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A novel environmental risk-free microwave discharge electrodeless lamp (MDEL) in advanced oxidation processes
Degradation of the 2,4-D herbicide

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Abstract

A novel microwave discharge electrodeless lamp (MDEL) has been developed for wastewater treatment with Advanced Oxidation Processes (AOPs) using environment risk-free gases (*e.g.*, xenon, nitrogen, helium, oxygen, hydrogen and argon alone or a mixture thereof) that provide the needed light plasma source when microwave irradiated. The MDEL was optimized through an examination of the light intensity of the emitted radiation in the UV–visible spectral region at controlled pressures and gas-mixture ratios and to test whether the gases self-ignite on irradiation with microwaves. The usefulness of the MDEL was assessed by examining the degradation of aqueous 2,4-dichlorophenoxyacetic acid (2,4-D) in the absence and presence of TiO_2 particles irradiated simultaneously by both microwave (MW) and by UV radiation emitted from the microwave-triggered (2.45 GHz) electrodeless lamp. The decomposition efficiencies for the disposal of the 2,4-D herbicide are compared with the MDEL in close contact (inside) with the 2,4-D solution or the 2,4-D/TiO_2 dispersion and with the MDEL located outside the reactor. Degradation of 2,4-D with the MDEL was monitored spectroscopically and by the loss of total organic carbon (TOC) using no less than seven different protocols, namely (i) MW irradiation alone, (ii) MDEL (outside), (iii) Hg lamp/TiO_2, (iv) Hg lamp/MW/TiO_2, (v) MDEL (outside)/TiO_2, (vi) MDEL (inside), and (vii) MDEL (inside)/TiO_2. Most efficient in the degradation of 2,4-D were the MDEL/TiO_2 systems with the MDEL lamp inside the reactor in contact with the 2,4-D/TiO_2 aqueous dispersion followed closely by the MDEL alone (no TiO_2) also in contact with the 2,4-D solution.

Keywords: Electrodeless lamp; Microwave; Advanced oxidation processes; Photodegradation; Herbicide; 2,4-Dichlorophenoxyacetic acid

1. Introduction

Ever since the early studies by Gedye et al. [1] and Giguere et al. [2] in the use of microwave radiation (MW) in organic syntheses, several additional chemical reactions have been promoted by microwaves as witnessed by two recent monographs [3,4]. The location of the heat source resulting from microwave irradiation is an essential feature in these MW-assisted chemical reactions. Several studies have been reported in the last few years on the enhanced efficiency of photo-assisted degradations of organic substrates using a combination of UV light and microwave radiation in the treatment of aqueous wastewaters containing a rhodamine B dye [5,6], 2,4-dichlorophenoxyacetic acid [7], bisphenol A [8], 4-chlorophenol [9] and other model compounds [10].

Microwave radiation provides not only a heat source (the thermal effect) but also a specific effect (the non-thermal effect), as suggested by Marken and coworkers [11,12], that lead to enhanced photo-assisted degradation of several substrates. A recent study on the photo-assisted TiO_2 degradation of bisphenol A carried out at near-ambient temperatures (21 °C) confirmed the significant role of this microwave non-thermal effect [13], which can lead to increased number of charge carriers on the metal oxide TiO_2 as well as induced formation of trap sites that can prolong carrier lifetimes and lead to additional quantities

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of $^{\bullet}$OH radicals produced in the TiO_2 photo-assisted oxidation of water [14]. Thus, microwave radiation is not merely a heat source. Accordingly, microwave radiation effects on metal-oxide photomediators such as TiO_2 can be very effective in the field of environmental abatement technologies.

Our earlier studies told us that introducing UV radiation in photo-assisted processes through a port in the microwave applicator or through fiber optics was rather inefficient. Accordingly, we proposed [7,15–17] the use of a microwave discharge electrodeless mercury lamp as the UV light source that should have significant advantages in wastewater treatments. They are (a) the relatively long lifetime of the electrodeless lamp, (b) no complications in lamp shape because it is electrodeless, (c) no variations in light intensity, (d) the ignition time to lighting is shorter than for a typical electrode lamp, (e) the energy can be supplied externally with the reactor absorbing no microwave radiation, (f) facile lamp replacement, and (g) both UV and MW radiations are available simultaneously by using microwave energy alone.

Research with microwave discharge electrodeless lamps have had their impetus pointed mostly toward solar-simulation lamps [18], as an energy source in photosynthesis [4,19] and in disinfections [20–22], and most recently in wastewater treatments involving TiO_2-assisted processes [23–25]. Mercury has generally been used as principal element in electrode and electrodeless light sources. However, concerns with released mercury that gets converted into organic mercury and inorganic mercury in the environment along with increased demands that mercury be eliminated from end products so as to attenuate environmental contamination necessitates the development of a Hg-free UV light source that will be environmental friendly and useful.

In the development of a novel microwave discharge electrodeless lamp (MDEL) system that could be used in Advanced Oxidation Processes (*e.g.*, in photo-assisted or photocatalyzed degradations) and become an integral part of the microwave technology, it was necessary that the device (a) have a simple structure, (b) contribute significantly to the overall efficiency of degradation processes, and (c) be of relatively low cost (capital and operating). Note that no detailed cost analysis was done in the present study. A metallic electrode lamp device would not be suitable in the presence of microwave radiation in the microwave applicator.

