

Environmental remediation by an integrated microwave/UV illumination technique

VI. A simple modified domestic microwave oven integrating an electrodeless UV-Vis lamp to photodegrade environmental pollutants in aqueous media

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Abstract

A simple device is described based on a modified domestic microwave oven that incorporates an UV-Vis lamp encased in Teflon to photodegrade environmental pollutants in aqueous media. The performance of this device was examined using the photodegradation of the agrochemical pollutant 2,4-dichlorophenoxyacetic acid (2,4-D) as the test process driven by a coupled photocatalytic/microwave method in an aqueous TiO₂ dispersion. The aqueous dispersion was contained in a high-pressure Teflon batch (TB) reactor that also integrated a double glass cylindrical plasma lamp (DGCPL) as the source of the UV-Vis radiation. This DGCPL lamp contained mercury gas with a minute amount of neon gas and was powered solely by microwave radiation. The coupled microwave-UV-Vis irradiation of the TB-DGCPL reactor led to an enhancement of the decomposition of the 2,4-D target substrate in the modified microwave oven relative to the photocatalytic method alone. Specifically, the rates of degradation were $2 \times 10^{-3} \text{ mM min}^{-1}$ (photocatalytic/microwave method (PD/MW)) and $1.1 \times 10^{-3} \text{ mM min}^{-1}$ (photocatalytic method (PD)) even though the light irradiance was some six-fold greater in the latter method. That is, the coupled PD/MW method was about 10 times more efficient than the PD method alone.

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1. Introduction

In a series of recent articles we reported that the degradation of pesticides, dyes, endocrine disruptors, surfactants and polymers can be achieved by combining microwave radiation with a photocatalytic technique that uses TiO₂ particulates [1–4]. A relatively simple, inexpensive and easy to use microwave-cooking oven can supply the microwave radiation. To achieve efficient degradation of polluting agrochemicals (and other environmental substrates) necessitates three basic elements: light, oxygen, and water. Of these, UV-Vis radiation is the most important element. The dy-

namics of the decomposition of organic pollutants using the TiO₂-mediated photocatalytic method (PD) can be improved by simultaneous irradiation of the aqueous dispersion by UV light and microwave radiation (PD/MW). The irradiation effect of microwaves is not just a thermal effect; there is also a significant non-thermal component [2–4]. For instance, the number of •OH radicals formed increases significantly when UV illumination is coupled with microwave irradiation as attested earlier by ESR studies [5]. This increase did not originate from the thermal factor, but rather from the non-thermal component. Accordingly, it was meaningful to test a modified domestic microwave-cooking oven to photodegrade the agrochemical 2,4-dichlorophenoxyacetic acid (2,4-D) as the test substrate.

Incorporating a suitable electrode UV lamp in a microwave-cooking oven is not only difficult, but also unsafe because the lamp can be broken by the electric discharge

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between the microwave oven and the metallic components of the lamp. To circumvent this safety issue, the UV source could be positioned externally to the microwave oven requiring a significantly greater number of inlets and outlets. Moreover, a suitable (batch-type) reactor system would be needed. The inner pressure in such a reactor can be rather high owing to the boiling water in the aqueous dispersion as a result of microwave radiation. Accordingly, metallic and/or polymeric materials must be chosen appropriately to construct a suitable batch reactor. However, since such materials are opaque to transmission of the UV-Vis radiation, a different approach was examined.

We demonstrated previously the suitability of microwave radiation coupled with UV-Vis light to decompose dyes (viz. rhodamine-B [6,7]) and the agrochemical 2,4-dichlorophenoxyacetic acid [2] in a research/industrial device that incorporated a microwave-powered plasma lamp. The detailed properties of this lamp were reported earlier [7]. In this article we examine the suitability and usefulness of a domestic microwave oven that was minimally modified to incorporate a Teflon batch (TB) reactor containing an electrodeless double glass cylindrical plasma lamp (DGCPL) and whose radiation could drive the photodegradation of a variety of pollutants. Results show complete photodegradation of an aqueous solution of the 2,4-D target pollutant (0.04 mM or 8.8 mg l⁻¹ (ppm); 3.8 mg l⁻¹ in TOC) in relatively short time (ca. 20 min) occurring through zero-order kinetics.

