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Microwave assisted photocatalytic degradation of high concentration azo dye Reactive Brilliant Red X-3B with microwave electrodeless lamp as light source

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Abstract

A device for microwave assisted photocatalysis (TiO_2/MWL) was described based on a modified domestic microwave oven that incorporated a novel microwave electrodeless lamp as the source of UV–vis irradiation to photodegrade environmental pollutants of high concentration in aqueous media. The performance of this device was examined using the photodegradation of azo dye Reactive Brilliant Red X-3B driven by a coupled UV–vis/microwave irradiation in an aqueous TiO_2 dispersion. The coupled UV–vis/microwave irradiation led to effective degradation of higher concentration dyes in TiO_2/MWL than in conventional photocatalysis. Higher photodegradation efficiency, higher rate constant (k) of surface reaction between dyes and hydroxyl radicals and slighter influence of the initial dye concentration on photodegradation were found in TiO_2/MWL. For 400 mg/L X-3B, removal of color and total organic carbon (TOC) reached 100% and 65% after 180 min, respectively. Meanwhile, the biodegradability of dye solution indicated by the value of BOD_5/COD increased from initial 0.03 to 0.35 which indicated that TiO_2/MWL could be used as a pre-treatment process of biotreatment as well. Moreover, photodegradation rate could be enhanced evidently in TiO_2/MWL by inorganic oxidizing species (H_2O_2, $Na_2S_2O_8$ and $Fe(NO_3)_3$).

Keywords: Photodegradation; Microwave electrodeless lamp; Reactive Brilliant Red X-3B; Biodegradability; Inorganic oxidizing species

1. Introduction

Heterogeneous photocatalysis, as one of the most promising Advanced Oxidation Processes (AOPs), has attracted much attention in the past two decades because this process can be operated at an ambient temperature and mineralize refractory or toxic organic compounds to carbon dioxide, water and mineral acids [1]. Nevertheless, by far, few practical applications of photocatalytic degradation on the industrial scale have been reported due to some barriers. Most of the photoinduced positive holes (h^+) and electrons (e^-) have recombined before they are trapped by hydroxyl or oxygen, which leads to low quantum efficiency (less than 5%). Consequently, low quantum efficiency results in low degradation rate of photocatalysis so that large reactor and long reaction time, which are not economical, are needed when photocatalysis is applied. There is a limiting concentration of reactants above which photocatalytic efficiency decreases. The limiting concentration is usually less than 100 mg/L. However, the concentrations of contaminants in real wastewaters are mostly much higher than this value. Titanium dioxide (TiO_2) powder is generally used as one of the most popular photocatalysts due to its nontoxicity, chemical inertness, and low costs. Although it has been proven that a great number of organic pollutants can be effectively mineralized by it, the separation and reuse of TiO_2 powder from treated water are still a difficulty in widely extending its practical application.

Microwave energy has been used more and more on synthetic organic chemistry because of its great ability to accelerate reactions and to improve yields and selectivity [2].

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Recently, microwave irradiation has been used to assist photocatalytic reactions [3–10]. Kataoka found that the photocatalytic oxidation of ethylene proceeded faster (83.9%) in the presence of microwave irradiation than in its absence [3]. Horikoshi proved by electron spin resonance (ESR) that about 20% more •OH radicals were generated by photocatalysis with microwave irradiation than photocatalysis alone [4]. Although photocatalytic degradation is effectively accelerated by microwave, traditional Hg lamp could not be laid in microwave field because the metal electrodes of the lamp will be damaged under microwave irradiation. The problem could be solved if microwave electrodeless lamp (MWL) substitutes traditional lamp as light source because it has no metal electrodes. MWL comprises an envelope or bulb containing a plasma-forming medium. When the MWL is placed in a microwave energy field, the gases within the envelope ionize, a low-pressure plasma discharge forms, heating and beating the envelope, vaporizing materials to emit light. MWL has some unique advantages such as, good photochemical efficiency, long life, low cost, and simple photocatalytic equipment [11,12]. The light intensity can be adjusted by variations in MW power level and irradiation wavelengths can be adjusted by the changes in ratio and nature of the gases in MWL [5]. Církva and Hájek [2] found that MWL showed higher photochemical efficiency than traditional lamp in the photochemical reaction of perfluorohexylethene with tetrahydrofuran. Horikoshi proved that photocatalysis with MWL (a double quartz cylindrical plasma photoreactor) was about 10 times more efficient than the photocatalysis using traditional lamp [9].

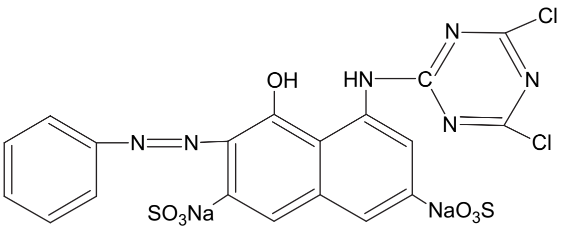
In our previous research [13], the effects of some important parameters on degradation rate in microwave assisted photocatalysis with MWL as light source (TiO_2/MWL) were investigated in detail. It was found that the effect of initial dye concentration on degradation rate in TiO_2/MWL was slighter than that in conventional photocatalysis. Therefore, higher concentration dye could be degraded effectively in TiO_2/MWL than in the latter. This is very valuable in that real wastewater could be degraded by TiO_2/MWL without dilution. Further investigation about TiO_2/MWL photocatalytic degradation of high concentration dye is needed, which is important for the practical application of the innovative photocatalysis.

