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Photo-oxidation of *o*-chloroaniline in the presence of TiO_2 and IO_3^-: A study of photo-intermediates and successive IO_3^- dose

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Abstract

The photocatalytic oxidation in TiO_2 and IO_3^- has been found to be an effective process to degrade the aromatic organic pollutant, *o*-chloroaniline (*o*-ClA). The degradation of *o*-ClA is mainly attributed to the $^{\bullet}OH$ attack. Several organic intermediates were identified and the existence of aromatic intermediates would not accumulate in the solution as their degradations were observed. A relatively high level of iodoaniline was solely owing to the use of IO_3^- which could experience further decay under UV/TiO_2 condition. Further investigation on second IO_3^- dose has indicated a faster *o*-ClA degradation, but the degree of degradation depends on the time interval between each dose. It is observed that the disappearance of *o*-ClA and intermediates was the fastest when shorter interval of second IO_3^- dose (i.e., 5 min). Slower degradation at longer IO_3^- interval (i.e., 20 min) is possibly due to consumption of radicals from first dose and the inhibition of iodide, the eventual reduction product of IO_3^-. With the inclusion of the photo-products, the degradation pathway of *o*-ClA has been proposed accordingly.

Keywords: TiO_2; IO_3^-; *o*-ClA; GC/MS; Intermediates; Degradation pathyway

1. Introduction

The photocatalytic process illuminated by TiO_2 has been widely employed in the removal of organic pollutants. The use of inorganic oxidants (e.g., H_2O_2, ClO_3^-, BrO_3^- and $S_2O_8^{2-}$) in UV/TiO_2 system could increase the quantum efficiencies either by inhibiting electron–hole pair recombination through scavenging conduction-band electrons at the surface of TiO_2 or offering additional oxygen atom as an electron acceptor to form the superoxide radical ion ($^{\bullet}O_2^-$) or reactive radical intermediates [1]. Besides, additional oxidants could induce the generation of other radical species. Wang and Hong [2] have worked on the photodecay of 2-chlorobiphenyl in periodate solution. They claimed that the photolytic decomposition of periodate involves the formation of a number of highly reactive radical and non-radical intermediates such as $IO_3^{\bullet}$, $^{\bullet}OH$, IO_3^- and $IO_4^{\bullet}$. Apart from the judgment on degradation kinetics of the target compound, the influence of the inorganic additives must be accurately examined before application as some of them may affect the degradation adversely at specific conditions.

Researches on organic photodegradation generally emphasize on either the initial stage, by measuring the reacted substrate, or to the final stage of the overall reaction by measuring CO_2 formation [3,4]. Although decay of target compound is possible to observe in most cases, the destination of compounds remains unanswered and it cannot be proposed as a trouble-free method without the knowledge of the photoproducts. The target compound is possibly transformed to other form of organics. Such transformation might result in the generation of more toxic organics than their parent compound after the treatment. To ensure the photodegradation is a clean process, the identification of degradation products could provide valuable evident. Organics are expected to breakdown into simpler structures, and subsequently, mineralization is the target of the process. The degradation pathway can be precisely proposed according to the information of photoproducts. However, the identification of photoproducts could be varied from researchers as the photoreaction is condition dependent. Sanchez et al. [5] have conducted the degradation of *p*-chloroaniline by ionizing radiation and the formation of aminophenol, chlorophenol, anilne, phenol and formaldehyde were reported. Apart from those, the photodecay of *p*-chloroaniline by Mailhot et al. [6] have generated chlorocataechol and chloronitrobenzene in the presence

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of Fe(III). Therefore, the examination of photoproducts in each process is necessary.

In this study, the photo-oxidation in UV/TiO_2/IO_3^- has been examined in the presence of a dye intermediate, *o*-chloroaniline (*o*-ClA). An in-depth study of IO_3^- and its successive dosing have been discussed in the paper and the degradation pathway of *o*-ClA was proposed according to the detection of organic intermediates.

2. Materials and methods

2.1. Material used

The probe *o*-ClA (99.8%; C_6H_6ClN) having a molecular weight of 127.57 and water solubility of 0.5 g per 100 mL at 20 °C was purchased from Fluka. TiO_2-P25 (Degussa) containing 80% anatase and 20% rutile phase with a BET surface area of 50 $m^2 g^{-1}$ and a density of 3.85 g cm^{-3} was chosen for the study. Potassium iodate, (KIO_3) (AR Grade; 99.7 + % purity) was purchased from International Laboratory USA. Intermediates including 2-chloro-1,4-benzoquinone, 2-iodoaniline, 2-chloronitrobenzene and 1,4-benzoquinone were purchased from Aldrich with the best available purity. Acetonitrile in HPLC grade; ethyl acetate, methanol and acetone in ACS reagent grade were purchased form Tedia. The water used in the preparation of all the solutions was generated from a Millipore Waters Milli-Q water purification system. All chemicals were used without further purification.

