



Decomposition of two haloacetic acids in water using UV radiation, ozone and advanced oxidation processes

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ARTICLE INFO

Article history:

Received 5 April 2007

Received in revised form 23 April 2008

Accepted 9 June 2008

Available online 13 June 2008

Keywords:

Ozone

Haloacetic acid

Advanced oxidation process

Ozonation

Halegenated organics

Ozone/UV radiation

ABSTRACT

The decomposition of two haloacetic acids (HAAs), dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA), from water was studied by means of single oxidants: ozone, UV radiation; and by the advanced oxidation processes (AOPs) constituted by combinations of O₃/UV radiation, H₂O₂/UV radiation, O₃/H₂O₂, O₃/H₂O₂/UV radiation. The concentrations of HAAs were analyzed at specified time intervals to elucidate the decomposition of HAAs. Single O₃ or UV did not result in perceptible decomposition of HAAs within the applied reaction time. O₃/UV showed to be more suitable for the decomposition of DCAA and TCAA in water among the six methods of oxidation. Decomposition of DCAA was easier than TCAA by AOPs. For O₃/UV in the semi-continuous mode, the effective utilization rate of ozone for HAA decomposition decreased with ozone addition. The kinetics of HAAs decomposition by O₃/UV and the influence of coexistent humic acids and HCO₃⁻ on the decomposition process were investigated. The decomposition of the HAAs by the O₃/UV accorded with the pseudo-first-order mode under the constant initial dissolved O₃ concentration and fixed UV radiation. The pseudo-first-order rate constant for the decomposition of DCAA was more than four times that for TCAA. Humic acids can cause the H₂O₂ accumulation and the decrease in rate constants of HAAs decomposition in the O₃/UV process. The rate constants for the decomposition of DCAA and TCAA decreased by 41.1% and 23.8%, respectively, when humic acids were added at a concentration of 1.2 mg TOC/L. The rate constants decreased by 43.5% and 25.9%, respectively, at an HCO₃⁻ concentration of 1.0 mmol/L.

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1. Introduction

In addition to trihalomethanes, haloacetic acids (HAAs) are another major group of disinfection by-products (DBPs) in chlorinated drinking water [1]. Owing to their carcinogenic risks, people show great concerns about drinking water hygiene. In the past, the main efforts focused on the mechanisms and the effective control of HAAs formation by reducing precursors [2,3] or using alternative disinfectants [4,5]. Recently, some treatment techniques, such as microbial degradation [6–8], activated carbon adsorption [9], etc., have been tried for the elimination of HAAs formed in drinking water. However, the research on decomposition of HAAs with AOPs was comparatively rare.

Advanced oxidation processes (AOPs), which are characterized by the generation of very reactive hydroxyl radicals, with

a higher oxidation potential (2.8 V) than that of O₃ (2.07 V), H₂O₂ (1.78 V), MnO₄⁻ (1.69 V), have emerged as a highly efficient method for the decomposition of many refractory pollutants [10–12]. Among the many AOPs studied, the combinations of ozone and ultraviolet (O₃/UV), O₃ and hydrogen peroxide (O₃/H₂O₂), and H₂O₂ and UV (H₂O₂/UV), etc., have been considered as the most potential processes, and some commercial plants using these processes have been established for drinking water and wastewater treatments [13–15]. The AOPs involving UV irradiation demonstrate to be effective for the dehalogenation of chlorinated organics [16–20], in which alkyl-oxidation, dealkylation, and dechlorination-hydroxylation (minor in catalytic oxidation process without UV-light) are the leading pathways with steric hindrance effect. The efficiency of AOPs in decomposing HAAs and other organics is affected by many factors, among which, the most essential ones include the types of reactions and the kinetics of reactions.

The objective of this study is to determine the feasibility of adopting single oxidants: ozone, UV radiation; and the advanced oxidation processes constituted by combinations of O₃/UV radiation, H₂O₂/UV radiation, O₃/H₂O₂, O₃/H₂O₂/UV radiation and to

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investigate the kinetics of HAAs decomposition and the influence of its coexistent radical scavengers (humic acids and HCO_3^-) on the decomposition process by effective AOPs. HAAs include nine compounds, among which, dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA) are generally of higher concentration level in chlorinated drinking water [21] and higher carcinogenic risks, and are chosen as the target pollutants.

