

## Effects of Combined and Sequential Addition of Dual Oxidants (H<sub>2</sub>O<sub>2</sub>/S<sub>2</sub>O<sub>8</sub><sup>2-</sup>) on the Aqueous Carbofuran Photodegradation

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Carbofuran (2,3-dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate) (CBF) is a widely used insecticide. Traditional methods like hydrolysis and direct photolysis cannot remove CBF effectively. In this study, the photodecay of 0.1 mM CBF in UV/H<sub>2</sub>O<sub>2</sub>, UV/S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, and UV/H<sub>2</sub>O<sub>2</sub>/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> and sequential addition of a second oxidant were studied under UV light at 254 nm. The degradations of CBF follow pseudo-first-order decay kinetics. Direct photolysis was slow, but the corresponding degradation rate was increased with the addition of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) or potassium peroxydisulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>). In the UV/H<sub>2</sub>O<sub>2</sub> reaction, the optimum reaction rate was 0.9841 min<sup>-1</sup> at 10 mM H<sub>2</sub>O<sub>2</sub> (pH 7); however, retardation is observed if H<sub>2</sub>O<sub>2</sub> is overdosed. Such retardation is not observed in the UV/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> system, but a nonlinear increment of removal efficiency is identified. The UV/H<sub>2</sub>O<sub>2</sub>/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> process on the other hand shows the best performance in CBF degradation, but it has a less effective mineralization than that of the sole UV/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> reaction.

**KEYWORDS:** Photolysis; advanced oxidation process; mineralization; endocrine disruptor; carbofuran

### INTRODUCTION

Carbofuran (2,3-dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate) (CBF), one of the derivatives of the carbamate pesticides, is a widely used insecticide and nematicide in agricultural application. More than 5 million pounds of CBF were applied in the United States in 1995 (1). The recommended maximum contamination level for CBF is  $7 \times 10^{-6}$  mM, but the detected CBF concentration in groundwater in different U.S. states is at levels between 1 and  $500 \times 10^{-6}$  mM (2). The use of CBF has become of major concern due to its heavy use and also to its high toxicity. Therefore, it is important to develop the treatment technology for removing CBF. It was known that traditional methods like hydrolysis and microbial degradation could remove CBF, but they were generally ineffective; it was reported that the half-lives of the compound in water ranged from 690 days at pH 5 to 1 week at pH 9 (3).

A technology in water and wastewater treatment using advanced oxidation processes (AOPs) is considered to be fast and effective in this respect; it has shown great potential in the treatment of pollutants and a wide range of applications in groundwater treatment and municipal wastewater sludge destruction (4). It is also considered very effective for the mineralization of a great variety of organic compounds, including refractory organics like herbicides (5), which convert the constituents of organic pollutants into simple, relatively harmless, and inorganic molecules (i.e., CO<sub>2</sub>, H<sub>2</sub>O). The use of AOPs involves combinations of high oxidation-potential sources (H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>), UV irradiation, and/or catalyst (Fe<sup>2+</sup>, Fe<sup>3+</sup>, and

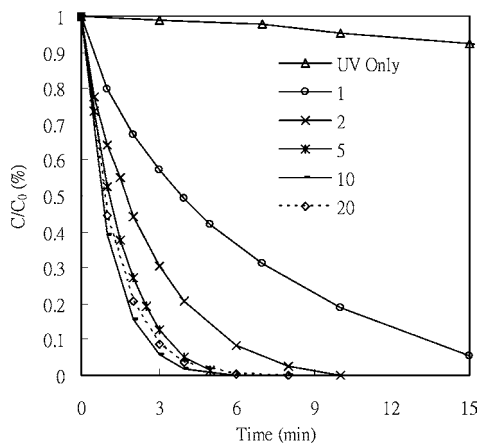
TiO<sub>2</sub>). The aim of these processes is to generate a highly reactive hydroxyl radical (<sup>•</sup>OH), the most powerful oxidizing species after fluorine. It reacts unselectively with most of the organic and inorganic substances present in water.

