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Ozonation of 3,3´-dichlorobenzidine in aqueous solution: degradation efficiency and kinetics

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ABSTRACT

The degradation efficiency and kinetics of 3,3´-dichlorobenzidine (DCB) in aqueous solution by ozonation was investigated in this study. In laboratory-scale experiments, the primary factors affecting the degradation of DCB were investigated. The results showed that pH strongly influenced the degradation process, with a maximum apparent rate of 0.235 min^{-1} obtained at pH 4. The reactivity of DCB decreased in the order $(C_{12}H_{10}Cl_2N_2)_2 > (C_{12}H_{10}Cl_2N_2)_2 \cdot HCl > (C_{12}H_{10}Cl_2N_2)_2 \cdot 2HCl$. The degradation rate of DCB increased with increasing ozone dosage and reaction temperature but decreased with increasing initial DCB concentration. We derived a reaction kinetics model of DCB degradation by ozonation in aqueous solution by interpreting the experimental data, and this model showed good stability. The efficiency of DCB degradation by ozonation was also evaluated. DCB could be removed efficiently by ozonation, with greater than 85% removal after 50 min at pH 4 and 16–30˚C with a DCB concentration of 1.2–6.5 mg/L and an ozone dosage of 3.7–5.1 mg/min. Most of the intermediate products could not be mineralised by direct oxidation by ozone. The addition of *tert*-butyl alcohol or Cl^- had little effect on the degradation rate of DCB, which indicated that degradation of DCB occurred via direct oxidation by ozone.

Keywords: 3,3´-Dichlorobenzidine; Ozonation; Influencing factors; Removal efficiency; Kinetics model

1. Introduction

3,3´-Dichlorobenzidine (DCB) and its salts have been used as intermediates in the manufacture of azo dyes and diarylide pigments, such as Pigment Yellows 12, 13, 14, 17, 34, 55 and 83, Pigment Oranges 13 and 34, and Pigment Red 38 [1,2]. DCB-based azo dyes and diarylide pigments exhibit a number of properties that make them superior to other similarly coloured pigments, such as a high tinting strength, bright colour and moderate price. These dyes can be used as substitutes for lead chromate pigments [3], and no cost-effective substitutes exist for DCB in these important applications.

However, DCB poses potential threats to human health and ecological security due to its highly toxic, carcinogenic and mutagenic nature [4]. The International Agency for Research on Cancer has designated DCB a category 2B compound (probable human

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carcinogen) [1]. A health and environmental assessment conducted by the United States Environmental Protection Agency (US EPA) indicated that DCB is carcinogenic to rodents and most likely to humans as well [3]. One cohort study of male manufacturing workers in the United States who were exposed to mixtures of benzidine and DCB revealed an increased risk of leukaemia and bladder cancer among the exposed workers [5]. Makena and Chung [6] demonstrated that DCB-mutated TA102 cells in the presence of rat liver S9 mix led to genotoxicity by causing DNA breakage. DCB can be biodegraded into a more stable compound, benzidine, when released into the environment [7]. Benzidine is listed in the First Annual Report on Carcinogens and has been classified as a Group A compound (known human carcinogen) by the US EPA [8].

Because of the properties and resulting safety and environmental challenges posed by DCB, this compound is no longer produced in some developed countries, such as the United States and Germany. Nonetheless, these countries import DCB from developing countries to produce DCB-based azo dyes and pigments. China and India are the main DCB producers in the world, and the annual production capacity of DCB in China is currently over 3.5×10^4 metric tonnes. The production of 1 ton of DCB hydrochloride results in the generation of 12–15 ton of wastewater. DCB can reach the environment through a variety of sources; however, the primary source is wastewater from the manufacture of DCB, DCB-based azo dyes and diarylide pigments [9]. DCB can be transported over long distances bound to sediment and is stable in sediment-water systems. In an 11-year field study, high levels of DCB were measured as far as 6 km from the single known source in Lake Macatawa, Michigan [9]. Hence, DCB must be effectively removed from industrial wastes before they are discharged.

The literature contains few published studies on the removal of DCB from wastewater. However, numerous studies on the removal of aromatic amines from wastewater have been reported. Casero et al. [10] studied the oxidation of various carcinogenic aromatic amines using Fenton's reagent. Using a composite process involving micro-electrochemical oxidation, air-stripping and aerobic biological processes, Xia et al. [11] reported the treatment of 2,2′,5,5′-tetrachlorobenzidine (TCB) wastewater. He and Wu [12] studied micro-electrolysis and biochemical processes to treat dyeing wastewater from DCB production. Currently in China, the wastewater from DCB production is treated primarily using biological methods. However, DCB has been reported to be stable under both aerobic and anaerobic conditions over a period of approximately four weeks. Nyman et al. [13] demonstrated that DCB undergoes sequential dehalogenation when incubated in sediments under anaerobic conditions, and the reductive dehalogenation of DCB is known to produce benzidine, which is more toxic than the parent compound. Therefore, the biodegradation of DCB has been examined as a part of a comprehensive fate study [14]. The chemical oxidation of organics can lead to ring-cleavage and subsequently to the complete breakdown of the molecule. However, the decontamination of large volumes of aqueous solution is inconvenient due to the large quantities of chemical reagents required. Therefore, a pressing demand exists for DCB-removal procedures that are inexpensive and highly efficient.

Ozone, which is a clean and strong oxidising agent, can oxidise most compounds effectively without creating further pollution, and this compound is widely used in research regarding the treatment of toxic and non-biodegradable organic wastewater [15–17]. Under certain conditions, ozone can decompose into $^{\cdot}$OH, which is a stronger oxidising agent than ozone. The decreased cost of ozone production makes the practical application of ozonation possible. Given the limited data available in the literature on the treatment of DCB-contaminated water, we studied the degradation of DCB in aqueous solution by ozonation in this study. The main purpose of this study was to evaluate the efficiency of ozonation in the detoxification of industrial DCB wastes. We concentrated on determining the optimal experimental conditions for the ozonation of DCB, and the removal efficiencies of DCB and total organic carbon (TOC) were also evaluated. Furthermore, the variation in the apparent reaction rate constants was studied, and a kinetic model based on the mechanisms of ozone decomposition and DCB degradation was derived. *tert*-Butyl alcohol (TBA) and chloride ion were used as $^{\cdot}$OH inhibitors to determine the major pathway involved in DCB degradation.

2. Experimental

2.1. Materials

DCB (99% purity, used without further purification, Yan Cheng Ouhua Chemical Industry, China) and high-performance liquid chromatography (HPLC)-grade acetonitrile (TianJin Yongda Chemical Reagent, China) were used; all other chemicals were of analytical grade. All solutions were prepared with deionised water. Ozone gas was generated from air or oxygen gas using a corona discharge ozone generator. The chemical characteristics of DCB are listed in Table 1.