2. Experimental

2.1. Chemicals and stock solutions

An ozonizer OS-1N (Mitsubishi Electric, Japan) connected with an oxygen generator was used for O_3 generation. Methyl *tert*-butyl ether (MTBE), methanol, DCAA and TCAA were obtained from Fisher Chemicals. 1,2-dibromopropane of >99% purity was purchased from Acros Organics. Sodium sulfate, sulfuric acid, humic substances, sodium bicarbonate and sodium indigo disulfonate were purchased from Beijing Chemical Reagents Company.

The concentrations of DCAA and TCAA stock solutions were 50–100 mg/mL, respectively.

2.2. Comparison of AOPs

The efficiency of O_3 , UV, O_3/UV , $\text{O}_3/\text{H}_2\text{O}_2$, and $\text{H}_2\text{O}_2/\text{UV}$, and $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$ on decomposition of DCAA and TCAA was compared in a reactor as shown in Fig. 1. The major reaction chamber is a cylindrical stainless steel column with an effective volume of 2 L. Its diameter and height are 100 and 300 mm, respectively. Inside the reaction column is a quartz well containing a UV lamp with a diameter of 30 mm and a height of 300 mm—a 15-W low-pressure mercury vapor lamp (254 nm). Liquid was recycled unless the experiments were designed to be done with continuous addition of O_3 to the reactor). The O_3 inlet valve was open only when the initial O_3 was added into the system for the batch experiments with initial O_3 .

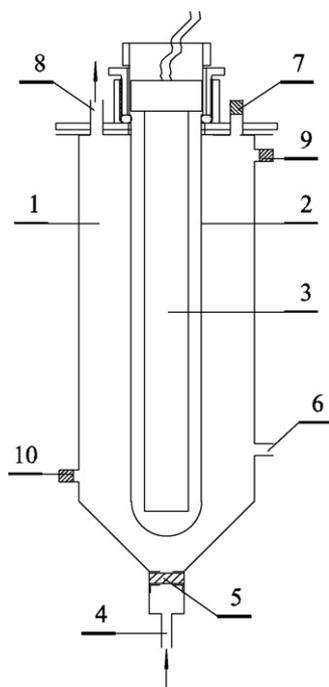


Fig. 1. Schematic diagram of reactor system: 1, reaction chamber; 2, quartz well; 3, UV lamp; 4, inlet of the ozone; 5, porous plate; 6, sampling and drainage spot; 7, inlet of raw water; 8, outlet of the exhaust gas; 9 and 10, liquid recycle spots.

Table 1

Experimental conditions applied in comparison experiments

| Parameter | Value |
|---|----------------|
| Ozone adding (mg/min) | 0.3 ± 0.06 |
| Initial H_2O_2 concentration (mg/L) | 2.5 |
| Wavelength of UV lamp (nm) | 254 |
| Power input of UV lamp (W) | 15 |
| Reaction volume (L) | 2 |
| Initial DCAA concentration (mg/L) | 2.0 |
| Initial TCAA concentration (mg/L) | 2.0 |
| Temperature ($^{\circ}\text{C}$) | 18–26 |

In the semi-continuous experiments of O_3/UV , ozone-containing gas was fed into the reactor through a porous titanic plate with an average pore size of 15–20 μm (Beijing General Research Institute for Non-ferrous Metals), situated at the bottom of the reactor, after 2.0 L of raw water spiked with the target HAAs was introduced into the reactor. Excess O_3 in the effluent gas was absorbed by 2% KI solution for the determination of ozone production and consumption. The UV lamp was turned on at the beginning of ozonation.

For the $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$, $\text{O}_3/\text{H}_2\text{O}_2$ and $\text{H}_2\text{O}_2/\text{UV}$ experiments, H_2O_2 was added into raw water before the start of ozonation and/or the UV radiation. All other operation was similar to that in the semi-continuous experiments of O_3/UV . The experimental conditions for the comparison of different oxidation techniques are given in Table 1.