The production and consumption of azo dyes account for over 50% of the total dyes around the world. Reactive Brilliant Red X-3B is a kind of typical azo dye. Therefore, X-3B was chosen as a representative model compound to obtain detailed information of TiO_2/MWL. The dye concentration in solution usually was 400 mg/L, maximal concentration being 1500 mg/L, which is higher compared with those commonly adopted in conventional photocatalysis (20–100 mg/L). In order to preclude the separation procedure of powder TiO_2, a novel grain TiO_2 (GT01) rather than the well-known P25 TiO_2 was used. The mechanism of TiO_2/MWL photocatalytic degradation of high concentration dye was discussed. The biodegradability of dye solution was detected during photocatalytic reaction besides color and TOC. Moreover, the acceleration effects of inorganic oxidizing species were investigated.

2. Experimental section

2.1. Chemical

The azo dye Reactive Brilliant Red X-3B was a commercial dye and was used without further purification. The catalyst used in this experiment was one kind of grain TiO_2 (GT01) from HSD. Co., China. GT01 was made by adding about 10% bonding agent (Al_2O_3) and then calcining at 300 °C. The particle diameter of GT01 was 180–250 μm, which was small enough for suspension by bubbling air through but large enough for settlement by gravity. BET surface area of GT01 was 194.4 m^2/g and its density was 900 kg/m^3. X-ray diffraction analysis showed that GT01 was mainly anatase TiO_2. The dosage of GT01 was 4 g/L. Other chemicals used were of analytical grade.



Reactive brilliant red X-3B (chemical formula = $C_{19}H_{10}O_7N_6C_{12}S_2Na_2$)

2.2. Equipment

The microwave source was a domestic microwave oven (Haier Co. Ltd.; power, 700 W; frequency, 2.45 GHz), and the microwave was maintained continuously during the reaction. The photocatalytic reactor was a cylindrical glass reactor (capacity, 1000 mL). Air (0.25 m^3/h) was bubbled into the solution through a sintered glass filter fixed at the bottom of the reactor not only for offering oxygen but also for mixing the catalyst and the solution. The photocatalytic reactor was placed inside of the erect microwave oven as illustrated in Fig. 1. Solution temperature was kept at 38 ± 1 °C by means of circulating solution to a cooler with a peristaltic pump. X-3B (750 mL) solution was added into the whole system,

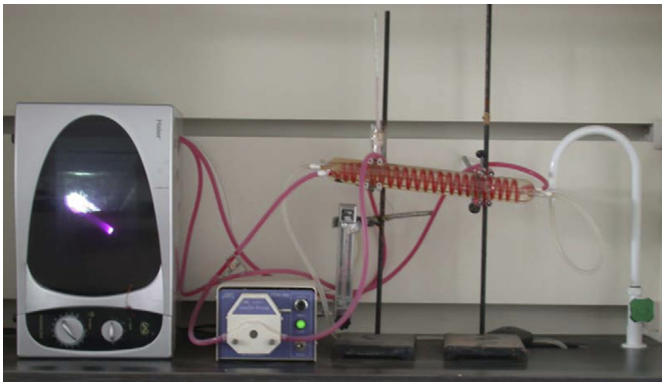


Fig. 1. Experimental setup of microwave assisted photocatalysis with microwave electrodeless lamp as the light source.

among which 125 mL was in the circulation pipe and 625 mL was in the photocatalytic reactor. A U-shaped MWL, which was easily fixed, was designed for the experiment. The MWL was made of quartz and filled with mercury and argon. 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 immerged in solution during the reaction.

2.3. Estimation of the power of microwave electrodeless lamp

The power of MWL could not be measured directly just as in conventional lamp. MWL emits UV–vis light by absorbing microwave energy. So, the power of MWL is equal to the power of microwave absorbed by it. In this experiment, the power of microwave absorbed by MWL could be measured by monitoring the temperature of the solution and the reactor. Microwave irradiation can linearly raise the temperature of the solution and the reactor in the initial stage of reaction if solution is not cooled by circulation. The temperature of the reactor is equal to the temperature of the solution in the reactor. Slope obtained from the straight lines can estimate the microwave power absorbed by the solution and reactor by means of the following equation [14].

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

where P is the power of microwave absorbed by the solution and reactor (W), m_w and m_r are the mass of water and reactor (water: 750 g, reactor: 680 g), c_w and c_r are the heat capacities of water and reactor (water: 4.184 J/g °C, reactor: 0.796 J/g °C), ΔT is the temperature rise (°C), and t is the irradiation time (s). When MWL is inside of microwave oven and not immerged in water, power (P_1) absorbed by water and reactor would be lower than the power (P_2) without MWL due to MWL absorbing partial microwave energy. P_1 and P_2 were 411.9 and 440.0 W, respectively. It could be calculated that the power of MWL was 28.1 W. During the reaction, the power of MWL was less than 28.1 W because the power of microwave absorbed by MWL was reduced due to partial immersion of MWL in solution.

