Degradation efficiencies of azo dye Acid Orange 7 by the interaction of heat, UV and anions with common oxidants: Persulfate, peroxymonosulfate and hydrogen peroxide

Shiying Yang [a,b,*], Ping Wang [b], Xin Yang [b], Liang Shan [b], Wenyi Zhang [b], Xueting Shao [b], Rui Niu [b]

[a] Key Laboratory of Marine Environment and Ecology, Ministry of Education, Qingdao 266100, China
[b] College of Environmental Science and Engineering, Ocean University of China, Qingdao 266100, China

ARTICLE INFO

ABSTRACT

In this paper, the degradation of azo dye Acid Orange 7 (AO7) by three common peroxides (persulfate (PS), peroxymonosulfate (PMS) or hydrogen peroxide (H_2O_2)) under various activation conditions, i.e., heat (25–80 °C), UV light (254 nm), or anions (SO_4^{2-}, NO_3^-, CO_3^{2-}, HCO_3^-, HPO_4^{2-}, and Cl^-), was investigated. The order of AO7 degradation efficiencies by heat activation is PS ≫ PMS > H_2O_2. PS oxidation activated by heat (>50 °C) is an effective degradation technology, while PMS and H_2O_2 are hardly activated. When assisted by UV, peroxides could all be activated and degrade AO7 quickly. The order is PS > H_2O_2 > PMS. We activated peroxides, for the first time, by using some anions and compared the subsequently degradation efficiencies of AO7. It was found that PMS could be activated by some anions, but PS and H_2O_2 cannot. The activation efficiencies of PMS by SO_4^{2-} and NO_3^- are negligible, whereas remarkable by HCO_3^-, HPO_4^{2-}, Cl^- and CO_3^{2-}. For HCO_3^-, HPO_4^{2-} and Cl^-, the activation efficiencies become higher with the increase of anion concentration. For CO_3^{2-}, however, the activation efficiency is higher at lower concentration.

1. Introduction

Textile dyes and other industrial dyestuffs constitute one of the largest groups of organic compounds that represent an increasing environmental danger owing to their non-biodegradability, toxicity and potential carcinogenic nature [1]. Over 15% of the total world production of dyes is lost during the dyeing process and is released in the textile effluents [2]. Azo dyes, which contribute to about 70% of all used dyes, is difficult degraded by biological treatment methods due to their complex structure and the stability. Common treatment processes like adsorption and flocculation are not efficient methods because they result in solid waste, thus creating other environmental problems requiring further treatment [3].

Advanced oxidation processes (AOPs) have been developed to degrade biorefractory organics in drinking water and industrial effluents. Almost all of the AOPs are based on the generation of hydroxyl radicals (•OH) [4] which can degrade a broad range of organic pollutants quickly and non-selectively [5,6]. Some of the AOPs are based on H_2O_2, such as Fenton's reagent [7–10], and UV/H_2O_2 [11–14]. H_2O_2 can be activated by iron or UV to yield the radical •OH [15]. Good reviews have been published to describe the application of H_2O_2 in wastewater treatment [16,17].

Sulfate radical ($SO_4^{•-}$)-based AOPs, in which PS or PMS is used as oxidant, came forth recently for the degradation of non-biodegradable contaminants [18–26]. PS and PMS can be activated to generate $SO_4^{•-}$ which is also a powerful oxidant and can oxidize most organics in wastewater. Huang et al. [27] studied the degradation of 59 volatile organic compounds by PS and found that most organics can be degraded. Anipsitakis et al. [28] successfully used PMS as oxidant to degrade chlorophenols, polyaromatic hydrocarbons (PAHs) and pesticides.

The three peroxides mentioned above (PS, PMS and H_2O_2) are similar in structure and they all have O–O bond. One hydrogen atom in H_2O_2 is replaced by SO_3 to generate HSO_5^- and two hydrogen atoms in H_2O_2 are replaced by SO_3 to form $S_2O_8^{2-}$. Due to the influence of SO_3, O–O bond is lengthened and the bond energy decreases. The distances of the O–O bonds in HSO_5^-, solid H_2O_2 and $S_2O_8^{2-}$ are 1.453, 1.460 and 1.497 Å, respectively [29]. The bond energy in PS is estimated 140 kJ/mol [30], while in H_2O_2 is 213.3 kJ/mol [31]. No value reference is available for PMS and it is estimated that PMS may be between PS and H_2O_2 in the bond energy. Moreover, PMS has an unsymmetric structure for only one H is replaced by SO_3. As the SO_3 can attract electrons, electron cloud of O–O bond leans to SO_3 side to make O of H-side carry positive charges. These peroxides are strong oxidizers, with standard oxidation–reduction potential (E^0) 2.01 V (PS) [32], 1.82 V (PMS) and 1.776 V (H_2O_2) [33],

* Corresponding author at: Key Laboratory of Marine Environment and Ecology, Ministry of Education, No. 238 Songling Road, Qingdao 266100, China.
Tel.: +86 0532 66781020; fax: +86 0532 66786519.
E-mail address: shiningpup@hotmail.com (S. Yang).

respectively. They all present limited ability to oxidize organics independently [17,24,34]. But under heating, UV or metal activation conditions, these peroxides can generate free radicals $SO_4^{\bullet-}$ and $^{\bullet}OH$ [28,32,35], with oxidation–reduction potentials of +2.5 to +3.1 V vs. NHE [36] and +1.8 to +2.7 V vs. NHE [4], respectively, which can oxidize most of the organics in water. Due to different structures and properties, these three peroxides have different decomposition rates and present diverse abilities to degrade organics under specific activation condition. Anipsitakis and Dionysiou [37] have studied the efficiency of organics degradation by these three peroxides under nine transition metal activation. It was found that Co(II) and Ru(III) were the best metal catalysts for the activation of PMS. Fe(III) and Fe(II) were the most efficient transition metals to activate H_2O_2. Additionally, Ag(I) showed the best efficiencies toward activating PS. However, the difference among these peroxides (PS, PMS, H_2O_2) under heat or UV activation conditions has not been studied yet. PMS can be activated by reductive anions and halide ions in water [33,38], to generate free radicals and OX^- (X = Cl, Br or I). Moreover, in the research of metal-activated PMS, researchers neglected the influence of anions [39,40] and did not deeply study organics degradation which was caused by oxidative species from the combination of PMS with anions. As far as we are concerned, no researcher has studied whether PMS could be activated by other anions, and none has studied the degradation of organics by PMS under anion activated condition. Therefore, the main objectives of this paper are: (1) to compare the degradation efficiencies of AO7, a model organic contaminant and commonly used as a model compound for the study of the dye degradation [1,3,41,42], by these three peroxides (PS, PMS and H_2O_2) under heat or UV activation condition; (2) to study whether common anions (SO_4^{2-}, NO_3^-, CO_3^{2-}, HCO_3^-, HPO_4^{2-}, and Cl^-) can activate these peroxides and consequently degrade AO7; (3) to determine the effects of the dosage of peroxides and anions on the degradation of AO7. These issues are useful to choose and improve the performance of $SO_4^{\bullet-}$ or $^{\bullet}OH$ based AOPs for dye wastewater treatment.

