

Oxidative decomposition of azo dye C.I. Acid Orange 7 (AO7) under microwave electrodeless lamp irradiation in the presence of H₂O₂

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Abstract

A novel microwave electrodeless lamp (MWL) rather than traditional electrode lamp (TEL) was used in a H₂O₂/MWL system as light source. This technique provided a new way to study the simultaneous effect of both UV–vis light and microwave irradiations. This study showed that H₂O₂/MWL process was 32% more effective than H₂O₂/TEL process in degrading azo dye Acid Orange 7 (AO7). Further study found that the degradation of AO7 by the H₂O₂/MWL process was initiated by the attack of HO• radicals generated by the photolysis of H₂O₂. However, the direct photolysis of AO7 by MWL irradiation was not negligible. Effect of operation parameters, such as the initial concentrations of AO7 and H₂O₂ and pH, were investigated. A kinetic model of degradation of AO7 by H₂O₂/MWL process was found, in which not only the HO• oxidation but also direct photolysis were considered. The kinetic model was consistent with the experiment results. The degradation of AO7 by H₂O₂/MWL corresponded to a pseudo-first order reaction. The apparent reaction constant (k_{ap}) was a function of initial concentrations of H₂O₂ and AO7 and pH of the solution.

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Keywords: Microwave electrodeless lamp (MWL); H₂O₂; Acid Orange 7 (AO7); Kinetics

1. Introduction

Textile dyes and other industrial dyestuffs constitute one of the largest groups of organic compounds that represent an increasing environmental danger. The release of these colored wastewaters in the environment not only is a considerable source of non-aesthetic pollution and eutrophication but also can generate dangerous by-products through oxidation, hydrolysis, or other chemical reactions taking place in the wastewater phase. Due to the large degree of aromatics present in dye molecules and the stability of modern dyes, conventional biological treatment methods are ineffective for discoloration and degradation. Nevertheless, traditional physical techniques (adsorption on activated carbon, ultrafiltration, reverse osmosis, coagulation by chemical agents, ion exchange on synthetic adsorbent resins, etc.) just transfer organic compounds from water to another phase [1].

Advanced oxidation processes (AOPs) have received increasing attention in the last decade since they are able to deal with the problem of dye destruction in aqueous systems. AOPs are related to the formation of hydroxyl radicals (HO•), which will attack numerous organic compounds dissolved in wastewater quickly and nonselectively. AOPs such as Fenton and photo-Fenton catalytic reactions [2,3], H₂O₂/UV process [4,5] and photocatalysis [6,7] have been studied in order to reduce the color and organic load of dye-containing effluent wastewaters. Although heterogeneous photocatalysis is the most destructive emerging technology, the separation of TiO₂ from the water is a difficult problem needing to be resolved. From this point of view, the use of homogeneous H₂O₂/UV appears to be a good alternative [8]. But, under UV irradiation, the molar extinction coefficient of hydrogen peroxide at 254 nm is only 19.6 M⁻¹ s⁻¹. Therefore, in order to generate as many HO• radicals as possible, a large amount of hydrogen peroxide must be added into the reacting system [9].

Several studies have proved that microwaves can lead to the improvement of several types of oxidation processes. Kataoka et al. [10] found that the photocatalytic oxidation of ethylene

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proceeded faster (83.9%) in the presence of the microwave irradiation than in the absence of it. Horikoshi et al. [11] illustrated that simultaneous photocatalysis and microwave radiation was more effective in the degradation of the Rhodamine-B dye than photocatalysis alone. Han et al. [9] showed that microwave irradiation could also considerably enhance the oxidative degradation of phenol in the $\text{H}_2\text{O}_2/\text{UV}$ reacting system even under suppression of the thermal effect. Although microwaves effectively accelerate $\text{H}_2\text{O}_2/\text{UV}$ degradation efficiency, traditional electrode lamps (TEs) were not suitable to be laid in the microwave field because the metal electrodes of the lamp would be damaged under microwave irradiation. The problem will be solved if a microwave electrodeless lamp (MWL) substitutes TEs as light source. Círka and Hájek [12] applied MWL to the photochemical reaction of perfluorohexylethene with tetrahydrofuran. Comparative experiments with conventional mercury lamps showed the higher efficiency of microwave electrodeless lamps providing a high yield of product in a shorter reaction time. Klán et al. [13] also confirmed that MWL could feasibly be used in light-induced photofragmentation reaction valerophenone. Horiyoshi et al. [14] found that an MWL was more effective in microwave-assisted photocatalytic degradation of 2,4-dichlorophenoxyacetic acid than an electrode Hg lamp.

The aim of this research was to evaluate whether the MWL could be useful to degrade wastewater in $\text{UV}/\text{H}_2\text{O}_2$ process. Azo dye Acid Orange 7 (AO7) was used as the model compound to obtain detailed information of the novel process. Experimental optimization of the process and kinetics was examined.

2. Experimental

2.1. Materials and analysis

AO7 was obtained from Beijing Xuanwu Chemistry Co. and used without further purification. Unless otherwise indicated, the initial pH of solution was not adjusted. H_2O_2 (30%, w/w, in H_2O) was purchased from Beijing Chemistry Co. All other chemicals used were analytical grade.

