

# Decolorization of Reactive Red 2 by advanced oxidation processes: Comparative studies of homogeneous and heterogeneous systems

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Received 18 March 2005; received in revised form 3 August 2005; accepted 9 August 2005

Available online 22 September 2005

## Abstract

This study investigated the decolorization of the Reactive Red 2 in water using advanced oxidation processes (AOPs): UV/TiO<sub>2</sub>, UV/SnO<sub>2</sub>, UV/TiO<sub>2</sub> + SnO<sub>2</sub>, O<sub>3</sub>, O<sub>3</sub> + MnO<sub>2</sub>, UV/O<sub>3</sub> and UV/O<sub>3</sub> + TiO<sub>2</sub> + SnO<sub>2</sub>. Kinetic analyses indicated that the decolorization rates of Reactive Red 2 could be approximated as pseudo-first-order kinetics for both homogeneous and heterogeneous systems. The decolorization rate at pH 7 exceeded pH 4 and 10 in UV/TiO<sub>2</sub> and UV/TiO<sub>2</sub> + SnO<sub>2</sub> systems, respectively. However, the rate constants in the systems (including O<sub>3</sub>) demonstrated the order of pH 10 > pH 7 > pH 4. The UV/TiO<sub>2</sub> + SnO<sub>2</sub> and O<sub>3</sub> + MnO<sub>2</sub> systems exhibited a greater decolorization rate than the UV/TiO<sub>2</sub> and O<sub>3</sub> systems, respectively. Additionally, the promotion of rate depended on pH. The variation of dye concentration influenced the decolorization efficiency of heterogeneous systems more significant than homogeneous systems. Experimental results verified that decolorization and desulfuration occurred at nearly the same rate. Moreover, the decolorization rate constants at pH 7 in various systems followed the order of UV/O<sub>3</sub> ≥ O<sub>3</sub> + MnO<sub>2</sub> ≥ UV/O<sub>3</sub> + TiO<sub>2</sub> + SnO<sub>2</sub> > O<sub>3</sub> > UV/TiO<sub>2</sub> + SnO<sub>2</sub> ≥ UV/TiO<sub>2</sub> > UV/SnO<sub>2</sub>.

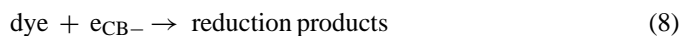
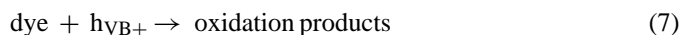
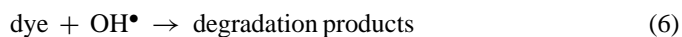
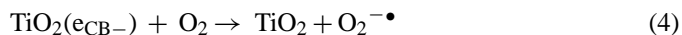
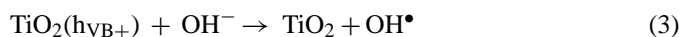
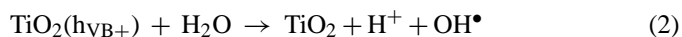
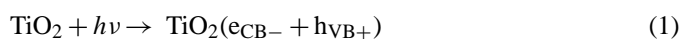
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**Keywords:** Reactive Red 2; Advanced oxidation processes; TiO<sub>2</sub>; SnO<sub>2</sub>; O<sub>3</sub>; MnO<sub>2</sub>; Decolorization

## 1. Introduction

The strong color of textile effluent creates both environmental and aesthetic problems. Azo dyes, which contain one or more azo bonds, are the most widely used synthetic dyes and generally are major pollutants in dye wastewaters. Due to their toxicity and slow degradation, these dyes are classified as environmentally hazardous materials. Research and development of advanced oxidation processes (AOPs) for textile effluent have made significant progress during recent years, particularly the TiO<sub>2</sub>- and O<sub>3</sub>-based processes [1–10]. AOPs primarily involve the generation of a very powerful and non-selective oxidizing agent, the hydroxyl radical (OH•), for destroying hazardous pollutants. The principle of photocatalytic degradation is well known since UV illumination onto a photocatalyst excites to produce an electron and hole pair with a high-energy state, which migrate to the particle surface and initiate various chemical redox reactions [11]. The previous literature has discussed the detailed mecha-

nism of UV/TiO<sub>2</sub> [12] and the reactions causing dye degradation can be summarized as follows [6]:



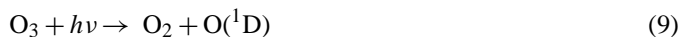
However, the rapid recombination of photoproduced electrons and holes in semiconductors significantly reduces photocatalytic efficiency. To enhance the photocatalytic efficiency of semiconductors, Serpone et al. [13] proposed an interparticle electron transfer process (IPET), which couples two semiconductors with different redox energy levels to increase charge

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separation for the corresponding conduction and valance bands. This process can enhance photocatalytic reaction efficiency [8,13,14].