Our strategy was then to develop a MDEL device that would use environmental risk-free gases that can self-ignite (no trigger needed) and that can generate suitable UV and visible wavelengths for photo-assisted and/or photocatalytic reactions in the presence of appropriate mediators or photocatalysts. The performance of the MDEL so developed was examined using the photodegradation of the agrochemical pollutant 2,4-dichlorophenoxyacetic acid (2,4-D) as the test process, which is driven by coupled microwave/UV radiation (the microwave/photo-assisted process) or by UV light alone (the photo-assisted degradation). The highly toxic synthetic phytohormone (toxin) [26] 2,4-dichlorophenoxyacetic acid (2,4-D) is a typical and widely used agrochemical herbicide.

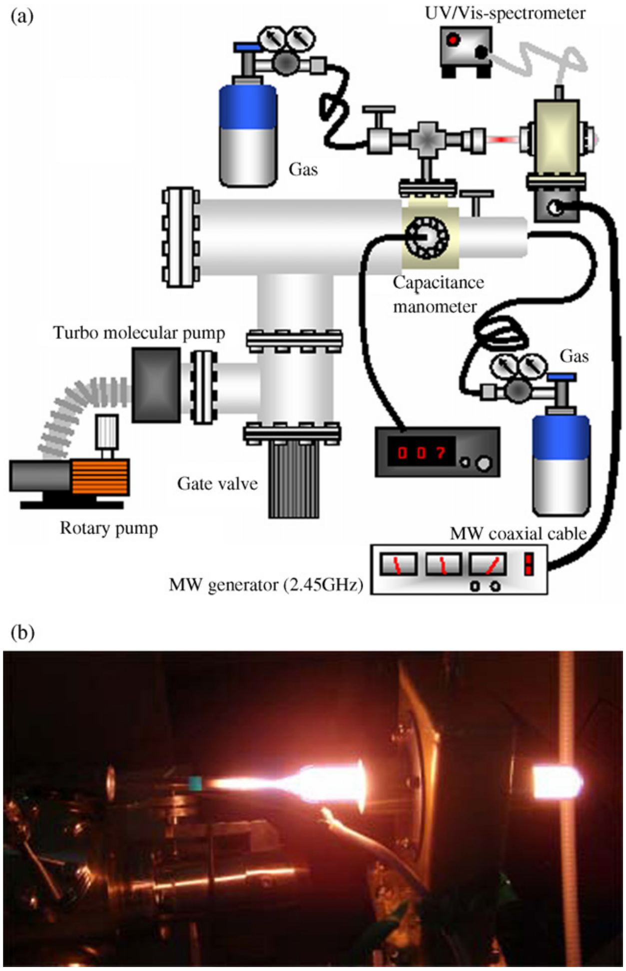

Fig. 1. (a) Experimental setup for the examination of optimized conditions for a microwave discharge electrodeless lamp (MDEL); (b) photograph of nitrogen/argon mixed plasma light with the source of the MW radiation.

2. Experimental

2.1. Preparation of the microwave discharge electrodeless lamp (MDEL)

Optimized conditions to obtain the best gas mixture ratios and internal gas pressures in the MDEL system were examined using the device illustrated in Fig. 1a. A quartz ampoule (Ichikawa Pressure Industrial Ltd.) was connected to vacuum and was then arranged in the microwave waveguide. The size of the MDEL was 145 mm (length) × 18 mm (diameter). The initial internal pressure in the ampoule was set at 10^{-3} Torr (or *ca.* 0.13 Pa) using the turbo molecular pump assisted by a rotary pump. Subsequently, the target gas (Xe, N_2, He, O_2, H_2, and Ar, or a binary gas mixture thereof) was introduced into the ampoule with the amount adequately adjusted by the mass controller. The pressure inside the ampoule was monitored with a capacitance manometer. The gas-mixture ratios were calculated from the volume ratio of each gas.

The UV–visible spectra of the emitted light plasma and the corresponding light intensities for each gas (and mixture) subjected to microwave irradiation were monitored through a fiber optic connected to a UV–visible spectrophotometer. The most suitable gas and gas-mixture ratio and gas pressure for the MDEL device was determined using three criteria: (1) light intensity, (2) spectral pattern and (3) self-ignition of the gases by MW irradiation alone. Microwave radiation was generated using an ARIOS Inc. generator (Model MP-201; frequency, 2.45 GHz; maximal power, 200 W), which together with the waveguide were connected through a coaxial cable. The applied power of the microwave was 80 W for all experiments, unless noted otherwise. Fig. 1b displays a photograph of the luminescence emitted by the MDEL subsequent to MW irradiation.

2.2. *Chemical reagents*

Titanium dioxide was Degussa P-25 (specific surface area, 53 m^2 g^{-1} by the BET method; particle size, 20–30 nm by TEM microscopy; composition 83% anatase and 17% rutile by X-ray diffraction). Reagent grade 2,4-dichlorophenoxyacetic acid (purity >98%) was supplied by Wako Pure Chemicals Co. Ltd. All other chemicals were of reagent grade quality.