2.2. Preparation of samples

The photodegradation of *o*-ClA was performed in a photochemical reactor with a ventilation fan installed at the bottom (Rayonet^{TM} RPR-200 manufactured by the Southern New England Ultraviolet Company). The installation of eight UV lamps at 300 nm emitting 5.6×10^{-6} E l^{-1} s^{-1} photons was used in this study. The *o*-ClA stock at 1.423 mM was prepared by transfering 150 μm of 1.21 g/L *o*-ClA into 1 L DDW. Thorough mixing was done by magnetic stirring for overnight and sonication in ultra-sound bath for 1 h. The initial concentration of *o*-ClA was set at 0.285 mM for kinetic study while it was raised to 0.95 mM for the intermediate identification. From the results of our previous study, the dosage of TiO_2 was fixed at 0.1 g L^{-1} and 0.156 mM of IO_3^- was used unless specified otherwise. Quartz beaker containing 150 mL mixture of *o*-ClA, TiO_2 and IO_3^- was placed at the centre of a photoreactor with stirring during the experiment. Samples were taken out at pre-determined time and filtered through a 0.45 μm membrane. Further extraction was required for GC/MS quantification, where an equal volume of ethyl acetate and hexane mixture was used as the solvent. The vials containing 1 mL of extraction solvent and 0.2 g of NaCl was filled with 1 mL of filtered sample. Thorough mixing was performed by a mixer Barnstead Thermolyne Type 37600. After the extraction, the vials were left stationary until the two layers were established; the top layer was then taken out by a glass dropper for GC/MS analysis.

2.3. Chemical analysis

Remaining *o*-ClA after photoreaction was determined by HPLC (Waters) with a Restek column packed with pinnacle octylamine (5 μm, 0.46 cm × 25 cm), in which the mobile phase was a mixture of acetonitrile (40%) and water (HPLC grade; 60%) at a flow rate of 1.0 mL min^{-1}. The decrease of iodate and the generation of chloride was monitored by the ion chromatography (Dionex Series 4500i) composed of an anion column (Dionex Ionpac AS11 (4 mm × 250 mm) and AG11 (4 mm × 50 mm), and a suppressor (ASRS-II) in auto suppression recycling mode. A mixture of 0.8 mM of $NaHCO_3$ and 0.8 mM of $NaCO_3$ was used as the mobile phase eluting at 1 mL min^{-1}. The total organic carbon (TOC) concentration was analyzed by a Shimadzu TOC-5000A analyzer equipped with an ASI-5000A autosampler to determine the mineralization degree of the organic pollutants during the advanced oxidation process.

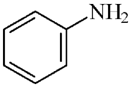
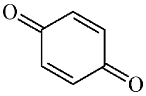
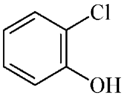
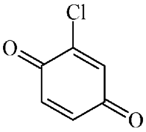
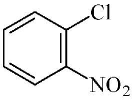
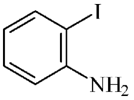
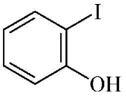
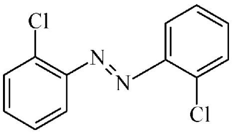
Aromatic intermediates were identified by gas chromatography–mass spectrometry (GC/MS) with a Hewlett-Packard system composed of a HP 3800 gas chromatograph connected with Varian factor four capillary column (VF-5 ms 30 m × 0.25 mm), coupled with a Varian 1200L quadrupole MS/MS operating in EI mode at 900 V. Helium gas in the constant flow of 1 ml min^{-1} was used as the carrier gas. An autosampler was installed and 1 μL of sample was injected from the injector port (280 °C) in the splitless mode. Separation of intermediates were ramped by a temperature program with an initial temperature at 50 °C for 1 min, rising to 200 °C at 5 °C min^{-1} and remained for 3 min, then it finally reached to 260 °C at the same rate and remained for another 2 min. Unknown peaks were identified by the library provided from National Institute of Standards and Technology (NIST) [7]. Quantification of intermediates was conducted by comparing to their corresponding external standards. While those compounds were not commercially available, their relative abundance was predicted by their corresponding ion intensity with the probe compound, *o*-ClA, from the MS analysis. Details of intermediates were shown in Table 1.

