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## Decolorization and kinetics of photo-oxidizing cationic blue X-GRL by UV/H<sub>2</sub>O<sub>2</sub> system

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**Abstract:** Azo dye cationic blue X-GRL, which is non-biodegradable toxic organic compound, is decolorized and subsequently mineralized by UV/H<sub>2</sub>O<sub>2</sub>/N<sub>2</sub> or UV/H<sub>2</sub>O<sub>2</sub>/air (O<sub>2</sub>) system. The effects of initial solution concentration, initial solution pH, and some ions produced during the degradation on the rate of decolorization of cationic blue X-GRL were investigated. The photodegradation of cationic blue X-GRL approximately follows first order kinetics. The regression curve of the natural logarithm of concentration versus reaction time becomes less linear with initial concentration increasing. Oxygen and appropriate OH<sup>·</sup> generator can accelerate reaction rate. The effect of reaction atmosphere, initial concentration, light intensity on the optimal dosage of H<sub>2</sub>O<sub>2</sub> were studied. It was found that the optimal H<sub>2</sub>O<sub>2</sub> dosage was determined by UV light intensity. These intermediates of cationic blue X-GRL decolorization are biodegradable.

**Key words:** decolorization; cationic blue X-GRL; kinetics; photooxidation; ultraviolet; hydrogen peroxide

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### Introduction

Recently, the industrial textile wastewater has been considered to be a serious pollution problem throughout the world. About 10000 different dyes and pigments are used in the textile industry (Spadaro, 1994). Azo dyes, whose color is determined by the azo bonds, are the largest and the most important class, constituting more than 50% of all the dyes. Several methods have been developed for treatment of the azo dyes. Biological processes is ineffective for most azo dyes. Research at the U. S. Environmental Protection Agency has verified that 11 out of 18 studied azo dyes were substantially non-biodegraded by the activated sludge process (Shaul, 1988). Alternative physical processes, such as coagulation and adsorption, can only transfer the solution pollutant from wastewater to other media and cause secondary pollution, and such methods have limited applicability to water-soluble dyes. Heterogeneous photocatalytic oxidation of toxic refractory by semiconductors is a promising technology, due to the non-toxic, insoluble, inexpensive, and high reactive nature of TiO<sub>2</sub> under solar light irradiation. Chen and Davis *et al.* (Chen, 1993; Davis, 1994; Vinodgopal, 1994) have shown that several kinds of wastewaters that contain dyes can be treated effectively by TiO<sub>2</sub>/UV oxidation. However, low efficiency, loss of catalyst, and filtering TiO<sub>2</sub> powder are obstacle to practical application. Advanced oxidation processes have been considered as effective technologies for treating refractory organic chemicals including dyes in wastewater. For example, UV combined with ozone or hydrogen peroxide can eliminate the refractory organic compounds and avoid secondary treatment problem (Legrini, 1993). Hydrogen peroxide is photodegraded directly to form OH<sup>·</sup> by UV light. The hydroxyl radicals attack organic compounds relatively non-selectively, and thus oxidize them by hydrogen atom abstraction or by addition to double bonds (Stefan, 1996). The latest commercial units with this process have been developed for on-site oxidation of organic contaminants in groundwater. As for UV/H<sub>2</sub>O<sub>2</sub>, UV/O<sub>3</sub>

system, the effects of pH, wavelength, light intensity and the molecular structure of dyes on decolorization of some azo dyes have been studied in detail (Shu, 1995; 1996). However, these technologies are very expensive to be applied to practical industrial wastewater, especially for developing countries. Nevertheless, it may be cost-effective means of pretreating wastewater.

In this work, non-biodegradable cationic blue X-GRL was photodegraded by UV/H<sub>2</sub>O<sub>2</sub> treatment. The objective is to investigate the kinetic key factor of UV/H<sub>2</sub>O<sub>2</sub> system, the biodegradability of these byproducts of photo-oxidizing bio-resistant organics.

## 1 Experimental section

### 1.1 Materials

Hydrogen peroxide solution 30% was purchased from East Chemical Factory of Tianjin, China. The azo dye cationic blue X-GRL was got from reputable supplier and was used without further purification. Fig.1 shows the chemical structure of dye. Ultra-pure water was used in all experiments. All the other chemicals were analytical grade.