A Hitachi (UV-3010) spectrometer recording the spectra over the 200–650 nm range was used for the determination of AO7 concentration and to follow its kinetics of discoloration with irradiation time. The calibration curve was established to correlate the absorbance at 485 nm to AO7 concentration. The decrease of total organic carbon (TOC) was monitored by a TOC analyzer (Phoenix 8000, Tekmar-Dohrmann Co., USA). The concentration of H_2O_2 was measured by iodimetry.

2.2. Estimation of power of microwave electrodeless lamp

The power of an MWL cannot be measured directly just as traditional lamps. MWLs emit UV–vis light by absorbing microwave energy, so the power of an MWL equals the microwave power absorbed by it. In this experiment, the microwave power absorbed by the MWL could be measured by monitoring the temperature of the solution and the reactor

with and without the MWL. Microwave irradiation can linearly raise the temperature of the solution and the reactor in the initial stage of reaction if the solution is not cooled by circulation. The slope obtained from the straight lines can be used to estimate the microwave power absorbed into the solution and the reactor by means of the following equation [9]:

$$P = (c_w m_w + c_r m_r) \frac{\Delta T}{t} \quad (1)$$

where P is the microwave power absorbed by the solution and the reactor (w), m_w and m_r are the mass of the solution and the reactor, c_w and c_r are the heat capacity of the solution and the reactor, ΔT is the temperature rise ($^{\circ}\text{C}$), and t is the irradiation time (s). When the MWL is inside of the microwave oven and outside of the reactor, the microwave power absorbed by the solution and the reactor is defined as P_1 . When the MWL is taken out from the system, the microwave power absorbed by the solution and the reactor is defined as P_2 . P_1 is lower than P_2 because some microwave energy was absorbed by the MWL. P_1 and P_2 were 440.0 and 411.9 W in this system, respectively. It could be calculated that the power of the MWL was 28.1 W. During reaction, the power of the MWL was less than 28.1 W because the microwave power absorbed by the MWL reduced to some extent due to the MWL being partially immersed in the solution.

2.3. Degradation procedures

The microwave source was a domestic microwave oven (Haier Co. Ltd.; power, 700 W; frequency, 2.45 GHz), and the microwave was continuous during the reaction. The reactor was a cylindrical glass container (D : 10 cm; H : 15 cm). Air ($0.15 \text{ m}^3/\text{h}$) was bubbled through a sintered glass filter fixed at the bottom of the reactor and into the solution to mix the solution. The reactor was laid inside of the erect microwave oven as illustrated in Fig. 1. The solution temperature was kept at $38 \pm 1^{\circ}\text{C}$ by means of circulating solution to a cooler by a peristaltic pump. Seven hundred and fifty milliliters 100 mg/L AO7 solution was added in the whole system, among which 125 mL was in the cooling circulation pipe and 625 mL was in the reactor. The MWL, which was made of quartz and filled with mercury and argon, was U-shaped. The UV–vis radiation emitted by the light source of the MWL is depicted in Fig. 2. The MWL floated on the solution and about 60% was immersed in solution.

In this study, we have performed comparative experiments of the MWL and a TEL. A 30-W ultraviolet lamp (Beijing ELR Co.) was used as the contrast, surrounded by a 5 mm-thick quartz glass tube shell placed at the center of the reactor (D : 9 cm; H : 30 cm).

In order to compare the effects of photolysis by microwave electrodeless lamp, direct reaction with H_2O_2 and degradation by $\text{H}_2\text{O}_2/\text{UV}$, AO7 was degraded by employing the following three processes: (1) microwave electrodeless lamp irradiation alone (MWL); (2) direct reaction with H_2O_2 under microwave irradiation ($\text{H}_2\text{O}_2/\text{MW}$); (3) microwave-assisted $\text{H}_2\text{O}_2/\text{UV}$ –vis with an MWL as light source ($\text{H}_2\text{O}_2/\text{MWL}$).

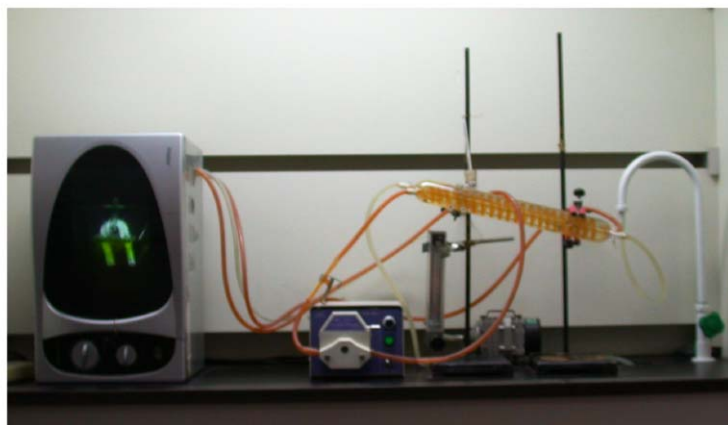
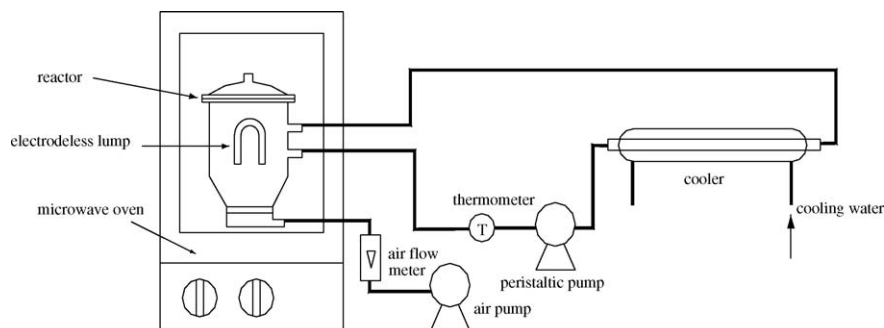


Fig. 1. Experimental set-up for $\text{H}_2\text{O}_2/\text{MWL}$ degradation of AO7.

