

# Effect of operating parameters on microwave assisted photocatalytic degradation of azo dye X-3B with grain TiO<sub>2</sub> catalyst

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## Abstract

In this paper, the photocatalytic decomposition of azo dye reactive brilliant red X-3B was investigated in microwave assisted photocatalysis with microwave electrodeless lamp as light source (MWL/TiO<sub>2</sub>). A novel grain TiO<sub>2</sub> (GT01) rather than the well-known P25 TiO<sub>2</sub> had been tested to determine whether its photocatalytic efficiency was good enough for use in water purification. The results showed that although GT01 was not so good as P25, it was easier separated from water and was more applicable. The effect of different operating parameters in MWL/TiO<sub>2</sub> with GT01 as catalyst on photocatalytic oxidation was discussed. The photodegradation was favored with low initial pH, high temperature and high light intensity. The optimal amount of GT01 under our experimental condition was 4 g/l. Some inorganic ions like CO<sub>3</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> also affected the photocatalytic efficiency. The order was CO<sub>3</sub><sup>2-</sup> > SO<sub>4</sub><sup>2-</sup> > NO<sub>3</sub><sup>-</sup>. Moreover, microwave irradiation changed the effect of operating parameters. The effect of initial pH, reactant concentration, and dissolved oxygen was weakened, whereas the effect of temperature and light intensity was magnified.

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**Keywords:** Microwave assisted photocatalysis; Microwave electrodeless lamp; Grain TiO<sub>2</sub>; Reactive brilliant red X-3B; Operating parameters

## 1. Introduction

In the past two decades, considerable attention has been focused on Heterogeneous photocatalytic oxidation for the degradation of organic pollutants, since the process results in complete mineralization with operation at mild conditions of temperature and pressure [1–3]. However, very few commercial applications of this technology are available at present due to low quantum efficiency and difficult separation and reuse of catalyst. Most of the photoinduced positive holes (h<sup>+</sup>) and electrons (e<sup>-</sup>) had recombined before they were trapped by hydroxyl or oxygen and quantum efficiency was usually less than 5%. Titanium dioxide (TiO<sub>2</sub>) powder is generally used as one of the most popular photocatalysts in photocatalytic oxidation for water and wastewater treatment because of its nontoxicity, chemical inertness, and low costs.

Although it has been proven that a great number of organic compounds can be effectively mineralized under near-UV irradiation, the recovery of TiO<sub>2</sub> powder from treated water is still a difficulty in widely extending its application in practice [4].

In order to enhance the quantum efficiency, many measures were taken. 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 [5]. Recently, some researchers have started to investigate photocatalytic reactions assisted with microwave irradiation [6–13]. Kataoka and co-workers found that the photocatalytic oxidation of ethylene proceeded faster (83.9%) in the presence of the microwave irradiation than in the absence [6]. Hori-hoshi et al. proved by electron spin resonance (ESR) that about 20% more •OH radicals were generated by photocatalysis with microwave irradiation than photocatalysis alone [7]. Although microwave effectively accelerates photocatalytic degradation, traditional Hg lamp was not laid in microwave

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field because the metal electrodes of the lamp were spoiled under microwave irradiation. The measures to avoid electrode spoilage would complicate equipment. The problem will be solved if microwave electrodeless lamp (MWL) substitutes traditional lamp as light source. Moreover, MWL has some unique advantages, such as, good photochemical efficiency, long life, low cost, and simple photocatalytic equipment [14,15]. The light intensity can be adjusted by variations of MW power level and irradiation wavelengths can be adjusted by the ratio and nature of the gases in electrodeless lamp [8]. Hori-hoshi et al. proved that photocatalysis with electrodeless lamp (a double quartz cylindrical plasma photoreactor) was about 10 times more efficient than the photocatalysis using traditional lamp [12].

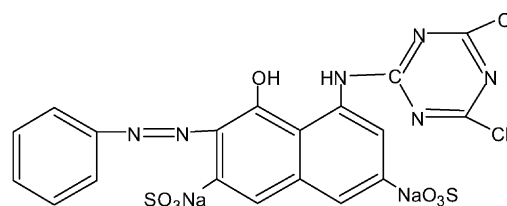
To preclude the separation procedure, the immobilization of the TiO<sub>2</sub> catalysts on certain supporting materials such as glass, fiber, or stainless steel has been frequently adopted. Unfortunately, a significant loss in the contact area between the immobilized photocatalyst and a light source limits its efficiency in the photocatalytic degradation of the organic substrates [16–18]. Moreover, the life of immobilized TiO<sub>2</sub> catalysts is short because TiO<sub>2</sub> easily fall off from supporting materials. Zhang [19] and Li [4] prepared TiO<sub>2</sub> microsphere by sol-gel and by sol-spraying-calcination, respectively. These grain TiO<sub>2</sub> had high efficiency and their separations from water were easy. Moreover, grain TiO<sub>2</sub> has a longer life than immobilized TiO<sub>2</sub>.

