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Photocatalytic oxidation of carbamazepine in triclinic-WO_3 suspension: Role of alcohol and sulfate radicals in the degradation pathway

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ABSTRACT

The photocatalytic oxidation of carbamazepine (CBZ, an antiepileptic drug frequently detected in surface water and WWTP effluent) in WO_3 suspension under the irradiation of 420 nm lamps has been investigated. The addition of $S_2O_8^{2-}$ to this process can significantly accelerate the CBZ degradation. It was interesting to observe that conventional radical quenchers like methanol and ethanol promoted the photocatalytic oxidation of CBZ at low concentration (<100 mM), while the tert-butanol inhibits or accelerates the CBZ degradation depending on its concentration. To explore this, the decomposition of CBZ with and without the presence of methanol was investigated in details through the comparison of evolution of intermediates/products, and the comparison of generated radicals by ESR spectroscopy in the process. Sulfate radicals are believed to play a major role during CBZ decay with the presence of methanol in this process. It was found the rate enhancement of methanol is likely due to the competition between quenching effect and cleaning effect on the catalyst surface. In addition, the reaction mechanism reveals that CBZ degradation is mainly dominant by the electrophilic attack of radicals at olefinic double bond in the central heterocyclic ring, leading to ring-opening and formation of various intermediates.

1. Introduction

Carbamazepine (CBZ) is a widely prescribed antiepileptic and psychotropic drug. The worldwide consumption of CBZ is estimated to be 1014 tons per year [1] and CBZ is excreted with <3% remaining in its original form [2]. CBZ is one of the most frequently detected pharmaceuticals in WWTP (Wastewater treatment plant) effluents, surface water, and even drinking water at concentrations up to 6.3 μg/L [3,4], 3.09 μg/L [5], and 30 ng/L [6], respectively, indicating the inadequacy of the treatment methods applied in the WWTPs. Previous studies reported the removal efficiency of CBZ in WWTP is generally below 10% [1]. The persistence of CBZ in ecosystem and its potential to interfere with aquatic organism [7–9] cause a growing public interest in its treatment. Furthermore, some of the photodegradation products of CBZ, such as acridine, are reported to exert more adverse effects than CBZ itself [2,10]. In consequence, attempts to remove CBZ or its metabolites in aquatic environment have provoked the investigation on effective treatment technologies of CBZ.

Previous studies have examined the removal of CBZ through adsorption [11], treatment with laccase [12], photodegradation of CBZ by direct photolysis [10,13], chemical oxidation with chlorine dioxide [2], ozone [14], Mn [VII] and Fe [VI] [15], and photocatalysis [16,17]. Previous studies focused on CBZ degradation by TiO_2-based photocatalysis under UV irradiation [16,17]. UV light only accounts for a small portion (~5%) of the solar spectrum in comparison to the visible region (~45%). As an alternative to widely used TiO_2 [18] or ZnO [19] photocatalyst in wastewater purification, tungsten oxide (WO_3) has attracted considerable attention recently due to the ease of its preparation, response to visible light and long-term stability during irradiation [20–22]. The conduction band level of WO_3 (+0.5 V vs NHE) is more positive than the reduction potential of O_2. This fact led us to believe that WO_3 is unattractive in environmental cleanup. Therefore, the reports on WO_3 used as a sole catalyst for the degradation of organic pollutants in aqueous phase have been limited [23–25]. In our previous study, WO_3 has demonstrated high photocatalytic activity toward the degradation of monuron under the illumination of 420 nm lamps and the addition of some inorganic oxidants such as $S_2O_8^{2-}$ resulted in higher quantum efficiency [26].

This study presents for the first time the degradation of CBZ by combining $S_2O_8^{2}$-assisted and WO_3-based photocatalysis under the irradiation of 420 nm lamps, with special emphasis on the

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degradation pathways and the roles of radical scavengers in this process.

2. Experimental

2.1. Chemicals

The probe CBZ was purchased from Tokyo Chemical Industry. 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) and carbamazepine 10,11-epoxide were obtained from Aldrich Sigma and Fluka, respectively. Atrazine and benzoic acid were obtained from Chem-Service. Nitrobenzene was purchased from International laboratory (USA). WO_3 powder was prepared from commercial WO_3 (ACROS Organics) by adding the WO_3 particles to Distilled Deionized Water (DDW) under sonication for 40 min to form WO_3 suspension, then the WO_3 suspension was steam dried to obtain WO_3 powder. The mean diameter of as-prepared WO_3 powder was measured to be 379.8 nm by Zeta Plus/Zeta Potential Analyzer (Brookhaven Instruments Corporation). BET surface area of as-prepared WO_3 is 2.3308 m^2/g (Micromeritics ASAP2020M, USA). The WO_3 is triclinic according to XRD pattern in good agreement with the JCPDS 32-1395 standard card [26]. Potassium persulfate ($K_2S_2O_8$) and hydrogen peroxide (H_2O_2) was purchased from International Laboratory while $NaHCO_3$ was obtained from BDH. All other chemicals are in analytic purity and all solvents are HPLC grade and used without further purification. The DDW used in the preparation of all solutions was obtained from a Millipore Waters Milli-Q water purification system.

2.2. Photodegradation reaction

The photodegradation of CBZ was conducted in a computerized Luzchem CCP-4V photochemical reactor. To ensure a thorough mixing, 150 mL of solution was dispensed into a 300 mL quartz cylinder with mechanical stirring before and during the illumination. Luzchem LZC-420 lamps were installed in the photoreactor. The experimental installation and the emission spectra of the lamps were stated previously [27]. Samples were withdrawn at a predetermined interval and filtered through a 0.2 μm PTFE membrane to ensure the solution was free from particles prior to quantification. All experiments were carried out at room temperature (air-conditioned) at 23 ± 1 °C in duplicate, and the error is less than 3.0%.

For the tests involving UV irradiation, Luzchem CCP-4V photochemical reactor was equipped with phosphor-coated low-pressure mercury lamps, emitting 253.7 nm monochromatic UV at a light intensity of 1.5×10^{-6} Einstein L^{-1} s^{-1}.

There was no pH adjustment during the photodegradation reaction. The pH value of CBZ solution, the CBZ solution after the addition of WO_3 and persulfate was around 6.0, 5.6 and 4.6, respectively. The addition of alcohol exerted insignificant influence on the pH value of the solution.

2.3. Detection of radicals using ESR spectroscopy

Radicals generated in $WO_3/S_2O_8^{2-}$/UV–vis system with and without the presence of methanol were detected by ESR spectroscopy using DMPO as a spin trap agent. Radicals were initiated by mixing 0.3 g/L WO_3, 2 mM $K_2S_2O_8$ and 0.1 M DMPO under the irradiation of UV–vis. All spectra were obtained using a Bruker EMX100 ESR spectrometer with 100 kHz modulation frequency, 9.86 GHz resonance frequency, 20 mW microwave power, 1.0 G modulation amplitude, 5 ms of time constant and receiver gain of 5.02×10^4.

