

Kinetics of Chlorine Dioxide Oxidation of Benzidine in Wastewater

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Reaction kinetics of benzidine oxidation with ClO_2 in the wastewater were investigated systematically by detecting concentrations of benzidine with HPLC at regular intervals. The results showed that the reaction was first-order with respect to both ClO_2 and benzidine and the entire reaction was of second-order. Under condition of pH 6.5 and water temperature 298 K, the second-order reaction rate constant k was $5.721 \times 10^{-4} \text{ L (mmol s)}^{-1}$. The reaction activation energy was 51.1 kJ mol^{-1} , revealing that the reaction could take place under usual water treatment conditions. The rate constants increased with the reaction pH increasing, then decreased. Hydrazobenzene, azobenzene and *para*-benzoquinone were detected by GC-MS as intermediates of the free benzidine- ClO_2 reaction.

Key Words: Chlorine dioxide, Benzidine, Kinetics, Intermediates.

INTRODUCTION

Benzidine derivatives, is a kind of non-natural organic pollutant, could be generated from tannery wastewaters containing large amounts of dyes and pigments after illumination, heating or biological treatment. The compounds are highly toxic, carcinogenic, mutagenic, teratogenic, stable in water, almost non-biodegradable and irremovable with conventional water treatment technology, thus internationally recognized as priority pollutants¹. It is essential that benzidines in tannery wastewater are removed. Therefore, it is of importance to investigate how to better remove benzidines from wastewater to protect human health and the environment. There are only some preliminary research works of benzidine derivatives treatment technology by far and the reaction kinetics still remained unclear.

Chlorine dioxide (ClO_2) is a strong oxidant that exhibit good performance in both organic and inorganic pollutant removal. Furthermore, it hardly forms any harmful organic halide such as trihalomethanes (THMs) while reacting with organic compounds in water². Thus, ClO_2 is widely used in drinking water and industrial wastewater oxidation treatments. Chlorine dioxide oxidation method is currently accepted as the most prominent technology for water treatment. However, the reports about benzidine treatment with the method are limited. In this work, ClO_2 oxidation method was applied to clarify the oxidation kinetics of benzidine removal in water.

EXPERIMENTAL

Benzidine (AR), diluted from solution of benzidine dissolved in methanol with dichloromethane; chlorine dioxide, generated from $\text{NaClO}_2/\text{K}_2\text{S}_2\text{O}_8$ in 10 % H_2SO_4 . ClO_2 of above 99.8 % purity was degassed before resolved in cold water and restored in sealed brown bottle and dark place as stock solution. The ClO_2 solution was calibrated and serially diluted before use.

1100 Series HPLC (Agilent Co., USA); 6890-5973 GC-MS (Agilent Co., USA); HJ-6 heating magnetic stirrer (Hongkai Instrument Co., Jiangsu, China); ZD-2 potentiometric titrimeter (Shanghai Leici Analytical Instrument Co., Shanghai, China).

Methods: pH value and temperature of the system were kept constant during the reaction procedure. pH value was controlled by a pH-stat apparatus (consists of 3, 4 and 5 in Fig. 1). Briefly, pH sensor was used to adjust the added acid and base solution volume (diluted H_2SO_4 and NaOH solution) during reaction to maintain the pH value, heating system of the magnetic stirrer was used to control the temperature within $\pm 0.1 \text{ }^\circ\text{C}$.

The reaction was carried out in dark and constant temperature. pH values of ClO_2 solution, benzidine solution and $\text{Na}_2\text{S}_2\text{O}_3$ solution were adjusted with diluted H_2SO_4 (HCl will cause Cl^- contamination) before the experiments. Appropriate volume of ClO_2 was added to benzidine solution for oxidation reaction before turn-on the magnetic stirrer. 0.05 mol L^{-1} $\text{Na}_2\text{S}_2\text{O}_3$ was used as terminating reagent after reaction.

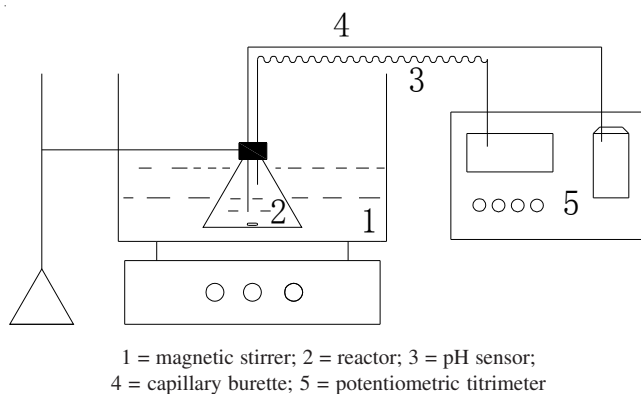


Fig. 1. Experimental equipment chat on benzidine oxidized by ClO_2

Analytical methods

Determination of ClO_2 concentration: Concentration of ClO_2 was determined by successive iodimetric technique³.