3. Results and discussions

3.1. The identification of organic intermediates and the reduction of TOC

Several organic intermediates degraded from *o*-ClA were identified in the UV/TiO_2/IO_3^- process. Fig. 1a showed the profiles of six organic intermediates matched with the NIST library. As indicated in Fig. 1b, the decay of *o*-ClA was quite fast in the first 10 min leading to the formation of intermediates at the early stage of the photoreaction. Nevertheless, their increasing trend was maintained shortly and declined gradually. After 15 min of reaction time, four organic intermediates, 2-chlorophenol (CP), 2-chloronitrobenzene (CNB), 2-chloro-1,4-benzoquinone (CBQ) and bis(2-chlorophenyl)-diazene (BCD) were identified at low detection levels. For example, the CNB showed the highest level with a maximum at 0.0025 mM, which was only about

Table 1
Information on organic intermediates of *o*-ClA (*Note*: NA means commercial standard is not available) [7]

Identified intermediates (nomenclature)	Molecular weight	Structural formula	MS spectrum (>50%)	Purchased from
Aniline (AL)	93.13		93	Acro
1,4-Benzoquinone (BQ)	108.09		108, 54, 26	Acro
2-Chlorophenol (CP)	128.56		128	Riedel-de Haen
2-Chloro-1,4-benzoquinone (CBQ)	142.54		142, 54, 26, 82, 53, 60	Acro
2-Chloronitrobenzene (CNB)	157.55		75, 111, 157, 99	International Lab.
2-Iodoaniline (IA)	219.02		219, 65, 127, 92	Aldrich
2-Iodophenol (IP)	220.01		220	Aldrich
Bis(2-chlorophenyl)-diazene (BCD)	251.11		111, 139	NA

1/380 times of the original probe compound. Beside the CNB, other intermediates also presented at only ppb levels. It is reasonable that the concentration of intermediates was lower than the initial *o*-ClA level as they were degraded from the same source. Because the decay of *o*-ClA was fast, the exceptional low level and low accumulation of intermediates was due to the fast decay of themselves in the process and led to a fast mineralization. Side product 2-iodoaniline (IA) and a typical oxidative product 1,4-benzoquinone (BQ) were also identified at the later time of reaction. Among all the identified intermediates, IA was the only component that kept increasing in the process indicating a longer reaction time was required. In view of this, the photodegradation of IA was carried out separately in UV/TiO_2 (without using IO_3^- to minimize the interference). As showed in Fig. 2, the decay of IA could be observed and about 92% of IA disappeared in 240 min. In addition, two organic compounds, 2-iodophenol (IP) and aniline (AL), were detected by the GC/MS analysis. After incorporating the profile of intermediates into Fig. 2, their levels were also found very low comparing with the initial [IA], where IP was found decreasing within the reaction time. Although the decay of aniline was not observed in this study, its degradation and mineralization were reported by Kumar and Mathur [8] and Sauleda and Brillas [9], respectively.

Besides, the detection of IC has also indicated the generation of chloride at 60 and 120 min were 0.343 mM and 0.518 mM respectively. As the initial *o*-ClA was at around 0.9 mM, the chloride concentration was comparable to the *o*-ClA. In addition, the measurement of TOC in Fig. 1a has shown a decreasing trend in the presence of UV/TiO_2/IO_3^-. It is noted that about 50% of TOC was reduced during the 300-min reaction time. This has proven that the process does not only reduce the amount of target compound; it could finally breakdown the aromatic organic into non-toxic CO_2 and H_2O.

3.2. Mechanistic pathway

Based on the profiles of intermediates, the degradation pathway of *o*-ClA was proposed in Fig. 3. Those organic intermediates were mainly degraded via the $^\bullet$OH attack by the addition to the aromatic ring [10,11]. Since the nature of $^\bullet$OH is highly electrophilic, it preferentially attacks at the position with the highest electron density of the target molecule [12,13]. Besides, H-abstraction and direct electron abstraction from the aromatic compound by $^\bullet$OH to give a resonance-stabilized cation radical are also important mechanisms to participate the degradation pathway [14,15].