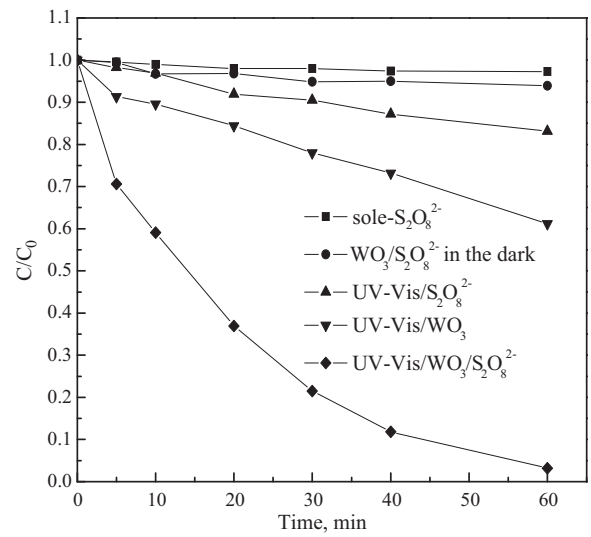


Fig. 1. CBZ degradation under different reaction (notes: initial CBZ concentration is 0.025 mM, WO_3 loading is 0.3 g/L, the initial concentration of H_2O_2 and $S_2O_8^{2-}$ is 2 mM, initial pH value is natural without adjustment, 12 lamps of 420 nm) conditions.

2.4. Chemical analysis

The remaining CBZ, atrazine (ATZ), nitrobenzene (NB) and benzoic acid (BA) after reaction was determined by HPLC, which was comprised of a Waters 515 HPLC pump, Waters 2489 Dual λ Absorbance Detector, a RESTEK C18 column (pinnacle DB, 250 mm × 4.6 mm, and 5 μm particle size), and a Waters 717plus Autosampler. The maximum adsorption wavelength (λ_{max}) was selected as 210, 221, 267 and 228 nm for CBZ, ATZ, NB and BA, respectively. A mixture of 60% acetonitrile and 40% water was used as the mobile phase running at a flow rate of 1 mL/min for CBZ, ATZ and BA. The $S_2O_8^{2-}$ residual was measured by the iodometric method [28].

The identification of intermediates was carried out at an initial CBZ concentration of 0.19 mM. A Thermo Quest Finnigan LCQ Duo Mass Spectrometer system was used with RESTEK C18 column (pinnacle DB, 250 mm × 4.6 mm, and 5 μm particle size). The LC detection system consisted of a photodiode array UV–visible detector. The reaction intermediates were identified by using LC-ESI-MS/MS operating at a positive mode with collision energy of 30%. A gradient method with a flow rate of 0.8 mL/min was used with two mobile phase (A: 5 mM ammonia acetate (pH 4.6); B: 100% acetonitrile). Phase A was maintained at 85% during the first 2 min, then B was steadily increased from 15% to 85% in the next 34 min. Finally, the mobile phase turned to the initial composition until the end of the run.

3. Results and discussion

3.1. Degradation of CBZ under different conditions

The degradation of CBZ was investigated under various conditions as demonstrated in Fig. 1. The removal of CBZ (<3%) in sole-$S_2O_8^{2-}$ system is insignificant after 60 min and the presence of WO_3 slightly increase the removal efficiency of CBZ (around 6%). The adsorption of CBZ on the surface of WO_3 is negligible (<1%). It is expected that CBZ elimination is also not effective (<17%) in UV–vis/$S_2O_8^{2-}$ system after 60 min since $S_2O_8^{2-}$ shows poor absorption of the light around 420 nm (see Fig. S1). CBZ degradation was found to follow pseudo-first-order kinetics in UV–vis/WO_3 and UV–vis/$WO_3/S_2O_8^{2-}$ systems. The removal efficiency of 0.025 mM

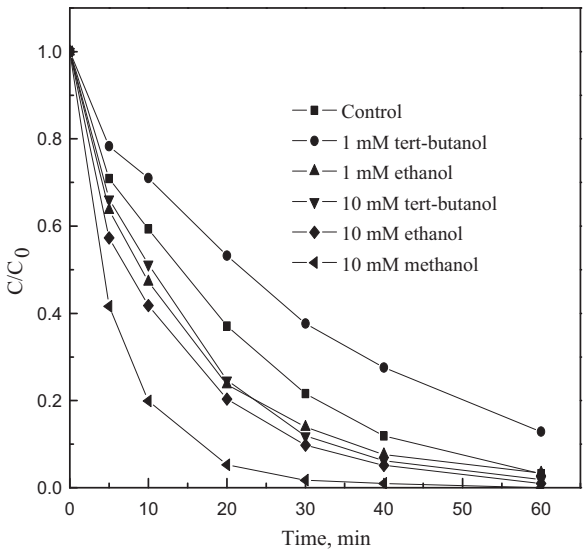


Fig. 2. Effect of various radical scavengers on CBZ (notes: initial CBZ concentration is 0.025 mM, WO_3 loading is 0.3 g/L, the initial concentration of $S_2O_8^{2-}$ is 2 mM, initial pH value is around 4.5, 12 lamps of 420 nm) degradation.

CBZ is around 39% in UV–vis/WO_3 process after 60 min of reaction. As also shown in Fig. 1, the addition of 2 mM $S_2O_8^{2-}$ markedly accelerated the degradation of CBZ, where the observed first-order rate constant ($k_{observed}$) was increased from 0.0082 to 0.055 min^{-1}. The $S_2O_8^{2-}$ ions can serve as electron acceptors to prevent the recombination of electron and hole by trapping the electron on the conduction band of WO_3. At the same time, $S_2O_8^{2-}$ ions may become the sources to offer sulfate radicals and additional hydroxyl radicals (Eqs. (1) and (2)) [29–31].

$$S_2O_8^{2-} + e_{CB} \rightarrow SO_4^{\bullet -} + SO_4^{2-} \quad (1)$$

$$SO_4^{\bullet -} + H_2O \leftrightarrow HO^{\bullet} + SO_4^{2-} + H^+ \quad (2)$$