Benzidine determination with HPLC: The reacted solution was transferred to 100 mL separating funnel, extracted by 5 mL dichloromethane for three times. The extract was dehydrated and concentrated before filtrated with 0.45 μm filter membrane. A mini-injector was served for sampling and the concentration of the residual benzidine was determined by means of HPLC. HPLC parameters: methanol:water (85:15 v/v); Hypersil ODS column, 250 mm long, 4.6 mm diameter; flow rate: 1.0 mL min^{-1} ; sample volume: 5 μL ; column pressure: 5.00 MPa; G1314A ultraviolet detector wavelength: 254 nm.

Reaction intermediates identification with GC-MS: The reacted solution after colour interferences removal was transferred to 100 mL separating funnel, extracted by 5 mL dichloromethane for three times. The extract was dehydrated and concentrated to 1 mL, then subjected to GC-MS determination. GC-MS parameters: GC silica capillary column (30 m \times 0.25 mm \times 0.25 μm); temperature program: 323 K (3 min) \rightarrow 5 K min^{-1} \rightarrow 473 K (2 min) \rightarrow 10 K min^{-1} \rightarrow 553 K (5 min); carrier gas: high purity helium; MS electron ionization (EI): 70 eV; scanning range: 35-400; detector voltage: 220 V.

RESULTS AND DISCUSSION

Kinetics of the reaction between ClO_2 and benzidine

Reaction order of benzidine: With benzidine (BD) initial concentration ($[\text{BD}]_0$) of 0.25 mmol L^{-1} , 298 K and pH 6.5, plot of $-\ln(C_t/C_0)$ (C_t - the concentration of benzidine at the time t , C_0 - the initial concentration of benzidine) vs. t (time) was obtained and shown in Fig. 2. A good linearity was obtained between $-\ln(C_t/C_0)$ and t , illustrating that the reaction was the first-order with respect to benzidine.

Reaction order of ClO_2 : The slope in Fig. 2 was the apparent rate constant k' of the reaction. A linear equation of $y = -3.3457 + 0.9788x$ ($R = 0.9788$) was obtained between $\ln k'$ and $\ln[\text{ClO}_2]_0$ as shown in Fig. 3 and the slope was the order of ClO_2 in the reaction, namely, approximate first order.

Determination of the second order reaction rate constant k : Based on the above experimental results, oxidation reaction of benzidine with ClO_2 could be characterized as follows:

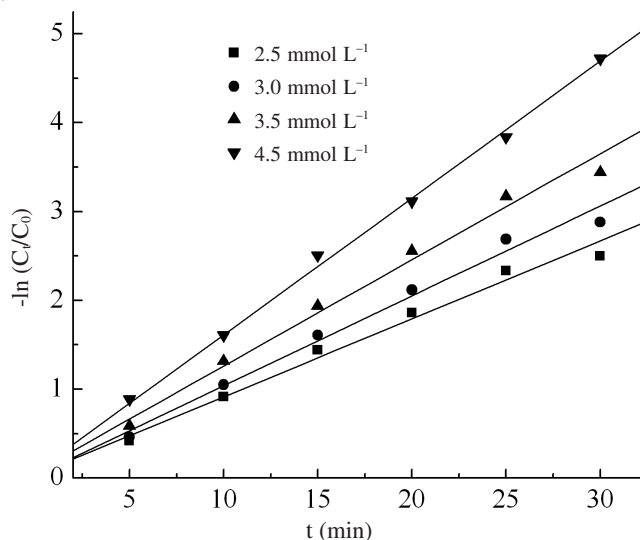


Fig. 2. Relation between $-\ln(C_t/C_0)$ and time 298 K; pH: 6.5; $[\text{BD}]_0 = 0.25 \text{ mmol L}^{-1}$; $[\text{ClO}_2]_0 = 2.5 \text{ mmol L}^{-1}$ (■), 3.0 mmol L^{-1} (●), 3.5 mmol L^{-1} (▲), 4.5 mmol L^{-1} (▼)