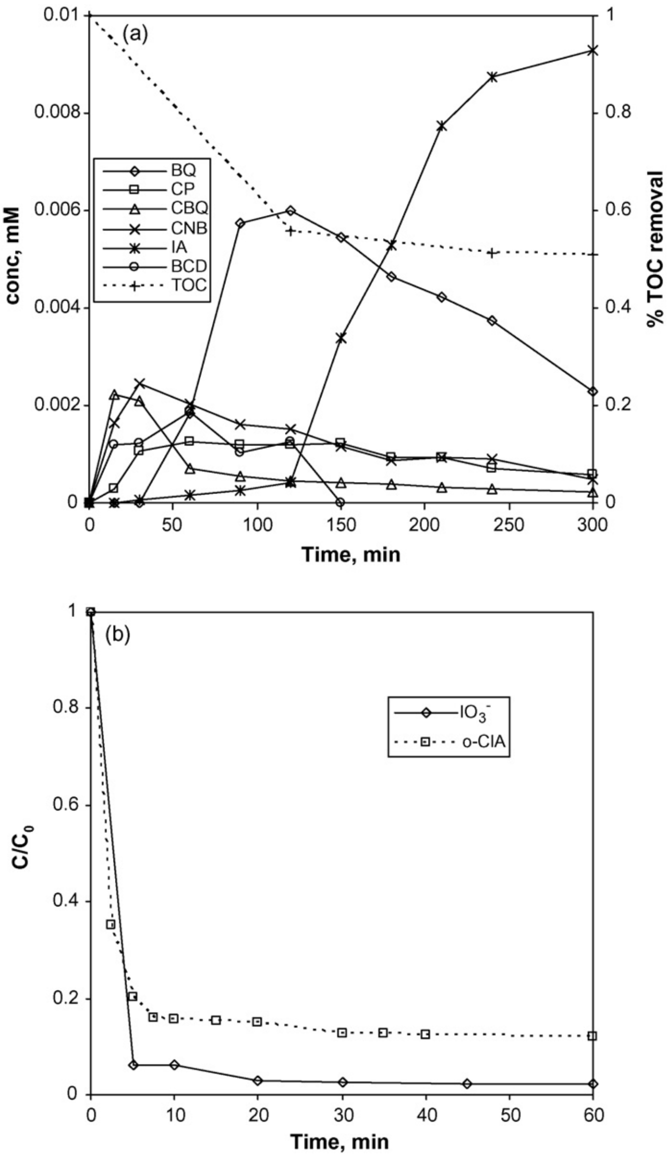


Fig. 1. (a) The intermediates and TOC profiles of $UV/TiO_2/IO_3^-$. (b) The consumption of IO_3^- and the *o*-ClA decay. (*Note*: [*o*-ClA] = 0.95 mM; $[TiO_2] = 0.1\ g\ L^{-1}$; $[IO_3^-] = 0.78$ mM; solution pH 7; irradiation time = 300 min.)

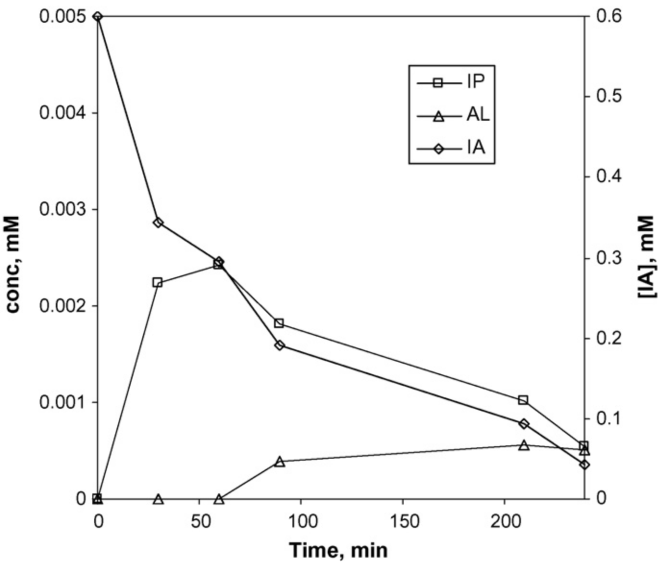


Fig. 2. Photodegradation of iodoaniline in UV/TiO_2 system. (*Note*: [IA] = 0.93 mM; $[TiO_2] = 0.1\ g\ L^{-1}$; solution pH 7.)

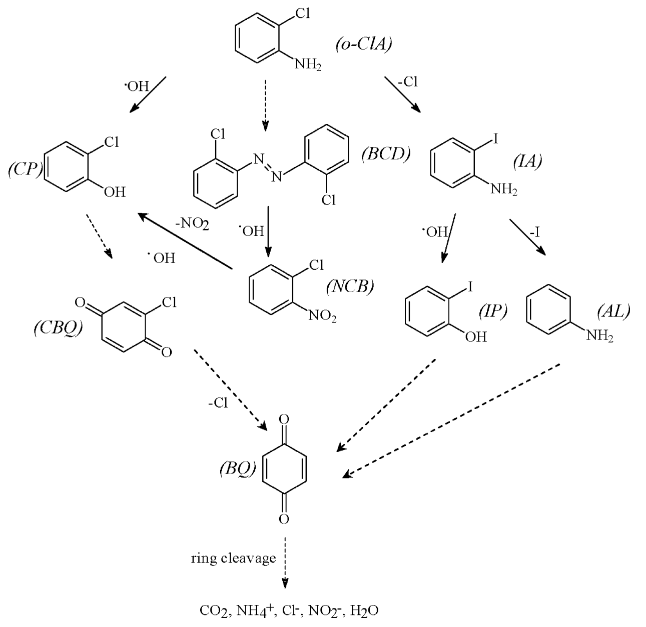
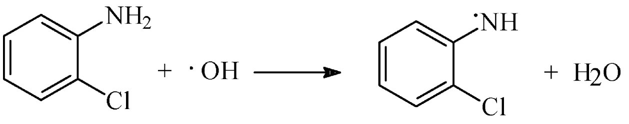
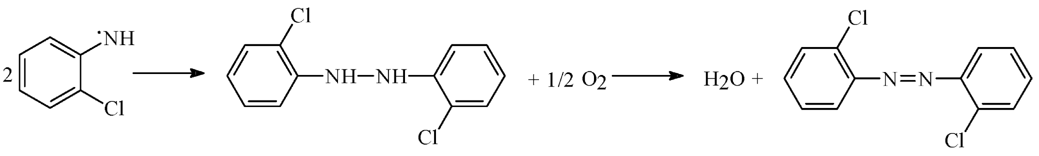