Table 1
Selected properties of DCB

Compound	Formula	MW (g/mol)	Melt. Pt. (℃)	S_w (mg/L)	pK_{a1}	pK_{a2}	Log K_{ow}
DCB	$C_{12}H_{10}Cl_2N_2$	253.13	132–133	3.99	1.6	3.2	3.5

2.2. Apparatus and ozonation experiments

The experimental apparatus consisted of a cylindrical Pyrex glass reactor (diameter: 58 mm; height: 530 mm) coupled to an ozone generator (NPF3W, Shandong NIPPON Photoelectricity Equipment Co., China), an air pump (ACO-002, Zhejiang Shenshen Industrial Co., China) and an exhaust treatment system. The airflow rate to the ozone generator was monitored and adjusted with a rotameter incorporated into the ozone generator. The generated ozone/air mixed gas was delivered into the reactor via a ceramic sand core diffuser plate at the bottom. The DCB solutions were buffered with phosphate at an ionic concentration of 0.1 mol/L. Samples were collected using a transfer pipette at various time points and filtered through qualitative filter paper. Sodium thiosulphate solution ($Na_2S_2O_3$, 0.1 mol/L) was added to stop the reaction after the sampling was complete.

In the mineralisation experiments, a high ozone dosage (11.1 mg/min) was generated from oxygen and the O_3/O_2 mixture was delivered into the reactor containing 1,000 mL of DCB aqueous solution (100 mg/L). The samples were passed through a membrane filter (0.45 μm pore size) and periodically analysed for TOC.

2.3. Analytical methods

DCB was analysed by high-pressure liquid chromatography (LC-20AT, Shimadzu, Japan). A 10 μL aliquot was injected to determine the concentration of DCB using acetonitrile/water (70:30 v/v) as the mobile phase. The analytes were separated using a C18 column (150 × 4.6 mm, DIKMA Diamonsil) at a flow rate of 1.0 mL/min and a column temperature of 25℃. A UV detector was used at a wavelength of 285 nm. The pH was measured with a PHS-25 instrument (Shanghai Rex Analytical Instrument Co., China). Low input gas mass concentrations of ozone were determined by the iodometric method [18] and higher concentrations were detected directly using an ozone concentration detector (IDEAL-2000, Zibo Ideal Computer Software Co., China). The UV_{285} absorption values were measured with an ultraviolet spectrophotometer (UV-2450PC, Shimadzu, Japan) at 285 nm. The TOC was determined by the combustion catalytic oxidation method using a TOC analyser (TOC-L CPH, Shimadzu, Japan).

3. Results and discussion

3.1. Effect of pH

The pH of aqueous solutions is usually considered one of the most important factors influencing ozonation. To elucidate the effects of pH on the degradation rate and the detoxification of DCB by ozonation, the experiments were repeated over the pH ranges 1.00–9.01 and 2.04–6.01, respectively. The UV and HPLC spectra during degradation process of DCB under different pH are described in Appendix. As shown in Fig. 1(a), the DCB degradation rate increased as the pH was increased from 1.00 to 4.01 and then decreased as the pH was increased beyond 4.01. The removal rates of DCB were 38.3, 97.1 and 4.3% after 15 min of ozonation when the pH values were 1.00, 4.01 and 9.01, respectively. As shown in Fig. 1(b), the removal rates of UV_{285} and DCB followed similar trends in the pH range 2.04–6.01; however, the removal rate of UV_{285} lagged behind that of DCB's. UV_{285} refers to the ultraviolet absorption of the DCB solution at 285 nm, and it reflects the concentration of aromatic organic compounds in the ozonation system. The maximum removal rate of UV_{285} was obtained at pH 4, with more than 90% removed after 40 min. The removal rate of UV_{285} lagged behind that of DCB because intermediates, such as diaminobiphenyl, 3-hydroxy-4,4´-diaminobiphenyl, benzidine and aniline [7,13], were produced during the initial stage of ozonation. With continued ozonation, the aromatic compounds would be oxidised to generate ring-cleavage products, thereby leading to an increase in the removal rate of UV_{285}.

In general, ozone reacts with organic compounds via either direct oxidation by ozone or indirect oxidation by ·OH [19]. The ozone molecule itself is stable and is the primary reactive species in acidic solutions [20]. When the solution becomes more alkaline, the rate of ozone decomposition into radicals increases. These radicals include the hydroxyl radical (·OH) [21], which is a stronger oxidant than ozone, with a redox potential of 2.80 V. The higher DCB degradation rate under acidic conditions indicates that the ozonation mechanism occurred via direct oxidation by ozone. Although at basic pH a fraction of ozone is transformed into hydroxyl radicals, this is compensated in acid media by the higher redox potential (2.07 V

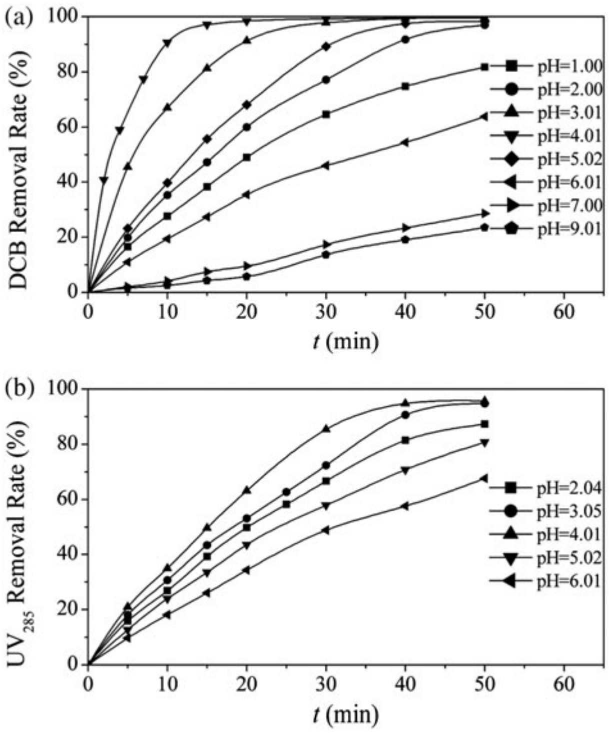

Fig. 1. (a) Effect of the pH on the degradation of DCB and (b) the removal rate of UV_{285} by ozonation ($Q_{O_3} = 5.04$ mg/min; $C_0 = 6$ mg/L; $T = 20$℃; solution volume = 1 L).

compared with 1.24 V in alkaline media) and the higher concentration of ozone.

Direct oxidation by ozone molecules strongly depends on the molecular structure of the organic compound [22]. DCB is a weak organic base and undergoes two-step dissociation, with $pK_{a1} = 1.6$ and $pK_{a2} = 3.2$ [14], to give arylamine and hydrochloride species in solution. In general, when $pH < pK_{a1}$, DCB exists predominantly in the dicationic form in aqueous solution. When $pK_{a1} < pH < pK_{a2}$, cationic DCB is the predominant species, whereas undissociated DCB is predominant when $pH > pK_{a2}$ (Fig. 2).

As shown in Fig. 3, the apparent reaction rate constant (k_{obs}) of DCB increased significantly as the pH was increased from 1.00 to 4.01, which indicates that the undissociated DCB was more easily oxidised by ozone than the cationic DCB and dicationic DCB. Therefore, the reaction occurred primarily between ozone molecules and undissociated DCB at pH 4.01. The activity of the reaction between ozone and different forms of DCB decreased in the order $(C_{12}H_{10}Cl_2N_2)_2 > (C_{12}H_{10}Cl_2N_2)_2{\cdot}HCl > (C_{12}H_{10}Cl_2N_2)_2{\cdot}2HCl$. The maximum k_{obs} value of 0.235 min^{-1} obtained at pH 4.01 was 6.9 times and 35.8 times greater than the k_{obs} values at pH 1.00 and 7.00, respectively. The rate was higher at pH 4.01 because the concentration of undissociated DCB reached a maximum at pH 4.01 and the further increases in pH accelerated the self-decomposition rate of ozone. Thus, the optimal pH during these experiments was 4.0.