In this paper, a novel grain TiO<sub>2</sub> was used as the catalyst in microwave assisted photocatalysis with microwave electrodeless lamp as light source (MWL/TiO<sub>2</sub>). An azo dye reactive brilliant red X-3B was chosen as a model compound to obtain detailed information of the innovative photocatalysis. Many factors are involved during the degradation of X-3B in MWL/TiO<sub>2</sub>. The important operating parameters that affect the overall photocatalytic oxidation efficiency were investigated in detail, including amount of catalyst, initial concentration of reactant, initial pH, oxygen, temperature, light intensity and anions. Moreover, the influence of microwave irradiation is also investigated.

## 2. Experimental

### 2.1. Chemical

The azo dye reactive brilliant red X-3B was commercialized and was used without further purification. The Grain TiO<sub>2</sub> used in this experiment is GT01 (HSD Co., China). The particle diameter of GT01 is 180–250 μm, which is small enough for suspension by bubbling air through but large enough for settlement by gravity. The BET surface area of GT01 is 194.4 m<sup>2</sup>/g and density is 900 kg/m<sup>3</sup>. The X-ray diffraction analysis shows that GT01 is mainly anatase. P25 (BET area, ca. 50 m<sup>2</sup>/g, average diameter, 30 nm) was obtained from Germany Degussa Corporation. Other chemicals used were analytical grade.



Reactive brilliant red X-3B (chemical formula = C<sub>19</sub>H<sub>10</sub>O<sub>7</sub>N<sub>6</sub>Cl<sub>2</sub>S<sub>2</sub>Na<sub>2</sub>)

### 2.2. Photocatalytic experiments

The microwave source was a domestic microwave oven (Haier. Co. Ltd.; power, 700 W; frequency, 2.45 GHz), and the microwave was continuous during reaction. The photocatalytic reactor was a cylindrical glass reactor (capacity, 1000 ml). Air (0.25 m<sup>3</sup>/h) was bubbled through a sintered glass filter (pore size, 50–70 μm) fixed at the bottom of the reactor and into the solution not only for offering oxygen but also for mixing the catalyst and the solution. The photocatalytic reactor was laid 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 by a peristaltic pump. 750 ml X-3B solution was added in the

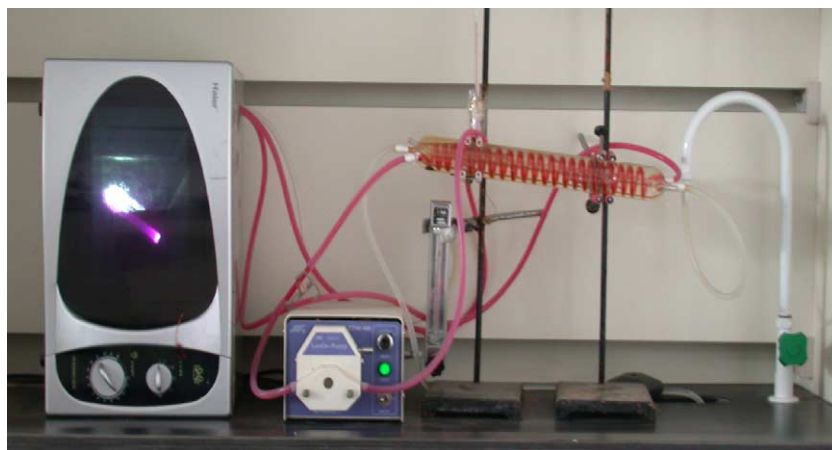


Fig. 1. Experimental setup of microwave assisted photocatalysis with electrodeless lamp as light source.

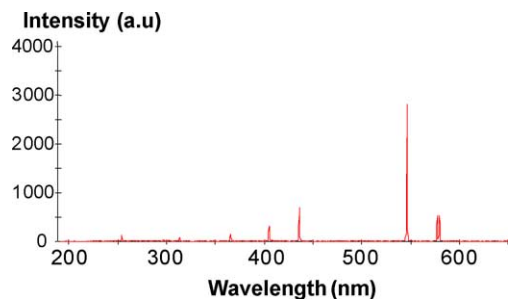


Fig. 2. Ultraviolet and visible wavelengths produced by the microwave electrodeless lamp.

whole system, among which 125 ml was in the cooling circulation pipe and 625 ml was in the photocatalytic reactor. Microwave electrodeless lamp (MWL), which was made of quartz and filled with mercury and argon, was designed as U-shaped. The UV–vis radiation emitted by the light source of MWL is depicted in Fig. 2. The MWL floated on the solution and about 60% was immersed in solution.

### 2.3. Analysis

The samples were filtered by 0.45- $\mu\text{m}$  membranes before analyzed. The temporal concentration changes of X-3B during experimental processes were determined by a UV-3010 spectrometer (Hitachi Co., Japan) at 540 nm. The quantity of dissolved oxygen in the X-3B solutions during reaction was measured with an ORION 826 detector.