2. Materials and methods

2.1. Materials

Sodium persulfate (PS, $Na_2S_2O_8$, 99.0%), hydrogen peroxide (H_2O_2, 30%), Oxone ($KHSO_4 \cdot K_2SO_4 \cdot KHSO_5$, containing 42% $KHSO_5$), sodium chloride (NaCl, 99.8%), sodium sulfate (Na_2SO_4, 99.0%), sodium bicarbonate ($NaHCO_3$, 99.5%), sodium carbonate (Na_2CO_3, 99.5%), potassium phosphate dibasic trihydrate ($K_2HPO_4 \cdot 3H_2O$, 99.0%), sodium nitrate ($NaNO_3$, 99.0%), potassium iodide (KI, 99.0%), sodium thiosulfate ($Na_2S_2O_3$, 99.0%) and AO7 (4-(2-hydroxy-1-naphthylazo) benzenesulfonic acid, 99.0%) were purchased from Shanghai Chemical Reagent Company, China and used without purification. All experiments were carried out using double distilled water.

2.2. Reactor and procedures

The degradation experiments were conducted in a jacketed reactor of 450 mL capacity at batch mode, and all comparisons were made using the same batch. Stirring and the temperature of the reacting solution were kept constant throughout the experiments. The temperature of the reaction was controlled by recirculation water.

In the UV activation experiment, a 6 W low pressure Hg UV lamp (λ_{max} = 254 nm, product type ZSZ-6-A, ShangHai Anting Scientific Instrument Factory), was used as the UV light source. Its fluence rate is about 9 μW/cm^2 measured by the normal method in Chinese Standard GB 19258-2003. Unless otherwise specified, the initial concentration of AO7 was fixed at 20 mg/L (0.057 mmol/L) and the

initial peroxide/AO7 molar ratio was 10:1. At given intervals, the solution was sampled. Samples were quickly cooled down to room temperature in the heat experiments.

2.3. Analysis

The degradation of AO7 was monitored by measuring the absorbance at 484 nm (UNICO 2100 spectrophotometer) as a function of reaction time. The concentration of peroxide (PS, PMS or H_2O_2) was determined by an iodometric titration with thiosulfate [43].

Although some studies have revealed that pH value and ionic strength can influence the degradation rate [44], some anions, such as the common buffer HPO_4^{2-}, could also react with PMS to produce active species resulting in AO7 degradation as will be shown in Section 3 of this paper. So as to avoid potential complications, all experiments were performed without buffers or ionic strength control. Initial and final pH value was monitored in all degradation experiments.

Every experiment was carried out three times and the results obtained were nearly similar, with variance not greater than 5%. The data referred in this paper is the mean value.

3. Results and discussion

3.1. Heat activation

3.1.1. Effects of temperature

A typical degradation of AO7 with one of the three heat-activated peroxides (PS, PMS, H_2O_2) against time is presented in Fig. 1. Experiments in Fig. 1(a)–(e) were conducted at 25, 50, 60, 70, and 80 °C, respectively. AO7 is not self-decomposed at elevated temperature (80 °C) according to our experiment results. The results in Fig. 1 indicated that these peroxides at room temperature were not effective. The reaction rate of peroxides with organic matter at ambient temperatures (e.g., 25 °C) was very slow. It can be concluded from Fig. 1(b)–(e) that: (1) H_2O_2 hardly degrades AO7 even at high temperature (80 °C); (2) PMS does not degrade AO7 under lower temperature either (below and at 70 °C), but there is 18.37% of AO7 degradation after 3 h under higher temperature (at 80 °C); (3) AO7 could be degraded by PS when the temperature is higher than 50 °C; (4) the degradation rate of AO7 by PS is faster with the temperature rising. At 80 °C, AO7 is nearly 99% decolorized within 40 min.

The initial pH value of AO7 solution was 6.5. When the PS or H_2O_2 was added, the pH of the solution was not changed. When the PMS was added, however, the pH value decreased from 6.5 to 3.3. PMS was from Oxone ($KHSO_4 \cdot K_2SO_4 \cdot KHSO_5$), which contains acidic $KHSO_4$. After reaction, the final pH value in the case of PS decreased to 3.8, possibly due to the release of protons when $SO_4^{\bullet-}$ reacts with water and the formation of acid products [45,46].

The remaining amount of peroxides at 70 °C is listed in Fig. 1(f). In terms of amount, PMS and H_2O_2 remained unchanged and PS reduced, which indicated that PS other than PMS and H_2O_2 was activated. It can be deduced that the oxidant dissociation profiles are in agreement with the AO7 degradation profiles for all those three oxidation systems. The order for degradation efficiency of the heat-activated peroxides tested here is PS ≫ PMS > H_2O_2. It may be attributed to their different O–O bond energy. H_2O_2 is hardly activated by heating due to its extremely large bond energy, which is much higher than that of PMS or PS as mentioned above. Although PMS could be activated under higher temperature, its efficiency is quite low. PS can be activated to generate sulfate free radical $SO_4^{\bullet-}$. The $SO_4^{\bullet-}$ radical, a powerful oxidant with oxidation–reduction potentials of +2.5 to +3.1 V vs. NHE [36], can effectively degrade the biorefractory organic compounds.
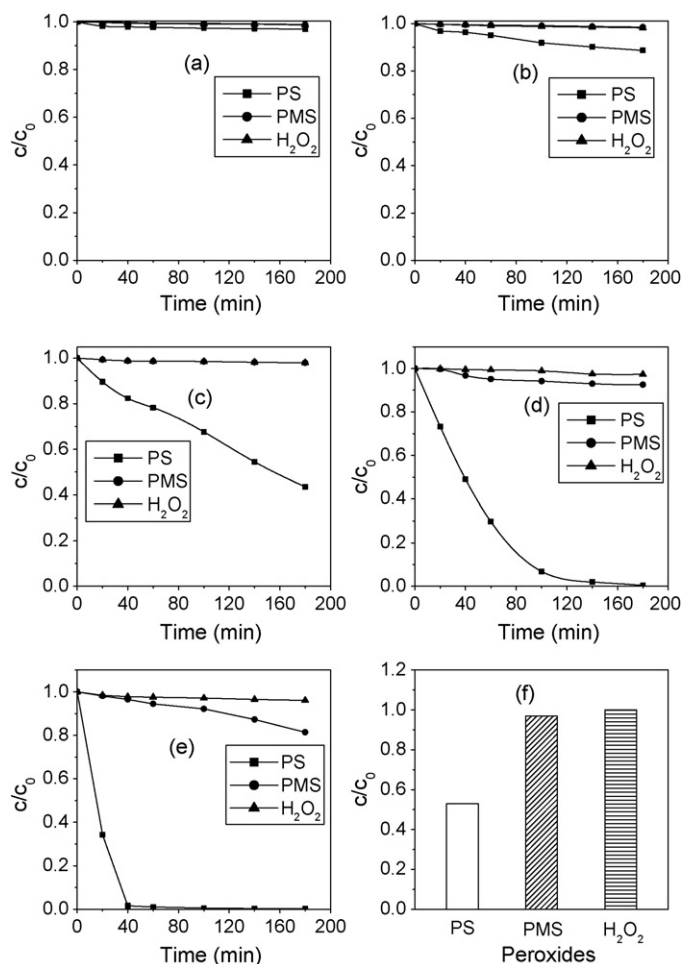
Fig. 1. Degradation of AO7 by three peroxides under various temperatures. (a) 25 °C; (b) 50 °C; (c) 60 °C; (d) 70 °C; (e) 80 °C; (f) the remaining of peroxides at (d). The initiation concentration of AO7 is 20 mg/L; the molar ratio peroxide/AO7 is 10/1.

