



Effects of chloride ion on degradation of Acid Orange 7 by sulfate radical-based advanced oxidation process: Implications for formation of chlorinated aromatic compounds

Ruixia Yuan, Sadiqua N. Ramjaun, Zhaohui Wang*, Jianshe Liu**

College of Environmental Science and Engineering, Donghua University, Shanghai, 201620, China

ARTICLE INFO

Article history:

Received 15 June 2011

Received in revised form 22 August 2011

Accepted 4 September 2011

Available online 19 September 2011

Keywords:

Azo dyes

Sulfate radicals

Decoloration

AOX formation

Chlorinated aromatic compounds

ABSTRACT

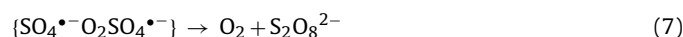
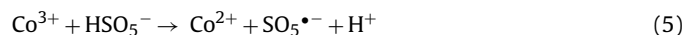
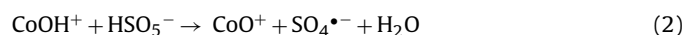
Sodium chloride is a common salt used during textile wet processes. Here a dual effect of chloride (i.e. inhibitory and accelerating effect) on azo dye (Acid Orange 7, AO7) degradation in an emerging cobalt/peroxymonosulfate (Co/PMS) advanced oxidation process (AOP) was reported. Compared to •OH-based AOPs, high concentrations of chloride (>5 mM) can significantly enhance dye decoloration independent of the presence of the Co²⁺ catalyst, but did greatly inhibit dye mineralization to an extent which was closely dependent upon the chloride content. Both UV–vis absorbance spectra and AOX determination indicated the formation of some refractory byproducts. Some chlorinated aromatic compounds, including 3-chloroisocoumain, 2-chloro-7-hydroxynaphthalene, 1,3,5-trichloro-2-nitrobenzene and tetrachlorohydroquinone, were identified by GC–MS measurement in both Co/PMS/Cl[−] and PMS/Cl[−] reaction systems. Based on those experimental results, two possible branched (SO₄^{•−} radical-based and non-radical) reaction pathways are proposed. This is one of the very few studies dealing with chlorinated organic intermediates formed via chlorine radical/active chlorine species (HOCl/Cl₂) attack on dye compounds. Therefore, this finding may have significant technical implications for utilizing Co/PMS reagent to detoxify chloride-rich azo dyes wastewater.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Dyeing industrial wastewater contains large amount of chloride ions with high non-biodegradable organic concentration, which can seriously inhibit the effectiveness of aerobic and anaerobic biological treatment of wastewater [1,2]. Recently, advanced oxidation processes (AOPs) are gaining significant importance in detoxification of dyeing wastewaters [3–5]. However, previous investigations have proved that the presence of chloride could make AOPs treatment of saline waters to be inefficient [6–8]. Since •OH (2.8 V) can oxidize Cl[−] to less reactive chlorine species, Cl₂/2Cl[−] (1.36 V) and HOCl/Cl[−] (1.48 V), the involvement of Cl[−] can inhibit the •OH-based radical chain reactions, thus significantly reducing the overall efficiency of the AOPs. Whereas our very recent study indicated that higher concentrations of chloride (>50 mM) in sulfate radical (SO₄^{•−}) based AOP could enhance the decoloration rate of an azo dye–AO7, although the underlying reaction mechanism has not been well elucidated [9].

SO₄^{•−} as a major oxidizing specie with high standard redox potential (2.5–3.1 V), may react selectively via electron transfer with organics over a wide pH range (2–8), and completely destroy the pollutants present in wastewater or convert them into simple harmless compounds [10]. This emerging AOP has attracted great scientific and technological interest in environmental application. Many transition metals such as Co(II) and Fe(II) can efficiently activate peroxymonosulfate (PMS) to produce sulfate radicals as followings (Eqs. (1)–(8)) [11–14]:



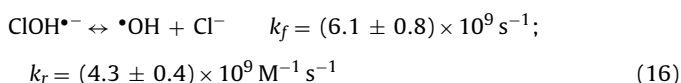
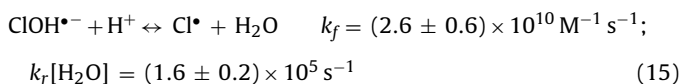
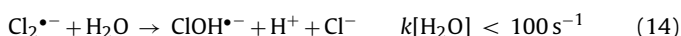
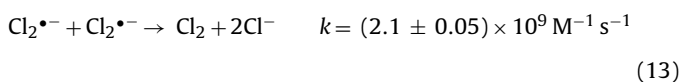
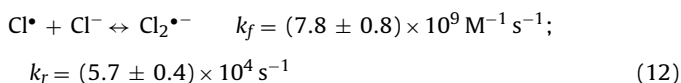
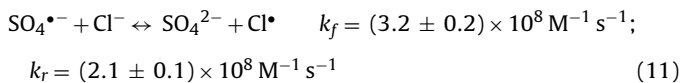
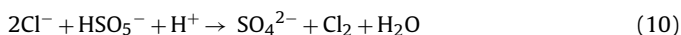
From a thermodynamic point of view, both PMS and sulfate radical also can oxidize chloride ions to active chlorine species HOCl/Cl₂

* Corresponding author.

** Co-corresponding author.

E-mail addresses: zhaohuiwang@dhu.edu.cn (Z. Wang), liujianshe@dhu.edu.cn (J. Liu).

or chlorine radicals. Chloride ions may be involved in PMS decomposition reaction via either *non-radical pathways* (Eqs. (9) and (10)) or *sulfate radical-based pathways* (Eqs. (11)–(16)) [15,16].