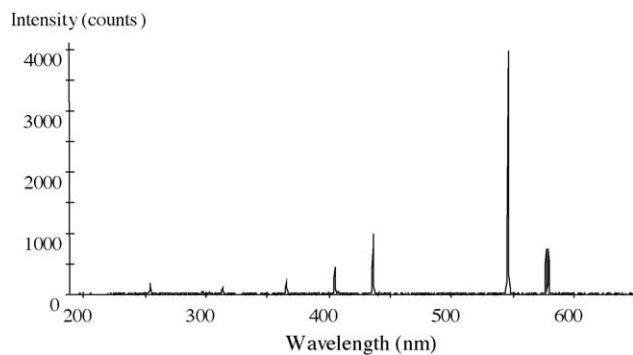


Fig. 2. Ultraviolet and visible wavelengths produced by the microwave electrodeless lamp.

3. Results and discussion

3.1. Comparison of MWL and TEL

AO7 was degraded by $\text{H}_2\text{O}_2/\text{MWL}$ and $\text{H}_2\text{O}_2/\text{TEL}$ under the same conditions, respectively. Fig. 3 indicates that the MWL is more effective than the TEL in AO7 degradation. From the pseudo first-order expression for the data of Fig. 3, the AO7 degradation rate constant of $\text{H}_2\text{O}_2/\text{MWL}$ was found to be 32% higher than that of $\text{H}_2\text{O}_2/\text{TEL}$. Fig. 2 shows that the light emission of MWL is mainly in the range of the visible region (>400 nm) and is much weaker in the UV region. Clearly, the

better performance of the MWL is not due to light emission. Han et al. [9] considered that microwave irradiation induced a violent rotation and migration for the motion of polar molecules, which can lead the molecules to a more highly excited state resulting in acceleration of the rate of reactant decomposition. We cannot preclude synergism of microwave irradiation and light irradiation. Further study of the mechanism is under investigation.

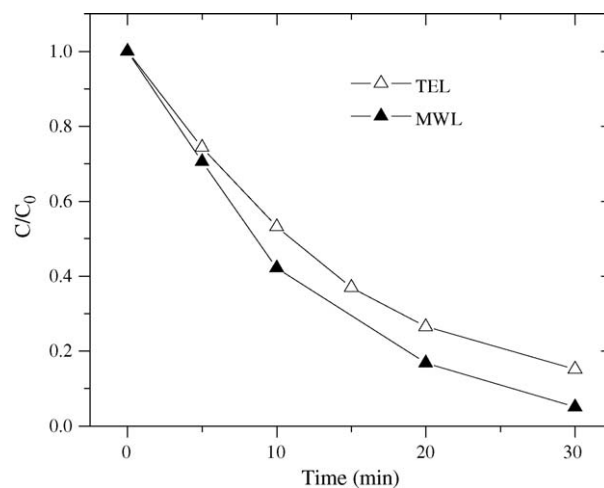


Fig. 3. Comparative experiments with microwave electrodeless lamp and traditional electrode lamp in $\text{H}_2\text{O}_2/\text{UV}$ system. Experimental conditions: $[\text{AO7}]_0 = 100$ mg/L, $[\text{H}_2\text{O}_2]_0 = 5$ mmol/L.