## 3. Results and discussion

### 3.1. The comparison of GT01 with P25

The photocatalytic efficiency of GT01 was investigated by comparing with P25. Both GT01 and P25 were 4 g/l and other experimental conditions were same. The disappearance rates of concentration of X-3B in initial 40 min followed the order GT01 > P25 as Fig. 3 illustrated. However, after 40 min the order changed to P25 > GT01. The disappearances of X-3B in MWL/TiO<sub>2</sub> with GT01 and P25 can be approximated as pseudo-first-order kinetics and the kinetics were 0.0203

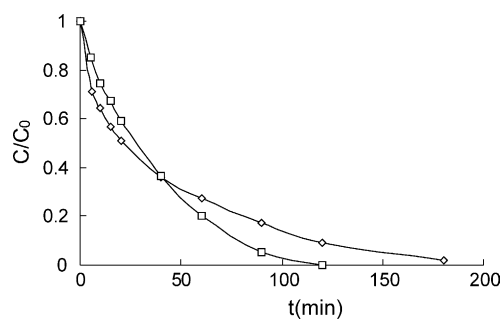


Fig. 3. The time change of X-3B in the solution at different catalyst: ( $\diamond$ ) GT01; ( $\square$ ) P25. GT01: 4 g/l; P25: 4 g/l; X-3B: 400 mg/l.

and 0.0253  $\text{min}^{-1}$ , respectively. At same dosage, the external surface area of GT01 irradiated by light is less than that of P25 due to the diameter of GT01 is larger than that of P25. This indicated that, though photocatalytic efficiency of GT01 was not as good as that of P25 in terms of per gram, photocatalytic efficiency of GT01 per external surface area irradiated by light was higher than that of P25.

The experiment demonstrated a quick settling time of the GT01 before and after the photoreaction. Before the photoreaction minimum-settling velocity was 67  $\text{mm min}^{-1}$  and it slightly decreased to 62  $\text{mm min}^{-1}$  after 180 min photoreaction. Compared with P25 (minimum settling velocity: 3.3–3.8  $\text{mm min}^{-1}$ ) [4], GT01 can be easily separated from the solution only by gravity and no other measures were needed. Wearing and tearing was unavoidable due to wash of air and water, but the loss of GT01 during reaction no more than 5%. Moreover, wearing and tearing did not result in a decreasing in photocatalytic efficiency of GT01 because interior of GT01 also was TiO<sub>2</sub>, which resolved the problem of inactivation of immobilized catalyst resulted from TiO<sub>2</sub> falling off from the supporting materials. Since GT01 can be easily suspended by air bubbling during the photoreaction and quickly settle down under gravity after the reaction, the operation in the photoreactor becomes much easier from an engineering point of view.

### 3.2. Effect of catalyst dosage

The effect of TiO<sub>2</sub> powder concentration on the photocatalytic degradation of organics in the absence of microwave irradiation in aqueous solution has already been studied in the literatures [20,21]. The necessity to optimize this factor was pointed out. Catalyst concentration has an optimum value, as using excess catalyst reduces the amount of photo-energy being transferred in the medium due to opacity offered by the catalyst particles [3].

Fig. 4 shows the change of X-3B as a function of reaction time in MWL/TiO<sub>2</sub> detected at different catalyst dosages 0.5, 1, 2, 4 and 6 g/l. On the whole, it was observed that along with the increase of catalyst dosage from 0.5 to 4 g/l, the disappearance rate of X-3B in solution increased. However, the catalyst concentration amounting 6 g/l did not further enhance the

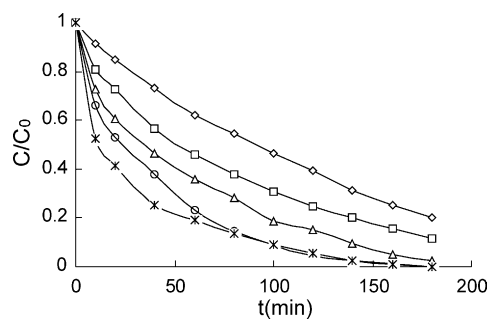


Fig. 4. The time change of X-3B in the solution at different catalyst dosage: ( $\diamond$ ) 0.5 g/l; ( $\square$ ) 1 g/l; ( $\Delta$ ) 2 g/l; ( $\circ$ ) 4 g/l; ( $\times$ ) 6 g/l. X-3B: 400 mg/l.