3.1.2. Effects of peroxide dosage

The influence of oxidant/contaminant molar ratios on the oxidation of AO7 with PS, PMS and H_2O_2 was investigated at the temperature of 70 °C. The reactions at oxidant/contaminant molar ratios of 10:1, 50:1, 100:1 are shown in Fig. 2(a)–(c). Fig. 2(a) shows that AO7 can be degraded by PS at various molar ratios. In Fig. 2(b), it is presented that AO7 is nearly not degraded by PMS at molar ratios of 10:1, but can be more rapidly degraded when the molar ratio rises to 100:1. As shown in Fig. 2(c), there is nearly no AO7 degradation when H_2O_2 is present even with a much higher H_2O_2/AO7 molar ratio of 100:1. The first-order kinetics model is used to describe the kinetic of AO7 degradation by peroxides under various peroxides/AO7 molar ratio. The results show that all the dates are well-fitted pseudo-first-order model and the R^2 is greater than 0.99. The first-order reaction rate constants of the degradation of AO7 by PS, PMS and H_2O_2 at various molar ratios are presented in Fig. 2(d). There are no linear correlation between the PS concentration and the rate constant of AO7 degradation. As the concentration of PS increases, the more $SO_4^{\bullet-}$ is generated in the solution. At the same time, the reaction of $SO_4^{\bullet-}$ with each other is enhanced. Reaction is as follows [47]:

$$SO_4^{\bullet-} + SO_4^{\bullet-} \rightarrow S_2O_8^{2-}, \quad k = 4 \times 10^8 \text{ L/(mol s)} \tag{1}$$
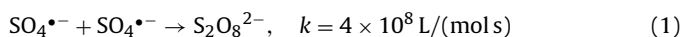
The rate constant of AO7 degradation by PMS seems to increase rapidly when the molar ratio is greater than 50:1. The degradation efficiency is PS ≫ PMS > H_2O_2 whatever the ratios of peroxides/AO7 is.
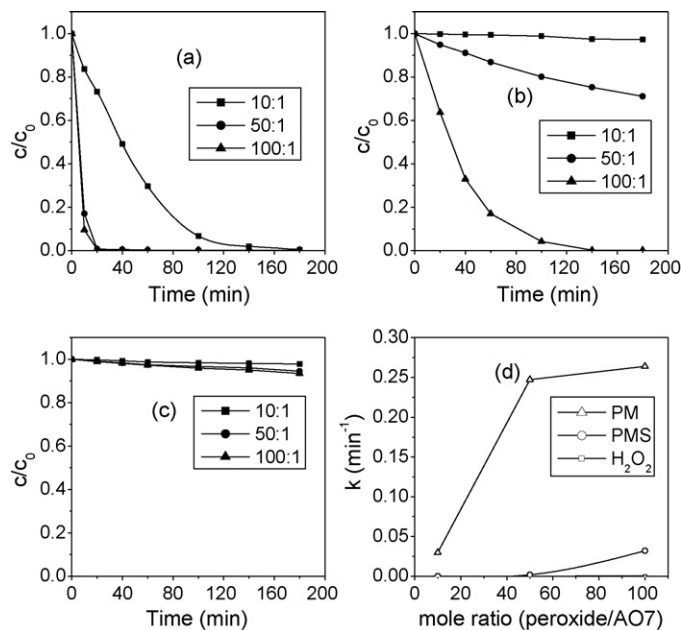
Fig. 2. Effect of the dosage of peroxides on degradation AO7 under heat-activated condition (70 °C). (a) PS; (b) PMS; (c) H_2O_2; (d) rate constants of AO7 degradation by peroxides at various molar ratios. The initiation concentration of AO7 is 20 mg/L; the molar ratio peroxide/AO7 is 10/1, 50/1, and 100/1.
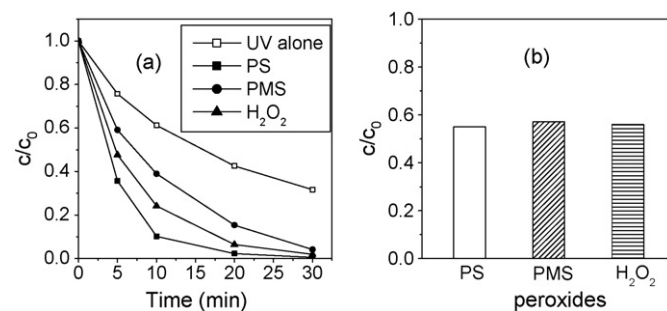
3.2. UV activation

3.2.1. Effects of peroxide

A typical degradation of AO7 with UV and UV-activated three peroxides (PS, PMS and H_2O_2) is presented in Fig. 3(a). As indicated in it, although AO7 could be degraded by UV alone, its degradation rate is improved by adding these peroxides. The degradation rates of the three peroxides are in the order of PS > H_2O_2 > PMS.