2.3. Kinetics study

The experiments for kinetics study were conducted using the same reactor in batch mode. The recirculation pump was turned on after 2 L of deionized water was added into the reactor. 5 mL of solution was sampled for the analysis of initial dissolved O_3 after O_3 gas stopped coming into the system. Then a given amount of HAA stock solution was quickly injected into the reaction chamber, through a silicon rubber septum plugged in the sampling spot. At the same time, the UV lamp was turned on to initiate the treatment. For the study of the effects of radical scavengers on HAA decomposition, HAA stock solutions containing humic acids or bicarbonate of given concentrations were prepared beforehand.

2.4. Analysis

O_3 in the gas stream was measured iodometrically, and the residual dissolved O_3 was followed by the Indigo method [22]. The indigo disulfonate (IDS) content of the commercial product was calibrated by titrations with potassium permanganate. After the residual O_3 and H_2O_2 were quenched with $\text{Na}_2\text{S}_2\text{O}_3$, analysis of HAAs in the sample was carried out by HP6890GC/5973MSD according to U.S. EPA Method 552.3. The concentration of H_2O_2 was monitored by the colorimetric method [23] after the residual dissolved O_3 in the sample was quenched by stripping with nitrogen gas.

3. Results and discussion

3.1. Comparison of oxidation processes

In the semi-continuous experiments, the HAAs decomposition in HAAs mixture system was compared using O_3 , UV, O_3/UV , $\text{O}_3/\text{H}_2\text{O}_2$, $\text{H}_2\text{O}_2/\text{UV}$ and $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$, and the normalized remaining concentrations against oxidation time are shown in Fig. 2. Single O_3 or UV treatment did not result in perceptible decomposition of HAAs within the applied reaction time. The $\text{O}_3/\text{H}_2\text{O}_2$, $\text{H}_2\text{O}_2/\text{UV}$,

O_3/UV and $O_3/H_2O_2/UV$ were effective in different degrees for the decomposition of DCAA although the former two processes showed a much lower reaction rate. The amount of TCAA decomposed by O_3/H_2O_2 and H_2O_2/UV within 30 min was <20%, indicating that these two processes are not effective enough for the decomposition of TCAA. Both O_3/UV and $O_3/H_2O_2/UV$ could remove >50% TCAA within 30 min, although the reaction rates were much lower than those for DCAA. TCAA was of relatively lower decomposition rates than DCAA, because the three chlorine atoms on its α -carbon provide greater space block, protecting carbon atom against attack from the radicals [18,24], and there is no hydrogen atom on α -carbon of TCAA, posing a higher oxidation state, thus more difficult to be oxidized than DACC.

Although the $O_3/H_2O_2/UV$ had a higher rate than O_3/UV for the decomposition of the two HAAs, the difference between O_3/UV and $O_3/H_2O_2/UV$ in reaction rate was not so remarkable. Since the O_3/UV technique is comparatively simpler and has a lower running cost, it was selected for the following studies.

The ratios of O_3 consumed to HAAs decomposed by O_3/UV in the semi-continuous experiment with ozone adding velocity of 0.28 ± 0.06 mg/min were shown in Fig. 3. It indicated that ozone consumption per mg of HAA decomposed increased with the time after O_3 was added, which meant that effective utilization rate of ozone for HAA decomposition decreased with continuous ozone

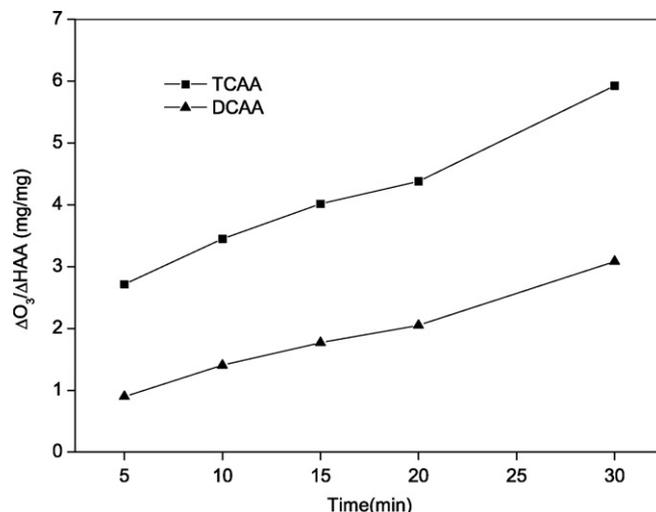


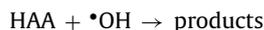
Fig. 3. Changes of O_3 consumption ratio with time.

addition. Therefore in the semi-continuous mode it is not advisable to add O_3 continuously into the system to improve HAAs decomposition by O_3/UV . For 90% DCAA decomposed, the ozone consumption ratio was 1.49 mg/mg. The ozone consumption ratio for TCAA was as much as two to three times that of the ratio for DCAA at a given O_3 adding velocity and continuous adding time.