3.2. Effect of radical scavengers on CBZ decay

It is believed that both hydroxyl radical and sulfate radical play an important role in UV–vis/WO_3/$S_2O_8^{2-}$ process. To investigate the photodegradation mechanism of CBZ, four radical scavengers were utilized to assess the contribution of various radicals to the CBZ decay. In general, tert-butanol selectively quenches hydroxyl radical, while ethanol and methanol can react with hydroxyl and sulfate radicals with high kinetic rate constants [32–35]. The reaction of $SO_4^{\bullet -}$ with tert-butanol is much slower compared to methanol and ethanol [32]. As demonstrated in Fig. 2, the CBZ degradation was noticeably inhibited with the presence of 1 mM tert-butanol. However, it is surprising to observe that the addition of ethanol and methanol did not retard but accelerate the CBZ degradation. It is also interesting to note the increase of the [tert-butanol] from 1 to 10 mM promoted CBZ degradation. Fig. 2 also shows the increase of ethanol concentration resulted in the enhancement of CBZ degradation rate and UV–vis/WO_3/$S_2O_8^{2-}$ process exhibited better performance in the presence of 10 mM methanol ($k_{observed}$ = 0.1273 min^{-1}) than that of 10 mM ethanol ($k_{observed}$ = 0.0728 min^{-1}). The accelerating effect of methanol on the degradation of another model compound, atrazine, was also observed (see Fig. S2). However, it was found the presence of 10 mM methanol noticeably inhibited NB degradation in UV–vis/WO_3/$S_2O_8^{2-}$ system (see Fig. S3). In order to evaluate the role of methanol in CBZ degradation by UV–vis/WO_3/$S_2O_8^{2-}$ process, the influence of methanol on CBZ degradation has been investigated in separate processes such as UV–vis/WO_3 and UV/$S_2O_8^{2-}$. It was observed that the presence of 10 mM methanol strikingly retarded CBZ degradation by UV–vis/WO_3 and UV–vis/WO_3/H_2O_2 processes (see Fig. S4). Sulfate radicals and hydroxyl radicals are believed to play a major role for the CBZ reduction in UV/$S_2O_8^{2-}$ and UV/H_2O_2 processes, respectively, since the photodecomposition of CBZ was not observed under the irradiation of sole-UV. The investigation on the effect of methanol on CBZ decay in both UV/$S_2O_8^{2-}$ and UV/H_2O_2 systems may help elucidate the role of methanol in CBZ decomposition in UV–vis/WO_3/$S_2O_8^{2-}$ system, where both hydroxyl and sulfate radicals are believed to exist simultaneously. The addition of methanol significantly hampered CBZ degradation in UV/$S_2O_8^{2-}$ and UV/H_2O_2 processes (see Fig. S5). It was also reported that methanol inhibited the degradation of Methyl Orange by Fe(II)/persulfate process [30]. However, the quenching effect of methanol is much more effective in UV/H_2O_2 system than that in UV/$S_2O_8^{2-}$. More than 60% of CBZ removal was achieved in 20 min by UV/$S_2O_8^{2-}$ with the presence of 100 mM methanol (CBZ removal efficiency is 92.3% in UV/$S_2O_8^{2-}$ system without methanol); while 100 mM methanol significantly retards the CBZ decay from 90.5% to 5.0% in the UV/H_2O_2 process. This is because methanol reacts much faster with hydroxyl radical (4.56–9.7 × 10^8 M^{-1} s^{-1} [33,34]) than with sulfate radicals (1.1–2.5 × 10^7 M^{-1} s^{-1} [35,36]). The fact that methanol exerting a negative influence on CBZ decomposition in both UV–vis/WO_3 and UV/$S_2O_8^{2-}$ processes implies that the positive role of methanol is likely related to the interaction between WO_3 and $S_2O_8^{2-}$ ions in UV–vis/WO_3/$S_2O_8^{2-}$ process (Table 1).

3.3. Effect of methanol concentration

To investigate the positive role of methanol in UV–vis/WO_3/$S_2O_8^{2-}$ process, the influence of methanol concentration on the degradation rate of $S_2O_8^{2-}$ and CBZ has been examined. Without the involvement of methanol, the consumption of $S_2O_8^{2-}$ was negligible in UV–vis/WO_3/$S_2O_8^{2-}$. A continuous increase of $S_2O_8^{2-}$ consumption was observed at elevated methanol concentration as illustrated in Fig. 3a. Fig. 3b shows the enhancement of CBZ decay as the methanol increases from 0 to 10 mM, where the presence of 10 mM methanol doubles the CBZ decay rate (from 0.055 to 0.127 min^{-1}). Further increment of methanol concentration, however, will start to retard the CBZ degradation. It is noteworthy that at 20 mM of methanol, the CBZ decay was still much faster (0.0943 min^{-1}) than that of no methanol (0.055 min^{-1}). The genuine retardation of CBZ decay (0.0467 min^{-1}) was not revealed until the methanol increased over 100 mM.

3.4. Detection of radicals involved in WO_3/$S_2O_8^{2-}$/UV–vis process with and without methanol

To investigate the reaction mechanism of CBZ degradation in WO_3/$S_2O_8^{2-}$/UV–vis system with and without the presence of methanol, ESR spectroscopy was utilized with DMPO as a spin trap agent to detect the generated radicals in the processes with and without the presence of methanol (see Fig. 4). Though, the generation of sulfate radical was unable to be quantified because of the low fluxes of the radicals in the solution. The radical signals with four symmetrical characteristic peaks of 1:2:2:1 of DMPO-OH were detected successfully in WO_3/$S_2O_8^{2-}$/UV–vis process with and without the presence of methanol, which verifies the formation of hydroxyl radicals in the process. Fig. 4 also shows that, in the absence of methanol, stronger signals of DMPO-OH were observed at 30-min than that at 15-min of light irradiation, indicating the radical concentration increases with time. In the presence of methanol, however, the signal was significantly reduced. This

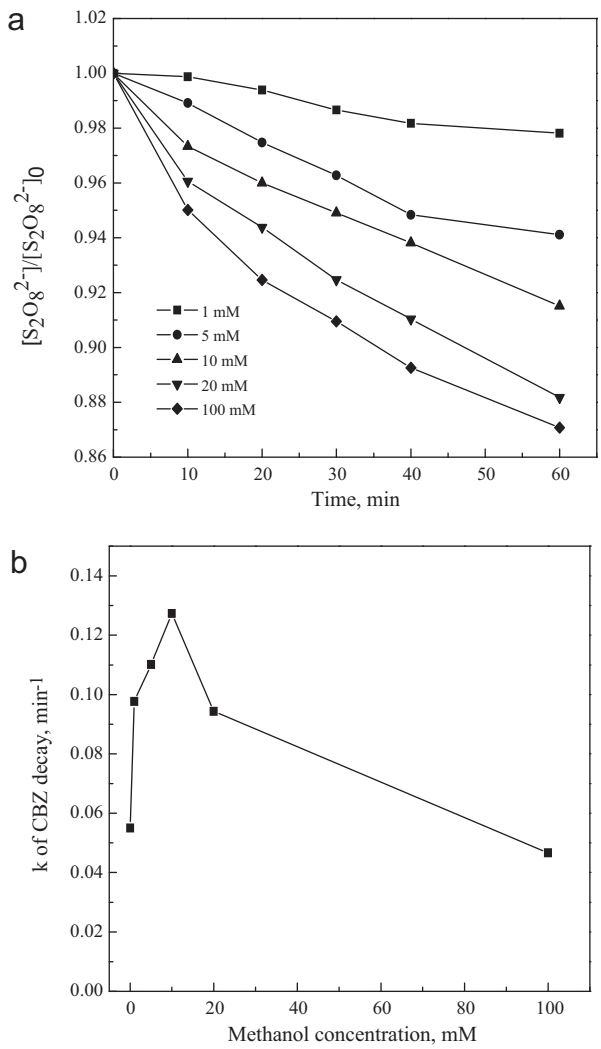


Fig. 3. (a) Effect of methanol concentration on the decomposition of $S_2O_8^{2-}$. (b) Effect of methanol concentration on the decay rate constants of CBZ (notes: initial CBZ concentration is 0.025 mM, WO_3 loading is 0.3 g/L, the initial concentration of $S_2O_8^{2-}$ is 2 mM, initial pH value is around 4.8 without adjustment, 12 lamps of 420 nm) ions.

