Chemical Engineering Journal 158 (2010) 578–583

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Decolorization of C.I. Reactive Black 5 in UV/TiO_2, UV/oxidant and UV/TiO_2/oxidant systems: A comparative study

Chien-Hwa Yu[a], Chung-Hsin Wu[b,*], Tsung-Han Ho[b], P.K. Andy Hong[c]

[a] Department of Civil and Environment Engineering, Nanya Institute of Technology, Taoyuan, Taiwan, ROC
[b] Department of Chemical and Materials Engineering, National Kaohsiung University of Applied Sciences, 415 Chien Kung Road, Kaohsiung 807, Taiwan, ROC
[c] Department of Civil and Environmental Engineering, University of Utah, USA

ARTICLE INFO

Article history:
Received 29 October 2009
Received in revised form 29 January 2010
Accepted 1 February 2010

Keywords:
Decolorization
TiO_2
H_2O_2
$Na_2S_2O_8$
$NaBrO_3$
$NaIO_4$

ABSTRACT

This study evaluated the effectiveness of decolorizing C.I. Reactive Black 5 (RB5) in UV/TiO_2, UV/oxidant and UV/TiO_2/oxidant systems in the presence of oxidants H_2O_2, $Na_2S_2O_8$, $NaBrO_3$, and $NaIO_4$. The effects of pH, oxidant dosage and ethanol addition on decolorization were determined. Decolorization rate constants (k) were of pseudo-first-order in all systems. In UV/TiO_2 and UV/oxidant systems, the k values followed the order pH 4 > pH 7 > pH 10. At pH 7 with 1 mM of oxidant added, the k values followed the order UV/$NaIO_4$ (0.377 min^{-1}) > UV/$Na_2S_2O_8$ (0.156 min^{-1}) > UV/H_2O_2 (0.105 min^{-1}) > UV/$NaBrO_3$ (0.101 min^{-1}) > UV (0.002 min^{-1}). In UV/oxidant systems, decolorization effectiveness increased with increasing $Na_2S_2O_8$ and $NaBrO_3$ doses but reached optima with $NaIO_4$ and H_2O_2 at 1 and 6 mM, respectively. Addition of oxidants to UV/TiO_2 resulted in quenching of conduction band electrons and generation of reactive radical intermediates, enhancing decolorization. In UV/TiO_2/oxidant systems, decolorization rate constants varied with oxidant following the order $NaIO_4$ (0.558 min^{-1}) > $Na_2S_2O_8$ (0.044 min^{-1}) > $NaBrO_3$ (0.036 min^{-1}) > H_2O_2 (0.035 min^{-1}) > absence of oxidant (0.033 min^{-1}). In UV/oxidant systems, addition of ethanol inhibited decolorization, which indicated the involvement of hydroxyl radicals in the decolorization pathway with UV/H_2O_2 and UV/$Na_2S_2O_8$ systems, as well as probable involvement of other radicals with UV/$NaBrO_3$ and UV/$NaIO_4$ systems. Direct oxidation by photogenerated holes was likely significant in UV/TiO_2 and UV/TiO_2/oxidant systems.

1. Introduction

Wastewater of the textile dyeing industry is of elevated temperature and varied pH, containing a high concentration of color substances. Many dyes pose environmental hazards because of their toxicity. Azo dyes containing one or more azo bonds are synthetic dyes that are extensively used and are major pollutants in the wastewater. Conventional processes of physical (adsorption, filtration, and flotation), chemical (coagulation, oxidation, reduction, and electrolysis), and biological methods have been applied to treat wastewater containing organic dyes and pigments. However, finding a convenient method for all dyestuff wastewaters is difficult [1].

Advanced oxidation processes (AOPs) are alternative approaches for decolorizing and reducing recalcitrant loads in textile wastewaters. AOPs are based on the generation of hydroxyl radicals, which are highly reactive and nonselective oxidants toward organic compounds. As broadly accepted, photogenerated valence holes are formed when TiO_2 particles are irradiated by UV light, which leads to oxidation of OH^- or H_2O by holes resulting in hydroxyl radicals that are capable of destroying most organic species [2]. Oxygen acts efficiently as an electron trap, preventing the recombination of photogenerated electrons and holes. When oxygen is limited, the rapid recombination of electrons and holes in TiO_2 would markedly reduce its photocatalytic actions.

In lieu of oxygen, inorganic oxidants such as IO_4^-, $S_2O_8^{2-}$, BrO_3^-, ClO_3^- and H_2O_2 can quench conduction band electrons and form reactive radical intermediates, thereby enhancing photodegradation of organic substrates by valence holes [3–7]. These oxidants improve the performance of UV/TiO_2 by reducing the probability of recombination of the photogenerated electrons and holes, thus availing more holes for oxidative degradation of organic contaminants. Selvam et al. [5] found enhanced photodegradation of 4-fluorophenol by UV/TiO_2 following this order according to oxidants $IO_4^- > BrO_3^- > S_2O_8^{2-} > H_2O_2 > ClO_3^-$. For 4-chloro-2-methylphenol by UV/TiO_2 [3], enhanced photodegradation followed the order according to oxidants $IO_4^- > BrO_3^- > H_2O_2 > O_2 > ClO_3^-$. Syoufian and Nakashima [6] found the effect of oxidants on degradation rates of methylene blue by UV/TiO_2 following the order $S_2O_8^{2-} > IO_4^- > BrO_3^- > H_2O_2 > ClO_3^-$.