Some treatment techniques of CBF have been proposed by using ultrasonic irradiation (1), direct photolysis (6), UV/O<sub>3</sub> or Fenton reagent (7), anodic Fenton treatment (AFT) (8), and TiO<sub>2</sub> as a photocatalyst (9). They have shown that AOPs are useful in treating CBF and giving a more effective performance than using single oxidants. They concluded that hydroxyl radical is effective in degrading CBF by using the above AOP processes. However, the information regarding the decay of organics by a new approach, UV/peroxydisulfate or sulfate radical, is very limited. In this study, the treatment performances of CBF using the UV/H<sub>2</sub>O<sub>2</sub>, UV/S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, and UV/H<sub>2</sub>O<sub>2</sub>/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> systems were investigated and compared; in addition, the effect of pH on each process was studied as well, so that a representative conclusion could be realized.

### MATERIALS AND METHODS

The probe CBF (98%) was obtained from Sigma-Aldrich Lab-orchemikalien GmbH. All stock and working solutions including hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, A.R. grade, Asia Pacific Specialty Chemicals Ltd., 30%), potassium peroxydisulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, International Laboratory USA, 99.5%), and acetonitrile [high-performance liquid chromatography (HPLC) grade] were prepared in 18 MΩ deionized distilled water from a Bamstead NANOpure water treatment system. All chemicals were used as received without further purification. For pH adjustment, 0.1 M sulfuric acid and/or 0.1 M sodium hydroxide was used, and all of the experiments were carried out in an air-conditioned room at 24 ± 1 °C.

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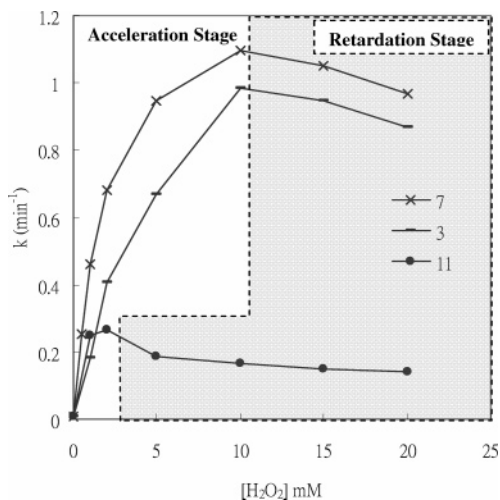
**Figure 1.** UV irradiation of 0.1 mM CBF degradation with different  $\text{H}_2\text{O}_2$  dosages (1–20 mM) at pH 3. The UV light was at 254 nm under a light intensity of  $1.5 \times 10^{-6}$  Einstein  $\text{L}^{-1} \text{s}^{-1}$ .

In the UV photolysis experiments, exactly 500 mL of 0.1 mM CBF mixture was irradiated in a 750 mL (100 mm i.d.  $\times$  130 mm H) quartz beaker with magnetic stirring. The quartz beaker was placed in the center of the UV photoreactor, Rayonet RPR-200 (Southern New England Ultraviolet Co.). The reactor was equipped with eight phosphor-coated low-pressure mercury lamps, emitting 253.7 nm monochromatic UV at a light intensity of  $1.5 \times 10^{-6}$  Einstein  $\text{L}^{-1} \text{s}^{-1}$ . Samples after UV exposure were mixed with an excess of sodium nitride (10) to quench the radicals before the quantification of the probe compound, intermediates, and total organic carbon (TOC).

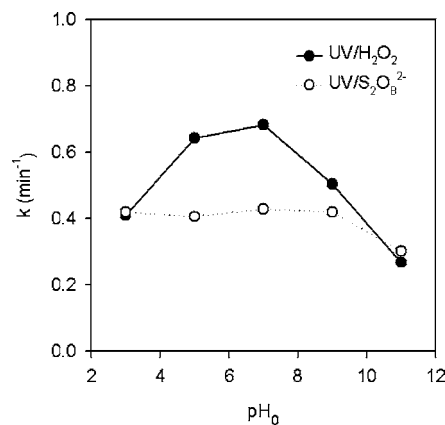
Analysis of CBF degradation was performed by liquid chromatography (LC). The LC system used in this project was Water486. Chromatographic separation was carried out in a reverse phase column (Econosphere C18 5  $\mu\text{m}$ , 250 mm long  $\times$  4.6 mm i.d.) from Alltech (IL). The mobile phase was composed of a mixture of 60% acetonitrile with 40% water. The flow of the mobile phase was adjusted by the Waters 515 HPLC pump at 1 mL  $\text{min}^{-1}$ . Injection samples were made manually using a 250  $\mu\text{L}$  Hamilton syringe (Hamilton, Bonaduz, Switzerland). Analyses of mineralization of CBF were performed by a TOC analyzer. The TOC analyzer used in this project was TOC-5000A (Shimadzu) with an ASI-5000A autosampler (Shimadzu).