These radical-based chain reactions and elementary reactions with unknown rate constants (e.g. Eqs. (1)–(8)) indeed complicate kinetic analysis in the Co/PMS/Cl⁻ systems. In this context, identification of reaction intermediates may be an alternative choice for clarifying the underlying reaction mechanism. All reactive chlorine species, including chlorine atom, dichloride radical and free chlorine, can add to some unsaturated bonds of the compounds present during oxidation processes, generating chlorinated hydrocarbons, therefore leading to an undesirable increase of the parameter AOX (halogenated organic compounds adsorbable on activated carbon) [17]. In the Co/PMS/Cl⁻ systems, it was observed that chlorine radicals may participate in phenol and 2,4-dichlorophenol transformation reactions [18]. Similarly, some chlorinated organic compounds or AOX are expected if Co/PMS is applied to decolor dye wastewater containing high concentration of Cl⁻. Kiwi et al. measured amount of AOX during Acid Orange 7 (AO7) oxidation in photoassisted and dark Fenton processes in the presence of Cl⁻ anions, but did not give detailed information of reaction intermediates formed by mass spectral identification [8]. Also, information of both decoloration and mineralization of the dye wastewater in a wide salinity range is lacking.

To improve the understanding of chloride effects on SO₄^{•-}-based treatment, AO7 was selected as a model nonbiodegradable azo dye to monitor its degradation and resulting intermediates, because it is a common dye used in industrial applications and laboratory studies and its degradation products in varied AOPs have been extensively characterized. The main objectives of this paper are (1) to test the effect of different concentration of chloride ions on the extent of decoloration and mineralization of AO7; (2) to study whether AOX can be formed during dye oxidation processes by chloride addition; and (3) to propose and compare the different dye degradation mechanisms under salt-free and hypersaline environment by detecting the intermediate products.

2. Experimental

2.1. Materials

Acid Orange 7 (C₁₆H₁₁N₂O₄SNa) and Oxone[®] ([2KHSO₅·KHSO₄·K₂SO₄] salt, 95%) were purchased from Sigma-Aldrich. NaCl and CoSO₄·7H₂O were of laboratory reagent grade and used without further purification. All sample solutions were prepared using deionized water from Barnstead UltraPure instrument. The salinity was varied by addition of sodium chloride (NaCl). Stock solutions of all chemicals were freshly prepared. Prior to each experiment, certain aliquots were transferred to the reactor vessel to obtain the specific concentrations.

2.2. Experimental procedures

All reactions were initiated by mixing appropriate concentrations of AO7, cobalt salt, chloride ion and Oxone[®] in this order immediately without the pH being controlled. The final experimental conditions, including the concentrations of PMS, Co²⁺ and AO7, have been set based on our preliminary experiments (please see Figs. SI-1 and SI-2) to obtain optimum conditions. The time scan mode of a Hitachi U-2900 spectrophotometer was used to in situ monitor the dye decoloration at 485 nm. A Shimadzu TOC-V_{CPH} analyzer was employed for TOC (total organic carbon) measurement. At the given reaction time intervals, samples taken from the solution for TOC analysis were immediately quenched with sodium nitrite. The AOX determinations were carried out by instrumental analysis (AOX, multi X[®] 2000, Jena, Germany) after enrichment on activated carbon (European Standard EN 1485 H14, 1996).

GC/MS analysis was performed to identify the intermediate products formed during the AO7 degradation process. The experiments were carried out at two different chloride ion concentrations (without Cl⁻ for 1# and in the presence of 200 mM Cl⁻ for 2# and 3#). To determine whether the cobalt is involved in the degradation at extremely high concentration of chloride, the initial concentration of cobalt was different (in the presence of 0.2 mM Co²⁺ for 1# and 2#, without Co²⁺ for 3#). Prior to GC-MS analysis, the unbuffered solutions (100 mL) were quenched by 50 mL of NaNO₂ solution (0.1 M) and filtered with 0.22 μm membrane. Samples were pretreated using SPE (solid-phase extraction), SPME (solid-phase microextraction) methods (details in Table SI-1) to extract and concentrate compounds of different polarity and volatility. Spectra were obtained with a gas chromatograph (Agilent 7890A), equipped with DB-5 MS capillary column (30 mm × 320 μm × 0.5 μm film thickness), interfaced directly to the mass spectrometer (5975A inert XL MSD with Triple-Axis Detector) used as a detector. Electron impact (EI) mode at 70 eV was used and the mass range scanned was 30–400 *m/z*. The substance analysis was undertaken with reference to the NIST08 mass spectral library database.

3. Results and discussion

3.1. Effects of Cl⁻ concentration on dye degradation rate

Fig. 1 showed that in PMS/Cl⁻ system AO7 was still rapidly degraded even in the absence of Co²⁺ ion, although the decoloration rate is lower than that with the catalyst. This Co-independent PMS decomposition suggests that PMS would react with chloride to produce active chlorine species HOCl/Cl₂ (Eqs. (9) and (10)), which are able to decolor dyes rapidly. Since the amount of HOCl/Cl₂ based on PMS decomposition by chloride was dependent upon chloride and PMS concentration, dye bleaching rate consequently increased exponentially with chloride and PMS content (Fig. SI-3).

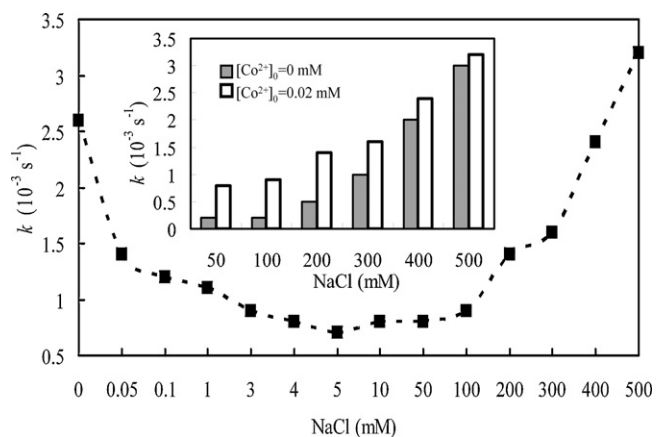


Fig. 1. Effects of chloride ions on AO7 bleaching rate constants (k) in the solution. Experimental conditions: $[AO7]_0 = 0.1$ mM; $[PMS]_0 = 0.5$ mM; $[Co^{2+}]_0 = 0.02$ mM. Inset: plots of combined effect of chloride ions and catalyst Co^{2+} on the decoloration rate (k) with the initial concentration of AO7 0.1 mM and PMS 0.5 mM. All rate constants are pseudo-first order rate constants.