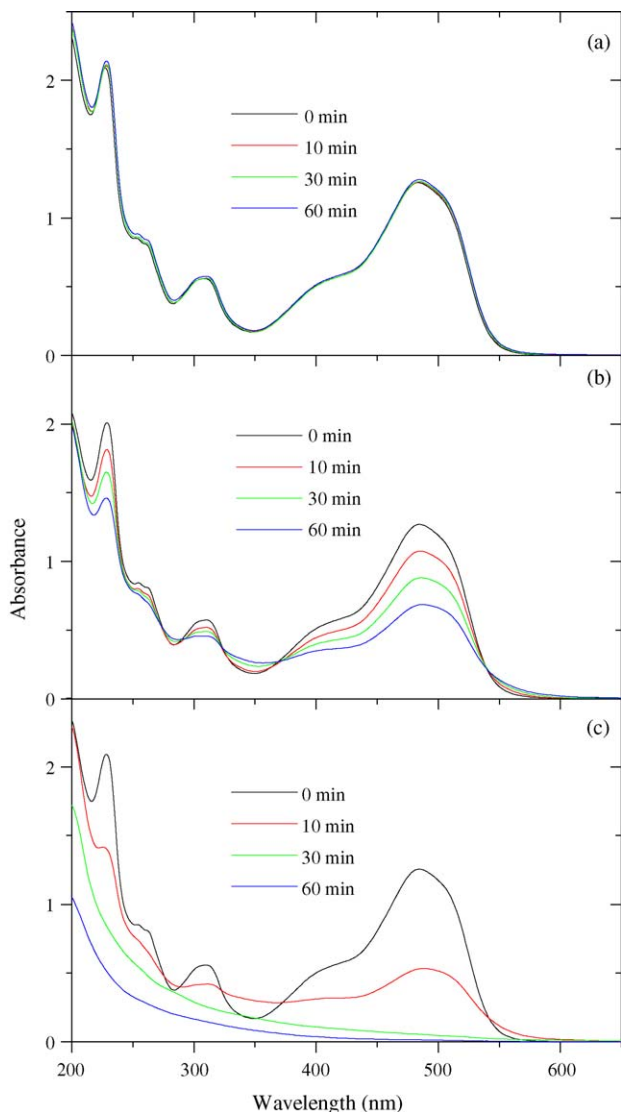


Fig. 4. UV-vis spectral changes of AO7 in solution as a function of irradiation time. (a) $\text{H}_2\text{O}_2/\text{MW}$; (b) MWL; (c) $\text{H}_2\text{O}_2/\text{MWL}$. Experimental conditions: $[\text{AO7}]_0 = 100 \text{ mg/L}$, $[\text{H}_2\text{O}_2]_0 = 5 \text{ mmol/L}$, initial pH 7.2 (natural). Insert: 2.5-fold diluted.

3.2. UV-vis spectral changes of AO7 solution with irradiation time

Fig. 4 shows typical UV-vis spectra obtained during $\text{H}_2\text{O}_2/\text{MWL}$, $\text{H}_2\text{O}_2/\text{MW}$ and MWL degradation of aqueous solutions of AO7. No degradation of AO7 within 60 min occurred by $\text{H}_2\text{O}_2/\text{MW}$ (Fig. 4(a)). However, irradiation of MWL alone (Fig. 4(b)) led to about 45% of AO7 being transformed after this time. With the $\text{H}_2\text{O}_2/\text{MWL}$ (Fig. 4(c)), about 95% of AO7 solution was discolored after only 30 min, with the solution displaying no spectral features. The absorption spectrum features of AO7 at 485, 310 and 228 nm correlate with the structural features of azo linkage, naphthalene and benzene rings of AO7, respectively [15]. The relevant first-order kinetics of the transformation of AO7 at three spectral wavelengths are listed in Table 1. These data show that $\text{H}_2\text{O}_2/\text{MWL}$ is more effective than MWL irradiation alone in degradation of AO7. The ratios

Table 1

Summary of rates of discoloration of AO7 solution by the three methods used

Degradation method	$k_{228 \text{ nm}}$ (10^{-2} min^{-1})	$k_{310 \text{ nm}}$ (10^{-2} min^{-1})	$k_{485 \text{ nm}}$ (10^{-2} min^{-1})
$\text{H}_2\text{O}_2/\text{MW}$	–	–	–
MWL	0.47	0.31	0.97
$\text{H}_2\text{O}_2/\text{MWL}$	2.16	2.09	8.45
Ratio ($k_{\text{H}_2\text{O}_2/\text{MWL}}/k_{\text{MWL}}$)	4.6	6.7	8.7

of the disappearance kinetics at the three spectral wavelengths in the $\text{H}_2\text{O}_2/\text{MWL}$ are $k_{228 \text{ nm}}/k_{310 \text{ nm}}/k_{485 \text{ nm}} = 1/1.0/3.9$. These ratios imply that degradation in the $\text{H}_2\text{O}_2/\text{MWL}$ method are different from those in the MWL photolytic degradation for AO7, inasmuch as the relevant ratios for the latter method are $k_{228 \text{ nm}}/k_{310 \text{ nm}}/k_{485 \text{ nm}} = 1/0.7/2.1$.

3.3. Temporal changes of pH

Fig. 5 shows temporal changes of pH during $\text{H}_2\text{O}_2/\text{MWL}$, $\text{H}_2\text{O}_2/\text{MW}$ and MWL degradation of aqueous solutions of AO7. $\text{H}_2\text{O}_2/\text{MWL}$ caused significant decrease of the pH during 60 min reaction, from pH 7.2 at $t=0$ to ca. pH 3.8 at $t=60$ min. MWL irradiation has less effect on pH, which at the end of the experiment reached the value of 6.6. The pH was not changed by $\text{H}_2\text{O}_2/\text{MW}$. The drop of pH with time was associated with the formation of acid products. This indicates that $\text{H}_2\text{O}_2/\text{MWL}$ destroyed AO7 to small molecular products more effectively than MWL irradiation alone.

3.4. Temporal change of total organic carbon

Total organic carbon (TOC) values are the total concentration of organics in solution and the changes of TOC mirror the degree of mineralization as a function of irradiation time. Results of TOC measurements obtained during the three treatment methods of aqueous solution of AO7 are presented in Fig. 6. It was

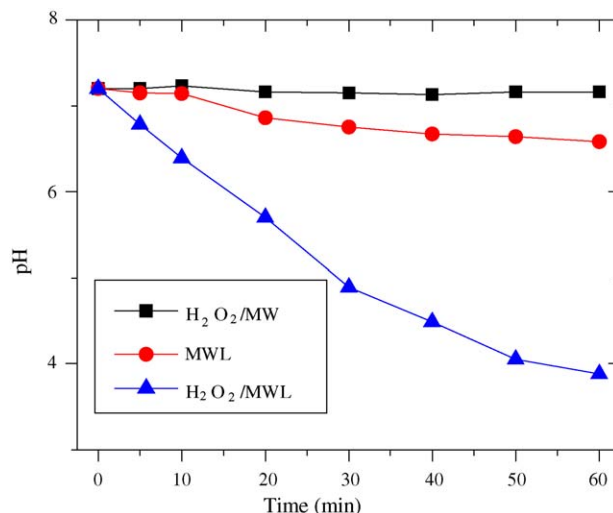


Fig. 5. Change of pH of solution with irradiation time. Experimental conditions: $[\text{AO7}]_0 = 100 \text{ mg/L}$, $[\text{H}_2\text{O}_2]_0 = 5 \text{ mmol/L}$, initial pH 7.2 (natural).