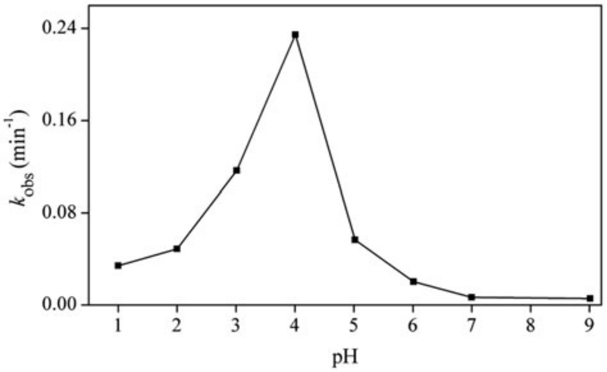

Fig. 3. Relationship between k_{obs} and pH ($Q_{O_3} = 5.0411$ mg/min; $C_0 = 6$ mg/L; $T = 20$℃; solution volume = 1 L).

3.2. Effect of the initial DCB concentration

The initial concentration of the pollutant has an important effect on the actual application of the ozonation process and directly affects the method used for water treatment and the time required for processing. The effect of the initial concentration on the degradation of DCB was evaluated at different DCB concentrations, with the other experimental conditions held constant (see Appendix). The results are shown in Fig. 4. As evident in Fig. 4(a), the initial DCB concentration strongly influenced the DCB degradation rate, and increases in the initial concentration led to significant decreases in the removal efficiency. The removal rates of DCB were 92.1, 89.1, 77.6 and 65.7% after 30 min with initial concentrations of 1.27, 2.44,

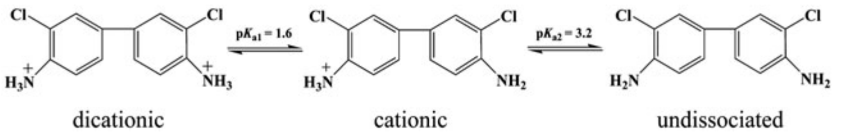

Fig. 2. Dissociation of DCB.

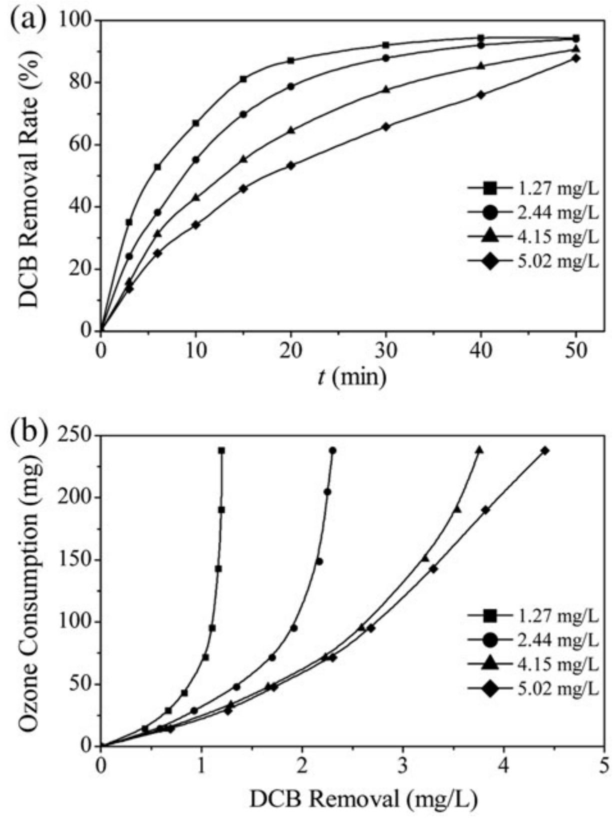

Fig. 4. (a) Effect of the initial concentration on the degradation of DCB. (b) Ozone consumption with DCB removal ($Q_{O_3} = 4.76$ mg/min; pH 4; $T = 20$°C; solution volume = 1.2 L).

4.15 and 5.02 mg/L, respectively. However, the amount of DCB that was degraded increased from 1.17 to 3.22 mg/L as the initial DCB concentration was increased from 1.27 to 4.15 mg/L, and no significant difference was observed in the amount of DCB degraded for initial DCB concentrations of 4.15 and 5.02 mg/L over a reaction time of 30 min.

These results were obtained because, as the initial concentration of DCB increased, the molar ratio of ozone to DCB decreased, which resulted in a decreased removal rate of DCB. However, the reaction rate of DCB with ozone increased, and more DCB was removed. In addition, the ozone mass transfer rate in aqueous solution increased, which enhanced the utilisation rate of ozone. As shown in Fig. 4(b), more ozone was consumed for the same DCB removal at low concentrations, and the same removal with high concentrations of DCB could be achieved by extending the ozonation time. However, the consumption of ozone increased due to the low DCB concentration and the generation of intermediates during the later part of the reaction. Thus, the treatment of wastewater with a high initial DCB concentration would be more efficient and economical.

3.3. Effect of the ozone dosage

The effect of the ozone dosage on the degradation of DCB in aqueous solution was investigated with different ozone dosages, with the other conditions fixed (see Appendix). The experimental results are presented in Fig. 5. The results revealed that the increase in the ozone dosage positively affected the degradation of DCB. After 50 min of ozonation, approximately 72, 85, 91 and 95% of the DCB had been removed, and the amount of DCB that was degraded increased gradually, with 2.89, 3.42, 3.77 and 3.83 mg/L degraded at influent ozone gas dosages of 3.75, 4.33, 4.76 and 5.04 mg/min, respectively. The influence of the ozone dosage on DCB removal was significant during the initial stage of the reaction because of the high DCB concentration; the difference became smaller as DCB was consumed.

In the case of a smaller gaseous ozone dosage or during the initial stage of reaction, the consumption rate of ozone was fast due to the higher DCB concentration and the reaction rate was controlled by the supply of ozone. An increase in the gaseous ozone dosage ensures the supply of ozone and increases the gas–liquid contact area, thereby accelerating the mass transfer rate of ozone and increasing the aqueous-phase ozone concentration [23]. Therefore, the ozone dosage had a substantial influence on the degradation of DCB. However, as the aqueous-phase ozone concentration approached the maximum value or as the concentration of DCB decreased, the ozone dosage was relatively abundant and the process was controlled by the rate of the chemical reaction [24].

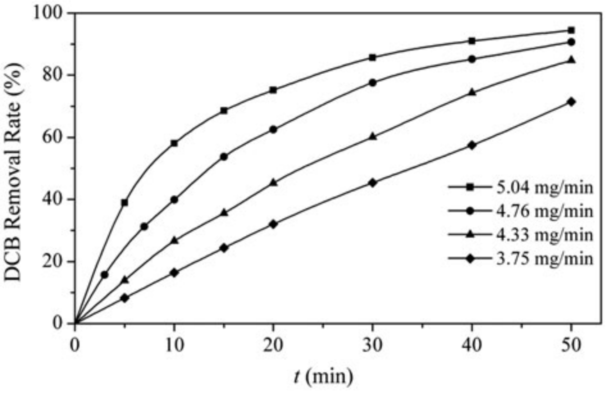

Fig. 5. Effect of the ozone concentration on the degradation of DCB (pH 4.00; $C_0 = 4.1$ mg/L; $T = 20$°C; solution volume = 1.2 L).