2. Experimental

A photograph of the Teflon batch reactor is shown in Fig. 1a, whereas Fig. 1b illustrates the schematic that shows the details of the reactor assembly held in place by two oppositely located flat stainless steel plates and stainless steel guiding posts mounted on the plates (SUS-304 stainless steel). The maximum temperature and pressure of the reactor can reach values greater than 200 °C and 3 MPa. Accordingly, a release valve was used to release the pressure whenever it exceeded 3 MPa. The double glass cylindrical plasma lamp was located inside the Teflon casing. The dimensions of the DGCPL UV-Vis light source were 4.8 cm (external diameter) by 7 cm (height). It contained mercury gas and a minute quantity of neon gas introduced as a purge gas in the DGCPL after bringing the system to vacuum (ca. 10⁻⁴ Pa). The Teflon casing is transparent to microwave radiation, so that the electrodeless DGCPL lamp that produced the UV-Vis light absorbed the microwave radiation. The gap between the Teflon casing and the SUS-304 stainless steel upper plate (lid) was sealed with a silicone O-ring. As noted in Fig. 1a, the microwave oven (Matsushita Electric Industrial Co. Ltd.; power, 700 W; frequency, 2.45 GHz) irradiated the reactor from the right side. Note that the release valve and the thermometer/fiber optic were installed through the top plate and through the upper part of the oven. The

turntable, typically found in microwave-cooking ovens, was removed to prevent rotation of the reactor and to avoid damage to the fiber optic/thermometer and to the tube with the release valve. The whole TB-DGCPL assembly was placed on Teflon jacks, whose role was to insulate and prevent electric discharges between the SUS-304 stainless steel and the microwave oven.

The photocatalyst was Degussa P-25 TiO₂ (specific surface area, 53 m² g⁻¹ by the BET method; particle size, 20–30 nm by TEM observations; composition, 83% anatase and 17% rutile by X-ray diffraction). The 2,4-D substrate was of high-purity grade and was used as supplied by Wako Pure Chem. Co. Ltd. A 10 ml aqueous dispersion composed of a solution of 2,4-dichlorophenoxyacetic acid (0.04 mM, initial pH 4.9) and TiO₂ particles (loading, 50 mg) was introduced into the reactor under air-equilibrated conditions after mixing the dispersion with a supersonicator for ca. 2 min.

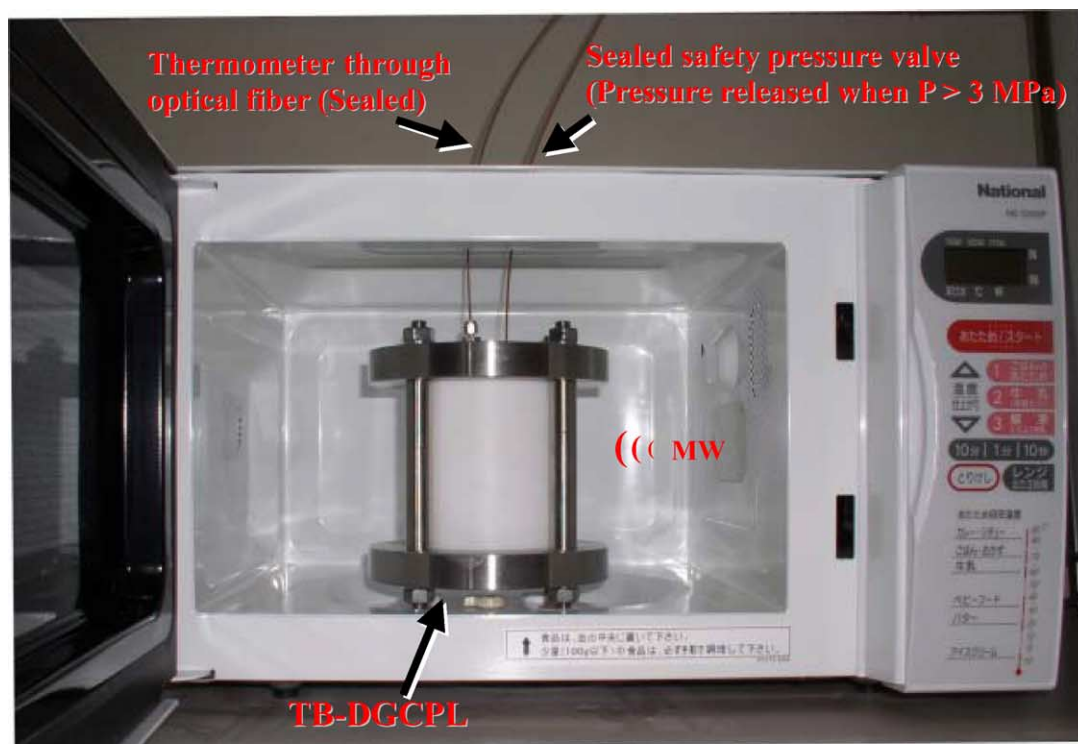
The performance of this relatively simple experimental reactor was evaluated by examining the degradation of 2,4-D using the following four techniques: (i) photocatalytic degradation using TiO₂ irradiated with the DGCPL UV-Vis light coupled with microwave irradiation (PD/MW); (ii) photocatalytic degradation with TiO₂ irradiated with an external electrode Hg lamp (PD); (iii) photocatalytic degradation using TiO₂ irradiated by microwave radiation alone (blank experiment, TiO₂/MW); and (iv) microwave irradiation of the 2,4-D solution in the absence of the TiO₂ photocatalyst (blank experiment, MW).

