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ORIGINAL PAPERS

Development of a Hg-free UV light source incorporating a Kr/Br_2 gas, and its application for wastewater treatments

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Abstract

Mercury lamps are typically the major light sources in water treatments. However, the use of mercury has raised some concerns with regard to the Minamata Convention on Mercury. As such, Hg-free microwave discharged electrodeless lamps (MDELs) that incorporate a rare gas and a halogen gas (R/H-MDEL) have been investigated with such Hg-free mixture filler gases as Kr/Cl_2, Xe/Cl_2, and Kr/Br_2 (R/H). Of these, only the Kr/Br_2-MDEL lamp is self-ignited at an inner pressure of 15 Torr when irradiated with microwave radiation. Accordingly, a novel Kr/Br_2 three-layer MDEL (Kr/Br_2-MDEL) photoreactor was fabricated to assess the optimal gas composition and gas pressure toward its performance vis-à-vis the treatment of model wastewaters contaminated with the tartrazine dye in aqueous media and with *Escherichia coli* (*E. coli*) bacteria. The extent of degradation of the tartrazine dye and sterilization of *E. coli* increased with irradiation time, with microwave radiation power (100, 200, and 300 W), and with increased sample flow rate 0.4 L min^{-1} to 0.8 L min^{-1}. The tartrazine-contaminated wastewater was treated at a flow rate of 0.4 L min^{-1} for 60 min of microwave irradiation by three different protocols that resulted in UV (62%) >> UV/ROS (24%) > ROS (0%); ROS denotes reactive oxygen species. After 5 min irradiation of the *E.coli* wastewater, also at 0.4 L min^{-1}, the order was UV (99.5%) ≈ UV/ROS (99.3%) >> ROS (14.5%). For comparison, the photosterilization of *E. coli* with an equivalent Hg/Ar-MDEL light source was also nearly complete (99.7%). Thus, the suitability of the environmentally friendlier Kr/Br_2 gas fill to replace Hg/Ar filler gas in MDELs for the photoelimination of organic pollutants and microbial disinfection in aqueous media has been demonstrated.

Keywords Hg-free MDEL · Kr/Br_2-MDEL · Microwave discharged electrodeless lamp · Tartrazine dye · *E. coli* bacteria

1 Introduction

The microwave-assisted photochemical and photocatalytic protocols toward wastewater treatments were highlighted in several studies nearly a decade ago [1–5]. Protocols typically used in such treatments involved mercury-type electrode lamps that were subsequently replaced by electrodeless discharge lamps (EDLs) as the light sources, which when placed inside a microwave field effectively produced UV–Vis radiation; they are referred to as MDELs. Such microwave discharge electrodeless light sources use simultaneously both UV and microwave radiations to degrade effectively organic compounds and destroy microorganisms often found in contaminated waters [6].

An International Treaty known as The Minamata Convention on Mercury, established in 2013 and enacted in 2017, aimed to regulate the manufacture, import, and export of products containing mercury [7]. This Convention required that all countries regulate the manufacturing and sales of mercury lamps by 2020. Accordingly, current commercially available UV lamps that contain mercury as the inner filler gas will see their usage regulated by the enacted mercury regulations. In response to such regulations, there has been a significant shift from mercury-containing fluorescent lamps to light-emitting diode (LED) lamps that use semiconductors and electroluminescence to generate light. In certain processes, however, such as treatment of contaminated

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wastewaters and air purification, LED lamps are poor substitutes for mercury-containing lamps because of the lack of generating significant low-wavelength UV radiation. Despite their being used widely as luminescent devices with lifetimes longer than current mercury UV lamps, there are no LEDs that emit high-intensity ultraviolet radiation.

Our research efforts reported previously have focused on novel MDELs that use advanced oxidation processes (AOPs) toward water treatment and air purification [6, 8, 9]. In some cases, these MDELs contained traces of mercury that posed some concerns to the environment with regard to Hg-toxicity exposure in the form of organic and inorganic mercury. Following the empowering of the Minamata Convention on Mercury in 2017, our research efforts have focused on developing useful environment-friendlier Hg-free light sources for water treatment applications. For instance, in 2017, we developed Hg-free MDELs containing nitrogen, oxygen, xenon, argon, and helium, either as lone filler gases or as mixed filler gases [10]. A year later, we demonstrated the possibility of replacing the Hg/Ar filler gas in MDEL lamps with the N_2/SF_6, N_2/Ar, and Xe/N_2 gas mixtures [11]. The latter filler gases are relatively inexpensive, are chemically stable, and are safe gases that have proven as suitable filler base gases in Hg-free light sources for wastewater treatments. However, when compared with a low-pressure Hg/Ar electrodeless light source, these MDEL lamps proved less efficient; for example, the N_2/SF_6 MDEL light source was about 25% less efficient toward the photolytic decomposition of the rhodamine-B dye in aqueous media. Thus, the search for other eco-friendlier filler gas mixtures that would prove more efficient has motivated the present study.

The noble gases Kr and Xe are environment-friendly, inert, and easily ionized gases, more so at low pressures than they are at higher pressures [12]. Their inertness makes them attractive substitutes in MDELs since they do not interfere with the lamp's operation. Moreover, upon ionization, these gases generate excimer molecules that when excited emit UV light at different wavelengths. Excimer formation uses dielectric barrier discharge (DBD) to generate incoherent UV radiation as the light source for photophysical and photochemical reactions [12]. Despite the several studies regarding rare-gas dimeric excimers (e.g., Ar_2*, Kr_2* and Xe_2*) [13–15] and rare-gas halide (RH*) excimers (e.g., KrCl*, XeCl*, XeBr*, XeI*), [16–19] only scant studies have highlighted their applicability in (microwave/UV)-induced photolytic decomposition of pollutants in contaminated wastewaters. In this regard, Bi and co-workers [20] demonstrated the decomposition of aqueous solutions of quinoline and indole using a microwave discharged KrBr*-excilamp.