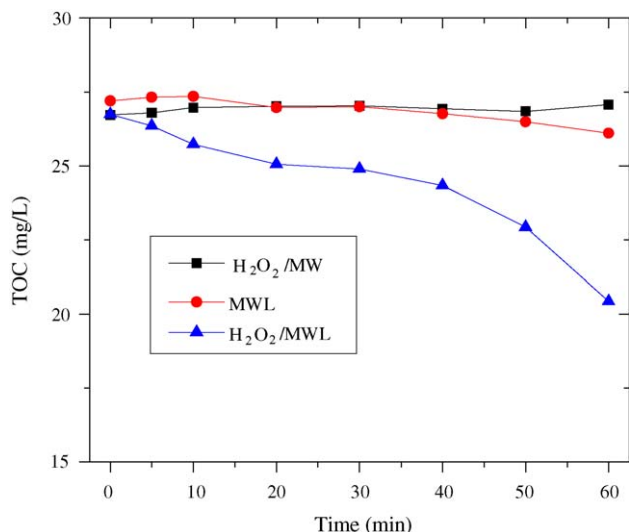


Fig. 6. Change of TOC of solution with irradiation time. Experimental conditions: $[AO7]_0 = 100$ mg/L, $[H_2O_2]_0 = 5$ mmol/L, initial pH 7.2 (natural).

observed that TOC was also not influenced by H_2O_2 /MW. MWL irradiation also had a bad performance on mineralization. Even after 60 min irradiation, less than 2% TOC was removed. By contrast, decay of TOC by H_2O_2 /MWL was more significant. About 30% TOC was removed after same time. However, in the initial 30 min, the rate of TOC removal also was very low in H_2O_2 /MWL. Less than 7% TOC is removed, whereas the color removal ratio reaches 95% more. After 30 min, the rate of TOC removal markedly increased. At that time, the AO7 solution was almost discolored completely. Clearly, this indicated that discoloration was the first degradation step.

3.5. Temporal change of H_2O_2 concentration

Fig. 7 shows the temporal change of H_2O_2 concentration in H_2O_2 /MWL. The H_2O_2 concentration decreased linearly

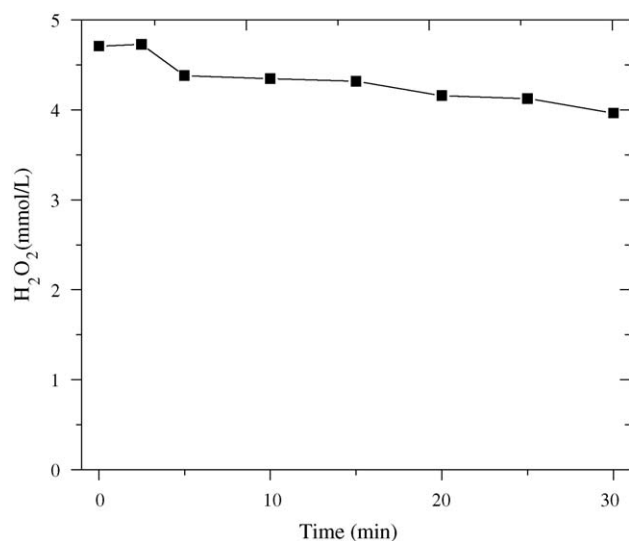


Fig. 7. Change of H_2O_2 concentration with irradiation time. Experimental conditions: $[AO7]_0 = 100$ mg/L, $[H_2O_2]_0 = 5$ mmol/L, initial pH 7.2 (natural).

Table 2

Pseudo-first order rate constants for discoloration of AO7 by H_2O_2 /MWL at different initial concentrations of AO7 and H_2O_2 and various pHs

No.	$[H_2O_2]_0$ (mmol/L)	$[AO7]_0$ (mg/L)	pH	k_{ap} (10^{-2} min^{-1})	R^2
1	5	80	7.2	15.91	0.999
2	5	100	7.2	8.45	0.994
3	5	170	7.2	4.96	0.993
4	5	250	7.2	2.83	0.991
5	1	100	7.2	4.28	0.999
6	2	100	7.2	5.09	0.998
7	4	100	7.2	8.31	0.999
8	12	100	7.2	16.05	0.999
9	20	100	7.2	14.17	0.992
10	5	100	3	10.65	0.992
11	5	100	5	9.07	0.999
12	5	100	9	7.34	0.992
13	5	100	11	6.62	0.998

with reaction time. At 30 min, the H_2O_2 concentration reduced 0.75 mmol/L. At same time, 0.27 mmol/L AO7 was discolored. This indicated that 1 mol AO7 discoloration consumed 2.8 mol H_2O_2 .