While in $Co/PMS/Cl^-$ system decoloration of AO7 declined significantly with increasing concentration of sodium chloride from 0.05 to 5 mM. Similar inhibitory effects have been reported in Ozonation [19], UV/H_2O_2 [20] and UV/TiO_2 processes [21]. However, further addition of Cl^- (>5 mM) apparently accelerated dye degradation and the bleaching rate in presence of 500 mM Cl^- was even larger than that without chloride ions. This dual effect of chloride on dyes bleaching has not been observed in other AOPs systems which are mainly based on $\bullet OH$ -radicals. In $Co/PMS/Cl^-$ system, the dye degradation can be attributed to three kinds of active species: (1) $SO_4^{\bullet-}$ radicals (Eqs. (1)–(8)); (2) Cl^\bullet , $Cl_2^{\bullet-}$ and $ClOH^{\bullet-}$ (Eqs. (11), (12), (14) and (15)) and (3) $HOCl$ and Cl_2 (Eqs. (9) and (10)). The variation tendency of dye degradation rate (k) is not only related to the percentage of each oxidant species, but also to their reaction kinetic constants with dye. Consumption of $SO_4^{\bullet-}$ radicals by Cl^- and formation of less reactive chlorine radicals should be responsible for the adverse effect of chloride on Co/PMS performance. However, the formation of $HOCl$ and Cl_2 (Eqs. (9) and (10)) would make the dye bleaching rate higher with the addition of large amount of chloride ions similar to PMS/Cl^- system. Therefore the dye degradation can be enhanced at higher chloride concentration. However, this dual effect of chloride has been not observed in H_2O_2 -based AOPs such as Fenton and photo-Fenton systems [8], possibly because chloride alone could not activate H_2O_2 to oxidize organics.

3.2. Spectral change of AO7

Representative UV/Vis spectra obtained from the dye solution as a function of reaction time are shown in Fig. 2. The absorption spectrum of AO7 in water is characterized by two bands in the visible region, with their maxima located at 485 nm and 430 nm corresponding to the hydrazone form and the azo form of the dye, respectively, and by two bands in the ultraviolet region located at 230 nm and 310 nm due to the benzene and naphthalene rings of AO7, respectively.

It is observed that the absorbance at 485 nm almost completely disappears regardless of chloride ion, indicating the destruction of azo chromophore. In Fig. 2A, a new absorbance peak ($\lambda = 251$ nm) appears at 2 min, but subsequently disappears after 30 min. However, in the presence of chloride, the intensities of the absorbance peaks at 230 nm and 310 nm decrease much more slowly with respect to that of the azo bond within 2 h. Previous reports have indicated that the ultraviolet bands located at 228 and 310 nm correspond to $\pi-\pi^*$ transitions in the benzoic and naphthalene rings of AO7, respectively [22]. It implies that some intermediates generated from chromophore cleavage may still contain benzoic- and naphthalene-type rings. Besides, there were some new peaks observed during the decomposition of the dye and their absorbance maxima increased continuously from 249 nm to 260 nm, which were not observed in the absence of chloride. These differences indicate the possible formation of new breakdown products like chlorinated aromatic compounds. Repeta et al. reported that chlorinated aromatic acids display strong absorption bands (240–400 nm) in the ultraviolet and near-ultraviolet regions [23]. Our following GC–MS analysis also proved that at least nineteen chlorinated compounds were produced during AO7 degradation, in accordance with spectral results.

3.3. Identification of reaction intermediates

3.3.1. AO7 intermediates (Co/PMS , No Cl^-)

The reaction intermediates of AO7 without any chloride present in the reacting solution (Figs. SI-4 and SI-5) can be classified into six groups: (I) two naphthalene-type compound, 1-nitro-2-naphthalenol (1) and coumarin (2), which are primary degradation intermediate accompanying AO7 cleavage in the vicinity of the azo bond; (II) four fused heterocyclic compounds, such as 1(3H)-isobenzofuranone (3), 1,3-indanedione (4), phthalimide (5) and phthalic anhydride (6); (III) two aromatic compounds, such as phthalic acid (7), benzoic acid (8), which might be the degradation products of the partial oxidation of the aforementioned naphthalene-type and heterocyclic compounds, and their formation has been also reported by several previous studies concerning AO7 photocatalytic degradation [24,25]; (IV) two

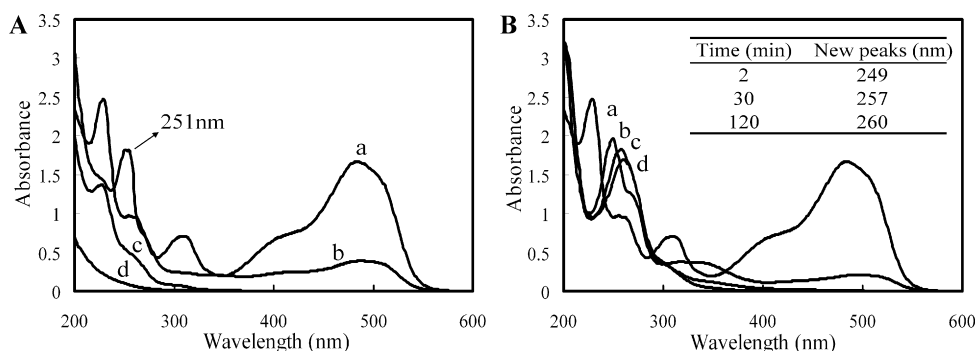


Fig. 2. UV-vis spectral changes of AO7 in solutions containing PMS (5 mM) and Co^{2+} (0.1 mM) in the presence of different concentrations of chloride as a function of time. Experimental conditions: (A) $[AO7]_0 = 0.08$ mM; $[NaCl]_0 = 0$ mM; (B) $[AO7]_0 = 0.08$ mM; $[NaCl]_0 = 200$ mM, initial pH 6.5 (natural). Reaction times: (a) 0 min, (b) 2 min, (c) 30 min, and (d) 120 min.

mono-heterocyclic compounds, including 1-nitrosopiperidine (**9**) and butyrolactone (**10**); (V) two alkane compounds, such as hexane (**11**) and 3-methylpentane (**12**); and (VI) one small molecule organic acid compound, formic acid (**13**), whose further oxidation yielded CO₂, H₂O. The major intermediates detected from the sulfate radical attack on AO7 were similar with those identified in hydroxyl radical oxidation processes such as the Fenton reagent [25], sonolytic oxidation [26] and photocatalysis [22,24]. Other reaction intermediates, such as 2-naphthol and *p*-benzoquinone proposed by Velegraki et al. [26] and other investigators [25], were not detected in our study and this might have been due to the different degradation mechanisms involving in different radicals as well as to the different experimental conditions and analytical techniques employed in various studies.

