

# Kinetics of Chlorine Dioxide Oxidation of Benzidine in Tannery Wastewater

*Xiangyu Cao*<sup>–</sup>

School of Light Industry and Textile, Qiqihar University, Qiqihar 161006, Heilongjiang, P. R. China

**Abstract:** Reaction kinetics of benzidine oxidation with  $\text{ClO}_2$  in the wastewater was investigated systematically by detecting concentrations of benzidine with HPLC at regular intervals. The results show that the reaction was first-order with respect to both  $\text{ClO}_2$  and benzidine, and the entire reaction was of second-order. Under condition of pH 6.5 and water temperature 298K, the second-order reaction rate constant  $k$  was  $5.721 \times 10^{-4} \text{L}/(\text{mmol} \cdot \text{s})$ . The reaction activation energy was  $51.1 \text{kJ} \cdot \text{mol}^{-1}$ , revealing that the reaction could take place under usual water treatment conditions. The rate constants first increased with the increasing reaction pH value, and then decreased. Diphenoquinonediimine, diphenoquinonediimine and diphenoquinone were detected by GC-MS as intermediates of the protonated benzidine- $\text{ClO}_2$  reaction, however, hydrazobenzene, azobenzene and para-benzoquinone as intermediates of the free benzidine- $\text{ClO}_2$  reaction. The end product of the free and proton state benzidine oxidized by  $\text{ClO}_2$  was unsaturated organic diacid. The two possible pathways for the benzidine- $\text{ClO}_2$  reaction were proposed based on the mechanism of the single electron transfer (SET).

**Key words:** chlorine dioxide; benzidine; kinetics; reaction pathway

## 1 Introduction

Benzidine derivatives, as 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 pollutants.<sup>1</sup> There are only some preliminary research works of benzidine derivatives treatment technology by far, and the reaction kinetics still remained unclear.

$\text{ClO}_2$  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 water.<sup>2</sup> Thus,  $\text{ClO}_2$  is widely used in drinking water and industrial wastewater oxidation treatments.  $\text{ClO}_2$  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,  $\text{ClO}_2$  oxidation method was applied to clarify the oxidation kinetics of benzidine removal in water, providing theoretical principles for further application of  $\text{ClO}_2$  oxidation method to toxic organic pollutant removal.

## 2 Experimental

### 2.1 Reagents and Apparatus

#### 2.1.1 Main reagents

Benzidine, A R, diluted from solution of benzidine dissolved in methanol with dichloromethane;  $\text{ClO}_2$ , generated from  $\text{NaClO}_2/\text{K}_2\text{S}_2\text{O}_8$  in 10%  $\text{H}_2\text{SO}_4$ .  $\text{ClO}_2$  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  $\text{ClO}_2$  solution was calibrated and serially diluted before use.

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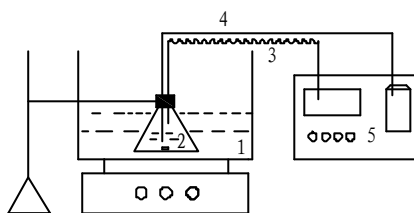
<sup>–</sup> Corresponding author. E-mail: cxy0720@126.com

### 2.1.2 Apparatus

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 titrimer (Shanghai Leici Analytical Instrument Co., Shanghai, China).

### 2.2 Research 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  $\text{H}_2\text{SO}_4$  and NaOH solution) during reaction to maintain the pH value, heating system of the magnetic stirrer was used to control the temperature within  $\pm 0.1^\circ\text{C}$ .



1-magnetic stirrer; 2-reactor; 3-pH sensor; 4-capillary burette; 5-potentiometric titrimer

**Fig. 1 Experimental equipment chat on benzidine oxidized by  $\text{ClO}_2$**

The reaction was carried out in dark and constant temperature. PH values of  $\text{ClO}_2$  solution, benzidine solution and  $\text{Na}_2\text{S}_2\text{O}_3$  solution were adjusted with diluted  $\text{H}_2\text{SO}_4$  (HCl will cause  $\text{Cl}^-$  contamination) before the experiments. Appropriate volume of  $\text{ClO}_2$  was added to benzidine solution for oxidation reaction before turn-on the magnetic stirrer.  $0.05 \text{ mol}\cdot\text{L}^{-1}$   $\text{Na}_2\text{S}_2\text{O}_3$  was used as terminating reagent after reaction.