3.6. Effect of operation parameters

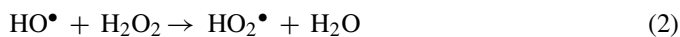
3.6.1. Effect of initial AO7 concentration

It is important from an application point of view to study the dependence of removal efficiency on the initial concentration of dye. Table 2 shows the degradation of AO7 at four different initial concentrations (the concentration of H_2O_2 was 5 mmol/L for all runs); Increase in the initial concentration of dye from 80 to 250 mg/L decreased the discoloration apparent reaction constant from 15.91×10^{-2} to $2.83 \times 10^{-2} \text{ min}^{-1}$. The rise in dye concentration induced an inner filter effect on light. Consequently, the solution became more and more impermeable to UV radiation with increasing of initial dye concentration and lowered hydroxyl radicals concentration [16]. Moreover, at higher dye concentrations, higher concentrations of intermediates were formed. These intermediates were also highly reactive toward hydroxyl radicals.

3.6.2. Effect of H_2O_2 dosage

The H_2O_2 concentration is crucial for the degradation rate. The rate of degradation increased with increasing concentrations of hydrogen peroxide as Table 2 shows. The addition of H_2O_2 from 1 to 12 mmol/L increased the discoloration k_{ap} from 4.28×10^{-2} to $16.05 \times 10^{-2} \text{ min}^{-1}$. The reason for this is that at higher concentrations of hydrogen peroxide, more UV is absorbed by hydrogen peroxide and the rate of hydroxyl radicals is higher, which leads to a higher rate of oxidation of AO7. However, above 12 mmol/L, the rate of degradation decreased with increasing concentrations of hydrogen peroxide. Increase of H_2O_2 concentration from 12 to 20 mmol/L decreased the discoloration k_{ap} from 16.05×10^{-2} to $14.17 \times 10^{-2} \text{ min}^{-1}$. At high concentrations, H_2O_2 acts as a hydroxyl radical quencher as follows, consequently lowering the concentration of hydroxyl

radicals [17]:



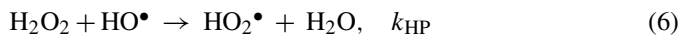
3.6.3. Effect of initial pH

The effect of pH on discoloration was studied in the pH range 3–11. The results are shown in Table 2. The pH of solution was adjusted using H_2SO_4 and NaOH . From the results, it is clear that the process is more efficient in acid medium (pH 3). Increase of pH from 3 to 11 decreased the discoloration k_{ap} from 10.65×10^{-2} to $6.62 \times 10^{-2} \text{ min}^{-1}$. Muruganandham and Swaminathan [17] also found that $\text{H}_2\text{O}_2/\text{UV}$ discoloration of azo dye Reactive Orange 4 was more efficient in acid medium (pH = 2–4) and further increase of pH from 3 to 8 decreased the discoloration. He considered that the lowering of the removal rate in this pH range was due to a reduction of hydroxyl radical concentration. Under this condition H_2O_2 undergoes photodecomposition to water and oxygen rather than hydroxyl radical (Eq. (27)):



3.7. Kinetic study

From the data above, it is clear that the degradation of AO7 by the $\text{H}_2\text{O}_2/\text{MWL}$ system is initiated by the attack of HO^\bullet radicals generated by photolysis of H_2O_2 . However, the direct photolysis of AO7 by MWL irradiation is not negligible, which is different from traditional electrode lamp irradiation. Hydroxyl radicals may react with AO7, H_2O_2 , and the intermediate products of the degradation process. From the initial oxidation of the AO7 until complete mineralization, a complex set of reactions took place. The following main reactions may be considered:



where I_{HP} and I_{S} are the rates of photons absorbed by H_2O_2 and the substrate AO7, respectively. Φ_{HP} and Φ_{S} are the quantum yields of respective photolysis. k_{HP} , k_{S} and k_{Int} are the bimolecular rate constants for the corresponding reactions with hydroxyl radicals. In this reaction scheme, reactions implying HO_2^\bullet or $\text{O}_2^{\bullet-}$ radicals have not been considered, as their reactivity is much lower than that of HO^\bullet [18].

Considering the simplified mechanism proposed, the rate of AO7 consumption (r) is given by the sum of the rates of direct photolysis reaction (7) and reaction with HO^\bullet (8):

$$r = -\frac{d[\text{S}]}{dt} = I_{\text{S}}\Phi_{\text{S}} + k_{\text{S}}[\text{S}][\text{HO}^\bullet] \quad (10)$$

The net rate of formation of HO^\bullet can be derived by the reactions (5), (6), (8) and (9) as follows:

$$r_{[\text{OH}^\bullet]} = \frac{d[\text{HO}^\bullet]}{dt} = 2I_{\text{HP}}\Phi_{\text{HP}} - k_{\text{HP}}[\text{H}_2\text{O}_2][\text{HO}^\bullet] - k_{\text{S}}[\text{S}][\text{HO}^\bullet] - k_{\text{Int}}[\text{Int}][\text{HO}^\bullet] \quad (11)$$

With the steady-state approximation for Eq. (11), the concentration of HO^\bullet is given by Eq. (12):

$$[\text{HO}^\bullet] = \frac{2I_{\text{HP}}\Phi_{\text{HP}}}{k_{\text{HP}}[\text{H}_2\text{O}_2] + k_{\text{S}}[\text{S}] + k_{\text{Int}}[\text{Int}]} \quad (12)$$

So, the oxidation rate of the substrate (r) is expressed as:

$$r = I_{\text{S}}\Phi_{\text{S}} + \frac{2I_{\text{HP}}\Phi_{\text{HP}}k_{\text{S}}[\text{S}]}{k_{\text{HP}}[\text{H}_2\text{O}_2] + k_{\text{S}}[\text{S}] + k_{\text{Int}}[\text{Int}]} \quad (13)$$