---

* Corresponding author. Tel.: +886 5 5347311; fax: +886 5 5334958.
E-mail address: chunghsinwu@yahoo.com.tw (C.-H. Wu).

1385-8947/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2010.02.001

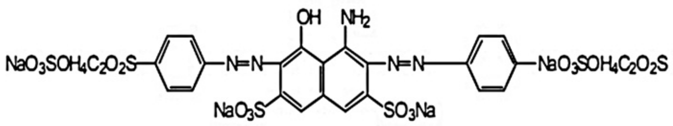

Fig. 1. Chemical structure of RB5.

Photodefluorination rates of pentafluorobenzoic acid by UV/ZnO followed the order according to ions $IO_4^- > S_2O_8^{2-} > BrO_3^- > ClO_3^-$ [4]. The photodegradation of phenol by UV/TiO_2 was enhanced by oxidants following the order $BrO_3^- > H_2O_2 > S_2O_8^{2-}$ [7]. Enhanced degradation was shown to vary with the contaminant kind, the catalyst and the dosage of oxidant. C.I. Reactive Black 5 (RB5), a representative reactive diazo dye, is commonly found at concentrations higher than other reactive dyes in dyebath effluents [8]; RB5 was therefore selected as the parent compound in this investigation. No studies have yet reported the promotion of decolorization of RB5 by UV/TiO_2 with added H_2O_2, $S_2O_8^{2-}$, BrO_3^- and IO_4^-. The influence of inorganic oxidants must be assessed prior to application to avoid adverse effects under different experimental parameters. Accordingly, H_2O_2, $Na_2S_2O_8$, $NaBrO_3$ and $NaIO_4$ were selected as oxidant additives. The objectives of this study were to (i) determine the effectiveness of decolorizing RB5 in UV/oxidant systems, (ii) evaluate the effects of pH and oxidant dosage, (iii) compare decolorization of UV/TiO_2 and UV/TiO_2/oxidant systems and (iv) understand the effects of added ethanol in UV/oxidant and UV/TiO_2/oxidant systems.

2. Materials and methods

2.1. Materials

TiO_2 (Degussa P-25) was used directly without treatment. The crystal phases of Degussa P-25 were anatase/rutile at the ratio 3/1. The specific surface area, average particle size and pH at the zero point of charge (pH_{zpc}) of Degussa P-25 were 50 m^2/g, 30 nm and 6.6, respectively [9]. The parent compound, RB5, purchased from Everlight Chemical Company, was employed without further purification. Fig. 1 presents the chemical structure of RB5. The CAS number, color index, formula, molecular weight and maximum UV absorption wavelength of RB5 was 17095-24-8, 20505, $C_{26}H_{21}N_5Na_4O_{19}S_6$, 991.82 g/mol and 597 nm, respectively. Ethanol (C_2H_5OH) was utilized as a scavenger of hydroxyl radical ($^\bullet OH$). Solution pH was controlled by addition of HNO_3 and NaOH via an automatic titrator. Reagents HNO_3, NaOH, NaCl, H_2O_2, $Na_2S_2O_8$, $NaBrO_3$, $NaIO_4$ and ethanol were obtained from Merck. All reagents were of analytical grade and used as purchased.

2.2. Decolorization experiments

The RB5 concentration in all experiments was 20 mg/L. Reaction pH was maintained at pH 7 for all runs except in those undertaken to delineate the effect of pH. Decolorization experiments were conducted in a 3-L hollow cylindrical glass reactor. A 15-W UVC lamp (254 nm, 10 mW/cm^2, Philips) was placed inside a quartz tube as an light source. Wu et al. [10] demonstrated that the UV-screening effect of 1 g/L TiO_2 was negligible, and this was found at the highest decolorization rate for RB5. Hence, a dose of 1 g/L TiO_2 was used. In experiments with UV/oxidant, decolorization effectiveness using 1–24 mM of different oxidants was evaluated. To evaluate enhanced decolorization, oxidant (1 mM) was added in UV/TiO_2. Ethanol was dosed at 1.2 g/L to study its effect. Reaction temperature was controlled at 25 °C in all experiments. The reaction medium was continually stirred at 300 rpm to maintain TiO_2 suspension. Aliquots of 15 mL were withdrawn from the photoreactor at prescribed intervals. The suspended TiO_2 particles were separated by filtration through a 0.22-μm filter (Millipore). The RB5 concentration was measured using a spectrophotometer (Hitachi U-2001) at 597 nm. The decolorization efficiency was calculated from the difference between the dye concentrations before and after treatment. Most experiments were performed in duplicate and the values shown are averages.

