Anilines Oxidation with Chlorine Dioxide in Wastewater

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Abstract: Oxidative behaviors of three toxic pollutants including aniline, p-toludine and p-chloroaniline with ClO₂ in water were studied with HPLC. The removal rates of anilines were used as criteria in this experiment. Effects of the ClO₂ concentration, pH and reaction time on the removal rate of anilines were discussed. The results show that for 1 mmol L⁻¹ aniline, p-toludine and p-chloroaniline, the optimal process conditions were as follows: ClO₂ concentration as 5 mmol L⁻¹, pH as 8, 8-9 and 7-8 and the reaction time as 60, 30 and 20min for aniline, p-toludine and p-chloroaniline respectively. The removal rates of anilines were higher than 90%, revealing that the oxidative method of ClO₂ is very feasible and efficient for anilines removal. Two intermediates p-aminophenol and azobenzene were detected by means of GC-MS. And, the possible reaction pathway was proposed.

Key words: anilines; chlorine dioxide; oxidation; reaction pathway

1 Introduction

Anilines, as a widely used material in light and textile industries such as printing & dyeing and tannery, have become one of the important components in the toxic and harmful wastewater. They are hardly biodegradable, highly toxic, carcinogenic and mutagenic. Conventional activated sludge process would decompose them incompletely, and somewhat inhibit the biodegradation of other organic compounds.

Several methods have been proposed for decomposition of anilines¹⁻⁶, such as activated carbon adsorption, chemical oxidation, photocatalytic oxidation, electrochemical process and supercritical fluid extraction. Among these methods, chemical oxidation is arguably predominant decomposition method because of simplicity. ClO₂ oxidation is an effective chemical oxidation method for organic pollutants removal, and do not produce trihalomethanes (THMs) after oxidation⁷. ClO₂ oxidation has a wide potential application in wastewater treatment for chemical industry. In the present work, with anilines as model, the parameters and mechanism of anilines oxidation by ClO₂ were studied, providing the reference for further industrial application.

2 Experimental

2.1 Reagents and Apparatus

2.1.1 Reagents

Aniline, p-toludine and p-chloroaniline, A R; ClO₂, prepared by the reaction between sodium chlorite and sulphuric acid followed by saturated sodiumchlorite washing, purity of ClO₂ was above 99%; All other reagents were of A. R. quality.

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);

2.2 Research Methods

The reaction was carried out in dark and constant temperature. Solution of ClO₂, anilines and the

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quenching agent Na₂S₂O₃ were adjusted to the desired pH prior to the start of each experiment. Experiment procedure was as follows: add a certain volume of anilines solution with an injector into the reactor. Then start the beater and inject a certain volume of ClO₂ solution. Allow the reaction to proceed for a desired duration, and then terminate the reaction by addition of Na₂S₂O₃. Then transfer all the solution in the reactor into a 100 ml separating funnel. Extract this solution with benzene three times. And then combine the extraction. Sample with a mini-injector and determine the concentration of the residual aniline by means of HPLC, thus calculating the rate of removal.

2.3 Analytical Methods

2.3.1 Determination of ClO₂ concentration

Concentration of ClO₂ was determined by successive iodimetric technique⁸.

2.3.2 Anilines determination with HPLC

The HPLC condition was: flowing phase: 85% methanol (chromatogram purity) solution; filling of separation column: Hyper ODS2 C₁₈, 250mm long, 4.6 mm diameter; flux: 1.0 ml·min⁻¹; pressure: 5.00 MPa; sample volume: 10μl; wavelength of detector: UV₂₅₄.

3 Results and discussions

3.1 The effect of ClO₂ concentration on anilines removal

![Graph showing the effect of ClO₂ concentration on anilines removal rate](image)

Fig. 1 The effect of ClO₂ concentration on anilines removal rate

The level of anilines oxidation was directly affected by the ClO₂ concentration. The influence of ClO₂ concentration was evaluated under the initial anilines concentration of 1 mmol·L⁻¹, pH 8.0, room temperature and 60 min reaction time, as is shown in Fig. 1.

It can be seen that the removal rates of anilines increase dramatically with the ClO₂ concentration from 0 to 5 mmol·L⁻¹ and then level off. The removal rate was 70%–80% and above 90% with 3 mmol·L⁻¹ and 5 mmol·L⁻¹ ClO₂ respectively, which exhibits the effectiveness of ClO₂ oxidation on anilines removal. Thereby, 5 mmol·L⁻¹ ClO₂ was used for further study.

3.2 The effect of reaction time on anilines removal

Reaction time is also an important factor affecting the anilines removal rate. The influence of reaction time was evaluated under the initial anilines concentration of 1 mmol·L⁻¹, pH 8.0, room temperature and ClO₂ concentration of 5 mmol·L⁻¹, as is shown in Fig. 2.