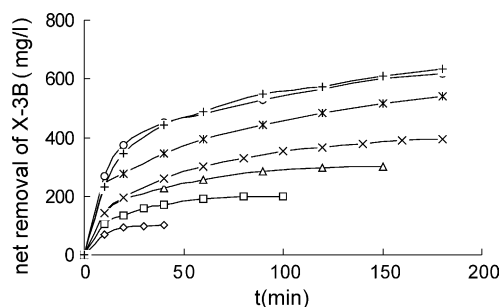


Fig. 5. The net degradation of X-3B at different initial concentration: ( $\diamond$ ) 100 mg/l; ( $\square$ ) 200 mg/l; ( $\triangle$ ): 300 mg/l; ( $\times$ ) 400 mg/l; ( $*$ ) 600 mg/l; ( $\circ$ ) 1000 mg/l; (+) 1500 mg/l. GT01: 4 g/l.

rate. In the initial 60 min a better X-3B removal at 6 g/l than at 4 g/l due to the adsorption on catalyst is more than the latter. The main goal of photocatalysis applied for treatment of wastewaters is to destroy contaminants rather than to separate it from the solution. So, 4 g/l was the optimum amount of GT01 in terms of photodegradation under our experimental condition.

### 3.3. Effect of initial concentration of X-3B

Fig. 5 illustrates the net degradation (initial concentration reduce temporal concentration) of X-3B in MWL/TiO<sub>2</sub> at different initial concentrations of X-3B 100, 200, 300, 400, 600, 1000 and 1500 mg/l. It was found that the net degradation significantly increased with the increase of the initial concentration of X-3B until 1000 mg/l. Beyond 1000 mg/l, increasing initial concentration did not further enhance the net degradation. For conventional photocatalysis, the initial concentrations of reactants usually were not higher than 100 mg/l. Beyond this value negative effect of high concentration would occur and the photocatalytic efficiency would decrease. The concentration of 1000 mg/l is a so high concentration for conventional photocatalysis that the solution needs diluting. However, in MWL/TiO<sub>2</sub> 1000 mg/l X-3B did not result in a decrease in photocatalytic efficiency. This denoted that MWL/TiO<sub>2</sub> effectively weakened the negative effect of high concentration.

The reasons why MWL/TiO<sub>2</sub> can overcome the negative effect of high concentration reactant happened in conventional photocatalysis can be explained in terms of the following two aspects. Firstly, microwave irradiation accelerated the photocatalytic degradation. One of the important factors for the efficient photodegradation of organic pollutants using TiO<sub>2</sub> photocatalysis is dependent on the concentration of hydroxyl radicals. Horihoshi et al. [10] considered that specific interactions of the microwave radiation with the UV-illuminated TiO<sub>2</sub> particle surface may give rise to the generation of additional surface defects that can directly increase the concentration of hydroxyl radicals or some other but equivalent reactive oxygen species in the aqueous dispersion. Moreover, chemical processes performed under microwave radiation are believed to be affected by superheat-

ing, polarization, dielectric properties, hot spots formation, nuclear spin rotation, and spin alignment [15]. On the other hand, microwave enhances the reactants mobility and diffusion leading to increased exchange of reactants between catalyst surface and solution. Too much reactant or intermediates adsorbing on TiO<sub>2</sub> surface are one of reasons that high concentration reactants inhibit the photodegradation due to screening light to irradiate on catalyst surface. The diffusion effect of microwave also destroys the screen effect and ensures enough light on TiO<sub>2</sub>. Secondly, the microwave electrodeless lamp was good photochemical efficiency. MWL was directly immersed in solution, which shortened the optical path and utilized more light energy. The light emission of MWL is mainly in the range of visible region and weak in UV region as Fig. 2 illustrated. Both UV radiation to activate the TiO<sub>2</sub> particles and visible radiation wavelengths to excite the X-3B are present. That is, the dye can be photodegraded concurrently by both a photocatalytic process and photosensitization. It has been approved by Horihoshi et al. [8,9]. Consequently, photodegradation of high concentration pollutant organic substances become more efficient in MWL/TiO<sub>2</sub>.

### 3.4. Effect of initial pH

Medium pH has a complex effect on the rates of photocatalytic oxidation and the observed effect is generally dependent on the type of the pollutant as well as the zero point charge (ZPC) of the semiconductor used in the oxidation process [3]. In this experiment, the pH was adjusted before reaction by addition of NaOH or HCl (0.1 mol/l) to solution. Fig. 6 shows temporal changes of X-3B in the solution at different initial pH values. The rate of photocatalytic oxidation slowly increases with the decrease of pH. It is also known that, in photocatalytic reactions pH has an effect on the electrostatic charge of TiO<sub>2</sub> surface, which determines the density of TiOH<sub>2</sub><sup>+</sup> groups. For pH values higher than the PZC of titania, the surface becomes negatively charged and it is the opposite for pH < PZC, according to the following equilibria [22]:

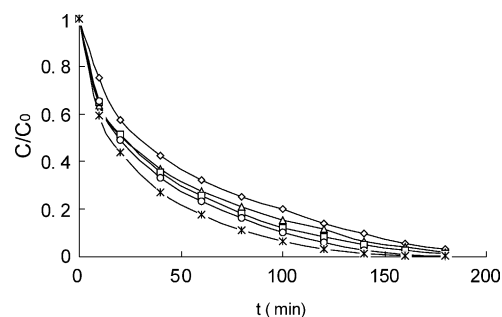


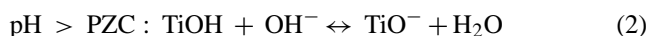
Fig. 6. The time change of X-3B in the solution at different initial pH: ( $\diamond$ ) pH 11; ( $\triangle$ ) pH 9; ( $\square$ ) pH 6.7; ( $\circ$ ) pH 5; ( $*$ ) pH 3. GT01: 4 g/l; X-3B: 400 mg/l.