3.3.2. AO7 intermediates (Co/PMS/Cl⁻ & PMS/Cl⁻)

The intermediates detected under a chloride-rich environment not only included the oxidation products measured in Co/PMS system, but also included several chlorinated organic products, regardless of the presence of Co²⁺ (Figs. SI-6–SI-11). These chlorinated intermediates can be grouped into four kinds: (I) five naphthalene-type compounds, including 4-chloro-1,2-naphthalenedione (**14**), 2,4-dichloro-1-naphthalenol (**15**), 6-chlorochromone (**16**), 3-chloroisocoumarin (**17**), and 3,4-dichloroisocoumarin (**18**); (II) two heterocyclic compounds, including 5-chloroisobenzofuran-1,3-dione (**19**) and 5-chlorobenzofuran (**20**); (III) twelve aromatic compounds, such as 4-chlorophthalic acid (**21**), 1,2-benzenedicarbonyl dichloride (**22**), 1,2-dichlorobenzene (**23**), 1,4-dichlorobenzene (**24**), 1,3,5-trichlorobenzene (**25**), 1,2-dichloro-3-nitrobenzene (**26**), 1,3,5-trichloro-2-nitrobenzene (**27**), 2,4-dichlorophenol (**28**), 2,5-dichlorohydroquinone (**29**), 2,4,6-trichlorophenol (**30**), 2,3,5,6-tetrachlorophenol (**31**) and tetrachlorohydroquinone (**32**); and (IV) one low molecule chlorinated product: tetrachloromethane (**33**). Some of these intermediates mentioned above such as 2,4-dichlorophenol, 2,4,6-trichlorophenol, tetrachlorohydroquinone and tetrachloromethane have been identified as the phenol degradation products in Co/PMS/Cl⁻ system [18]. To our best knowledge, none of previous studies dealing with dye degradation gives information on these chlorinated by-products. Such information is only available for several experiments with much simpler molecules. To quantify total chlorinated by-products, AOX value was tested.

3.4. AOX formation

AOX is an important parameter for wastewaters from cleaning agents and disinfectants. Photochemical reactions are capable of transforming Cl⁻ into Cl[•] radical, leading to the chlorination of organic compounds [8]. Chlorine atoms are electrophilic (the element is electronegative, and Cl[•] will readily take up an electron to complete its octet) and thus readily add to the double bond of organic compounds. Chlorination by HOCl/Cl₂ can also generate AOX [17,19].

To determine the effect of chloride concentration on AOX formation, experiments were carried out at different chloride ion concentrations (0 mM Cl⁻, 0.2 mM Cl⁻ and 100 mM Cl⁻). Fig. 3 presents results of AOX measurement under different experimental conditions. Prior to oxidative treatment, no AOX was detected as expected, due to the absence of chlorine atom in the AO7 molecular structure. AOX type products were formed once the dye in aqueous solution was mixed with 0.1 mM Co²⁺, 10 mM PMS and 0.2 mM Cl⁻. The amount of AOX formed was dependent upon reaction time and the chloride content in solution. The increase of Cl⁻ concentration led to an increase in the yields of AOX as seen in Fig. 3. The maximum AOX production was 3.5 mg/L in the presence of 100 mM

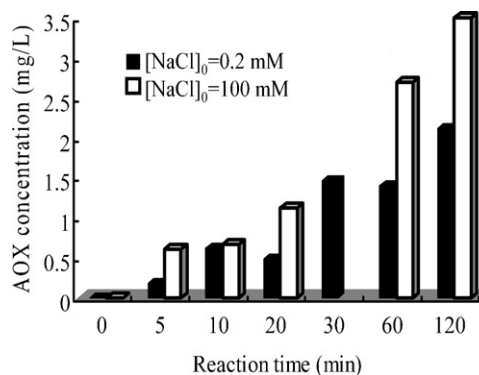


Fig. 3. AOX concentration of the dye wastewater during the Co/PMS treatment ([AO7]₀ = 0.2 mM; [PMS]₀ = 10 mM; [Co²⁺]₀ = 0.1 mM) containing different concentrations of chloride.

Cl⁻, comparable to those detected in •OH-based Fenton oxidation processes of AO7 [8].

AOX formation in the presence of Cl⁻ can be explained by reactions (17)–(19):

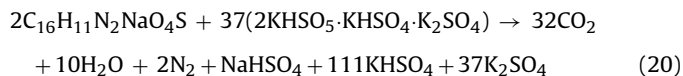


Sulfate/chlorine radicals attack on the aromatic ring of dye itself or its byproducts, or direct chlorination by Cl₂/HClO yields RCl type organohalogenes. The formation of AOX has already been observed in other AOPs systems such as Fenton reaction [8] and UV/H₂O₂ oxidation [17]. Kiwi et al. [8] reported that Fenton and photo-Fenton degradation of AO7 may produce chlorinated byproducts due to the radical chain reactions of chloride ion with hydroxyl radicals, although their molecular structures have not been well identified. Baycan et al. [17] observed a de novo synthesis of AOX in the presence of 1000 mg/L or 10000 mg/L Cl⁻ during UV/H₂O₂ oxidation of acetone and sodium dodecyl sulfate (ABS). It should be pointed out that AOX only represents a fraction of the chlorinated organic compounds. They are considered recalcitrant and expected to be completely mineralized with longer oxidative treatment.

