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RESEARCH ARTICLE

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Photodegradation of rhodamine B dye using a microwave electrodeless UV lamp (MWUVL)

Abstract The photodegradation of organic dye rhodamine B (RhB) in an aqueous solution was studied using a microwave electrodeless UV lamp (MWUVL). The 185 nm vacuum UV (VUV) intensity of the MWUVL amounted to 12% of the total UV output, about 1.7 times as high as that of the conventional low-pressure mercury lamp. An acidic condition was preferred for the degradation of RhB. Precipitate was generated during RhB degradation when the initial concentration of RhB solution was above 60 $mg \cdot L^{-1}$. For 100 $mg \cdot L^{-1}$ RhB at pH 4.0, the mass of precipitate produced was nearly half of the initial amount of RhB in the solution after irradiation for 75 min. The corresponding degradation ratio of RhB reached up to 99.4% and COD reduced 77.4%. The photodegradation of RhB is mainly achieved by direct photolysis of RhB by 185 nm and OH radical oxidation.

Keywords microwave electrodeless UV lamp (MWUVL), photodegradation, 185 nm, rhodamine B (RhB), direct photolysis

1 Introduction

Microwave electrodeless UV lamps (MWUVLs) have been of great interest as a new type of UV light source in recent decades. Unlike the conventional lamps energized by the electric field between the electrodes, MWUVLs do not use any electrode. The filling gas in the lamp absorbs the microwave (MW) energy and then forms stable UV-emitting discharge plasma. Due to such a unique discharge pattern, MWUVLs possess lots of advantages over conventional lamps, e.g. long lifetime, high UV intensity and adaptable lamp shapes, etc. [1–3], thus being proposed by researchers as a prospective tool for photochemistry [4–6].

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Lately, attempts in applying MWUVL to photodegradation of organic pollutants in an aqueous solution have been described in many papers [7–9]. Their ideas of developing the photochemical reactor with MWUVL are similar: the electrodeless lamp, in most cases filled with mercury vapor and an inert gas like argon, together with the reaction mixture are placed in a modified domestic microwave oven; the MW field of the oven generates the UV discharge in the lamp with the resulting, simultaneous UV and MW irradiation of the reaction mixture. Investigations have shown that the MW irradiation can accelerate the photodegradation rate of organic pollutants [8–10]. Whereas, for such a coupled MW-UV irradiation arrangement, part of the MW energy also goes into heating the reaction mixture, causing less MW power for the electrodeless lamp and thereby may attenuate the UV output. On the other hand, to keep the photoreaction proceeding at an appropriate temperature, generally, there has to be a reaction mixture circulation device with water cooling located outside the oven. It can also be noticed that the MWUVLs covered in literatures hitherto are almost studied with the UV wavelength (λ) being or above 253.7 nm, where a catalyst or an oxidant (*e.g.* TiO_2 and H_2O_2) is usually needed to achieve the degradation. However, the vacuum UV (VUV, $\lambda < 200$ nm) region of MWUVL, which has higher photon energy and hence does not necessarily require catalyst or oxidant to accomplish the degradation process, has not yet been reported concerning its characteristics or application to photochemistry.

In this paper, we present a different MWUVL photoreactor with the reaction mixture placed outside the MW field to avoid the thermal effect of MW and to allow more MW energy for the electrodeless lamp. The 185 nm VUV emission of the MWUVL was measured and employed to photodegrade of the organic dye rhodamine B (RhB) in water.

2 Experimental

2.1 Chemicals

Rhodamine B (RhB) dye of analytical grade (see structure given in Fig. 1) was obtained from Shanghai No. 3 Reagent

Factory and used as received. Dissolving RhB in distilled water with a mass concentration between 20 and 400 $mg \cdot L^{-1}$ derived RhB solution. H_2O_2 (30%, w/w, in H_2O) was purchased from Shanghai Taopu Chemical Factory. H_2SO_4, NaOH and absolute ethanol were all of analytical grade.