## RESULTS AND DISCUSSION

**Rate Constants and pH Dependency for the Photodegradation of CBF by  $\text{H}_2\text{O}_2$ .** Under direct photolysis by UV, only 8 and 57% of 0.1 mM CBF was removed at the irradiation time of 15 and 60 min (data not shown for the latter), respectively. With the aid of 2 mM  $\text{H}_2\text{O}_2$ , however, CBF can be completely degraded within 10 min at pH 3 (see **Figure 1**). The CBF decay rate is strongly dependent on the dosage of  $\text{H}_2\text{O}_2$ , as shown in **Figure 2**; the pseudo-first-order rate constant increased from 0.1825 to 0.9841  $\text{min}^{-1}$  when the  $\text{H}_2\text{O}_2$  concentration increased from 1 to 10 mM, respectively. However, further increasing the  $\text{H}_2\text{O}_2$  dosage beyond 10 mM can retard the reaction. Therefore, two different reaction stages have been identified as follows: (i) the accelerating and (ii) the retardation stages. It has been proved that  $\text{H}_2\text{O}_2$  acts as both promoter and scavenger of hydroxyl radical (11). At low to optimal  $\text{H}_2\text{O}_2$  dosages, hydroxyl radicals are generated and assisted the degradation of CBF (eq 1 and 2). However, at very high  $\text{H}_2\text{O}_2$  dosages, the excess  $\text{H}_2\text{O}_2$  molecules scavenge the valuable hydroxyl radicals in the solution and form a much weaker oxidant hydroperoxyl radical ( $\text{HO}_2^\bullet$ ) (eq 3), which could further scavenge another hydroxyl radical (eq 4) (12). The excessive hydroxyl and hydroperoxyl radicals could also recombine into  $\text{H}_2\text{O}_2$

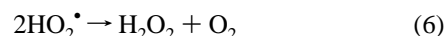
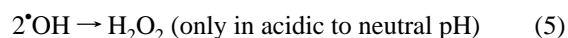
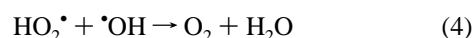
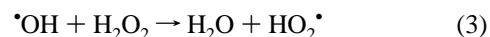


**Figure 2.** Variation of pseudo-first-order rate constants with various  $\text{H}_2\text{O}_2$  concentrations under various initial pH values in UV/ $\text{H}_2\text{O}_2$  system for 0.1 mM CBF degradation.

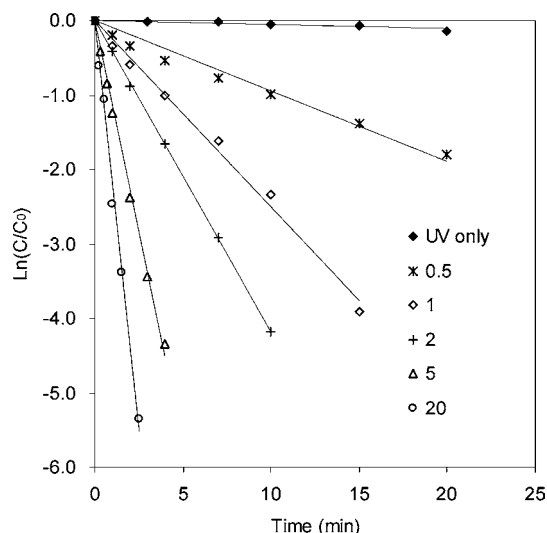


**Figure 3.** Variation of pseudo-first-order rate constants with initial pH values in UV/ $\text{H}_2\text{O}_2$  and UV/ $\text{S}_2\text{O}_8^{2-}$  systems for 0.1 mM CBF degradation. The initial concentrations of  $\text{H}_2\text{O}_2$  and  $\text{S}_2\text{O}_8^{2-}$  were both 2 mM.

(eq 5 and 6) (13), which reduce the overall oxidative power of all oxidants in the solution.