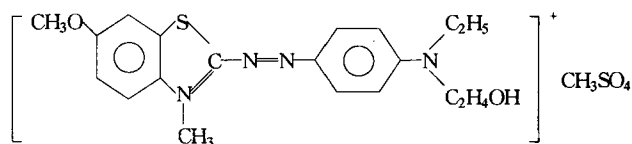


Fig.1 The chemical structure of cationic blue X-GRL

### 1.2 Procedures

A solution containing regular concentration of cationic blue X-GRL was prepared with Ultra-pure water, and then the solution was mixed in the reactor with selected volumes 30% hydrogen peroxide solution. In all experiments, a total reaction solution volume of 410 ml was used. Samples were taken from sampling port at given time intervals for analysis.

### 1.3 Equipment and analyses

Degradation of cationic blue X-GRL was performed in the main cylindrical glass body, which has gas inlet and outlet, sample outlet ports. Complete mixing of the solution was achieved by gas bubbling. 500 W or 300 W medium pressure mercury lamp was located at the quartz jacket of center of the reactor. A 254 nm low pressure mercury lamp was used for 1.5-liter reactor. Concentration of cationic blue X-GRL was analyzed quantitatively at its maximal wavelength 610 nm with COLE PARMAR colorimeter. Total organic carbon concentration of solutions were analyzed with a Dohrmann TOC-180 carbon analyzer. A DiGi510 pH meter was used to measure pH.

## 2 Results and discussions

### 2.1 Decolorization of cationic blue X-GRL by UV/H<sub>2</sub>O<sub>2</sub> system

Cationic blue X-GRL was decolorized and its intermediates were mineralized by OH<sup>•</sup> generated from photolysis of H<sub>2</sub>O<sub>2</sub> rather than by direct photolysis. As is known, OH<sup>•</sup> is main oxidant in UV/H<sub>2</sub>O<sub>2</sub> system. Fig.2 shows corresponding UV-VIS spectra of reaction solution at selected concentration of hydrogen peroxide. It depicts the entire processes of cationic blue decolorization. The initial dark blue cationic blue X-GRL solution gradually turned colorless. Subsequently, TOC

began to decrease markedly. The pH of the initial aqueous solution, which varied from 4.47 to 5.94 depending on the  $\text{H}_2\text{O}_2$  concentrations, decreased to 2.80 after photodegradation (Fig.3), indicating that organic and inorganic acids were released during degradation of cationic blue X-GRL. The mineralization of cationic blue X-GRL occurred in three stages: first, the azo bond is broken by hydroxyl radical, then further reaction of hydroxylated intermediates with  $\text{OH}^\cdot$  leads to aromatic ring cleavage, and finally, products from ring cleavage subsequently are oxidized to  $\text{CO}_2$ .

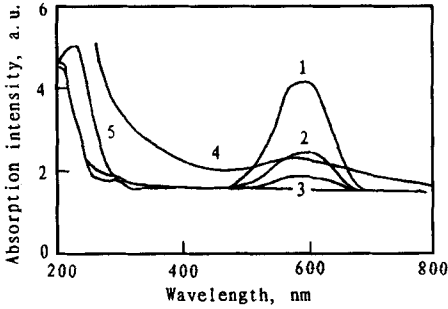


Fig.2 UV/VIS absorption spectra of cationic blue X-GRL degradation solution (UV + 97.94 mmol  $\text{H}_2\text{O}_2$ , initial concentration 150 ppm, reaction volume 1400 ml)  
1: 0 min; 2: 10 min; 3: 20 min; 4: 40 min; 5: 80 min

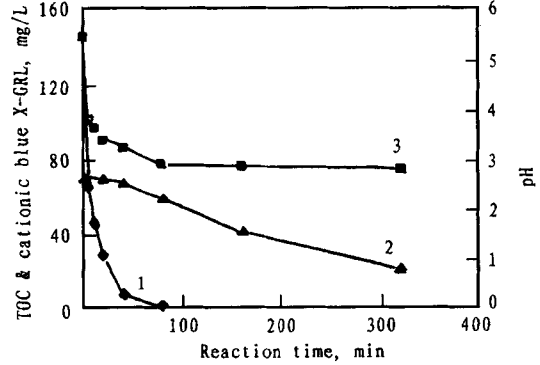


Fig.3 The photodegradation of cationic blue X-GRL by UV/ $\text{H}_2\text{O}_2$  system (UV + 97.94 mmol  $\text{H}_2\text{O}_2$ , initial concentration 150 ppm, reaction volume 1400 ml)  
1. cationic blue X-GRL; 2. TOC; 3. pH