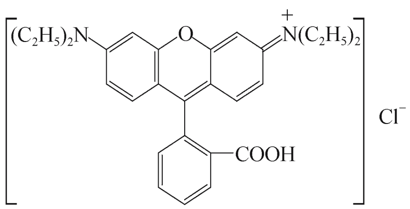

Fig. 1 Chemical structure of RhB

2.2 Experimental set-up

The experimental set-up with MWUVL based on a domestic microwave oven (LG Co., 850 W, 2.45 GHz,) is shown in Fig. 2. The electrodeless lamp was made of a quartz tube ($D = 20$ mm, $L = 150$ mm) and sealed up with low-pressure mercury and argon. Main modifications to the microwave oven were two 8-mm holes drilled in the left-side oven wall for the water circulating through a glass vessel (approx. 130 mL) which was laid inside the oven and a 20.5-mm hole at the bottom to erect the electrodeless lamp by using a Teflon ring as a bracket. The water circulating was used to remove the excess MW power so that to prevent the magnetron from being destroyed by overheating [11]. As illustrated in Fig. 2, the electrodeless lamp stretched downwards with the lower part outside the oven and immersed into the RhB solution (100 mL) with magnetic stirring right under the oven.

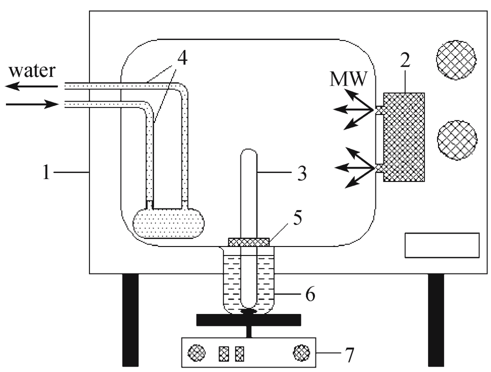

Fig. 2 Schematic diagram of the experimental set-up
1) Microwave oven; 2) magnetron; 3) electrodeless lamp; 4) water circulating in a glass vessel; 5) lamp bracket; 6) beaker (100 mL); 7) magnetic stirrer.

2.3 Analytical methods

An Acton VM-505 VUV monochrometer was used in measuring the emission spectrum of MWUVL. The concentration of RhB remaining in the aqueous solution after irradiation was determined by visible absorbance at $\lambda_{max} = 553$ nm using a Scinco S-3100 UV-Vis spectroscopy. The degradation ratio of RhB (η) was calculated by the equation given below

$$\eta = \frac{C_0 - C}{C_0} \times 100 \tag{1}$$

where C_0 and C are the initial and final concentration of RhB respectively. The pH of RhB solution was adjusted by H_2SO_4 and NaOH with a PHS-2C pH-meter (Shanghai Weiye Instrument Co.). The chemical oxygen demand (COD_{Cr}) was measured according the standard potassium dichromate method. The photoproduct was analyzed by Fourier transform-infrared spectroscopy (FT-IR) (Nicolet5DX) and gas chromatography/mass spectrometry (GC/MS) (Finnigan MAT ITD800) as a function of irradiation time.

3 Results and discussion

3.1 Characteristics of MWUVL

It was observed that the MWUVL was ignited within 1–2 seconds of turning on the microwave oven and the lower part of the lamp, outside the oven though, was lit almost simultaneously with the upper part inside the MW field. This can be attributed to the conductivity of MW energy by plasma. In our case, the plasma first formed in the upper part of the lamp conducted a sufficient portion of MW energy towards the lower part and then ignited the entire lamp immediately [3]. Meanwhile, the plasma in the lower part of the lamp would also inevitably transmit a small amount of MW irradiation to the RhB solution through the quartz lamp envelope. The thermal effect of MW here, however, was found to be insignificant considering that the solution temperature did not exceed 60°C during the degradation and that the infra-red radiation of the lamp could produce heat in the solution as well.

The emission spectrum of MWUVL recorded by the VUV monochrometer is given in Fig. 3. As expected, it resembled that of the conventional low-pressure mercury lamp in the mercury lines dominating 253.7 and 185 nm, but the relative intensity of 185 nm VUV amounted to 12% of the total UV output, about 1.7 times as high as that of the conventional lamp (generally 7%). Therefore, under MW powered electrodeless discharge, the emission efficiency of mercury line at 185 nm was greatly enhanced compared with the conventional electric discharge pattern.

3.2 Effects of initial pH

RhB solution (20 $mg \cdot L^{-1}$) with different initial pH was irradiated under MWUVL for 4 min and the results are shown in Fig. 4. The degradation ratio of RhB decreased with the increase in pH value, so the acidic condition is preferred for