3.2. Homogeneous oxidation of HAA by O_3/UV

The batch experimental results for the homogeneous decomposition of HAA by O_3/UV are shown in Fig. 4. It is clear that the degradation rates of HAAs increased with the increase of initial ozone concentrations.

As shown in Fig. 2, the effect of HAA decomposition by direct UV irradiation or direct ozonation was negligible. The decomposition of HAAs should be caused by the attack of $\bullet OH$ radicals formed through photolysis of ozone [12]. The reaction of $\bullet OH$ with HAAs is assumed to be first-order with respect to each reactant, yielding an overall second-order kinetics:



Therefore, the reaction rate can be expressed in the form:

$$\frac{dC}{dt} = -kC[\bullet OH] \quad (1)$$

where C , $[\bullet OH]$ and k are the HAA concentration, the $\bullet OH$ concentration, the second-order reaction rate constant, respectively. If the reaction system is in a steady state (by assuming $[\bullet OH]$ to be constant), then the reaction becomes of pseudo-first-order, and Eq. (1) can be rewritten in the following form:

$$\frac{dC}{dt} = -k'C \quad (2)$$

where k' is the pseudo-first-order rate constant, reflecting the effect of initial ozone concentration and UV radiation.

The pseudo-first-order rate constant k' under different initial O_3 concentrations was obtained with correlation coefficients higher than 0.93 by plotting $\ln(C_0/C)$ versus reaction time (Table 2), indicating that the assumption of pseudo-first-order reaction is suitable. It is clear that k' increased with the increase of initial dissolved O_3 . And the rate constant of DCAA is more than four times that of TCAA.

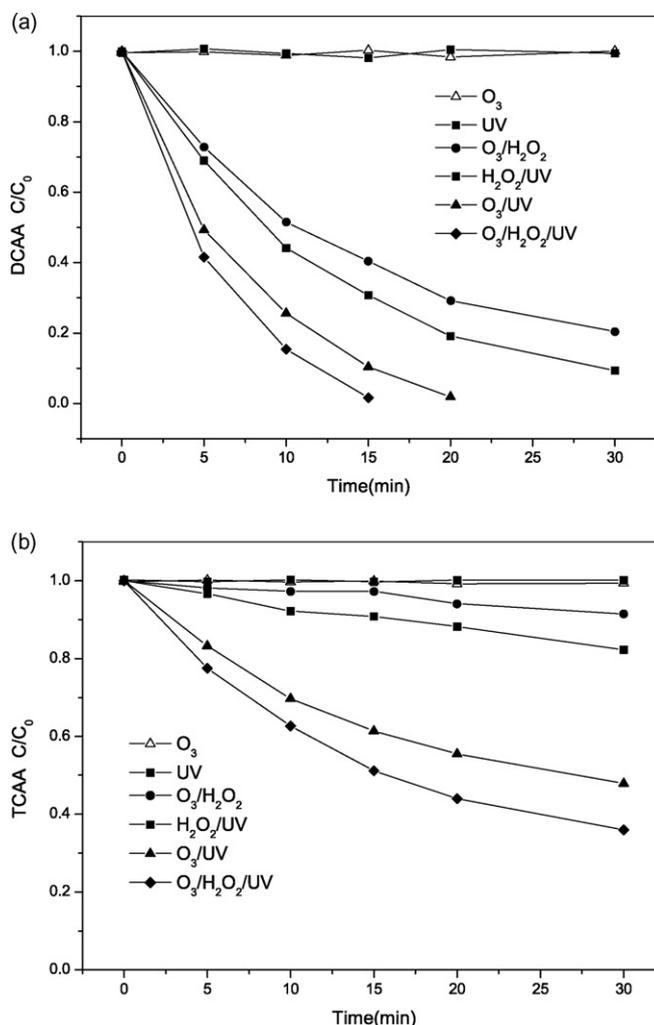


Fig. 2. (a) Comparison of HAA decomposition efficiency of different methods; (b) comparison of HAA decomposition efficiency of different methods.

