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Microwave Discharge Electrodeless Lamps (MDELs). Part IX. Novel microwave MDEL photoreactor for the photolytic and chemical oxidation treatment of contaminated wastewaters

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Abstract

This article reports on the fabrication and enhanced performance of a novel microwave discharge electrodeless lamp (MDEL) consisting of a three layer cylindrical structure that has been found effective in the degradation of wastewater containing the 2,4-D herbicide and the near total sterilization of bacteria-contaminated pond water (*E. coli* and other microorganisms) through photolysis with the emitted vacuum-UV (185 nm) and UVC (254 nm) light from the MDEL and through chemical oxidation with reactive oxygen species (ROS) produced by the photolysis of dioxygen and air oxygen through one of the photoreactors. Flow rates of the 1.0-L contaminated waters were 0.6 and 1.2 L min^{-1}. The integrated UV/ROS_{O2} and UV/ROS_{Air} methods used to carry out the degradation and sterilization processes were more effective than either the UV method alone or the ROS_{O2} and ROS_{Air} methods for short time periods (5 or 8 min). At the lower flow rate, 79 % of 2,4-D degraded by the UV/ROS_{O2} method and 55 % by UV/ROS_{Air} after 8 min. At the faster flow rate of 1.2 L min^{-1}, degradation of 2,4-D in the 1.0 L volume of water was 84 % and 77 % complete by the UV/ROS_{O2} and the UV/ROS_{Air} method, respectively, after 8 min of irradiation. The number of kills of *E. coli* bacteria was nearly quantitative (98 and 99 %) by the UV/ROS_{O2} and UV/ROS_{Air} methods after treating the contaminated water for 5 min. The decrease of total viable microorganisms in pond water was 90 % and 80 % after 5 min of microwave irradiation at a flow rate of 1.2 L min^{-1} by the integrated methods UV/ROS_{O2} and UV/ROS_{Air}, respectively. The rate of flow of oxygen gas through the photoreactor impacted the extent of degradation and the related dynamics of the 2,4-D herbicide.

Keywords: Microwave discharge electrodeless lamps; MDELs; 2,4-dichlorophenoxyacetic acid; Ozone; *E. coli*; photolysis

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1.0 Introduction

Recent years have witnessed increased practical applications of microwave discharge electrodeless lamps (MDELs) as a result of their high performance, their miniaturization and the lower costs of the magnetron. MDELs have proven useful as light sources in the photochemical syntheses of organic substrates and in environmental remediation. Distinctive features that make MDEL devices attractive are (a) the relatively long lifetime of the electrodeless lamp, (b) no complications in lamp shape because the lamps are electrodeless, (c) no variation in light intensity, (d) the ignition time for lighting the MDEL device is shorter than for a typical electrode lamp, (e) the UV radiation can be supplied external to the reactor to avoid absorption of the microwave radiation by the reactor contents, (f) the facility of lamp replacement, and finally (g) both UV and MW radiations can be used simultaneously to induce oxidative/degradative processes toward the destruction of organics and microorganisms using only the microwave energy source. Recent studies have used such a lamp device to effect the remediation of contaminated waters.[1, 2]

As part of our long-standing strategy, we have developed novel MDEL and microwave equipment for the treatment of wastewaters. The MDEL device in our earlier studies consisted of MDELs surrounding the tubular reactor.[3–5] Also examined were the suitability and usefulness of a commercial microwave domestic oven minimally modified to incorporate a Teflon batch (TB) reactor containing an electrodeless double glass cylindrical plasma lamp (DGCPL), whose radiation could drive the degradation of a variety of pollutants.[6] The MDEL lamp was easily ignited using low microwave power levels because the microwave radiation was directly focused onto the MDEL device. However, although this MDEL device can be used to photolyse wastewater through the emitted light directed at the interior of the MDEL device, the light directed at the exterior is lost photon energy. In addition, vacuum-UV light emitted by the MDEL device generated ozone through the photolysis of air oxygen, which can cause deterioration of the equipment and of the microwave applicator.

To overcome the above issues, the MDEL was located directly in the aqueous media, such that all of the emitted light radiation from the MDEL could be used for the photolysis of wastewater. The MDELs required no electric wiring because the MDEL devices contain no metallic electrodes as is the case in commercial mercury UV lamps. A mercury-free MDEL device has also been proposed.[7] Unfortunately, a non-insignificant portion of the applied microwaves that activate this type of MDEL device are also absorbed by the wastewater, which decreases the microwave energy converted into photon energy. To resolve this problem, in another study we included a tungsten wire to improve the ignition efficiency of the MDELs.[8] In addition, a metallic condensing cone that concentrates the microwave radiation (equivalent to an optical lens) was likewise developed and used as part of a system to activate the MDEL in the photo-oxidative treatment of wastewaters by aiding self-ignition of the lamp on irradiation at low microwave power levels.[9] Small grain-shaped MDELs (10 × 5 mm) were also fabricated as light sources for remediating polluted aqueous media as self-ignition could occur at low microwave power levels, thereby demonstrating some advantages of miniaturizing the

