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The roles of active species in photo-decomposition of organic compounds by microwave powered electrodeless discharge lamps

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ABSTRACT

Knowledge of the effective radiation spectrum irradiating substrates from microwave powered electrodeless discharge lamps (MEDLs), and the active species that directly oxidize substrates in the photolytic process, is fragmentary and unclear. In this work, we conducted a comparative study using MEDLs made with quartz envelopes (MEDL-quartz) and with borosilicate Pyrex envelopes (MEDL-Pyrex) targeting the degradation of Rhodamine B (RhB) *via* radical-extinguishing tests. We found that UVC/UVB radiation is essential to generate •OH and H_2O_2 in the MEDL-quartz system. The degradation of RhB mostly originates from •OH species, which account for a contribution of 53.8%, while the remaining contribution is attributed to oxidation by H_2O_2 and direct photolysis. This degradation is influenced by several parameters. Acidic and neutral pHs, but not extreme alkaline pH, benefit the degradation. To ensure a high intensity of UVC/UVB, the optimum ratio of the MEDL volume to the aqueous solution volume (V_L/V_S) is 0.4. Concentrations of 0.15–0.20 mmol/L of RhB are suitable to obtain an effective quantum absorbance in the MEDL-quartz system, showing a high decomposition rate of 5.6×10^{-3} (mmol/L)min^{-1}. Moreover, two other substrates, Reactive Brilliant Red X-3B and Safranine T, were tested and found to be efficiently degraded in the MEDL-quartz system.

Introduction

Using microwave (MW) powered electrodeless discharge lamps (MEDLs) to degrade refractory environmental contaminants has attracted increasing interest in the past few decades (Park et al., 2010). MEDLs have often been utilized as a kind of light source in photochemical reactions since they can simultaneously provide ultraviolet, visible (UV–vis) and MW irradiation, and show high reaction rates with substrates (Ju et al., 2011). Meanwhile, MEDLs exhibit great advantages, such as the absence of electrodes, low price, low energy cost, and simple reactor configuration in the degradation of pesticides, dyes, endocrine disruptors and other non-biodegradable compounds (Bae and Jung, 2010; Hong et al., 2006; Ta et al., 2006; Xia et al., 2008).

Photocatalytic degradation by MEDLs coupled with solid catalysts suspended in aqueous solution (Ju et al., 2012; Xiong et al., 2013) or coated as films on the surface of MEDLs (Yu

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et al., 2013b) has been widely investigated. The study of the mechanism shows that MEDLs can improve the photocatalytic activity due to their effects on the surface of catalysts, such as titanium dioxide. This occurs *via* three pathways (Horikoshi et al., 2002; Zhang et al., 2008): (1) UV–induced generation of electron/hole pairs. (2) Visible light-induced dye self-photosensitization and then adsorption of excited dye on the catalyst surface when Coulombic interactions between the excited substrate and charged catalyst surface are overcome. (3) Direct photolytic degradation.

However, some studies reported that high decomposition efficiencies could also be observed for MEDL irradiation without any catalysts or additives (Ai et al., 2004; Sun et al., 2010; Zhang et al., 2006b; Zhao et al., 2011). A variety of studies have tried to elucidate the mechanism of photolysis by MEDL irradiation. Ju et al. (2013) reported that the photolysis degradation course without catalysts was initiated by UV–Vis light and was •OH and O_2^- dependent. Horikoshi et al. (2011) found that the 185 nm wavelength led to an excitation of perfluoroalkoxy acids as well as their subsequent cleavage, and this radiation caused photolysis of water, yielding the reactive oxygen species •OH radical, H. radical and aqueous electron, e^-. Yu et al. (2013a) found that air irradiated by MEDLs could generate a number of $_1O_2$ and •OH species in the photodegradation of H_2S in the gas phase. On the other hand, from the viewpoint of economy, the process of photolytic degradation by MEDLs without solid catalysts saves energy, in comparison to that with catalyst-coupled MEDLs. This is because the latter method requires a catalyst-synthesis procedure before the reaction, such as sol–gel preparation and heat treatment, and faces the added complication of a catalyst-separation procedure after reaction. Therefore photolytic degradation by MEDLs without catalysts seems a promising direction in future studies and applications.