Fig. 3. The proposed degradation mechanism of *o*-ClA in the presence of $UV/TiO_2/IO_3^-$. (*Note*: Dashed arrow represents reactants could take more than one step to reach the products. Abbreviations were indicated as italic.)

The proposed scheme showed three possible products have been degraded from the primary oxidation of *o*-ClA in $UV/TiO_2/IO_3^-$. The $^{\bullet}OH$ could replace the amino group of *o*-ClA to form CP. Or alternatively, dimerization of *o*-ClA is possible via subsequent processes. Solar et al. [16] have verified that $^{\bullet}OH$ attack to the amino-group could result in the aniline-radical formation (Eq. (1)) by the pulse radiolysis. Kumar and Mathur [17] have further discussed the combined of this radical could finally yield the dimer (BCD in our case) as shown in Eq. (2):



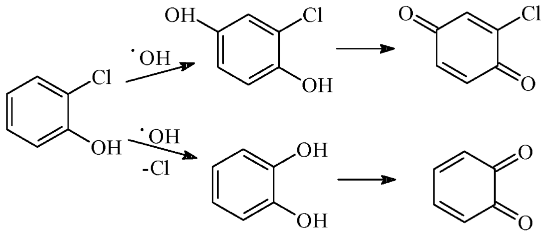
(1)



(2)

As IO_3^- was used as an oxidant, an iodide related intermediate was identified. Chloride on *o*-ClA was found to be replaced by iodide and formed the IA. This product was identified at 30 min of reaction time. Such delay in IA formation may due to the less reactive substitution reaction comparing to the radical attack and the low level iodide in the solution at the beginning.

Since the primary intermediates were already in ppb level, further decay would lead to even lower level of secondary and tertiary products which are undetectable. Also, it is observed that BQ was accumulated and the amount was relatively higher than other intermediates. The generation of BQ was result from the decay of CP, BCD and IA. The degradation of CP has been proposed by Bandara et al. [18] and Ma et al. [19]. Although *ortho*- and *para*-site in CP are both electron rich, they revealed that $^\bullet$OH attack is preferential at *para*-site. This is due to the steric strain is lower in *para*-site and the inductive electron-withdrawing effect of the chlorine atom might render attachment of the electrophilic $^\bullet$OH to the *ortho*-relative to the *para*-position. Ilisz et al. [20] have reported chlorohydroquinone (CHQ) as the major product from the decay of CP while another minor product, catechol, (CHQ:catechol ~5:1) was also formed by the addition in ortho position followed by Cl abstraction (Eqs. (3) and (4)) [21,22]:



(3)

(4)

Subsequently, CHQ may dissociate two hydrogen atoms to give 2-chloro-1,4-benzoquinone (CBQ) which concurred with our observation. CBQ could further decay to BQ by dechlorination process.

Another primary photo-intermediate, BCD, was detected in the process but its concentration dropped to zero in 150 min. This compound is apparently not persistent in the photoreaction and can subsequently be oxidized to CNB. Although the direct formation of CNB from ClA photodegradation has been elsewhere reported [6]; the formation of CNB via a two-step process involving the transformation of BCD is identified in this study. Canle et al. [23] described the reaction of CNB via the addition of $^\bullet$OH to the aromatic ring, followed by elimination of OH^- from the $^\bullet$OH adduct and deprotonation of the radical cation. The $^\bullet$OH can further attack the nitro group of CNB and transform CNB into CP. This mechanism has also been reported by Ishikawa et al. [24].