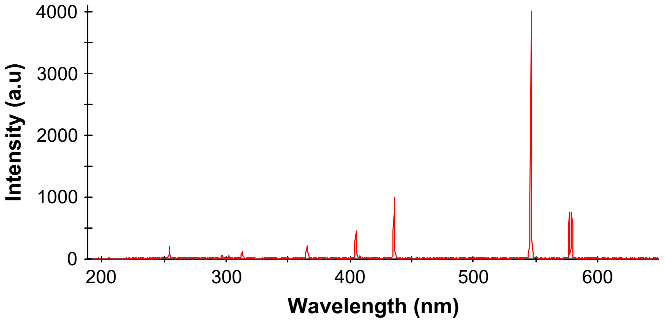


Fig. 2. The emission spectra of the microwave electrodeless lamp.

2.4. Analysis

The samples were filtered through 0.45 μm membrane before being analyzed. The UV–vis spectra of the samples were recorded from 200 nm to 700 nm using a U-3010 UV–vis spectrophotometer (Hitachi Co., Japan). The concentration of the dye was determined by measuring the absorbance at a fixed wavelength (540 nm) according to the calibration curve established. Total organic carbon (TOC) in water was measured by a Phoenix 8000 TOC analyzer (Tekmar–Dohrmann Co., USA). Biochemical oxygen demand for 5 days (BOD_5) of samples was measured by a BOD measuring device (OITOP IS 12, WTW Co., Germany). Chemical oxygen demand (COD) was measured by a CTL-12 COD analyzer (Chende Huatong Co., China).

3. Results and discussion

3.1. Influence of initial concentration of X-3B

For conventional photocatalysis without microwave irradiation, the initial concentrations of dyes subjected to degradation usually were not higher than 100 mg/L. At higher dye concentrations, larger amounts of the dye absorbed onto catalyst are thought to inhibit the reaction between dye molecules and oxidative species to some extent because less oxidative species are produced [15]. The other possible reason is that a large amount of UV may be absorbed by the dye molecules rather than TiO_2 particles, which reduce the photocatalytic efficiency [16]. This is the so-called UV-screening effect of dye itself [17]. However, it was found that higher concentration dye could be degraded effectively in TiO_2/MWL than in photocatalysis without microwave irradiation. Fig. 3 illustrates the removal of X-3B ($C_0 - C$) with time in TiO_2/MWL at different initial concentrations 100, 200, 300, 400, 600, 1000 and 1500 mg/L. It was found that the removal of X-3B increased

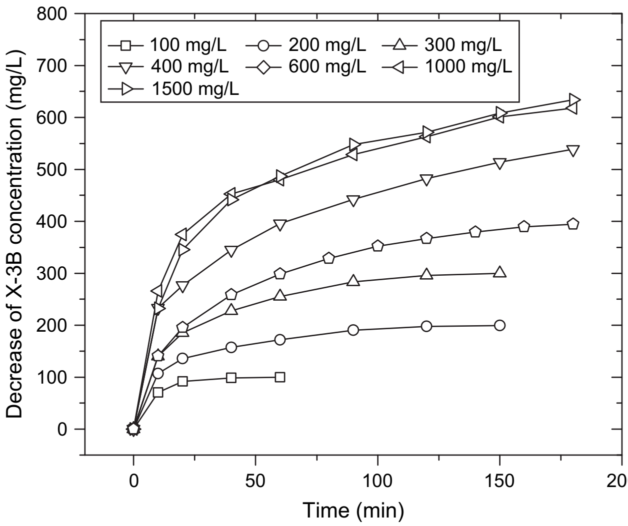


Fig. 3. The removal of X-3B in TiO_2/MWL with time at different initial concentrations.

with the increasing of initial concentration from 100 mg/L to 1000 mg/L. When the initial concentration was beyond 1000 mg/L, the removal did not increase further as shown in Fig. 3. This indicates that 1000 mg/L was the maximal concentration that could be degraded effectively, which is at least 10 times than that involved in photocatalysis without microwave irradiation.