The remaining amount of PS, PMS and H_2O_2 are shown in Fig. 3(b). It shows that those peroxides dissociated after UV irradiation 30 min as illustrated in the following equations:

$$S_2O_8^{2-} \rightarrow 2SO_4^{\bullet-} \tag{2}$$

$$HSO_5^- \rightarrow SO_4^{\bullet-} + {}^{\bullet}OH \tag{3}$$

$$H_2O_2 \rightarrow 2{}^{\bullet}OH \tag{4}$$

The remaining amount of those peroxides is nearly equal. Its order is PMS > H_2O_2 > PS. The initial pH values in the presence of PS, PMS and H_2O_2 were 6.3, 3.3 and 6.5, respectively. After 30 min, the pH values decreased to 3.7, 3.1 and 4.8, which was due to acid products formed in the process of degradation of AO7 and the protons released in the reaction of $SO_4^{\bullet-}$ with water [45,46].

Fig. 3. The degradation of AO7 by peroxides under UV activation condition. (a) The degradation of AO7; (b) the remaining of peroxides. The initiation concentration of AO7 is 20 mg/L; the molar ratio peroxide/AO7 is 10/1; the wavelength of UV is 254 nm.
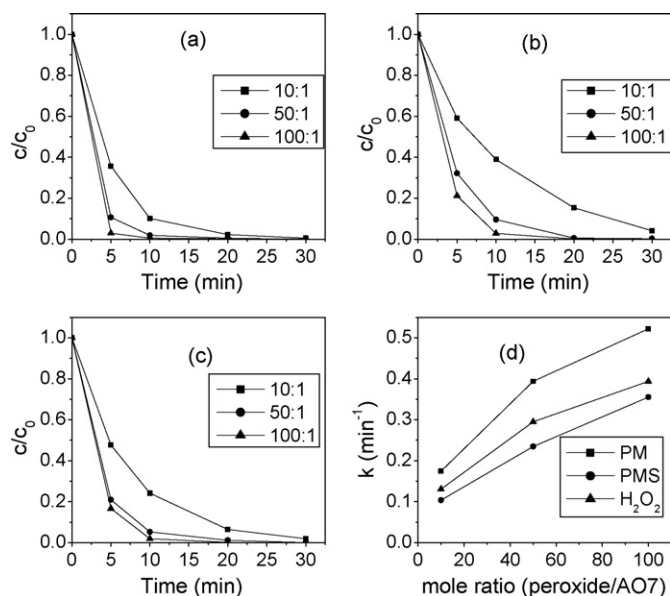
Fig. 4. Effect of the dosage of peroxides on degradation AO7 under UV-activated condition. (a) PS; (b) PMS; (c) H_2O_2; (d) rate constants of AO7 degradation by peroxides at various molar ratios. The initiation concentration of AO7 is 20 mg/L; the molar ratio peroxide/AO7 is 10/1, 50/1, 100/1; the wavelength of UV is 254 nm.

However, it has been [48] studied that the order of the absorbance of these peroxides at 254 nm was PS > PMS > H_2O_2. Although an absorbance of PMS at 254 nm is higher than that of H_2O_2 under the same condition, the slight difference between them, which is less than 0.01, suggests that the decomposition of PMS is not faster than that of H_2O_2 under UV light irradiation. While Anipsitakis and Dionysiou [48] also found that the rate of 2,4-dichlorophenol degradation by PMS was faster than that by H_2O_2. This might be attributed to the generation of Cl^- generated during 2,4-dichlorophenol degradation under UV-irradiation PMS system, as the formed Cl^- interacts with PMS to produce OCl^- which could also degrade organic compound [38]. PS, PMS and H_2O_2 can generate free radicals either via heterolytic cleavage with metal catalyzer, or via homolytic cleavage under UV irradiation. Aparicio et al. [49] found that PMS was more likely to exhibit heterolytic cleavage due to its non-symmetrical structure. Therefore, it is speculated that it might be easier for PS and H_2O_2 to generate homolytic cleavage than that for PMS.

3.2.2. Effects of peroxide dosage

The influence of oxidant/contaminant molar ratios on the AO7 oxidation by PS, PMS and H_2O_2 under UV activation condition was investigated. The degradation of AO7 at oxidant/contaminant molar ratios of 10:1, 50:1, and 100:1 are shown in Fig. 4. Fig. 4(a)–(c) illustrates that the degradation rate of AO7 increases with oxidant dosage rising. Moreover, the first-order reaction rate constants were exhibited in Fig. 4(d). It indicates that the order for degradation efficiency of AO7 by these three peroxides is PS > H_2O_2 > PMS under various molar ratios.

3.3. Anion activation

3.3.1. Effects of anion

Fig. 5(a)–(f) presents the degradation of AO7 by peroxides under anion activation conditions ((a) SO_4^{2-}, (b) NO_3^-, (c) CO_3^{2-}, (d) HCO_3^-, (e) HPO_4^{2-}, and (f) Cl^-). As indicated in this figure, AO7 degradation by PS and H_2O_2 is very low, but the condition with the presence of PMS is significantly different. As PMS has very limited ability to oxidize organics, we may consider that it can be activated by the anions (CO_3^{2-}, HCO_3^-, HPO_4^{2-}, Cl^-) in water to produce
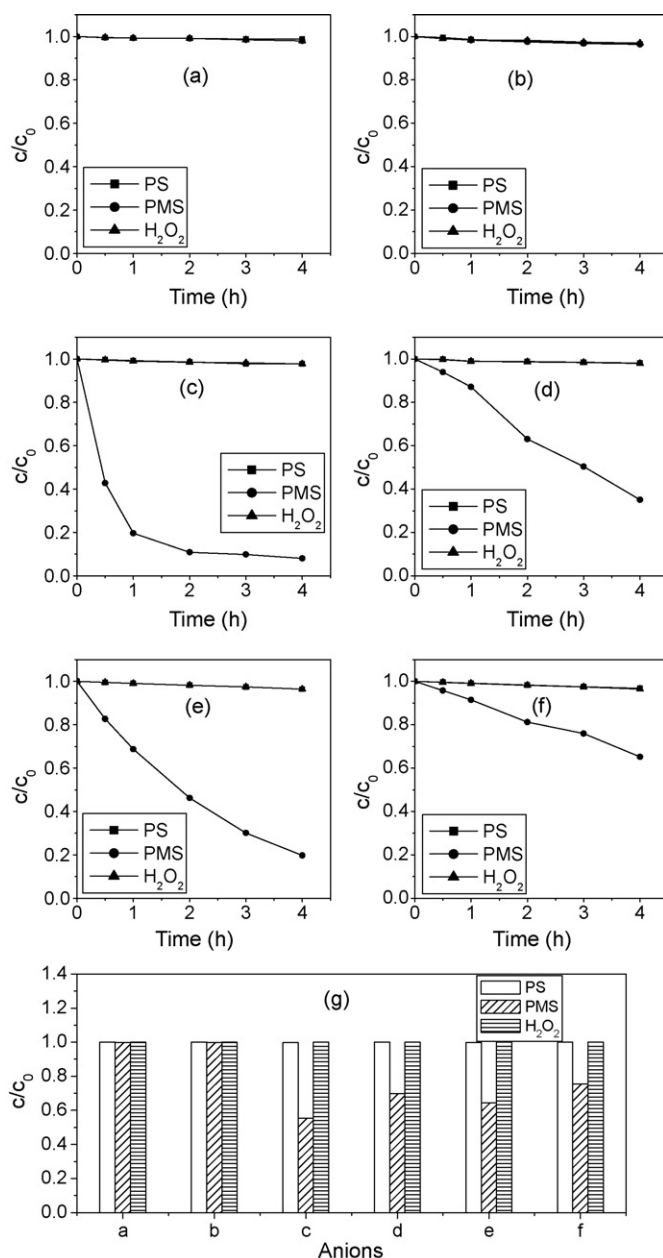
Fig. 5. Degradation of AO7 by peroxides under anions activated conditions. (a) SO_4^{2-}; (b) NO_3^-; (c) CO_3^{2-}; (d) HCO_3^-; (e) HPO_4^{2-}; (f) Cl^-; (g) the remaining of peroxides after 4 h. The initiation concentration of AO7 is 20 mg/L; the molar ratio peroxide/AO7 is 10/1; the concentration of anions is 0.01 mol/L.