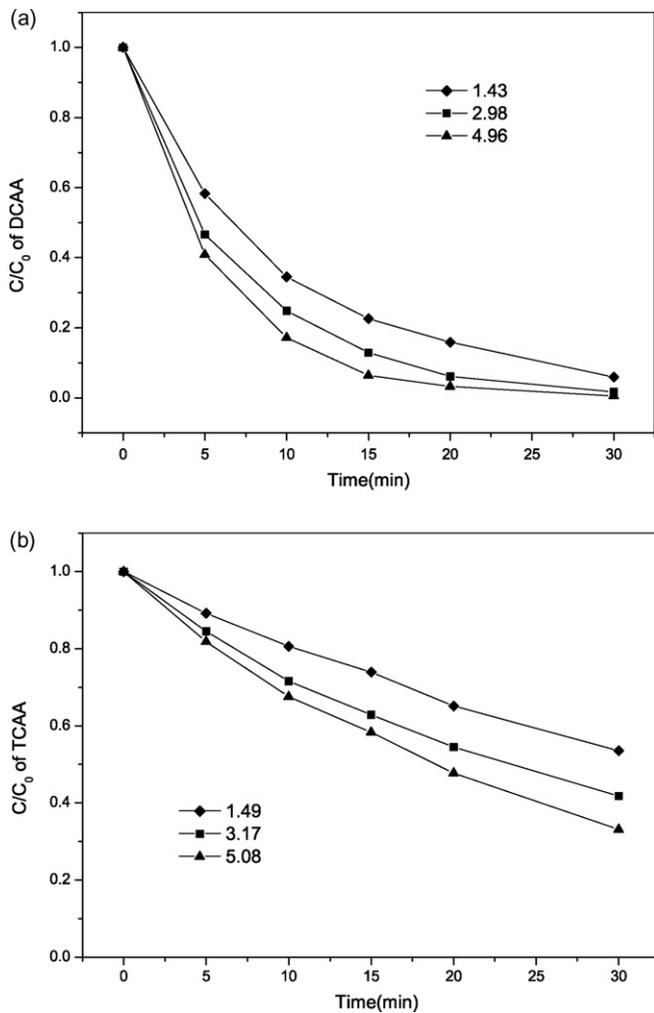


Fig. 4. (a) Variation of DCAA concentrations with time; (b) variation of TCAA concentrations with time.

From Table 2, the following empirical equations were obtained:

$$k'_{DCAA} = 0.0799C_{O_3}^{0.4921}$$

$$k'_{TCAA} = 0.0165C_{O_3}^{0.5029}$$

Table 2
Rate constants under different conditions

| System description | C _O (mg L ⁻¹) | C _{TOC} (mg L ⁻¹) | C _{HCO₃⁻} (mmol L ⁻¹) | k' / min ⁻¹ | |
|---|---|---|---|------------------------|--------|
| | | | | DCAA | TCAA |
| Homogeneous | 1.43 | | | 0.0952 | |
| | 2.98 | | | 0.1370 | |
| | 4.96 | | | 0.1755 | |
| Homogeneous | 1.49 | | | | 0.0209 |
| | 3.17 | | | | 0.0300 |
| | 5.08 | | | | 0.0369 |
| Heterogeneous | 1.55 | | | 0.0886 | 0.0172 |
| | 3.25 | | | 0.1259 | 0.0222 |
| | 5.20 | | | 0.1511 | 0.0265 |
| Heterogeneous (in the presence of humic acids) | 3.15 | 1.2 | | 0.0712 | 0.0167 |
| | 3.15 | 2.5 | | 0.0579 | 0.0140 |
| | 3.15 | 5.0 | | 0.0480 | 0.0116 |
| Heterogeneous (in the presence of HCO ₃ ⁻) | 3.19 | | 1.0 | 0.0692 | 0.0164 |
| | 3.19 | | 2.5 | 0.0533 | 0.0134 |
| | 3.19 | | 5.0 | 0.0407 | 0.0109 |

where k'_{DCAA} and k'_{TCAA} are the rate constants (min⁻¹) of DCAA and TCAA, respectively; C_{O_3} is the initial concentration of the dissolved ozone (mg/L).