### 2.3 Analytical Methods

#### 2.3.1 Determination of $\text{ClO}_2$ concentration

Concentration of  $\text{ClO}_2$  was determined by the successive iodimetric technique<sup>3</sup>.

#### 2.3.2 Benzidine determination with HPLC

The reacted solution was transferred to 100mL separating funnel, extracted by 5mL dichloromethane for three times. The extract was dehydrated and concentrated before filtrated with  $0.45\mu\text{m}$  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 (85:15v/v); Hypersil ODS column, 250mm long, 4.6 mm diameter; flow rate:  $1.0 \text{ mL}\cdot\text{min}^{-1}$ ; sample volume:  $5\mu\text{L}$ ; column pressure: 5.00MPa; G1314A ultraviolet detector wavelength: 254 nm.

#### 2.3.3 Reaction intermediates identification with GC-MS

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

## 3 Results and discussions

### 3.1 Kinetics of the reaction between $\text{ClO}_2$ and benzidine

### 3.1.1 Reaction order of benzidine

With benzidine initial concentration of  $0.25 \text{ mmol} \cdot \text{L}^{-1}$ , 298K 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.

### 3.1.2 Reaction order of $\text{ClO}_2$

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  $\text{ClO}_2$  in the reaction, namely, approximate first order.

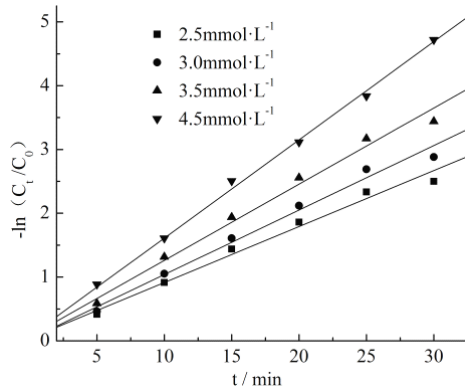


Fig. 2 Relation between  $-\ln(C_t/C_0)$  and time

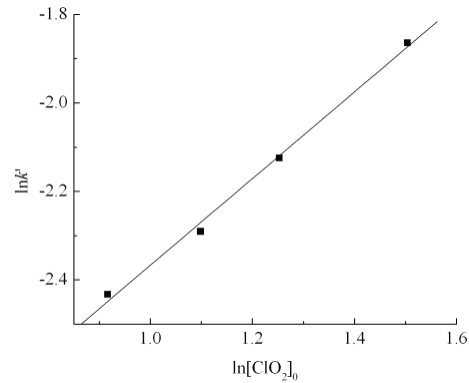


Fig. 3 Relation between  $\ln k'$  and  $\ln[\text{ClO}_2]_0$

### 3.1.3 Determination of the second order reaction rate constant $k$

Based on the above experimental results, oxidation reaction of benzidine with  $\text{ClO}_2$  could be characterized as follows:

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

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  $\text{ClO}_2$  concentration could be treat as a constant, i.e.:

$$\ln \frac{[\text{BD}]_0}{[\text{BD}]} = k'[\text{ClO}_2]t \quad (3) \quad k = k' / [\text{ClO}_2]_0 \quad (4)$$

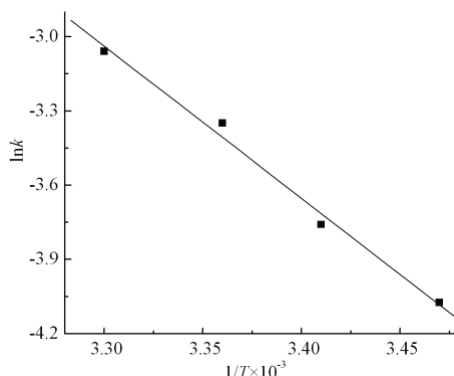
Where  $k'$  is apparent rate constant,  $k$  is second order reaction rate constant.

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

### 3.2 Effect of temperature on reaction rate constant

Under condition of  $[\text{BD}]_0 = 0.25 \text{ mmol} \cdot \text{L}^{-1}$ ,  $[\text{ClO}_2]_0 = 2.5 \text{ mmol} \cdot \text{L}^{-1}$  and pH 6.86, second order reaction rate constants  $k$  were  $2.833 \times 10^{-4}$ ,  $3.883 \times 10^{-4}$ ,  $5.850 \times 10^{-4}$  and  $7.817 \times 10^{-4} \text{ L}/(\text{mmol} \cdot \text{s})$  with water temperature  $T = 288, 293, 298$  and  $303\text{K}$ , 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  $E_a=51102.8\text{J}\cdot\text{mol}^{-1}\approx 51.1\text{kJ}\cdot\text{mol}^{-1}$ ,  $A=5.143\times 10^5\text{ L}/(\text{mmol}\cdot\text{s})$ . Apparently,  $\text{ClO}_2$  oxidation of benzidine could proceed under common water treatment conditions.