Table 1

Summary rates of disappearance of X-3B at different initial pH by photocatalysis with and without microwave irradiation

Degradation method	$k_{\text{pH } 3}$ ( $\text{min}^{-1}$ )	$k_{\text{pH } 5}$ ( $\text{min}^{-1}$ )	$k_{\text{pH } 6.7}$ ( $\text{min}^{-1}$ )	$k_{\text{pH } 9}$ ( $\text{min}^{-1}$ )	$k_{\text{pH } 11}$ ( $\text{min}^{-1}$ )
MWL/TiO <sub>2</sub>	0.0261	0.0235	0.0203	0.0178	0.0167
Photocatalysis <sup>a</sup>	0.0146	0.0138	0.0115	0.0089	0.0059

<sup>a</sup> 30 W Hg lamp as light source.

The adsorption of X-3B is mainly through the sulfogroup, which is favored in positive charge surface [23]. Adsorption of X-3B on GT01 also slowly increases with pH decrease (the data were not showed). The increased adsorption results in the good photodegradation. Other research [24] indicated that pH had strong effect on degradation of X-3B in traditional photocatalysis. So, X-3B was photocatalytic degradation with 30 W Hg lamp as light source without microwave irradiation under same conditions. Relevant first-order kinetics of the disappearance of X-3B with and without microwave irradiation are listed in Table 1. The  $k$  decrease 41 and 65% with pH increase from 3 to 11, respectively. These data show microwave irradiation efficiently weakened the effect of initial pH.

### 3.5. Effect of dissolved oxygen

Presence of electron acceptors (oxygen) is recommended so as to prevent the recombination reaction between the generated positive holes and electrons. Generally, aeration is used for this purpose as it also provides uniform mixing suspension of the catalyst. In order to investigate the effect of dissolved oxygen on photodegradation in MWL/TiO<sub>2</sub>, air, highly pure nitrogen and industrial oxygen were bubbled into the solution during experiment, respectively. Fig. 7 compares the rates of photodegradation for air-, nitrogen- and oxygen-purged X-3B/GT01 dispersions with same gas flow (0.25 m<sup>3</sup>/h).

The photodegradation rates of X-3B in MWL/TiO<sub>2</sub> with three gas follow the order O<sub>2</sub> > air > N<sub>2</sub>. Curiously, although the photodegradation rate of X-3B with N<sub>2</sub> purging is lowest, the rate is much larger than expectation. After 180 min reaction, about 90% of X-3B in the solution are removed. The average amounts of dissolved oxygen air-, nitrogen- and

oxygen-purged solutions were 4.5, 1.2 and 18.4 mg/l, respectively. Recombination of photogenerated valence band holes with conduction band electrons after UV irradiation of TiO<sub>2</sub> particles is known to compete with the formation of reactive species ( $\bullet\text{OH}$  and  $\bullet\text{OOH}$  radicals). Molecular oxygen interaction with electrons not only decreases the recombination of holes with electrons but also yields to  $\bullet\text{OOH}$  radicals. Consequently, the photodegradation rate is governed by quantity of dissolved oxygen in solution. It was found in previous study [25] that without microwave irradiation the photocatalytic efficiency decrease remarkably in the absence of oxygen or low oxygen. Surprisingly, the low dissolved oxygen concentration in nitrogen-purged solution during reaction did not decrease remarkably oxidation rate in this experiment. Hori-hoshi et al. [7,10] also found that under low oxygen (nitrogen-purging) the photodegradation rate in the presence of microwave irradiation was higher than that of absence of microwave irradiation. It is clearly showed that the novel MWL/TiO<sub>2</sub> keeping a good photodegradation rate under low oxygen concentration was due to the microwave irradiation. As above mentioning, specific interactions of microwave radiation with the UV-illuminated TiO<sub>2</sub> particle surface give rise to the generation of additional surface defects [10] that can prohibit the recombination of holes with electrons. So, the concentration of  $\bullet\text{OH}$  radicals or some other but equivalent reactive oxygen species in the aqueous dispersion is high even under low oxygen concentration. Moreover, the microwave non-thermal distribution might enhance rate of oxygen transference. In conventional photocatalysis the rate of oxygen transference is so low that a high dissolved oxygen concentration in solution is necessary for sufficient oxygen absorbing on TiO<sub>2</sub>. In MWL/TiO<sub>2</sub> the high transference rate decreases the need of concentration of dissolved oxygen in solution.