As mentioned earlier, IP and AL have been detected as the primary products of IA and were also included in the degradation pathway. This suggested that IA could be decayed either through $^\bullet$OH attack to the amino group or by the deiodination. The study of halogen compounds has revealed that the chemical properties within the halide group are similar except florine which has high electronegativity. Clark [25] has stated that the bond enthalpies between H and halide are getting weaker from Cl to I. The increase in size has pulled the atoms further apart and weakens the attraction within. Therefore, it is feasible that IP undergoes analogous oxidation as CP and generates BQ as the product.

The profile of BQ in Fig. 1a has revealed a relatively higher concentration comparing to other intermediates. Although the decay of *o*-ClA could be routed to yield various species, the pathway would finally end up to the same products, BQ. The degradation of BQ has been examined by many researchers [26,27]. It has been verified that further decay of BQ could initiate the ring cleavage leading to the formation of short chain organic acids such as oxalic acid, formic acid, maleic acid and malonic acid, etc. In addition, the ions formation (NH_4^+, NO_2^- and Cl^-) as the end-products has also been reported in our previous study and other researchers [28].

3.3. Second iodate dosing

3.3.1. Kinetic description

It has previously proven that IO_3^- is a very powerful oxidant when working with UV/TiO_2 [29]. Recall from Fig. 1b that the consumption of IO_3^- was extremely fast. Within 5 min of reaction time, about 96% of IO_3^- was utilized in the solution. Therefore, the possibility of second IO_3^- dosing was proposed to improve the process performance. Solution of *o*-ClA containing 0.1 g L^{-1} of TiO_2 and 0.158 mM of IO_3^- was mixed and was irradiated at the same condition as indicated before. An additional 0.158 mM of IO_3^- was dosed at pre-selected time intervals to the solution. The performance of *o*-ClA by second iodate dose was depicted in Fig. 4. With the inclusion of single IO_3^- dose, it can be compared that the overall *o*-ClA removal was enhanced by the second IO_3^- dose. Fast degradation of *o*-ClA could be observed at the beginning of second dosing, but the decay was slow down at a later stage. In addition, it was observed that the removal efficiency of *o*-ClA depended on the time of second dosing: the earlier the second dosing, the faster and higher the degradation. When the second dose was applied at 20 min, additional 11% of *o*-ClA was removed in

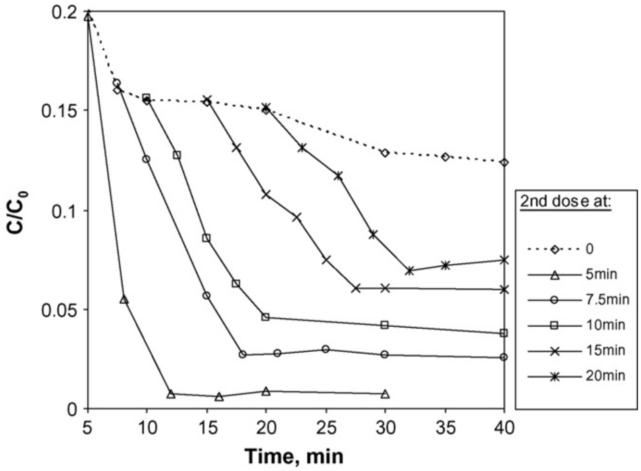


Fig. 4. Effect of second iodate dosing. (*Note*: Each dose of IO_3^- was controlled at 0.156 mM; $[o\text{-ClA}]_0 = 0.285$ mM; solution pH 7; $[TiO_2] = 0.1$ g L^{-1}.)