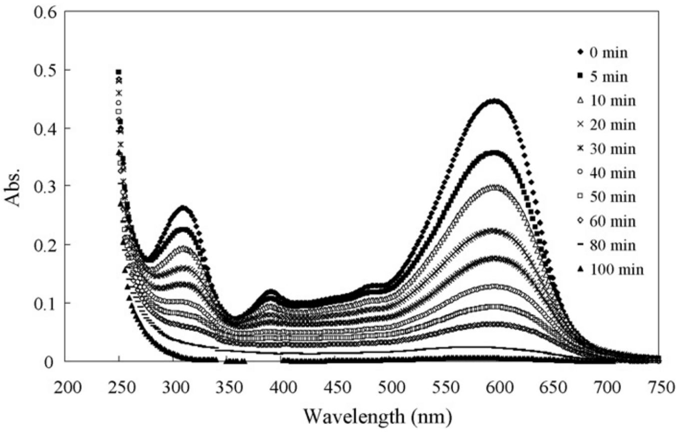

Fig. 2. UV–vis spectral changes of RB5 in UV/TiO_2 system ([RB5] = 20 mg/L, pH 7 and [TiO_2] = 1 g/L).

3. Results and discussion

3.1. Decolorization in UV/TiO_2 system

The UV–vis spectral changes of RB5 at pH 7 during reaction in the UV/TiO_2 system are displayed in Fig. 2. Before treatment, the UV–vis spectrum of RB5 exhibits two main absorption bands – one in the UV region (310 nm) and another in the visible region (597 nm). The UV band is characteristic of two adjacent rings, whereas the visible band is associated with a long conjugated π system that is internally linked by two azo groups [11]. The intensity of visible band at 597 nm declines rapidly while the UV band at 310 nm disappeared much slower. The decolorization rate constants (k) of RB5 in the UV/TiO_2 systems were found to fit pseudo-first-order kinetics, as reported previously by various investigators on dye decolorization [1,10,12–16]. The rates of disappearance of absorbance at 310 and 597 nm were 0.024 and 0.033 min^{-1}, respectively. Initially, the hydroxyl radicals attack the azo groups and open the N=N bond that are more easily destroyed than are the aromatic structures. The markedly higher rate of decay of the visible band is attributed to preferential hydroxylation of the azo-links during the oxidation process, which leads to rapid disappearance of chromophores in the dye structure [17]. Lucas and Peres [14] observed similar results for BR5 in a photo-Fenton system. During decolorization, the absorbance values decreased all over the spectral window and no specific peaks remained after 100 min of reaction (Fig. 2). Kritikos et al. [18] showed products of photocatalytic degradation of RB5 to be aromatic rings (such as benzaldehyde) and short-chain aliphatic oxygenated hydrocarbons (including butanoic and propanoic acids).

Textile wastewater contains not only organic contaminants but also a large amount of inorganic anions. These ions increase the ionic strength of the medium and thus affect the catalytic activity of the photocatalyst. We evaluated the effect of adding NaCl to the UV/TiO_2 system (Fig. 3). The k values were 0.033, 0.045 and 0.052 min^{-1} when 0, 1 and 5 g/L NaCl were added to the UV/TiO_2 system, respectively. Addition of NaCl increased the ionic strength of the aqueous phase, driving organic compounds to the

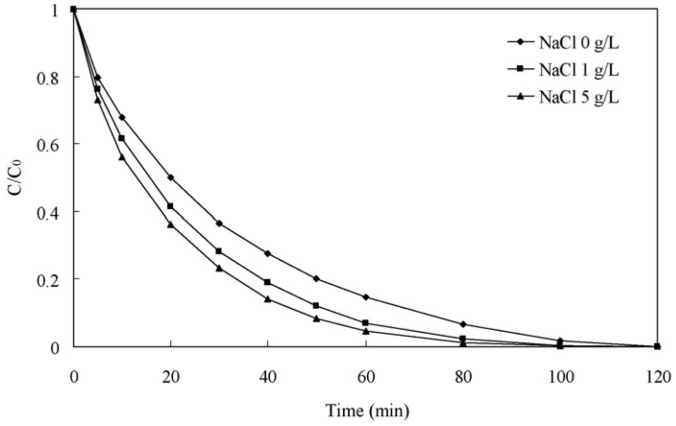

Fig. 3. Effects of NaCl addition in UV/TiO_2 system ([RB5] = 20 mg/L, pH 7 and [TiO_2] = 1 g/L).

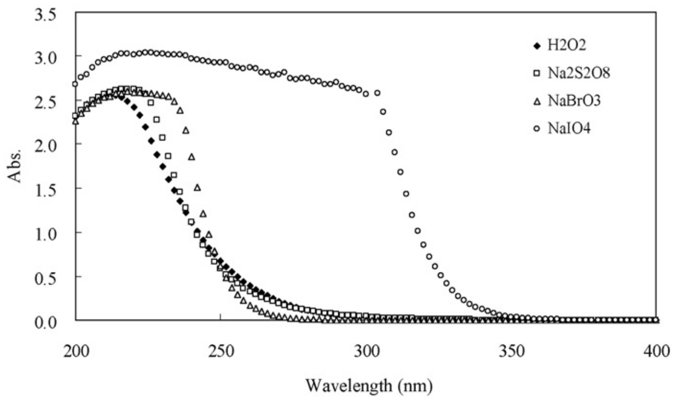

Fig. 4. UV absorption spectra of H_2O_2, $Na_2S_2O_8$, $NaBrO_3$ and $NaIO_4$ ([oxidant] = 1 mM).

liquid–solid interface in the UV/TiO_2 system. Wang et al. [19] indicated that adding 0.01 M NaCl did not influence the reaction of UV/TiO_2; however, adding 0.01 M Na_2SO_4 promoted photocatalytic activities. Clearly, increasing the ionic strength enhanced reaction in the UV/TiO_2 system. In UV/TiO_2, addition of NaCl favored partitioning of RB5 to the TiO_2 surface, increasing adsorption of RB5; decolorization was thus accelerated. This is in agreement with a previous study on C.I. Reactive Red 2 with UV/TiO_2 [16].