### 3.6. Effect of ions

Effect of ions is a very important factor that needs to be considered because real industrial effluents will have different types of salts at different levels of concentration and generally these are in ionized forms. In order to simulate these conditions, some mine salt as Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub> and NaNO<sub>3</sub>, were added separately to solution. The concentrations of these anions were 5 mmol/l. Fig. 8 shows the time change of X-3B during reaction with different anions.

CO<sub>3</sub><sup>2-</sup> anions caused a significant inhibition effect on photocatalytic rate. The X-3B disappearance kinetic  $k$  drop to 0.0062 from 0.0203 min<sup>-1</sup>. The study on photodegradation of humic acids by Wiszniowski et al. [27] indicated that

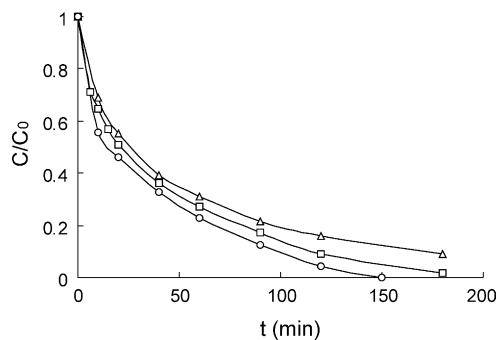


Fig. 7. The time change of X-3B in the solution at different purged gas: ( $\Delta$ ) nitrogen; ( $\square$ ) air; ( $\circ$ ) oxygen. GT01: 4 g/l; X-3B: 400 mg/l.

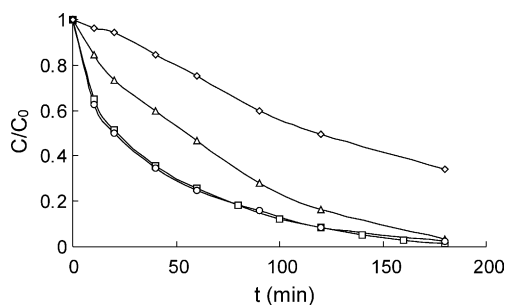
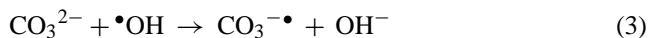
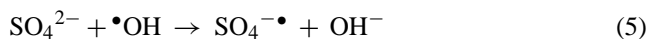


Fig. 8. The time change of X-3B in the solution at different inorganic ions: (□) blank; (△) Na<sub>2</sub>SO<sub>4</sub>; (○) NaNO<sub>3</sub>; (◇) Na<sub>2</sub>CO<sub>3</sub>. GT01: 4 g/l; X-3B: 400 mg/l.

CO<sub>3</sub><sup>2-</sup> or HCO<sub>3</sub><sup>2-</sup> ions addition brought about pH changes that weakened the adsorption of humic acids on TiO<sub>2</sub> and inhibited the photocatalytic oxidation. In this experiment, CO<sub>3</sub><sup>2-</sup> ions (5 mmol/l) brought about the pH of X-3B rise to 11.2 from 6.7. Increase of pH makes GT01 surface more negative and weakens adsorption of X-3B on GT01 surface (see the above). However, the kinetic *k* drops to 0.0163 from 0.0203 min<sup>-1</sup> with increase of pH from 6.7 to 11 by adding NaOH as Table 1. Clearly, The pH change was not the primary reason for inhibitory effect of CO<sub>3</sub><sup>2-</sup> anions. The inhibitory effect was mainly attributed to the scavenging character of this anion on the •OH photogenerated radicals during the photocatalysis according to literature [26].



The addition of SO<sub>4</sub><sup>2-</sup> (5 mmol/l) also led to inhibition of photocatalytic oxidation. The inhibitory effect of SO<sub>4</sub><sup>2-</sup> was lower than that of CO<sub>3</sub><sup>2-</sup> and the *k* merely dropped to 0.0147 min<sup>-1</sup>. We believed that SO<sub>4</sub><sup>2-</sup> was competed significantly with X-3B for adsorption site on catalyst surface because the similarity of SO<sub>4</sub><sup>2-</sup> with sulfogroup in X-3B structure. SO<sub>4</sub><sup>2-</sup> was adsorbed onto positively charged TiO<sub>2</sub> surface by electrostatic attraction. Meanwhile, the TiO<sub>2</sub> surface charge becomes more negative due to the adsorption of SO<sub>4</sub><sup>2-</sup>. (SO<sub>4</sub><sup>2-</sup> holds the positive site on the surface of TiO<sub>2</sub>), leading to the decreased adsorption of X-3B onto TiO<sub>2</sub>. The adsorbed SO<sub>4</sub><sup>2-</sup> reacted with the positive holes (h<sup>+</sup>) and hydroxyl radical (•OH) [28] as shown in Eqs. (4) and (5), which inhibited the photodegradation:



Although SO<sub>4</sub><sup>2-</sup> significantly decreased the adsorption of X-3B and SO<sub>4</sub><sup>2-</sup> scavenges h<sup>+</sup> and •OH, the rate of photocatalytic oxidation decreased slightly. This is due to the product SO<sub>4</sub><sup>•-</sup>. SO<sub>4</sub><sup>•-</sup> is less reactive than •OH and h<sup>+</sup>. However, it also is a very strong oxidant (*E*<sup>0</sup> = 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 neu-

tral molecules [29]. Therefore, as an oxidant agent SO<sub>4</sub><sup>•-</sup> compensated photodegradation in a way.

The photodegradation rate of X-3B after adding NO<sub>3</sub><sup>-</sup> is almost same as that of without inorganic salts. On the one hand, the effect of NO<sub>3</sub><sup>-</sup> on adsorption of X-3B is very lower than that of CO<sub>3</sub><sup>2-</sup> and SO<sub>4</sub><sup>2-</sup>. So, negative effect of NO<sub>3</sub><sup>-</sup> on photodegradation is not strong. On the other hand, the photolysis of NO<sub>3</sub><sup>-</sup> at wavelengths λ > 280 nm is also known to result in the formation of •OH hydroxyl radicals according to the follow equations. The formation of •OH has a positive effect on photodegradation.



The negative effect resulted from decrease adsorption counteracts the positive effect resulted from the formation of •OH. Consequently, the net effect of NO<sub>3</sub><sup>-</sup> on photodegradation is slight.

### 3.7. Effect of temperature and light intensity

In the range of 20–80 °C, usually weak dependence of the degradation rates on temperature has been observed [4,30]. However, strong effect of solution temperature on photodegradation is found in MWL/TiO<sub>2</sub> as Fig. 9 showed. The disappearance kinetic of X-3B increases from 0.0203 to 0.059 min<sup>-1</sup> with the temperature increase from 38 to 58 °C. It was clear that photocatalysis under microwave irradiation was sensitive to temperature. Müller et al. [31] found that the emission spectrum of electrodeless lamp was dependent on the temperature. Generally, the short wavelengths (less than and equal to 254 nm) are suppressed with increasing temperature, whereas the long wavelengths (>254 nm) are enhanced. However, the light irradiances of short wavelengths for MWL are very smaller than long wavelengths and they played only a minor role in the photochemical process [9]. Accordingly, the gross light intensity increases with increasing temperature. The increase light intensity certainly accelerates photodegradation.

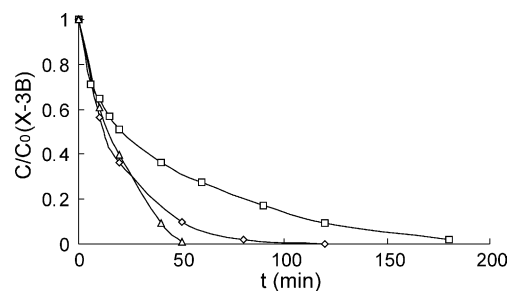


Fig. 9. The time change of X-3B in the solution at different temperature and number of lamp: (□) one lamp at 38 °C; (△) one lamp at 58 °C; (◇) two lamp at 38 °C. GT01: 4 g/l; X-3B: 400 mg/l.

Light intensity is critical parameter affecting photodegradation rate. For conventional photocatalysis usually linear variation is observed at low intensity and beyond a certain magnitude of intensity, the rate of the reaction shows a square root dependence on the intensity [3]. In this experiment, the light intensity is adjusted by changing the number of MWL. The disappearance kinetic of X-3B increases from 0.0203 to 0.043 min<sup>-1</sup> when the number of lamp increase from one to two. The light intensity of two lamps is two times of that one lamp, whereas the kinetic is 2.15 times of the latter. This indicates that microwave irradiation increases the effect of light intensity on photodegradation.

#### 4. Conclusions

GT01 had a good performance in MWL/TiO<sub>2</sub> degradation X-3B and was easily separated from treated water. The concentration of 4 g/l was the optimum dosage of GT01 under the experimental condition in terms of photocatalytic oxidation rate. The photodegradation increased with a decrease in pH of solution and with an increase of dissolved oxygen. Microwave irradiation weakened the effect of pH, reactant concentration and dissolved oxygen on photodegradation. Consequently, MWL/TiO<sub>2</sub> had good efficiency under limited quantities of molecular oxygen and high concentration of X-3B in the solution. The significant inhibition in the presence of CO<sub>3</sub><sup>2-</sup> was attributed to scavenging hydroxyl radical. Same reasons resulted in inhibitory effect after adding SO<sub>4</sub><sup>2-</sup>. However, the inhibitory effect of SO<sub>4</sub><sup>2-</sup> was not as severe as that of CO<sub>3</sub><sup>2-</sup> because product SO<sub>4</sub><sup>-•</sup> effectively destroyed X-3B and compensated the photodegradation. The effect of NO<sub>3</sub><sup>-</sup> was negligible. Moreover, MWL/TiO<sub>2</sub> is more sensitive to temperature and light intensity than conventional photocatalysis. A high photodegradation rate was found at high temperature and with high light intensity.