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devices.[10]

The penetration depth of the 185-nm radiation in water is shorter than the 254-nm wavelength, and the 185-nm light irradiance decreases by ca. 50% from the surface of the water at a distance of 2 mm.[11] Accordingly, the photodegradation of organic pollutants in water by the 185-nm VUV light likely takes place near or at the lamp surface. An advantage of miniaturization of MDEL systems is the greater surface area achieved for light irradiation of the contaminated model wastewaters even in a small flow-through reactor. Nonetheless, even if these MDEL devices were used, a certain portion of the microwave energy is also absorbed by the wastewaters. Moreover, the vacuum-UV (185 nm) and UVC (254 nm) light wavelengths emitted by the MDELs compete in the photolytic process and in the formation of reactive oxygen species (ROS).

This study reports on a novel MDEL device that consists of a three-layer cylindrical structure with the MDEL unit looped around the tubular reactor through which the wastewaters flow. Photolysis of oxygen gas occurred in the reactor volume outside the MDEL generating chemical oxidative ROS species. One of the advantages of this device is that it also permits passing the produced ROS gas (e.g., ozone) through the solution during the successive photolyses and ROS treatment of a wastewater contaminated with a herbicide (2,4-D) and with such bacteria as *E coli*. The problem of microwave energy loss in treating wastewaters was also resolved.

2.0 Experimental setup

2.1 MDEL device to drive the photolysis and chemical oxidation of wastewaters

A novel device that includes a microwave discharge electrodeless lamp (MDEL) and two photoreactors was fabricated to effect the photolysis of wastewaters and gaseous substrates using vacuum-UV transparent synthetic quartz as the envelope for the Hg/Ar gas-filled device (**Figure 1a**). Subsequent to evacuating the MDEL quartz envelope to 1×10^{-3} Pa, the system was purged with argon gas (133 Pa) followed by addition of a small quantity of liquid mercury (ca. 0.3 mg). Specifically, the device consists of three chambers with the middle chamber being the MDEL (14.0 cm long, 3.0 cm diameter), while the innermost (20.0 cm long; inner dia., 0.8 cm) and outermost (20.0 cm long; diameter, 5.3 cm) chambers are used in the photolysis of waters and gases (air or O_2), respectively. Two quartz walls used to make the gases flow in a one-way direction were setup inside the outer photolysis reactor (**Figures 1b** and **1c**). Air or oxygen gas was introduced into the quartz tube (2.8 cm long; inner diameter, 0.5 cm) installed in the outer chamber through the lower part of the device. The volume of the photolysis reactor for air or O_2 gas was 161 cm^3, while the volume of the photolysis reactor for the wastewaters was ca. 6.8 cm^3.

High-purity grade 2,4-dichlorophenoxyacetic acid (2,4-D; $LD_{50\text{-rat}}$ = 370 mg kg^{-1}) was obtained from Wako Pure Chemical Industries Ltd. It was dissolved in ion-exchanged water (pH 6.4) and served as our model contaminant in the wastewaters. The time profiles of the microwave-/UV-assisted degradation of 2,4-D were obtained with a JASCO liquid chromatograph (HPLC) equipped with a JASCO UV-2070 UV/Visible diode array multi-wavelength detector, and a

JASCO Crestpak C-18S column; the eluent was a mixed solution of CH_3OH/H_2O (1:4 v/v).