3.3. Heterogeneous oxidation of HAAs by O₃/UV

The batch treatment results of the mixture of the two HAAs are presented in Fig. 5. The mixture contains each HAA of 2.0 mg/L as initial concentration. Similar to the homogeneous systems, the apparent pseudo-first-order rate constant for each HAA in the mixture system was obtained, and the results are also listed in Table 2. By comparison, the rate constants were smaller than those of the homogeneous systems under experimental conditions, indicating that the two HAAs in heterogeneous systems consumed more •OH radicals causing low •OH radicals concentration in steady state.

Similarly, the rate constants of the mixture system could be obtained as follows:

$$k'_{DCAA} = 0.0735C_{O_3}^{0.4443}$$

$$k'_{TCAA} = 0.0147C_{O_3}^{0.3564}$$

The rate constants of DCAA and TCAA decreased by 8.0–13.9% and 15.2–27.7%, respectively, when an initial dissolved O₃ concentration

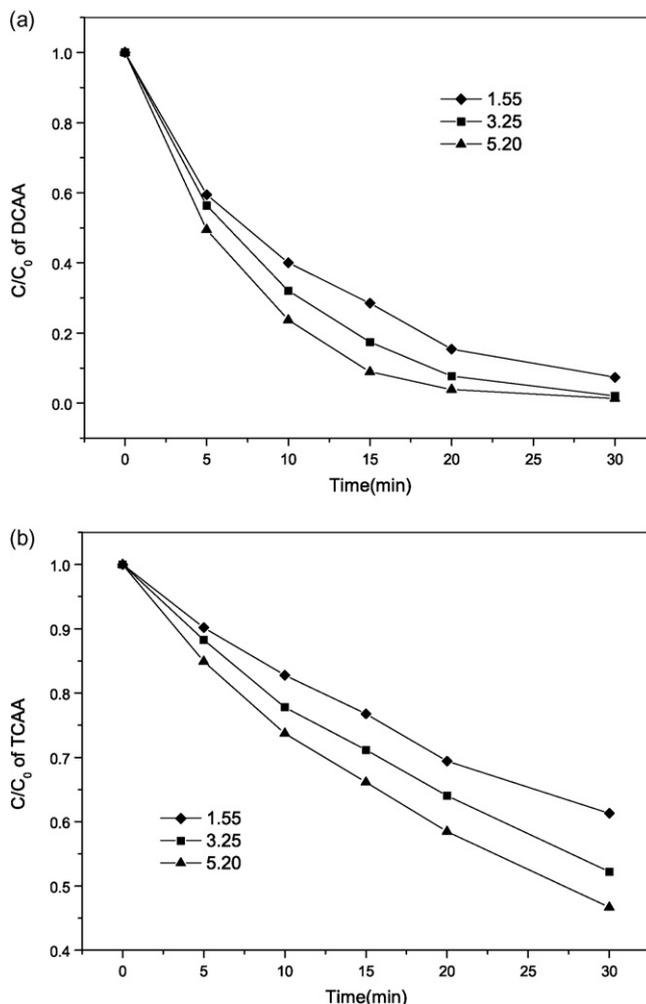


Fig. 5. (a) Variation of DCAA concentrations with time in the mixture system; (b) variation of TCAA concentrations with time in the mixture system.

ranged from 1.0 to 4.0 mg/L as compared to those in homogeneous oxidation. The effect of coexistent TCAA on DCAA decomposition was not as large as the one of DCAA on TCAA decomposition.

3.4. The influence of humic acids and bicarbonate ion

Previous studies indicated that humic acids and bicarbonate, which are ubiquitous in drinking water, are radical scavengers [25]. On the other hand, the reactions of ozone with humic acids might also generate species that promote the conversion of O_3 into $\cdot OH$ [25,26]. So it is important to determine the effects of these substances on HAA decomposition.

In the batch experiments of O_3/UV , the remarkable effect of humic acids on HAAs decomposition and the accumulation of hydrogen peroxide were observed when an initial dissolved O_3 concentrations ranged from 3.08 to 3.22 mg/L in the presence of 1.2, 2.5, 5.0 mg/L of TOC, and the results are given in Figs. 6 and 7, respectively. The rate constants are also listed in Table 2.