3.5. AO7 mineralization

All experimental results obtained from UV–vis spectroscopy, GC–MS and AOX measurements show that chlorinated organic intermediates were generated when certain concentrations of chloride were present in Co/PMS systems. Therefore, using TOC values rather than decoloration rates seems more reasonable to evaluate the degradation efficiencies of Co/PMS/Cl⁻ system.

The approximate stoichiometry of AO7 mineralization in the presence of Oxone[®] can be expressed as:



The stoichiometric amount of Oxone[®] needed to mineralize 0.2 mmol of AO7 is 3.7 mmol (less than Oxone[®] dosage used in this study). Therefore, complete mineralization of AO7 should be expected under the present experimental conditions (AO7, 0.2 mM; PMS, 10 mM; Co²⁺, 0.1 mM). As shown in Fig. 4, 81.8% of AO7 could be mineralized without the addition of NaCl after 6 h oxidation treatment. However, under similar conditions but in the presence of salt (0.2–200 mM of NaCl), TOC removal was reduced with increasing chloride concentrations. For example, the decrease of TOC was only 6.65% with a chloride concentration of 10 mM.

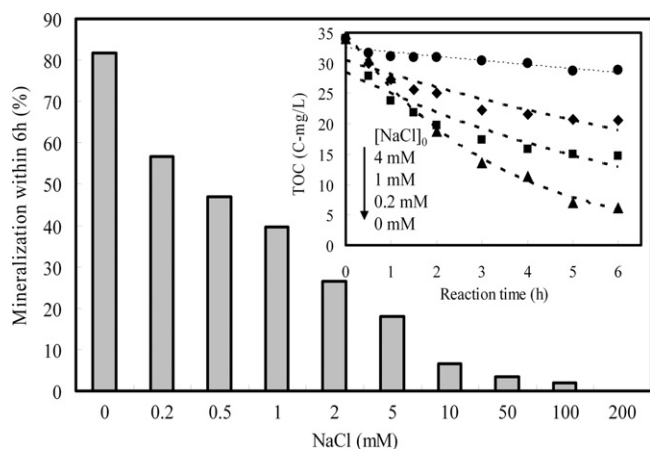


Fig. 4. TOC removal of dye wastewater containing different chloride concentrations after 6 h oxidation treatment. *Inset:* influence of chloride ions on mineralization of dyes. Experimental conditions: $[AO7]_0 = 0.2 \text{ mM}$; $[Co^{2+}]_0 = 0.1 \text{ mM}$; $[PMS]_0 = 10 \text{ mM}$.

AO7 was hardly mineralized after 6 h oxidation when the concentration of NaCl was up to 200 mM, although complete decoloration could be reached within 1 h. The inhibitory effects of chloride on dye mineralization would be attributed to (1) the consumption of the oxidant PMS and $SO_4^{\bullet-}$ radicals by Cl^- ions, resulting to the

less reactive inorganic radicals (e.g. $Cl^{\bullet}/Cl_2^{\bullet-}$); and (2) generation of more refractory organohalogen compounds as identified with GC-MS and AOX measurements.

3.6. Proposed reaction mechanism

Based on the kinetic results and degradation products identified by GC/MS methods and previous researches [25,27], two possible branched pathways for AO7 degradation by sulfate radicals under a chloride-rich environment are proposed.

3.6.1. $SO_4^{\bullet-}$ radical-based reaction pathway

The sulfate radical is a primary oxidizing species via Co^{2+} -mediated PMS reduction, and may react with dye molecule via addition to the aromatic ring followed by hydrolysis. The hydroxylation intermediates are the major products formed by sulfate radical attack on aromatics [28]. The overall decomposition of AO7 dye via sulfate radical-based pathway is illustrated in Fig. 5. The oxidation decomposition of AO7 can be described by a series of consecutive degradation steps. AO7 was firstly decomposed to aromatic intermediates, further oxidized to ring opening products and organic acids, and finally mineralized to CO_2 , H_2O and inorganic salts as pointed out in the literature [25,27]. Sulfonated molecules are non-volatile and highly soluble in water therefore cannot be analyzed by GC/MS. After 120 min of oxidation, the reaction