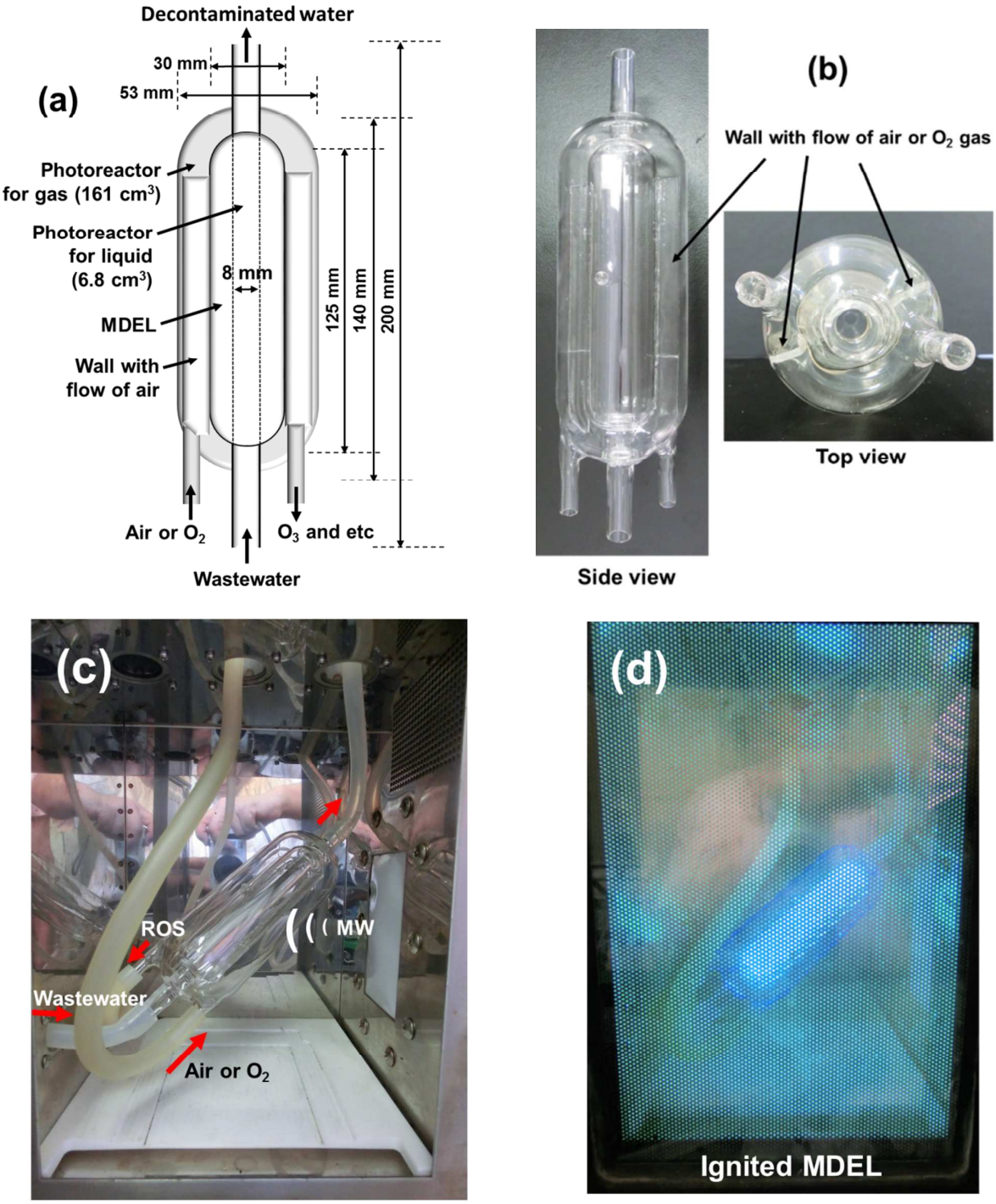

Figure 1. Schematic (a) and photograph (b) of the MDEL device for the decontamination of wastewaters through photolysis and chemical oxidation. (c) Setup of the MDEL reactor within a microwave multimode applicator and (d) ignition of the MDEL by the 60-W microwave radiation.

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A small pond located on the Sophia University Campus was our model of natural water stemming from accumulated rainwater. The pond is surrounded by plants; leaves accumulated at the bottom of the pond gave the water a brownish color. The decrease in *Escherichia coli* (*E. coli*) bacteria or total viable microorganisms was ascertained by a colony count using desoxycholate agar and plate count agar (Atect Co.) in a Petri dish (diameter 90 mm): subsequent to addition of 1 mL of water, it was covered, and then kept in the incubator at 35 ºC for 24 h, after which the number of colonies was assessed. The rate of bacterial decrease was estimated from the decrease in the initial number of colonies before processing.

The 1.0-L air-equilibrated water contaminated with the 2,4-D herbicide (2.2 mg L^{-1}; ca. 0.01 mM; initial pH, 5.9) or pond water was circulated through the inner photoreactor using silicon tubing and a peristaltic pump. Air or oxygen was introduced into the outer photolysis reactor using a compressor (Ryobi Ltd, ACP-50) at a flow rate of 0.25 L min^{-1}. Pure oxygen gas (≥ 99.9 %) was accessed from an oxygen tank at flow rates 0.15, 0.30, and 0.40 L min^{-1}. Continuous microwave irradiation of the MDEL reactor was provided by a Tokyo Rikakikai Co., Ltd MWO-1000S apparatus consisting of a multimode applicator and a 2.45 GHz microwave magnetron. Air oxygen or pure oxygen is converted into reactive oxygen species (ROS) such as ozone, for example. Such ROS are then bubbled through the wastewater using a frit connected to the silicon tubing to effect the chemical oxidation of the contaminants in the wastewaters.