2.3. *Degradation procedures*

Continuous microwave irradiation of the dispersions was achieved using the ARIOS MP-201 apparatus. A 30-mL air-equilibrated aqueous 2,4-D solution (0.050 mM) containing the TiO_2 particles (loading, 50 mg) was introduced into the cylindrical high-pressure reactor. A suitable 2,4-D/TiO_2 aqueous dispersion was achieved by sonication for *ca.* 30 s followed by insertion of the MDEL lamp into the cylindrical reactor connected to the top side of the multimode MW applicator. It was then sealed with two Teflon rings and a stainless steel cap. The dispersion was continually stirred during the microwave and/or UV irradiations. The increase in pressure inside the reactor was monitored using the pressure gauge connected to the stainless steel cap. Microwave power was continuously 200 W in the degradation experiments involving the 2,4-D herbicide (see Fig. 2a and b). Degradation of the 2,4-D herbicide was followed by UV spectroscopy. When TiO_2 dispersions were examined, the TiO_2 particles were removed by centrifugation followed by filtration with a 0.2 μm filter/syringe prior to spectroscopic analysis.

3. Results and discussion

3.1. *Preparation of the MDEL lamp*

Typical UV–visible spectra of the light plasma generated from Xe gas are displayed in Fig. 3(i) with the internal pressure of the lamp controlled in the range 18–186 Pa (0.14–1.40 Torr); the figure reports spectra at 18 (0.14), 41 (0.31) and 58 (0.44) Pa (Torr). The light intensity of the light plasma for Xe was greatest at pressures from 40 to 60 Pa (0.30–0.45 Torr). Of import, the Xe light plasma was observed under microwave irradiation only between 30 and 60 Pa (0.23–0.45 Torr) pressures. At other pressures it was necessary to use a Tesla coil (atmospheric discharge coil) to trigger the light plasma. Also significant is the spectral shape of the Xe-loaded MDEL emitted radiation that resembles closely that from a traditional Xe electrode lamp. The tendency of the spectral intensity to decrease is caused by the increased pressure inside the lamp above the threshold of 60 Pa (0.45 Torr) as a result of self-quenching above this threshold.

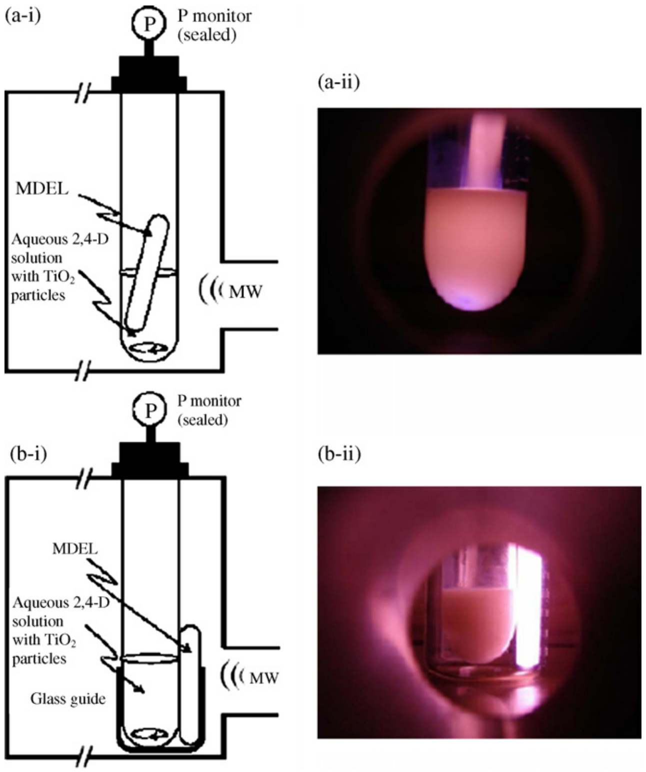

Fig. 2. (a-i) Experimental details of the setup of the microwave discharge electrodeless lamp (MDEL) used in the photo-assisted decomposition of 2,4-D in aqueous TiO_2 dispersions; (a-ii) actual photograph of the N_{20}/Ar_{80} MDEL lamp in the TiO_2 dispersed 2,4-D solution (subscripts refer to ratio of gases); (b-i) experimental image of MDEL degradation system on the location of outside; (b-ii) photograph of the outside setup of MDEL and the aqueous 2,4-D/TiO_2 dispersion.

UV–visible spectra of the light plasma generated from the N_2-loaded MDEL device using microwave radiation were observed in the pressure range 47–1130 Pa (0.35–8.50 Torr). Spectral patterns at three selected pressures (102, 401 and 1130 Pa; *i.e.*, 0.77, 3.02 and 8.50 Torr) are illustrated in Fig. 3(ii). No significant variations in the spectral patterns were seen at these pressures. Emitted wavelengths for the nitrogen plasma were mainly concentrated in the UVB/UVA range of 300–400 nm. With the absorption edge of TiO_2 at *ca.* 387–400 nm, the N_2-loaded MDEL is most adapted to photo-activate this metal-oxide photocatalyst in advanced oxidation processes. The light intensity below 400 nm of the N_2 gas light plasma was greater than that emitted by the Xe gas under otherwise similar conditions. Moreover, the cost of N_2 gas is definitely more economical than Xe gas. Based on these two criteria then, it is evident that a MDEL purged with N_2 gas is the more suitable one. This contrasts a recent study by Jinno et al. [27] who report that a pure Ar discharge and a pure N_2 discharge are both unstable and thus require a small amount of nitrogen to improve the stability of the Ar discharge. Details of the physical mechanism of