The present study focused on examining the Kr/Br_2, Xe/Cl_2 and Kr/Cl_2 filler gas mixtures as potential substitutes for mercury in the earlier MDEL light sources so as to attain and fabricate suitable R/H-MDELs for the photolytic and photocatalytic oxidative treatments of contaminated wastewaters. The optimal filler gas mixture was incorporated in a three-layer cylindrical structure with the MDEL unit looped around the tubular reactor through which the wastewater flowed. Photolysis of oxygen gas occurred in the reactor volume outside the MDEL that generated highly oxidizing reactive oxygen species (ROS). One of the advantages of this three-layer device is that it permitted to pass the produced ROS gas (e.g., ozone) through the solution during successive photolyses and ROS treatments of a model wastewater contaminated with the tartrazine dye and with such bacteria as *E. coli* (Fig. 1).

2 Experimental section

2.1 Determination of Hg-free gas mixture for MDEL fabrication

The best mixed filler gases examined in fabricating a rare gas/halogen-MDEL (R/H-MDEL) light source contained the Kr/Br_2, Kr/Cl_2, and Xe/Cl_2 mixed gases with internal pressures of 150 and 15 Torr. The self-ignition, the lighting efficiency, and the emission spectra were measured subsequent to irradiation with the electromagnetic wave energy from an AC (alternating current) dielectric barrier discharge (DBD) power source. The R/H-MDEL was fabricated using a quartz bulb (length, 4.0 cm; diameter, 2.5 cm) that was then filled with a filler gas mixture, while the two related electrodes were connected to an AC power source (Logy Electric Co., Ltd; LHV-13AC; output voltage, 10 kV; current, 120 mA; frequency, 9–12 kHz). Later, the UV–Vis emission spectra were monitored within the wavelength range 200–400 nm using a fiber optic cable (fixed distance, 10.0 cm from the lamp) connected to a high-sensitivity UV–Vis Spectrophotometer (Ocean Optics Inc, Maya2000Pro). The quartz used in this series of studies was SupraSil (Heraeus Quarzglas GmbH & Co. KG), which transmits more than 85% of UV light at 190 nm.

2.2 Performance evaluation of MDEL in water purification

The R/H-MDELs, fabricated for evaluating their suitability toward water purification treatments, were of the same size and structure as the previously fabricated Hg/Ar-MDEL light source, a size that was earlier found to be compatible with the microwave equipment [6]. The device consisted of three chambers: the middle chamber being the MDEL (length, 12.5 cm; diameter, 3.0 cm), while the innermost (length, 20.0 cm; inner diameter, 0.8 cm) and outermost (length, 14.0 cm long; diameter, 5.3 cm) chambers were used in the photoremediation of waters and air, respectively

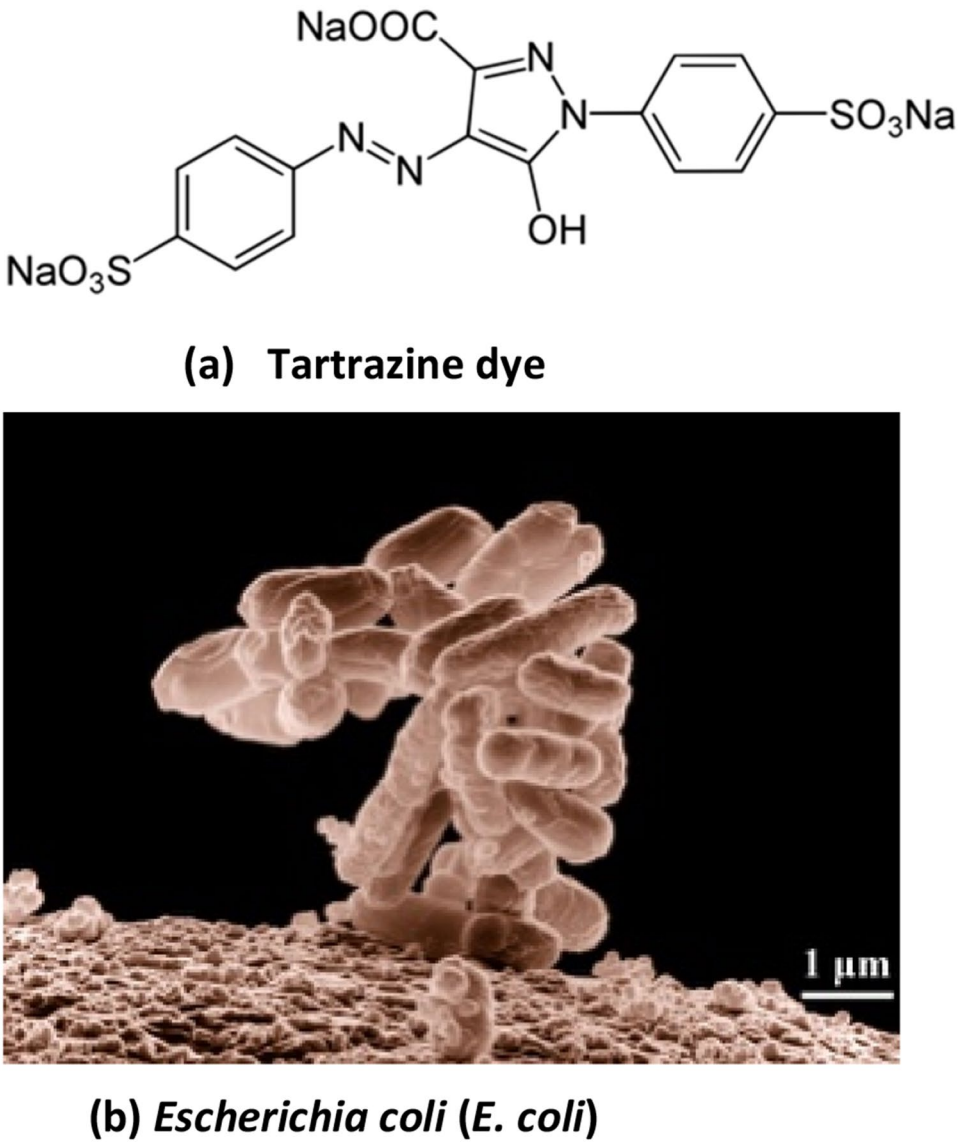
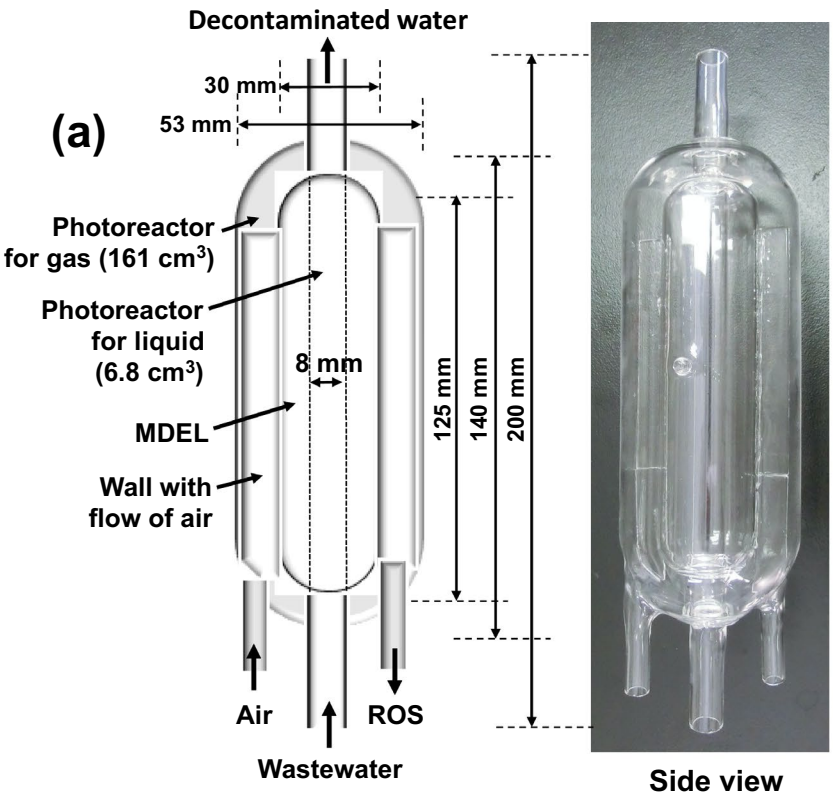