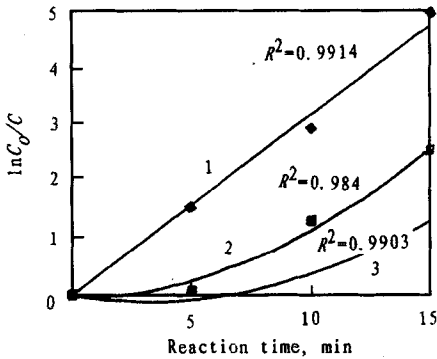


Fig.4 The regression curve of cationic blue X-GRL decolorization under different initial concentration  
1.  $C_0 = 150$  ppm; 2.  $C_0 = 300$  ppm;  
3.  $C_0 = 400$  ppm

The decolorization of cationic blue X-GRL was performed in UV/ $\text{N}_2$ , UV/air ( $\text{O}_2$ ) system respectively. It was found that the former reaction rate was slower than the latter one. Oxygen is oxidant to further oxidize hydroxylated product to accelerate decolorization rate. The regression curve type of the natural logarithm changed from straight line to parabola with initial chemical concentration increasing (Fig.4). The reaction follows pseudo-first order kinetics. The figure apparently shows that the decolorization is more and more difficult at primary stage (reaction time 5 min) with reaction compound increasing. When  $[\text{OH}^\cdot]$  can be treated as a constant if hydrogen peroxide dosage is appropriate with respect to given available UV light intensity (see later discussion), assuming that the hydroxyl radical

concentration reaches equilibrium instantaneously, the increase of the initial chemical concentration causes the competition of reaction chemical for the  $\text{OH}^\cdot$  decreasing the reaction rate. Meanwhile, the photon can move more far distance in solution with initial chemical concentration decreasing so that the chance of photon hitting  $\text{H}_2\text{O}_2$  is increased to generate more  $\text{OH}^\cdot$ , the reaction rate is increased.

## 2.2 Biodegradability

Azo dye cationic blue X-GRL is nonbiodegradable and inhibitory for bacteria. After the solution was exposed to UV irradiation with H<sub>2</sub>O<sub>2</sub> for 20 min and its color faded away in N<sub>2</sub> or air atmosphere, the BOD of solution was increased to 14.25 mg/L from zero, while the COD was decreased to 57.60 from 225 mg/L. That is, the ratio of BOD/COD was changed from 0 to 0.28. The result implies that biodegradability of the solution can be increased by UV/H<sub>2</sub>O<sub>2</sub> photo-oxidation reaction due to converting nonbiodegradable organics to biodegradable forms. The result indicates that reaction solution become biodegradable with the azo bond cleaving.

## 2.3 The optimal H<sub>2</sub>O<sub>2</sub> dosage under various conditions

The following several experiments were completed in order to optimize H<sub>2</sub>O<sub>2</sub> dosage: (1) different H<sub>2</sub>O<sub>2</sub> dosages were tested in N<sub>2</sub> atmosphere; (2) different H<sub>2</sub>O<sub>2</sub> dosages were tested in air atmosphere; (3) different H<sub>2</sub>O<sub>2</sub> dosages were tested at various initial chemical concentrations; (4) different H<sub>2</sub>O<sub>2</sub> dosages were tested at various light intensity.