The literature has reported ozonation of water with or without UV [7,10,15–17]. O<sub>3</sub> may attack the dyes via two different reaction pathways: (1) direct ozonation by the ozone molecule and (2) radical ozonation by highly oxidative free radicals such as hydroxyl radicals, which are formed by ozone decomposition in the aqueous solution [16]. However, this method can be costly owing to the production cost of O<sub>3</sub> and also because of the low solubility in aqueous solutions. These difficulties have stimulated research on how to improve ozonation efficiency for various applications, such as UV/O<sub>3</sub> [7] and catalytic ozonation [18,19]. Combining O<sub>3</sub> with UV achieves a net enhancement of dyes degradation due to direct and indirect production of hydroxyl radicals following O<sub>3</sub> decomposition and H<sub>2</sub>O<sub>2</sub> formation, respectively [15]:



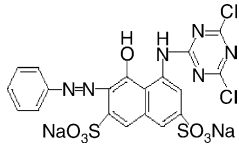
UV, TiO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> can promote the degradation of Reactive Red 2 by photocatalytic oxidation [20]. Neppolian et al. [21] performed the photocatalytic degradation of Reactive Yellow 17, Reactive Red 2 and Reactive Blue 4 using TiO<sub>2</sub>, ZnO, ZrO<sub>2</sub>, WO<sub>3</sub> and CdS. CdS is less active than TiO<sub>2</sub> and ZnO. ZrO<sub>2</sub> and WO<sub>3</sub> are not associated with any significant photodegradation of the dyes. Hu et al. [5] verified that decolorization and desulfuration occurred at almost the same rate in the first step of the photodegradation of Reactive Red 2. Although several works have compared the degradation efficiency of various azo dyes using different commercial or synthetic photocatalysts [5,20,21], comparisons of homogeneous and heterogeneous advanced oxidation systems for the decolorization of azo dyes has attracted relatively little attention. Accordingly, the present study utilized TiO<sub>2</sub>, SnO<sub>2</sub> and O<sub>3</sub> as catalysts to degrade Reactive Red 2. The decolorization efficiencies of various systems were compared. This work investigated the effect of IPET on decolorizing azo dye in the suspension of coupled-photocatalyst and the influence of MnO<sub>2</sub> in the O<sub>3</sub> systems. Moreover, the influence of decolorization efficiency by the variation of dye concentration in homogeneous and heterogeneous systems was also evaluated. Finally, the experiments with chloride ions additives were performed to determine the effects of chloride ions concentration in the UV/O<sub>3</sub> system.

## 2. Materials and methods

### 2.1. Materials

TiO<sub>2</sub> was obtained from Degussa P-25 and SnO<sub>2</sub> was purchased from Riedel-de Haen. The photocatalysts were used directly without treatment. The model azo dye Reactive Red 2, obtained from Aldrich Chemical Company, was used with-

Table 1  
Structure and properties of Reactive Red 2 (Wu [8])

C.I. number	18200
Structure	
Formula	C <sub>19</sub> H <sub>10</sub> Cl <sub>2</sub> N <sub>6</sub> Na <sub>2</sub> O <sub>7</sub> S <sub>2</sub>
Molecular weight (g/mol)	615
λ <sub>max</sub> (nm)	538

out further purification. Table 1 summarizes the structure and properties of Reactive Red 2 [8]. For the supply of chloride ions, sodium chloride (Merck) was chosen. Other experimental chemicals were analytical grade. Water used was deionized and double distilled with MINIQ. A dielectric barrier discharge (DBD) reactor was used for ozone generation. Moreover, a stainless steel wire (5.0 mm diameter) as inner electrode was suspended along the axis of a Pyrex-glass tube (inner diameter: 20.0 mm). The effective length of the DBD reactor was 137 mm. Glass pellets with a diameter of 5 mm were used as the packing materials, and were placed in the plasma region between two electrodes. High voltage was applied to the inner electrodes. The DBD reactor employed the same power consumption (8 W) under a gas flow rate of 500 ml/min. The ozone feeding then was fixed at 2060 ppm in this work. The schematic diagram of the ozone generator and photoreactor was presented as Fig. 1. The inner diameter and height of the photoreactor were 143 and 230 mm, and those of the quartz tube were 36 and 210 mm, respectively.

### 2.2. Decolorization experiments

Decolorization experiments were performed in a 3-l hollow cylindrical glass reactor. The inner tube was made of quartz with an 8 W, 365 nm UV-lamp (Philips) placed inside it to provide the irradiation source. Light intensity of the UV-lamp was 4.32 mW/cm<sup>2</sup>. In heterogeneous systems, the total photocatalyst used was 0.5 g/l in all experiments. In the coupled systems, the weight ratio of photocatalyst was 1:1. The reaction system was stirred constantly at 300 rpm and aerated air at a flow rate of 500 ml/min to keep the photocatalysts suspended. The Reactive Red 2 concentration was 20 ppm in all experimental runs, and the solution pH was controlled at 4, 7 or 10 using HNO<sub>3</sub> and NaOH via an automatic titrator. A 15-ml aliquot was withdrawn from the photoreactor at pre-determined intervals. The photocatalyst suspension was separated by centrifugation at 5000 rpm for 10 min, then filtrated using a 0.22 μm filter. Decolorization of Reactive Red 2 was detected using a spectrophotometer (HACH DR/4000U) at 538 nm. Additionally, anion concentration was detected via ionic chromatography (Metrohm 790 Personal IC, column: Metrosep A Supp 5) to determine the sulfate and chloride dissociation concentrations during decolorization. Vaporization, adsorption, and direct photolysis reactions were also conducted to compare the decolorization efficiency of Reactive Red 2 with that in photocatalytic reactions. In O<sub>3</sub>-base systems,