As showed, the rate of HAAs decomposition greatly decreased with the increase of coexistent humic acids concentration, indicating that humic acids played as a radical scavenger in this system. The rate constants of DCAA and TCAA decreased by 41.1% and 23.8%, respectively, when humic acids was added at a concentration of 1.2 mg TOC/L as compared to those in the absence of humic acids. From the concentration of humic acids and the reaction rate con-

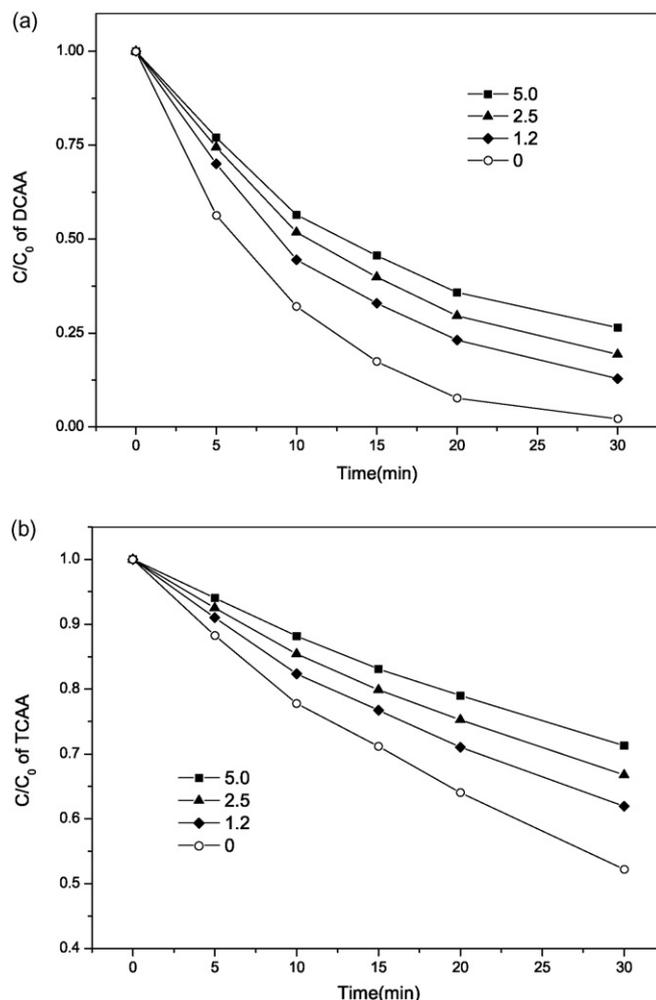


Fig. 6. (a) Effects of humic acids on DCAA decomposition; (b) effects of humic acids on TCAA decomposition.

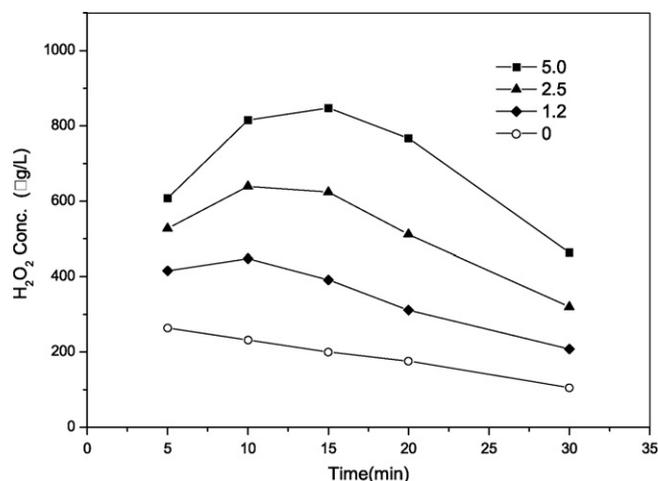


Fig. 7. Effect of humic acids on H_2O_2 formation.

stants, the following empirical equations were obtained:

$$k'_{DCAA} = 0.04315 + 0.08268 \exp\left(\frac{-C_{HS}}{0.7092}\right)$$

$$k'_{TCAA} = 0.00988 + 0.01229 \exp\left(\frac{-C_{HS}}{1.1349}\right)$$

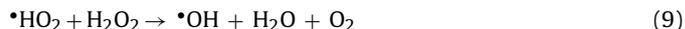
where C_{HS} is the concentration of humic acids (TOC mg/L).