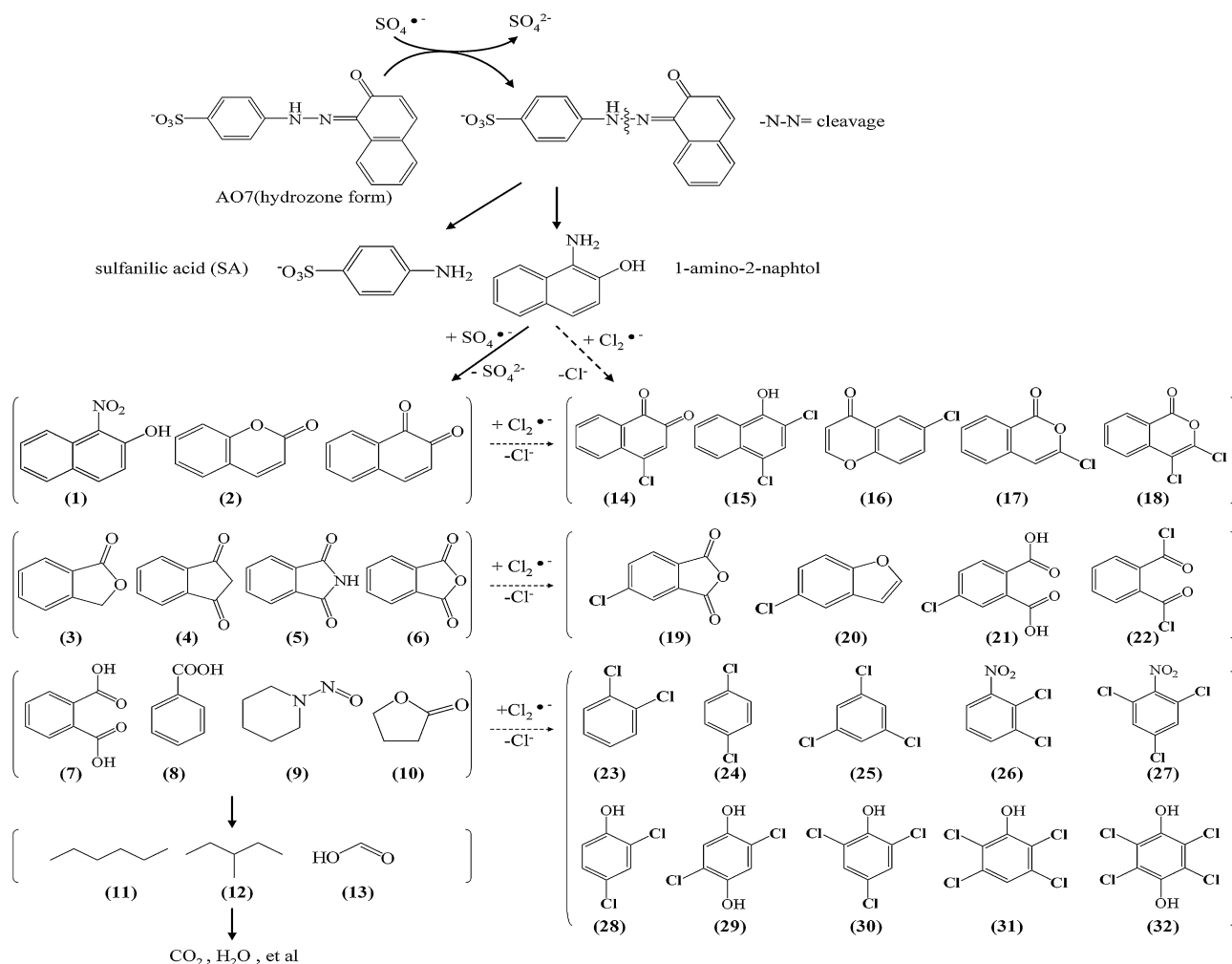


Fig. 5. $SO_4^{\bullet-}$ radical-based reaction pathway of AO7 oxidative degradation using Co/PMS system in the presence of chloride ions. The identified byproducts by GC-MS were numbered in parentheses (see details in Supporting Information).

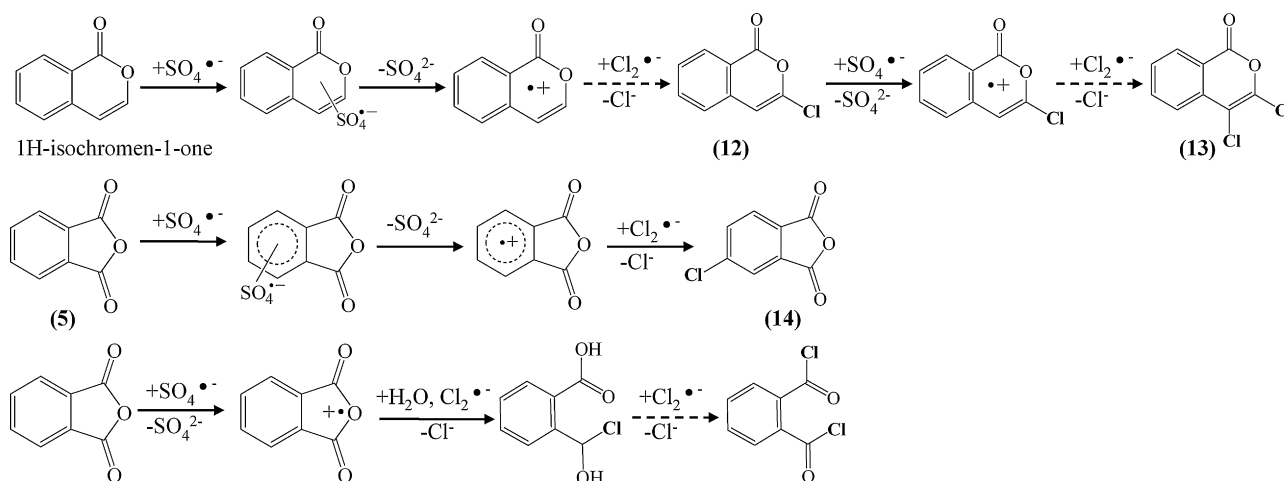


Fig. 6. Sulfate/chlorine radicals attack on degradation intermediates of AO7.

mixture nearly exclusively consists of aliphatic compounds presumably due to further oxidation of AO7 and its ring intermediates.

In the presence of chloride, the secondary chlorine radicals such as Cl^\bullet , $\text{Cl}_2^{\bullet-}$ and $\text{ClOH}^{\bullet-}$, were generated by scavenging $\text{SO}_4^{\bullet-}$ radical by Cl^- ion [29]. These chlorine radicals are generally less reactive than the primary $\text{SO}_4^{\bullet-}$ radical, leading to slower degradation of AO7 dye. $\text{Cl}^\bullet/\text{Cl}_2^{\bullet-}$ may react with dye and its intermediates by one-electron oxidation, H-abstraction and addition to unsaturated C–C bonds [30]. A termination reaction of chlorine radical with AO7 oxidation intermediates radicals, such as quinone radical, leads to the formation of the chlorinated derivatives as detected from the transformation of phthalic anhydride provided in Fig. 6. The first step in all cases is the addition of a sulfate radical to the aromatic ring of byproducts of dye decomposition [18]. The formation of the corresponding cation radicals take place via elimination of the sulfate group, followed by chlorination by $\text{Cl}_2^{\bullet-}$, as shown in more details in Fig. 6.