The results are shown in Fig.5. Clearly, there is a same result for N<sub>2</sub>, 300 ppm/300W; O<sub>2</sub>, 300 ppm/300W; and air, 300 ppm/300W, respectively. The optimum H<sub>2</sub>O<sub>2</sub> dosage is in the range of about 88.11–117.48 mmol. For N<sub>2</sub>, 300 ppm/500W, the optimal H<sub>2</sub>O<sub>2</sub> dosage is in the range of 117.48–146.85 mmol. Therefore, the optimal H<sub>2</sub>O<sub>2</sub> dosage increases with UV light intensity increasing. It implies that the optimal H<sub>2</sub>O<sub>2</sub> dosage is determined by UV light intensity in UV/H<sub>2</sub>O<sub>2</sub> system. The mechanism of UV/H<sub>2</sub>O<sub>2</sub> photo-oxidation organics is the chain reaction arising from OH<sup>•</sup> which is from the photolysis of H<sub>2</sub>O<sub>2</sub>, that is,  $\text{H}_2\text{O}_2 + h\nu \longrightarrow 2\text{OH}^\bullet$ . The reaction is different from the mol ratio reaction of the chemical additive with initial chemical. At appropriate H<sub>2</sub>O<sub>2</sub> concentration, all of the UV light was absorbed, and therefore, UV light intensity becomes rate-limiting. At lower concentrations, H<sub>2</sub>O<sub>2</sub> absorbs only a small fraction of the incident light, and so the decolorization rate is slow. At higher concentrations, H<sub>2</sub>O<sub>2</sub> becomes a strong OH<sup>•</sup> radicals scavenger, competing with cationic blue X-GRL. In addition, the perhydroxyl (HO<sub>2</sub><sup>•</sup>) radical formed by reaction of H<sub>2</sub>O<sub>2</sub> with hydroxyl radical is a much weaker oxidant in comparison with hydroxyl radical. Hence the decolorization rate is reduced.

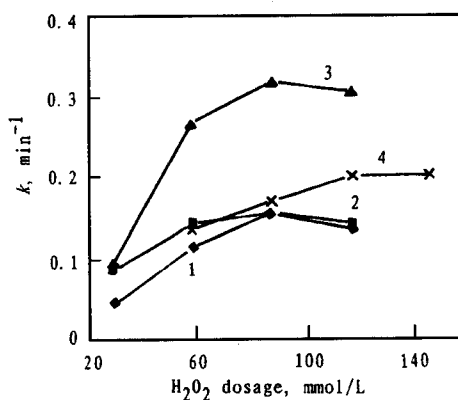


Fig.5 Decolorization rate constant for various H<sub>2</sub>O<sub>2</sub> dosages under different conditions (reaction atmosphere, initial concentration, light source power are shown in the figure)  
 1. N<sub>2</sub> + 300ppm/300W; 2. O<sub>2</sub> + 300ppm/300W; 3. N<sub>2</sub> + 150ppm/300W; 4. N<sub>2</sub> + 300ppm/500W

## 2.4 The effect of scavenger and generator of OH<sup>•</sup> on decolorization

Dye auxiliary is scavenger of OH<sup>•</sup>. Fig. 6 indicates that the auxiliary Tanadel can be degraded at almost the same rate as cationic blue X-GRL under the same conditions. The maximum absorption wavelength of Tanadel is 220 nm, so it only weakly absorbs 254 nm UV. Its degradation is also caused by OH<sup>•</sup>. Therefore, the auxiliary acts as a competitor in the reaction of cationic blue X-GRL with OH<sup>•</sup> and it notably affects the decolorization. Table 1 shows the effects of various Tanadel concentrations on the decolorization rate constant and half-life of cationic blue X-GRL. It is observed that the decolorization rate decreases with increasing Tanadel concentration.

The results also verify that auxiliary is a scavenger of  $\text{OH}^\cdot$  radical and any other active oxidative species, and that it inhibits the decolorization of cationic blue X-GRL.

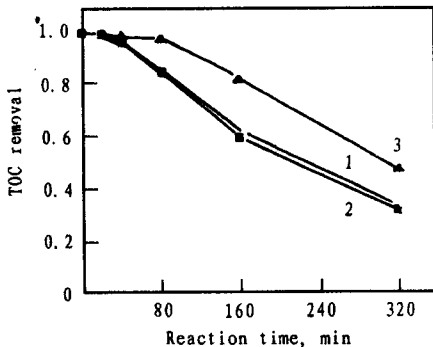


Fig. 6 The TOC removal of cationic blue X-GRL and Tanadel at the same condition (97.94 mmol  $\text{H}_2\text{O}_2$  + UV reaction volume 1400 ml, 254 nm UV source)

1. tanadel 150 ppm; 2. cationic blue X-GRL 150 ppm; 3. Cationic blue X-GRL + tanadel