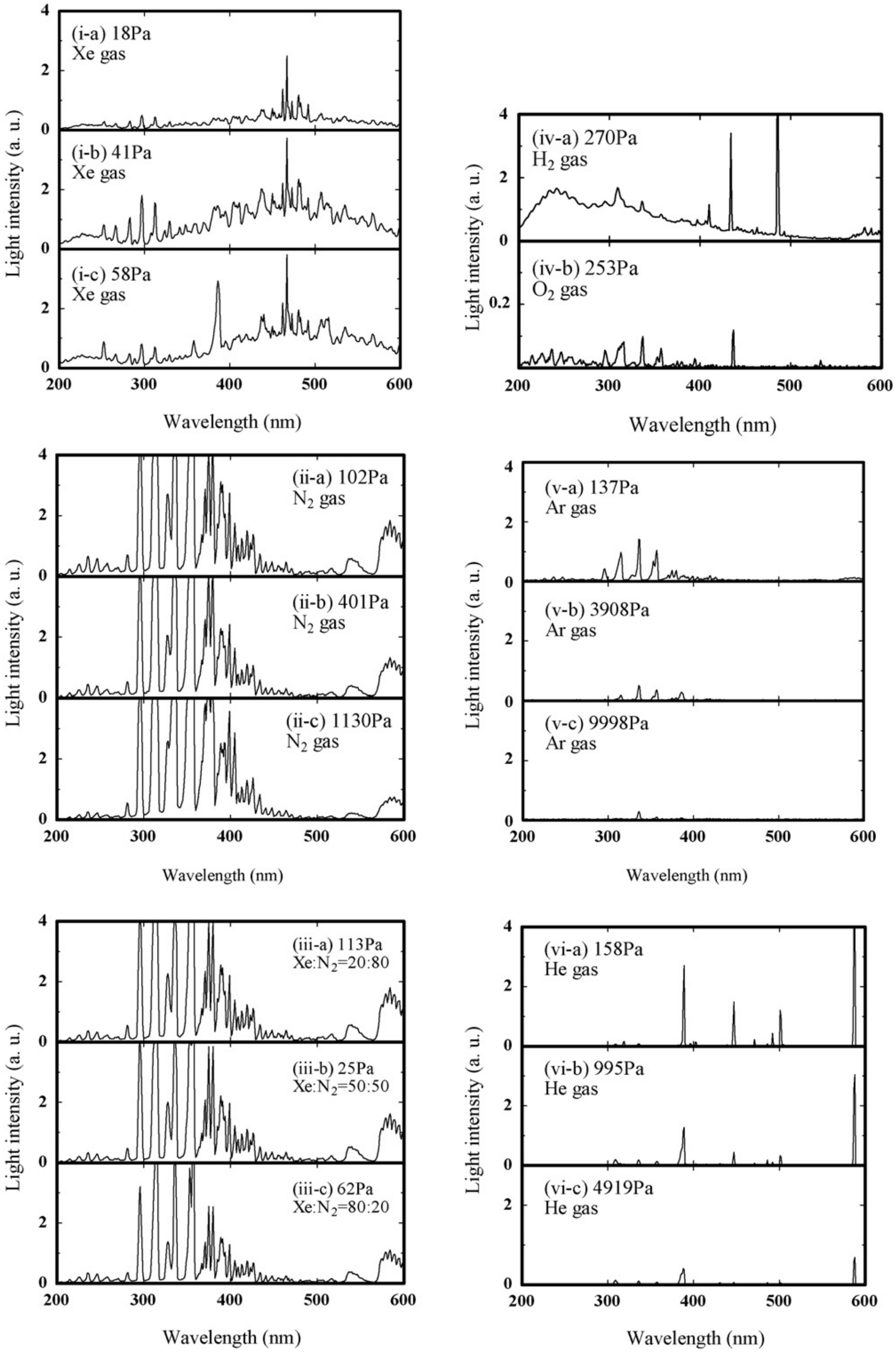

Fig. 3. UV and visible wavelengths emitted by the MDEL lamp at applied MW powers of 80 W: lamp purged at the pressures noted with (i) Xe gas, (ii) N_2 gas, (iii) mixed Xe/N_2 gases, (iv) H_2 gas and O_2 gas, (v) Ar gas, and (vi) He gas. For (i) spectra were measured at 5 Pa steps, whereas for cases (ii), (iii), (v), and (vi) spectra were measured every 10 Pa.

MW-excited N_2 and N_2/Ar gas discharges have been reported recently by Ferreira and coworkers [28,29]. It appears that N_2^+ ions dominate over a wide range of Ar content, a consequence of charge transfer processes between Ar^+ and N_2 and of the effective associative ionization from the $N_2(A^3\Sigma_u{}^+)$ metastable state. However, details of the Xe/N_2 plasma discharge remain elusive and were not a goal of this study.

The UV–visible spectral patterns of the emitted light plasma from a gas mixture composed of various volume ratios (20:80, 50:50 and 80:20) of Xe and N_2, respectively, were examined at various pressures; total pressure inside the quartz ampoule ranged from 25 to 812 Pa (0.19–6.11 Torr). Typical spectra are shown in Fig. 3(iii) in which the principal peaks are mostly of nitrogen origins {compare with patterns in Fig. 3(ii)}. No light plasma spectral patterns from the Xe gas are evident as no pattern commensurate with Xe emission appears in the vicinity of 400–500 nm. Contrary to the case of pure nitrogen, the mixed Xe/N_2 gas mixture did not self-ignite when the lamp device was subjected to microwave radiation. Ignition again required a Tesla coil at all the pressures examined. Even if Xe gas were mixed with N_2 in the MDEL it would not be a suitable candidate as a light source because of the latter factor and the increased cost of the Xe gas.