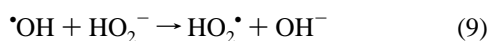
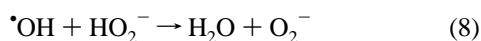
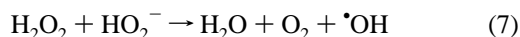
The pH dependency on the CBF photodegradation at 2 mM  $\text{H}_2\text{O}_2$  is summarized in **Figure 3**, where kinetic rate constants at five different initial pH levels were determined and the optimal pH condition was found to be 7. For those reactions moving toward acidic or alkaline pH, their rate constants will gradually decrease and form a hillock pattern. The rate increment from acidic to neutral (i.e., 3–7) pH level is known due to the increase of  $\text{OH}^-$ , which induces a higher generation of  $\text{OH}^\bullet$ , and therefore the degradation efficiency. However, the decreas-



**Figure 4.** Photodecay of 0.1 mM CBF in different  $S_2O_8^{2-}$  concentrations (mM) at pH 3.

ing reaction rate constants at  $pH \geq 7$  can be explained by the following reasons: the instability of  $H_2O_2$  at high pH levels (14). Because of the self-decomposition of  $H_2O_2$  at neutral to high pH,  $O_2$  is the major product and the oxidizing ability of  $O_2$  is trivial as compared to  $\cdot OH$  and/or  $H_2O_2$ . Besides, the self-decomposition of  $H_2O_2$  forms a barrier to the creation of  $\cdot OH$  radical and greatly inhibits the degradation of CBF.

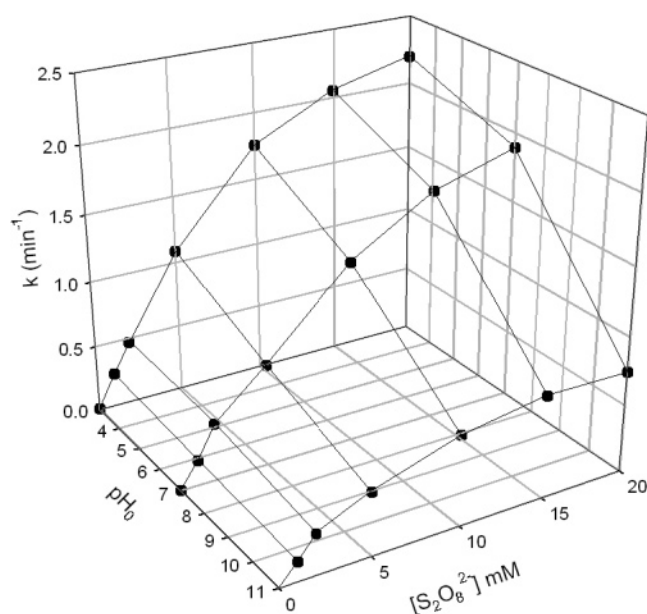
According to Muruganandham and Swaminathan (15), at basic condition,  $HO_2^-$  anion exists as the conjugated base of  $H_2O_2$ . The anion will react with  $\cdot OH$  radical and residual  $H_2O_2$  as indicated in eqs 7–9. Because the reaction rate of  $HO_2^-$  reacted with  $\cdot OH$  is higher than that of  $H_2O_2$  (16), the scavenging effect of  $\cdot OH$  is more prevailing.



Furthermore, the molar extinction coefficient of  $HO_2^-$  upon UV absorption at high pH was higher than that of generating  $\cdot OH$  from the cleavage of  $H_2O_2$  (eq 1). Because of light attenuation, the generation of  $\cdot OH$  was greatly reduced (16).

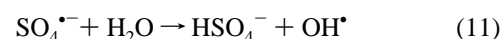
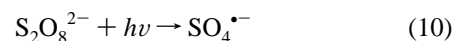
**Rate Constants and pH Dependency for the Photodegradation of CBF by  $S_2O_8^{2-}$ .** Because of the potential quenching effect of using  $H_2O_2$  when the process is not well-controlled (such as overdosing), another oxidant, peroxydisulfate ion ( $S_2O_8^{2-}$ ), has been selected for investigation as an alternative. **Figure 4** demonstrated that the use of  $S_2O_8^{2-}$  instead of  $H_2O_2$  could successfully eliminate the drawback of retardation. The concentration of  $S_2O_8^{2-}$  was found to be an important parameter for the degradation of CBF in the UV/ $S_2O_8^{2-}$  system. The decay of CBF followed pseudo-first-order kinetics and was summarized in **Figure 5**. For different  $S_2O_8^{2-}$  concentrations that increased from 0.5 to 15 mM, the reaction rate constants increased from 0.0907 to 2.0387  $\text{min}^{-1}$ , respectively. This is likely because sulfate radicals and hydroxyl radicals are generated simultaneously and improved the degradation of CBF (17).