active species, which cause the degradation of AO7. The remaining concentration of peroxides was shown in Fig. 5(g). It is found that the concentrations of PS and H_2O_2 exhibit no change and that of PMS reduce, which indicate that PMS other than PS and H_2O_2 is activated. The result is in agreement with the degradation rate of AO7 with PS, PMS and H_2O_2 and also indicates that only PMS is activated by anions.

The active species may be generated as a result of anion decomposition of PMS, which has unsymmetric structure. It will be easily attacked by nucleophile [33]. As shown in Fig. 5(c)–(d), degradation rate of AO7 resulted from PMS activated by HPO_4^{2-} and CO_3^{2-} is faster than that resulted from PMS activated by HCO_3^-. This might be because HPO_4^{2-} and CO_3^{2-} have two nucleophilic atoms O^- which can attack O–O, while HCO_3^- has only one. From Fig. 5(d) and (f), we can conclude that the AO7 degradation rate via HCO_3^-

Table 1
The initial and final pHs of the solution under anions activated peroxides.

| Anions	Peroxide	pH values	
		Initial	Final
SO_4^{2-}	PS	6.4	6.4
	PMS	3.3	3.2
	H_2O_2	6.5	6.5
NO_3^-	PS	6.4	6.4
	PMS	3.3	3.3
	H_2O_2	6.5	6.5
CO_3^{2-}	PS	11.4	11.4
	PMS	11.3	11.2
	H_2O_2	11.4	11.4
HCO_3^-	PS	8.5	8.5
	PMS	8.3	8.0
	H_2O_2	8.5	8.5
HPO_4^{2-}	PS	8.6	8.6
	PMS	8.4	8.2
	H_2O_2	8.6	8.6
Cl^-	PS	6.4	6.4
	PMS	3.3	3.2
	H_2O_2	6.5	6.5

activated PMS is higher than that by Cl^- activated PMS, and the electronegativity of O^- (3.44), which is greater than that of Cl^- (3.16), is considered to be the major reason responsible for the phenomenon.

The activated species under Cl^- activated PMS condition is HOCl. Lente et al. [38] studied the reaction of PMS with halogen and found out that combination of PMS with halogen could generate OX^- (X = Cl, Br or I). Reaction is as follows:
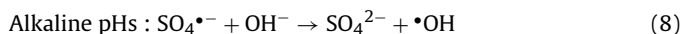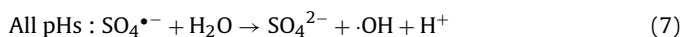
$$HSO_5^- + X^- \rightarrow HSO_4^- + OX^- \tag{5}$$

Delcomyn et al. [50] studied that the combination of PMS with Cl^- was used to produce OCl^- to inactivate biological agents.

However, the activated species under CO_3^{2-}, HCO_3^-, HPO_4^{2-} activated PMS condition remains obscure. To our knowledge, there are no author studied the reaction of CO_3^{2-}, HCO_3^-, HPO_4^{2-} with PMS. We speculated that the active species maybe $SO_4^{\bullet-}$. Connick et al. [51] investigated the reaction between PMS and HSO_3^- and found that $SO_4^{\bullet-}$ and $SO_3^{\bullet-}$ could be generated from that interaction, inducing the degradation of organics. Reaction is as follows:

$$HSO_5^- + HSO_3^- \rightarrow SO_4^{\bullet-} + SO_3^{\bullet-} + H_2O \tag{6}$$
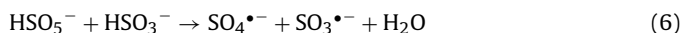
$SO_4^{\bullet-}$ could react with H_2O and OH^- to convert into $^\bullet OH$ as shown in the following equations:

$$\text{All pHs}: SO_4^{\bullet-} + H_2O \rightarrow SO_4^{2-} + \cdot OH + H^+ \tag{7}$$

$$\text{Alkaline pHs}: SO_4^{\bullet-} + OH^- \rightarrow SO_4^{2-} + {}^\bullet OH \tag{8}$$

The rate constants for Eqs. (7) and (8) are of $k[H_2O] < 2 \times 10^{-3}\ s^{-1}$ [52] and $(6.5 \pm 1.0) \times 10^{-3}\ L/(mol\ s)$ [53], respectively. Based on this, $SO_4^{\bullet-}$ starts to decompose and transform into $^\bullet OH$ rapidly at the solution pH value >8.5, and $^\bullet OH$ will become the dominator when the solution pH value is lager than 10.7 subsequently [54]. The initial and final pH values of the solution were listed in Table 1. In the case of the system containing CO_3^{2-}, the pH value of the solution is higher than 11, where $^\bullet OH$ plays a major role in the degradation process. While in the solution with HCO_3^-, HPO_4^{2-} and Cl^- (8.0 < pH value < 8.6), $SO_4^{\bullet-}$ is the major species responsible for the organic oxidation. Those anions (CO_3^{2-}, HCO_3^-, HPO_4^{2-} and Cl^-) are radical scavengers in aqueous phase. The rate constants of $^\bullet OH$ with CO_3^{2-} and $SO_4^{\bullet-}$ with HCO_3^-, HPO_4^{2-}, Cl^- are $3.9 \times 10^8\ L/(mol\ s)$ [4], $2.8–9.1 \times 10^6\ L/(mol\ s)$ [54], $1.2 \times 10^6\ L/(mol\ s)$ [55] and $2.5 \times 10^8\ L/(mol\ s)$ [56], respectively.