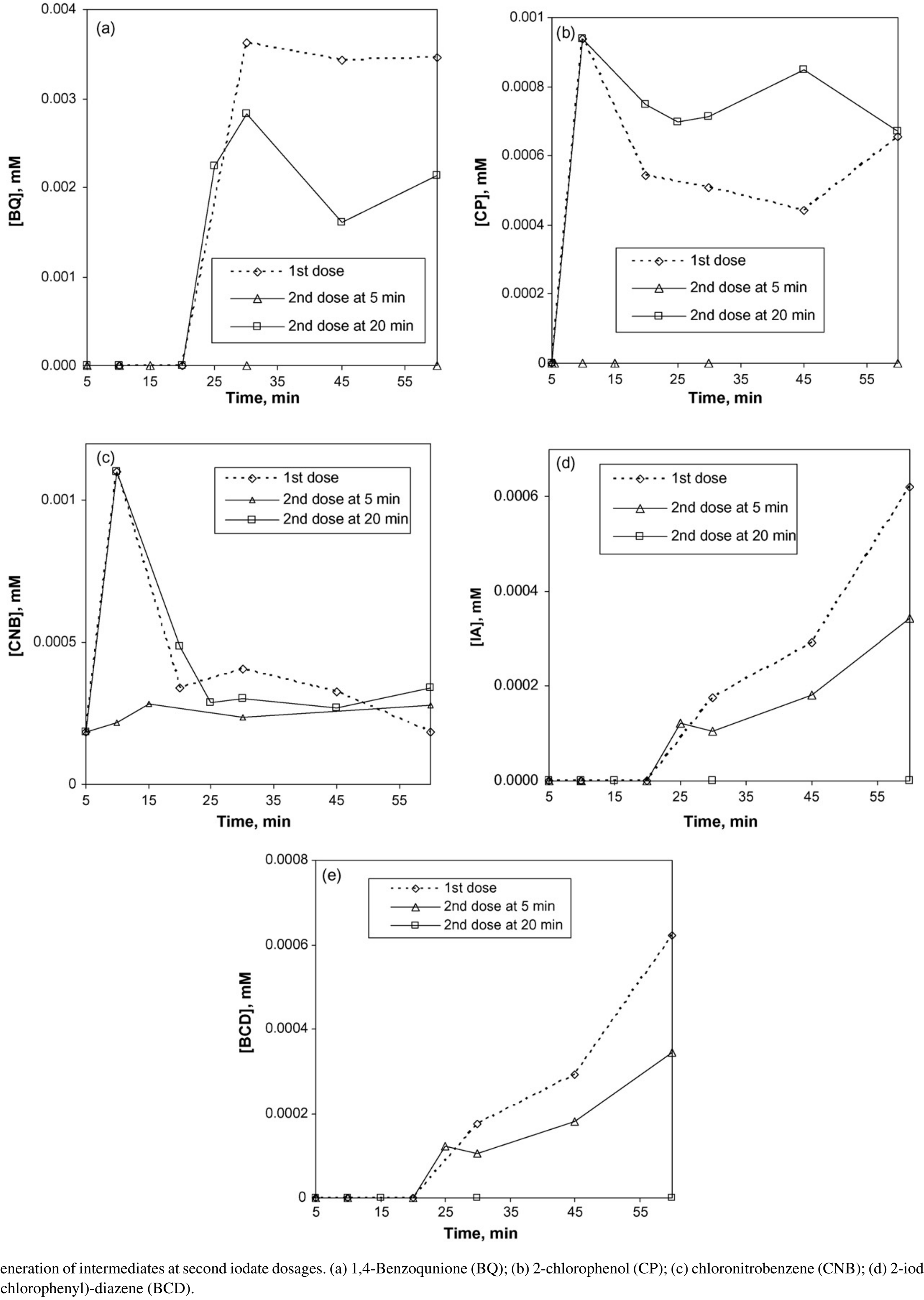


Fig. 5. Generation of intermediates at second iodate dosages. (a) 1,4-Benzoqunione (BQ); (b) 2-chlorophenol (CP); (c) chloronitrobenzene (CNB); (d) 2-iodoaniline; (e) bis(2-chlorophenyl)-diazene (BCD).

11 min, while 19% more of *o*-ClA was removed in 7 min when the dosing time was shorten to 5 min. Such observation is possibly attributed to the intermediates effect. In the presence of IO_3^- in the UV/TiO_2 system, the fast initial decay of *o*-ClA has led to formation of intermediates. The increase amount of intermediates would compete for further decay with the *o*-ClA resides in the solution implying the chance to oxidize *o*-ClA is thus reduced. A more detail study on the intermediate effect will be discussed in the next section.

3.3.2. *Intermediates from second IO_3^- dosing*

The second dosing time of IO_3^- at 5 and 20 min were selected for the intermediate examination. The *o*-ClA decay can be referred to Fig. 4 (symbols of △ and *) while the examination of four selected intermediates were illustrated in Fig. 5a-e. During an 1-h reaction, it was generally observed that the profile of intermediates was found to be similar between the single dose and the second dose at 20 min while the second dose at 5 min has given quite a different performance. In a shorter dosing interval, several major intermediates in $UV/TiO_2/IO_3^-$ including BQ, CP and IA were not detected in all the samples while CNB and BCD were barely identified in relatively lower level than the other runs. To ensure a higher percentage removal of *o*-ClA and intermediates, successive dosing is encouraged at shorter time interval. The IO_3^- profile of second dosing has been monitored in Fig. 6. When $[IO_3^-]$ was dropped to about 0.01 mM within 5 min time, the second dosing could boost-up the system to ensure the source of oxidant was adequate for organic destruction. However it was surprised to note the second dose at 20 min did not significantly reduce the *o*-ClA and the generation of CP was even higher than the single dosing.