Generally, knowledge on the mechanism of photolytic degradation by MEDLs is fragmentary, and a number of questions remain. For example, in the MEDL-irradiated photolysis process, what kinds of species are actually generated under the hybrid irradiation of UVC (100–280 nm), UVB (280–315 nm), UVA (315–400 nm) and visible (400–1000 nm) radiation? What is the importance of each part of the spectrum? What species are responsible for substrate degradation? And by what degree does each species contribute to the degradation? Solving these questions would lead to a better understanding of the mechanism of photolytic degradation by MEDLs.

In this study, the role of the radiation spectrum in the photo-decomposition of a basic dye, Rhodamine B (RhB), was evaluated by a comparative study between two systems, *i.e.*, MEDLs made with quartz (MEDL-quartz) envelopes and MEDLs with Pyrex envelopes (MEDL-Pyrex). The UVC/UVB transmittance for Pyrex envelopes is very low, therefore MEDL-Pyrex emitted UVA and visible light only, without UVC/UVB. Radical-extinguishing tests were conducted to explore the degradation contributions of different radicals, such as HO_2/O_2^-, H_2O_2 and •OH. Factors that might affect the degradation were also investigated. Moreover, the degradation of two other targets, an azo dye, Reactive Brilliant Red X-3B (X-3B), and a cationic dye, Safranine T (SaT), was compared to that of RhB to check the effectiveness of the MEDL system.

1. Experimental

1.1. Material and methods

RhB (CAS No.: 81-88-9, molecular mass: 479.0 g/mol) and X-3B (CAS No.: 17804-49-8, molecular mass: 615.3 g/mol) were purchased from Sinopharm Chemical Reagent Co., Ltd., China. SaT (CAS No.: 477-73-6, molecular mass: 350.8 g/mol) was purchased from Tianjing Kermel Co., Ltd., China. Their maximal absorbance wavelengths are around 550 nm, 538 nm and 554 nm, respectively. H_2O_2 (30%), methanol, potassium dichromate, silver sulfate, ferrous ammonium sulfate, 1,10-phenanthroline monohydrate, benzoquinone, isopropanol, catalase, H_2SO_4, HCl and NaOH were of analytical grade. Double-distilled water was used throughout the experiments.

A customized MW oven used in this experiment has been described in our previous work (Hong et al., 2007). The oven has a frequency of 2.45 GHz that is generated from its resonant cavity, and is powerful enough to irradiate MEDLs inside the solution-containing flask in the MW field. A MEDL-quartz (fused quartz, high-purity silica) or a MEDL-Pyrex (soda–lime glass), was evacuated to 1×10^{-3} Pa, then purged with 133 Pa of Argon. After that, 15 mg of liquid mercury was added. The cylinder-like MEDLs were 15 or 20 mm in outer diameter, 50 mm in length, around 7 or 12 cm^3 each in volume measured by the draining method (Aopu Co., China). The MEDL-quartz emits photons in both UV and visible ranges (254, 313, 365, 405, 436, 546 and 577–579 nm), while the MEDL-Pyrex emits photons in the UVA and visible ranges, with negligible photons in the UVB/UVC ranges (Fig. 1).

1.2. General procedure

A batch reaction was conducted *via* the following procedures. Aqueous substrate solution was pumped into a MEDL-containing flask inside the MW oven at a flow rate of 0.72 mL/sec. The total volume of the solution, including that in the flask, reservoir outside the MW oven and peristaltic tubing, was 200 mL, while keeping a constant volume of 50 mL in the flask for photo-reaction. Reaction time started when the MW oven was activated. Samples were withdrawn every few minutes. For pH study or radical-extinguishing tests, desired reagents were added into the flask before reaction. The change of the ratio of lamp volume to solution volume (V_L/V_S) was achieved through changing the volume of reaction solution (30, 50 and 70 mL) as well as the quantity of MEDLs used in the reaction. Blank spectra were subtracted from the corresponding data. Experiments were conducted three times. Values were given as means of triplicates.

The formation of oxidative species and their roles in the degradation processes were investigated by the addition of appropriate quenchers. Benzoquinone, isopropanol and