In the early stage of the degradation (decolorization stage), decolorization is much faster than mineralization. So, we can write:

$$[\text{S}]_0 \approx [\text{S}] + [\text{Int}] \quad (14)$$

The difference between k_{S} and k_{Int} was supposed to be negligible ($k_{\text{S}} \approx k_{\text{Int}}$) [16]. Hence it can be written as:

$$k_{\text{S}}[\text{S}] + k_{\text{Int}}[\text{Int}] = k_{\text{S}}[\text{S}]_0 \quad (15)$$

According to Lambert-Beer's law,

$$I_{\text{S}} = I_0(1 - 10^{-A}) \frac{\varepsilon_{\text{S}}[\text{S}]}{\sum \varepsilon_i C_i} \quad (16)$$

$$I_{\text{HP}} = I_0(1 - 10^{-A}) \frac{\varepsilon_{\text{HP}}[\text{H}_2\text{O}_2]}{\sum \varepsilon_i C_i} \quad (17)$$

$$A = \exp(-2.3L(\varepsilon_{\text{HP}}[\text{H}_2\text{O}_2] + \varepsilon_{\text{S}}[\text{S}] + \varepsilon_{\text{Int}}[\text{Int}])) \quad (18)$$

$$\sum \varepsilon_i C_i = \varepsilon_{\text{HP}}[\text{H}_2\text{O}_2] + \varepsilon_{\text{S}}[\text{S}] + \varepsilon_{\text{Int}}[\text{Int}] \quad (19)$$

where I_0 is the incident UV-light intensity, L is the optical path length of the system; ε_{HP} , ε_{S} and ε_{Int} are the molar extinction coefficients for H_2O_2 , AO7 and the intermediate product, respectively. Due to the high absorbance of the AO7 and H_2O_2 in the process, it can be written as:

$$(1 - 10^{-A}) \approx 1 \quad (20)$$

The difference between ε_{S} and ε_{Int} was supposed to be negligible ($\varepsilon_{\text{S}} \approx \varepsilon_{\text{Int}}$). Hence it can be written as:

$$\varepsilon_{\text{S}}[\text{S}] + \varepsilon_{\text{Int}}[\text{Int}] = \varepsilon_{\text{S}}[\text{S}]_0 \quad (21)$$

So, the oxidation rate of the substrate (r) is simplified as:

$$r = \frac{I_0}{\varepsilon_{\text{HP}}[\text{H}_2\text{O}_2] + \varepsilon_{\text{S}}[\text{S}]_0} \left\{ \varepsilon_{\text{S}}\Phi_{\text{S}} + \frac{2k_{\text{S}}\varepsilon_{\text{HP}}\Phi_{\text{HP}}[\text{H}_2\text{O}_2]}{k_{\text{HP}}[\text{H}_2\text{O}_2] + k_{\text{S}}[\text{S}]_0} \right\} [\text{S}] \quad (22)$$

If

$$\frac{I_0}{\varepsilon_{\text{HP}}[\text{H}_2\text{O}_2] + \varepsilon_{\text{S}}[\text{S}]_0} \left\{ \varepsilon_{\text{S}}\Phi_{\text{S}} + \frac{2k_{\text{S}}\varepsilon_{\text{HP}}\Phi_{\text{HP}}[\text{H}_2\text{O}_2]}{k_{\text{HP}}[\text{H}_2\text{O}_2] + k_{\text{S}}[\text{S}]_0} \right\} = k_{\text{ap}} \quad (23)$$

Eq. (22) is simplified as following:

$$r = k_{\text{ap}}[S] \quad (24)$$

where k_{ap} is the apparent reaction constant of substrate AO7 degradation. Mostly, $[\text{H}_2\text{O}_2]_0 \gg [\text{S}]_0$. One mole AO7 discoloration consumes 2.8 mol H_2O_2 . Hence it can be written as:

$$[\text{H}_2\text{O}_2] = [\text{H}_2\text{O}_2]_0 - 2.8([\text{S}]_0 - [\text{S}]) \approx [\text{H}_2\text{O}_2]_0 \quad (25)$$

So,

$$k_{\text{ap}} = \frac{I_0}{\varepsilon_{\text{HP}}[\text{H}_2\text{O}_2]_0 + \varepsilon_{\text{S}}[\text{S}]_0} \left\{ \varepsilon_{\text{S}}\phi_{\text{S}} + \frac{2k_{\text{S}}\varepsilon_{\text{HP}}\phi_{\text{HP}}[\text{H}_2\text{O}_2]_0}{k_{\text{HP}}[\text{H}_2\text{O}_2]_0 + k_{\text{S}}[\text{S}]_0} \right\} \quad (26)$$

This kinetic model indicates that the degradation of AO7 corresponds to a pseudo-first order reaction, which is consistent with the experiment results above. It can also be concluded that the apparent reaction constant (k_{ap}) is a function of the initial concentration of H_2O_2 and AO7. As discussed above, pH also affects the degradation of AO7. In this kinetic model, the effect of pH on k_{ap} was reflected by variation of some parameters with pH change, such as k_{HP} , k_{S} , ϕ_{HP} and ϕ_{S} .