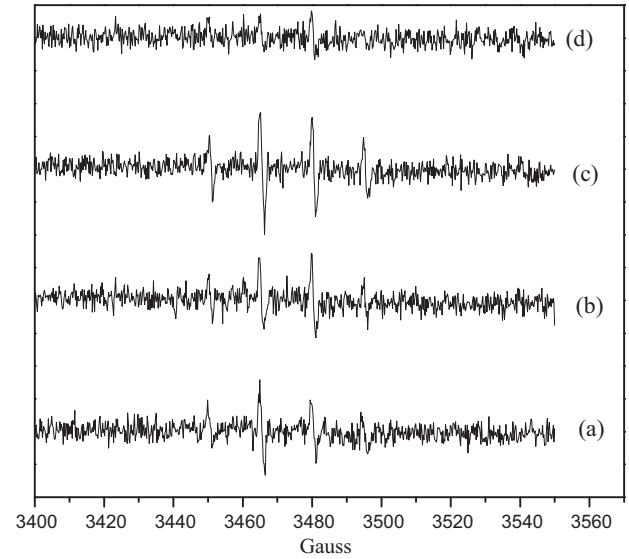


Fig. 4. ESR spectra change with increasing irradiation time for UV–vis/WO_3/$S_2O_8^{2-}$ system: (a) 15 min without the presence of methanol; (b) 15 min with the presence of methanol; (c) 30 min without the presence of methanol; (d) 30 min with the presence of methanol.

suggests that methanol effectively quenched hydroxyl radicals, and the reasons for methanol in promoting CBZ's decay are dominated by other mechanisms (to be discussed).

3.5. Identification and evolution of intermediates and products

It is believed that sulfate radicals are the dominant oxidant in UV/$S_2O_8^{2-}$ process with the presence of tert-butanol, which is an effective quencher for hydroxyl radicals but not for sulfate radicals [37]. Therefore, the investigation on the transformation products of CBZ generated in (i) UV–vis/WO_3/$S_2O_8^{2-}$ process with and without the addition of methanol, and (ii) in UV/$S_2O_8^{2-}$ process with tert-butanol may disclose the details of the mechanism of CBZ degradation by UV–vis/WO_3/$S_2O_8^{2-}$ process with methanol. During CBZ degradation in each of these three systems, same 14 intermediates were detected by LC-MS/MS (Table 2). Chemical structures were proposed for each intermediate/product on the basis of the molecular ion masses and MS^2 fragmentation patterns (MS^2 spectra for each intermediate/product provided in the supporting information). Among the intermediates, there are seven isomers (compounds 3, 4 and 12; compounds 8 and 11; and compounds 9 and 13). Compounds 3, 4 and 12 can be identified on the basis of the different MS^2 fragmentation patterns. The proposed structures of these three isomers are in accordance with previously published studies [14,15]. However, compounds 8 and 11 and compounds 9 and 13 show similar MS^2 fragmentation patterns. The identification of these two pairs of isomers is based on their yields. Compared to the two outside benzene rings, the olefinic double bond on the central heterocyclic ring shows higher reactivity toward electrophilic attack by radicals, leading to higher yield of the intermediates/products from the electrophilic attack at the olefinic double bond than that of other intermediates/products from other pathways. Since the yield of compound 8 and 9 is much higher than that of compound 11 and 13, compound 9 is assigned as 10,11-dihydro-dihydroxycarbamazepine and compound 8 may result from further hydroxylation of compound 9 on the outside benzene ring. Compound 13 is tentatively attributed to 10,11-dihydro-2,10-dihydroxycarbamazepine and the fragmentation patterns of compound 11 resembles closely that of 10,11-dihydro-2,4,10-trihydroxylcarbamazepine. The identity of compound 6 was confirmed by comparing its retention time and mass fragmentation pattern to that of the authentic compound (Carbamazepine 10, 11-epoxide). Compounds 1, 2, 3 and 10 are believed to derive from cyclization reaction [38] and their structures have been proposed in previous contributions [10,15].

The evolution profiles of major intermediates/products were organized and shown in Fig. 5a–c (trace intermediates/products not included). To achieve 99% decay of 0.19 mM CBZ, it

Table 1
Summary of the first-order rate constants of CBZ degradation by UV–vis/WO_3/$S_2O_8^{2-}$ process with the presence of various alcohols.

Alcohols	R^2	$k_{observed}$ (min^{-1})
Control	0.993	0.055
1 mM TBT	0.993	0.033
1 mM ethanol	0.982	0.061
10 mM TBT	0.998	0.069
10 mM ethanol	0.973	0.0728
10 mM methanol	0.981	0.1273

Notes: initial CBZ concentration is 0.025 mM, WO_3 loading is 0.3 g/L, the initial concentration of $S_2O_8^{2-}$ is 2 mM, initial pH value is around 4.5, 12 lamps of 420 nm.

Table 2
Intermediates and products detected by LC-MS/MS during CBZ degradation by UV–vis/$WO_3/S_2O_8^{2-}$ process.

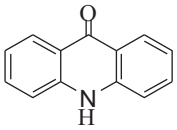
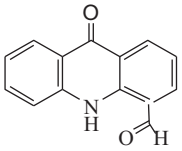
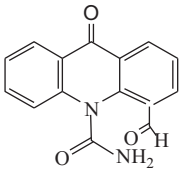
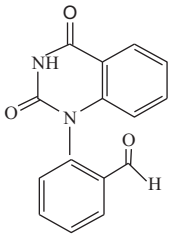
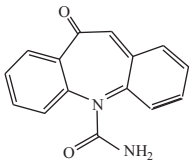
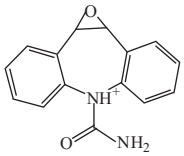
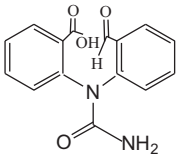
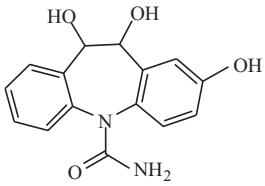
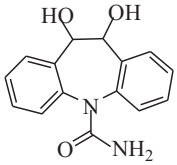
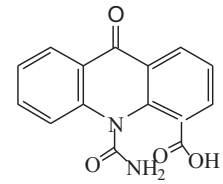
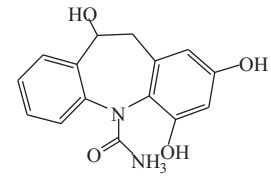
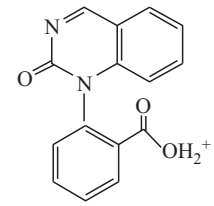
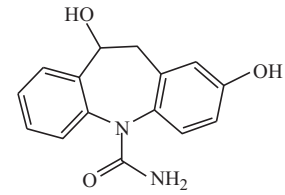
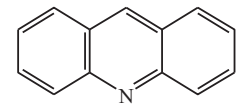
Product ID	ESI(+)MS *m/z*	ESI(+)MS^2 *m/z*	UV absorbance (λ_{max})	Proposed structure
1	196	196	219, 252	
2	224	224, 196	219, 255	
3	267, 249	249, 239, 224, 196	225, 241, 312	
4	267	249, 224	227, 272, 345	
5	251	251,223,208, 180	227, 275, 343	
6	253	253, 236, 210, 180	219, 238, 279	
7	285, 267	267, 239, 224, 196	224, 263, 321	
8	287	287, 253, 236, 223, 196, 180	220	
9	271	253, 210	221	