Furthermore, when the  $S_2O_8^{2-}$  concentration increased beyond 15 mM, the increment of CBF decay rate slowed down slightly. According to Qiao et al. (13), at higher  $S_2O_8^{2-}$  dosages,

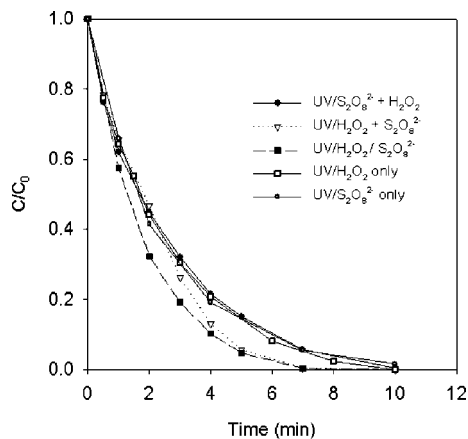


**Figure 5.** Variation of pseudo-first-order rate constants with various  $[S_2O_8^{2-}]$  concentrations under different initial pH values in UV/ $S_2O_8^{2-}$  system for 0.1 mM CBF degradation.

excessive generation of hydroxyl radicals (eqs 10 and 11) would be recombined to form less reactive  $H_2O_2$  (eq 5), which is a known quencher of  $OH\cdot$  radical (eq 3). Therefore, the rate increment of CBF degradation is slightly slowed down at higher  $S_2O_8^{2-}$  dosages. However, such a recombination effect of the radical is likely not very effective due to the low steady-state concentrations of the radicals; higher decay rates of CBF at higher  $S_2O_8^{2-}$  dosages are still expected.



Photodecay rates of CBF at different initial pH levels were also investigated. It was interesting to find that the variation of rate constant pattern at different pH levels was insignificant at low  $S_2O_8^{2-}$  dosages of 2 mM, as shown in **Figure 3**. However, at a higher  $S_2O_8^{2-}$  dosage of 5 mM, the impact of initial pH level to the reaction rate became critical, as shown in **Figure 5**. The highest reaction rate constant was observed at pH 3, and then, the rate decreased with the increase of pH levels. The higher decay performance at low pH might be due to the presence of one of the major decay products of CBF, ammonium ( $NH_4^+$ ). Katsumata et al. (18) reported that  $NH_4^+$  and  $CO_2$  are the decay end products of CBF in photocatalytic oxidation process, where the hydroxyl radical can attack the carbamate group and further attack on the furan ring and lead to the cleavage of ring and demethylation. The aromatic intermediate then further oxidizes through a ring rupturing reaction into aliphatic compounds and degrades to  $NH_4^+$  and  $CO_2$ . At a low pH level, ammonia ( $NH_3$ ) would convert to  $NH_4^+$  since the  $pK_a$  of  $NH_3$  is 9.25. Therefore, at a low pH level,  $NH_4^+$  becomes dominant; it could enhance the decay rate of CBF due to the generated photoproducts (nitrate and nitrite). The  $NH_4^+$  could be photo-oxidized into nitrite ( $NO_2^-$ ) and nitrate ( $NO_3^-$ ) in an oxidizing environment (19); a recent study has shown that photoinduced degradation under the  $NO_3^-/NO_2^-$  system is taking a major role in the fate of pesticides in water (20). Shankar et al. (21) found that the lower the pH level is, the