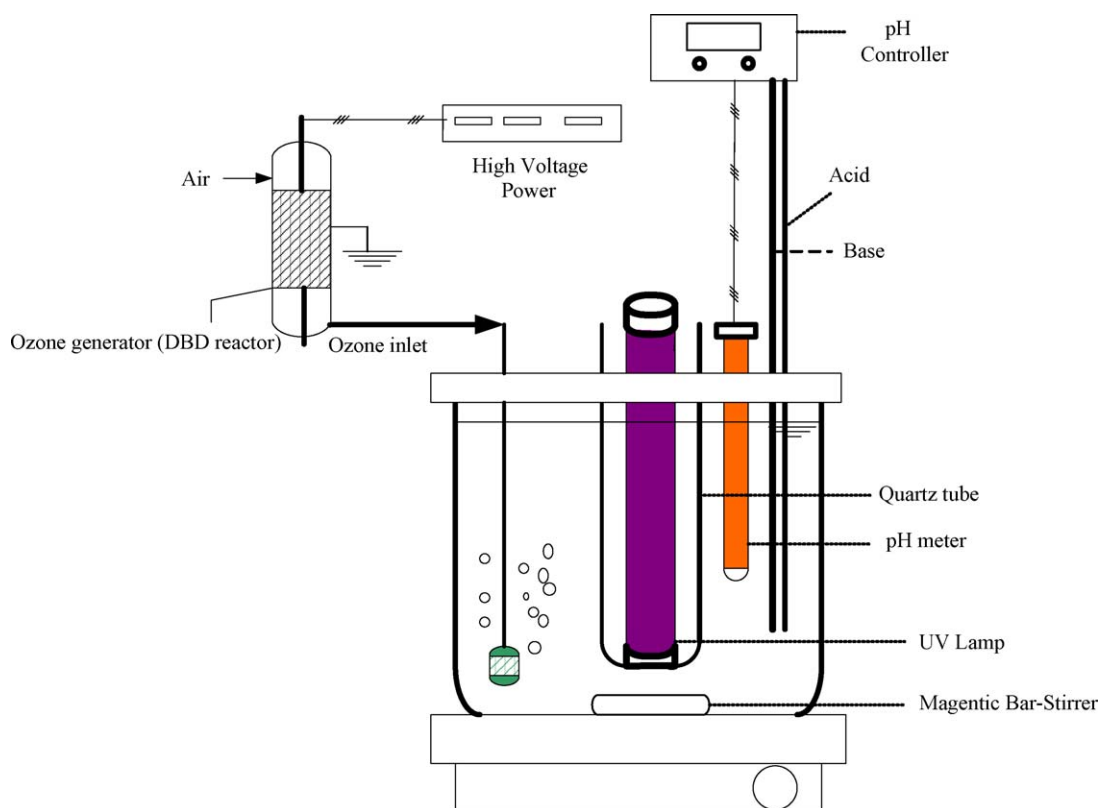


Fig. 1. Diagram of the ozone generator and photoreactor.

O<sub>3</sub> was aerated into the reactor at a flow rate of 500 ml/min. Except for no photocatalyst being added, the other procedures and agents were the same as for heterogeneous systems.

### 3. Results and discussion

#### 3.1. Decolorization of azo dye in heterogeneous and homogeneous systems

Owing to no significant degradation occurring in the vaporization, adsorption, and direct photolysis reactions, the disappearance of Reactive Red 2 could be attributed to photocatalytic reactions. Fig. 2 shows the decolorization efficiency of Reactive Red 2 (20 ppm) by heterogeneous AOPs under different conditions. Fig. 2 reveals that the catalytic activity of SnO<sub>2</sub> in this study was negligible. This phenomenon is attributed to the band

gap energy (4.13 eV) of SnO<sub>2</sub>, which is insufficient for initiating photocatalytic reaction after UV irradiation (365 nm) [8]. Fig. 3 shows the decolorization efficiency of Reactive Red 2 by the O<sub>3</sub>-based processes at different pH. Plotting ln(C<sub>0</sub>/C) against time provides the decolorization rate constants (*k*) (Fig. 4). The *k* values of azo dyes in heterogeneous and homogeneous photocatalytic systems fit a pseudo-first-order kinetic, and several investigations found that the dye decolorization rates generally can be approximated as pseudo-first-order kinetics [1,3,5,6,8]. The decolorization efficiency of heterogeneous and homogeneous photocatalytic systems thus can be compared via the *k* values (Table 2).

In heterogeneous photocatalytic systems, the decolorization rate at pH 7 exceeded that at pH 4 and 10 in UV/TiO<sub>2</sub> and UV/TiO<sub>2</sub> + SnO<sub>2</sub> systems, respectively (Table 2). Interpreting how pH influences dye decolorization efficiency in heteroge-

Table 2  
Decolorization rate constants (*k*, h<sup>-1</sup>) of Reactive Red 2 in different systems

Systems	pH 4		pH 7		pH 10	
	<i>k</i>	<i>r</i> <sup>2</sup>	<i>k</i>	<i>r</i> <sup>2</sup>	<i>k</i>	<i>r</i> <sup>2</sup>
UV/TiO <sub>2</sub>	0.29	0.994	0.33	0.983	0.29	0.982
UV/SnO <sub>2</sub>	< 0.01	–	< 0.01	–	< 0.01	–
UV/TiO <sub>2</sub> + SnO <sub>2</sub>	0.20	0.987	0.34	0.996	0.32	0.981
O <sub>3</sub>	1.84 (2.68)	0.975, 0.984	3.55	0.902	7.63 (7.79)	0.994, 0.885
O <sub>3</sub> + MnO <sub>2</sub>	4.51	0.986	5.36	0.938	6.13	0.998
UV/O <sub>3</sub>	5.23	0.974	5.71	0.985	8.38	0.996
UV/O <sub>3</sub> + TiO <sub>2</sub> + SnO <sub>2</sub>	5.17 (4.99)	0.983, 0.994	5.20	0.924	8.31 (8.33)	0.996, 0.930

Note: Values in parentheses denote the dissociation rate constants of sulfate in different reaction systems.