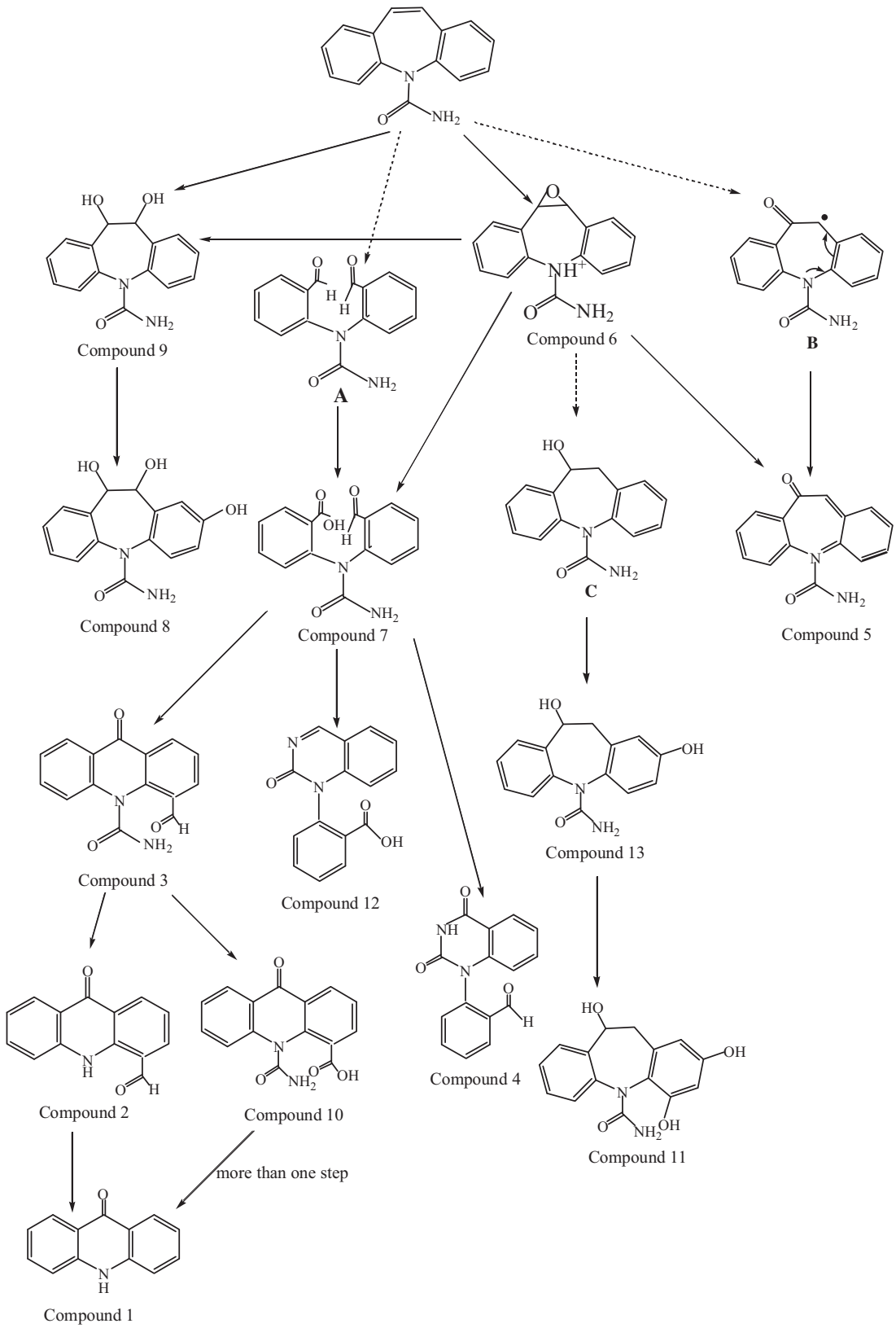
Table 2 (*Continued*)

Product ID	ESI(+)MS m/z	ESI(+)MS^2 m/z	UV absorbance (λ_{max})	Proposed structure
10	283	265, 240, 222, 196	224, 313	
11	287	253,223, 208, 180	219	
12	267	249, 221	226, 272, 348	
13	271	253, 210, 180	219	
14	180	180	211, 249	

required 4.5 and 32 h, with and without the presence of 10 mM methanol, respectively, in UV–vis/WO_3/$S_2O_8^{2-}$system. As also indicated in Fig. 5a and b, the formation/degradation profiles of the intermediates/products generated with and without the presence of methanol are quite different. The yield of compounds 3, 5 and 7 is much higher during CBZ degradation in UV–vis/WO_3/$S_2O_8^{2-}$system with the presence of methanol than that in the absence of methanol. To make a further comparison between these two scenarios, the mass balance of CBZ and all detectable intermediates for these two scenarios was also investigated (see Fig. S6). Although CBZ removal was similar at the end of the reaction in these two scenarios, only around 36% mass reduction was achieved in the presence of methanol while 91% mass elimination was observed without the addition of methanol, indicating the accumulation of intermediates/products in the presence of methanol. All the experimental results described above may imply different reaction mechanisms involved in CBZ decay or different contribution of various active species to CBZ decomposition in these two scenarios. On the other hand, the formation/degradation profiles of the intermediates/products generated in UV–vis/WO_3/$S_2O_8^{2-}$ process (with methanol) and in that of UV/$S_2O_8^{2-}$ process (with tert-butanol) are similar as shown in Fig. 5b and c. This implies that the sulfate radicals make major contribution to CBZ degradation in UV–vis/WO_3/$S_2O_8^{2-}$ process with the presence of methanol as they do in UV/$S_2O_8^{2-}$ process with the presence of tert-butanol.

3.6. Proposed CBZ degradation pathways

Reaction pathways for CBZ degradation by UV–vis/WO_3/$S_2O_8^{2-}$ process are proposed in Scheme 1. Four primary intermediates (compounds **5**, **6**, **7** and **9**) were generated upon CBZ's degradation, which were initiated by electrophilic attack at the olefinic double bond on the central heterocyclic ring by hydroxyl radicals or sulfate radicals. At the initial stage, two benzene rings remain intact. Hydroxyl radical is capable of reacting with olefinic double bond in various ways [39]: (1) addition to double bond in pairs to give saturated glycols; (2) addition to double bonds singly to give epoxides; (3) dehydrogenation to give olefin radicals and union with olefin radicals to give alcohol; and (4) oxidation to cause the breakdown of the double bond and generate two aldehydes or ketones. Compound **9** comes from the first way and compound **6** is derived from the second way. The fourth way resulted in the formation of "intermediate A" which is further oxidized to produce compound **7**. Oxidation reaction between radicals and the olefinic double bond on the central heterocyclic ring may lead to the formation of carbon-centered radical "intermediate B", which was transformed to compound **5** via rearrange reaction. In addition, there is another possibility that compounds **5**, **7**, and **9** might not directly come from CBZ but from compound **6**. To verify this, compound **6** was used as the starting probe in WO_3/$S_2O_8^{2-}$/UV–vis process as an independent test, where all the compounds **5**, **7**, and **9** were detected. Under these circumstances, compounds **5**, **7** and **9** are secondary derivatives and only compound **6** is the primary intermediate directly