Liang et al. [40] found that there was hardly any interference emerging in the TCE degradation with the Cl^- concentration less than 0.2 mol/L, when PS was used as oxidant in the presence of Cl^-. However, it has been reported that Cl^- exhibited interference in the analysis of dissolved organic carbon (DOC) by the wet PS oxidation method at a Cl^- level greater than 0.02 mol/L [57]. Liang et al. [40] suggested that the interference of Cl^- was related to the generation rate of $SO_4^{\bullet-}$. When $SO_4^{\bullet-}$ were generated at a lower rate, the interference of Cl^- can be ignored unless its concentration is at higher level (>0.2 mol/L). In this study, the generation rate of $SO_4^{\bullet-}$ was much smaller than that of the wet PS oxidation method. Furthermore, anions concentration tested here was very low, which is about 0.01 mol/L, and the rate constants of $SO_4^{\bullet-}$ with HCO_3^-, HPO_4^{2-} are less than that of Cl^- with $SO_4^{\bullet-}$. As a result, the interference of these anions (HCO_3^-, HPO_4^{2-} and Cl^-) on the degradation of AO7 could be negligible. In the term of CO_3^{2-}, it is speculated that it could inhibit the degradation of AO7 due to the fast generation rate of free radical and the high rate constant of CO_3^{2-} with $^\bullet OH$ ($3.9 \times 10^8\ L/(mol\ s)$). The speculation was confirmed in the following Section 3.3.2.

In the current study, it is the first time to illustrate that organic contaminant (AO7) can be degraded by anions (CO_3^{2-}, HCO_3^-, HPO_4^{2-}, and Cl^-) activated PMS. As water generally contains these anions, application of PMS activated by anions will be of great significance for organics degradation and sterilization of salt-bearing water.
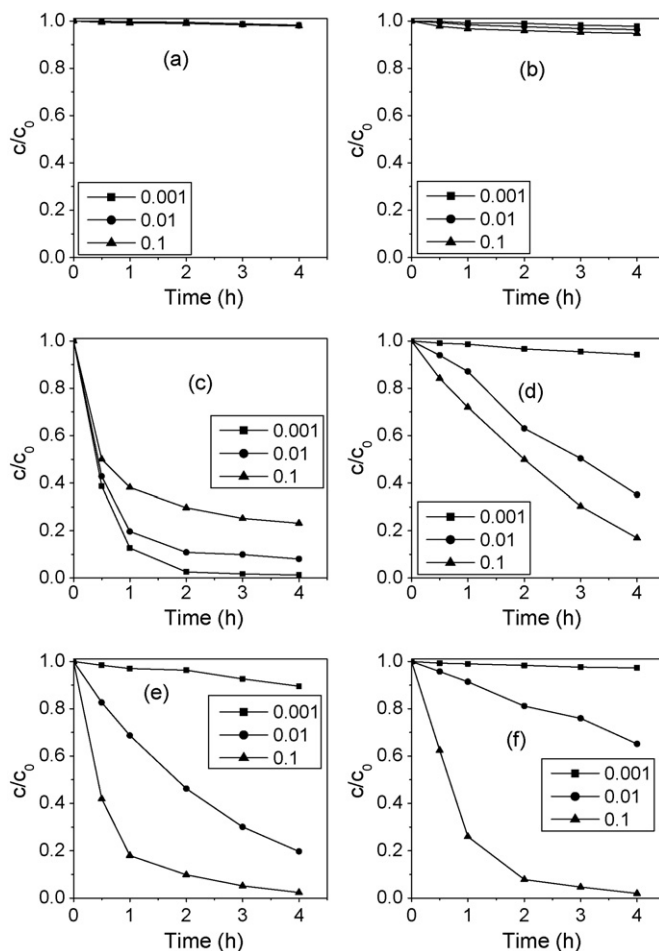
Fig. 6. Influence of the dosage of anions on the degradation of AO7 by PMS under anion activation conditions. (a) SO_4^{2-}; (b) NO_3^-; (c) CO_3^{2-}; (d) HCO_3^-; (e) HPO_4^{2-}; (f) Cl^-. The initiation concentration of AO7 is 20 mg/L; the molar ratio peroxide/AO7 is 10/1; the concentrations of anions are 0.001, 0.01 and 0.1 mol/L, respectively.

3.3.2. Effects of anion dosage

The influence of the anion dosage (0.001–0.1 mol/L) was shown in Fig. 6(see (a)–(f)). From Fig. 6(a) and (b), we can notice that there is less degradation of AO7 by PMS under NO_3^- and SO_4^{2-} conditions even at higher concentration (0.1 mol/L). From Fig. 6(d)–(f), we can find that HCO_3^-, HPO_4^{2-} and Cl^- could activate PMS to degrade AO7, but such effect is not obvious at low concentration (0.001 mol/L). With the increasing concentration of anions (HCO_3^-, HPO_4^{2-} and Cl^-), the degradation of AO7 become faster. However, as shown in Fig. 6(c), CO_3^{2-} just shows the opposite direction, producing the best degradation effect at low concentration (0.001 mol/L). Its degradation rate decreases with the concentration increasing. It is speculated that: (1) CO_3^{2-} could activated PMS to generate $SO_4^{\bullet-}$ which rapidly reacted with OH^- to produce $^\bullet OH$, even at low concentration. (2) CO_3^{2-} could quench $^\bullet OH$ and inhibit the degradation of AO7. The results confirmed this speculation in Section 3.3.1. As rates of reaction of HCO_3^-, HPO_4^{2-} and Cl^- respective with PMS are all lower to cause fewer radicals to be generated, radical scavenging reaction is not obvious.

4. Conclusions

This study compares the degradation efficiencies of AO7 by three common peroxides (PS, PMS and H_2O_2) under various activation conditions, i.e., heat (25–80 °C), UV (254 nm), and anions (SO_4^{2-}, NO_3^-, CO_3^{2-}, HCO_3^-, HPO_4^{2-}, and Cl^-). The order for degradation efficiency of the heat-activated peroxides tested here is $PS \gg PMS > H_2O_2$, H_2O_2 is hardly activated by heating. Although PMS could be activated under higher temperature condition (80 °C), its efficiency is quite low. The order for degradation efficiency of the UV (254 nm) activated peroxides tested here is $PS > H_2O_2 > PMS$. Very interestingly, PMS can be activated by anions (such as CO_3^{2-}, HCO_3^-, HPO_4^{2-}, Cl^-) in water to generate active species for degrading AO7, while PS and H_2O_2 cannot be activated by anions. PMS can be activated by CO_3^{2-} under lower concentration.