From the figure, the removal rates of anilines increase greatly during the first 20 min, then level off. The increased removal rates were different for different anilines. During the first 20 min, the removal rates were 64.42%, 84.74% and 93.72% for aniline, p-aminotoluene and p-chloroaniline. The removal rate of p-chloroaniline was almost constant thereafter. Thus, the appropriate reaction time of p-chloroaniline was selected as 20 min.
While for p-aminotoluene, 30 min reaction time resulted in the almost maximum removal rate of 94.33%, further increased reaction time gave little influences and removal rate of 96.68% was obtained with 40 min reaction time. Therefore, 30 min was chosen as the optimal reaction time of p-aminotoluene.

Among the three pollutants, aniline removal rate increased slowest with the reaction time. The removal rates of aniline were 92.35% and 95.01% with 60 min and 90 min reaction time respectively. The most suitable reaction time for aniline was selected as 60 min.

![Graph showing the effect of reaction time on anilines removal rate](image)

**Fig. 2 The effect of reaction time on anilines removal rate**

### 3.3 The effect of system pH value on anilines removal

The system pH value influences not only ClO₂ oxidation ability, but also the presence state of anilines, thus regarded as another key factor of anilines removal. The influence of pH value was studied under the initial anilines concentration of 1 mmol·L⁻¹, ClO₂ 5 mmol·L⁻¹, room temperature and 60 min. The result is shown in Fig. 3.

![Graph showing the effect of system pH value on anilines removal rate](image)

**Fig. 3 The effect of system pH value on anilines removal rate**

The removal of anilines was more effective in acidic conditions (pH 5.0 and pH 5.8) and basic conditions (pH 8.0 and pH 9.0, except pH 10.0) than neutral condition (pH 7.0), because of the variation of ClO₂ oxidization ability with the change of pH value in water. ClO₂ would obtain 5 mol electrons and be partially reduced to Cl⁻ in acidic condition, and obtain 1 mol electrons to ClO₂⁻ in neutral condition. Therefore, the redox potential of ClO₂ is higher in acidic condition while comparing with neutral
condition, the higher oxidation ability finally leads to the higher anilines removal rate. The anilines itself is weakly basic, and presents as hardly oxidizable proton state in acidic and neutral conditions. While in basic conditions, anilines are present at free and easily oxidizable state. However, the removal rate of p-aminotoluene was not increased with the pH from 9.0 to 10.0, but decreased from 95.74% to 78.62%, probably due to ClO₂ oxidation ability loss after disproportionation reaction.

From Fig. 3, a high aniline removal rate of 92.36% was obtained with pH value of 8.0. Because p-aminotoluene is more basic than aniline, the higher pH value is needed for the presence of free p-chloroaniline in order to obtain optimal removal. The optimal removal rate of p-aminotoluene was above 94% with pH value 8-9. p-chloroaniline is less basic than aniline and p-aminotoluene, thus lower pH value was needed for the presence of free state p-chloroaniline in order to obtain optimal removal. The removal rate of p-chloroaniline was above 92% with pH value 7-8.

Generally, effective anilines removal rate could be obtained with ClO₂ oxidation in a wide range of pH value.

3.4 Discussion of the aniline-ClO₂ reaction pathways

GC-MS technique was employed to determine intermediates of reaction between ClO₂ and aniline. p-aminophenol and azobenzene were detected as intermediates under water treatment conditions. It is known that reaction between ClO₂ and phenol followed single-electron-transfer mechanism. 9,10 Reaction products of ClO₂ and phenol have been reported to be quinones and then simple organic and inorganic acid. Azobenzene was combining product of two aniline neutral radicals and which indicated the presence of this radical. Research has proved that azobenzene could be further degraded by ClO₂. Based on the results of GC-MS and characteristics of the aniline molecule, possible pathways of reaction between ClO₂ and aniline were proposed in Fig.4.

![Fig.4 Proposed pathways of reaction between aniline and ClO₂](image)

4 Conclusions

Research on the aniline, p-toluidine and p-chloroaniline indicated it was feasible to anilines oxidation with ClO₂. For 1mmol·L⁻¹ anilines, the optimal process conditions were as follows: ClO₂ concentration 5mmol·L⁻¹, pH8 for aniline, pH8-9 for p-toluidine and pH7-8 for p-chloroaniline, reaction time were 60,30 and 20min respectively. The removal rates of anilines were more than 90%. Effective anilines removal rate could be obtained with ClO₂ oxidation in a wide range of pH value. Two intermediates p-aminophenol and azobenzene were detected by means of GC-MS. And the possible reaction pathway was proposed.

References