Therefore, any further increase in the ozone dosage would have little effect on the degradation of DCB. The optimal ozone dosage during these experiments was 4.76 mg/min.

3.4. *Effect of reaction temperature*

The effect of the reaction temperature on degradation was investigated over the temperature range of 15–30℃ (see Appendix). As shown in Fig. 6, the DCB degradation rate increased as the reaction temperature was increased from 15 to 30℃. The DCB removal rates were 83.5 and 95.7% of the maximum at reaction temperatures of 15 and 26℃, respectively, after 50 min. However, the influence of the reaction temperature became insignificant when the reaction temperature was higher than 26℃, and the DCB removal rate was only 96.9% at 30℃.

The rate of the reaction between DCB and ozone gradually increased with increasing reaction temperature; thus, the DCB degradation rate increased. However, an increase in the temperature had two negative effects on the degradation of DCB. First, the aqueous ozone concentration decreased as the temperature increased [25]. Second, the increase in the temperature resulted in greater decomposition of ozone in solution [26]. As a result, the increase in the reaction temperature had a positive effect on the degradation of DCB despite the lower concentration of ozone in aqueous solution at higher temperatures.

3.5. *Effects of TBA and Cl^-*

The oxidation of organics with ozone mainly consists of two pathways: a direct pathway with molecular ozone and a radical pathway via the hydroxyl radical derived from ozone [15]. TBA is a scavenger of ·OH and can inhibit the chain reaction between ·OH and DCB [27]. The reaction rate constant ($k_{\cdot OH,\ TBA}$) for TBA with ·OH is 6×10^8 L/(mol s); however, the reaction rate constant ($k_{O3,\ TBA}$) for TBA with ozone is less than 3×10^{-3} L/(mol s) [19]. Therefore, TBA was used to investigate whether direct oxidation by ozone was a major process in the degradation of DCB [28]. DCB wastewater contains high concentrations of Cl^-, which is a scavenger of ·OH and one of the primary factors that negatively affects advanced oxidation technology in practical applications [29].

To further investigate the major oxidation pathway during the degradation of DCB, experiments were conducted with and without ·OH scavengers. To completely eliminate the role of ·OH in the degradation of DCB by ozonation, TBA or Cl^- was added to the solution in excess (TBA: 85.75 mg/L; Cl^-: 2912.2 mg/L) [30]. The effects of TBA and Cl^- on the degradation rate of DCB are shown in Fig. 7. The results demonstrate that the removal rates of DCB by ozonation were 86.5 and 85.1% in the presence of TBA and Cl^-, respectively, and 87.5% in the absence of TBA and Cl^- after 50 min. No conspicuous effect of TBA or Cl^- on the degradation rate of DCB was observed, thereby indicating that the degradation of DCB occurred via the direct oxidation mechanism.

3.6. *Establishment of a reaction kinetics model*

The kinetics of the degradation of DCB by ozonation can be described as

$$-dc/dt = kC^m \times C_{O_3}^n \tag{1}$$

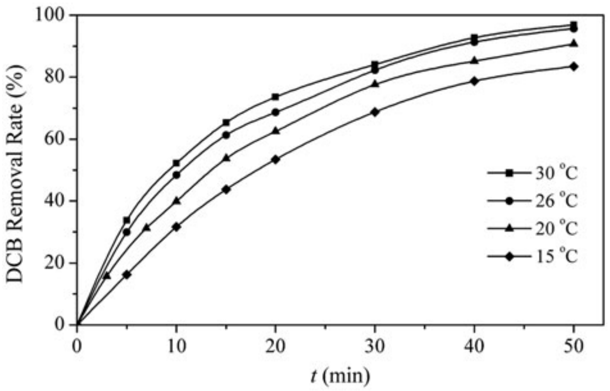

Fig. 6. Effect of temperature on the degradation of DCB (Q_{O_3} = 4.76 mg/min; pH 4.00; C_0 = 4.1 mg/L; solution volume = 1.2 L).

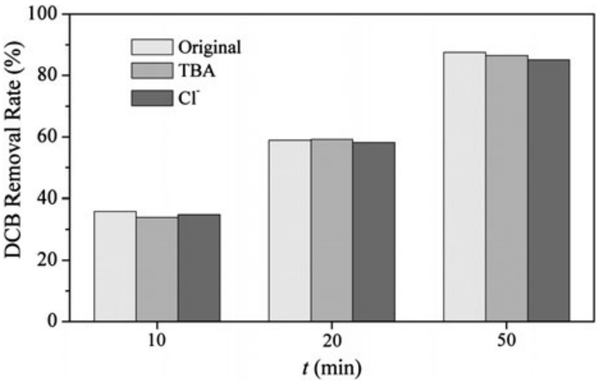

Fig. 7. Effects of TBA and Cl^- on the degradation of DCB (Q_{O_3} = 4.76 mg/min; C_0 = 4 mg/L; T = 16℃; solution volume = 1.2 L).

If the aqueous-phase ozone concentration is assumed to be constant in the BSTR reactor, then the degradation reaction kinetics can be simplified as follows:

$$-\mathrm{d}c/\mathrm{d}t = k_{\mathrm{obs}}C^{m} \tag{2}$$

where C is the DCB concentration, t is the reaction time, k is the total rate constant, k_{obs} is the observed rate constant and m and n are the influence indices for the DCB concentration and ozone, respectively.

As shown in Fig. 8, we found that the degradation of DCB by ozonation fit well with a first-order kinetic equation over a period of 50 min. The degradation reaction kinetics could therefore be simplified as,

$$-\mathrm{d}c/\mathrm{d}t = k_{\mathrm{obs}}C \tag{3}$$

Table 2 presents the k_{obs} and correlation coefficients (r) for different initial DCB concentrations, ozone dosages and reaction temperatures. The data in Table 2 show that k_{obs} was strongly influenced by the initial DCB concentration, the ozone dosage and the reaction temperature. Thus, k_{obs} could be represented by a modified Arrhenius equation, as follows [31]:

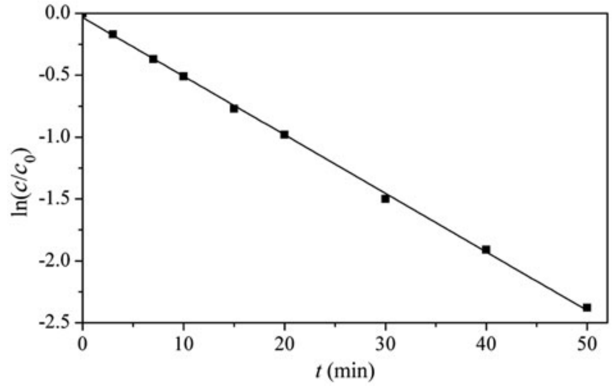

Fig. 8. Fitted curve of $\ln(C/C_0) - t$ ($Q_{O_3} = 4.76$ mg/min; $C_0 = 4$ mg/L; $T = 20$℃; solution volume = 1.2 L).