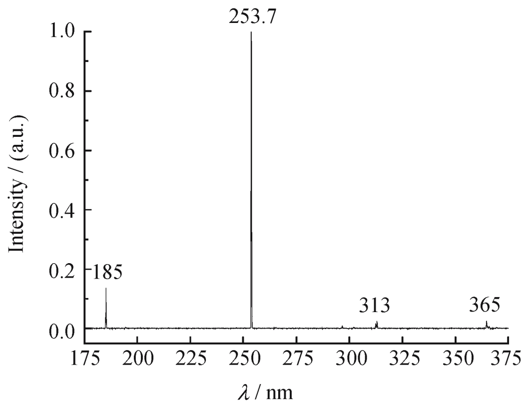

Fig. 3 UV emission spectrum from MWUVL

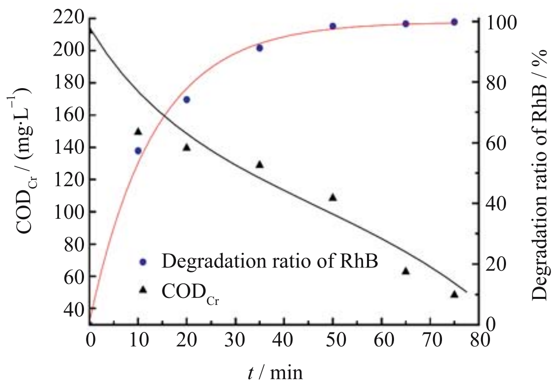

Fig. 5 Evolution of degradation ratio of RhB and COD_{Cr} vs. irradiation time

its degradation. Unless indicated otherwise, an initial pH of 4 was chosen for the following experiments.

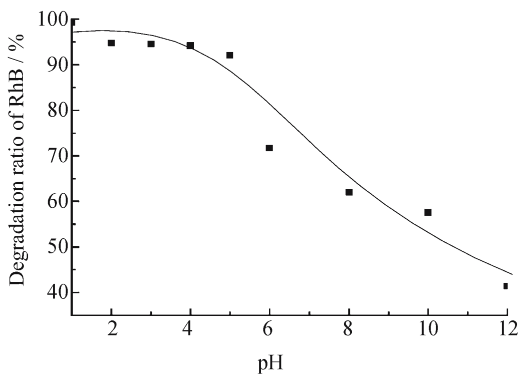

Fig. 4 Effects of initial pH on the degradation ratio of RhB

3.3 Degradation process of 100 mg·L^{-1} RhB

For RhB solution of 100 mg·L^{-1}, other than the observation of decolourization of the solution, precipitate, consisting of tiny henna particles, was found generated and it could be dissolved in ethanol with a jujube color. This phenomenon has not yet been described in literatures by far. The generation mechanism of this precipitate photoproduct shall be discussed hereafter in Sections 3.5 and 3.6.

Considering that the precipitate produced after MWUVL irradiation could be easily removed through a filter paper, the filtrate was selected to estimate the photodegradation efficiency of RhB only. Figure 5 illustrates the temporal variation of degradation ratio of RhB and COD_{Cr} of the filtrate. There was an exponential relationship between the degradation ratio of RhB and irradiation time. After irradiation for 75 min, the degradation ratio of RhB reached 99.4% and COD_{Cr} reduced from primarily 212 to 48 mg·L^{-1} with a removal efficiency of 77.4%.

The temporal changes in UV-Vis absorption spectra during the photodegradation of RhB solution are depicted in Fig. 6. The characteristic absorption peaks at 260, 355 and 553 nm of RhB weakened rapidly with irradiation time and vanished almost completely at 75 min, indicating that the aromatic conjugated system or the chromophoric group of RhB molecule was successfully destroyed under UV irradiation of MWUVL. Besides, an obvious blue shift of the visible absorption peak from 553 to 520 nm was observed, which may be ascribed to the stepwise deethylation of RhB [12].

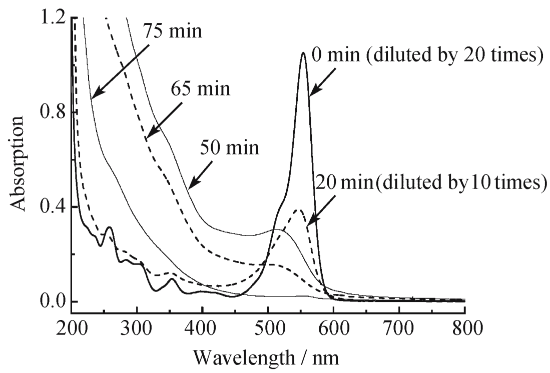

Fig. 6 Temporal changes in UV-Vis absorption spectra during the degradation of RhB solution

To obtain the production of the precipitate generated after MWUVL irradiation, the precipitate derived through filtration was dissolved in absolute ethanol and then dried at 80°C under an infrared lamp. Figure 7 shows the mass of precipitate (m_P) as a function of irradiation time. The precipitate gradually increased with irradiation time and after 75 min, there produced 4.7 mg precipitate in the solution, nearly as much as 50% of the initial amount of RhB (10 mg). At that time, the corresponding COD_{Cr} removal ratio of the filtrate was 77.4% as mentioned above. It implies that the generation of precipitate might play an important role in reducing the COD_{Cr} in the aqueous medium. And in the practical application, if possible, higher degradation efficiency within shorter treating time could be anticipated if the precipitate is removed timely for further UV irradiation of the solution.