3.2. Decolorization in UV/oxidant systems

The pH affects production of hydroxyl radicals and therefore decolorization. Table 1 presents the effects of pH on the RB5 decolorization in UV/oxidant systems. With 1 mM of added oxidant, all *k* values of the UV/oxidant systems increased as pH decreased. Buxton et al. [20] demonstrated that the oxidation potential of hydroxyl radicals decreased as pH increased. This is consistent with the *k* value being lowest at the highest test pH of 10. At pH 7, the decolorization rates of RB5 followed the order UV/$NaIO_4$ > UV/$Na_2S_2O_8$ > UV/H_2O_2 > UV/$NaBrO_3$ > UV. To affirm the role of oxidant in decolorization using the UV/oxidant system, UV absorption spectra of all oxidants at the same concentration were analyzed. As shown in Fig. 4, $NaIO_4$ has strong UV absorption. Oxidants that absorb more UV are more effective for degradation because strong UV absorption promotes formation of reactive radical species. Accordingly, UV/$NaIO_4$ that absorbed most strongly exhibited the highest decolorization performance. This agreed with the results of Selvam et al. [5] that found the photodegradation efficiencies of 4-fluorophenol following the order UV/IO_4^- > UV/$S_2O_8^{2-}$ > UV/H_2O_2 > UV/BrO_3^-. Moreover, the extent of organic carbon removal of 2,4-dichlorophenol followed the order of UV/$S_2O_8^{2-}$ > UV/HSO_5^- > UV/H_2O_2 [21]. Contrarily, Ravichandran et al. [4] found the photodefluoridation of pentafluorobenzoic acid following the order UV/IO_4^- > UV/H_2O_2 > UV/$S_2O_8^{2-}$ > UV/BrO_3^-. These results suggested the ability of oxidants to enhance photodegradation varied with the contaminant kind and the oxidant dose, as the latter's effect was further explored below.

Table 1
Effects of pH on the RB5 decolorization rate constants ([RB5] = 20 mg/L and [oxidant] = 1 mM).

	pH 4 *k* (min^{-1})	pH 7 *k* (min^{-1})	pH 10 *k* (min^{-1})
UV/TiO_2	0.076 (0.969)	0.033 (0.997)	0.026 (0.994)
UV/H_2O_2	0.118 (0.989)	0.105 (0.997)	0.103 (0.992)
UV/$Na_2S_2O_8$	0.197 (0.995)	0.156 (0.992)	0.127 (0.996)
UV/$NaBrO_3$	0.155 (0.998)	0.101 (0.995)	0.093 (0.997)
UV/$NaIO_4$	Too fast	0.377 (0.998)	0.243 (0.991)

( ), r^2 value.

Fig. 5(a) and (b) plots the effects of H_2O_2 dosage in UV/H_2O_2 and UV/TiO_2/H_2O_2 systems, respectively. The *k* value of 1, 3, 6, 12, 24 mM H_2O_2 added to the UV/TiO_2 system was 0.035, 0.035, 0.033, 0.028 and 0.018 min^{-1}, respectively. Table 2 lists the *k* values of different oxidant dosages in UV/oxidant systems. To clarify the effects of oxidant dosage, the reaction mechanisms at work in the UV/oxidant systems must be introduced.

Eq. (1) describes the key reaction of the UV/H_2O_2 system. Furthermore, H_2O_2 may act as an $^{\bullet}OH$ scavenger and form hydroperoxyl radicals, which are detrimental to photolysis (Eq. (2)). Several studies have shown that the degradation rate of organic compounds increases with increasing H_2O_2 concentration up to a

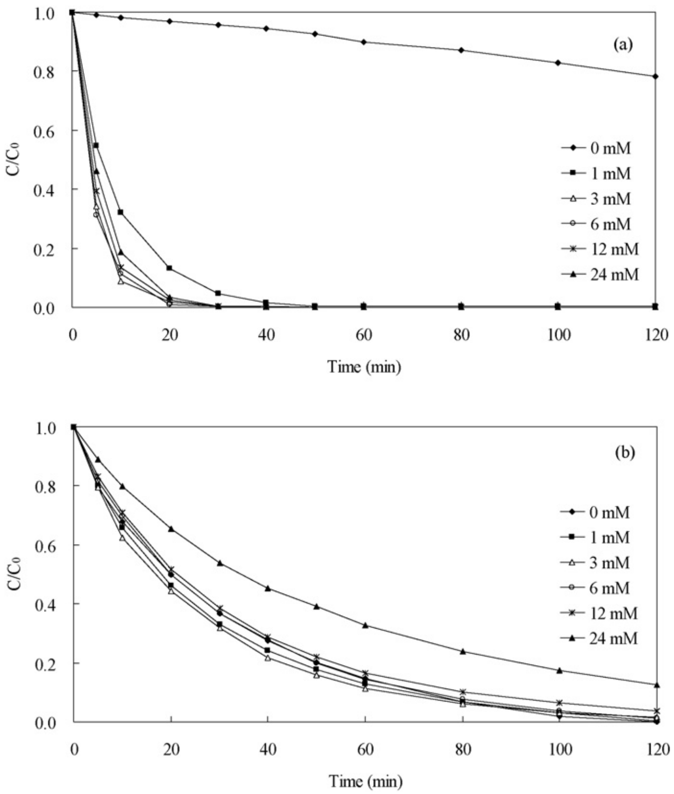

Fig. 5. Effects of H_2O_2 dosage in UV/H_2O_2 and UV/TiO_2/H_2O_2 systems: (a) UV/H_2O_2 and (b) UV/TiO_2/H_2O_2 ([RB5] = 20 mg/L, pH 7 and [TiO_2] = 1 g/L).