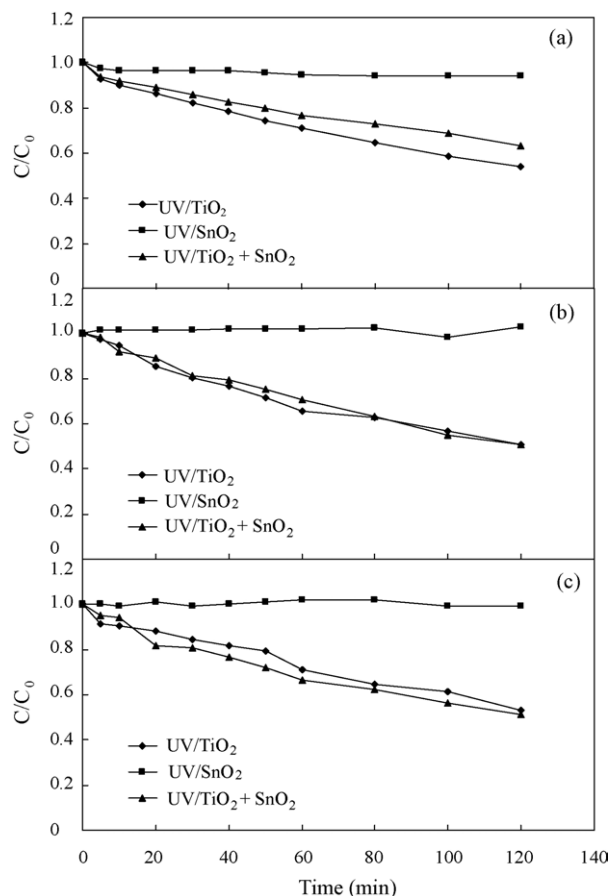


Fig. 2. Decolorization of Reactive Red 2 (20 ppm) by heterogeneous AOPs under different conditions: (a) pH 4, (b) pH 7 and (c) pH 10 (total photocatalyst = 0.5 g/l and  $T = 25^\circ\text{C}$ ) (b) and (c) cited from Wu [8]).

neous systems is very difficult owing to its multiple roles. The pH influences not only the surface properties of the photocatalyst, but also dye dissociation and OH radical formation. The point of zero charge (pzc) of  $\text{TiO}_2$  (Degussa P25) is at pH 6.8. Moreover, the photocatalyst surface is charged positively under  $\text{pH} < \text{pH}_{\text{pzc}}$ . The azo dye used in this study was anionic dye, and was negatively charged owing to the sulfonate groups under experimental conditions. Accordingly, electrostatic interactions between the photocatalyst surface and dye anions lead to adsorption formation at low pH. In contrast, little adsorption formed on the surfaces of  $\text{TiO}_2$  at pH 10. However, in alkaline solution OH radicals can be more easily generated by oxidizing more hydroxide ions available on the photocatalyst surface, thus enhancing the process efficiency [2]. Thereby, the Reactive Red 2 decolorization efficiency by UV/ $\text{TiO}_2 + \text{SnO}_2$  was  $\text{pH } 7 > \text{pH } 10 > \text{pH } 4$ . Because several reaction mechanisms can contribute to dye decolorization, for example OH radical attack, direct oxidation by the positive holes, and direct reduction by the electrons, the effect of pH on decolorization efficiency differed from that of photocatalysts and photodegradation model substrates [8].

Comparing the results listed in Table 2 could demonstrate that IPET significantly improved dye decolorization efficiency under alkaline conditions. At pH 10, the  $k$  value of Reactive Red 2 for UV/ $\text{TiO}_2 + \text{SnO}_2$  ( $0.32 \text{ h}^{-1}$ ) was larger than that of UV/ $\text{TiO}_2$