Weaver et al. [30] have outlined the reduction pathway of IO_3^- under the UV illumination. During the process, it would generate other radical species such as $IO_2^{\bullet}$ and $HIO_3^{\bullet -}$, yielding I^- as the end-product. Enhancing the photodecay is straightforward by the extra radicals, but the effect of I^- should not be overlooked. Ohtaki et al. [31] have reported a inhibiting degradation in UV/TiO_2 process when halide ions were exist in the system. The gradual increment of $[I^-]$ can significantly deteriorated the photodegradation. As indicated in Fig. 7, the slowest degradation was found in the solution containing iodide. The UV/TiO_2 was retarded by 25% when 0.15 mM iodide was added. It can be assumed that the generation of I^- as the reductive products of IO_3^- has functioned as a radical scavenger in the system. Such an effect is minimal at shorter time interval as large amount of radical species were still participating in the organic oxidation. However, after a longer reaction time, the accumulated I^- was dominant over the IO_3^- and the radical concentrations ($IO_2^{\bullet}$ and $HIO_3^{\bullet -}$) which significantly retard the *o*-ClA decay even the source of IO_3^- was refilled.

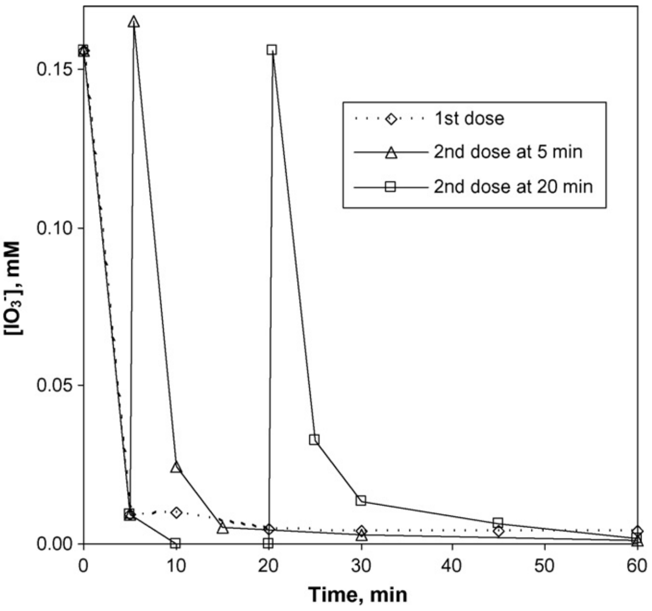


Fig. 6. Profile of iodate at second dosages.

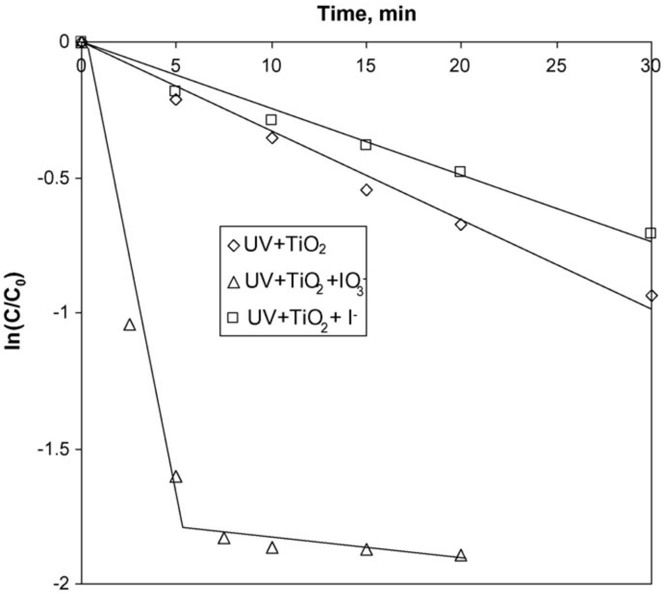


Fig. 7. Effect of iodide ion on the photodegradation of *o*-ClA. (*Note*: [*o*-ClA] = 0.285 mM; $[TiO_2] = 0.1\ g\ L^{-1}$; $[IO_3^-] = 0.156$ mM; $[I^-] = 0.15$ mM.)

4. Conclusion

In the decay of *o*-ClA under the $UV/TiO_2/IO_3^-$ process, the aromatic intermediates have been detected. The degradation was mainly initiated by radical attack and the mechanistic pathway was proposed accordingly. Although different organics were formed, all of them can be eventually oxidized to BQ, which can be subsequently decayed into simple organic acids and ionic products through ring cleavage. Second dosing of IO_3^- was proven useful in further improving the *o*-ClA decay, but the time interval for the second dose was critical to the process. Experimental data has indicated the shorter time interval is beneficial to both *o*-ClA and product decay. The final product from IO_3^- reduction, I^-, was believed to be the main species to scavenge the photo-oxidation in the system.

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