml; [RhB] = 0.05 mM; TiO_2 loading, 232 mg; pH, 4.2). The DQCPP was illuminated by continuous MW radiation. A cooling device located external to the MW oven maintained the RhB/TiO_2 dispersion at a temperature between about 55 and 67 °C.

The extent of MW absorption during the experiments was estimated from the difference between the current of incident MW radiation versus the current of reflected MW radiation (in mA): (a) with the DQCPP contained in the MW oven (0.240 $mA_{incidence}$/0.130 $mA_{reflection}$); (b) in the presence of the DQCPP reactor with the circulated RhB/TiO_2 dispersion (0.240 $mA_{incidence}$/0.12–0.14 $mA_{reflection}$). In the absence of the DQCPP device, the absorption of MW radiation in the oven was estimated from the ratio 0.240 $mA_{incidence}$/0.185 $mA_{reflection}$. In essence, the fraction of MW radiation absorbed by the MW-powered lamp and by the dispersion was ca. 0.055 mA (in terms of current).

The decrease in the spectral absorbance of the RhB dye in the UV–VIS region during the degradation of RhB was monitored on a JASCO UV/VIS/NIR V-560V spectrophotometer. The temporal decrease of total organic carbon (TOC) from the RhB solution was assayed on a Shimadzu TOC-5000A analyzer.

3. Results and discussions

The UV–VIS radiation emitted by the light source of the DQCPP reactor containing a mixture of mercury and neon gases is depicted in Fig. 2. When subjected to 320 W of

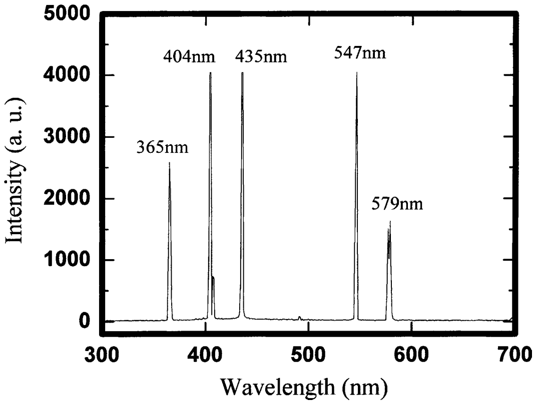

Fig. 2. Ultraviolet and visible wavelengths produced by the MW-powered electrodeless DQCPP lamp system containing Hg/Ne gases.

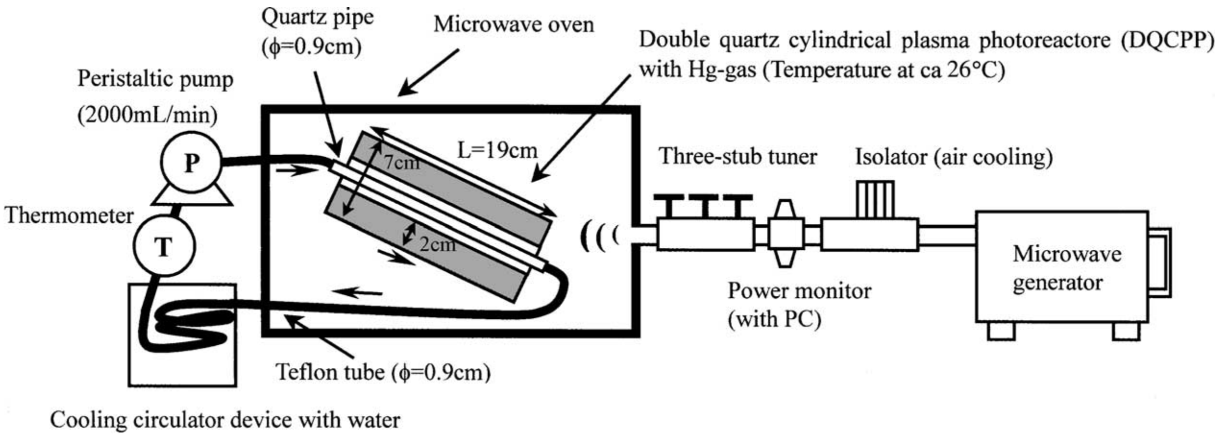

Fig. 1. Experimental set-up of a double quartz cylindrical plasma photoreactor (DQCPP) used in the photocatalytic decomposition of RhB dye cooperative UV–VIS and MW irradiations.