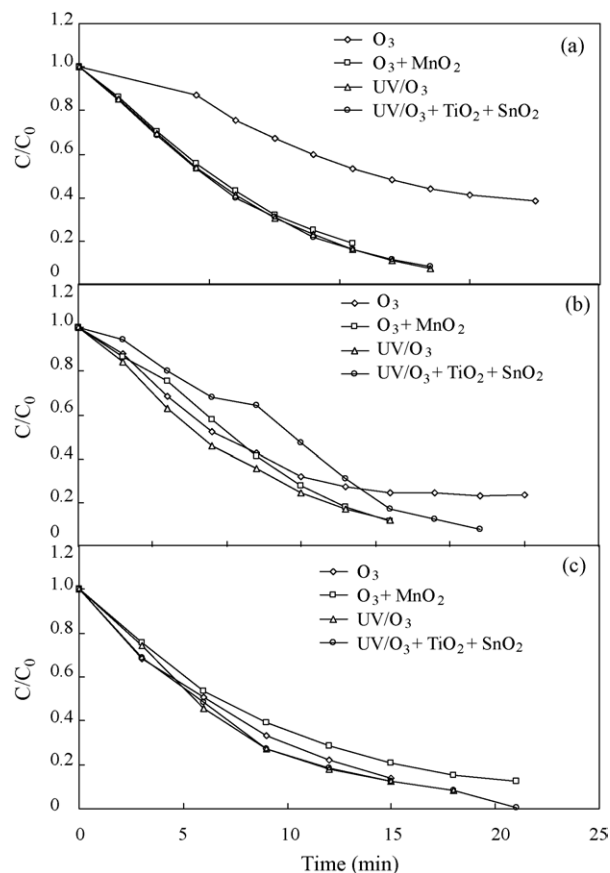


Fig. 3. Decolorization of Reactive Red 2 (20 ppm) by the  $\text{O}_3$ -based processes under different conditions: (a) pH 4, (b) pH 7 and (c) pH 10 (total photocatalyst = 0.5 g/l,  $\text{O}_3$  flow rate = 500 ml/min and  $T = 25^\circ\text{C}$ ).

( $0.29 \text{ h}^{-1}$ ) and UV/ $\text{SnO}_2$ . The improvement in charge separation achieved by coupling two semiconductor systems with different energy levels increases the rate of photocatalytic degradation. Several researchers have demonstrated that the photocatalytic activity of the coupled semiconductor system exceeded that of single semiconductor systems [8,13,14]. Although  $\text{SnO}_2$  exhibited low activity because the UV light energy was insufficient to excite it in a single semiconductor system,  $\text{SnO}_2$  acted as a suitable photogenerated-electrons scavenger in the coupled semiconductor system.

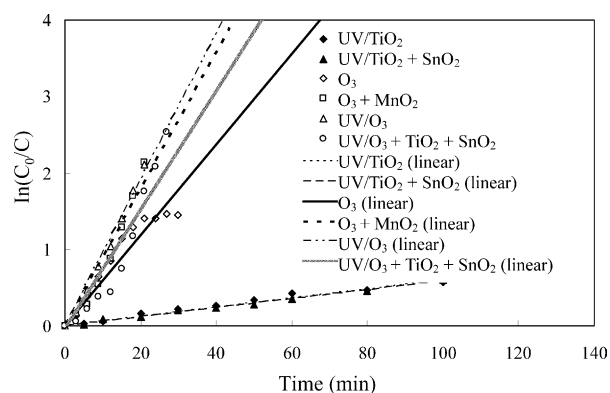


Fig. 4. The pseudo-first-order rate constants of different systems at pH 7.

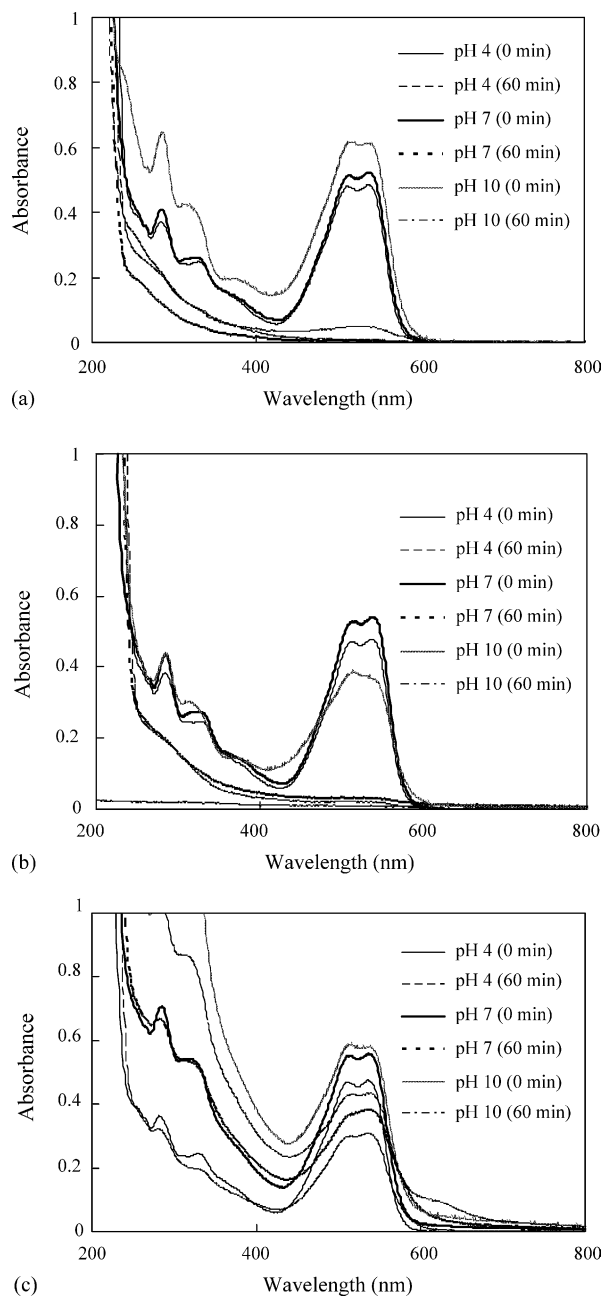


Fig. 5. UV-vis spectral changes of Reactive Red 2 (20 ppm) in various systems: (a) UV/O<sub>3</sub>, (b) O<sub>3</sub> + MnO<sub>2</sub> and (c) UV/TiO<sub>2</sub> + SnO<sub>2</sub> (total photocatalyst = 0.5 g/l, O<sub>3</sub> flow rate = 500 ml/min, reaction time = 60 min and T = 25 °C).