It was found that the degradation of X-3B at different concentrations was approximated as pseudo-first-order kinetics with respect to the concentration of X-3B.

$$r = -\frac{\mathrm{d}C}{\mathrm{d}t} = k_{\mathrm{app}}C \tag{2}$$

where r (mg/L/min) is the rate of disappearance of X-3B and C (mg/L) is the concentration of X-3B in solution. K_{app} is the apparent rate constant (min^{-1}) of pseudo-first-order reaction. Whose integration gives, for $C = C_0$ at $t = 0$:

$$-\ln\left(\frac{C}{C_0}\right) = k_{\mathrm{app}}t \tag{3}$$

k_{app} values for each initial concentrations were found from the slopes of the straight line obtained by plotting $-\ln([C]/[C]_0)$ versus reaction time. The k_{app} values for different initial concentrations are listed in Table 1. When the initial concentration of X-3B was 100 mg/L, k_{app} was 0.145 min^{-1}. Some k_{app} values of photodegradation of dyes in photocatalysis without microwave irradiation are listed in Table 2. Compared with reported k_{app} values ranging from 0.01 to 0.057 min^{-1} in the literatures [18–23] for dye concentrations less than 100 mg/L with comparable or high wattage conventional electrode lamps as light sources, the k_{app} appears more than 2.5 times higher. This indicates that photodegradation efficiency of TiO_2/MWL was enhanced by the coupled UV–vis/microwave irradiation.

Langmuir–Hinshelwood rate expression has been successfully used for heterogenous photocatalytic degradation to determine the relationship between the degradation rate and the concentration of the organic substrate [24–27].

$$r = -\frac{\mathrm{d}C}{\mathrm{d}t} = \frac{kK_{\mathrm{S}}C}{1 + K_{\mathrm{S}}C_0} \tag{4}$$

Table 1

Apparent reaction constants (k_{app}) of photodegradation of X-3B in TiO_2/MWL at different initial dye concentrations

Initial concentrations of X-3B (mg/L)	k_{app}(min^{-1})	R^2
100	0.1445	0.9904
200	0.0538	0.9859
300	0.0332	0.9838
400	0.0199	0.9892
600	0.0112	0.9692
1000	0.0083	0.9374
1500	0.0062	0.9215

k reflects the surface reaction rate constant between the dyes and hydroxyl radicals (mg/L/min), K_{S} represents the equilibrium constant (L/mg) for the adsorption of the organic substrate onto the catalyst. The relationship between k_{app} and C_0 can be expressed as a linear Eq. (5), from Eqs. (2) and (4):

$$\frac{1}{k_{\mathrm{app}}} = \frac{1}{kK_{\mathrm{S}}} + \frac{C_0}{k} \tag{5}$$

when initial concentrations are plotted versus $1/k_{\mathrm{app}}$, k and K_{S} can be calculated according to Eq. (5). k and K_{S} are 8.9 mg/L/min and 0.49 L/mg, respectively. Some k values of photodegradation of dyes in photocatalysis without microwave irradiation are listed in Table 3. Compared to reported k values in the literature ranging from 0.39 to 5.085 mg/L/min for dye pollutants [19,21,22,28–30], the value 8.9 mg/L/min in TiO_2/MWL appears higher. This indicates that microwave irradiation accelerates the reaction between X-3B and hydroxyl radicals.

For different C_0 the k_{app} values are different, which decrease with increasing C_0. Influence of C_0 on photodegradation could be expressed by variation of k_{app} with the change in C_0. From Eq. (5), it can be found that higher k indicates slighter influence of C_0 on photodegradation. Because k in TiO_2/MWL is higher than that in photocatalysis without microwave irradiation, it can be concluded that influence of C_0 on photodegradation in TiO_2/MWL is slighter than in the latter.

Above results clearly show that TiO_2/MWL not only could degrade higher concentration dyes but also have higher photodegradation efficiency and slighter influence of C_0 on photodegradation than photocatalysis without microwave irradiation. The reason can be explained in terms of the following two

Table 2

Summary of apparent rate constants (k_{app}) of photodegradation of dyes without microwave irradiation

Dye	Light resource	Catalyst	k_{app}(min^{-1})	References
Reactive Black 5 (90 mg/L)	75 W low-pressure UV lamp	P25	0.055	[18]
X-3B (59 mg/L)	125 W high pressure Hg lamp	TiO_2	0.0106	[19]
Procion Yellow HE4R (100 mg/L)	Eight 15 W UV lamps	P25	0.0351	[20]
Direct 80, 3BL (40 mg/L)	400 W high pressure Hg lamp	TiO_2 (from Aldrich)	0.0261	[21]
Reactive Yellow 2, X-6G (20 mg/L)	400 W high pressure Hg lamp	TiO_2 (from Aldrich)	0.0305	[21]
Reactive Black 5 (100 mg/L)	Hg UV lamp (0.50 μ photons/min)	TiO_2	0.057	[22]
Solophenyl Green, BLE (50 mg/L)	Low-pressure Hg lamp (3 W of radiant flux)	P25	0.029	[23]

Table 3
Summary of rate constants (*k*) of reaction between dyes and hydroxyl radicals in photocatalysis without microwave irradiation