**Fig. 4 Relation between rate constant and temperature**

### **3.3 Effect of pH value on reaction rate constant**

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

### **3.4 Reaction Mechanism of $\text{ClO}_2$ Oxidation of Benzidine**

According to the two-step dissociation equilibrium of benzidine, the presence state of benzidine would change with the variation of pH value in solution. Based on calculation, benzidine presents as proton state and free state at the pH value of 2.0 and 6.5 respectively. Therefore, solution pH values of 2.0 and 6.5 were investigated to study the oxidation of proton state and free state benzidine with  $\text{ClO}_2$ . Intermediates were identified by GC-MS technique to illustrate the possible mechanism of the reaction.

#### **3.4.1 Reaction intermediates identification of $\text{ClO}_2$ oxidation of benzidine**

The colorless benzidine solution turned to yellow-green immediately after addition of  $\text{ClO}_2$ , then gradually pale yellow and brown-yellow, finally colorless at pH 2.0 and turned to light red gradually, then pale yellow slowly and almost colorless finally during the oxidation reaction at pH 6.5, which meant a series colored intermediates generated during the oxidation reaction.<sup>5, 6</sup> The GC-MS results showed that the sequences of the main intermediates of the protonated benzidine- $\text{ClO}_2$  reaction were diphenoquinone diimine, diphenoquinone dioxime and diphenoquinone, however the sequence of the main intermediates of the free benzidine- $\text{ClO}_2$  reaction were hydrazobenzene, azobenzene and para-benzoquinone.

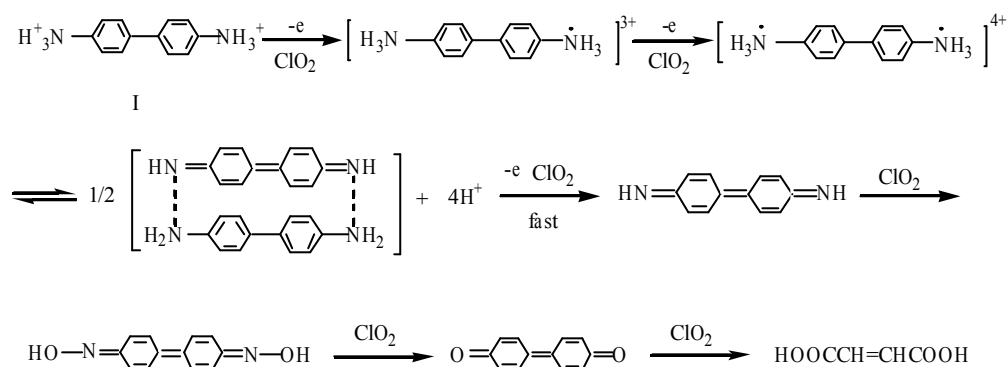
#### **3.4.2 Discussions of possible reaction mechanism**

Based on the above-mentioned GC-MS results,  $\text{ClO}_2$  oxidation characteristics and benzidine presence state, possible mechanism of  $\text{ClO}_2$  oxidation of benzidine was proposed.