Table 2
Fitted k_{obs} based on experimental results

C_0 (mg/L)	Q_{O_3} (mg/min)	T (K)	k_{obs} (min^{-1})	r
1.27	4.76	293	0.1119	0.9966
2.44	4.76	293	0.0759	0.9994
4.15	4.76	293	0.0478	0.9988
5.02	4.76	293	0.0366	0.9978
4.15	3.75	293	0.0214	0.9964
4.15	4.33	293	0.0332	0.9936
4.15	5.04	293	0.0582	0.9838
4.15	4.76	288	0.0370	0.9970
4.15	4.76	299	0.0613	0.9963
4.15	4.76	302	0.0663	0.9937

$$k_{\mathrm{obs}} = A\exp(-E_{\mathrm{a,obs}}/RT)Q_{O_3}^{\alpha}C_0^{\beta} \tag{4}$$

Then, transformation of the equation logarithmically leads to Eq. (5):

$$\ln k_{\mathrm{obs}} = \ln A - E_{\mathrm{a,obs}}/RT + \alpha \ln Q_{O_3} + \beta \ln C_0 \tag{5}$$

where $E_{\mathrm{a,obs}}$ is the observed activation energy, A is a pre-exponential factor, T is the reaction temperature, Q_{O3} is the ozone dosage, C_0 is the initial DCB concentration and α and β are the exponential constants for the ozone dosage and the initial DCB concentration, respectively.

According to Eq. (5), $E_{\mathrm{a,obs}}$, A, α and β can be calculated by linear regression analysis, as shown in Fig. 9. The following modified Arrhenius equation was obtained on the basis of the data in Table 2.

$$k_{\mathrm{obs}} = 190.3\exp(-30460.0/RT)Q_{O_3}^{3.408}C_0^{-0.794} \tag{6}$$

with $E_{\mathrm{a,obs}} = 30{,}460.0$ J/mol ($r = 0.9918$), $\alpha = 3.408$ ($r = 0.9977$) and $\beta = -0.794$ ($r = 0.9778$).

With the integration of Eqs. (3) and (6), the reaction kinetics model can be represented as follows:

$$C = C_0\exp(-190.3\exp(-30460.0/RT)Q_{O_3}^{3.408}C_0^{-0.794}t) \tag{7}$$

The reaction kinetics model of DCB ozonation in aqueous solution is a suitable tool for predicting the process efficiency and for designing reactors.

3.7. Degradation efficiency and stability of the kinetics model

To investigate the stability of the kinetics model and the efficiency of DCB degradation by ozonation, we performed additional 10 experiments under the following experimental conditions: pH 4; DCB concentration, 1.2–6.5 mg/L; ozone dosage, 3.7–5.1 mg/min; and temperature, 16–30℃. Table 3 shows the relative deviation between the calculated concentration and the experimental concentration at different reaction times and the amount of DCB degraded after 50 min.

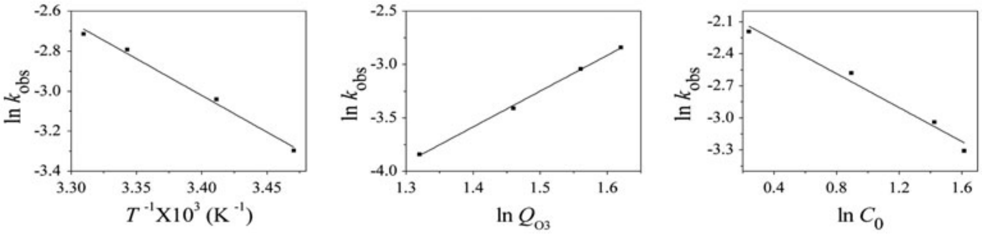

Fig. 9. The fitted curve of $\ln k_{obs}$ with T^{-1}, $\ln Q_{O_3}$ and $\ln C_0$.

Table 3
The stability of the model and DCB degradation efficiency

C_0 (mg/L)	Q_{O_3} (mg/min)	T (℃)	t (min)	Experimental determined concentration (mg/L)	Calculated concentration (mg/L)	Relative deviation (%)	DCB degradation rate (%)
3.98	4.76	20	30	1.08	0.94	6.8	88.8
2.44	4.33	25	10	1.09	1.30	−8.5	94.1
4.12	4.76	16	20	1.93	1.88	1.4	86.4
4.16	5.04	16	30	1.15	1.00	6.6	85.1
4.40	5.04	19	50	0.23	0.30	−12.6	94.7
3.94	4.76	28	7	2.86	2.46	7.6	86.5
4.14	4.76	17	40	0.65	0.80	−10.7	87.5
1.24	3.75	20	50	0.076	0.084	−5.0	93.9
2.50	4.76	20	10	1.56	1.21	12.8	95.5
6.49	4.76	19	15	2.94	4.06	−15.9	89.9

As shown in Table 3, the relative deviation was less than 16%, which indicates that the kinetics model exhibited good stability. The removal rate of DCB reached over 85% after 50 min, which indicates that DCB in aqueous solution was removed efficiently by ozonation under the specified experimental conditions.

3.8. Analysis of mineralisation

To investigate the mineralisation degree of DCB, we conducted experiments with high concentrations of DCB and O_3 gas. The TOC of the solution at different ozonation times was measured after filtration using a membrane filter. The removal rates of DCB and TOC by ozonation are shown in Fig. 10. Clearly, the removal rates of TOC and DCB increased rapidly within 4 min, reaching maximum values of 97.7 and 99.9% at 4 min, respectively. Thereafter, the removal rate of DCB tended to stabilise. However, the removal rate of TOC decreased significantly from 4 to 15 min and tended to stabilise at 14.1% after 30 min.

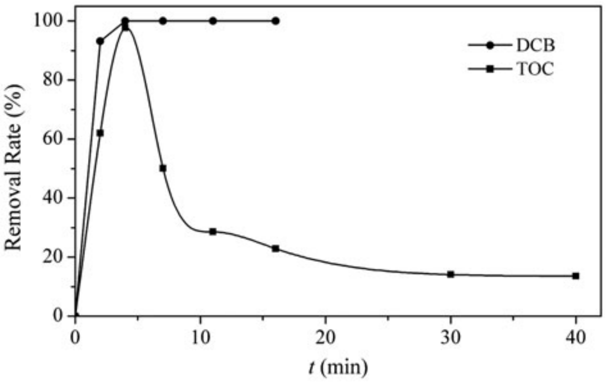

Fig. 10. Removal rates of DCB and TOC by ozonation (Q_{O_3} = 11.1 mg/min; C_0 = 24 mg/L; pH 4.04; T = 16℃; solution volume = 1.0 L).