Dye	Light resource	Catalyst	*k* (mg/L/min)	References
Reactive Black 5	25 W low-pressure Hg fluorescent lamp	PC500	0.757	[30]
Reactive Yellow 145	25 W low-pressure Hg fluorescent lamp	PC500	0.39	[30]
Reactive Black 5	75 W low-pressure UV lamp	P25	2.45	[21]
X-3B	125 W high pressure Hg lamp	TiO_2	1.5961	[19]
Acid Red 27	Hg UV lamp (30 W)	P25	1.39	[28]
Reactive Black 5	Hg UV lamp (0.50 μ photons/min)	TiO_2	5.085	[22]
Reactive Black 5	20 W black light fluorescent lamp	P25	4.47	[29]

aspects. Firstly, microwave irradiation accelerates the photocatalytic degradation. In this experiment, the temperature of solution was suppressed by cooling. Evidently, assistance of microwave in TiO_2/MWL is due to non-thermal effects of microwave such as polarization, dielectric properties, hot spots formation, nuclear spin rotation, and spin alignment [12]. On the one hand, reaction rate between X-3B and hydroxyl radicals is enhanced by microwave irradiation as discussed above. On the other hand, more •OH radicals are generated by photocatalysis with microwave irradiation than photocatalysis alone [4]. One of the important factors for the efficient photodegradation of organic pollutants using TiO_2 photocatalysis is dependent on the concentration of hydroxyl radicals. Specific interactions of the microwave radiation with the UV–vis-illuminated TiO_2 particle's surface might give rise to the generation of additional surface defects that can directly increase the concentration of hydroxyl radicals or some other equivalent reactive oxygen species in the aqueous dispersion [7]. Moreover, microwave enhances the reactants' mobility and diffusion leading to increased exchange of reactants between catalyst surface and solution. One of the reasons why high concentration reactants inhibit the photodegradation is attributed to too much reactants or intermediates absorbed onto TiO_2 surface, thereby screening light to irradiate on catalyst surface. The diffusion of microwave also avoids the screen and ensures enough light irradiating on TiO_2. Secondly, the MWL is more efficient to utilize the simultaneous effect of both UV–vis light and microwave irradiations. MWL was directly immerged in solution, which shortened the optical path and utilized more light energy. In this experiment, the light emission of MWL is mainly in the range of visible region and weak in UV region as illustrated in Fig. 2. Accordingly, both UV radiation to activate the TiO_2 particles and visible radiation to excite the X-3B are present. That is, X-3B can be photodegraded concurrently by both UV photocatalytic process and visible light photosensitization.

3.2. Color removal

In order to distinguish the contribution of microwave, MWL and photocatalysis, X-3B was degraded by employing the following three processes: (1) microwave irradiation alone; (2) photolysis of MWL without TiO_2; (3) photocatalytic degradation by TiO_2/MWL. In all three processes, temperature and airflow were adjusted at the same values.

Fig. 4 shows the evolution of the UV–vis absorption spectrum of X-3B when the dye was degraded by the three treatment processes. No degradation occurred under microwave irradiation alone as shown in Fig. 4a. This was consistent with other results [4]. Microwave energy is substantially lower than that of UV irradiation ($E_{MW} = 1.6 \times 10^{-3}$ eV, $E_{UV} = 4.1$ eV) and, is not sufficient to cleave chemical bonds [2]. Microwave energy only results in the transition of molecular rotational energy [31]. Wondrously, about 58% of the X-3B was effectively degraded in MWL after 180 min, as displayed in Fig. 4b. The light of MWL is mainly in the range of visible region and decolorization of X-3B under visible light is very slow. Clearly, microwave irradiation accelerated the MWL photolysis of X-3B. The results shown in Fig. 4c illustrate that the decolorization efficiency of TiO_2/MWL was better than that of MWL and the color removal nearly reached 100% at 180 min.

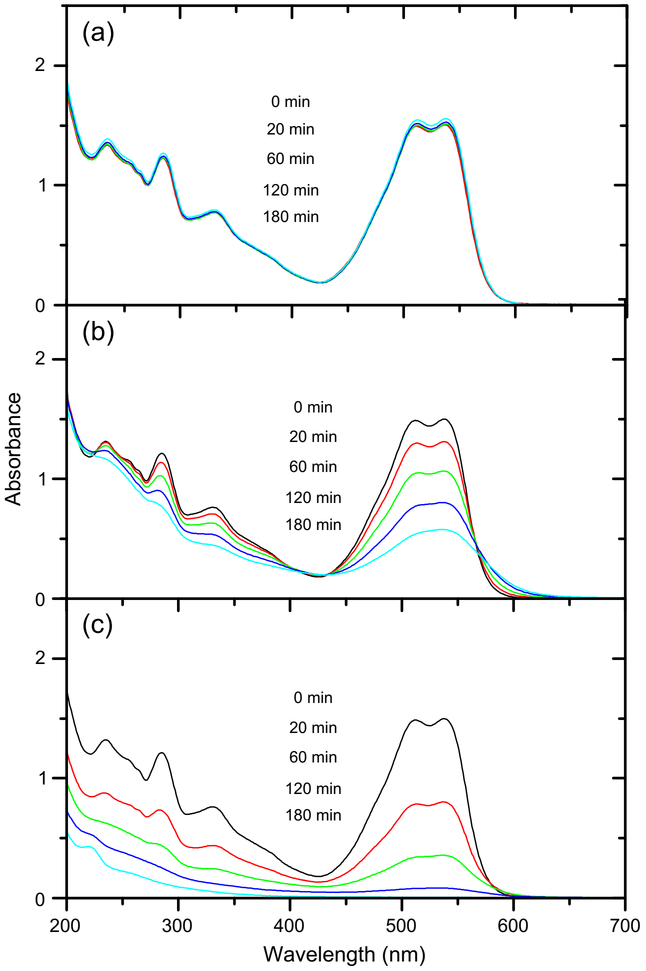


Fig. 4. Temporal changes in the absorption spectral patterns in the degradation of X-3B of (a) microwave irradiation, (b) MWL, (c) TiO_2/MWL. X-3B: 400 mg/L; sample dilution ratio: 1:5.