References

[1] C.M. Du, T.H. Shi, Y.W. Sun, X.F. Zhuang, Decolorization of Acid Orange 7 solution by gas–liquid gliding arc discharge plasma, J. Hazard. Mater. 154 (2008) 1192–1197.
[2] H.N. Liu, G.T. Li, J.H. Qu, H.J. Liu, Degradation of azo dye Acid Orange 7 in water by Fe⁰/granular activated carbon system in the presence of ultrasound, J. Hazard. Mater. 144 (2007) 180–186.
[3] A. Azam, A. Hamid, Effects of gap size and UV dosage on decolorization of C.I. Acid Orange 7 by UV/H₂O₂ process, J. Hazard. Mater. 133 (2006) 167–171.
[4] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Rose, Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (•OH/•O⁻) in aqueous solution, J, Phys. Chem. Ref. Data 17 (1988) 513–780.
[5] G.B. Tabrizi, M. Mehrvar, Integration of advanced oxidation technologies and biological processes: recent developments, trends, and advances, J. Environ. Sci. Health A 39 (2004) 3029–3081.
[6] M. Klavarioti, D. Mantzavinos, D. Kassinos, Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes, Environ. Int. 35 (2009) 402–417.
[7] H. Zhang, H.J. Choi, P. Canazo, C.P. Huang, Multivariate approach to the Fenton process for the treatment of landfill leachate, J. Hazard. Mater. 161 (2009) 1306–1312.
[8] A.A. Burbano, D.D. Dionysiou, M.T. Suidan, Effect of oxidant-to-substrate ratios on the degradation of MTBE with Fenton reagent, Water Res. 42 (2008) 3225–3239.
[9] E. Elmolla, M. Chaudhuri, Optimization of Fenton process for treatment of amoxicillin, ampicillin and cloxacillin antibiotics in aqueous solution, J. Hazard. Mater. 170 (2009) 666–672.
[10] R.L. Kruger, R.M. Dallago, D.M. Luccio, Degradation of dimethyl disulfide using homogeneous Fenton's reaction, J. Hazard. Mater. 169 (2009) 443–447.
[11] H.Y. Shu, M.C. Chang, Decolorization and mineralization of a phthalocyanine dye C.I. Direct Blue 199 using UV/H₂O₂ process, J. Hazard. Mater. 125 (2005) 96–101.
[12] K. Li, M.I. Stefan, J.C. Crittenden, Trichloroethene degradation by UV/H₂O₂ advanced oxidation process: product study and kinetic modeling, Environ. Sci. Technol. 41 (2007) 1696–1703.
[13] C. Wu, K.G. Linden, Degradation and byproduct formation of parathion in aqueous solutions by UV and UV/H₂O₂ treatment, Water Res. 42 (2008) 4780–4790.
[14] B. Xu, N.Y. Gao, H. Cheng, S.J. Xia, M. Rui, D.D. Zhao, Oxidative degradation of dimethyl phthalate (DMP) by UV/H₂O₂ process, J. Hazard. Mater. 162 (2009) 954–959.
[15] G. Andreottola, L. Dallago, E. Ferrarese, Feasibility study for the remediation of groundwater contaminated by organolead compounds, J. Hazard. Mater. 156 (2008) 488–498.
[16] E. Neyens, J. Baeyens, A review of classic Fenton's peroxidation as an advanced oxidation technique, J. Hazard. Mater. 98 (2003) 33–50.
[17] P.R. Gogate, A.B. Pandit, A review of imperative technologies for wastewater treatment I: oxidation technologies at ambient conditions, Adv. Environ. Res. 8 (2004) 501–551.
[18] S.Y. Yang, Y.Y. Chen, H.Z. Xu, P. Wang, Y.H. Liu, M.D. Wang, A novel advanced oxidation technology: activated persulfate (in Chinese), Prog. Chem. 20 (2008) 1433–1438.
[19] S.Y. Yang, X. Yang, P. Wang, W.Y. Zhang, L. Shan, Advances in activation methods of persulfate oxidation (in Chinese), Modern Chem. Ind. 29 (2009) 13–19.
[20] S.Y. Yang, P. Wang, X. Yang, G. Wei, W.Y. Zhang, L. Shan, A novel advanced oxidation process to degrade organic pollutants in wastewater: microwave-activated persulfate oxidation, J. Environ. Sci. 21 (2009) 1175–1178.
[21] S.X. Li, D. Wei, N.K. Mak, Z.W. Cai, X.R. Xu, H.B. Li, Y. Jiang, Degradation of diphenylamine by persulfate: performance optimization, kinetics and mechanism, J. Hazard. Mater. 164 (2009) 26–31.
[22] Y.F. Huang, Y.H. Huang, Identification of produced powerful radicals involved in the mineralization of bisphenol A using a novel UV–Na₂S₂O₈/H₂O₂–Fe (II, III) two-stage oxidation process, J. Hazard. Mater. 162 (2009) 1211–1216.
[23] Y.H. Huang, Y.F. Huang, C.I. Huang, C.Y. Chen, Efficient decolorization of azo dye Reactive Black B involving aromatic fragment degradation in buffered Co²⁺/PMS oxidative processes with a ppb level dosage of Co²⁺-catalyst, J. Hazard. Mater. 170 (2009) 1110–1118.
[24] G.P. Anipsitakis, D.D. Dionysiou, Degradation of organic contaminants in water with sulfate radicals generated by the conjunction of peroxymonosulfate with cobalt, Environ. Sci. Technol. 37 (2003) 4790–4797.
[25] J.H. Sun, X.Y. Li, J.L. Feng, X.K. Tian, Oxone/Co²⁺ oxidation as an advanced oxidation process: Comparison with traditional Fenton oxidation for treatment of landfill leachate, Water Res. 43 (2009) 4363–4369.
[26] R.H. Waldemer, P.G. Tratnyek, R.L. Johnson, J.T. Nurmi, Oxidation of chlorinated ethenes by heat-activated persulfate: kinetics and products, Environ. Sci. Technol. 41 (2007) 1010–1015.
[27] K.C. Huang, Z.Q. Zhao, G.E. Hoag, A. Dahmani, P.A. Block, Degradation of volatile organic compounds with thermally activated persulfate oxidation, Chemosphere 61 (2005) 551–560.
[28] G.P. Anipsitakis, D.D. Dionysiou, M.A. Gonzalez, Cobalt-mediated activation of peroxymonosulfate and sulfate radical attack on phenolic compounds. Implications of chloride ions, Environ. Sci. Technol. 40 (2006) 1000–1007.
[29] J. Flanagan, W.P. Griffith, A.C. Skapski, The active principle of caro's acid, HSO₅⁻: k-ray crystal structure of KHSO₅·H₂O, J. Chem. Soc., Chem. Commun. 23 (1984) 1574–1579.
[30] I.M. Kolthoff, I.K. Miller, The chemistry of persulfate. I. The kinetics and mechanism of the decomposition of the persulfate ion in aqueous medium, J. Am. Chem. Soc. 73 (1951) 3055–3059.
[31] W. Reints, D.A. Pratt, H.G. Korth, P. Mulder, O–O bond dissociation enthalpy in di(trifluoromethyl) peroxide (CF₃OOCF₃) as determined by very low Pressure pyrolysis. Density functional theory computations on O–O and O–H bonds in (fluorinated) derivatives, J. Phys. Chem. A 104 (2000) 10713–10720.
[32] C.J. Liang, C.J. Bruell, M.C. Marley, K.L. Sperry, Thermally activated persulfate oxidation of trichloroethylene (TCE) and 1,1,1-trichloroethane (TCA) in aqueous systems and soil slurries, Soil Sediment. Contam. 12 (2003) 207–228.
[33] E.A. Betterton, M.R. Hoffmann, Kinetics and mechanism of the oxidation of aqueous hydrogen sulfide by peroxymonosulfate, Environ. Sci. Technol. 24 (1990) 1819–1824.
[34] E.R. Bandala, M.A. Peláez, D.D. Dionysiou, S. Gelover, J. Garcia, D. Macías, Degradation of 2,4-dichlorophenoxyacetic acid (2,4-ᴅ) using cobalt-peroxymonosulfate in Fenton-like process, J. Photochem. Photobiol. A 186 (2007) 357–363.
[35] G.S. Wang, S.T. Hsieh, C.S. Hong, Destruction of humic acid in water by UV light-catalyzed oxidation with hydrogen peroxide, Water Res. 34 (2000) 3882–3887.
[36] P. Neta, R.E. Huie, A.B. Ross, Rate constants for reactions of inorganic radicals in aqueous solution, J. Phys. Chem. Ref. Data 17 (1988) 1027–1284.
[37] G.P. Anipsitakis, D.D. Dionysiou, Radical generation by the interaction of transition metals with common oxidants, Environ. Sci. Technol. 38 (2004) 3705–3712.
[38] G. Lente, J. Kalmár, Z. Baranyal, A. Kun, I. Kék, D. Bajusz, M. Takács, L. Veres, I. Fábián, One-versus two-electron oxidation with peroxomonosulfate ion: reactions with iron(II), vanadium(IV), halide ions, and photoreaction with cerium(III), Inorg. Chem. 48 (2009) 1763–1773.
[39] X.Y. Chen, X.L. Qiao, D.G. Wang, J. Lin, J.W. Chen, Kinetics of oxidative decolorization and mineralization of acid orange 7 by dark and photoassisted Co²⁺-catalyzed peroxymonosulfate system, Chemosphere 67 (2007) 802–808.
[40] C.J. Liang, Z.S. Wang, N. Mohanty, Influences of carbonate and chloride ions on persulfate oxidation of trichloroethylene at 20 °C, Sci. Total Environ. 370 (2006) 271–277.
[41] Y.X. Chen, S.Y. Yang, K. Wang, L.P. Lou, Role of primary active species and TiO₂ surface characteristic in UV-illuminated photodegradation of acid orange 7, J. Photochem. Photobiol. A 172 (2005) 47–54.