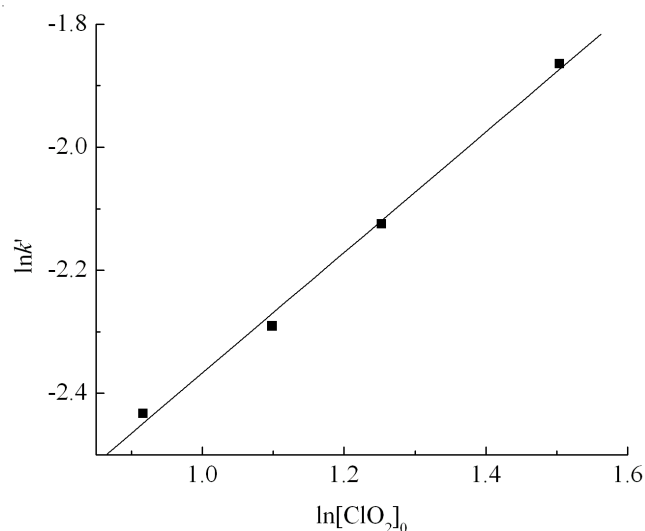


Fig. 3. Relation between $\ln k'$ and $\ln[\text{ClO}_2]_0$

$$-\frac{d[\text{BD}]}{dt} = k[\text{BD}][\text{ClO}_2] \quad (\text{where BD is benzidine}) \quad (1)$$

With respect to the initial condition, $t = 0$, $[\text{BD}] = [\text{BD}]_0$, it can be integrated as:

$$\ln \frac{[\text{BD}]_0}{[\text{BD}]} = k \int_0^t [\text{ClO}_2] dt \quad (2)$$

$[\text{ClO}_2]_0 \gg [\text{BD}]_0$, so the ClO_2 concentration could be treat as a constant, i.e.:

$$\ln \frac{[\text{BD}]_0}{[\text{BD}]} = k[\text{ClO}_2]t \quad (3)$$

$$k = k' / [\text{ClO}_2]_0 \quad (4)$$

where k' is apparent rate constant, k is second order reaction rate constant.

Under condition of 298 K and pH 6.5, second order rate constant k of reaction was calculated as an average value of $5.721 \times 10^{-4} \text{ L (mmol s)}^{-1}$ from eqn. 4.

Effect of temperature on reaction rate constant: Under condition of $[\text{BD}]_0 = 0.25 \text{ mmol L}^{-1}$, $[\text{ClO}_2]_0 = 2.5 \text{ mmol L}^{-1}$ and pH 6.5, second order reaction rate constants k were 2.833×10^{-4} , 3.883×10^{-4} , 5.850×10^{-4} and $7.817 \times 10^{-4} \text{ L (mmol s)}^{-1}$ with water temperature $T = 288, 293, 298$ and 303 K , respectively. As shown in Fig. 4, a linear equation of $\ln k = 17.245 - 6146.6 (1/T)$ ($R^2 = 0.9902$) was obtained, which means the relation between reaction rate constant k and absolute temperature is in good accordance with Arrhenius empirical equation. The slope of the equation is $-E_a/R$ and intercept is $\ln A$. The reaction activation energy was calculated as $E_a = 51102.8 \text{ J mol}^{-1} \approx 51.1 \text{ kJ mol}^{-1}$, $A = 5.143 \times 10^5 \text{ L (mmol s)}^{-1}$. Apparently, ClO_2 oxidation of benzidine could proceed under common water treatment conditions.

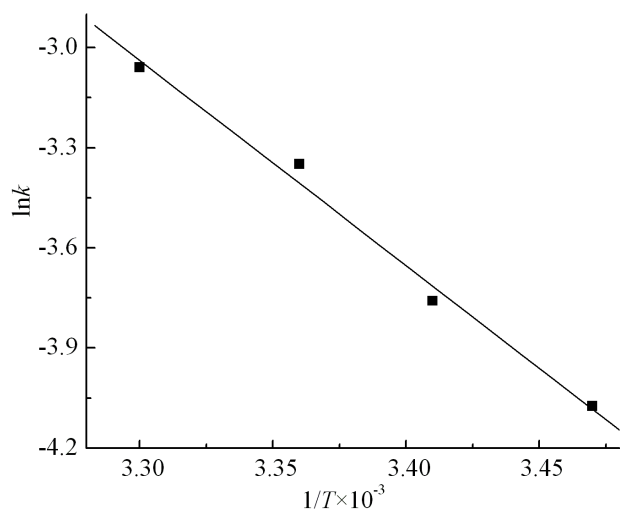


Fig. 4. Relation between rate constant and temperature. pH: 6.5; $[\text{BD}]_0 = 0.25 \text{ mmol L}^{-1}$; $[\text{ClO}_2]_0 = 2.5 \text{ mmol L}^{-1}$; Temp. 288 K, 293 K, 298 K, 303 K