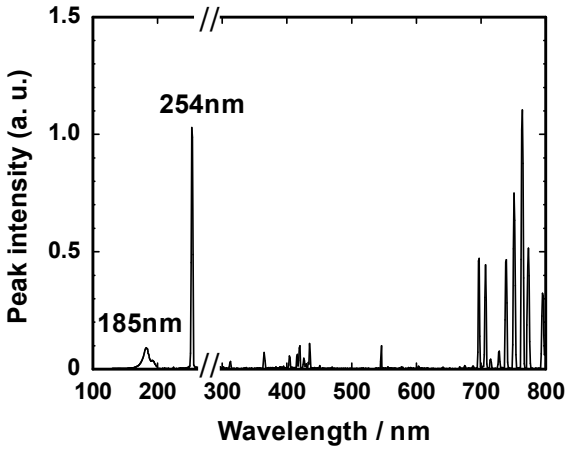

Figure 2. Vacuum-UV, UV, visible and near-IR wavelengths emitted by the MDEL device exposed to microwave irradiation. Reproduced from ref. [**9**]; Copyright 2009 by The Royal Society of Chemistry.

The optimal quantities of mercury and argon gas in the MDEL device exposed to microwave radiation were determined in an earlier study[9] by examining the spectral peak intensities of the vacuum-UV (185 nm), UV (254 nm), and visible and near-IR wavelengths emitted by the MDEL device (**Figure 2**). Oxygen absorbs the 185-nm radiation and is transformed into ozone, whereas the 254-nm emitted light is absorbed by ozone to generate activated oxygen atoms, $O(^1D)$.[12] The 185-nm radiation cleaves most molecular bonds in organic compounds, ultimately generating water vapor

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and carbon dioxide gas.[13]

2.2 Methodologies

Three different methodologies were considered to evaluate the MDEL system using the degradation of the 2,4-D herbicide or the sterilization of bacterial microorganisms (**Figure 3**). Vacuum-UV and UV light from the MDEL was used in the photolysis of the wastewaters through the occurrence of chemical oxidation with the ROS gaseous species (ozone, $O(^1D)$) – referred to as the UV/ROS method. The performance of this MDEL device was then assessed by the UV or the ROS method in comparison with the UV/ROS method. The input microwave applied power was maintained at 60 W throughout.

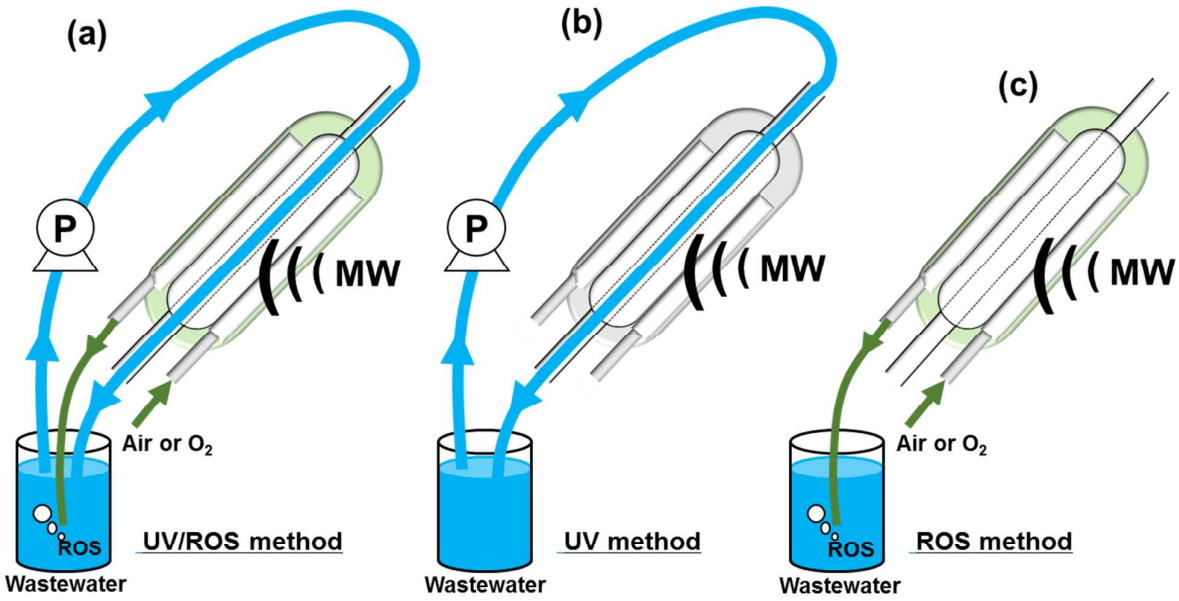

Figure 3. Cartoons illustrating the microwave-irradiated MDEL system used in the degradation of the 2,4-D herbicide in aqueous media and in the sterilization of bacteria-contaminated pond water under three different methods: (a) UV/ROS, (b) UV, and (c) ROS. Note that only in (a) and (b) were the waters circulated through the innermost MDEL reactor.