Fig. 1 **a** Structure of the tartrazine dye. b Photograph of *E. coli* {source: photograph by Eric Erbe, digital colorization by Christopher Pooley, both of the USDA, ARS, EMU}. Image released by the Agricultural Research Service, U.S. Department of Agriculture, ID K11077-1. Public Domain: https://commons.wikimedia.org/w/index.php?curid=958857 (accessed Sept. 7, 2020)

(Fig. 2a). Two quartz walls used for gas flow in a one-way direction were setup inside the outer photolysis reactor through which air or oxygen gas was introduced into the quartz tube (length, 2.8 cm; inner diameter, 0.5 cm) installed in the outer chamber through the lower part of the device; the Kr/Br_2-MDEL setup was then located in a microwave multimode applicator (Fig. 2b). The outer photolysis reactor had a capacity of 161 cm^3 of air, while the inner photolysis reactor could contain ca. 6.8 cm^3 of wastewaters.

The photolytic procedure implicated two model wastewater systems: the first consisted of an aqueous tartrazine dye solution (0.01 mM) in untreated natural water, while the second contained *E. coli,* also in untreated natural water. The microwave apparatus (Tokyo Rikakikai Co., Ltd MWO-1000S) consisted of a multimode applicator and a 2.45 GHz microwave magnetron that provided the continuous microwaves to irradiate the R/H-MDEL setup. Unless noted otherwise, three different methods were used to evaluate the Kr/Br_2-MDEL system using the degradation of tartrazine dye and *E. coli* sterilization in the model wastewaters (Fig. 3).

The model solutions (400 mL) flowed through the Kr/Br_2-MDEL inner photoreactor using a silicone tubing and a peristaltic pump (flow rates, 0.4 and 0.8 L min^{-1}). The photodecomposition proceeded directly by the generated vacuum-UV and UV light (UV) emitted by the Kr/Br_2-MDEL source. Air was introduced into the outer layer of the R/H-MDEL using a compressor (Ryobi Ltd, ACP-50), which caused the air oxygen to be transformed into reactive oxygen species in gaseous forms (ROS: ozone and activated oxygen atoms) resulting from the UV radiation emitted by the Kr/Br_2-MDEL (method denoted UV/ROS). For comparison, the UV-only and ROS-only decomposition methods were also employed to assess the