The absorption spectral changes of Reactive Red 2 in UV/O<sub>3</sub>, O<sub>3</sub> + MnO<sub>2</sub> and UV/TiO<sub>2</sub> + SnO<sub>2</sub> systems are displayed in Fig. 5. Reactive Red 2 showed a major absorption peak at 538 nm and it decreased after 60 min photocatalytic reaction. The main absorption peak declined, but some intermediates may have been generated after photocatalytic reaction but this study did not further elucidate this possibility. However, the EC 50 values, after the decolorization of the solution of Reactive Red 2, indicated that the intermediates produced in photocatalytic degradation were not toxic [5,20].

In the O<sub>3</sub>-based processes, decolorization rate constants in various systems followed the order UV/O<sub>3</sub> ≥ UV/O<sub>3</sub> +

TiO<sub>2</sub> + SnO<sub>2</sub> > O<sub>3</sub> + MnO<sub>2</sub> > O<sub>3</sub> and the pH effects illustrated the trend pH 10 > pH 7 > pH 4 (Table 2). The solution pH alters the chemical composition of the ozone; for example OH radicals were formed from ozone decomposition at high pH, while the molecular ozone remains the same as for main oxidant at a low pH. Alaton et al. [4] indicated that increasing the ozonation system pH would increase the OH radical production rate because of the following reactions:



Ozone has oxidation potential of 2.07 V, while the OH radical has oxidation potential of 2.80 V; notably direct oxidation is slower than radical oxidation. Therefore, the *k* values of dye increased with the pH [1,9].

Ozonation combined with UV radiation is considered a more effective process for remove organics than ozonation alone. The combined process is more effective because UV radiation enhances the ozone decomposition, yielding freer OH radicals and thus producing a higher ozonation rate. The *k* value of Reactive Red 2 at pH 4 for UV/O<sub>3</sub> (5.23 h<sup>-1</sup>) significantly exceeded that for O<sub>3</sub> (1.84 h<sup>-1</sup>). The ozonation process in the acid condition mainly occurs via the direct oxidation reaction, which is selective. Accordingly, UV promotion is more significant in the acidic than in the alkaline condition. Several researches also indicated that UV improved ozonation efficiency [7,10,15]. However, Shu and Huang [17] demonstrated UV did not significantly enhance the degradation ability of the ozonation reaction, since UV light is highly absorbed by azo dyes, only limited amounts of free radicals can be produced to decompose azo dyes.

The *k* value of UV/O<sub>3</sub> exceeded those of UV/O<sub>3</sub> + TiO<sub>2</sub> + SnO<sub>2</sub> in the experimental conditions. This finding can be explained as follows: a significant quantity of UV light may be absorbed by the photocatalyst particles, and thus reduces the decolorization efficiency; that is a UV-screening effect of photocatalyst particles [20]. Restated, the path length of photons entering the solution decreased with increasing concentration of photocatalyst particles. Since the decolorization ability of UV/O<sub>3</sub> exceeded that of UV/TiO<sub>2</sub>, this effect reduces the photoactivity for OH radical formation.

Except for the UV light enhancing the efficiency of ozonation, several investigations also reported that a heterogeneous catalytic ozonation process achieved similar promotion of ozonation [18,19]. This study found that MnO<sub>2</sub> catalytic ozonation of Reactive Red 2 at pH 4 had a greater *k* value than ozonation alone, but catalytic efficiency is not observed at pH 10. The experimental results indicated that the solution pH is a dominant influence on MnO<sub>2</sub> catalytic ozonation. The *k* value of Reactive Red 2 increases clearly when ozonation at acid condition in the presence of MnO<sub>2</sub> might due to a surface manganese-dye complex, which is easily decolorized by ozone. The characteristics of the MnO<sub>2</sub> catalytic ozonation can be attributed to the formation of surface complexes that are oxidized by dissolved ozone also



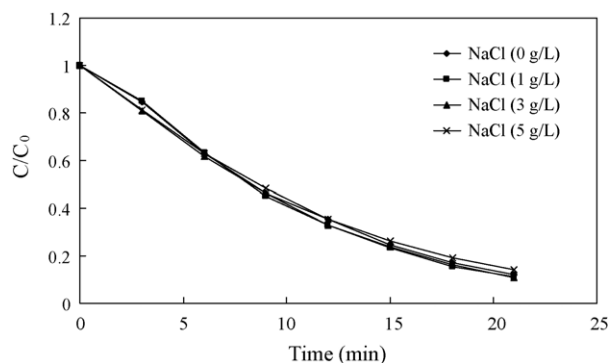


Fig. 6. The effect of NaCl addition in the UV/O<sub>3</sub> system (Reactive Red 2 = 20 ppm, O<sub>3</sub> flow rate = 500 ml/min, pH 7 and T = 25 °C).

having been proposed by previous studies [18,19]. Andreozzi et al. [18] found that the  $\text{pH}_{\text{pzc}}$  of MnO<sub>2</sub> was 5.6 and MnO<sub>2</sub> exhibited almost no catalytic activity during oxalic acid ozonation at pH exceeding the  $\text{pH}_{\text{pzc}}$  of MnO<sub>2</sub>.