3.0 Results and discussion

3.1 Evaluation of the photoreactor/MDEL system

The microwave power level needed for self-ignition of the MDEL device was obtained using a multimode applicator; under a circulating aqueous solution (temperature, ca. 24 ºC) self-ignition occurred at ca. 35 W of microwave power. However, ignition was unstable even at 50 W power, but remained stable on increasing the microwave power to 60 W subsequently used throughout the study as the minimum power level. With water and air (oxygen gas) capable of absorbing vacuum-UV and UV light (see above), changes in emitted light irradiance with increasing MW power was then measured at 340 nm through the orifice of the multimode applicator with and without the presence of circulated water; results are displayed in **Figure 4a.**

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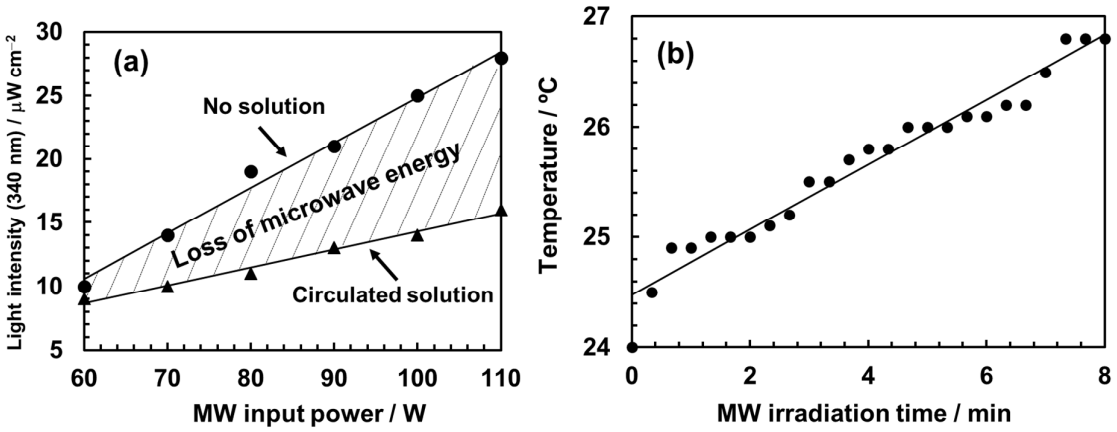
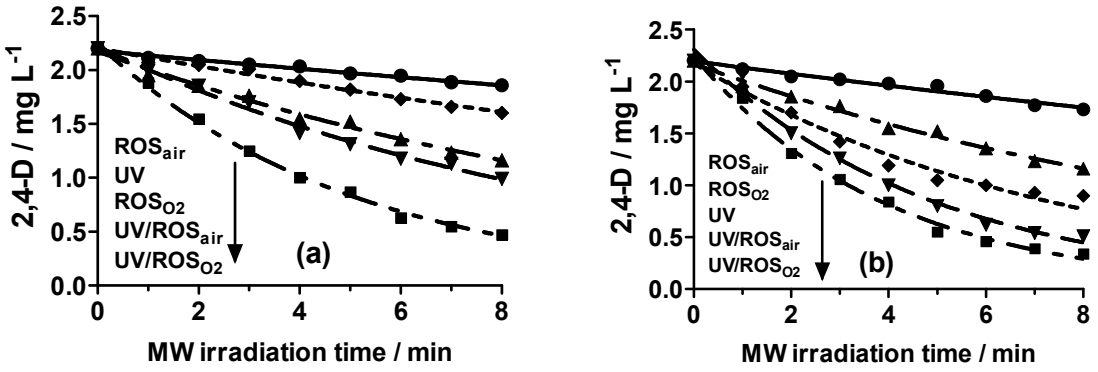


Figure 4. (a) Plot of light irradiance (μW cm^{-2}) against microwave input power (W) with and without circulated water. (b) Temporal change of temperature for the circulated water under microwave irradiation.

Light irradiance increased by 0.14 μW cm^{-2} per watt of microwave power with increase in the circulating water flow, while in the absence of water the increase was 0.36 μW cm^{-2} per watt of MW power. Thus, the weaker light irradiance is due to the absorption of the microwaves by the water circulated through the silicon tubing (not an absorber of microwaves) in the multimode applicator (see **Figure 1c**). Accordingly, when devising a microwave applicator it is important to account for the loss of microwave energy in the presence of aqueous media. The temperature of the circulated water increased by 2.8 ºC after microwave irradiation for 8 min (**Figure 4b**), a result of radiation heating by the MDEL light source and microwave dielectric heating.