4. Conclusion

Although the MWL used in our experiment has a weak UV region, our study has displayed that MWL as the light source is more effective in the UV-vis/ H_2O_2 system than TEL to treat wastewaters. Other research [19] found that light intensity and irradiation wavelengths of MWL could be adjusted according to requirement. The lamp even gave over three times as much UV radiation as the traditional electrode lamp [12]. The simultaneous irradiation of polluted water by both MW and UV-vis light makes it possible to use the simplified effective H_2O_2 /MWL for practical application. On the basis of the proposed kinetic model, the pseudo-first rate constant (k_{ap}) is affected by varying the initial concentration of AO7, H_2O_2 and pH, which is consistent with the experiment results.

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References

- [1] I.K. Konstantinou, T.A. Albanis, TiO_2 -assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations, *Appl. Catal. B: Environ.* 49 (2004) 1–14.
- [2] M. Pérez, F. Torrades, X. Domènech, J. Peral, Fenton and photo-fenton oxidation of textile effluents, *Water Res.* 36 (2002) 3237–3244.
- [3] X.R. Xu, H.B. Li, W.H. Wang, J.D. Gu, Degradation of dyes in aqueous solutions by the Fenton process, *Chemosphere* 57 (2004) 595–600.
- [4] C. Galindo, A. Kalt, UV/ H_2O_2 oxidation of azodyes in aqueous media: evidence of a structure—degradability relationship, *Dyes Pigments* 42 (1999) 199–207.
- [5] M. Neantu, I. Siminiceanu, A. Yediler, A. Kettrup, Kinetics of decolorization and mineralization of reactive azo dyes in aqueous solution by the UV/ H_2O_2 oxidation, *Dyes Pigments* 53 (1999) 93–99.
- [6] G. Liu, T. Wu, J. Zhao, H. Hidaka, N. Serpone, Photoassisted degradation of dye pollutants 8. Irreversible degradation of alizarin red under visible light irradiation in air-equilibrated aqueous TiO_2 dispersions, *Environ. Sci. Technol.* 33 (1999) 2081–2087.
- [7] J. Zhao, T. Wu, K. Wu, K. Oikawa, H. Hidaka, N. Serpone, Photoassisted degradation of dye pollutant 3. Degradation of the cationic dye rhodamine B in aqueous anionic surfactant/ TiO_2 dispersions under visible light irradiation: evidence for the need of substrate adsorption on TiO_2 particles, *Environ. Sci. Technol.* 32 (1998) 2394–2400.
- [8] P.K. Malik, S.K. Sanyal, Kinetics of decolorisation of azo dyes in wastewater by UV/ H_2O_2 process, *Separat. Purif. Technol.* 36 (2004) 167–175.
- [9] D.H. Han, S.Y. Cha, H.Y. Yang, Improvement of oxidative decomposition of aqueous phenol by microwave irradiation in UV/ H_2O_2 process and kinetic study, *Water Res.* 38 (2004) 2782–2790.
- [10] S. Kataoka, D.T. Tompkins, W.A. Zeltner, et al., Photocatalytic oxidation in the presence of microwave irradiation: observations with ethylene and water, *J. Photochem. Photobiol. A: Chem.* 148 (2002) 323–330.
- [11] S. Horikoshi, H. Hidaka, N. Serpone, Environmental remediation by an integrated microwave/UV-illumination method. 1. Microwave-assisted degradation of rhodamine-B dye in aqueous TiO_2 dispersions, *Environ. Sci. Technol.* 36 (2002) 1357–1366.
- [12] V. Círka, M. Hájek, Microwave photochemistry. Photoinitiated radical addition of tetrahydrofuran to perfluorohexylethene under microwave irradiation, *J. Photochem. Photobiol. A: Chem.* 123 (1999) 21–23.
- [13] P. Klán, J. Literák, M. Hájek, The electrodeless discharge lamp: a prospective tool or photochemistry, *J. Photochem. Photobiol. A: Chem.* 128 (1999) 145–149.
- [14] S. Horiyoshi, H. Hidaka, N. Serpone, Environmental remediation by an integrated microwave/UV-illumination technique 4. Non-thermal effects in microwave-assisted degradation of 2,4-dichlorophenoxyacetic acid in UV-irradiated $\text{TiO}_2/\text{H}_2\text{O}$ dispersions, *J. Photochem. Photobiol. A: Chem.* 159 (2003) 289–300.
- [15] M. Styliadi, D.I. Kondarides, X.E. Verykios, Visible light-induced photocatalytic degradation of Acid Orange 7 in aqueous TiO_2 suspensions, *Appl. Catal. B: Environ.* 47 (2004) 189–201.
- [16] M.A. Behnajady, N. Modirshahla, M. Shokri, Photodestruction of Acid Orange 7 (AO7) in aqueous solutions by UV/ H_2O_2 : influence of operational parameters, *Chemosphere* 55 (2004) 129–134.
- [17] M. Muruganandham, M. Swaminathan, Photochemical oxidation of reactive azo dye with UV- H_2O_2 process, *Dyes Pigments* 62 (2004) 269–275.
- [18] F.S. García, J. Luciano, A.L. Capparelli, A.M. Braun, E. Oliveros, Evaluations of the efficiency of photodegradation of nitroaromatics applying the UV/ H_2O_2 technique, *Environ. Sci. Technol.* 36 (2002) 3936–3944.
- [19] P. Müller, P. Klán, V. Círka, The electrodeless discharge lamp: a prospective tool for photochemistry. Part. Temperature- and envelope material-dependent emission characteristics, *J. Photochem. Photobiol. A: Chem.* 158 (2003) 1–5.