At the beginning of the ozonation reaction, the colour of the solution changed from colourless to black brown and quickly became darker. The solution then gradually became pale and eventually became colourless at 16 min. Correspondingly the residue attached to the membrane after filtration was the same colour as the solution and the trend for the colour of the solution was similar to the trend for the removal rate of TOC. It is reasonable that in the oxidation reaction, ozone can react with amino groups by reacting with the lone pair on nitrogen, forming a nitroxyl radical ($NO–OO^-$) [32]. The generated nitroxyl radical then immediately transformed to various macromolecular oligomers or polymers after further condensation reactions. The coloured, water insoluble solid organic was generated through ozonation and left on the membrane after filtration, resulting in a rapid decrease in the measured TOC of the sample. Therefore, this measured TOC was not the true TOC of the solution. Because of the electron-withdrawing effect of the neighbouring Cl groups and the electron-donating effect of the amino groups, the electron density on the benzene ring is unevenly distributed. With ozone gas continually being added, the insoluble products underwent an ozone addition reaction and were gradually degraded into soluble, colourless ring-cleavage products, increasing the TOC of the solution. Furthermore, the ring-cleavage products were degraded into alcohols, aldehydes, carboxylic acids, etc. Analysis of the degradation process by liquid chromatography revealed that one major intermediate was generated and gradually disappeared. Under acidic conditions (pH of 4), the reaction occurred mainly via direct oxidation by ozone molecules. Although DCB could easily be removed, the direct ozonation rates of most of the intermediates were low, and complete mineralisation to H_2O and CO_2 was difficult. The removal rate of TOC was stable and only 14.1% after 30 min. Casero et al. assessed the chemical degradation of DCB by Fenton's reagent and insoluble products were also found in that experiment [10].

The removal of DCB from wastewater could be achieved by conversion into insoluble products, ring-cleavage products or mineralisation, but the actual execution of the different routes depends on the experimental conditions, especially the dosage of ozone. DCB can be easily removed by ozone, and from an economic point of view the ring-cleavage of DCB is expected to be superior in comparison to degradation through mineralisation.

4. Conclusions

DCB could be removed efficiently by ozonation in aqueous solution. The degradation of DCB was influenced by pH, the initial DCB concentration, the ozone dosage and the reaction temperature. The removal rate of DCB in aqueous solution reached more than 85% after 50 min at pH 4 and 16–30˚C with a DCB concentration of 1.2–6.5 mg/L and an ozone dosage of 3.7–5.1 mg/min. A reaction kinetics model for these conditions was developed, and the model showed good stability.

The pH strongly influenced the DCB degradation rate. The k_{obs} value first increased and then decreased quickly as the pH was increased from 1 to 9 because of the different reaction mechanisms of ozonation and the dissociation of DCB. The largest k_{obs}, 0.235 min^{-1}, was obtained at pH 4. The reactivity of DCB with ozone decreased in the order $(C_{12}H_{10}C_{12}N_2)_2 > (C_{12}H_{10}C_{12}N_2)_2{\cdot}HCl > (C_{12}H_{10}C_{12}N_2)_2{\cdot}2HCl$. The experimental results confirmed that the degradation of DCB occurred via direct oxidation by ozone. The detoxification of DCB was achieved by conversion into ring-cleavage products and most aliphatic compounds could not be mineralised via direct oxidation by ozone under our experimental conditions.

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Appendix

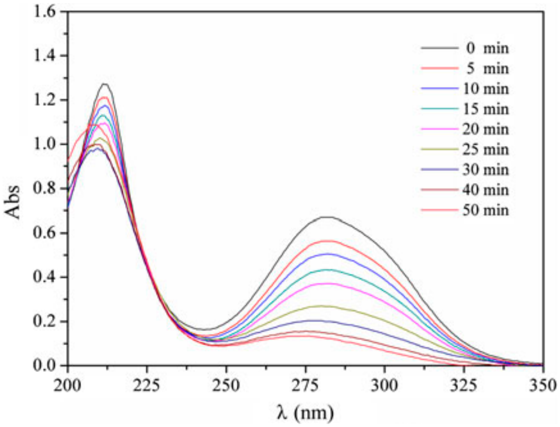
Original data of UV and HPLC spectra

UV spectra

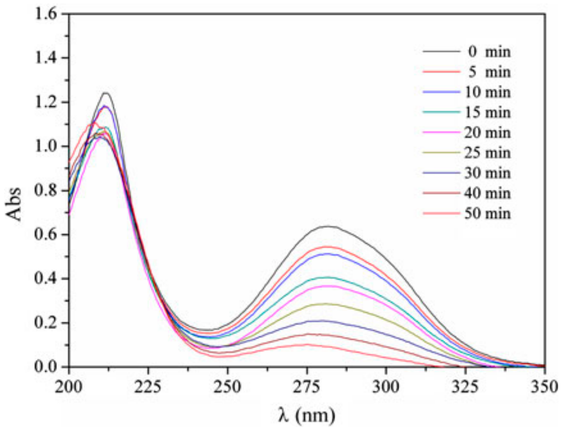
Measured at 285 nm

Effect of the pH on the degradation of DCB by ozonation (Q_O = 5.04 mg/min; C_0 = 6 mg/L; T = 20 ℃; solution volume = 1 L).

pH = 2.04



pH = 3.05



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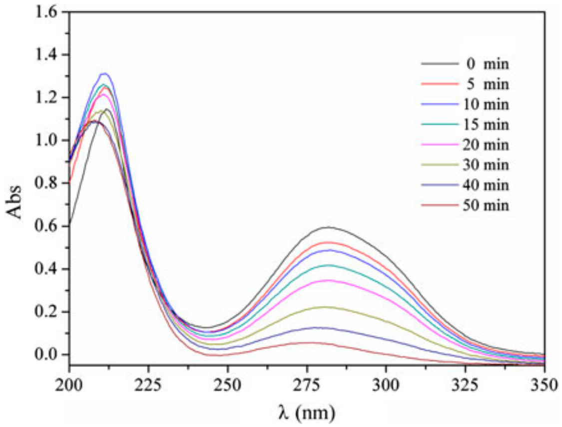
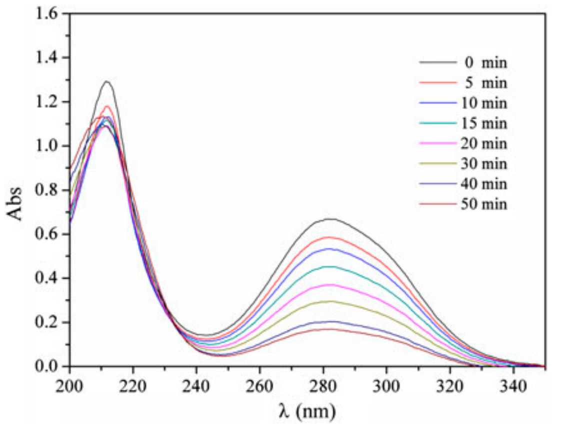
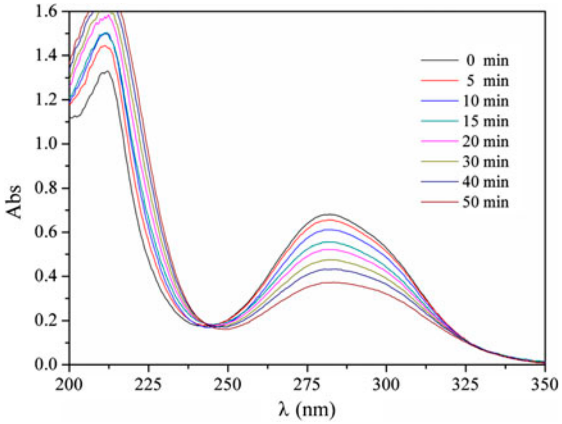