[42] S. Hammami, N. Bellakhal, N. Oturan, M.A. Oturan, M. Dachraoui, Degradation of acid orange 7 by electrochemically generated •OH radicals in acidic aqueous medium using a boron-doped diamond or platinum anode: a mechanistic study, Chemosphere 73 (2008) 678–684.

[43] N. Wahba, M.F.E. Asmar, M.M.E. Sadr, Iodometric method for determination of persulfates, Anal. Chem. 31 (1959) 1870–1871.

[44] C.J. Liang, Z.S. Wang, C.J. Bruell, Influence of pH on persulfate oxidation of TCE at ambient temperatures, Chemosphere 66 (2007) 106–113.

[45] M. Stylidi, D.I. Kondarides, X.E. Verykios, Pathways of solar light-induced photocatalytic degradation of azo dyes in aqueous TiO$_2$ suspensions, Appl. Catal. B 40 (2003) 271–286.

[46] M. Stylidi, D.I. Kondarides, X.E. Verykios, Visible light-induced photocatalytic degradation of acid orange 7 in aqueous TiO$_2$ suspensions, Appl. Catal. B 47 (2004) 189–201.

[47] R.E. Huie, C.L. Clifton, Rate constants for hydrogen abstraction reactions of the sulfate radical SO$_4{}^{•-}$ alkanes and ethers, Int. J. Chem. Kinet. 21 (1989) 611–619.

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

[49] F. Aparicio, R. Contreras, M. Galván, A. Cedillo, Global and local reactivity and activation patterns of HOOX (X = H, NO$_2$, CO$_2{}^-$, SO$_3{}^-$) peroxides with solvent effects, J. Phys. Chem. A 107 (2003) 10098–10104.

[50] C.A. Delcomyn, K.E. Bushway, M.V. Henley, Inactivation of biological agents using neutral oxone-chloride solutions, Environ. Sci. Technol. 40 (2006) 2759–2764.

[51] R.E. Connick, Y.X. Zhang, S.Y. Lee, R. Adamic, P. Chieng, Kinetics and mechanism of the oxidation of HSO$_3{}^-$ by O$_2$. 1. The uncatalyzed reaction, Inorg. Chem. 34 (1995) 4543–4553.

[52] D.E. Pennington, A. Haim, Stoichiometry and mechanism of the chromium(II)-peroxydisulfate reaction, J. Am. Chem. Soc. 90 (1968) 3700–3704.

[53] E. Hayon, A. Treinin, J. Wilf, Electronic spectra, photochemistry, and autoxidation mechanism of the sulfite–bisulfite–pyrosulfite systems. SO$_2{}^-$, SO$_3{}^-$, SO$_4{}^-$, and SO$_5{}^-$ radicals, J. Am. Chem. Soc. 94 (1972) 47–57.

[54] L. Dogliotti, E. Hayon, Flash photolysis of per[oxydi]sulfate ions in aqueous solutions. The sulfate and ozonide radical anions, J. Phys. Chem. 71 (1967) 2511–2516.

[55] P. Maruthamuthu, P. Neta, Phosphate radicals. Spectra, acid-base equilibriums, and reactions with inorganic compounds, J. Phys. Chem. 82 (1978) 710–713.

[56] R.E. Huie, C.L. Clifton, Temperature dependence of the rate constants for reactions of the sulfate radical, SO$_4{}^{•-}$, with anions, J. Phys. Chem. 94 (1990) 8561–8567.

[57] G.R. Aiken, Chloride interference in the analysis of dissolved organic carbon by the wet oxidation method, Environ. Sci. Technol. 26 (1992) 2435–2439.