Spectral patterns across the UV–visible region for the H_2 gas ($P = 270$ Pa; 2.03 Torr) and O_2 gas ($P = 253$ Pa; 1.90 Torr) light plasma are summarized in Fig. 3(iv). Plasma lines for H_2 gas are mostly concentrated at wavelengths 200–400 nm, and are appropriate to activate the TiO_2 photocatalyst. However, both H_2 and O_2 gases failed to self-ignite under microwave radiation necessitating the Tesla coil to ignite and emit the light plasma. The intensity of the O_2 light plasma was rather low and thus not very useful when compared to the nitrogen plasma.

The above data and discussion clearly indicate nitrogen gas as the most suitable medium to provide a light plasma source in the MDEL device because of low cost, UV-light spectral patterns and self-ignition under microwave radiation. However, when the MDEL device was tested in treating a wastewater containing a pollutant it became necessary to examine self-ignition more closely. Thus, microwave irradiation of the N_2-purged MDEL in wastewater treatment at N_2 pressures similar to those of Fig. 3(ii) proved ineffective (no self-ignition) because of the non-insignificant absorption of the microwaves by the wastewater. Accordingly, argon and helium gases were mixed with nitrogen because these gases are easily self-ignited by microwaves.

Results of low, middle and high Ar and He gas pressures are typical and are shown in Fig. 3(v) and (vi), respectively. In both cases, the light intensity is greater at low pressures owing to self-quenching events at the higher pressures. UV–visible spectral patterns of the Ar-loaded lamp were determined at pressures from 83 to 1014 Pa (0.62–7.62 Torr). Self-ignition of the MDEL device by microwave irradiation alone occurred in all instances, with light wavelengths concentrated mostly at 300–400 nm. Thus the argon plasma in itself would be suitable for TiO_2 photocatalyst activation. By contrast, experiments with He gas in the pressure range 20–14,532 Pa (0.15–109.3 Torr) showed that self-ignition of the He plasma occurred only within the range of pressures 298–805 Pa (2.24–6.05 Torr). Accordingly, argon gas was used to assist in the self-ignition of a N_2-loaded MEDL lamp device for wastewater treatment.

3.2. Optimization of the N_2/Ar-loaded MDEL

Various gas ratios of nitrogen and argon were examined for self-ignition and light plasma intensity in optimizing the conditions for a N_2/Ar-loaded MDEL. Ratios of nitrogen and argon were N_2:Ar = 75:25, 50:50 and 25:75 the results of which are portrayed in Fig. 4(i–iii). The pressure inside the MDEL quartz ampoule was adjusted to between 54 and 10,000 Pa (0.41–75.2 Torr). Note that the data reported in Fig. 4 were obtained by placing a pinhole attachment between the fiber optic and the light source so as to reduce the light intensity of the emitted light plasma {see, *e.g.* Fig. 3(iii)}. Consequently, the data in Fig. 3 cannot be compared to the results displayed in Fig. 4 for which the ideal pressure for each of the N_2/Ar ratios examined ranged between 700 Pa (5.26 Torr) and 5000 Pa (37.6 Torr). Significant Ar light plasma lines are seen mostly above 600 nm [27] and are not reported in Fig. 4. The MDEL device with a nitrogen-to-argon ratio of 25–75% at 682 Pa (5.13 Torr) self-ignited under MW radiation emitting light plasma with the highest intensity under these conditions.

The nitrogen content in the N_2/Ar gas mixture was adjusted to 10%, 1%, 0.1%, 0.05%, 0.025% and 0.01% and subsequently examined. The result from the 1% nitrogen content is shown in Fig. 4(iv). Although self-ignition improved by increasing the quantity of argon, the light intensity decreased substantially {compare data of Fig. 4(iii and iv)}.

The condition of 10–30% nitrogen in the gas mixture was suitable from the points of view of light intensity of the emitted light plasma and of self-ignition. Considering the changes in light intensities at each pressure examined for a 10–30% nitrogen content, it is evident from the results displayed in Fig. 4(iii) that the most suitable pressure was *ca.* 700 Pa (5.26 Torr). This pressure region fits very nicely with the required self-ignition by the microwave radiation alone. The UV spectral patterns for the 10–30% nitrogen content and for a pressure at *ca.* 700 Pa (5.26 Torr) are illustrated in Fig. 5. Clearly, the most suitable ratio of nitrogen-to-argon is 20% N_2 and 80% Ar on the basis of higher light intensities and on the observation that the gas mixture in the quartz ampoule can undergo self-ignition by microwave irradiation.

The UV spectral lines emitted by a mercury lamp at 297, 303, 313, and 365 nm are depicted in Fig. 5f for comparison. The wavelengths emitted by the self-ignited N_2/Ar gas mixture (see above) in the MDEL device are seen at 296, 315, 336, 353 and 357 nm emanating mostly from nitrogen. It is also evident that the UV light generated by the MDEL subjected to microwave radiation is concentrated in the range 300–400 nm. Consequently, we deduce that the N_{20}/Ar_{80}-loaded MDEL device is as suitable a light source for a photo-assisted reaction as is a Hg lamp. This nitrogen-to-argon gas ratio was thus used to examine the practicality and efficiency of degrading the test 2,4-D substrate.