3.6.2. Non-radical reaction pathway

The halide ions (e.g. Cl^- , Br^- and I^-) are directly oxidized through *two-electron transfer* producing reactive halogens (e.g. Cl_2/HClO) (Eqs. (9) and (10)) [31]. Chlorine in the form of a liquid or gas has been effectively used for the color removal processes of many dyes [32]. The first step of aquatic chlorination is electrophilic substitution on the aromatic ring, depending on the combined resonance and inductive effects of the ring substituents. HClO has higher instability due to pronounced ionic nature and thus more reactivity towards the aromatic nucleus [33]. Chlorination of anisole, *o*-methoxybenzoic acid, ethylbenzene [34] and other phenolic compounds [35] led to formation of notable array of organochlorines. Narender et al. [33] reported the selective oxychlorination of aromatic compounds using KCl as a chlorine source and Oxone[®] as an oxidant. They found that introduction of an electron donating group on the aromatic ring substantially increased the rate of ring chlorination while on electron-withdrawing group decreases it. It is noteworthy that the identified chloride-containing intermediates by Cl_2/HClO chlorination were very similar to those detected in Co/PMS/ Cl^- systems (see Figs. SI-6 and SI-7).

It should be noted that many chlorinated aromatic pollutants generated during the dye bleaching process are recalcitrant and have long half-lives. Some of them show a tendency to bioaccumulate due to their hydrophobicity and excellent ability to penetrate cell membranes while some are proven carcinogens and mutagens [36]. It is unlikely that the risk of yielding more toxic compounds

would be deemed worth the effectiveness that Co/PMS reagent represents. If these noncolored azo dye byproducts are released into water bodies as a discharge effluent, it will pose a high toxicological risk to exposed humans and aquatic biota [37].

4. Conclusions

Effects of chloride ion on degradation of an azo dye (Acid Orange 7) by the emerging cobalt/peroxymonosulfate (Co/PMS) advanced oxidation process were investigated in this study. A dual effect of chloride (i.e. inhibitory and accelerating effect) on dye bleaching kinetics was firstly observed. In contrast to the Fenton-based AOPs, chloride ions with high concentrations (>5 mM) can greatly increase the decoloration efficacy of AO7, regardless of the presence of the Co^{2+} catalyst. However, high dosage of chloride did significantly inhibit dye mineralization to an extent which was closely dependent upon the initial chloride concentrations. According to the results obtained from UV–vis spectroscopy, AOX determination and GC–MS measurements, some undesirable aromatic chlorinated compounds were generated in the presence of 200 mM NaCl, independent of the addition of cobalt catalyst. These interesting results above can be attributed to two possible branched ($\text{SO}_4^{\bullet-}$ radical-based and non-radical) pathways for AO7 degradation by sulfate radicals under a chloride-rich environment.

The present study indicates that the appreciable levels of salts in wastewater from the textile industries may reduce the level of dye mineralization and even lead to the formation of more toxic chlorinated compounds during AOPs treatment. Therefore, attempts to develop strategies for circumventing the adverse effects of chloride in Co/PMS system should be urgently taken prior to the large scale application of this emerging advanced oxidation technology.

Acknowledgments

The authors gratefully acknowledged the financial support from the Fundamental Research Funds for the Central Universities (2010B04-04-1), the Shanghai Leading Academic Discipline Project (B604) and Shanghai Tongji Gao TingYao Environmental Science & Technology Development Fund. This work was also partially supported by the priming scientific research foundation for the junior teachers of Donghua University (No. 113-10-0044049) and the PhD thesis innovation foundation of the Donghua University (No. 11D11311).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.09.007.