The effect of the DGCPL UV-Vis radiation on the photodegradation of the 2,4-D substrate was examined by comparing it with the radiation emitted by the external electrode Hg lamp (Ushio Inc., 250 W). For the latter experiment, the aqueous 2,4-D solution containing TiO₂ particles was first introduced into the Teflon reactor, followed by UV irradiation from the top of the Teflon reactor through a fiber optic light guide and maintained under agitation during the irradiation period.

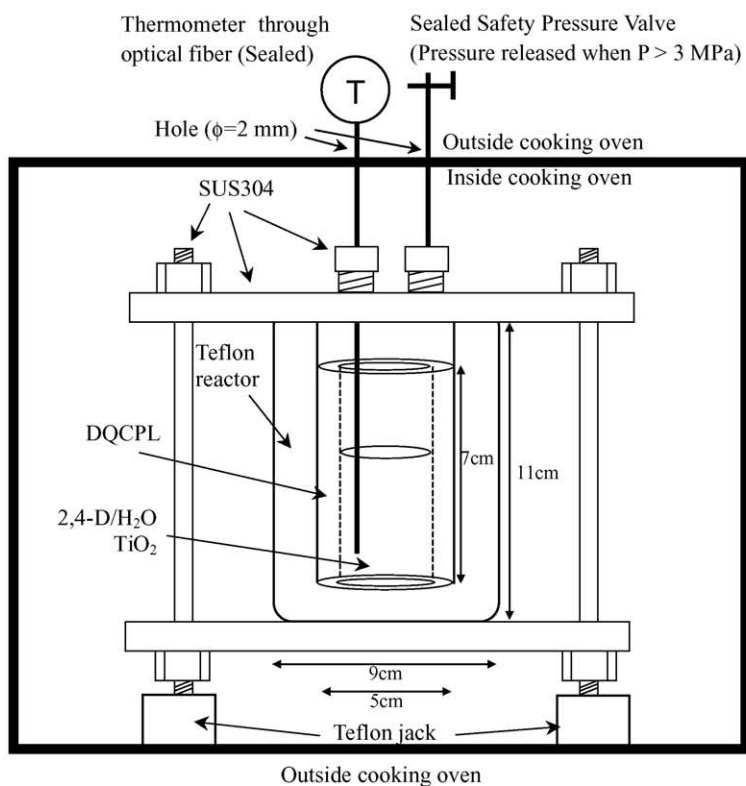
The temporal variations in the absorption spectral features occurring during the photodegradation of 2,4-D were monitored with a JASCO UV/Vis/NIR model V-560V spectrophotometer. The decrease of total organic carbon (TOC) was assayed using a Shimadzu TOC-5000A total organic carbon analyzer. The concentration of Cl⁻ ions produced was determined with a JASCO liquid chromatograph (HPLC) equipped with a CD-5 conductivity detector and an I-524 anion column. The UV-Vis wavelength spectral outputs of the light emitted by the DGCPL and by the Hg lamp were monitored using a Fastevert S-2400 UV spectrophotometer manufactured by Soma Optics Ltd.