3.3. Surface temperatures of N_2/Ar-loaded MDEL

Because microwave radiation produces heat as does the emitted light, it was imperative we also measure the temperature at the surface of the MEDL at several microwave input power. For this purpose we used other microwave generators with higher MW powers and a N_{20}/Ar_{80}-loaded MDEL arranged in a multimode cavity. The surface temperatures at the various microwave power input were measured outside the cavity 1 min after self-ignition of the lamp using an infrared thermometer (Model R-160; Anritsu Meter Co. Ltd.). They are summarized in Table 1. The surface temperature reached 120 °C on irradiation with microwaves at 200-W power.

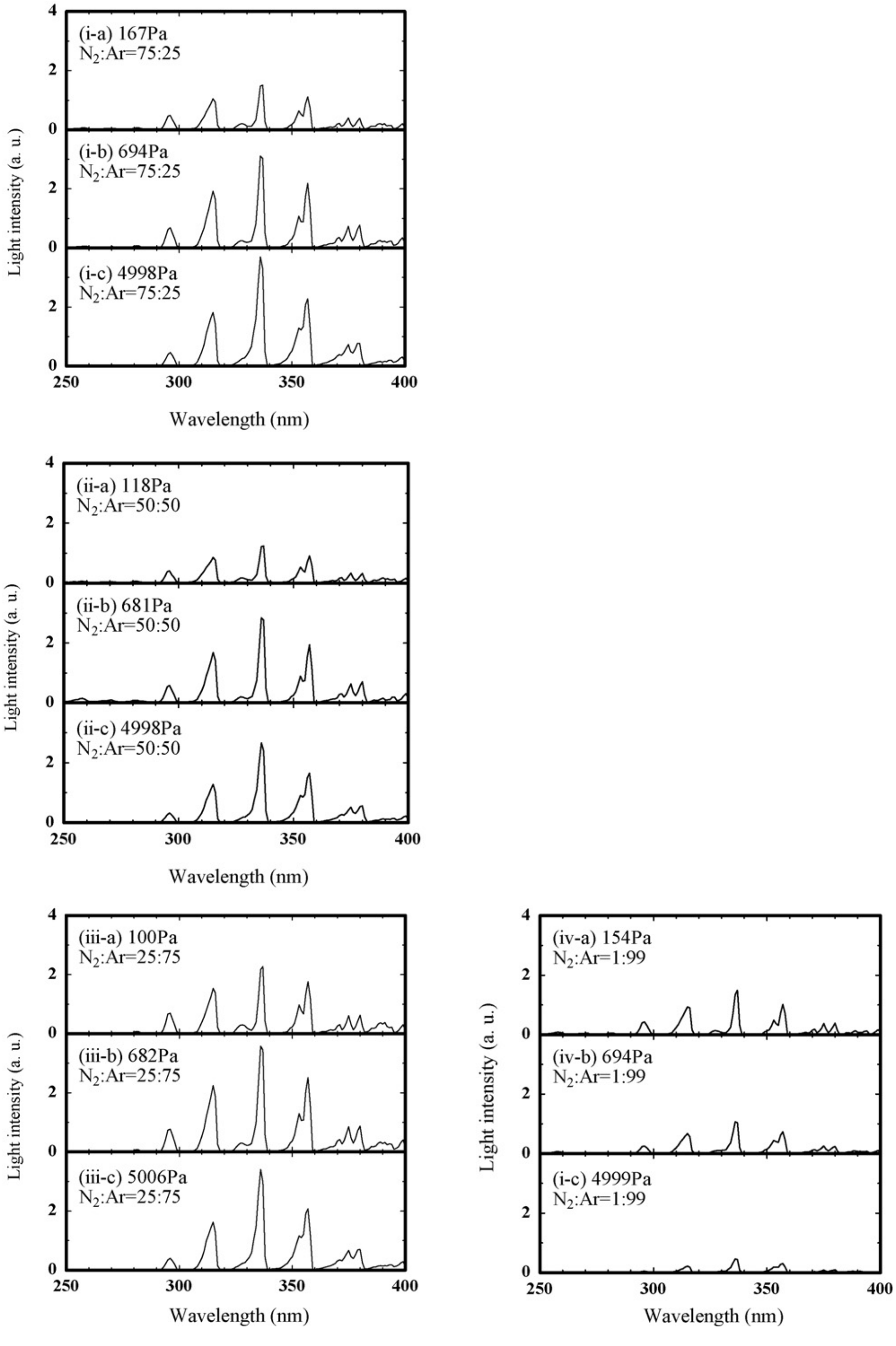

Fig. 4. Ultraviolet and visible wavelengths emitted by the microwave discharge electrodeless lamp with Xe and N_2 mixed gases at applied microwave powers of 80 W. The gas mixture ratio of N_2 and Ar were (i) 75: 25, (ii) 50: 50, (iii) 25: 75 and (iv) 1: 99. For cases (i–iii) spectra were measured in 100 Pa pressure steps.

3.4. Degradation of 2,4-D using the N_2/Ar-loaded MDEL light source

The photodegradation of an air-equilibrated 2,4-dichlorophenoxyacetic acid (2,4-D; 0.050 mM) aqueous dispersion in the presence of TiO_2 was carried out using the N_{20}/Ar_{80} MDEL light source and a traditional Hg electrode lamp. The photodecomposition of 2,4-D in the absence of TiO_2 was also examined with the same MDEL source under otherwise identical conditions. Degradation rates of 2,4-D were compared by arranging the MDEL to be inside or outside the cylindrical reactor.