References

- [1] Y. Dong, J. Chen, C. Li, H. Zhu, Decoloration of three azo dyes in water by photocatalysis of Fe(III)-oxalate complexes/H₂O₂ in the presence of inorganic salts, *Dyes Pigments* 73 (2007) 261–268.
- [2] S. Wang, A comparative study of Fenton and Fenton-like reaction kinetics in decolorisation of wastewater, *Dyes Pigments* 76 (2008) 714–720.
- [3] Z.H. Wang, W.H. Ma, C.C. Cheng, J.C. Zhao, Light-assisted decomposition of dyes over iron-bearing soil clays in the presence of H₂O₂, *J. Hazard. Mater.* 168 (2009) 1246–1252.
- [4] J. He, W. Ma, J. He, J. Zhao, J.C. Yu, Photooxidation of azo dye in aqueous dispersions of H₂O₂/α-FeOOH, *Appl. Catal. B: Environ.* 39 (2002) 211–220.
- [5] C.C. Chen, W.H. Ma, J.C. Zhao, Semiconductor-mediated photodegradation of pollutants under visible-light irradiation, *Chem. Soc. Rev.* 39 (2010) 4206–4219.
- [6] H. Lachheb, E. Puzenat, A. Houas, M. Ksibi, E. Elaloui, C. Guillard, J.-M. Herrmann, Photocatalytic degradation of various types of dyes (Alizarin S, Crocein Orange G, Methyl Red, Congo Red, Methylene Blue) in water by UV-irradiated titania, *Appl. Catal. B: Environ.* 39 (2002) 75–90.
- [7] H. Ghodbane, O. Hamdaoui, Decolorization of anthraquinonic dye, C.I. Acid Blue 25, in aqueous solution by direct UV irradiation, UV/H₂O₂ and UV/Fe(II) processes, *Chem. Eng. J.* 160 (2010) 226–231.
- [8] J. Kiwi, A. Lopez, V. Nadtochenko, Mechanism and kinetics of the OH-Radical intervention during Fenton oxidation in the presence of a significant amount of radical scavenger (Cl⁻), *Environ. Sci. Technol.* 34 (2000) 2162–2168.
- [9] Z.H. Wang, R.X. Yuan, Y.G. Guo, L. Xu, J.S. Liu, Effects of chloride ions on bleaching of azo dyes by Co²⁺/Oxone reagent: kinetic analysis, *J. Hazard. Mater.* 190 (2011) 1083–1087.
- [10] S.K. Ling, S. Wang, Y. Peng, Oxidative degradation of dyes in water using Co²⁺/H₂O₂ and Co²⁺/peroxymonosulfate, *J. Hazard. Mater.* 178 (2010) 385–389.
- [11] M.G. Antoniou, A.A. de la Cruz, D.D. Dionysiou, Degradation of microcystin-LR using sulfate radicals generated through photolysis, thermolysis, and e⁻ transfer mechanisms, *Appl. Catal. B: Environ.* 96 (2010) 290–298.
- [12] Q. Yang, H. Choi, S.R. Al-Abed, D.D. Dionysiou, Iron-cobalt mixed oxide nanocatalysts: heterogeneous peroxymonosulfate activation, cobalt leaching, and ferromagnetic properties for environmental applications, *Appl. Catal. B: Environ.* 88 (2009) 462–469.
- [13] Q. Yang, H. Choi, Y. Chen, D.D. Dionysiou, Heterogeneous activation of peroxymonosulfate by supported cobalt catalysts for the degradation of 2,4-dichlorophenol in water: the effects of support, cobalt precursor, and UV radiation, *Appl. Catal. B: Environ.* 77 (2008) 300–307.
- [14] P.R. Shukla, S. Wang, H.M. Ang, M.O. Tade, Photocatalytic oxidation of phenolic compounds using zinc oxide and sulphate radicals under artificial solar light, *Sep. Purif. Technol.* 70 (2010) 338–344.
- [15] C. 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.
- [16] X.-Y. Yu, Z.-C. Bao, J.R. Barker, Free radical reactions involving Cl[•], Cl₂^{•-}, and SO₄^{•-} in the 248 nm photolysis of aqueous solutions containing S₂O₈²⁻ and Cl⁻, *J. Phys. Chem. A* 108 (2004) 295–308.
- [17] N. Baycan, E. Thomanetz, F. Sengül, Influence of chloride concentration on the formation of AOX in UV oxidative system, *J. Hazard. Mater.* 143 (2007) 171–176.
- [18] 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.
- [19] M. Muthukumar, N. Selvakumar, Studies on the effect of inorganic salts on decolouration of acid dye effluents by Ozonation, *Dyes Pigments* 62 (2004) 221–228.
- [20] M. Muruganandham, M. Swaminathan, Photochemical oxidation of reactive azo dye with UV-H₂O₂ process, *Dyes Pigments* 62 (2004) 269–275.
- [21] M. Sömen, A. Özkan, Decolourising textile wastewater with modified titania: the effects of inorganic anions on the photocatalysis, *J. Photochem. Photobiol. A: Chem.* 147 (2002) 77–81.
- [22] M. Styliadi, D.I. Kondarides, X.E. Verykios, Visible light-induced photocatalytic degradation of Acid Orange 7 in aqueous TiO₂ suspensions, *Appl. Catal. B: Environ.* 47 (2004) 189–201.
- [23] D.J. Repeta, N.T. Hartman, S. John, A.D. Jones, R. Goericke, Structure elucidation and characterization of polychlorinated biphenyl carboxylic acids as major constituents of chromophoric dissolved organic matter in seawater, *Environ. Sci. Technol.* 38 (2004) 5373–5378.
- [24] M. Styliadi, D.I. Kondarides, X.E. Verykios, Pathways of solar light-induced photocatalytic degradation of azo dyes in aqueous TiO₂ suspensions, *Appl. Catal. B: Environ.* 40 (2003) 271–286.
- [25] H.-Z. Zhao, Y. Sun, L.-N. Xu, J.-R. Ni, Removal of Acid Orange 7 in simulated wastewater using a three-dimensional electrode reactor: removal mechanisms and dye degradation pathway, *Chemosphere* 78 (2010) 46–51.
- [26] T. Velegraki, I. Poullos, M. Charalabaki, N. Kalogerakis, P. Samaras, D. Mantzavinos, Photocatalytic and sonolytic oxidation of Acid Orange 7 in aqueous solution, *Appl. Catal. B: Environ.* 62 (2006) 159–168.
- [27] X. Chen, J. Chen, X. Qiao, D. Wang, X. Cai, Performance of nano-Co₃O₄/peroxymonosulfate system: kinetics and mechanism study using Acid Orange 7 as a model compound, *Appl. Catal. B: Environ.* 80 (2008) 116–121.
- [28] G.R. Peyton, The free-radical chemistry of persulfate-based total organic carbon analyzers, *Mar. Chem.* 41 (1993) 91–103.
- [29] G.P. Anipsitakis, T.P. Tufano, D.D. Dionysiou, Chemical and microbial decontamination of pool water using activated potassium peroxymonosulfate, *Water Res.* 42 (2008) 2899–2910.
- [30] J.E. Grebel, J.J. Pignatello, W.A. Mitch, Effect of halide ions and carbonates on organic contaminant degradation by hydroxyl radical-based advanced oxidation processes in saline waters, *Environ. Sci. Technol.* 44 (2010) 6822–6828.
- [31] G. Lente, J. Kalmár, Z. Baranyai, A. Kun, I. Kék, D. Bajusz, M. Takács, L. Veres, I. Fábrián, 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.
- [32] K. Hamada, M. Nishizawa, D. Yoshida, M. Mitsuishi, Degradation of an azo dye by sodium hypochlorite in aqueous surfactant solutions, *Dyes Pigments* 36 (1998) 313–322.
- [33] N. Narender, P. Srinivasu, S.J. Kulkarni, K.V. Raghavan, High efficient, para-selective oxychlorination of aromatic compounds using potassium chloride and oxone®, *Synth. Commun.* 32 (2002) 279–286.
- [34] A.T. Lebedev, G.M. Shaydullina, N.A. Sinikova, N.V. Harchevnikova, GC–MS comparison of the behavior of chlorine and sodium hypochlorite towards organic compounds dissolved in water, *Water Res.* 38 (2004) 3713–3718.
- [35] L.M. Rebenne, A.C. Gonzalez, T.M. Olson, Aqueous chlorination kinetics and mechanism of substituted dihydroxybenzenes, *Environ. Sci. Technol.* 30 (1996) 2235–2242.
- [36] D.V. Savant, R. Abdul-Rahman, D.R. Ranade, Anaerobic degradation of adsorbable organic halides (AOX) from pulp and paper industry wastewater, *Bioresour. Technol.* 97 (2006) 1092–1104.
- [37] D.P. Oliveira, P.A. Carneiro, C.M. Rech, M.V.B. Zanoni, L.D. Claxton, G.A. Umbuzeiro, Mutagenic compounds generated from the chlorination of disperse azo-dyes and their presence in drinking water, *Environ. Sci. Technol.* 40 (2006) 6682–6689.