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#### References

- [1] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, *Chem. Rev.* 95 (1995) 69.

- [2] A. Fujishima, T.N. Rao, D.A. Tryk, *J. Photochem. Photobiol. C: Photochem. Rev.* 1 (2000) 1.
- [3] P.R. Gogate, A.B. Pandit, *Adv. Environ. Res.* 8 (2004) 501.
- [4] X.Z. Li, H. Liu, L.F. Cheng, H.J. Tong, *Environ. Sci. Technol.* 37 (2003) 3989.
- [5] V. Cirkva, M. Hájek, *J. Photochem. Photobiol. A: Chem.* 123 (1999) 21.
- [6] S. Kataoka, D.T. Tompkins, W.A. Zeltner, et al., *J. Photochem. Photobiol. A: Chem.* 148 (2002) 323.
- [7] S. Horiyoshi, H. Hidaka, N. Serpone, *Environ. Sci. Technol.* 36 (2002) 1357.
- [8] S. Horiyoshi, H. Hidaka, N. Serpone, *J. Photochem. Photobiol. A: Chem.* 153 (2002) 185.
- [9] S. Horiyoshi, H. Hidaka, N. Serpone, *Environ. Sci. Technol.* 36 (2002) 5229.
- [10] S. Horiyoshi, H. Hidaka, N. Serpone, *J. Photochem. Photobiol. A: Chem.* 159 (2003) 289.
- [11] S. Horiyoshi, A. Saitou, H. Hidaka, N. Serpone, *Environ. Sci. Technol.* 37 (2003) 5813.
- [12] S. Horiyoshi, H. Hidaka, N. Serpone, *J. Photochem. Photobiol. A: Chem.* 161 (2004) 221.
- [13] S. Horiyoshi, H. Hidaka, N. Serpone, *J. Photochem. Photobiol. A: Chem.* 162 (2004) 33.
- [14] P. Klan, J. Literak, M. Hajek, *J. Photochem. Photobiol. A: Chem.* 128 (1999) 145.
- [15] J. Literak, P. Klan, *J. Photochem. Photobiol. A: Chem.* 137 (2000) 29.
- [16] J.A. Byrne, B.R. Eggins, N.M.D. Brown, B. McKinney, M. Rouse, *Appl. Catal. B: Environ.* 17 (1998) 25.
- [17] A. Rachel, M. Subrahmanyam, P. Boule, *Appl. Catal. B Environ.* 37 (2002) 301.
- [18] G.S. Shephard, S. Stochenstrom, D. Villiers, W.J. Engelbrech, G.F.S. Wessels, *Water Res.* 36 (2002) 140.
- [19] B.L. Zhang, B.S. Chen, K.Y. Shi, S.J. He, X.D. Liu, Z.J. Du, K.L. Yang, *Appl. Catal. B: Environ.* 40 (2003) 253.
- [20] J. Wiszniowski, D. Robert, J. Surmacz-Gorska, K. Miksch, J.V. Weber, *J. Photochem. Photobiol. A: Chem.* 152 (2002) 267.
- [21] P. Fernandez-Ibanez, S. Malato, F.J. Delas Nieves, *Catal. Today* 54 (1999) 195.
- [22] A.G. Rincion, C. Pulgarin, *Appl. Catal. B: Environ.* 51 (2004) 283.
- [23] C. Hu, Y.Z. Wang, H.X. Tang, *Appl. Catal. B: Environ.* 35 (2001) 95.
- [24] J. Wang, H. Zhao, *Chin. J. Appl. Chem.* 8 (2002) 792.
- [25] D. Chen, A.K. Ray, *Water Res.* 32 (1998) 3223.
- [26] C. Guillard, H. Lachheb, A. Houas, et al., *J. Photochem. Photobiol. A: Chem.* 158 (2003) 27.
- [27] J. Wiszniowski, D. Robert, J. Surmacz, et al., *Appl. Catal. B: Environ.* 53 (2004) 127.
- [28] C. Hu, C. Jimmy, Z. Hao, P. Wong, *Appl. Catal. B: Environ.* 46 (2003) 35.
- [29] S. Malato, J. Blanco, C. Richter, et al., *Appl. Catal. B: Environ.* 17 (1998) 347.
- [30] K. Hofstadler, R. Bauer, S. Novalic, G. Heiser, *Environ. Sci. Technol.* 28 (1994) 670.
- [31] P. Müller, P. Klán, V. Cirkva, *J. Photochem. Photobiol. A: Chem.* 158 (2003) 1.