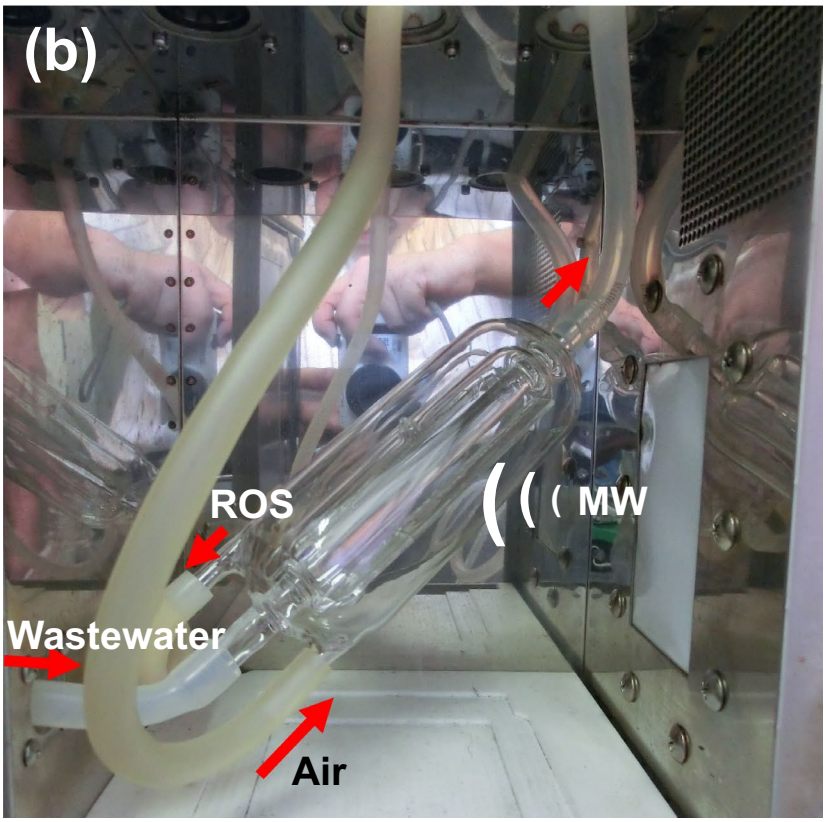


Fig. 2 **a** Schematic diagram and photograph of the Kr/Br_2-MDEL device for photolytic applications and oxidative remediation of wastewaters; **b** Kr/Br_2-MDEL setup within the microwave multimode applicator

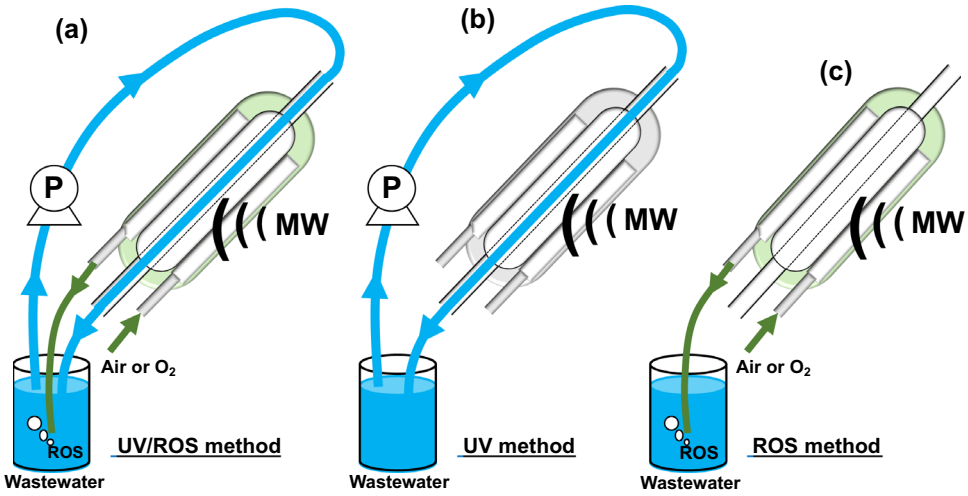


Fig. 3 Cartoons illustrating the microwave irradiation of the Kr/Br_2-MDEL system in aqueous media under three different protocols: **a** UV/ROS, **b** UV, and **c** ROS. Reproduced from Horikoshi et al. [6]. Copyright 2015 by the Royal Society of Chemistry and Owner Societies

decomposition and elimination of the contaminants in the aqueous media.

2.3 Model wastewaters

Analytical grade (purity 100%) tartrazine azo dye (Fig. 1) from Fujifilm Wako Chemical Co. was dissolved in ion-exchanged water (0.01 mM; 400 mL) and used as a contaminant in the model wastewater. A JASCO V-650 UV–Vis spectrophotometer was used to record the dye solution absorption spectra before and after degradation; the actual concentrations were subsequently determined from a calibration curve established at 427 nm. The degradation efficiency was determined from the initial and final concentrations as expressed in Eq. 1;

$$\text{Degradation efficiency } [\%] = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (1)$$

where C_0 is the initial concentration of tartrazine and C_t is the concentration at the specified time, t.

The model contaminated natural water sample was prepared to mimic the water collected from a stream in the Blantyre City of Malawi in South-eastern Africa. Malawi faces challenges of domestic and industrial wastewater treatment resulting from untreated wastewaters dumped into surrounding water resources. Specifically, industries in Blantyre City, the country's commercial hub, dispose both partially treated and untreated wastewaters into the Mudi stream [21]. A sample was collected from the Mudi Stream at 15.804615 Latitude and 35.029767 Longitude on August 19, 2019. The initial sample pH was 8.0 and the total organic carbon (TOC) was 59.5 mg L^{-1} measured with the Wagtech International digital multimeter. The quantity of *E. coli* was 5.5×10^4 CFU mL^{-1} (CFU, colony forming unit) as determined by the Association of Official Agricultural Chemists International (AOAC) Method (991.14), which uses the 3 M Petrifilm *E. coli* Count Plate method carried out within 6 h of sample collection.

The concentration of *E. coli* in artificial natural water was adjusted according to the collected water. A pure strain of *E. coli* DH5-α was provided by Sophia University's Microbiology Center. The bacteria were inoculated in 100-mL sterile Luria–Bertani (LB) broth and incubated at 37 °C for 24 h. The cells were then washed three times with saline solution (0.9%) by centrifugation at 4 °C for 3 min at 10,000 rpm. The volume of artificial natural water used in the sterilization experiment was also 400 mL. The decrease in *E. coli* bacteria was established by a colony count using the LB broth agar plates. Subsequent to the addition of 1 mL of water sample, the plates were covered and incubated at 37 °C for 24 h, after which the number of colonies was assessed. The sterilization efficiency of *E. coli* before and after irradiation was determined using Eq. 1, where C_0 is the initial concentration of *E. coli* bacteria (CFU mL^{-1}) and C_t is the concentration (CFU mL^{-1}) at the specified time, t.

3 Results and discussion

3.1 Optimal encapsulated gas in R/H-MDEL

In an initial consideration, we ascertained whether the R/H-MDELs system would light up using only electromagnetic energy from the AC power source. The nature of the filler gas material with low-ionization potential and sufficient vapor pressure is an essential factor to exhibit a UV emission discharge within the R/H-MDELs upon activation with the electromagnetic energy. Fortuitously, all excimer R/H-MDELs are self-ignited at both internal gas pressures of 15 and 150 Torr using the electromagnetic energy sources, which we attribute to the alternating current energy's higher

frequencies (range 9–12 kHz). The high frequencies cause faster vibration of the gas molecules, and a greater number of collisions that effect the rapid emission of UV light (Table 1).