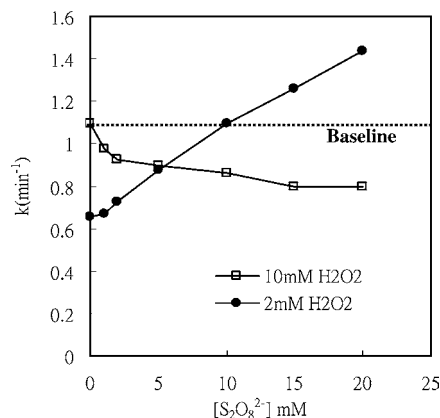


**Figure 6.** Different photo-oxidation systems for 0.1 mM CBF degradation at pH 3. The used dosages of  $\text{H}_2\text{O}_2$  and  $\text{S}_2\text{O}_8^{2-}$  were both 2 mM, if any (+ indicates that the second dose of oxidant is applied sequentially into the system at 2 min).

higher the concentrations of  $\text{NO}_3^-$  and  $\text{NO}_2^-$  are and the faster in degrading herbicide due to the generation of  $\cdot\text{OH}$  radical at high  $\text{NO}_3^-$  concentration (20). The enhancement of CBF decay therefore was observed at a lower pH level especially if the raw oxidant  $\text{S}_2\text{O}_8^{2-}$  is high. Additionally, the hydrolysis of the  $\text{S}_2\text{O}_8^{2-}$  ion in acidic, neutral, and alkaline medium is reported to be different. According to House (22), in general, hydrogen sulfate ( $\text{HSO}_4^-$ ) and  $\text{H}_2\text{O}_2$  can be produced in the hydrolysis of  $\text{S}_2\text{O}_8^{2-}$  (eqs 12 and 13). In acidic medium, the conversion of the product  $\text{H}_2\text{O}_2$  to  $\cdot\text{OH}$  in the presence of UV is a stable and efficient process (with a very low self-decomposition property as indicated before), which indirectly improves the CBF degradation.



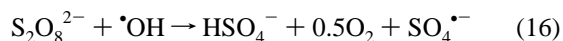
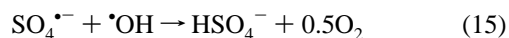
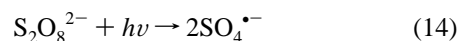
**UV/ $\text{H}_2\text{O}_2$ / $\text{S}_2\text{O}_8^{2-}$  Process.** The reaction rate constants of UV/ $\text{H}_2\text{O}_2$  and UV/ $\text{S}_2\text{O}_8^{2-}$  processes at pH 3 are 0.4127 and 0.4177  $\text{min}^{-1}$ , respectively. This similarity at oxidant concentration, pH, and removal efficiency serves as a good incentive for detailed investigation in the combined UV/ $\text{H}_2\text{O}_2$ / $\text{S}_2\text{O}_8^{2-}$  reaction. **Figure 7** showed that the combined system (UV/ $\text{H}_2\text{O}_2$ / $\text{S}_2\text{O}_8^{2-}$ ) has the best performance in removing CBF (with a rate constant of 0.5841  $\text{min}^{-1}$ ) than the other single oxidant reaction (i.e., UV/ $\text{H}_2\text{O}_2$  and UV/ $\text{S}_2\text{O}_8^{2-}$ ). This is apparently due to the extra addition of oxidants, which can generate more sulfate radical and hydroxyl radical to enhance the CBF degradation. In the UV/ $\text{H}_2\text{O}_2$ / $\text{S}_2\text{O}_8^{2-}$  reaction, the irradiation time for total CBF degradation is reduced to 8 min. However, it should be noted that the dual-oxidant system does not lead to a doubled overall performance; in fact, only about 42% of rate improvement is observed. It is highly possible that interference among different radicals could occur during the photolysis reaction. To verify this hypothesis, different sequences in adding oxidants on the CBF photodegradation were investigated and compared with the combined addition (simultaneously) of both oxidants. In order to investigate the cause of interference by the second oxidant, sequential addition of the second oxidant will be applied when 50% of CBF is removed by the first oxidant. For instance, the UV/ $\text{H}_2\text{O}_2$  process is interrupted by introducing 2 mM  $\text{S}_2\text{O}_8^{2-}$  at 2 min or vice versa.