Different structural units and groups in the dye molecules correlate with different absorption features. The absorbance features of X-3B at 235, 330 and 540 nm are, respectively, mainly attributed to benzene ring, naphthalene ring and azo linkage. The absorbance feature at 285 nm may be the fine multi-peaks of benzene ring and naphthalene ring [32]. The temporal changes in the spectral features of X-3B solutions were monitored at 235, 285, 330 and 540 nm. Relevant first-order kinetics of the transformation of X-3B at the four monitored wavelengths during three experimental processes are listed in Table 4. These data show that decolorization by the TiO_2/MWL photocatalysis is about 5.1 times faster than that of MWL photolysis. The ratios of the disappearance kinetics at the four spectral wavelengths in MWL photolysis are $k_{235\ nm}/k_{285\ nm}/k_{330\ nm}/k_{540\ nm} = 1/4.2/4.6/8.7$. Clearly, the disappearance of the spectral feature at 540 nm is relatively faster than for the other three spectral features. The ratios in TiO_2/MWL are $k_{235\ nm}/k_{285\ nm}/k_{330\ nm}/k_{540\ nm} = 1/1.4/1.7/1.9$. These ratios also infer that the events in TiO_2/MWL process are different from those in the MWL photolysis and TiO_2/MWL has the excellent ability not only to destroy azo linkage but also to destroy benzene ring and naphthalene ring.

3.3. TOC mineralization

Fig. 5 illustrates the extent of X-3B mineralization during the three processes, as witnessed by the temporal decay of TOC. Microwave irradiation did not eliminate TOC, even after 180 min of irradiation, which further testified that microwave irradiation alone was not able to degrade the dye. MWL photolysis reduced TOC of X-3B by about 12% after 180 min of irradiation and the removal of TOC is lower than that of color, which indicated that most X-3B molecules were transformed to other organic substances rather than being mineralized to CO_2 and water. Compared to microwave irradiation and MWL photolysis, TiO_2/MWL performed well in TOC elimination and about 65% TOC removal was achieved at 180 min.

3.4. Biodegradability

The ratio of BOD_5/COD is normally used to express the biodegradability of the wastewater. When the ratio is more than 0.3, it was thought that the wastewater could be effectively degraded by biological treatment. Our early research proved that photocatalysis could enhance biodegradability of dyes [33]. It is reasonable that TiO_2/MWL may be adopted as a pre-treatment process of biological treatment if it effectively enhances the biodegradability of dyes. Fig. 6a shows the changes in COD and BOD_5 of X-3B solution as a function of time.

The initial BOD_5/COD ratio of X-3B is very low (only 0.03), indicating that X-3B cannot be degraded by biological treatment. Fig. 6a shows that BOD_5 improved significantly with the decrease in COD. The contrary effect results in a strong increase in BOD_5/COD ratio as Fig. 6b illustrates, which implies that biodegradability of X-3B can be effectively enhanced by the treatment of TiO_2/MWL photocatalytic oxidation by converting nonbiodegradable organics to biodegradable forms. Due to the production of organic and inorganic acid anions, the solution's pH decreased for the duration of photocatalysis from 6.7 to 3.39. After 180 min of treatment the ratio of BOD_5/COD increased to 0.35, implying that the X-3B solution after TiO_2/MWL photocatalytic oxidation could be degraded effectively by biological treatment processes. However, the biodegradability did not increase linearly. At the beginning, the biodegradability increased slowly. However, it significantly improved after 90 min and the ratio of BOD_5/COD already increased to 0.3 at 120 min. Subsequently the increasing of the ratio becomes slow again. More than 95% colors were removed at 120 min, which indicates that decolorization led to the increase in biodegradability of the solution. The color of azo dyes results from the chromophore group (azo linkage). This indicates that low biodegradability of dye is contributed to azo linkage.

3.5. The effect of inorganic oxidizing species

One effective strategy for inhibiting e^-/h^+ recombination is to add other electron acceptors to the reaction system. The use of inorganic oxidizing species has been demonstrated to enhance the rates of degradation of different organic contaminants remarkably because they trap the photogenerated electrons more efficiently than O_2 [34]. For better results, these additives should fulfill the following criteria: dissociate into harmless by-products and lead to the formation of •OH or other oxidizing agents [35]. Herein, in order to further enhance TiO_2/MWL photodegradation efficiency, the effects of three inorganic oxidizing species (H_2O_2, $Na_2S_2O_8$ and $Fe(NO_3)_3$) on the degradation rate of X-3B were investigated.