The self-ignition of the R/H-MDELs under microwave irradiation was investigated using a microwave multimode applicator at an input power of 500 W. Under these conditions, only the Kr/Br_2-MDEL system is self-ignited under microwave irradiation at an inside pressure of 15 Torr (Table 1).

Figure 4 illustrates the photographs of the R/H-MDELs lighting up under the alternating current (AC) electromagnetic energy. The MDEL containing the Kr/Br_2 filler gas mixture yielded a red-colored radiation, while the MDELs with Kr/Cl_2 and Xe/Cl_2 filler gases resulted in a blue-colored radiation.

In the lighting experiments, the R/H-MDELs emitted a more intense light at 15 Torr pressure than at 150 Torr; under the latter pressure, lighting of the R/H-MDELs was unstable. A comparison of the light emission spectra of the R/H-MDELs containing Kr/Cl_2 Xe/Cl_2 and Kr/Br_2 at 15 Torr pressure in the range 200–400 nm is displayed in Fig. 5. An alternating current was used for all lighting for these R/H-MDELs. The relevant UV spectra were measured at a position 10.0 cm from the lamp surface. In addition, we also fabricated a Hg/Ar-MDEL of the same size as the R/H-MDELs with the gas characteristics of Hg/Ar-MDEL reported previously. It was subjected to otherwise identical conditions as the R/H-MDELs with the alternating current; its UV spectrum is overlaid on the R/H-MDEL's UV spectra of Fig. 5.

The principal emission band for the lamp filled with Xe/Cl_2 occurred at 308 nm [XeCl*], while that of Kr/Cl_2 occurred at 222 nm [KrCl*] [22]. The principal emitted line of Hg/Ar-MDEL was seen at 254 nm. The results show that the emission intensities for each of these R/H-MDELs are far greater (around 60,000 a.u.) than for the Hg/Ar-MDEL system (about 2700 a.u. greater). Despite these observations, the operating lifetimes of the Xe/Cl_2 and Kr/Cl_2 MDELs under gas static conditions do not exceed 100 h, which has stimulated the use and development of MDELs filled with heavier and less-reactive halogen-containing mixtures [23, 24]. By contrast, the Kr/Br_2-MDEL showed relatively weaker intensity than both the Xe/Cl_2 and Kr/Cl_2 lamps, but nonetheless a greater intensity (around 30,600 a.u.) than the Hg/Ar-MDEL. The Kr/Br_2 mixture contains the heavier and less-reactive Br_2 gas (versus Cl_2) which thus offers a longer operating life. Moreover, the emission line at 207 nm for the [KrBr*] is especially optimal for photobiological applications in that the absorption spectrum of DNA molecules exhibits two absorption maxima in the vicinity of 200 and 260 nm [25]. The coefficient of linear absorption in the region of the 207-nm line of [KrBr*] is about twofold greater than in the long-wavelength maximum [26]. Subsequently, we used the Kr/Br_2 mixture in the fabrication of Hg-free MDEL prototypes for further evaluation of wastewater treatment using the UV light generated from the Kr/

Table 1 Self-ignition test results for the excimer/halogen-MDELs (R/H-MDELs) using an applied alternating current at a frequency of 9–12 kHz (dielectric barrier discharge: DBD) versus irradiation with 2.45-GHz microwaves (microwave discharge: MWD) at an input power of 500 W

Purged gases	Ionization energy for gases (kJ mol^{-1})	Internal pressure (Torr)	Applied AC current (DBD)	MW irradiation (MWD)
Kr/Cl_2	1351/1251	150	Lighting	No lighting
		15	Lighting	No lighting
Xe/Cl_2	1170/1251	150	Lighting	No lighting
		15	Lighting	No lighting
Kr/Br_2	1351/1140	150	Lighting	No lighting
		15	Lighting	Lighting

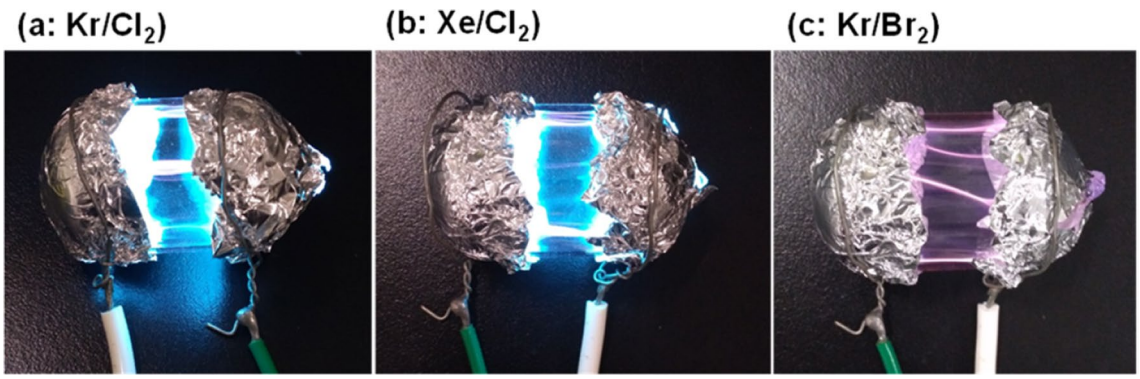


Fig. 4 Photographs of the dielectric barrier discharge (DBD) on MDEL with filler mixture gases: **a** Kr/Cl2, **b** Xe/Cl2, and **c** Kr/Br2 under alternating current (AC) energy