The spectrum of an aqueous solution of 2,4-D displays absorption bands at 285, 230 and 204 nm. Loss of UV absorption at 204 nm for the decomposition of 2,4-D solution was converted into concentration loss reported in Fig. 6a. It was remarkable to

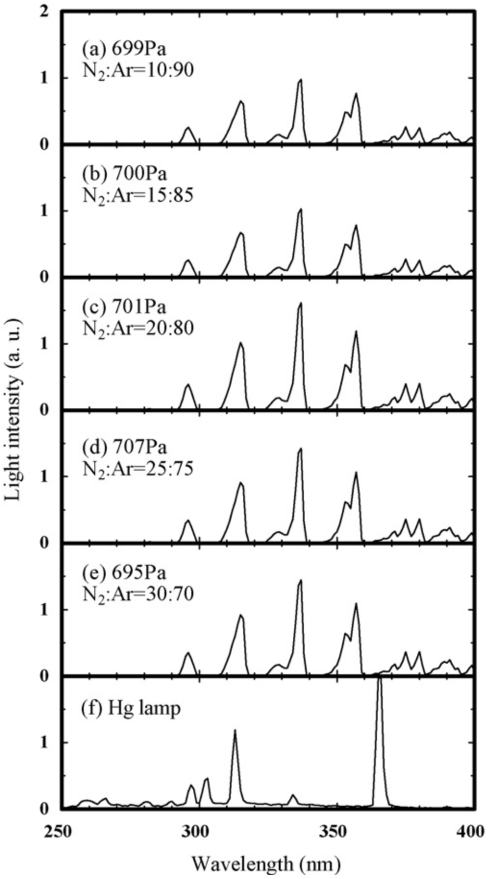

Fig. 5. Ultraviolet and visible wavelengths emitted by the microwave discharge electrodeless lamp with a gas mixture of N_2 and Ar at an applied microwave power of 80 W. The N_2 to Ar gas ratios were (a) 10:90, (b) 15:85, (c) 20:80, (d) 25:75, and (e) 30:70; (f) light emitted by a traditional 100-W Hg electrode lamp.

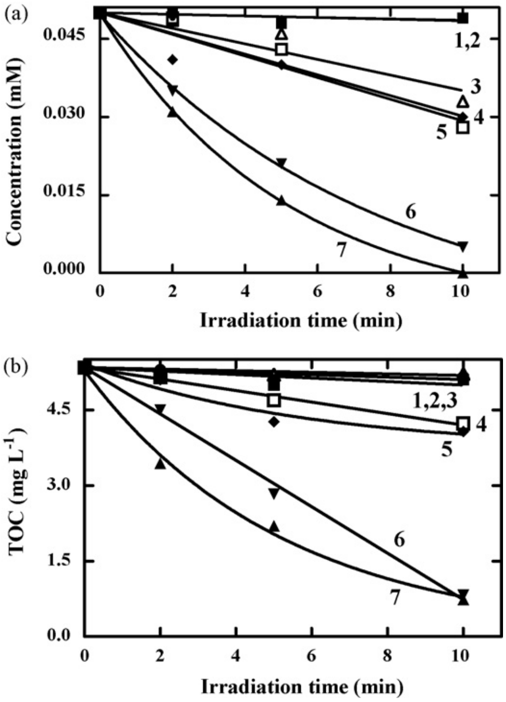

Fig. 6. (a) Temporal variations in the concentration of 2,4-D during its degradation in aqueous 2,4-D solutions (0.050 mM) using various protocols: (1) MW alone, (2) MDEL (outside), (3) Hg Lamp/TiO_2, (4) Hg lamp/MW/TiO_2, (5) MDEL (outside)/TiO_2, (6) MDEL (inside), and (7) MDEL (inside)/TiO_2 after irradiation for 2, 5 and 10 min. (b) Temporal decrease of total organic carbon (TOC) during the mineralization of the 2,4-D solution (initial TOC concentration, 5.34 mg L^{-1}).

observe that in the absence of TiO_2, the direct photodegradation of the 2,4-D herbicide using the MDEL lamp inside the reactor was nearly complete (*ca.* 90%).

The following points are worth noting on the degradation of 2,4-D irradiated by the MDEL system alone in the absence of TiO_2: (a) photodegradation of 2,4-D also takes place through direct irradiation by the short UV wavelengths from the MDEL light source, and (b) some thermal degradation of 2,4-D may also occur through the infrared light also emitted by the MDEL device. With the MDEL located outside the cylindrical reactor, the degradation of 2,4-D is slower probably owing to a decrease of the thermal component (infrared radiation is less) and because the UV wavelengths of the MDEL light plasma less than 320 nm are attenuated/screened through absorption by the Pyrex cylindrical reactor. The extent of decomposition of 2,4-D was 40% in the presence of TiO_2 with the outside MDEL source, compared to less than 5% by outside MDEL alone without TiO_2. Also, microwave irradiation of the 2,4-D aqueous solution had no effect with the pressure inside the reaction cylinder being 1.7 MPa after MW irradiation for 10 min. Irradiation by light emitted from a traditional Hg lamp and by the Hg lamp/MW coupled system was also rather ineffective (34% and 44%, respectively) even in the presence of TiO_2 after a 10-min period.

Table 1
Temperatures measured at the MDEL surface at various MW power using the infrared thermometer (see text)

MW input power (W)	Temperature[a] (°C)
200	120
280	160
350	210
450	250
540	260
630	310
709	400
795	>500
881	>500

[a] Error margin about ±8 °C.