##### **3.4.2.1 Reaction mechanism of $\text{ClO}_2$ oxidation of proton state benzidine**

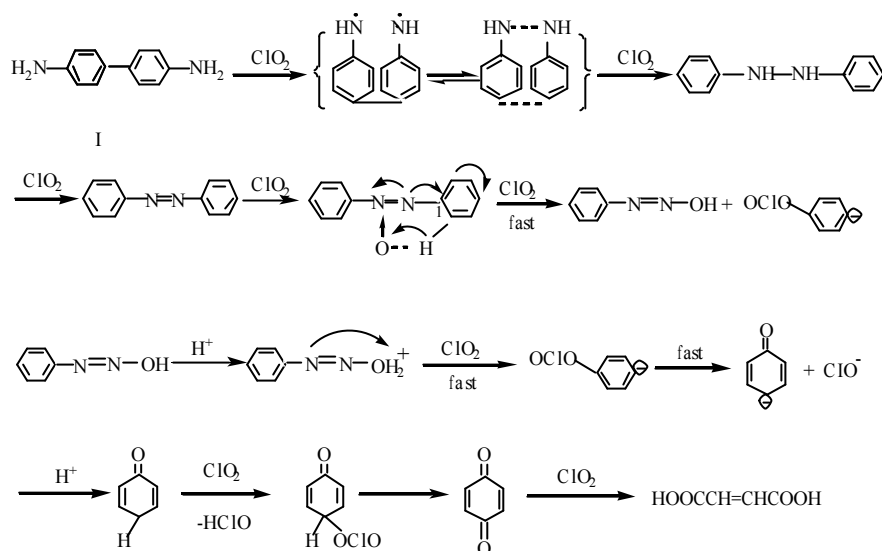
As shown in Fig.5, during the oxidation of proton state benzidine (I),  $\text{ClO}_2$  attacks benzidine via the abstraction of one electron from proton state benzidine, and then two electrons transfer occurs, leading to

the formation of benzidine cation-radicals (II) and (III). Benzidine cation-radicals react further to generate blue-green electron transfer complex (IV), and then immediately yellow diphenoquinone diimine(V). Diphenoquinone diimine is an unstable compound which prone to form diphenoquinone dioxime. Diphenoquinone dioxime would turn to diphenoquinone (strip HOCl and NO) in the presence of strong oxidant  $\text{ClO}_2$ , and finally be oxidized to unsaturated diacid.



**Fig. 5 Proposed pathway of the protonated benzidine- $\text{ClO}_2$  reaction**

### 3.4.2.2 Reaction mechanism of $\text{ClO}_2$ oxidation of free state benzidine



**Fig. 6 Proposed pathway of the free benzidine- $\text{ClO}_2$  reaction**

With benzidine (**I**) under the action of  $\text{ClO}_2$ , the  $\alpha$ -hydrogen atoms of N were shed, and it changes to diphenylhydrazine (**II**) after re-arrangement. The lone pair electrons of N atoms and the p-p conjugation of benzene ring allowed  $\alpha$ -hydrogen atoms of the N of diphenylhydrazine to be captured by oxygen of  $\text{ClO}_2$  to produce azobenzene (**III**). In this case, a conjugated system became broader and the system energy was reduced. As the reaction proceeded the lone pair electrons of the N atoms of azo group were easily attached by the oxygen of  $\text{ClO}_2$ , which resulted in transfer of the electron cloud density of azobenzene to the two benzene rings. The electrons of oxygen attracted the ortho-hydrogen of azo group.

Meanwhile, owing to reducing the electron cloud density of the 1' position on the benzene ring, leads to attack by  $\text{ClO}_2$  as nucleophilic reagent (seen in **IV**). After the process of reaction shown in Figure 6, benzoquinone (**V**) was produced. Benzoquinone could be further degraded by sufficient  $\text{ClO}_2$  to produce an organic acid (**VI**).

From the reaction mechanisms illustrated in Fig.5 and 6, whether for proton state or free state benzidine oxidation, the first step is the electron abstraction of N atom in amino group by  $\text{ClO}_2$ , which subject to single electron transfer mechanism.<sup>7,8</sup>

#### 4 Conclusions

The reaction between  $\text{ClO}_2$  and benzidine was first-order with respect to both  $\text{ClO}_2$  and benzidine, and the entire reaction was of second-order. Under condition of pH6.5 and 298K, the second-order reaction rate constant  $k$  was  $5.721 \times 10^{-4} \text{ L}/(\text{mmol} \cdot \text{s})$ . The rate constant  $k$  had the same change with the reaction temperature. The reaction activation energy was  $51.1 \text{ kJ} \cdot \text{mol}^{-1}$ , revealing that the reaction could take place under usual water treatment conditions. The rate constant  $k$  increased with the increasing reaction pH value, and then decreased. Sequences of the main intermediates of the protonated benzidine- $\text{ClO}_2$  reaction were diphenoquinone diimine, diphenoquinone dioxime and diphenoquinone, however the intermediates of the free benzidine- $\text{ClO}_2$  reaction were hydrazobenzene, azobenzene and para-benzoquinone by GC-MS technique. Based on the GC-MS results,  $\text{ClO}_2$  oxidation characteristics and benzidine presence state, the two possible pathways for the benzidine- $\text{ClO}_2$  reaction was proposed based on the mechanism of the single electron transfer (SET).

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