Table 1
Characteristics of the MW-powered DQCPP device

MW power (W)	GIR with DQCPP (mA)[a]	GIR without DQCPP (mA)[a]	MW absorption with DQCPP (mA)[b]	Relative MW absorption with DQCPP (10^{-4} mA W^{-1})	Light intensity at 250 nm (mW cm^{-2})	Light irradiance at 360 nm (mW cm^{-2})	Relative light irradiance (μW cm^{-2} W^{-1} of MW power)
30	0.005	0	0.005	1.67	0	0	0
40	0.015	0	0.015	**3.75**	0.010	0.104	2.60
100	0.045	0.020	0.025	2.50	0.028	0.327	3.27
125	0.060	0.020	0.040	3.20	0.047	0.507	**4.06**
175	0.080	0.040	0.040	2.29	0.052	0.600	3.43
220	0.105	0.050	0.055	2.50	0.069	0.723	3.29
320	0.110	0.055	0.055	1.72	0.083	0.860	2.69
400	0.120	0.055	0.065	1.63	0.094	1.092	2.73
510	0.135	0.080	0.055	1.08	0.111	1.351	2.65
700	0.190	0.080	0.110	1.57	0.122	1.761	2.52

[a] GIR, gap of incident radiation−reflected radiation.
[b] (GIR with reactor)−(GIR without reactor).

MW power, the DQCPP light source emitted ultraviolet and visible light wavelengths at 365, 404, 435, 547 and 579 nm. To the extent that the bandgap of the anatase form of TiO_2 is 3.20 eV (corresponding to 387.4 nm), the mercury peak at 365 nm can activate the TiO_2 particulates. The light irradiance from the mercury vapor at wavelengths shorter than 300 nm was about 10% or less of the irradiance seen in Fig. 2. Accordingly, these wavelengths are not reported as their influence on excitation of TiO_2 is not as important. The resulting characteristic features of the device sketched in Fig. 1 are listed in Table 1 for applied MW powers ranging from 30 to 700 W.

The different GIR of incident and reflection of microwaves are remarkable in this system. In other words, the GIR values reflect the extent (yield) of absorption of MW radiation.

The maximal MW absorption using DQCPP is displayed at an applied power of 40 W (column 5), subsequent to which absorption of microwaves decreased at greater applied power. This occurs because the MW radiation is converted to heat more than it is converted into light; any increase of applied MW power increased the quantity of reflected MW radiation. This heat conversion is caused by absorption of microwaves by the oven reactor. Originally, the increases of light intensity and MW absorption scaled with increase of MW energy. However, the relative MW absorption with DQCPP and the relative light irradiance (last column of Table 1) decreased with further increase of MW power. The decrease of this efficiency is due to increased MW absorption by the oven and to an increase in the amount of MW radiation reflected, which could be minimized in principle by fitting the oven with a MW stirrer.

The light irradiance at 360 nm at powers greater than 125 W scales inversely with MW power. At this power level the maximum light irradiance is 4.06 μW cm^{-2} W^{-1} of MW power. The MW power used in our experiments was 320 W for which the irradiance at 360 nm was 0.86 mW cm^{-2}.

The temporal decrease in absorbance of the RhB dye in the UV–VIS spectral region for irradiation times of 15 and 30 min is depicted in Fig. 3. Approximately 36% of RhB dye photodegraded in the presence of TiO_2 after 30 min exposure to UV radiation from a conventional a Ushio 250-W Hg lamp emitting a light irradiance of 1.8 mW cm^{-2} in the wavelength range 310–400 nm (maximum emission occurred at $\lambda = 360$ nm), that is nearly two-fold greater than the irradiance from the DQCPP lamp. The Hg lamp was located on the top of the MW oven. Note that the MW radiation was excluded and that the reaction temperature was 26 °C; the UV radiation was incident only on one side of the reactor. As well, the light irradiance from the Hg lamp was measured at the same position from the reactor as that from the DQCPP photoreactor. Otherwise, the experiment was carried out under conditions nearly identical to those used for the MW-powered lamp system with the DQCPP reactor.