H_2O_2 had an optimal dosage at 5 mmol/L under our experimental condition. The effects of $Na_2S_2O_8$ and $Fe(NO_3)_3$ improved with the increasing of their dosage from 0 to 10 mmol/L. So all the dosages of the three species were 5 mmol/L in order to compare their effects. Fig. 7 shows decolorization and mineralization of X-3B in TiO_2/MWL with the three inorganic oxidizing species. It was observed that

Table 4
Summary of kinetics of decolorization of X-3B during 180 min by microwave irradiation alone, MWL photolysis and TiO_2/MWL photocatalysis

Degradation method	$k_{235\ nm}$ (10^{-3} min^{-1})	$k_{285\ nm}$ (10^{-3} min^{-1})	$k_{330\ nm}$ (10^{-3} min^{-1})	$k_{540\ nm}$ (10^{-3} min^{-1})	$k_{average}$ (10^{-3} min^{-1})
Microwave irradiation	–	–	–	–	–
MWL	0.6	2.5	2.9	5.2	2.8
TiO_2/MWL	9.1	13.1	15.1	19.9	14.3
Ratio ($k_{TiO_2/MWL}/k_{MWL}$)	15.2	5.2	5.2	3.8	5.1

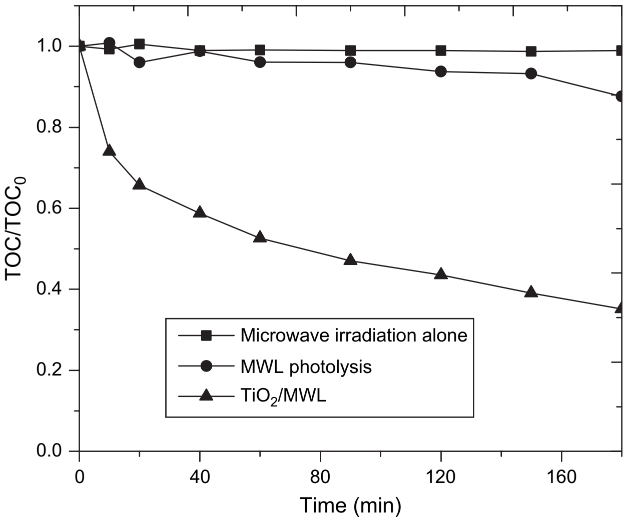


Fig. 5. Decrease of total organic carbon (TOC) in the decomposition of X-3B during three methods. X-3B: 400 mg/L.

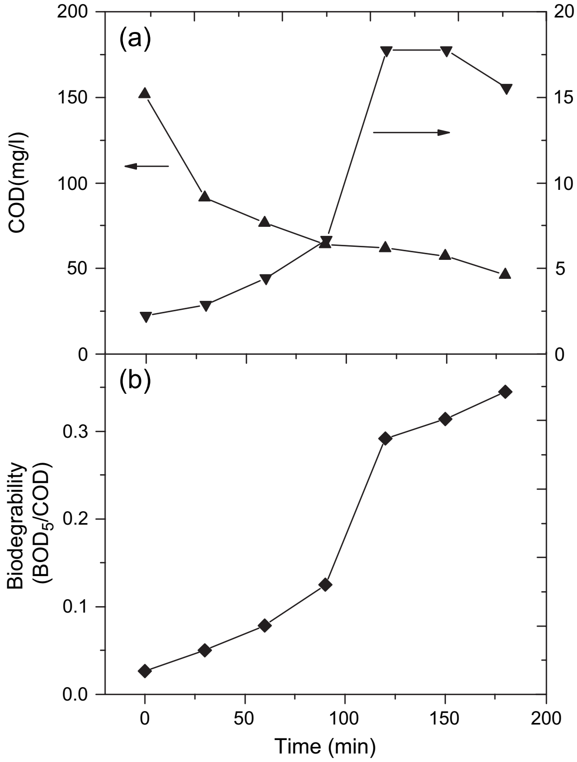


Fig. 6. Temporal changes of COD, BOD_5 (a) and biodegradability (b) of X-3B solution in TiO_2/MWL. X-3B: 400 mg/L.