Effect of pH value on reaction rate constant: The solution pH changes not only the oxidation potential of ClO_2 , but also presence state of benzidine in water as well. Thus, pH is a key factor affecting reaction rate. Under condition of $[\text{BD}]_0 = 0.25 \text{ mmol L}^{-1}$, $[\text{ClO}_2]_0 = 2.5 \text{ mmol L}^{-1}$ and 298 K, second order reaction rate constants k were 1.383×10^{-4} , 3.667×10^{-4} , 5.850×10^{-4} , 5.167×10^{-4} and $3.283 \times 10^{-4} \text{ L (mmol s)}^{-1}$ with pH value of 3.0, 4.66, 6.5, 8.0 and 9.5, respectively.

As shown in Fig. 5, second order reaction rate constant k was increased with the increase of pH value to pH 9.5 and then decreased down. The reaction rate constant k was affected by oxidation potential of ClO_2 as well as presence state of benzidine. The oxidation potential of ClO_2 was the predominant factor affecting the reaction rate constant k while presence state of benzidine remained unchanged. With pH value higher than 9, oxidation potential was decreased due to disproportionation reaction of ClO_2^4 .

Reaction intermediates identification of ClO_2 oxidation of benzidine: The colourless benzidine solution turned to light red gradually, then pale yellow slowly and almost colourless finally during the oxidation reaction at pH 6.5, which meant a series coloured intermediates generated during the oxidation reaction^{5,6}.

Since it was found that the reaction proceeded quickly and finished in about 60 min, some sampling time, such as

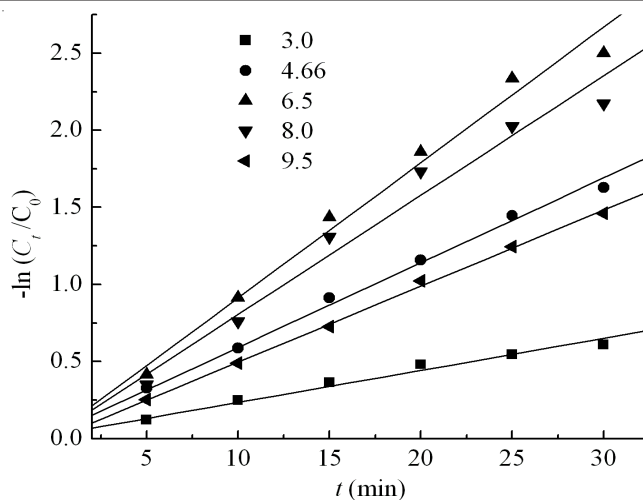


Fig. 5. Relation between $-\ln(C_t/C_0)$ and time under different reaction pH; 298K; $[\text{BD}]_0 = 0.25 \text{ mmol L}^{-1}$; $[\text{ClO}_2]_0 = 2.5 \text{ mmol L}^{-1}$; pH = 3.0 (■), 4.66 (●), 6.5 (▲), 8.0 (▼), 9.5 (◄)

0, 5, 18 and 60 min, were chosen to reveal the intermediates. Typical GC patterns of the reaction solution intermediates at different time, containing the residual benzidine and products formed, are provided as Fig. 6(a) to (d), respectively, where compounds related to the starting pollutant show retention time in the range from 6.27 to 21.98 min. Prior to the commencement of oxidation, the first GC chromatogram of the benzidine solution was collected [Fig. 6(a)]. This shows a clear trace at the retention time of 21.21 min. After reacted with ClO_2 for 5 min [Fig. 6(b)], the GC analysis revealed that the concentration of benzidine in the solution decreased dramatically and two new peaks appeared with retention time at 9.14 and 12.45 min, respectively. At 18 min of the reaction proceeded [Fig. 6(c)], The peak of the benzidine further decreased and the peak of the product at 9.14 min increased with the decrease at 12.45 min. At the termination of the procedure, 60 min, the peak of benzidine decreased continuously with time, while another new strong peak appeared with retention time at 6.42 min, but there were no other peaks that appeared [Fig. 6(d)].

It is evident that there are three intermediates mainly formed during the reaction and they were identified by EI mass spectra through above 95 % match with the NIST 02L MS library. The results reveals that the three intermediates are hydrazobenzene, azobenzene and *para*-benzoquinone. Furthermore, the identification of the products were established from a comparison of the GC-MS data with that of an authentic sample.

