Kinetics of Chlorine Dioxide Oxidation of Benzidine in Tannery Wastewater

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Abstract: Reaction kinetics of benzidine oxidation with ClO₂ 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 ClO₂ 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 5.721×10⁻⁴L/(mmol·s). The reaction activation energy was 51.1kJ·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, diphenoquinonedioxime and diphenoquinone were detected by GC-MS as intermediates of the protonated benzidine-ClO₂ reaction, however, hydrazobenzene, azobenzene and para-benzoquinone as intermediates of the free benzidine-ClO₂ reaction. The end product of the free and proton state benzidine oxidized by ClO₂ was unsaturated organic diacid. The two possible pathways for the benzidine-ClO₂ 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.¹ There are only some preliminary research works of benzidine derivatives treatment technology by far, and the reaction kinetics still remained unclear.

ClO₂ 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.² Thus, ClO₂ is widely used in drinking water and industrial wastewater oxidation treatments. ClO₂ 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, ClO₂ oxidation method was applied to clarify the oxidation kinetics of benzidine removal in water, providing theoretical principles for further application of ClO₂ 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; ClO₂, generated from NaClO₂/K₂S₂O₈ in 10% H₂SO₄. ClO₂ 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 ClO₂ solution was calibrated and serially diluted before use.

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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 Leci 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 H$_2$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 ±0.1°C.

![Experimental equipment that on benzidine oxidized by ClO$_2$](image)

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

Fig. 1 Experimental equipment that on benzidine oxidized by ClO$_2$

The reaction was carried out in dark and constant temperature. PH values of ClO$_2$ solution, benzidine solution and Na$_2$S$_2$O$_3$ solution were adjusted with diluted H$_2$SO$_4$ (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$^{-1}$ Na$_2$S$_2$O$_3$ was used as terminating reagent after reaction.

2.3 Analytical Methods

2.3.1 Determination of ClO$_2$ concentration

Concentration of ClO$_2$ was determined by the successive iodimetric technique$^3$.

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 0.45μm 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 mL·min$^{-1}$; sample volume: 5μL; 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 m×0.25 mm×0.25μm); temperature program: 323K (3min)→5K·min$^{-1}$→473K(2min)→10K·min$^{-1}$→553K (5min); 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 ClO$_2$ and benzidine
3.1.1 Reaction order of benzidine

With benzidine initial concentration of 0.25 mmol·L⁻¹, 298K and pH 6.5, plot of −ln(C/Co) (Cᵣ the concentration of benzidine at the time t, Co the initial concentration of benzidine) vs t (time) was obtained and shown in Fig. 2. A good linearity was obtained between -ln(Cᵣ/Co) and t, illustrating that the reaction was the first-order with respect to benzidine.

3.1.2 Reaction order of ClO₂

The slope in Fig. 2 was the apparent rate constant k' of the reaction. A linear equation of k' = 3.3457+0.9788·x (R=0.9788) was obtained between ln k' and ln[ClO₂]₀ as shown in Fig. 3, and the slope was the order of ClO₂ in the reaction, namely, approximate first order.

![Fig. 2 Relation between -ln(C/Co) and time](image1)

![Fig. 3 Relation between lnk' and ln[ClO₂]₀](image2)

3.1.3 Determination of the second order reaction rate constant k

Based on the above experimental results, oxidation reaction of benzidine with ClO₂ could be characterized as follows:

\[-\frac{d[BD]}{dt} = k'[BD][ClO₂] \quad \text{(where BD is benzidine)} \tag{1}\]

With respect to the initial condition, t=0, [BD] = [BD]₀, it can be integrated as:

\[\ln \frac{[BD]₀}{[BD]} = k' \int_0^t [ClO₂]dt \tag{2}\]

[ClO₂]₀ ≫ [BD]₀, so the ClO₂ concentration could be treat as a constant, i.e.:

\[\ln \frac{[BD]₀}{[BD]} = k'[ClO₂]t \tag{3}\]

\[k = k'[ClO₂]₀ \tag{4}\]

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 5.721×10⁻⁴ L/(mmol·s) from equation (4).

3.2 Effect of temperature on reaction rate constant

Under condition of [BD]₀ = 0.25 mmol·L⁻¹, [ClO₂]₀ = 2.5 mmol·L⁻¹ and pH 6.86, second order reaction rate constants k were 2.833×10⁻⁴, 3.883×10⁻⁴, 5.850×10⁻⁴ and 7.817×10⁻⁴ L/(mmol·s) with water temperature T = 288, 293, 298 and 303K, respectively. As shown in Fig. 4, a linear equation of lnk = 17.245-6146.6(1/T) (R²=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 In$A$. The reaction activation energy was calculated as $E_a=51102.8\, \text{J/mol}^{-1}\approx51.1\, \text{kJ/mol}^{-1}$, $A=5.143\times10^5\, \text{L/(mmol-s)}$. Apparently, ClO$_2$ oxidation of benidine could proceed under common water treatment conditions.