3.2 Degradation of the 2,4-D herbicide

The continuous degradation of aqueous 2,4-D polluted water (1.0 L) at a concentration of 0.10 mM and at flow rates of 0.6 and 1.2 L min^{-1} was examined with the novel MDEL system at a microwave power level of 60-W; results are displayed in **Figure 5a** and **5b**, respectively.



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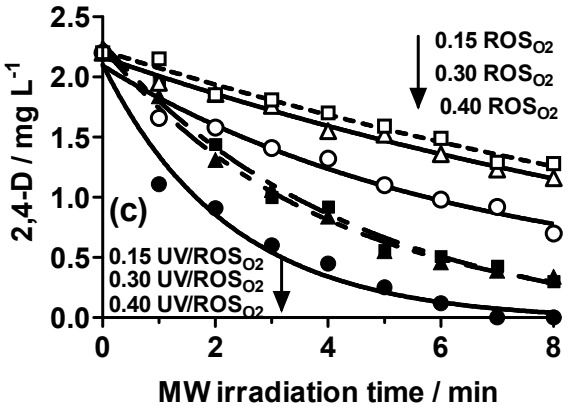

Figure 5. Plots illustrating the extent of 2,4-D remaining in aqueous solution by the UV/ROS_{O2}, UV/ROS_{Air}, UV, ROS_{O2} and ROS_{Air} method; (a) flow rate, 0.6 L min^{-1}; (b) flow rate, 1.2 L min^{-1}. (c) 2,4-D remaining in aqueous solution subsequent to treatment with the ROS_{O2} and UV/ROS_{O2} methods at an oxygen gas flow rate of 0.15, 0.30, and 0.40 L min^{-1}.

At the lower flow rate of 0.6 L min^{-1} in 2,4-D, 79 % degraded by the UV/ROS_{O2} method and 55 % by UV/ROS_{Air} after 8 min (**Figure 5a**). Note that when aqueous 2,4-D solution was circulated for 8 min, the entire 1.0-L of water passed 4.8 times (0.6 L min^{-1}) through the MDEL photolysis reactor. With oxygen gas as the source of ROS for the chemical oxidation of the contaminated wastewater, the degradation of 2,4-D by this method was 40 % more effective than with an air flow through the outermost photoreactor. The extent of degradation was 27 %, 47 % and 16 % by the UV, the ROS_{O2} and the ROS_{Air} method, respectively. The quantity of ROS produced when passing oxygen gas or air through the MDEL photoreactor exposed to microwave radiation was estimated by passing the gaseous species for 2 min in a 1.0 L volume of ion-exchanged water. The analyzed concentration of ozone in the ion-exchanged water (ozone meter; TGK Co.; model O3-1Z) was ca. 1.5 ppm with O_2 gas and ca. 0.5 ppm for air.

At the faster flow rate of 1.2 L min^{-1}, the 1.0-L volume of water flowed through the innermost photoreactor 9.6 times after 8 min. The extent of degradation of 2,4-D was 84 % and 77 % by the UV/ROS_{O2} and the UV/ROS_{Air} method, respectively, after 8 min of irradiation (**Figure 5b**). By contrast, the extent of decomposition was 59 %, 47 % and 22 % for the UV, the ROS_{Air} and the ROS_{O2} method, respectively.

The first-order kinetics of degradation of 2,4-D by all the methods used herein are summarized in **Table 1**. At the lower flow rate of 0.6 L min^{-1} the degradation decreased in the order UV/ROS_{O2} > UV/ROS_{air} > ROS_{O2} > UV > ROS_{air}, whereas at the faster flow rate of 1.2 L min^{-1} the order was UV/ROS_{O2} > UV/ROS_{air} > UV > ROS_{O2} > ROS_{air}.

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Table 1. First-order kinetics of the degradation of 2,4-D herbicide in aqueous media.