Conclusion

The reaction between ClO_2 and benzidine was first-order with respect to both ClO_2 and benzidine and the entire reaction was of second-order. Under condition of pH 6.5 and 298 K, the second-order reaction rate constant k was $5.721 \times 10^{-4} \text{ L (mmol s)}^{-1}$. The rate constant k had the same change with the reaction temperature. The reaction activation energy was 51.1 kJ mol^{-1} , revealing that the reaction could take place under usual water treatment conditions. The rate constant k increased with the reaction pH increasing, then decreased. Sequences

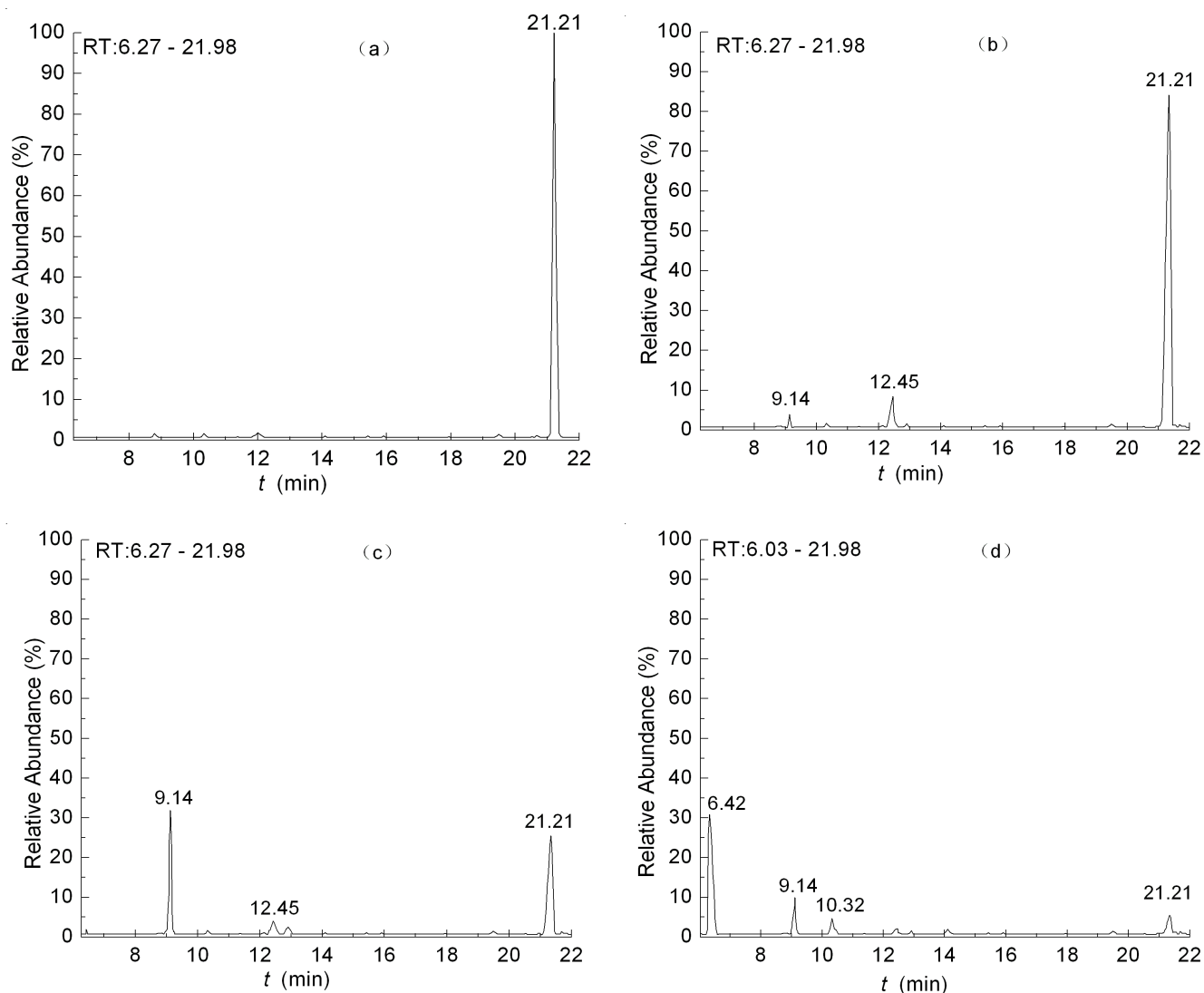


Fig. 6. Ion current chromatogram of benzidine reacted with ClO_2 under different time at pH 6.5; Reaction time: (a) 0 min; (b) 5 min; (c) 18 min; (d) 60 min

of the main intermediates of the free benzidine- ClO_2 reaction were hydrazobenzene, azobenzene and *para*-benzoquinone by GC-MS technique.

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