Table 2
Influence of oxidant dose on RB5 decolorization in UV/oxidant systems ([RB5] = 20 mg/L and pH 7).

	1 mM k (min^{-1})	3 mM k (min^{-1})	6 mM k (min^{-1})	12 mM k (min^{-1})	24 mM k (min^{-1})
UV/H_2O_2	0.105 (0.997)	0.207 (0.995)	0.213 (0.994)	0.185 (0.998)	0.177 (0.996)
UV/$Na_2S_2O_8$	0.156 (0.992)	0.328 (0.962)	0.576 (0.963)	Too fast	Too fast
UV/$NaBrO_3$	0.101 (0.995)	0.166 (0.964)	0.261 (0.936)	0.413 (0.997)	0.479 (0.999)
UV/$NaIO_4$	0.377 (0.998)0.297[a] (0.992)[a]	0.305 (0.998)	0.250 (0.999)	0.218 (0.990)	0.171 (0.980)

( ), r^2 value.
[a] $[NaIO_4] = 0.5$ mM.

threshold, beyond which degradation efficiency declines as H_2O_2 increasingly scavenges $^{\bullet}OH$ [3,15,22,23] resulting in hydroperoxyl radicals with reduced potency. Decolorization effectiveness increased with H_2O_2 concentration from 1 to 6 mM in the UV/H_2O_2 system, but increased no further beyond 6 mM (Table 2). The k value was highest at 3 mM of H_2O_2 with the UV/TiO_2/H_2O_2 system. Irmak et al. [3] observed similarly that the reaction rate was highest when 1 mM H_2O_2 was added to the UV/TiO_2/H_2O_2 system. Hence, the dose of H_2O_2 in the UV/H_2O_2 and UV/TiO_2/H_2O_2 systems must be carefully controlled:

$$H_2O_2 + h\nu \rightarrow 2\,^{\bullet}OH \tag{1}$$

$$H_2O_2 + {}^{\bullet}OH \rightarrow HO_2^{\bullet} + H_2O \tag{2}$$

Ivanov et al. [24] suggested that persulfate ions undergo photolysis under irradiation with light, generating sulfate free radicals (Eq. (3)). Sulfate free radicals react with water molecules to produce hydroxyl radicals (Eq. (4)) [2]. According to Eqs. (3) and (4), increasing the amount of $S_2O_8^{2-}$ increased the number of sulfate free radicals and $^{\bullet}OH$ formed, accelerating decolorization. Since the k value increased with the dose of $Na_2S_2O_8$ in UV/$Na_2S_2O_8$ (Table 2), $^{\bullet}OH$ scavenging by $S_2O_8^{2-}$ was not observed when doses 1–24 mM $Na_2S_2O_8$ were added (Eq. (5)):

$$S_2O_8^{2-} + h\nu \rightarrow 2SO_4^{\bullet -} \tag{3}$$

$$SO_4^{\bullet -} + H_2O \rightarrow SO_4^{2-} + H^+ + {}^{\bullet}OH \tag{4}$$

$$SO_4^{2-} + {}^{\bullet}OH \rightarrow SO_4^{\bullet -} + OH^- \tag{5}$$

Zuo and Katsumura [25] investigated the mechanisms of UV/$NaBrO_3$, as given by Eqs. (6)–(11). Similarly, for the UV/$Na_2S_2O_8$ system, k increased with increasing dose of $NaBrO_3$, which suggested that BrO_3^- did not scavenge $^{\bullet}OH$ in this study (Eq. (11)):