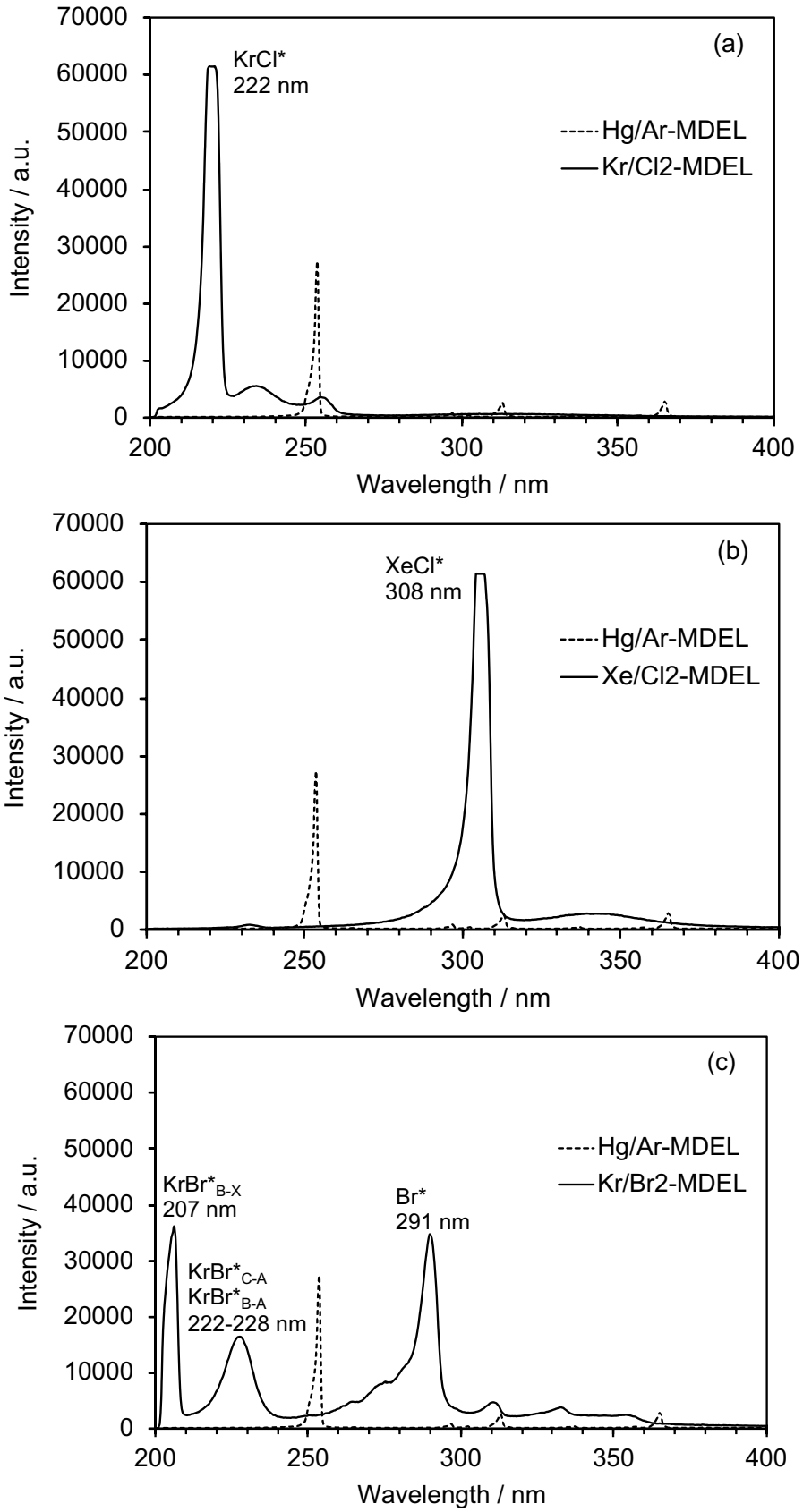


Fig. 5 Comparison of the UV spectral features of the emitted radiation generated from the dielectric barrier discharge (DBD) using an alternating current (AC) electromagnetic energy for the filler gas mixtures: **a** Kr/Cl_2, **b** Xe/Cl_2, and **c** Kr/Br_2 in the R/H-MDELs systems (solid lines) versus the Hg/Ar-MDEL (dotted line)

Br_2 gases within the MDEL that involved several reaction steps as described by Han and co-workers [25].

3.2 Photolytic degradation of tartrazine dye in aqueous media

To the extent that the Kr/Br_2 filler gas mixture was the most suitable to fabricate the R/H-MDEL system in the three-layer cylindrical structure, lamp performance was evaluated using the degradation of the tartrazine dye that contaminated our model wastewater (initial concentration, 0.010 mM). Initially, the lighting conditions of the lamp were determined using the 2.45-GHz microwaves to irradiate the circulating aqueous dye solution so as to improve its output. The minimum microwave applied power required to light the Kr/Br_2-MDEL was 100 W. Therefore, our first task was to ascertain to what extent increasing the microwave radiation to 200 and 300 W compared to the usage of 100-W microwaves with regard to any increases in the decomposition efficiency by the UV method. Figure 6a displays the time course of the loss of tartrazine dye at these three power levels. Degradation of the dye continued monotonically with irradiation up to 60 min, at which at least 62, 94, and 99% of tartrazine degradation was achieved at the thee power levels of 100, 200, and 300 W, respectively.

An important point to consider here is that doubling the microwave power from 100 to 200 W did not lead to a doubling of the decomposition efficiency, nor did tripling the microwave power to 300 W. That is, although increasing the microwave output increased the emitted light intensity, it did not lead to a linear increase in the corresponding decomposition rate, a phenomenon consistent with our earlier studies. In terms of energy efficiency, however, the use of 100-W microwaves appeared most suitable to degrade the dye. In this regard, using higher microwave power levels caused the temperature of the recirculating solution to increase and thus accelerate dye degradation. For instance, after 60 min of irradiation with 100-W microwaves, the temperature of the recirculated dye solution increased by 20 °C, a result of radiation heating by the Kr/Br_2-MDEL light source and by microwave dielectric heating.