As is known, carbonate ( $\text{CO}_3^{2-}$ ) and bicarbonate ( $\text{HCO}_3^-$ ) are effective  $\text{OH}^\cdot$  scavengers, while nitrate ( $\text{NO}_3^-$ ) and nitrite ( $\text{NO}_2^-$ ) can photolyze in UV light to form  $\text{OH}^\cdot$  (Haag, 1985). In this experiment, reaction mechanism of UV/ $\text{H}_2\text{O}_2$  decolorization of cationic blue X-GRL is verified by the determining the effect of these ions on the reaction rate, and the role of these inorganic ions as products of the photodegradation of cationic blue X-GRL was also investigated. As shown in Table 2, it is obvious that carbonate ion has a clearly negative effect on the decolorization. The reaction of  $\text{OH}^\cdot$  with  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  generates  $\text{HCO}_3^\cdot/\text{CO}_3^\cdot$  carbonate radicals as oxidation transients. They may disappear rapidly by attacking hydrogen peroxide, resulting in the formation  $\text{HO}_2/\text{O}_2^\cdot$  of hydroperoxy radical. Nevertheless, either  $\text{HO}_2/\text{O}_2^\cdot$  or  $\text{HCO}_3^\cdot/\text{CO}_3^\cdot$  is weaker oxidation. In contrast, at appropriate  $\text{NO}_3^-$  and  $\text{NO}_2^-$  concentrations, the decolorization of cationic blue X-GRL is accelerated. However, if their concentrations are too high, the rate of decolorization will be limited. As the formed  $\text{OH}^\cdot$  is quenched by excess  $\text{NO}_3^-$  or  $\text{NO}_2^-$ , the reaction rate is reduced.

Therefore, in practical wastewater treatment, carbonate and bicarbonate should be removed promptly by adjusting pH to acid condition or adding precipitating agent such as  $\text{Ca}^{2+}$  ion.

## 2.5 Effect of pH

Fig. 7 demonstrates the pH effect on the decolorization of cationic blue X-GRL. No significant change of the decolorization rate is observed in the pH range 2–7. At pH = 11, a lower reaction rate is found. Hydrogen peroxide is generally decomposed into water and oxygen rather than

Table 1 The decolorization rate constant and half-life of cationic blue X-GRL at various Tanadel concentrations (initial chemical concentration 150 ppm, reaction volume 1400 ml)

Tanadel, ppm	$k/\text{min}$	Half-life, min
50	0.055	12.603
100	0.0577	12.013
150	0.0424	16.348
200	0.0329	21.0683

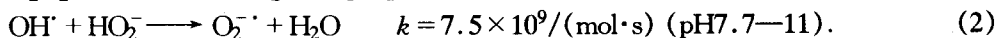
hydroxyl radicals in alkaline conditions without UV light. In addition, hydrogen peroxide is a weak acid which dissociates in alkaline media. The reaction rate constant of  $\text{OH}^\cdot$  radicals with

Table 2 The rate constants of cationic blue X-GRL decolorization at varying carbonate and nitrate and nitrite concentrations

Ions	Ion concentration, mmol	$k/\text{min}$	$r$
Without ion	0	0.0705	0.996
$\text{NO}_3^-$	$1.61 \times 10^{-1}$	0.0721	0.987
	$3.61 \times 10^{-2}$	0.0765	0.986
	$3.44 \times 10^{-1}$	0.0621	0.983
	$5.58 \times 10^{-2}$	0.0706	0.997
$\text{NO}_2^-$	$1.23 \times 10^{-1}$	0.0750	0.986
	$2.60 \times 10^{-1}$	0.0709	0.999
	$4.08 \times 10^{-1}$	0.0632	0.998
	$2.76 \times 10^{-1}$	0.0663	0.965
$\text{CO}_3^{2-}$	$1.68 \times 10^{-1}$	0.0623	0.982

hydroxyl radicals in alkaline conditions without UV light. In addition, hydrogen peroxide is a weak acid which dissociates in alkaline media. The reaction rate constant of  $\text{OH}^\cdot$  radicals with

hydroperoxide ion is much higher than that of OH<sup>•</sup> with hydrogen peroxide (Buxton, 1988). This reduces effectiveness of OH<sup>•</sup> radical attack on cationic blue X-GRL molecules. The following reaction scheme expresses the mechanism.



O<sup>-</sup>, HO<sub>2</sub><sup>-</sup> are weaker oxidant than OH<sup>•</sup> so the decolorization rate becomes slower at higher pH. Under the acidic conditions, the hydroxyl radical will have a higher oxidation potential, so the degradation rate is faster.