Fig. 7 indicates that the accumulation of H_2O_2 depended highly on the concentration of humic acids in the solution. It can be seen that up to 800 $\mu g/L$ of H_2O_2 accumulated in the solution at a TOC of 5.0 mg/L, whereas the concentration of H_2O_2 in the absence of humic acids did not exceed 250 $\mu g/L$.

According to Glaze et al. [27,28], the following reactions could be expected in the O_3/UV process:



Through the reactions H_2O_2 was formed. Simultaneously the reactions of H_2O_2 with O_3 and $\cdot HO_2$ radicals accelerate the formation of $\cdot OH$ radicals [29].



The cleavage of H_2O_2 by UV could also produce $\cdot OH$ radicals, but the UV absorption of H_2O_2 is poor [30].

Obviously, there were many different pathways for the generation of $\cdot OH$ radicals in the O_3/UV process, which was beneficial to the decomposition of the HAAs. Humic acids generally contain rich unsaturated structures, which could react with O_3 , thus consume much O_3 . The fast consumption of ozone by humic acids inhibited the reaction of hydrogen peroxide with ozone and other species produced by ozone, resulting in the decrease in $\cdot OH$ radicals and the accumulation of H_2O_2 . So when the effect of humic acids on HAAs decomposition in the O_3/UV process is remarkable, it is important to provide a favourable condition for transformation of H_2O_2 into $\cdot OH$ radicals.

The effect of the HCO_3^- concentration on the decomposition of HAAs in water at an initial dissolved O_3 concentrations of

3.19 ± 0.06 mg/L was investigated, and the HCO_3^- concentration ranging from 1.0 to 5.0 mmol/L, and the obvious pseudo-first-order rate constants are shown in Table 2. Compared with those in the absence of any scavenger, the rate constants of DCAA and TCAA decreased by 43.5% and 25.9%, respectively, at an HCO_3^- concentration of 1.0 mmol/L. According to the HCO_3^- concentrations and the reaction rate constants, the following empirical equations were obtained:

$$k'_{\text{DCAA}} = 0.04008 + 0.08526 \exp\left(\frac{-C_{\text{HCO}_3^-}}{1.3475}\right)$$

$$k'_{\text{TCAA}} = 0.01116 + 0.01101 \exp\left(\frac{-C_{\text{HCO}_3^-}}{1.9847}\right)$$

where $C_{\text{HCO}_3^-}$ is the concentration of HCO_3^- (mmol/L).

4. Conclusion

Single O_3 or UV did not result in perceptible decomposition of HAAs within the applied reaction time. Among the six methods of oxidation, O_3/UV is believed to be more suitable for the decomposition of DCAA and TCAA in water. Decomposition of DCAA was easier than TCAA by AOPs. For O_3/UV in the semi-continuous mode, effective utilization rate of ozone for HAA decomposition decreased with ozone addition, so to add O_3 continuously into the system is not an efficient method to improve HAAs decomposition. A pseudo-first-order reaction model could describe the decomposition of the two HAAs by O_3/UV under the constant initial O_3 concentration and fixed UV irradiation. Under experimental conditions, the pseudo-first-order rate constant for the decomposition of DCAA was more than four times that for TCAA.

Humic acids could cause the H_2O_2 accumulation and the decrease in rate constants of HAAs decomposition in the O_3/UV process, so it is important to provide a favourable condition for transformation of H_2O_2 into $\cdot\text{OH}$ radicals. The rate constants for the decomposition of DCAA and TCAA decreased by 41.1% and 23.8%, respectively, when humic acids were added at a concentration of 1.2 mg TOC/L. The rate constants decreased by 43.5% and 25.9%, respectively, at an HCO_3^- concentration of 1.0 mmol/L.

Acknowledgement

Financial support by the National Scientific and Technological Project of China during the 11th Five-Year Plan Periods of China (No. 2006BAJ08B08) is gratefully acknowledged.

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