The pressure in the closed reactor was also monitored during the degradation of 2,4-D. As expected, the pressure increased with increase in temperature. For instance, in the case of the MDEL/TiO_2 system, the pressure increased from an initial 0.1 to 2.0 MPa after only 10 min of microwave irradiation, whereas the pressure increased to 2.2 MPa when the MDEL system alone was used without TiO_2. However, when the MDEL (outside) setup was used for the degradation of 2,4-D the pressure increased to 1.8 MPa in the presence of TiO_2 but was 2.0 MPa without TiO_2. The increase in temperature of the solution was due to some extent to the emitted infrared light; however, heating was mostly due to microwave dielectric heating. Regardless, the surface

Table 2
Rates of degradation and mineralization (as TOC loss) of 2,4-dichlorophenoxyacetic acid in aqueous media

Protocols	Curves in Fig. 6	$R_{(\mathrm{degr})}$ 10^{-3} mM min^{-1}	$R_{(\mathrm{TOC})}$ mg L^{-1} min^{-1}
MW	1	0.16 ± 0.07	0.035 ± 0.011
Hg lamp/TiO_2	3	1.50 ± 0.22	0.016 ± 0.004
Hg lamp/MW/TiO_2	4	2.00 ± 0.24	0.114 ± 0.005
MDEL (outside)	2	0.13 ± 0.04	0.024 ± 0.007
MDEL (inside)	6	6.52 ± 1.02	0.46 ± 0.01
MDEL (outside)/TiO_2	5	2.08 ± 0.25	~0.92
MDEL (inside)/TiO_2	7	9.68 ± 0.33	1.02 ± 0.30

temperature of the lamp was only about 120 °C (see above and Table 1) so that thermal degradation of 2,4-D is an insignificant factor of the overall pathway to degradation.

When the MDEL was in contact with the aqueous 2,4-D solution or with the aqueous 2,4-D/TiO_2 dispersion the degradation efficiency was substantial as witnessed by the complete degradation of 2,4-D for the MDEL (inside)/TiO_2 system (Fig. 6a) after a 10-min period, and the 90% degradation in the absence of TiO_2. The results on the loss of total organic carbon are even more revealing as illustrated in Fig. 6b. With the MDEL (inside) and MDEL (inside)/TiO_2 arrangements, about 84% of TOC was lost after only 10 min of irradiation; the dynamics of the latter are somewhat faster (see Table 2). Evidently, mineralization of the 2,4-D and other by-products to carbon dioxide was nearly quantitative in very short time. No attempt was made in this study to examine the nature of the intermediates that formed during the photo-assisted degradation of the 2,4-D herbicide, as this was dealt with in an earlier study [7].

Results reported in Table 2 also indicate that although the kinetics of degradation of 2,4-D by the Hg lamp/MW/TiO_2 and the MDEL (outside)/TiO_2 protocols are nearly identical, the mineralization rate of 2,4-D by the latter setup is nearly an order of magnitude faster, as also appears to be the case when comparing the mineralization rates of the Hg lamp/TiO_2 system with the Hg lamp/MW/TiO_2 arrangement. Nonetheless, most important to note is that the arrangement in which the MDEL is in close contact with the 2,4-D solution is to be preferred. This notwithstanding, however, a possible disadvantage of the MDEL (inside) setups is that the conversion rate of the microwave radiation to light emitted may decrease as a result of absorption of the microwaves by the solution/dispersion. By contrast, with the MDEL (outside) setup, light intensity from the plasma source is greater and constant. In the latter case, however, the short UV wavelengths (<320 nm) are also screened by the Pyrex glass reactor. With the MDEL (inside) setup, all the UV wavelengths are available in causing a direct (no TiO_2) or indirect (with TiO_2) photodegradation of the 2,4-D herbicide. Clearly, there are merits and demerits on the location of the MDEL light source with respect to the reactor. However, the experimental results definitely demonstrate that the MDEL (inside) setups are the more suitable arrangements.

4. Concluding remarks

A novel microwave discharge electrodeless lamp (MDEL) device has been developed and its characteristic features determined as a function of the nature of the gas and gas mixtures, pressure ranges within which the light plasma emitted was most intense, and whether the gases or gas mixtures can be self-ignited on application of microwave radiation alone. The most suitable light plasma with lines concentrated in the 300–400 nm spectral range under our conditions was obtained with a nitrogen-to-argon ratio of 20–80% by volume at a pressure around 700 Pa. Such a system was then used to test the usefulness of such a light source that embodies UV radiation, microwave radiation and some thermal energy toward the degradation of the herbicide 2,4-dichlorophenoxyacetic acid. The degradation process was examined with the MDEL light source inside the reactor and outside the reactor, and with and without the presence of TiO_2 well known to assist in the photodegradation of a large class of organic pollutants. The arrangement in which the MDEL is located inside the reactor proved most efficient in degrading 2,4-D completely (100%) within a 10-min period in the presence of TiO_2; when no TiO_2 was present the degradation was also near completion at 90%. Significant mineralization of the herbicide was also evident from the loss of total organic carbon (TOC), which after 10 min showed that the MDEL (inside) arrangement accounted for *ca.* 85% loss of TOC with and without the TiO_2 photomediator, with the dynamics of degradation of the former being somewhat faster. Clearly, the MDEL device so developed should prove to be an attractive additional tool in the attenuation and disposal of environmental contaminants.

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