$$BrO_3^- + h\nu \rightarrow BrO^{\bullet} + O_2^- \tag{6}$$

$$BrO_3^- + h\nu \rightarrow BrO_2^{\bullet} + O^{\bullet -} \tag{7}$$

$$BrO_3^- + h\nu \rightarrow BrO_3^{\bullet} + e^- \tag{8}$$

$$BrO_3^{\bullet} \rightarrow BrO^{\bullet} + O_2 \tag{9}$$

$$O^{\bullet -} + H^+ \rightarrow {}^{\bullet}OH \tag{10}$$

$$BrO_3^- + {}^{\bullet}OH \rightarrow BrO_3^{\bullet} + OH^- \tag{11}$$

Weavers et al. [26] proposed Eqs. (10) and (12)–(16) as mechanisms that operate in UV/$NaIO_4$. The formation of various highly reactive radicals ($O^{\bullet -}$, $^{\bullet}OH$, $IO_3^{\bullet}$ and $IO_4^{\bullet}$) and non-radical intermediates (O_3, IO_4^- and IO_3^-) is responsible for the high activity of UV/$NaIO_4$. Increasing the concentration of IO_4^- increases the amount of radicals formed. A threshold of $NaIO_4$ at 1 mM was found with the UV/$NaIO_4$ system, above which decolorization rate decreased. Lee and Yoon [1] also reported that the k values of RB5 in the UV/$NaIO_4$ system increased as the IO_4^- concentration increased in the low range (0–5 mM) and decreased slightly when the IO_4^- concentration exceeded 5 mM. Since the RB5 concentration used in the work by Lee and Yoon [1] was higher (50 mg/L) than that in this study (20 mg/L), Lee and Yoon [1] identified a higher optimal $NaIO_4$ concentration (5 mM) than that in this study (1 mM). The presence of excess IO_4^- ions in solution may scavenge $^{\bullet}OH$ (Eq. (16)); therefore, the decolorization rate decreased when a high concentration of IO_4^- was added [1].

$$IO_4^- + h\nu \rightarrow IO_3^{\bullet} + O^{\bullet -} \tag{12}$$

$$IO_4^- + h\nu \rightarrow IO_3^- + O \tag{13}$$

$$O^{\bullet -} + H^+ \rightarrow {}^{\bullet}OH \tag{10}$$

$$O + O_2 \rightarrow O_3 \tag{14}$$

$$O_3 + IO_3^{\bullet} \rightarrow IO_4^{\bullet} + O_2 \tag{15}$$

$$IO_4^- + {}^{\bullet}OH \rightarrow IO_4^{\bullet} + OH^- \tag{16}$$

3.3. *Effects of added oxidant in UV/TiO_2 system*

In the heterogeneous photocatalytic system of UV/TiO_2, molecular oxygen acts as an electron acceptor, which prevents electron–hole recombination. Oxidants have dual functions as an oxidant and an electron scavenger. Eqs. (17)–(20) specify the acceptance of photogenerated electrons by H_2O_2 [15,27], $S_2O_8^{2-}$ [2,4,27,28], BrO_3^- [4,5,27] and IO_4^- [3,26,29] in UV/TiO_2:

$$H_2O_2 + e_{(CB)}^- \rightarrow OH^- + {}^{\bullet}OH \tag{17}$$

$$S_2O_8^{2-} + e_{(CB)}^- \rightarrow SO_4^{2-} + SO_4^{\bullet -} \tag{18}$$

$$BrO_3^- + 6\,e_{(CB)}^- + 6\,H^+ \rightarrow 3\,H_2O + Br^- \tag{19}$$

$$IO_4^- + 8\,e_{(CB)}^- + 8\,H^+ \rightarrow 4\,H_2O + I^- \tag{20}$$

Decolorization rates followed the order UV/TiO_2/$NaIO_4$ > UV/TiO_2/$Na_2S_2O_8$ > UV/TiO_2/$NaBrO_3$ > UV/TiO_2/H_2O_2 > UV/TiO_2 (Table 3). Adding inorganic oxidants increased the rate of decolorization by various means, such as, (i) prevention of electron–hole recombination via capturing conduction band electrons; (ii) increased formation of hydroxyl radicals formed, and (iii) production of other species that oxidize intermediate compounds. Numerous works have also found enhanced photodegradation rates using UV/TiO_2/oxidant over those using UV/TiO_2 [3–7,10,15,29,30]. The enhancement of these oxidants has been investigated for many organic compounds other than RB5.

Table 3
Effects of adding ethanol on the RB5 decolorization in various systems ([RB5] = 20 mg/L, pH 7, [TiO_2] = 1 g/L, [oxidant] = 1 mM and [ethanol] = 1.2 g/L).

	Without ethanol k (min^{-1})	With ethanol k (min^{-1})
UV/TiO_2	0.033 (0.997)	0.014 (0.992)
UV/H_2O_2	0.105 (0.997)	0.002 (0.993)
UV/$Na_2S_2O_8$	0.156 (0.992)	0.007 (0.908)
UV/$NaBrO_3$	0.101 (0.995)	0.044 (0.992)
UV/$NaIO_4$	0.377 (0.998)	0.109 (0.993)
UV/TiO_2/H_2O_2	0.035 (0.997)	0.015 (0.941)
UV/TiO_2/$Na_2S_2O_8$	0.044 (0.995)	0.015 (0.942)
UV/TiO_2/$NaBrO_3$	0.036 (0.991)	0.013 (0.997)
UV/TiO_2/$NaIO_4$	0.558 (0.925)	0.261 (0.998)

( ), r^2 value.

Results of prior studies on photocatalytic degradation of structurally different organic compounds under different experimental conditions have been consistent with results of RB5 in this study; specifically, all related studies have shown that $NaIO_4$ exerts a stronger enhancement than H_2O_2, $Na_2S_2O_8$, $NaBrO_3$ oxidants or absence of which in the use of UV/TiO_2 for degradation of organic contaminants.