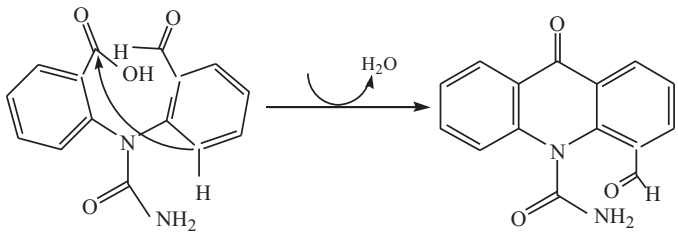


Scheme 1. Degradation pathways of CBZ by UV–vis/WO_3/$S_2O_8^{2-}$ process.

from CBZ degradation. The yield of compound **6** therefore should be higher than that of compounds **5**, **7** and **9**. Experimental results showed the yield of compounds **5**, **7** and **9** was much higher than that of compound **6** and only trace amount of compound **6** was detected. Theoretically, this may be due to a faster decay rate of compound **6** than that of CBZ. To verify this point, an additional test was conducted and the degradation rate of compound **6** was determined to be 0.0347 min^{-1}, which is slightly slower than that

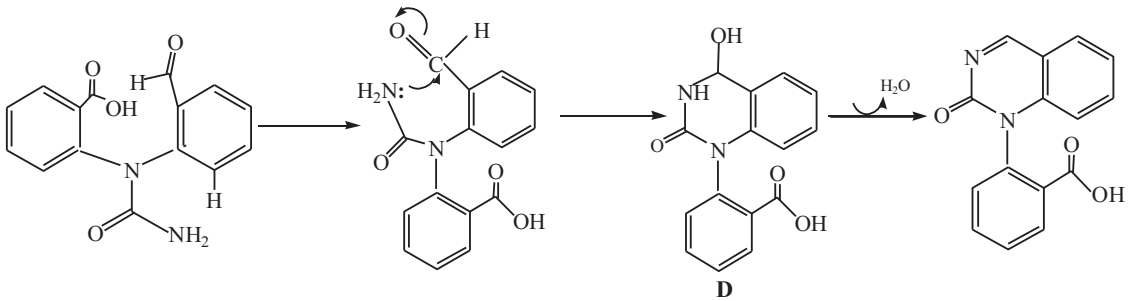
of CBZ under the same conditions. Therefore, compounds **5**, **7** and **9** are believed to come from two sources (i.e. CBZ and compound **6**). Compound **13** is believed to derive from compound **6** through the attack at benzene ring of "intermediate C" by hydroxyl radicals or sulfate radicals. Nitrogen group on the central heterocyclic ring has an electron-donating property, indicating the radical attack tends to happen on carbon 2 and carbon 4 on the benzene ring. Due to steric effect, the radical attack prefers taking place on carbon 2 (para-position), leading to the generation of compound **13**. The further hydroxylation on carbon 4 of compound **13** produces compound **11**. Compound **8** is believed to derive from compound **9** via the attack at the carbon 2 on the benzene ring by hydroxyl radicals. Compound **7** might be further evolved in three ways:

(1) Intramolecular cyclization via electrophilic aromatic substitution to generate compound **3** as Eq. (6):



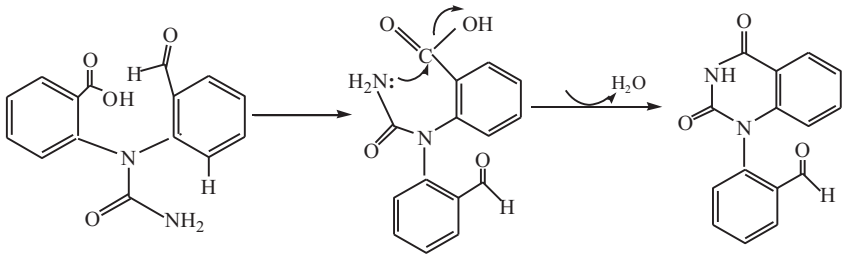
(6)

(2) The ring closure proceeds through intramolecular attack by nitrogen at the aldehyde. It is well documented that ammonia or primary amines can attack aldehydes or ketones to form imines [40]. In this case, the hydrogen-bearing nitrogen on the urea group attacks the aldehyde to form a hemi-aminal moiety in intermediate D as shown in Eq. (7). In this study, the formation of intermediate D was not observed probably because it was readily transformed into compound **12** with the elimination of H_2O.



(7)

(3) Intramolecular attack by hydrogen-carrying nitrogen at the carbonyl to produce compound **4** as indicated in Eq. (8):



(8)

The evolution of compound **3** may proceed in two ways: (1) the hydrolysis of the urea group on the central heteocyclic ring leading to the generation of compound **2**; and (2) the aldehyde group on the benzene ring further oxidized to produce compound **10**.

3.7. The role of methanol

The addition of methanol and ethanol was found to accelerate CBZ degradation in UV–vis/WO_3/$S_2O_8^{2-}$ system. It was observed that the addition of 10 mM chloroform also prompted the CBZ degradation by UV–vis/WO_3/$S_2O_8^{2-}$ process, where the pseudo-first-order rate constant of CBZ degradation was increased from 0.022 to 0.031 min^{-1} (see Fig. S7). The accelerating effect of methanol, ethanol and chloroform therefore is likely because of their solvent property in cleaning the water–WO_3 interface. Through this, the spent reagents and accumulated intermediates can be flushed away from the catalyst surface (i.e. activated sites) into the bulk solution. First, this will make the catalyst surface favorable to the adsorption of fresh $S_2O_8^{2-}$, and create more radicals, which can be evidenced indirectly by experimental results that $S_2O_8^{2-}$ decay rate increased with the enhancement of methanol concentration (see Fig. 3a). It was also observed methanol concentration exerted no influence on $S_2O_8^{2-}$ decomposition with the absence of CBZ in this system (data not shown). Secondly, this mechanism presents a better possibility of CBZ to react with radicals. Assuming the activated sites on WO_3 surface is fixed, without the presence of methanol, some activated sites would be occupied by the reacted CBZ (i.e. intermediates), and the chance for unreacted CBZ molecules in the bulk solution approaching the radicals nearby the catalyst surface is constrained. However, in the presence of methanol, the clean WO_3 surface could offer more activated sites available for fresh CBZ reacting with various radicals or active species. Thus, the CBZ decay rate increases as methanol is present in the solution.