3. Results and discussion

The UV-Vis radiation emitted by the DGCPL light source containing a mixture of mercury and neon gases in the mi-



(a)



(b)

Fig. 1. (a) Photograph of the experimental setup of a Teflon batch-type reactor with a double glass cylindrical plasma lamp (DGCPL) incorporated into a domestic microwave oven used in the photocatalytic decomposition of 2,4-D in which microwave irradiation was coupled to the UV-Vis irradiation emitted by the DGCPL source. (b) Schematic of the setup illustrating some of the details of the reactor.

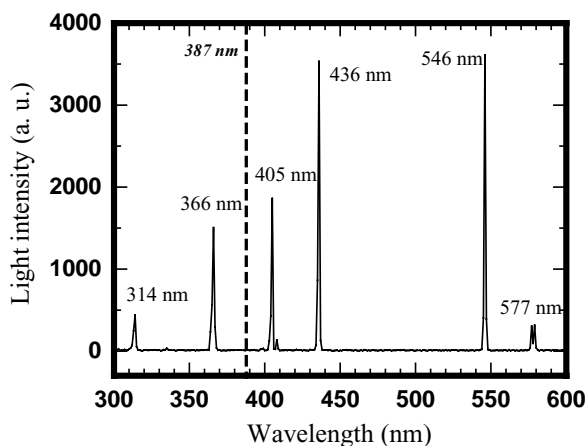


Fig. 2. Ultraviolet and visible wavelengths emitted by the microwave-powered electrodeless DGCPL lamp system.

crowave oven are depicted in Fig. 2. The measurement technique employed the naked DGCPL source placed in the microwave oven and an external UV-Vis spectrophotometer to monitor the radiation. The ultraviolet and visible light wavelengths emitted by the microwave-powered DGCPL light source were 314, 366, 405, 436, 546 and 577 nm. The bandgap energy of the anatase form of TiO_2 is 3.20 eV (corresponding to an absorption onset at 387 nm; dashed vertical line in Fig. 2) so that the 314 and 366 nm wavelengths can activate the TiO_2 particulates. The other wavelengths can be used to degrade dyes [4,6–10] and any other substrate that absorbs radiation in the visible part of the spectrum.

The light irradiance emitted by the naked electrodeless DGCPL light source was ca. 2 mW cm^{-2} , whereas the external electrode Hg lamp delivered an irradiance of ca. 12 mW cm^{-2} in the wavelength range 310–400 nm (maximal emission at $\lambda = 360 \text{ nm}$). Note that, the UV radiation from the DGCPL source falls entirely onto the Teflon batch reactor and thus onto the aqueous solution or dispersion. Even though the irradiance was some six times smaller for the DGCPL source, the degradation efficiency of 2,4-D was nonetheless greater (see below) when using the microwave radiation coupled with the UV light source.

The temporal decrease of the concentration of the 2,4-D, assayed by UV absorption losses at 204 nm, is illustrated in Fig. 3a. Clearly, the PD/MW method caused a relatively faster and complete degradation of the 2,4-D pollutant substrate (ca. 20 min) through zero-order kinetics ($2.0 \times 10^{-3} \text{ mM min}^{-1}$) compared to the PD method alone, which was relatively inefficient requiring ca. 20 min to degrade nearly 59% of the initial quantity of 2,4-D ($1.1 \times 10^{-3} \text{ mM min}^{-1}$). The degradation rate of 2,4-D by the PD/MW method was thus nearly two-fold faster than by the PD method, even though the light irradiance in the latter method was six times greater than in the PD/MW method. Thus, the microwave radiation in the coupled PD/MW technique had a significant effect (nearly 10-fold) on the overall degradation efficiency.