Fig. 6 presents the effect of NaCl concentration in the UV/O<sub>3</sub> system at pH 7. The experimental results displayed that the decolorization efficiency was nearly the same in the NaCl concentration between 0 and 5 g/l. The results of homogeneous systems differed from those of heterogeneous systems. Wang et al. [22] indicated that the NaCl and Na<sub>2</sub>SO<sub>4</sub> additions showed inhibitive effect to the reaction at pH 3. For chloride and sulfate ions, Degussa P25 TiO<sub>2</sub> had strong adsorption and reduced the reaction sites due to the presence of Ti-OH<sub>2</sub><sup>+</sup>. In homogeneous systems, the adsorption of chloride ions can be neglected; therefore, the addition of chloride ions did not influence the reaction.

Comparing the *k* values of Reactive Red 2 in TiO<sub>2</sub>- and O<sub>3</sub>-based processes under different conditions reveal that the *k* values in O<sub>3</sub>-based processes exceed those of TiO<sub>2</sub>-base processes by at least one order. Also, the energy inputted into TiO<sub>2</sub>-base processes and ozone alone systems was the same (8 W), nevertheless, the oxidation agent in ozone alone systems (free ozone + OH radicals) might exceed that in TiO<sub>2</sub>-base processes (OH radicals only). The results suggested that the decolorization efficiency per energy input in O<sub>3</sub>-based processes was higher than in TiO<sub>2</sub>-base processes.

### 3.2. Effects of azo dye concentration variation in heterogeneous and homogeneous systems

The effect of initial dye concentration on the rate of dye decolorization was examined by varying the initial concentration of Reactive Red 2 20 and 40 ppm at pH 10 in heterogeneous (UV/TiO<sub>2</sub> + SnO<sub>2</sub>) and homogeneous (O<sub>3</sub> and UV/O<sub>3</sub>) systems, and the results as illustrated in Fig. 7. The pseudo-first-order decolorization rate constant of 20 and 40 ppm Reactive Red 2 was calculated as 0.32 and 0.14 h<sup>-1</sup> in UV/TiO<sub>2</sub> + SnO<sub>2</sub>, 7.63 and 5.53 h<sup>-1</sup> in O<sub>3</sub> and 8.38 and 5.83 h<sup>-1</sup> in UV/O<sub>3</sub>, respectively. It can be found that, as the dye concentration increase, the decolorization rate constant decreases. Several studies have reported similar observations [20,21,23]. This can be explained by two explanations for this phenomenon exists. First, a significant

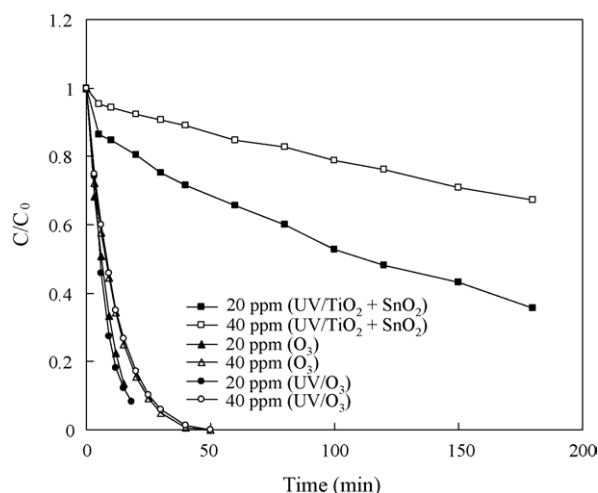


Fig. 7. Decolorization of Reactive Red 2 under different initial dye concentrations and reaction systems (total photocatalyst = 0.5 g/l, O<sub>3</sub> flow rate = 500 ml/min, pH 10 and T = 25 °C).

quantity of UV light may be absorbed by the high concentration dye molecules rather than by the photocatalyst particles, and thus reducing the decolorization efficiency, namely, the dye has a UV-screening effect. Hence, this effect thus reduces the photoactivity of photocatalyst for OH radical formation. Second, there are more dyes and reaction intermediates compete with the OH radicals and the reaction active sites of the photocatalyst in high initial concentration. Since the quantity of photocatalyst is constant, OH radical formation on the photocatalyst surface is also constant. Accordingly, the relative number of OH radicals attacking the dye molecules and its reaction intermediates decreases with increasing in the initial dye concentration. These results imply that as the initial concentration of dye increases, the requirement of photocatalyst needed for decolorization also increases. The effects of the dye and reaction intermediates competing with the OH radicals were similar in heterogeneous (UV/TiO<sub>2</sub> + SnO<sub>2</sub>) and homogeneous (O<sub>3</sub> and UV/O<sub>3</sub>) systems. The UV-screening effect of the dye was the same in heterogeneous and homogeneous systems; however, the UV-screening effect of the photocatalyst was stronger in the heterogeneous systems. Accordingly, the inhibitive effects of a high dye concentration were stronger in the heterogeneous system (Fig. 7). Furthermore, the direct ozonation of dye molecules in homogeneous systems was important in the addition of a high concentration of dye; hence, adding a high dye concentration negligibly inhibited.