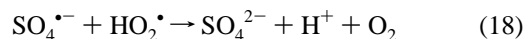
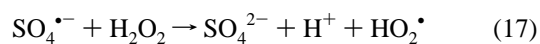
**Figure 7.** Variation of pseudo-first-order rate constants in UV/ $\text{H}_2\text{O}_2$ / $\text{S}_2\text{O}_8^{2-}$  system for 0.1 mM CBF degradation in various  $\text{S}_2\text{O}_8^{2-}$  concentrations with two different initial  $\text{H}_2\text{O}_2$  concentrations (2 and 10 mM) at pH 7.

**Sequential Addition of the Second Oxidant.** The comparison of the sequential addition (i.e.,  $\text{S}_2\text{O}_8^{2-}$  into UV/ $\text{H}_2\text{O}_2$  or  $\text{H}_2\text{O}_2$  into UV/ $\text{S}_2\text{O}_8^{2-}$  systems) and other processes is shown in **Figure 6**, where the reaction rate constants are ranked in descending order: UV/ $\text{H}_2\text{O}_2$ / $\text{S}_2\text{O}_8^{2-}$  > UV/ $\text{H}_2\text{O}_2$  +  $\text{S}_2\text{O}_8^{2-}$  > UV/ $\text{S}_2\text{O}_8^{2-}$  +  $\text{H}_2\text{O}_2$   $\cong$  UV/ $\text{S}_2\text{O}_8^{2-}$   $\cong$  UV/ $\text{H}_2\text{O}_2$ . With the addition of  $\text{S}_2\text{O}_8^{2-}$  into UV/ $\text{H}_2\text{O}_2$  after 2 min of irradiation (UV/ $\text{H}_2\text{O}_2$  +  $\text{S}_2\text{O}_8^{2-}$ ), its slower initial removal can be significantly boosted up and reach the same level of the UV/ $\text{H}_2\text{O}_2$ / $\text{S}_2\text{O}_8^{2-}$  process after 5 min. However, in the reverse case (i.e., the sequential addition of  $\text{H}_2\text{O}_2$  into UV/ $\text{S}_2\text{O}_8^{2-}$  or UV/ $\text{S}_2\text{O}_8^{2-}$  +  $\text{H}_2\text{O}_2$ ), no advantage was observed as compared to the single oxidant systems.

It was known that in the UV/ $\text{S}_2\text{O}_8^{2-}$  process, 2 mol of sulfate radical could be generated by direct photolysis of 1 mol of  $\text{S}_2\text{O}_8^{2-}$  ion (eq 14). However, in the sequential UV/ $\text{H}_2\text{O}_2$  +  $\text{S}_2\text{O}_8^{2-}$  process, abundant hydroxyl radicals, which already existed in the UV/ $\text{H}_2\text{O}_2$  system, could react with the freshly introduced  $\text{S}_2\text{O}_8^{2-}$  ion (eq 16). The  $\text{S}_2\text{O}_8^{2-}$  ion will directly react with  $\cdot\text{OH}$  radical and produce only 1 mol of sulfate radical. This explains why the combined reactions have no doubled enhancement, since the addition of  $\text{S}_2\text{O}_8^{2-}$  cannot produce as much  $\text{SO}_4^{\cdot-}$  as the UV/ $\text{S}_2\text{O}_8^{2-}$  process does (eq 16). In the absence of  $\text{SO}_4^{\cdot-}$  at the early stage, UV/ $\text{H}_2\text{O}_2$  +  $\text{S}_2\text{O}_8^{2-}$  will minimize the recombination effect of useful radicals as indicated in eq 15. A boosting up of the reaction can be observed after the addition of  $\text{S}_2\text{O}_8^{2-}$ .



On the other hand, for the UV/ $\text{S}_2\text{O}_8^{2-}$  +  $\text{H}_2\text{O}_2$  sequential process, no improvement of reaction as compared with the single oxidant systems was found. This is mainly due to  $\text{SO}_4^{\cdot-}$  that already existed in the solution, is scavenged by the new supply of  $\text{H}_2\text{O}_2$  (eqs 17 and 18), and formed a much weaker oxidant hydroperoxyl radical ( $\text{HO}_2^{\cdot}$ ).