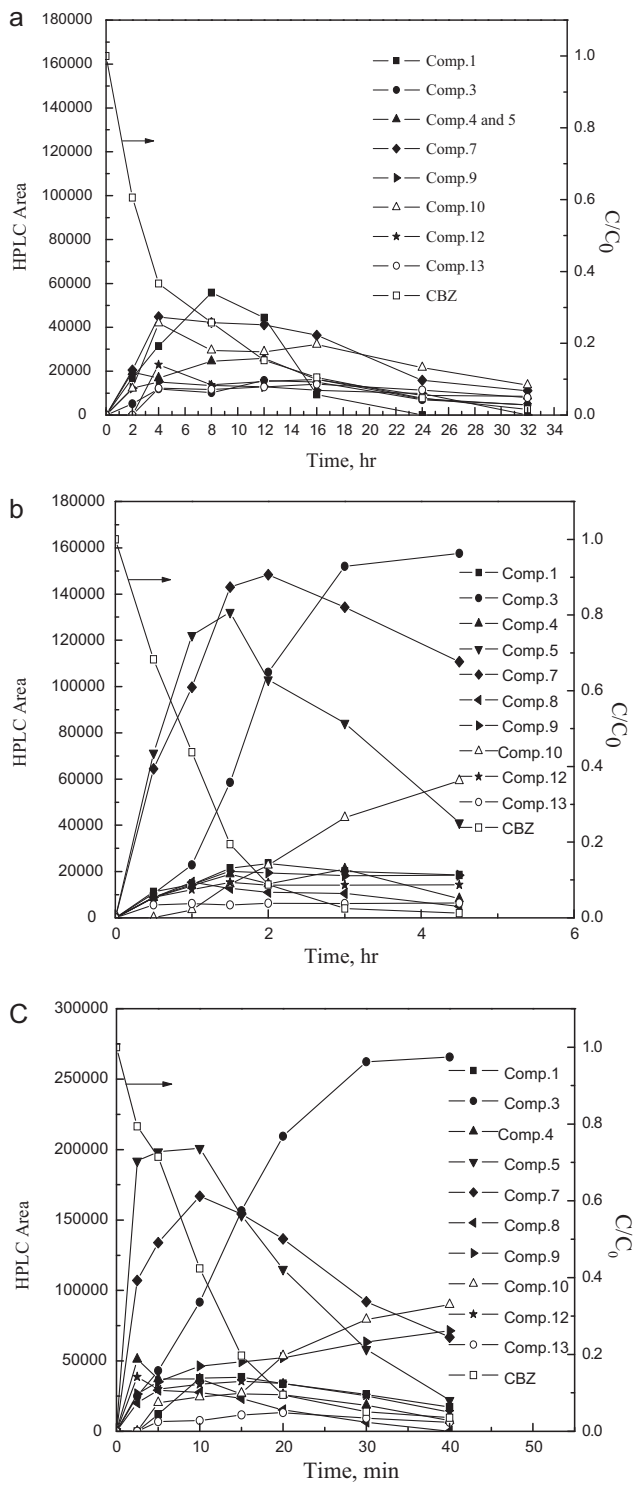


Fig. 5. (a) The evolution profiles of major intermediates/products generated without the presence of methanol. (b) The evolution profiles of major intermediates/products generated with the presence of methanol. (c) The evolution profiles of major intermediates/products generated during CBZ degradation by UV/$S_2O_8^{2-}$ process with the presence of tert-butanol (notes: for UV–vis/WO_3/$S_2O_8^{2-}$ process, the initial concentration of CBZ is 0.19 mM, WO_3 dosage is 0.3 g/L, the initial concentration of $S_2O_8^{2-}$ is 2 mM, initial pH value is 4.6, the concentration of methanol is 10 mM, 12 lamps of 420 nm; for UV/$S_2O_8^{2-}$ process, the initial concentration of CBZ is 0.19 mM, 4 lamps of 254 nm, the initial concentration of $S_2O_8^{2-}$ is 8 mM, initial pH value is 4.8, the concentration of tert-butanol is 10 mM).

Sulfate radical is more selective than hydroxyl radicals in H-abstraction reaction [32], which may partly rationalize the accumulation of some intermediates during CBZ degradation in the presence of methanol. Therefore, methanol, ethanol and tert-butanol may play a dual role in CBZ degradation by UV–vis/WO_3/$S_2O_8^{2-}$ process. One is radical quencher and another is cleaning agent of catalyst. The former has a negative role and the latter is positive for UV–vis/WO_3/$S_2O_8^{2-}$ process. For the cases of methanol and ethanol, the cleaning effect outplays the quenching effect at low concentration (for methanol, the concentration of methanol is below 100 mM), leading to the enhancement of CBZ degradation rate. Furthermore, the presence of methanol leads to faster decomposition of $S_2O_8^{2-}$ and generates more sulfate radicals. Based on Fig. 3a, 0.1697 mM $S_2O_8^{2-}$ was decomposed in the presence of 10 mM methanol, theoretically leading to the generation of 0.1697 mM $SO_4^{\bullet-}$. The reaction rate constant of methanol with $HO^\bullet$ ($4.6–9.7 \times 10^8\ M^{-1}\ s^{-1}$ [33,34]) is around 40 times higher than that with $SO_4^{\bullet-}$ ($1.1–2.5 \times 10^7\ M^{-1}\ s^{-1}$ [35,36]), indicating methanol could quench more hydroxyl radicals than sulfate radicals as evidenced by Fig. S4. The reaction rate constants of CBZ with $HO^\bullet$ and $SO_4^{\bullet-}$ are similar as determined in the supporting information ($k_{CBZ,\ OH} = 2.98 \times 10^9\ M^{-1}\ s^{-1}$, $k_{CBZ,SO_4} = 2.63 \times 10^9\ M^{-1}\ s^{-1}$). The reaction rate constant of CBZ with $SO_4^{\bullet-}$ ($2.63 \times 10^9\ M^{-1}\ s^{-1}$) is much higher than that of methanol with $SO_4^{\bullet-}$ ($1.1–2.5 \times 10^7\ M^{-1}\ s^{-1}$). Thus, $SO_4^{\bullet-}$ may be the key player in CBZ degradation by UV–vis/WO_3/$S_2O_8^{2-}$ process in the presence of methanol, as evidenced indirectly in Fig. 5b and c. Furthermore, the inhibiting effect of methanol on NB degradation (see Fig. S3) can also verify the major role of $SO_4^{\bullet-}$ in CBZ decomposition with the presence of methanol in UV–vis/WO_3/$S_2O_8^{2-}$ system because NB exhibits very low reactivity toward sulfate radical ($<10^6\ M^{-1}\ s^{-1}$)[41] while it is susceptible to $HO^\bullet$ oxidation ($3.9 \times 10^9\ M^{-1}\ s^{-1}$) [33].

For tert-butanol, however, quenching effect is dominant at a lower concentration (2 mM), while cleaning effect played a major role in CBZ decomposition at a higher concentration of 10 mM. It was also observed that CBZ decay rate in the presence of methanol is faster than that of ethanol at the same concentration, which can be explained by the reaction rate constants of $HO^\bullet$ and $SO_4^{\bullet-}$ with methanol and ethanol. It was reported that the reaction rate constant of $HO^\bullet$ with ethanol ($9.7 \times 10^8–1.9 \times 10^9\ M^{-1}\ s^{-1}$) is around two times higher than that with methanol ($4.6–9.7 \times 10^8\ M^{-1}\ s^{-1}$) [33,34]. The reaction rate constant of $SO_4^{\bullet-}$ with ethanol ($3.5–7.7 \times 10^7\ M^{-1}\ s^{-1}$) was reported to be around 3 times higher than with methanol ($1.1–2.5 \times 10^7\ M^{-1}\ s^{-1}$ [35,36]). It was noteworthy that the faster $S_2O_8^{2-}$ decomposition boosted CBZ degradation with methanol concentration ranging from 0 to 10 mM; while the further increment of $S_2O_8^{2-}$ decay rate (i.e. higher [methanol]) could not accelerate but inhibit CBZ degradation with methanol concentration higher than 10 mM as shown in Fig. 3b. Though higher methanol concentration can offer better cleaning effect and leads to a faster decomposition of $S_2O_8^{2-}$ and generating more sulfate radicals; overdosed methanol, however, can compete with CBZ for $HO^\bullet$ and $SO_4^{\bullet-}$ and results in an overall effect of CBZ retardation as observed.