### 3.3. Evolution of sulfate dissociation in heterogeneous and homogeneous systems

The temporal evolution of sulfate in heterogeneous (UV/O<sub>3</sub> + TiO<sub>2</sub> + SnO<sub>2</sub>) and homogeneous (O<sub>3</sub>) systems at pH 4 and 10 is displayed in Fig. 8. The *k* values of O<sub>3</sub> (7.63 h<sup>-1</sup>) and UV/O<sub>3</sub> + TiO<sub>2</sub> + SnO<sub>2</sub> (8.31 h<sup>-1</sup>) were similar to the dissociation constants of sulfate in O<sub>3</sub> (7.79 h<sup>-1</sup>) and UV/O<sub>3</sub> + TiO<sub>2</sub> + SnO<sub>2</sub> (8.33 h<sup>-1</sup>) at pH 10, respectively (Table 2). The results verified that decolorization and desul-

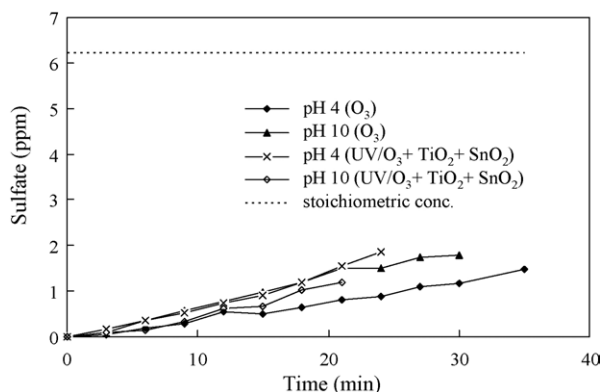


Fig. 8. Dissociated concentration of sulfate during decolorization reaction (Reactive Red 2=20 ppm, total photocatalyst=0.5 g/l, O<sub>3</sub> flow rate = 500 ml/min and  $T = 25^{\circ}\text{C}$ ).

uration occurred at almost the same rates in the first step of photodegradation. Consequently, the initial step of Reactive Red 2 can be proposed to be cleaving the bonds of the C–S in Reactive Red 2, leading to sulfate ion formation. Several studies investigating dyes with sulfonate groups in photocatalytic reactions also indicated that sulfonate group removal is an early step in the degradation process [5,8,20,24–26].

The Reactive Red 2 decolorization converts organic carbon to CO<sub>2</sub> and its intermediates, and while that of nitrogen, sulfur, and chloride heteroatoms are mineralized into inorganic ions. This study detected the formation of inorganic ions during the photocatalytic reaction in heterogeneous and homogeneous systems; however, only sulfate ions were monitored and that was similar to So et al. [20] who degraded the Reactive Red 2 by UV/TiO<sub>2</sub>, and the experimental results revealed that no chloride was obtained.

The stoichiometry dissociation of sulfate for 20 ppm Reactive Red 2 was 6.2 ppm. However, the quantities of sulfate ion released are lower than that expected from stoichiometry both in heterogeneous and homogeneous systems. Two reasons contributed such experimental results. First, sulfate released during decolorization might adsorb on the surface of photocatalyst, thereby, preventing dyes from releasing the expected stoichiometric quantities of sulfate. This study was similar to previous researchers denoted that the quantities of sulfate ions released from stoichiometry were below expectations from stoichiometry [8,24,26]. Such measured results might contribute from the previously observed partially irreversible adsorption of sulfate on the surface of photocatalyst and that had already observed [25]. Second, the sulfur and chloride heteroatoms might bind with intermediates and form sulfur-containing or chloro-containing compounds. Due to the dissociated concentration of sulfate in heterogeneous (UV/O<sub>3</sub> + TiO<sub>2</sub> + SnO<sub>2</sub>) system was greater than that of homogeneous (O<sub>3</sub>) system at pH 4; hence, it was implied that the adsorption of sulfate onto the surface of the photocatalyst was insignificant. Accordingly, this work suggested that the sulfur and chloride heteroatoms of Reactive Red 2 might bind with intermediates and form sulfur-containing or chloro-containing compounds both in heterogeneous and homogeneous systems.

#### 4. Conclusion

This study examined the decolorization of Reactive Red 2 in TiO<sub>2</sub>- and O<sub>3</sub>-based systems under different conditions. The decolorization rate constants of Reactive Red 2 in heterogeneous and homogeneous photocatalytic systems fit a pseudo-first-order kinetics. Moreover, the Reactive Red 2 decolorization efficiency by UV/TiO<sub>2</sub> + SnO<sub>2</sub> was pH 7 > pH 10 > pH 4. Although SnO<sub>2</sub> displayed low activity because the UV light energy was insufficient to excite it in a single semiconductor system, SnO<sub>2</sub> performed as a suitable photogenerated-electrons scavenger in the coupled semiconductor system. In the O<sub>3</sub>-based processes,  $k$  values in various systems followed the order of UV/O<sub>3</sub>  $\geq$  UV/O<sub>3</sub> + TiO<sub>2</sub> + SnO<sub>2</sub>  $\geq$  O<sub>3</sub> + MnO<sub>2</sub> > O<sub>3</sub> and the pH effects exhibited the trend of pH 10 > pH 7 > pH 4. UV radiation enhanced the ozone decomposition, yielding freer OH radicals resulting with higher ozonation rate. The experimental results also confirmed the rates of decolorization and desulfuration were almost identical in the first step of photooxidation. This work found that MnO<sub>2</sub> catalytic ozonation of Reactive Red 2 at pH 4 had a higher  $k$  value than ozonation alone, but catalytic efficiency is not observed at pH 10. This study suggested that the decolorization efficiency per energy input in O<sub>3</sub>-based processes exceeded that of TiO<sub>2</sub>-base processes.

#### Acknowledgement

The authors would like to thank the National Science Council of the Republic of China for financially supporting this research under Contract No. NSC 93-2621-Z-264-001.

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