pH = 5.02

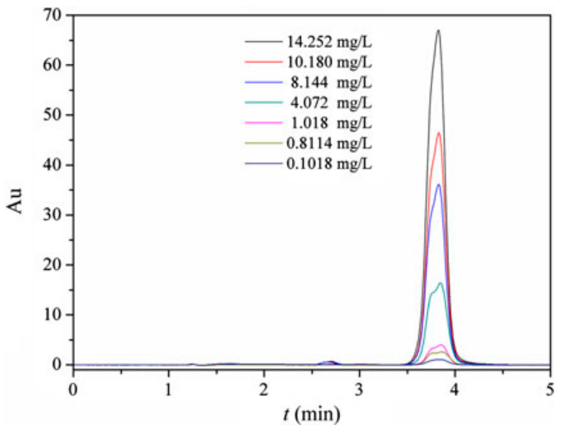


pH = 6.01



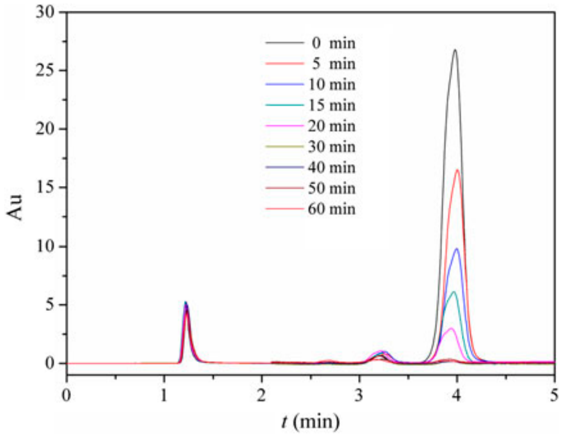
HPLC spectra

Measured at 285 nm
1. Standard curve of DCB

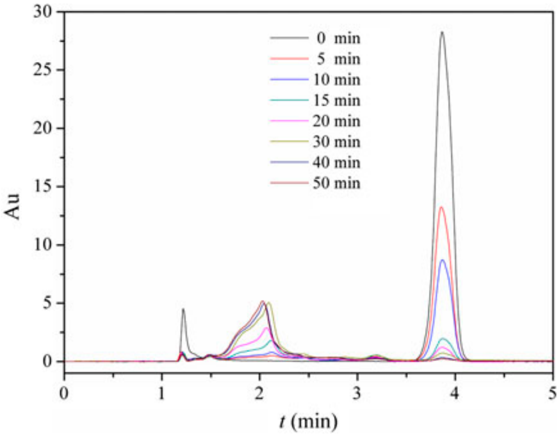


2. Effect of the pH on the degradation of DCB by ozonation (Q_{O3}= 5.04 mg/min; C_0 = 6 mg/L; T = 20 ℃; solution volume = 1 L).

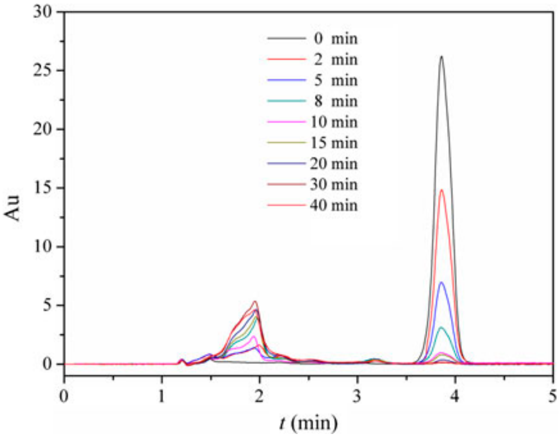
pH = 2.00



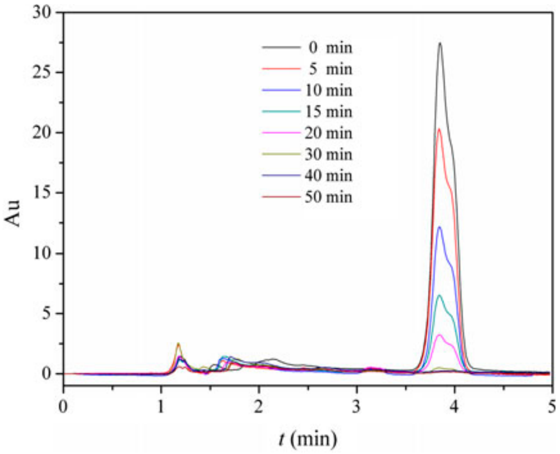
pH = 3.01



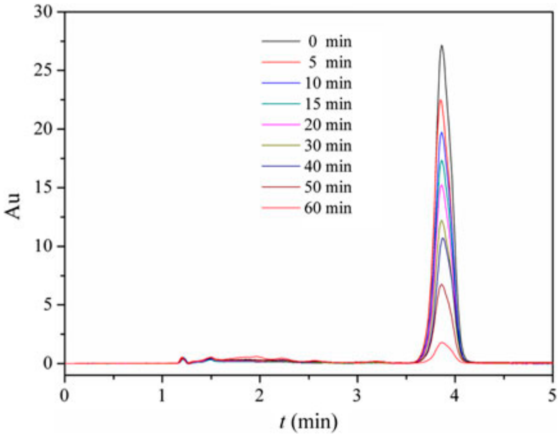
pH = 4.01



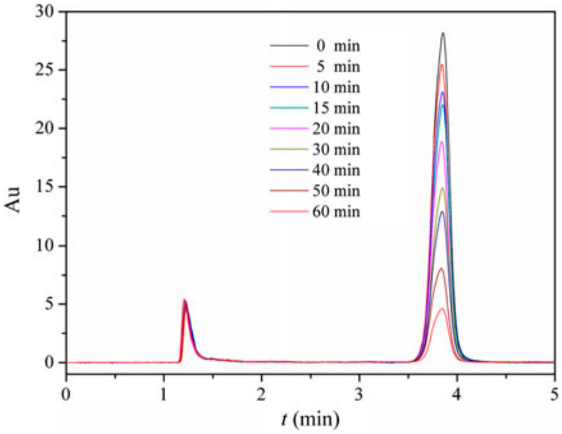
pH = 5.02



pH = 7.00

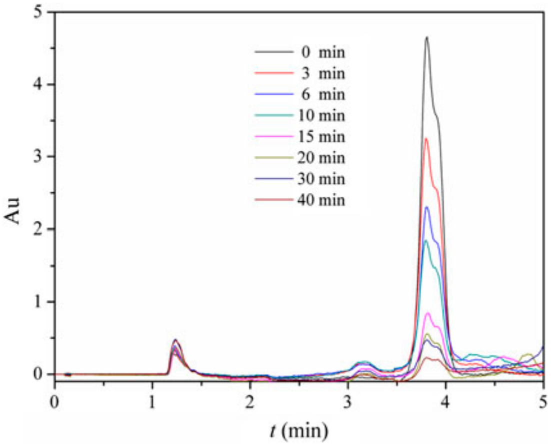


pH = 9.01

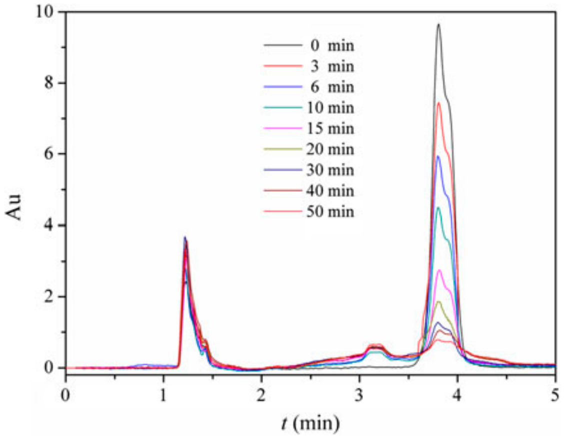


3. Effect of the initial concentration on the degradation of DCB (Q_O = 4.76 mg/min; pH = 4; T = 20 ℃; solution volume = 1.2 L).