4. Conclusions

The WO_3-based photocatalytic degradation of CBZ with the presence of persulfate has been investigated in this study. The results show the addition of $S_2O_8^{2-}$ significantly accelerated CBZ degradation in WO_3 suspension under the irradiation of 420 nm lamps. It is surprising to observe that radical quenchers such as methanol and ethanol promoted photocatalytic oxidation of CBZ

at low concentration (<100 mM) in this study. It was also found the presence of 1 mM tert-butanol inhibited CBZ degradation and the addition of 10 mM tert-butanol accelerated CBZ degradation. Although same 14 intermediates/products were detected during CBZ degradation with and without the presence of methanol, their evolution profiles, mass balance of CBZ and intermediates/products were quite different. The evolution profiles of CBZ and intermediates/products in UV–vis/WO_3/$S_2O_8^{2-}$ system with the presence of methanol are similar to that in UV/$S_2O_8^{2-}$ system with the presence of tert-butanol, indicating sulfate radicals played a major role in CBZ decay in UV–vis/WO_3/$S_2O_8^{2-}$ system with the presence of methanol. Methanol is believed to play a dual role (quenching agent and cleaning agent) in UV–vis/WO_3/$S_2O_8^{2-}$ system, in which sulfate radicals make dominating contribution to CBZ degradation in the presence of methanol.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2013.08.050.

References

[1] Y.J. Zhang, S.U. Geissen, C. Gal, Chemosphere 73 (2008) 1151–1161.
[2] T. Kosjek, H.R. Andersen, B. Kompare, A. Ledin, E. Heath, Environ. Sci. Technol. 43 (2009) 6256–6261.
[3] T.A. Ternes, Water Res. 32 (1998) 3245–3260.
[4] T. Heberer, J. Hydrol. 266 (2002) 175–189.
[5] A. Ginebreda, I. Munoz, M.L. de Alda, R. Brix, J. Lopez-Doval, D. Barcelo, Environ. Int. 36 (2010) 153–162.
[6] T. Heberer, K. Reddersen, A. Mechlinski, Water Sci. Technol. 46 (2002) 81–88.
[7] M. Nassef, S. Matsumoto, M. Seki, F. Khalil, I.J. Kang, Y. Shimasaki, Y. Oshima, T. Honjo, Chemosphere 80 (2010) 1095–1100.
[8] X.F. Zhou, C.M. Dai, Y.L. Zhang, R.Y. Surampalli, T.C. Zhang, Environ. Monit. Assess. 173 (2011) 45–53.
[9] G. Vernouillet, P. Eullaffroy, A. Lajeunesse, C. Blaise, F. Gagne, P. Juneau, Chemosphere 80 (2011) 1062–1068.
[10] S. Chiron, C. Minero, D. Vione, Environ. Sci. Technol. 40 (2006) 5977–5983.
[11] Z.R. Yu, S. Peldszus, P.M. Huck, Water Res. 42 (2008) 2873–2882.
[12] T. Hata, H. Shintate, S. Kawai, H. Okamura, T. Nishida, J. Hazard. Mater. 181 (2010) 1175–1178.
[13] V. Calisto, M.R.M. Domingues, G.L. Erny, V.I. Esteves, Water Res. 45 (2011) 1095–1104.
[14] D.C. McDowell, M.M. Huber, M. Wagner, U. Von Gunten, T.A. Ternes, Environ. Sci. Technol. 39 (2005) 8014–8022.
[15] L. Hu, H.M. Martin, O. Arcs-Bulted, M.N. Sugihara, K.A. Keatlng, T.J. Strathmann, Environ. Sci. Technol. 43 (2009) 509–515.
[16] T.E. Doll, F.H. Frimmel, Water Res. 39 (2005) 403–411.
[17] M.N. Chong, B. Jin, J. Hazard. Mater. 199 (2012) 135–142.
[18] L.G. Devi, S.G. Kumar, Cent. Eur. J. Chem. 9 (2011) 959–961.
[19] S.-M. Lam, J.-C. Sin, A.Z. Abdullah, A.R. Mohamed, Desalin. Water Treat. 41 (2012) 131–169.
[20] G.R. Bamwenda, H. Arakawa, Appl. Catal. A-Gen. 210 (2001) 181–191.
[21] Z. Haidong, O. Jian Zhen, M.S. Strano, R.B. Kaner, A. Mitchell, K. Kalantar-zadeh, Adv. Funct. Mater. 21 (2011) 2175–2196.
[22] C. Janaky, K. Rajeshwar, N.R. de Tacconi, W. Chanmanee, M.N. Huda, Catal. Today 199 (2013) 53–64.
[23] E.O. Scott-Emuakpor, A. Kruth, M.J. Todd, A. Raab, G.I. Paton, D.E. Macphee, Appl. Catal. B-Environ. 123 (2012) 433–439.
[24] D. Sanchez Martinez, A. Martinez-de la Cruz, E. Lopez Cuellar, Appl. Catal. A-Gen. 398 (2011) 179–186.
[25] K. Sayama, H. Hayashi, T. Arai, M. Yanagida, T. Gunji, H. Sugihara, Appl. Catal. B-Environ. 94 (2010) 150–157.
[26] W. Chu, Y.F. Rao, Chemosphere 86 (2012) 1079–1086.
[27] Y.F. Rao, W. Chu, Chem. Eng. J. 158 (2010) 181–187.
[28] C.J. Liang, C.F. Huang, N. Mohanty, R.M. Kurakalva, Chemosphere 73 (2008) 1540–1543.
[29] L.G. Devi, S.G. Kumar, Bulg. Chem. Commun. 40 (2008) 114–121.
[30] L.G. Devi, S.G. Kumar, K.M. Reddy, C. Munikrishnappa, J. Hazard. Mater. 164 (2009) 459–467.
[31] A. Hesselmann, J. Phys. Chem. A 115 (2011) 11321–11330.
[32] E. Hayon, A. Treinin, J. Wilf, J. Am. Chem. Soc. 94 (1972) 47–57.
[33] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, J. Phys. Chem. Ref. Data 17 (1988) 513–886.
[34] G.E. Adams, J.W. Boag, B.D. Michael, Trans. Faraday Soc. 61 (1965) 1417–1424.
[35] P. Neta, R.E. Huie, A.B. Ross, J. Phys. Chem. Ref. Data 17 (1988) 1027–1284.
[36] L. Dogliott, E. Hayon, J. Phys. Chem. 71 (1967), 3802-3808.
[37] L.G. Devi, K.S.A. Raju, S.G. Kumar, J. Environ. Monit. 11 (2009) 1397–1404.
[38] K. Dzierzbicka, A.M. Kolodziejczyk, J. Med. Chem. 46 (2003) 183–189.
[39] E.H. Farmer, C.G. Moore, J. Chem. Soc. (1951) 149–153.
[40] K. Peter, S. Voldhardt, N.E. Schore, Organic Chemistry, second ed., W.H. Freeman & Co, New York, 1987.
[41] P. Neta, V. Madhavan, H. Zemel, R.W. Fessenden, J. Am. Chem. Soc. 99 (1977) 163–164.