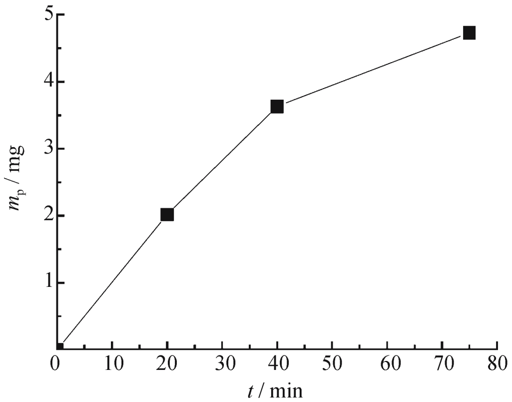

Fig. 7 Mass of precipitate (m_P) generated in the RhB solution at various irradiation times

3.4 Influences of initial concentration of RhB

Figure 8 displays the production of precipitate for RhB solution with various initial concentrations (C_0) after irradiation for 75 min. It was discovered that no precipitate was generated until C_0 climbed to 60 mg·L^{-1} and with further increase in C_0 the production of precipitate grew fast at first and then ascended slowly for C_0 above 100 mg·L^{-1} before a slight decrease occurred at 400 mg·L^{-1}. This is because for C_0 at a low level there were no sufficient fragments resulted from the photodegradation of RhB to form the precipitate; while for higher C_0 the production of precipitate would took place and increase with increasing C_0 and then would come to the saturation point owing to the limited amount of UV photons emitted from MWUVL.

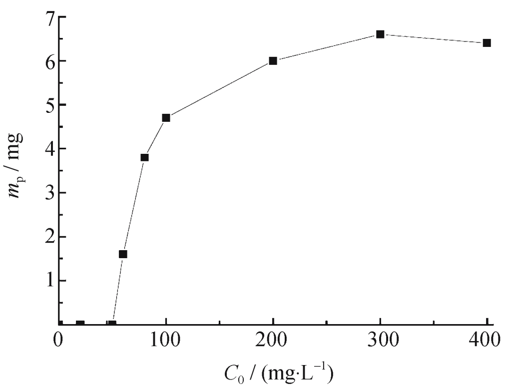

Fig. 8 Relationship between the initial concentration of RhB (C_0) and production of precipitate (m_P)

3.5 Analysis of photoproduct

As an important photoproduct for our MWUVL photodegradation experiment, the precipitates generated after 40 and 75 min irradiation of 100 mg·L^{-1} RhB solution were analyzed by FT-IR in comparison with that of RhB dye, as illustrated in Fig. 9. With increasing the irradiation time, most absorption peaks in 1,800–450 cm^{-1} range weakened or even disappeared eventually, accompanied by the emergence of some new absorption peaks. In addition, the characteristic absorption bands of –OH (3,400–3,200, 1,260–1,000 cm^{-1}) apparently strengthened both at 40 and 75 min. These distinctions in FT-IR spectral pattern between RhB and the precipitate provide a supplemental demonstration of the effective destruction of RhB structure by the UV irradiation of MWUVL and meanwhile, with further UV irradiation, the early generated precipitate would convert to more stable precipitate substance containing more –OH groups.

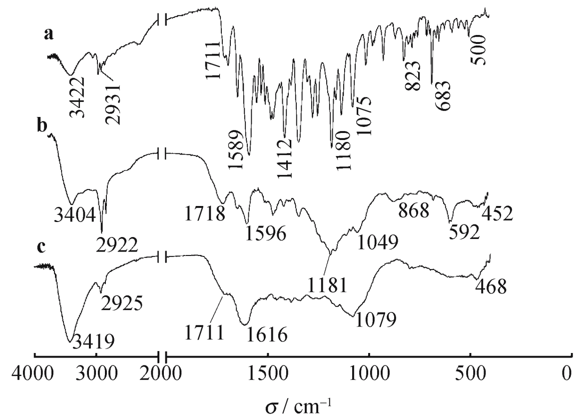

Fig. 9 FT-IR spectra of (a) RhB and precipitates generated in RhB solution after irradiating for (b) 40 min and (c) 75 min

However, no evident signal was detected for GC/MS analysis of the precipitate, so this precipitate photoproduct was probably composed of big molecule organic compounds with low volatility.