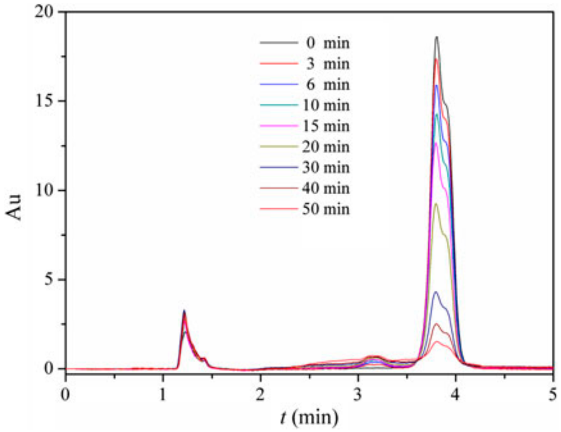
C_0 = 1.27 mg/L



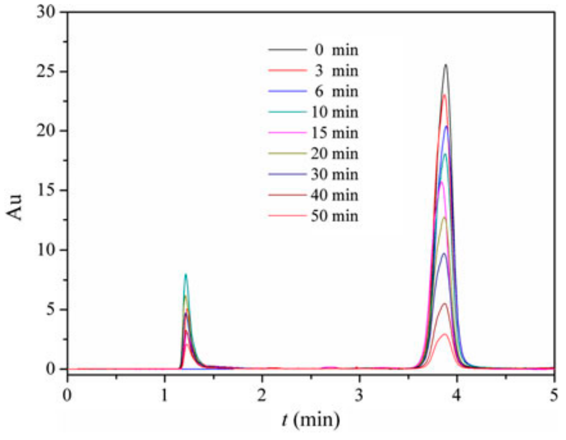
C_0 = 2.44 mg/L



C_0 = 4.05 mg/L

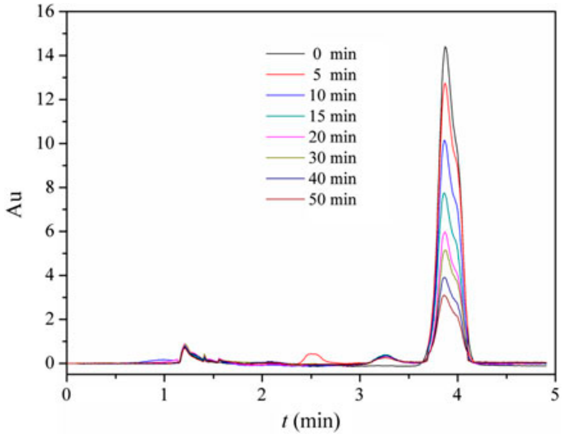


C_0 = 5.12 mg/L

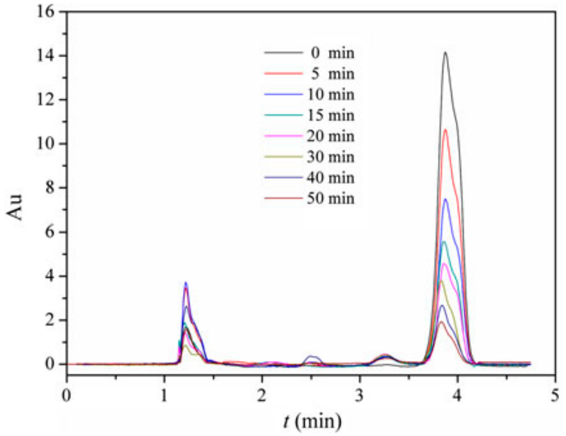


4. Effect of the ozone concentration on the degradation of DCB (pH = 4.00; C_0 = 4.1 mg/L; T = 20 ℃; solution volume = 1.2 L).

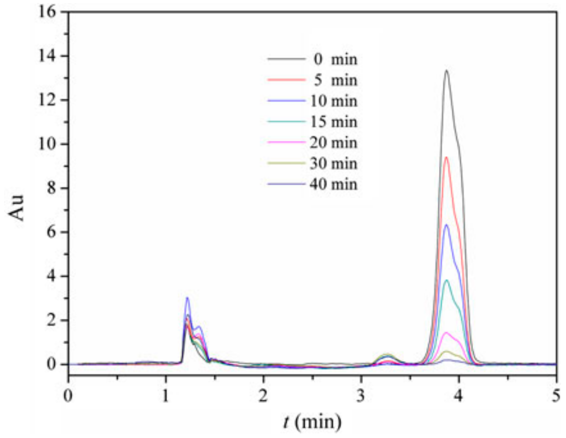
Q_{O3} = 4.33 mg/min



Q_{O3} = 4.76 mg/min

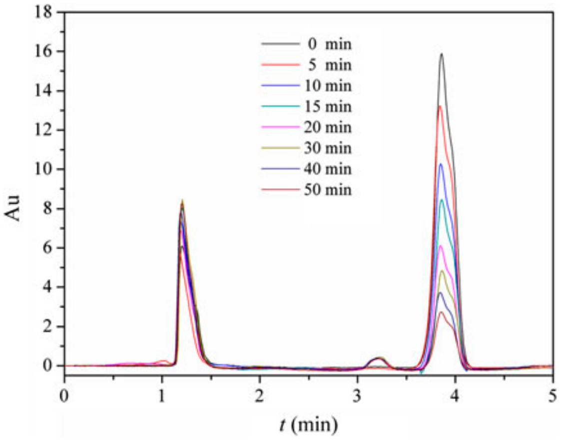


Q_{O3} = 5.04 mg/min

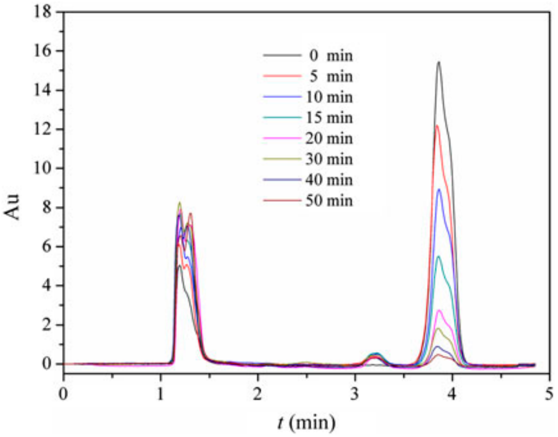


5. Effect of temperature on the degradation of DCB (Q_O = 4.76 mg/min; pH = 4.00; C_0 = 4.1 mg/L; solution volume = 1.2 L).

T = 17 ℃



T = 26 ℃



T = 30 ℃