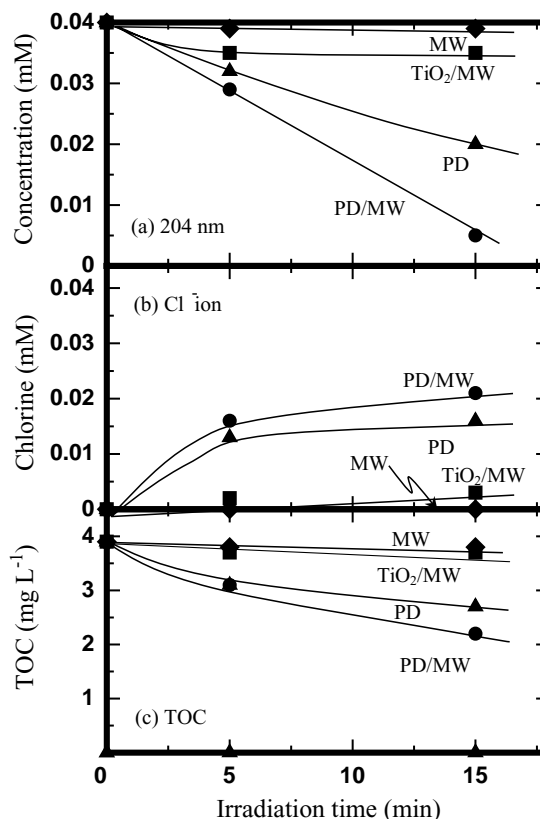


Fig. 3. (a) Plot showing the temporal loss of the 2,4-D target pollutant substrate (0.04 mM) as determined by UV spectral methods; (b) temporal formation of chloride ions; and (c) temporal decrease of TOC (initial concentration, 3.8 mg l^{-1}) during the photodegradation of aqueous 2,4-D solution by the PD/MW, PD, TiO_2/MW , and MW methods.

The difference in the *apparent* photodegradation of 2,4-D by the TiO_2/MW process relative to the MW method alone was caused by loss of 2,4-D from solution through adsorption on the surface of TiO_2 particles.

The temporal formation of Cl^- ions during the photodecomposition of 2,4-D is illustrated in Fig. 3b. The rate of dechlorination of 2,4-D (i.e. formation of chloride ions) using the PD/MW method was slightly greater than for the PD method. In any case, only one chlorine substituent was released into the bulk solution (expected 0.04 mM, observed 0.02 mM). The quantity of Cl^- ions obtained from the TiO_2/MW method was rather small, and none was obtained by microwave irradiation of a 2,4-D solution alone. Our earlier more extensive study [2] of the microwave-assisted photocatalyzed degradation of 2,4-D using a more intricate setup showed that the greater efficiency of the MW-assisted process is due to a non-thermal effect of microwave radiation on the break-up of the aromatic ring of 2,4-D (oxidation), but not apparently on the dechlorination process (reduction) for which MW radiation had only a negligible influence. Under the present conditions, however, it appears that microwaves may have a slight influence on the extent of dechlorination.

The temporal decrease of total organic carbon (initial concentration ca. 3.8 mg l^{-1}) is reported in Fig. 3c. The extent

of mineralization (TOC loss) of 2,4-D was ca. 49% with the PD/MW method, and somewhat less for the PD method (~35%; extrapolated to 20 min). For the TiO₂/MW and MW routes the extent of mineralization of 2,4-D was relatively insignificant.

4. Concluding remarks

Results reported herein demonstrate the usefulness of a simple modified microwave oven that incorporates a batch-type reactor in which the UV-Vis light radiation is supplied by an electrodeless double glass cylindrical plasma lamp. Such a microwave oven can find interesting and efficient use in degrading a large variety of polluting substrates typically found in aquatic ecosystems. Because of its relative ease of use and safety, it could find application in minimizing discarded domestic and agrochemical products otherwise discarded into the usual ecosystems (lakes, rivers); it would require some membrane filtering to avoid disposing of the TiO₂ particulates. The modified microwave oven can also handle a flow-through reactor for continuous operation of relatively larger volumes of polluted feed. Certainly the 2,4-dichlorophenoxyacetic acid could be disposed of in reasonably short time (ca. 20 min) compared to other methods. Moreover, the cost of operating such a simple device should be relatively small as the only power needed is the electrical power to drive the domestic microwave oven (in the present case, 700 W).

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