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 ClO_2 in water were studied with HPLC. The removal rates of anilines were used as criteria in this experiment. Effects of the ClO_2 concentration, pH and reaction time on the removal rate of anilines were discussed. The results show that for 1mmol·L^{-1} aniline, p-toludine and p-chloroaniline, the optimal process conditions were as follows: ClO_2 concentration as 5mmol·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 ClO_2 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 anilines[1-6], 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. ClO_2 oxidation is an effective chemical oxidation method for organic pollutants removal, and do not produce trihalomethanes (THMs) after oxidation[7]. ClO_2 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 ClO_2 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; ClO_2, prepared by the reaction between sodium chlorite and sulphuric acid followed by saturated sodiumchlorite washing, purity of ClO_2 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 ClO_2, anilines and the

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quenching agent $Na_2S_2O_3$ 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 ClO_2 solution. Allow the reaction to proceed for a desired duration, and then terminate the reaction by addition of $Na_2S_2O_3$. 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 ClO_2 concentration

Concentration of ClO_2 was determined by successive iodimetric technique[8].

2.3.2 Anilines determination with HPLC

The HPLC condition was: flowing phase: 85% methanol (chromatogram purity) solution; filling of separation column: Hyper ODS2 C_{18}, 250mm long, 4.6 mm diameter; flux: 1.0 ml·min^{-1}; pressure: 5.00 MPa; sample volume: 10μl; wavelength of detector: UV_{254}.

3 Results and discussions

3.1 The effect of ClO_2 concentration on anilines removal

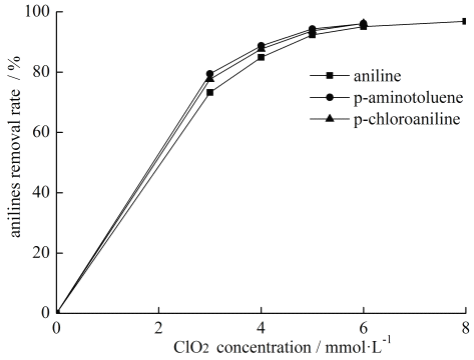

Fig. 1 The effect of ClO_2 concentration on anilines removal rate

The level of anilines oxidation was directly affected by the ClO_2 concentration. The influence of ClO_2 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 ClO_2 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} ClO_2 respectively, which exhibits the effectiveness of ClO_2 oxidation on anilines removal. Thereby, 5 mmol·L^{-1} ClO_2 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 ClO_2 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.

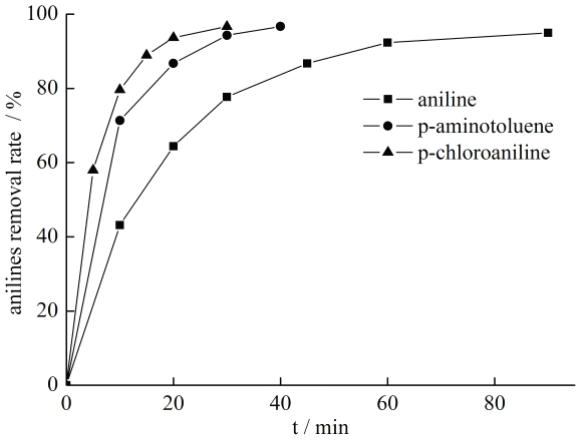

Fig. 2 The effect of reaction time on anilines removal rate

3.3 The effect of system pH value on anilines removal

The system pH value influences not only ClO_2 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}, ClO_2 5 mmol·L^{-1}, room temperature and 60 min. The result is shown in Fig. 3.

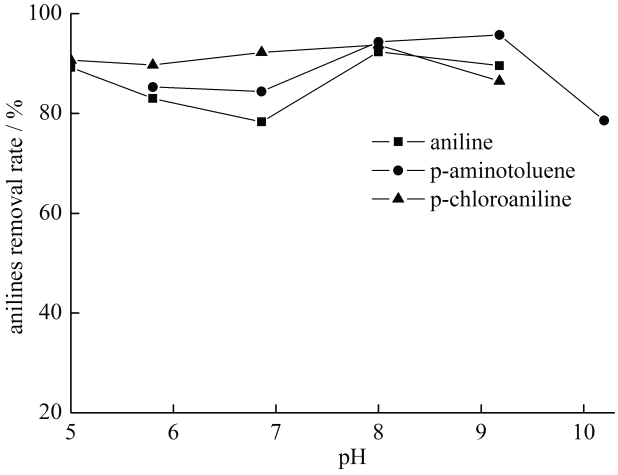

Fig. 3 The effect of system pH value on anilines removal rate

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 ClO_2 oxidization ability with the change of pH value in water. ClO_2 would obtain 5 mol electrons and be partially reduced to Cl^- in acidic condition, and obtain 1 mol electrons to ClO_2^- in neutral condition. Therefore, the redox potential of ClO_2 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 ClO_2 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 ClO_2 oxidation in a wide range of pH value.

3.4 Discussion of the aniline-ClO_2 reaction pathways

GC-MS technique was employed to determine intermediates of reaction between ClO_2 and aniline. p-aminophenol and azobenzene were detected as intermediates under water treatment conditions. It is known that reaction between ClO_2 and phenol followed single-electron-transfer mechanism. [9,10] Reaction products of ClO_2 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 ClO_2. Based on the results of GC-MS and characteristics of the aniline molecule, possible pathways of reaction between ClO_2 and aniline were proposed in Fig.4.

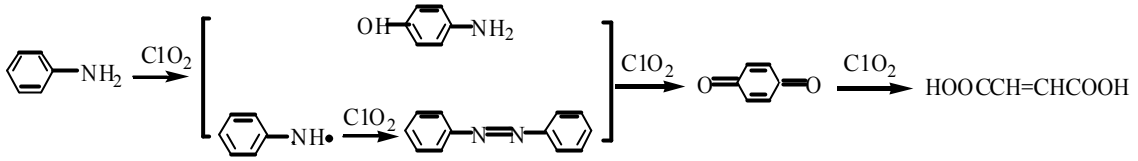

Fig.4 Proposed pathways of reaction between aniline and ClO_2

4 Conclusions

Research on the aniline, p-toludine and p-chloroaniline indicated it was feasible to anilines oxidation with ClO_2. For 1mmol·L^{-1} anilines, the optimal process conditions were as follows: ClO_2 concentration 5mmol·L^{-1}, pH8 for aniline，pH8-9 for p-toludine 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 ClO_2 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.

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