Next, the decomposition efficiency of the tartrazine dye was examined using the three protocols illustrated in Fig. 3 under a constant applied microwave power of 100 W and at a recirculating flow rate of 0.4 L min^{-1}; in addition, we also examined the UV/ROS protocol but without the ROS species being introduced into the wastewater sample (Fig. 6b) as was done for the UV/ROS protocol of Fig. 3a. Table 2 summarizes the extent to which tartrazine degraded, which decreased in the order $UV_{0.8}$ (70%) > $UV_{0.4}$ (62%) > UV/ROS (no ROS; 25%) ≈ UV/ROS (24%) > ROS (0%). The rates of degradation of the dye followed a similar order, $UV_{0.8}$ (9.3×10^{-5} mM min^{-1}) > $UV_{0.4}$ (8.3×10^{-5} mM min^{-1}) > > UV/ROS (no ROS; 4.5×10^{-5} mM min^{-1}) > UV/ROS (3.5×10^{-5} mM min^{-1}) > > ROS (0×10^{-5} mM min^{-1}). These results were somewhat unexpected. In our earlier study [6], the degradation of the 2,4-dichlorophenoxy acetic acid (2,4-D) herbicide carried out with a Hg/Ar-MDEL light source in a similar three-layered cylindrical structure followed the order UV/ROS (0.100 min^{-1}) > > UV (0.039 min^{-1}) > ROS (0.020 min^{-1}). Clearly, the lack of decomposition of tartrazine by the ROS method alone implies that the reactive oxygen species were insufficient to breakdown the chemical bonds within the tartrazine dye.

In the case of the UV/ROS protocol to degrade the tartrazine dye, air was circulated in the lamp to allow formation of ROS species that were subsequently introduced into the

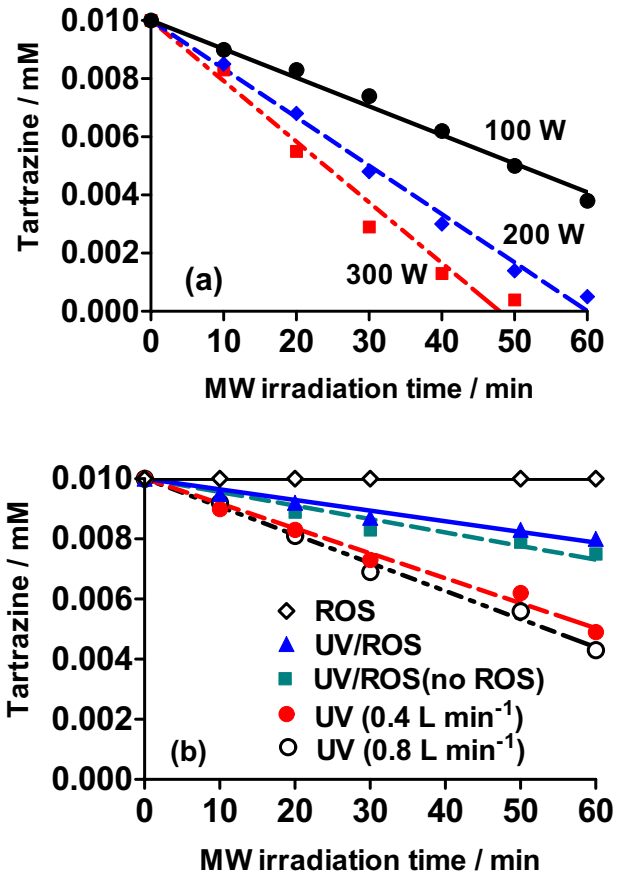


Fig. 6 Plots illustrating the degradation of tartrazine (initial concentration, 0.010 mM) with MW irradiation time up to 60 min of continuous recirculation of a 400-mL solution at a flow rate of 0.4 L min^{-1} through the Kr/Br_2-MDEL reactor located in the multimode microwave applicator using **a** the UV method (see Fig. 2) at microwave applied powers of 100, 200, and 300 W; **b** the degradation of the dye by the ROS, UV, UV/ROS, and UV/ROS (no ROS) protocols (see Fig. 3; for the UV protocol, the rate of decomposition was also examined at a flow rate of 0.8 L min^{-1}); microwave applied power was constant at 100 W

Table 2 Percent degradation and kinetics of degradation of the tartrazine dye (0.010 mM) in aqueous media at a flow rate of 0.4 L min^{-1} at various microwave power levels and using the protocols ROS, UV/ROS, UV, and UV/ROS (no ROS)

Parameters		100 W		200 W	300 W
Rate (10^{-5} mM min^{-1})		9.9 ± 0.2		16.7 ± 0.3	20.9 ± 0.8
% degradation after 60 min		62		95	99
Parameters*	ROS	UV/ROS	UV/ROS (no ROS)	UV	UV**
Rate (10^{-5} mM min^{-1})	0	3.5 ± 0.2	4.5 ± 0.3	8.3 ± 0.2	9.3 ± 0.2
% degradation after 60 min	0	24	25	62	70

*Microwave power level: 100 W

**Flow rate was 0.8 L min^{-1}

wastewater sample (see Fig. 3a); the flow of air also served to cool the lamp. It is possible that this cooling may have reduced the emission intensity of the lamp and thus may have decreased the efficiency of the UV/ROS protocol relative to the two UV protocols. To test this hypothesis, the decomposition of the tartrazine dye was examined under the UV/ROS experimental conditions whereby air was passed through the MDEL, but was not introduced into the aqueous solution {UV/ROS (no ROS) protocol}. As noted in Fig. 6b and Table 2, the rate of decomposition was slightly faster than the UV/ROS protocol of Fig. 3a, but nonetheless significantly less than the UV protocols at the different flow rates. Unmistakably, the ROS species had no effect on the degradation of the tartrazine dye.

The sample flow rate is another important operating parameter in microwave-assisted photolytic reactions. Increasing the flow rate from 0.4 to 0.8 L min^{-1} with 100-W microwaves increased the extent of degradation of tartrazine from 62 to 70% (Fig. 6b; Table 2). Consequently, the higher the flow rate, the more times the sample solution is recirculated within the reactor, and thus the greater exposure of the dye solution to the MW/UV radiation than was otherwise the case at the lower flow rate. Thus, it was more beneficial to operate at higher flow rates in the continuous-mode MDEL reactor.