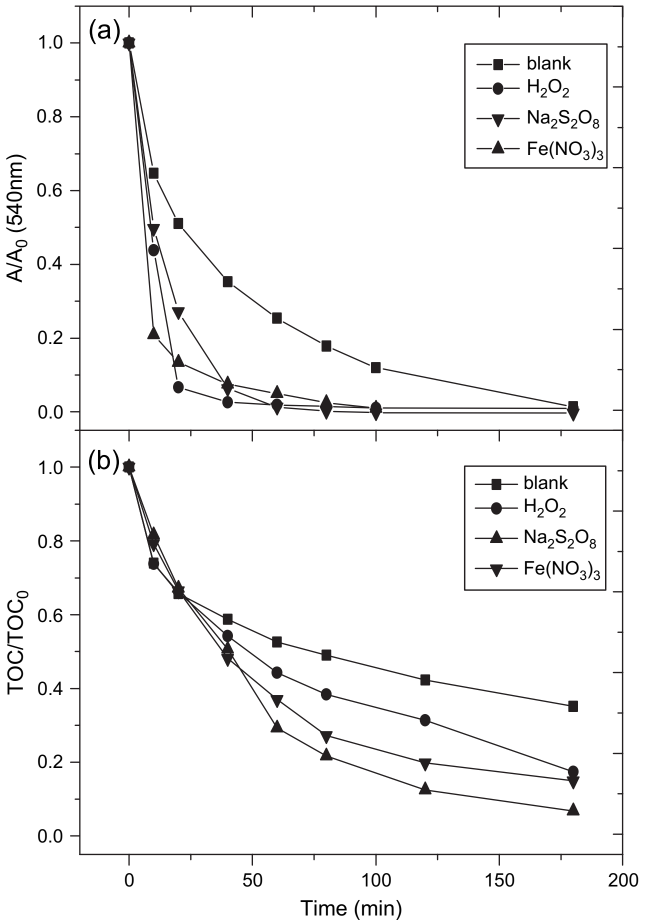


Fig. 7. Effects of adding inorganic oxidizing species on photodegradation. (a) Color removal, (b) TOC removal. X-3B: 400 mg/L; initial concentrations of H_2O_2, $Na_2S_2O_8$ and $Fe(NO_3)_3$: 5 mmol/L.

not only decolorization, but also mineralization was accelerated by adding the three inorganic oxidizing species. The effect order was $H_2O_2 > Na_2S_2O_8 > Fe(NO_3)_3$ in terms of color removal. The required reaction times for 90% color removal with H_2O_2, $Na_2S_2O_8$ and $Fe(NO_3)_3$ reduced 100, 80, and 70 min after adding oxidizing species, respectively. However, effect order of three inorganic oxidizing species on TOC removal was different from that on color removal and the order was $Na_2S_2O_8 > Fe(NO_3)_3 > H_2O_2$. The removals of TOC were enhanced 44.0%, 31.3% and 27.5% by $Na_2S_2O_8$, $Fe(NO_3)_3$, H_2O_2, respectively. TOC (93.3%) was removed at 180 min with 5 mmol/L $Na_2S_2O_8$.

The degradation rate improvement by adding inorganic oxidizing species is probably due to the following reasons. Firstly, the recombination of h^+ and e^- was inhibited by these oxidizing species because they could trap photoproduced e^- more effectively than molecular oxygen. For example, the minimum energy requirement of oxygen reduction to produce hydroxyl radical is 3.0 eV while that of hydrogen peroxide is 2.2 eV [36]. The reactions of inorganic oxidizing species with e^- are listed.

$$H_2O_2 + e^- \rightarrow \bullet OH + OH^- \tag{6}$$

$$S_2O_8^{2-} + e^- \rightarrow SO_4^{-\bullet} + SO_4^{2-} \tag{7}$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \tag{8}$$

Secondly, these oxidizing species produce •OH or other oxidizing agents which can degrade pollutants. For example, the direct photolysis of H_2O_2 by UV light can generate free radicals.

$$H_2O_2 + h\nu \rightarrow 2{\bullet}OH \tag{9}$$

For sodium persulfate, the product $SO_4^{-\bullet}$ is a very strong oxidant ($E^0 = 2.6$ eV) and engages in at least three reaction modes with organic compounds: by abstracting a hydrogen atom from saturated carbon, by adding to unsaturated or aromatic carbon, and by removing one electron from carboxylate anions and from certain neutral molecules [34]. For $Fe(NO_3)_3$, $Fe(OH)^{2+}$, the Fe^{3+}-hydroxyl species predominant in aqueous solutions in the pH range 2.5–5.5, is the most photoactive Fe^{3+} species in the 300–400 nm range. It can lead to the formation of •OH radicals in aqueous systems as follows [37]:

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + {\bullet}OH \tag{10}$$

The product Fe^{2+} may also combine with H_2O_2 generated by photocatalysis to enhance the oxidation of organics by Fenton reaction.

4. Conclusions

Although MWL performed well in decolorization, but badly in mineralization, it was convenient for microwave assisted photocatalysis due to its simultaneous irradiation of microwave and UV–vis light. The coupled UV–vis/microwave irradiation led higher concentration dyes to be effectively degraded in TiO_2/MWL than in conventional photocatalysis. Higher photodegradation efficiency and slighter influence of initial dye concentration on photodegradation were found in TiO_2/MWL. The assistance of microwave was due to producing more hydroxyl radicals, accelerating surface reaction between dyes and hydroxyl radicals, avoiding catalyst absorbing excessive dye on surface, etc. Not only excellent decolorization and mineralization were carried out in TiO_2/MWL, but also the biodegradability of X-3B solution was increased indicating that it could be used as a pre-treatment process of biotreatment. Moreover, X-3B degradation in TiO_2/MWL could be accelerated further by adding inorganic oxidizing species (H_2O_2, $Na_2S_2O_8$ and $Fe(NO_3)_3$).

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