3.3 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 benidine 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 298K, second order reaction rate constants $k$ were $1.383\times10^4$, $3.667\times10^4$, $5.850\times10^4$, $5.167\times10^4$ and $3.283\times10^4\, \text{L/(mmol-s)}$ 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 ClO$_2$ as well as presence state of benidine. The oxidation potential of ClO$_2$ was the predominant factor affecting the reaction rate constant $k$ while presence state of benidine remained unchanged. With pH value higher than 9, oxidation potential was decreased due to disproportionation reaction of ClO$_2$.\(^4\)

3.4 Reaction Mechanism of ClO$_2$ Oxidation of Benidine

According to the two-step dissociation equilibrium of benidine, the presence state of benidine would change with the variation of pH value in solution. Based on calculation, benidine 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 benidine with ClO$_2$. Intermediates were identified by GC-MS technique to illustrate the possible mechanism of the reaction.

3.4.1 Reaction intermediates identification of ClO$_2$ oxidation of benidine

The colorless benidine solution turned to yellow-green immediately after addition of 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.\(^5,\,6\) The GC-MS results showed that the sequences of the main intermediates of the protonated benidine-ClO$_2$ reaction were diphenoquinone diimine, diphenoquinone dioxime and diphenoquinone, however the sequence of the main intermediates of the free benidine-ClO$_2$ reaction were hydrazobenzen, azobenzene and para-benzoquinone.

3.4.2 Discussions of possible reaction mechanism

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

3.4.2.1 Reaction mechanism of ClO$_2$ oxidation of proton state benidine

As shown in Fig.5, during the oxidation of proton state benidine (I), ClO$_2$ attacks benidine via the abstraction of one electron from proton state benidine, 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 dioxidime. Diphenoquinone dioxidime would turn to diphenoquinone (strip HOCl and NO) in the presence of strong oxidant ClO_2 and finally be oxidized to unsaturated diacid.

\[
\begin{align*}
H^+_3N &\rightarrow \text{H}_2N\text{−NH}_3^+ &\xrightarrow{\text{ClO}_2} &\text{H}_3N \rightarrow \text{H}^+\text{−NH}_3 \\
& &\xrightarrow{\text{ClO}_2} &\text{H}_3N \rightarrow \text{H}^+\text{−NH}_3^+
\end{align*}
\]

Fig. 5 Proposed pathway of the protonated benzidine-ClO_2 reaction

3.4.2.2 Reaction mechanism of ClO_2 oxidation of free state benzidine

\[
\begin{align*}
\text{H}_3N &\xrightarrow{\text{ClO}_2} \text{H}_2N\text{−NH}_3 &\xrightarrow{\text{ClO}_2} &\text{H}_3N \rightarrow \text{H}^+\text{−NH}_3 \\
& &\xrightarrow{\text{ClO}_2} &\text{H}_3N \rightarrow \text{H}^+\text{−NH}_3^+
\end{align*}
\]

Fig. 6 Proposed pathway of the free benzidine-ClO_2 reaction

With benzidine (I) under the action of ClO_2, the a-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 a-hydrogen atoms of the N of diphenylhydrazine to be captured by oxygen of 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 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 ClO₂ 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 ClO₂ 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 ClO₂, which subject to single electron transfer mechanism. 7, 8

4 Conclusions

The reaction between ClO₂ and benzidine was first-order with respect to both ClO₂ and benzidine, and the entire reaction was of second-order. Under condition of pH6.5and 298K, the second-order reaction rate constant \( k \) was 5.721 \times 10^{-4} \text{ L/(mmol·s)}. The rate constant \( k \) had the same change with the reaction temperature. The reaction activation energy was 51.1kJ·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-ClO₂ reaction were diphenooquinone diimine, diphenooquinone dioxide and diphenooquinone, however the intermediates of the free benzidine-ClO₂ reaction were hydrazobenzene, azen benzene and para-benzoquinone by GC-MS technique. Based on the GC-MS results, ClO₂ oxidation characteristics and benzidine presence state, the two possible pathways for the benzidine-ClO₂ reaction was proposed based on the mechanism of the single electron transfer (SET).

References