Flow rate	k (min^{-1})				
	UV/ROS$_{O2}$	ROS$_{O2}$	UV/ROS$_{Air}$	ROS$_{Air}$	UV
0.6 L min^{-1}	0.20 ± 0.01	0.078 ± 0.003	0.10 ± 0.004	0.020 ± 0.001	0.039 ± 0.002
1.2 L min^{-1}	0.26 ± 0.01	0.078 ± 0.003	0.20 ± 0.01	0.028 ± 0.002	0.13 ± 0.01

An interesting observation of the data reported in **Table 1** concerns the comparison of UV/ROS$_{O2}$ *versus* [UV + ROS$_{O2}$] and the UV/ROS$_{air}$ *versus* [UV + ROS$_{air}$] methods. That is, degradation by the integrated UV/ROS$_{O2}$ method (0.20 min^{-1} at the lower flow rate and 0.26 min^{-1} at the faster flow rate) and the integrated UV/ROS$_{air}$ method (0.10 min^{-1} at the lower flow rate and 0.20 min^{-1} at the faster flow rate) degrade 2,4-D faster than the combined [UV + ROS$_{O2}$] (0.12 min^{-1} and 0.21 min^{-1}) and [UV + ROS$_{air}$] (0.059 min^{-1} and 0.16 min^{-1}). Clearly, when photolysis and chemical oxidation of the wastewater with the MDEL device are performed separately, the microwave power would necessarily have to be increased to achieve results similar to the more effective integrated methods.

The degradation of 2,4-D at different flow rates of oxygen gas that was converted into ROS species is reported in **Figure 5c**. Only a slight difference in the degradation dynamics of 2,4-D was observed at the flow rates 0.15 L min^{-1} and 0.30 L min^{-1} by the ROS$_{O2}$ method (k = 0.071 min^{-1} versus 0.078 min^{-1}, respectively). However, at the faster flow rate of 0.40 L min^{-1} in oxygen gas the first-order degradation dynamics of 2,4-D were nearly twofold greater (k = 0.13 min^{-1}). By comparison, no differences were observed in the degradation dynamics by the UV/ROS$_{O2}$ method at oxygen gas flow rates of 0.15 L min^{-1} and 0.30 L min^{-1} (k = 0.25 min^{-1}), whereas at the maximum flow rate of oxygen (0.40 L min^{-1}) the degradation dynamics of 2,4-D by UV/ROS$_{O2}$ were again nearly twofold faster (k = 0.46 min^{-1}). The extent of degradation of the herbicide was ca. 50 % after 1 min of MW irradiation with complete degradation occurring after only 7 min.

3.3 Sterilization of a wastewater contaminated with bacterial microorganisms

The top clear layer of the water in the pond was collected and subsequently sterilized for the presence of *E. coli* bacteria and total viable microorganisms with the use of the MDEL photoreactors. The initial average number of colonies of *E. coli* was 272 (± 8), while the average number of total viable microorganisms (TVMOs) in the pond water was 587 (± 11). All experiments were performed the same day. The experimental conditions were: microwave input power, 60 W; flow rate, 1.2 L min^{-1}; sample volume, 1.0 L.

The decrease in the number of *E. coli* bacteria with microwave irradiation time is reported in **Figure 6a**, while the quantitative data are reported in **Table 2**. Bacterial kills by the UV/ROS$_{O2}$ and UV/ROS$_{Air}$ methods were nearly total (98 and 99 %) after treating the water for 5 min.

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Approximately 97 % of the bacterial count decreased in the 5-min treatment by the UV method; that is, bacterial removal was nearly complete when the contaminated pond water flowed twice through the photolyzing reactor. Treatments were also performed with the ROS_{O2} and ROS_{Air} methods; the number of kills of *E. coli* was 85 % and 61 %, respectively, within the 5-min period. The decrease in bacterial count followed first-order kinetics (**Table 2**) and followed the order $UV/ROS_{O2} > ROS_{O2} > UV/ROS_{air} \approx UV > ROS_{air}$.

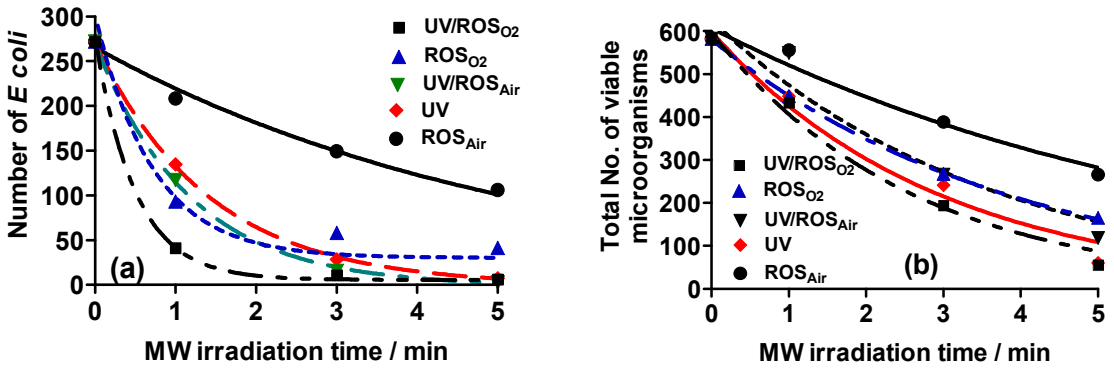

Figure 6. Sterilization of water contaminated with (b) *E. coli* bacteria and (a) total viable microorganisms in a natural pond water, and using the MDEL reactor.