3.3 Photolytic sterilization of *E. coli* bacteria in natural waters

The percent sterilization of the natural water sample contaminated with the *E. coli* bacteria was examined to assess the effect of flow rate based on the three methods of microwave irradiation (Fig. 3) namely, UV/ROS, UV, and ROS. Results are displayed in Fig. 7 and summarized in Table 3. The sterilization efficiency increased in all three cases with respect

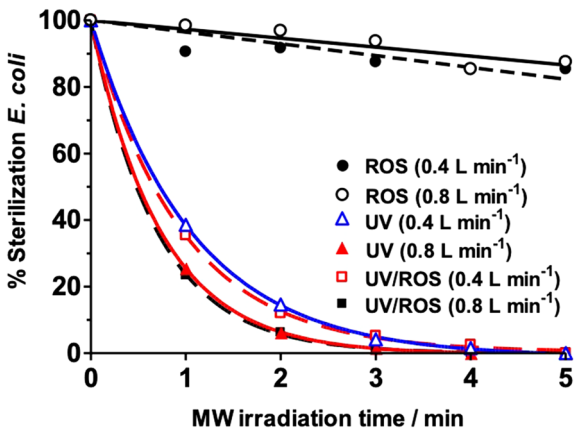


Fig. 7 Sterilization of the *E. coli* contaminated samples (10^4 CFU mL^{-1}) using the Kr/Br_2-MDEL light source under a 60-W microwave power using the three irradiation protocols (UV/ROS, UV, and ROS); flow rates were 0.4 and 0.8 L min^{-1}

to irradiation time. The least sterilization was obtained for the ROS method with a maximum of 14.3% at a flow rate of 0.4 L min^{-1} and 12.8% for the flow rate of 0.8 L min^{-1} after a 5-min irradiation period. Supplying air exposed the *E. coli* cells to the ROS species, thereby causing damage to the growing bacterial cells. Interestingly, the sterilization of *E. coli* occurred via zero-order kinetics when using the ROS protocol, while the kinetics were first order for the UV and UV/ROS protocols (Fig. 7; Table 3). For the latter two protocols, the sterilization of the *E. coli*-contaminated water was nearly quantitative (ca. 100%).

According to Baez and Shiloach, [27] the concentration of ROS may have increased at the faster flow rate to such an extent that the *E. coli* cells may have developed a defence mechanism for self-protection from the toxic effects of

Table 3 Percent sterilization and kinetics of the sterilization of *E. coli* bacteria in aqueous media with 60-W microwaves at two different flow rates

Flow rates	Parameters	UV/ROS	UV	ROS*
Kr/Br_2-MDEL (vol. 0.4 L)				
0.4 L min^{-1}	First-order kinetics k (min^{-1})	1.05 ± 0.03	0.94 ± 0.02	3.5 ± 0.4
	% of *E coli* killed after 5 min	99.3	99.5	14.3
0.8 L min^{-1}	First-order kinetics k (min^{-1})	1.44 ± 0.02	1.36 ± 0.01	2.7 ± 0.3
	% of *E coli* killed after 5 min	99.9	99.9	12.8
Hg/Ar-MDEL (volume, 1.0 L) from ref. [6]				
1.2 L min^{-1}	First-order kinetics k (min^{-1})	0.85	0.71	0.19
	% of *E coli* killed after 5 min	99	97	61

*Zero-order kinetics in mM min^{-1}

oxygen saturation. On the other hand, increasing the flow rate from 0.4 to 0.8 L min^{-1} increased the *E. coli* sterilization efficiency to nearly 100% within experimental error (Table 3) for the UV and UV/ROS methods after the 5-min treatment. Furthermore, a comparison of the reaction rates reveals no difference in the extent of sterilization between the UV and UV/ROS methods, albeit the rates are slightly faster at the faster flow rate. Clearly then, the UV method had a large non-insignificant effect on the degradation of *E. coli*. By contrast, in our earlier degradation study [6] of *E. coli* mediated by the otherwise similar Hg/Ar-MDEL setup (Table 3), the ROS method showed a greater effect than the sterilization using the Kr/Br_2-MDEL source, although the sterilization rate with respect to the UV method was significantly faster with the Kr/Br_2-MDEL irradiation source than it was with the Hg/Ar-MDEL—likewise for the UV/ROS method. Clearly, unlike the decomposition of the tartrazine dye, the ROS species had a significant effect on the sterilization of *E. coli*.

4 Concluding remarks

To follow the recommendations from The Minamata Convention on Mercury in avoidance of using mercury in applications, we have herein proposed the combination of a noble gas and a halogen gas (Kr/Br_2) as the optimal filler gas mixture to fabricate a microwave discharge electrodeless lamp (MDEL) activated either by the AC electromagnetic energy or by microwave irradiation. Although this mercury-free MDEL was somewhat inferior to the Hg/Ar-MDEL toward the degradation of organic pollutants in two different model wastewaters (2,4-D herbicide versus the tartrazine dye), the Kr/Br_2-MDEL light source was able to effectively kill nearly 100% of *the E. coli* bacteria as also shown earlier [6] when using a Hg/Ar-MDEL source. The present study also revealed that the UV radiation emitted by this novel Kr/Br_2-MDEL system was most effective in degrading polluted waters so that a simpler MDEL structure could be envisaged, which would see a simple encapsulation of the MDEL in a quartz bulb followed by microwave irradiation in the wastewaters to effect a suitable wastewater treatment. Lamp manufacturers who take costs into consideration may be concerned with the relative costs of krypton versus mercury that might affect the overall costs of manufacturing such MDELs. Currently, on a weight basis, the cost of krypton gas [28] is less than the cost of pure mercury [29] ($33.00 per 100 g versus $48.00 per 100 g, respectively). Moreover, it should be noted that the amount of gas enclosed in these R/H-MDELs is extremely small, with the internal pressure being but 15 Torr.

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Compliance with ethical standards

Conflict of interest The authors declare no conflict of interest.

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