3.6 Degradation mechanism

The RhB solution received 253.7 and 185 nm irradiation (see Fig. 3) simultaneously in our MWUVL experiment, yet the 253.7 nm irradiation only was unable to photodegrade the RhB dye referring to earlier studies [13]. In this regard, it can be deduced that the photodegradation of RhB was induced by the 185 nm VUV irradiation of MWUVL. It has been widely accepted in research papers that the degradation of organic pollutants in aqueous solutions under 185 nm irradiation is mainly attributed to the oxidation of ·OH radicals generated through the 185 nm photolysis of H_2O (see Eq. (2)), whereas the pathway of direct photolysis of the organic molecules by 185 nm is always considered negligible unless the concentration of the pollutant is high enough [14,15].

$$H_2O + h\nu\ (185\ \text{nm}) \rightarrow \cdot OH + \cdot H \tag{2}$$

In an attempt to investigate whether the precipitate photoproduct in our case is also caused by the attack of ·OH on RhB, we conducted a comparison experiment using a 253.7-nm conventional mercury lamp (185 nm filtered through the lamp envelope made of high boron glass) as the UV light source combined with 330 mg·L^{-1} H_2O_2 added in the 100 mg·L^{-1} RhB solution, where the ·OH oxidation is known to be the dominant degradation mechanism [13]. As consistent with the results described by Zheng and Xiang [16], no precipitate was observed for this experiment. Thus, we cannot simply use the theory of ·OH oxidation to explain the generation of precipitate in RhB solution under the 185 nm irradiation of MWUVL. Apart from the ·OH oxidation reactions, it is most likely that there occurred the direct photolysis of RhB by 185 nm and the possible pathways were summarized in Eqs. (3)–(7) set below. The RhB* molecules in singlet or triplet states excited by 185 nm photons were very unstable; their chemical bonds would be broken or they would turn back to the ground state [17]. The deethylation of RhB, mentioned in section 3.3, might take place at C–N of the chromophoric group with resulting $\cdot R_1$ and $\cdot CH_2CH_3$. $\cdot R_1$ would continue to absorb 185 nm photons and generate fragments of $\cdot I_i$ ($i = 1, 2, \ldots, n$) radicals, which subsequently collided together and formed oligomers [18]. These oligomers could be regarded as the main source of the precipitate produced under the 185 nm irradiation of MWUVL.

$$\mathrm{RhB} + h\nu\ (185\ \mathrm{nm}) \rightarrow \mathrm{RhB}^* \tag{3}$$

$$\mathrm{RhB}^* \rightarrow \mathrm{RhB} \tag{4}$$

$$\mathrm{RhB}^* \rightarrow \cdot\mathrm{R}_1 + \cdot\mathrm{CH_2CH_3} \tag{5}$$

$$\cdot\mathrm{R}_1 + h\nu\ (185\ \mathrm{nm}) \rightarrow \cdot I_i\ (i = 1, 2, \ldots, n) \tag{6}$$

$$\cdot I_i + \cdot I_{i'} \rightarrow \mathrm{oligomer} \tag{7}$$

In order to study the universality of such a precipitate phenomenon observed in our photodegradation experiment, many other organic dyes of different types, such as methyl violet, alizarin red and reactive brilliant red X-3B, were selected to carry out the identical MWUVL experiments. A large amount of precipitate was also found produced in the methyl violet solution, while for the other dyes no precipitate was observed after irradiation. This suggested that the generation of precipitate depends greatly on the chemical structure of the organic dye itself.

4 Conclusions

With the MWUVL energized by a modified microwave oven, we obtained 185 nm VUV light with much higher emission efficiency compared with the conventional mercury lamp and it proved to be very effective in photodegradation of RhB dye in an aqueous solution. For RhB with initial concentration above 60 mg·L^{-1}, precipitate was found to be generated in the solution during degradation, due to the direct photolysis of RhB by 185 nm incorporated with ·OH oxidation. Timely removal of the precipitate might as well be taken into account for achieving better degradation in treatment of such a kind of precipitate-producing organic pollutants. As for the making of MWUVL, the MW power supply needs to be improved for further studies, the microwave oven used here as the MW source in the experiment has many deficiencies, such as high energy consumption (850 W) and low density MW field.

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