Table 2. Kinetics of the sterilization of *E. coli* bacteria (initial average number, 272) and of the total viable microorganisms (TVMO; initial average number, 587) in aqueous media in the MDEL reactor.

Parameters	**First-order kinetics of the sterilization of *E. coli***				
	UV/ROS_{O2}	**ROS_{O2}**	**UV/ROS_{Air}**	**ROS_{Air}**	**UV**
k (min^{-1})	2.0 ± 0.2	1.4 ± 0.5	0.85 ± 0.04	0.19 ± 0.02	0.71 ± 0.02
% of *E coli* killed after 5 min	98	85	99	61	97
Parameters	**First-order kinetics of sterilization of *total viable microorganisms***				
	UV/ROS_{O2}	**ROS_{O2}**	**UV/ROS_{Air}**	**ROS_{Air}**	**UV**
k (min^{-1})	0.38 ± 0.04	0.26 ± 0.01	0.28 ± 0.07	0.15 ± 0.02	0.34 ± 0.05
% of TVMOs killed after 5 min	90	72	80	55	90

Figure 6b summarizes the data in the sterilization of the pond water contaminated with total viable microorganisms (TVMOs). The decreases of total viable microorganisms were 90 % and 80 % after 5 min of microwave irradiation at a flow rate of 1.2 L min^{-1} for the integrated methods

UV/ROS_{O2} and UV/ROS_{air}, respectively (see **Table 2**). The decrease of total viable microorganisms was 72 % and 55 % after 5 min by the ROS_{O2} and ROS_{Air} methods, whereas the UV method decreased the TVMOs by only 60 % within this time period. Fist-order kinetics of sterilization of the TVMOs in the pond water followed a somewhat different order than the sterilization of *E coli*.: $UV/ROS_{O2} \approx UV > UV/ROS_{air} \approx ROS_{O2} > ROS_{air}$. In addition, the malodorous natural pond water initially collected was refreshed after processing it through the MDEL photoreactor.

It is relevant to emphasize that sterilization of the bacteria-contaminated pond water occurred through a photolytic/chemical oxidation process and not thermally as the increase in temperature of the water was negligible (25.1 ºC to ca. 26.3 ºC) during the 5-min period the water flowed through the microwave phororeactor. Also significant, UV photolysis of *E. coli* bacteria and total viable microorganisms was more effective than chemical oxidation through ROS (i.e., chemical oxidation), in contrast to the degradation of 2,4-D solution.

4. Concluding remarks

Degradation of 2,4-D contaminated wastewater and sterilization of bacteria-contaminated pond waters were examined by photolysis and chemical oxidation using a novel MDEL photoreactor device fabricated such that it consisted of two photoreactors (one inner and the other outer) and a MDEL light source activated by microwave radiation. The microwave energy was effectively converted to vacuum-UV (185 nm) and UVC light (254 nm) as well as longer wavelengths in the visible spectral region by this hybrid MDEL device, with such wavelengths (185 nm and 254 nm) being used effectively in wastewater treatment. While performing successive photolyses and ROS treatment of the wastewaters by this novel MDEL device, it was possible to bubble ROS gas through the solution. In addition, the problem of microwave energy loss with wastewater present could be resolved. The extent of degradation of the 2,4-D herbicide with a more classical MDEL device (double quartz cylindrical photoreactor) was only 46 % effective for a reactor volume of 12.1 cm^3 and at a microwave power of 330 W for 30 min of irradiation,[5] whereas with the novel MDEL system (**Figure 1**) irradiated with 60-W microwaves, the extent of degradation of this herbicide (0.010 mM; 1.0 L; reactor volume, 6.8 cm^3; flow rate 1.2 L min^{-1}) was 84 % (UV/ROS_{O2}) and 77 % (UV/ROS_{air}) after 8 min (see **Figure 5b**). Clearly, the MDEL photoreactor system developed herein was far superior in terms of energy savings, short time needed, and temperatures very close to ambient for the treatment of wastewaters.

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Microwave Discharge Electrodeless Lamps (MDELs). Part IX. Novel microwave MDEL photoreactor for the photolytic and chemical oxidation treatment of contaminated waste waters

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Research Highlights

- A novel microwave discharge electrodeless lamp (MDEL) was developed for the photolysis and chemical oxidation of wastewater.
- The structure of this MDEL consists of a threefold cylinder.
- It was effective in the degradation of organic pollutants (*e.g.* 2,4-D) in aqueous solution.
- Was also effective in the drainage and sterilization of natural water compared with a classical MDEL device.

Graphic abstract