## 2.6 Energy efficiency

The efficiency of photochemical reaction can be expressed by the photolysis quantum yield. In aquatic photochemical reaction system, photolysis quantum yield is affected by such as light intensity, light path length, initial chemical concentration and radical diffuse limitation and so on. In general, photo-oxidation of contamination follows the first order kinetics, so eliminating the same chemical with the same initial concentration needs equal reaction time usually, that is, needs equal UV irradiation energy. Therefore, the energy consumption can express the efficiency of system energy. In this experiment, *EE/O* (electrical energy per order) is used to compare UV/H<sub>2</sub>O<sub>2</sub> system energy efficiency under different operational factors. *EE/O* refers to the energy (kWh) of removing one order contamination concentration in 3785L water according to Bolton and Cater specification (Bolton, 1994). Its equation is:

$$EE/O = P \times (t/60) \times 3785/V \times \log(C_i/C_f),$$

where *P* refers to the light source power, *t* refers to illumination time, *V* refers to reaction volume, *C<sub>i</sub>* and *C<sub>f</sub>* refers to initial concentration and final concentration in illumination time, respectively. Based on above equation, *EE/O* value is obtained by the time of removing 90% cationic blue X-GRL. The results are shown in Fig. 8. In different initial concentration conditions, *EE/O* values increase with initial concentration increasing because of the longer time for eliminating the same percentage contamination needs more longer time. It is attractive that the consumption of energy can be the same greatly with H<sub>2</sub>O<sub>2</sub> dosage increasing. On the contrast, the consumption of energy does not change by regular trend with the change of pH. However, the

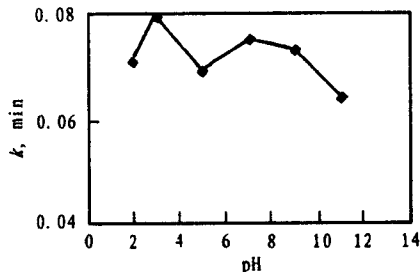


Fig. 7 The effect of pH on the decolorization of cation blue X-GRL (initial concentration 150 ppm, reaction volume 1400 ml, 254 nm UV source)

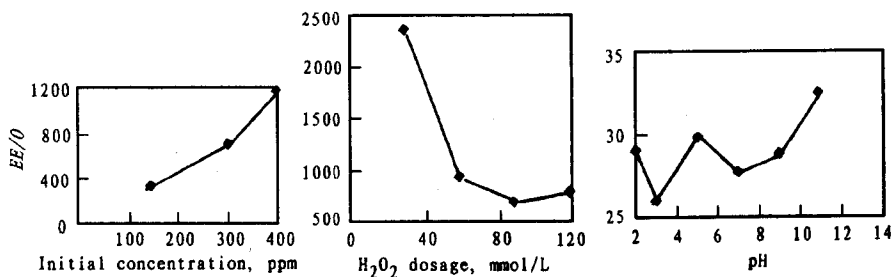


Fig. 8 Influence of *EE/O* value photo-oxidation cationic blue X-GRL on (a) H<sub>2</sub>O<sub>2</sub> dosage, (b) initial chemical concentration, (c) solution pH, initial concentration 150 ppm, reaction volume 1400 ml 254 nm low energy mercury lamp 15W

consumption of energy decreases with pH decreasing generally. Obviously,  $EE/O$  values from (a), (b) experiments are much higher than that one from (c) although there are bigger power light source. It indicates that photoreactor volume is a key factor, appropriate size reactor can degrade the consumption of energy. The reaction rate constants in (a), (b) conditions are 10 times that of (c) condition. However, the former  $EE/O$  are much higher than that of the latter.

### 3 Conclusions

A process utilizing UV irradiation combined with  $H_2O_2$  is available for eliminating bio-resistant and toxic organic compound. UV light intensity and  $H_2O_2$  concentration are key control factors in UV/ $H_2O_2$  system. The decolorization of cationic blue X-GRL follows pseudo-first order kinetics. Some inorganic ions that are generated from cationic blue X-GRL photooxidation can affect the reaction rate as seen in the experiment results of the effect of carbonate, nitrate and nitrite on the reaction. The dye auxiliary hinders the decolorization as  $OH^-$  scavenger. The optimum  $H_2O_2$  dosage is determined by available light intensity. Oxygen can accelerate decolorization rate. The reaction rate in depends on pH at the range of pH 2—7. Only above pH 9 is the reaction rate reduced markedly. In UV/ $H_2O_2$  system. It was found that lower  $EE/O$  was obtained by high light intensity, appropriate  $H_2O_2$  dosage and acid condition.

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