Table 3 presents the effects of ethanol addition to UV/TiO_2, UV/oxidant and UV/TiO_2/oxidant systems. Ethanol is known to scavenge $^\bullet OH$ radical [12,13]. Notably, excess ethanol (1.2 g/L) reduced the rate of decolorization of RB5 in UV/oxidant systems. For UV/H_2O_2 and UV/$Na_2S_2O_8$ systems, the k values were approximately 20 times lower than in the absence of ethanol (Table 3), indicating decolorization proceeded mainly via attack by $^\bullet OH$. However, decolorization was only partially reduced by 1.2 g/L of ethanol in UV/$NaBrO_3$ and UV/$NaIO_4$ systems, as evidenced by k values being only four times slower than without ethanol. This finding suggested other reactive species, which were less reactive with ethanol, were involved in decolorization. These species were most likely $BrO^\bullet$, $BrO_2{}^\bullet$ and $BrO_3{}^\bullet$, which could be produced in UV/$NaBrO_3$ (Eqs. (6)–(8)) and likely $O^{\bullet-}$, $IO_3{}^\bullet$, $IO_4{}^\bullet$ and O_3, that were produced in UV/$NaIO_4$ (Eqs. (12)–(15)). The k values using UV/TiO_2 and UV/TiO_2/ethanol were 0.033 and 0.014 min^{-1}, respectively. The inhibition by ethanol suggested a predominant pathway involving $^\bullet OH$ and plausibly another significant pathway via direct oxidation by photogenerated holes in UV/TiO_2. This finding was consistent with those of Daneshvar et al. [12,13] and Wu [15].

In UV/TiO_2/oxidant/ethanol systems excepting UV/TiO_2/$NaIO_4$/ethanol, the k values were approximately equal to that of the UV/TiO_2/ethanol system (Table 3). This suggested that the main decolorization pathway in UV/TiO_2/H_2O_2, UV/TiO_2/$Na_2S_2O_8$ and UV/TiO_2/$NaBrO_3$ systems involved $^\bullet OH$, as in UV/TiO_2; however, direct oxidation by photogenerated holes in UV/TiO_2/oxidant was probably significant. In UV/TiO_2/$NaIO_4$, the decolorization rate declined by about half when 1.2 g/L of ethanol was added. This suggested that decolorization proceeded primarily via $^\bullet OH$, but $O^{\bullet-}$, $IO_3{}^\bullet$, $IO_4{}^\bullet$, O_3 and photogenerated holes could also be involved in UV/TiO_2/$NaIO_4$.

4. Conclusions

This investigation studied how pH, oxidant dosage and the addition of ethanol affected decolorization of RB5 using UV/oxidant systems. The effects of oxidant addition on RB5 decolorization by UV/TiO_2 were evaluated. RB5 decolorization rates by UV/TiO_2 and UV/oxidant increased as pH was decreased. Increasing the ionic strength of the aqueous phase by NaCl drove RB5 to the liquid–solid interface in the UV/TiO_2 system; therefore, decolorization rate increased. Oxidants H_2O_2 and $NaIO_4$ when present at high concentrations scavenged $^\bullet OH$ in the UV/oxidant system; accordingly, optimal doses of these compounds existed for UV/H_2O_2 and UV/$NaIO_4$ systems. In UV/$Na_2S_2O_8$ and UV/$NaBrO_3$ systems, $^\bullet OH$ was not scavenged; therefore, decolorization rates increased with increasing oxidant doses. An oxidant functioned both as an oxidant and as an electron scavenger in UV/TiO_2/oxidant systems. Decolorization rates using UV/TiO_2/oxidant exceeded those using UV/TiO_2, with UV/TiO_2/$NaIO_4$ demonstrating fastest decolorization. In UV/TiO_2/oxidant systems, decolorization reaction involved $^\bullet OH$, and it probably involved photogenerated holes in direct oxidation.

Acknowledgments

The authors would like to thank the National Science Council of the Republic of China, Taiwan, for financial support of this research under Contract No. NSC 98-2221-E-212-002-MY3. Ms. Jhan of Da-Yeh University is appreciated for performing some of the experiments.

References

[1] C. Lee, J. Yoon, Application of photoactivated periodate to the decolorization of reactive dye: reaction parameters and mechanism, J. Photochem. Photobiol. A: Chem. 165 (2004) 35–41.

[2] I.K. Konstantinou, T.A. Albanis, TiO_2-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations – a review, Appl. Catal. B: Environ. 49 (2004) 1–14.

[3] S. Irmak, E. Kusvuran, O. Erbatur, Degradation of 4-chloro-2-methylphenol in aqueous solution by UV irradiation in the presence of titanium dioxide, Appl. Catal. B: Environ. 54 (2004) 85–91.

[4] L. Ravichandran, K. Selvam, M. Swaminathan, Effect of oxidants and metal ions on photodefluoridation of pentafluorobenzoic acid with ZnO, Sep. Purif. Technol. 56 (2007) 192–198.

[5] K. Selvam, M. Muruganandham, I. Muthuvel, M. Swaminathan, The influence of inorganic oxidants and metal ions on semiconductor sensitized photodegradation of 4-fluorophenol, Chem. Eng. J. 128 (2007) 51–57.

[6] A. Syoufian, K. Nakashima, Degradation of methylene blue in aqueous dispersion of hollow titania photocatalyst: study of reaction enhancement by various electron scavengers, J. Colloid Interface Sci. 317 (2008) 507–512.

[7] N. Kashif, F. Ouyang, Parameters effect on heterogeneous photocatalysed degradation of phenol in aqueous dispersion of TiO_2, J. Environ. Sci. 21 (2009) 527–533.