By contrast, using the integrated UV–VIS–microwave DQCPP light source we found that ca. 62% of RhB

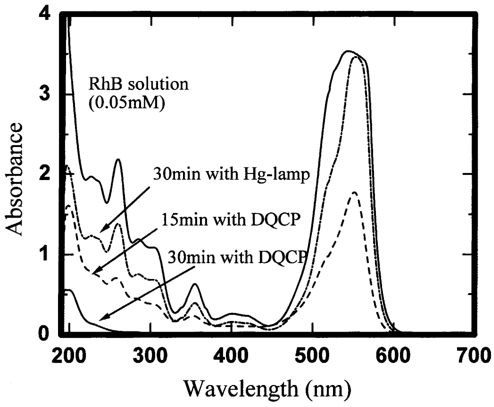

Fig. 3. Temporal changes in the UV–VIS spectral patterns observed during the degradation of RhB solution after irradiating for 15 and 30 min with a conventional Hg lamp and with the DQCPP light source.

photodegraded after only 15 min of irradiation. Further irradiation with this source for an additional 15 min led to the complete discoloration of the RhB solution. In fact, color fading of the RhB solution exposed to the Hg lamp was weaker than observed when exposed to the MW-powered light source, even though the irradiance emitted by the former source was nearly two-fold greater (see above). Note, however, that the DQCPP reactor was irradiated uniformly throughout the entire length (19 cm) of the sample tube. All of the RhB dye had been photoconverted to smaller organic intermediates after 30 min of exposure to the DQCPP integrated radiation. Only minor residual absorption was observed at wavelengths below 250 nm (Fig. 3), likely due to minor intermediates, the nature of which was outside the scope of this study.

The extent of photomineralization of the RhB solution was also assessed using assays of TOC. The initial TOC (18.6 ppm) decreased to 10.5 ppm (43% loss) and 7.0 ppm (62% loss) under MW–UV–VIS illumination for 15 and 30 min, respectively (see Fig. 4). Clearly, some 40% of TOC remain in the solution, which can be further mineralized photocatalytically for longer exposure times. The corresponding decrease in TOC under UV irradiation was 11 and 30%, respectively.

The photodegradation of RhB with the MW-powered lamp suggests feasibility. As reported earlier [4], integrating the photocatalytic method with MW irradiation can enhance the degradation of organic pollutants. In the present instance, however, not all the MW radiation was used to irradiate the solution/TiO_2 particles. The MW oven absorbed much of this radiation. The current system (Fig. 1) compensated for this loss of MW energy, in the form of electric power to the Hg/Ne lamp. An important feature of this MW-powered lamp is that the light irradiance can easily be adjusted by simple variations of the MW power level (Table 1). Moreover, changing the ratio and nature of the gases in the DQCPP reactor can vary the UV–VIS radiation wavelengths.

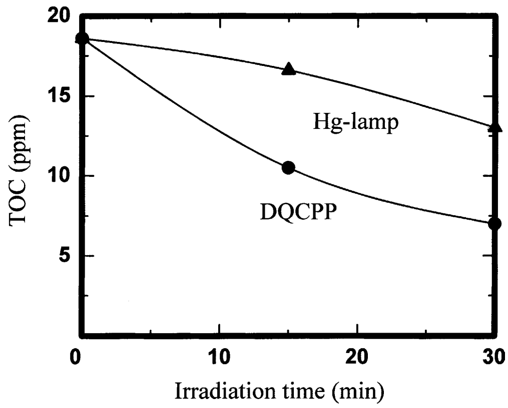

Fig. 4. Temporal decrease of TOC in the degradation of aqueous RhB solution (0.1 mM, 18.6 ppm) under two irradiation conditions.