**Table 1.** Result of TOC Analysis by UV/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> and UV/H<sub>2</sub>O<sub>2</sub>/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> Systems

time (min)	TOC removal (%)	
	UV/S <sub>2</sub> O <sub>8</sub> <sup>2-</sup>	UV/H <sub>2</sub> O <sub>2</sub> /S <sub>2</sub> O <sub>8</sub> <sup>2-</sup>
10	56.09	19.77
30	100	55.84
45	100	100
60	100	100

**Simultaneous Reaction (UV/H<sub>2</sub>O<sub>2</sub>/S<sub>2</sub>O<sub>8</sub><sup>2-</sup>) and Mineralization.** An interesting phenomenon has been found when optimizing the dosage for the UV/H<sub>2</sub>O<sub>2</sub>/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> process. The optimum H<sub>2</sub>O<sub>2</sub> dosage (10 mM) was first tested by varying the S<sub>2</sub>O<sub>8</sub><sup>2-</sup> dosage, where a declining reaction rate was identified when the [S<sub>2</sub>O<sub>8</sub><sup>2-</sup>] increased as shown at **Figure 7**. In order to verify if the radical is in excess and potentially induces the retardation stage as found at **Figure 2**, a much lower H<sub>2</sub>O<sub>2</sub> concentration (2 mM) was selected for further investigation. The results are also shown in **Figure 7**, which provided solid evidence suggesting that the S<sub>2</sub>O<sub>8</sub><sup>2-</sup> reaction was easily suppressed by the excessive H<sub>2</sub>O<sub>2</sub> or its photolysis product hydroxyl radicals (eqs 17 and 16) and leading to the retardation stage similar to that in **Figure 2**. In the case of a low H<sub>2</sub>O<sub>2</sub> concentration of 2 mM (**Figure 7**), the addition of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> could surprisingly improve the reaction. Because there is less H<sub>2</sub>O<sub>2</sub> available and less hydroxyl radicals can be generated, the scavenging effect of hydroxyl radical on sulfate radical becomes insignificant. In summary, the dosage of H<sub>2</sub>O<sub>2</sub> should not be too high in the process; when 2 mM is used, the corresponding S<sub>2</sub>O<sub>8</sub><sup>2-</sup> can be higher than 10 mM to achieve a better performance (above the baseline in **Figure 7**).

The effectiveness of mineralization by using different systems was evaluated by measuring the TOC in the solution. The mineralization efficiency in UV/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> system was higher than that in the UV/H<sub>2</sub>O<sub>2</sub>/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> system; see **Table 1**. In the UV/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> system, 56.09% TOC was removed after 10 min of irradiation time and a complete removal in 30 min. In the UV/H<sub>2</sub>O<sub>2</sub>/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> system, however, the complete removal took place at 45 min. As discussed previously, in the UV/H<sub>2</sub>O<sub>2</sub>/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> system, the sulfate radical and hydroxyl radical would scavenge each other and resulted in hindrance of the degradation of CBF and its intermediates. This implies that using the UV/H<sub>2</sub>O<sub>2</sub>/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> system is more difficult to break the furan ring of CBF and oxidize it into carbon dioxide. Therefore, the UV/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> process is suggested if zero (or low) discharge of organics is preferred. It exhibits the best mineralization performance with a slightly lower CBF degrade rate constant. For the UV/H<sub>2</sub>O<sub>2</sub>/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> process, on the other hand, it has a slightly lower mineralization due to the recombination of radicals at the later stage of the reaction. This process is recommended for treatment of specific targeted compound degradation (such as CBF), which offers faster decay; therefore, a smaller reactor can be used.

The UV/H<sub>2</sub>O<sub>2</sub>/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> system shows the best performance in CBF degradation, but it is highly dependent on the initial H<sub>2</sub>O<sub>2</sub> concentration. At a high initial H<sub>2</sub>O<sub>2</sub> concentration, the addition of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> would scavenge the hydroxyl radical where there is no enhancement in the overall reaction. At a low H<sub>2</sub>O<sub>2</sub> concentration, however, the addition of S<sub>2</sub>O<sub>8</sub><sup>2-</sup> can generate sufficient sulfate radicals, which enhance the degradation of CBF. The UV/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> shows the advantage among all other processes in terms of mineralization. Although the combined UV/H<sub>2</sub>O<sub>2</sub>/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> system has a lower mineralization, it offers the highest efficiency in removing CBF. The sequential addition

of the second oxidant has given strong evidence of the scavenging effect of the recombination of the robust radicals (sulfate and hydroxyl radicals), which is the major reason of retardation of the degradation of CBF and its intermediates.

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