[8] P. Pekakis, N.P. Xekoukoulotakis, D. Mantzavinos, Treatment of textile dyehouse wastewater by TiO_2 photocatalysis, Water Res. 40 (2006) 1276–1286.

[9] C.H. Wu, Photodegradation of toluic acid isomers by UV/TiO_2, React. Kinet. Catal. Lett. 90 (2007) 301–308.

[10] C.H. Wu, C.Y. Kuo, P.K.A. Hong, Effects of operational parameters on decolorization of C.I. Reactive Black 5 in UV/TiO_2 system, Water Sci. Technol., submitted for publication.

[11] R.M.C. Silverstein, G.C. Basdler, G.C. Morrill, Spectrophotometric Identification of Organic Compounds, Wiley, New York, 1991.

[12] N. Daneshvar, D. Salari, A.R. Khataee, Photocatalytic degradation of azo dye acid red 14 in water: investigation of the effect of operational parameters, J. Photochem. Photobiol. A: Chem. 157 (2003) 111–116.

[13] N. Daneshvar, D. Salari, A.R. Khataee, Photocatalytic degradation of azo dye acid red 14 in water on ZnO as an alternative catalyst to TiO_2, J. Photochem. Photobiol. A: Chem. 162 (2004) 317–322.

[14] S. Lucas, J.A. Peres, Decolorization of the azo dye Reactive Black 5 by Fenton and photo-Fenton oxidation, Dyes Pigments 71 (2006) 236–244.

[15] C.H. Wu, Effects of operational parameters on the decolorization of C.I. Reactive Red 198 in UV/TiO_2-based systems, Dyes Pigments 77 (2008) 31–38.

[16] C.H. Wu, Photodegradation of C.I. Reactive Red 2 in UV/TiO_2-based systems: effects of ultrasound irradiation, J. Hazard. Mater. 167 (2009) 434–439.

[17] N.H. Ince, G. Tezcanli, Reactive dyestuff degradation by combined sonolysis and ozonation, Dyes Pigments 49 (2001) 145–153.

[18] D.E. Kritikos, N.P. Xekoukoulotakis, E. Psillakis, D. Mantzavinos, Photocatalytic degradation of Reactive Black 5 in aqueous solutions: effect of operating conditions and coupling with ultrasound irradiation, Water Res. 41 (2007) 2236–2246.

[19] K.H. Wang, Y.H. Hsieh, C.H. Wu, C.Y. Chang, The pH and anion effects on the heterogeneous photocatalytic degradation of o-methylbenzoic acid in TiO_2 aqueous suspension, Chemosphere 40 (2000) 389–394.

[20] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ($OH^\bullet/O^{\bullet-}$) in aqueous solution, J. Phys. Chem. Ref. Data 17 (1988) 513–886.

[21] G.P. Anipsitakis, D.D. Dionysiou, Transition metal/UV-based advanced oxidation technologies for water decontamination, Appl. Catal. A: Environ. 54 (2004) 155–163.

[22] H. Kusic, N. Koprivanac, A.L. Bozic, I. Selanec, Photo-assisted Fenton type processes for the degradation of phenol: a kinetic study, J. Hazard. Mater. 136 (2006) 632–644.

[23] M. Tokumura, A. Ohta, H.T. Znad, Y. Kawase, UV light assisted decolorization of dark brown colored coffee effluent by photo-Fenton reaction, Water Res. 40 (2006) 3775–3784.

[24] K.L. Ivanov, E.M. Glebov, V.F. Plyusnin, Y.V. Ivanov, V.P. Grivin, N.M. Bazhin, Laser flash photolysis of sodium persulfate in aqueous solution with addition of dimethylformamide, J. Photochem. Photobiol. A: Chem. 133 (2000) 99–104.

[25] Z. Zuo, Y. Katsumura, Formation of hydrated electron and BrO_3(radical from laser photolysis of $BrO_3{}^-$ aqueous solution, J. Chem. Soc., Faraday Trans. 94 (1998) 3577–3580.

[26] L.K. Weavers, I. Hao, M.R. Hofmann, Degradation of triethanolamine and chemical oxygen demand reduction in wastewater by photoactivated periodate, Water Environ. Res. 69 (1997) 1112–1119.

[27] S. Qourzal, N. Barka, M. Tamimi, A. Assabbane, Y. Ait-Ichou, Photodegradation of 2-naphthol in water by artificial light illumination using TiO_2 photocatalyst:

identification of intermediates and the reaction pathway, Appl. Catal. A: Gen. 334 (2008) 386–393.

[28] E. Bizani, K. Fytianos, I. Poulios, V. Tsiridis, Photocatalytic decolorization and degradation of dye solutions and wastewaters in the presence of titanium dioxide, J. Hazard. Mater. 136 (2006) 85–94.

[29] W.A. Sadik, Effect of inorganic oxidants in photodegradation of an azo dye, J. Photochem. Photobiol. A: Chem. 191 (2007) 132–137.

[30] B. Gozmen, M. Turabik, A. Hesenov, Photocatalytic degradation of Basic Red 46 and Basic Yellow 28 in single and binary mixture by UV/TiO_2/periodate system, J. Hazard. Mater. 164 (2009) 1487–1495.