The presence of both UV radiation to activate the TiO_2 anatase particles and visible radiation wavelengths to excite the RhB dye leads to a "double-edged sword" in the photodegradation of dyestuffs from discharges of the textile industry, for which we have taken the RhB dye as a model substrate. That is, the dye can be photodegraded concurrently by both a photocatalytic process and by self-photosensitization.

The involvement of $^{\bullet}OH$ radicals produced by valence band hole oxidation of OH^- groups (or chemisorbed H_2O) on the TiO_2 surface in the photocatalytic oxidation of organic pollutants is now well established (reactions (1)–(5)) [1,7]. As well, peroxyl ($HOO^{\bullet}$) radicals produced by protonation of the superoxide radical anions, $O_2^{\bullet -}$, resulting from

$$TiO_2 + h\nu \rightarrow TiO_2(e^-_{CB} + h^+_{VB}) \quad (1)$$

$$h^+_{VB} + OH^-(H_2O) \rightarrow {}^{\bullet}OH(+H^+) \quad (2)$$

$$e^-_{CB} + O_2 \rightarrow O_2^{\bullet -} \quad (3)$$

$$O_2^{\bullet -} + H^+ \rightarrow HOO^{\bullet} \quad (4)$$

$$^{\bullet}OH\ (\text{or } HOO^{\bullet}) + RhB \rightarrow \text{products} \quad (5)$$

reduction of molecular oxygen by the conduction band electrons, are not precluded. It is relevant to note that hydroxyl radicals are also produced in the integrated MW/photocatalytic method reported earlier [4].

A process that also leads to the photodegradation of pollutants, particularly of such colored dyes as RhB, is photosensitization in which the dye absorbs the visible wavelengths from the Hg/Ne lamp (see Fig. 2) to yield an excited state of the dye, $^{1,3}dye^*$ (reaction (6)). Subsequently, the $^{1,3}dye^*$ inject(s) an electron onto the TiO_2 particle to give a conduction band electron and a dye radical cation ($^{1,3}dye^{\bullet +}$), reaction (7). The electron is next involved in reactions (3) and (8)–(10) producing the $^{\bullet}OH$ radical. Ultimately, the dye cation radical reacts with molecular oxygen or with the radical species $O_2^{\bullet -}$, $^{\bullet}OH$, or $HOO^{\bullet}$ to yield intermediate and/or mineralized products [8].

$$dye + h\nu \rightarrow {}^{1,3}dye^* \quad (6)$$

$$^{1,3}dye^* + TiO_2 \rightarrow {}^{1,3}dye^{\bullet +} + TiO_2(e^-_{CB}) \quad (7)$$

$$O_2^{\bullet -} + e^-_{CB} + 2H^+ \rightarrow H_2O_2 \quad (8)$$

or

$$2O_2^{\bullet -} + 2H^+ \rightarrow H_2O_2 + O_2 \quad (9)$$

$$H_2O_2 + e^-_{CB} \rightarrow OH^- + {}^{\bullet}OH \quad (10)$$

$$^{1,3}dye^{\bullet +} + O_2\ (\text{and/or } O_2^{\bullet -},\ \text{and/or } ^{\bullet}OH) \rightarrow \text{intermediates} \rightarrow \cdots \rightarrow \text{mineralized products} \quad (11)$$

To the extent that the MW energy supplied to the DQCPP device originates externally and the lamp is electrodeless, the device shown in Fig. 1 can easily be adapted to treat wastewaters where the more conventional UV–VIS-illuminated photoreactors might present some difficulties. The simultaneous irradiation of polluted streams by both MW and UV–VIS light presents such advantages that a simplified DQCPP device is available for practical applications. The maintenance of DQCPP was never required because electrodeless. The all radiated MW energy could not converted to prasma light. Therefore, the effect of the photocatalytic degradation under both MW and UV–VIS light irradiation (PD/MW) was partly recognized for the cationic RhB dye in the presence of TiO_2 catalyst. The manufactured device is expected to be commercialized in the near future.

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