Chlorine dioxide catalytic oxidation and online FTIR spectroscopic analysis of simulated *o*-chlorophenol wastewater

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Abstract An activated carbon- MnO_2 catalyst was prepared and used for chlorine dioxide catalytic oxidation of simulated *o*-chlorophenol wastewater. The COD removal efficiencies of chemical oxidation and catalytic oxidation are 28.6 and 93.5%, respectively. The COD removal efficiency of catalytic oxidation is greater than that of chemical oxidation at the same treatment condition. By using UV–Vis and online FTIR analysis technique, the intermediates during the degradation process were obtained. The benzene ring in *o*-chlorophenol was degraded into quinone and carboxylic acid, and finally changed into carbon dioxide and water during the catalytic oxidation. The degradation reaction mechanism of *o*-chlorophenol by chlorine dioxide catalytic oxidation was proposed based upon the experiment evidence.

Keywords Chlorine dioxide · Catalytic oxidation · *O*-chlorophenol · Wastewater treatment · Online FTIR analysis

Introduction

O-chlorophenol is an important intermediate and raw material in the synthesis of pesticides, medicines, and dyes. However, *o*-chlorophenol has the properties of an unpleasant odor, high skin irritation, and ease of absorption by skin. Therefore, the treatment of wastewater containing *o*-chlorophenol is an urgent environmental problem. Otherwise, it can lead to extreme environmental pollution. Various treatment techniques have been studied to remove or eliminate phenolic compounds from wastewaters, including chemical oxidation [1], solvent extraction [2], membrane

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techniques [3], adsorption [4], photodegradation [5, 6], coagulation flocculation [7], biological processes [8], and so on. However, such technologies usually involve complicated procedures and are not economically viable.

The catalytic oxidation process is an interesting technique to decompose toxic and/ or non-biodegradable organic compounds in wastewaters, which is able to oxidize organic pollutants into carbon dioxide or into products that can be eliminated by biological treatment. Ozone, oxygen, hydrogen peroxide, or a combination of these are frequently used as an oxidant. In fact, chlorine dioxide is an effective oxidant. However, there are few reports on the use of chlorine dioxide in the catalytic oxidization processes [9–13].

The ClO₂ catalytic oxidation is an interesting method for the treatment of high concentration and non-biodegradable organic wastewater. In this study, activated carbon-MnO₂ catalyst was prepared and used for chlorine dioxide catalytic oxidation of simulated *o*-chlorophenol wastewater. The benzene ring in *o*-chlorophenol was degraded into quinone and carboxylic acids, and finally changed into carbon dioxide and water during the catalytic oxidation. Then, the degradation reaction mechanism of *o*-chlorophenol by chlorine dioxide catalytic oxidation had been put forward based upon the experiment evidence.

Experimental

Materials

All the reagents used were of analytical grade. The ClO_2 solution was prepared by mixing a hydrochloric acid solution and a sodium chlorite solution before using. The concentration of chlorine dioxide solution is 9.38 g/L. Simulated wastewater containing *o*-chlorophenol was prepared by dissolving 2.00 mL *o*-chlorophenol in water in a 2,000 mL volumetric flask. The chemical oxygen demand (COD) of the wastewater was 2,085 mg/L.

The activated carbon- MnO_2 catalyst was prepared by the dipping-calcination method. First, the activated carbon was immersed into 8% $Mn(NO_3)_2$ aqueous solution for 24 h, then dried at 120 °C for 4 h and calcined at 300 °C for 4 h. The formed MnO_2 was loaded on the surface of activated carbon.

The wastewater treatment process

Simulated wastewater (100 mL) containing *o*-chlorophenol was added in a 250-mL flask. The pH value was adjusted by hydrochloric acid solution. The amounts of the catalysts and ClO_2 solution were added. The treatment was carried out at room temperature for a certain time under the condition of stirring and keeping from light. The COD of wastewater before and after treatment was measured by the international standard of ISO6060-1989.

UV–Vis spectrophotometric measurements were performed in a TU-1800PC UV– Vis spectrophotometer (Beijing Puxi Tongyong Instrument Company, Beijing, China). A complete spectrum of the water samples could be obtained in the range of 200–1,000 nm. The simulated wastewater containing o-chlorophenol, the effluent by chemical oxidation, and the effluent by catalytic oxidation were diluted by 2.1 times before determination.

FTIR analysis

FTIR spectra were obtained using a Bruker Tensor-27 FTIR spectrophotometer. FTIR spectra were recorded from 400 to $4,000 \text{ cm}^{-1}$ wavenumber range with averaging 32 scans at a resolution of 4 cm⁻¹. For the effluent by chemical oxidation and the effluent by catalytic oxidation, it was evaporated in a water bath at 80 °C. The solid samples were obtained and then determined by FTIR spectrophotometer.

Online FTIR analysis during the wastewater treatment

The online FTIR analysis was performed on a ReactIR 4000 spectrophotometer (Mettler-Toledo AutoChem, Inc., USA). FTIR spectra were recorded from 400 to 4,000 cm⁻¹ wavenumber range at a resolution of 8 cm⁻¹. An amount of 100 mL of simulated wastewater containing *o*-chlorophenol was added into a 250-mL flask. The pH value was adjusted to 1.2 by hydrochloric acid solution. Then, chlorine dioxide solution containing 100 mg chlorine dioxide, and 6 g of activated carbon-MnO₂ catalyst were added. The magnetic stirrer was under operation during the online FTIR measurement.

Results and discussion

The wastewater treatment process

The reaction conditions were as follows: the simulated wastewater containing o-chlorophenol, 100 mL; pH value, 1.2; the concentration of chlorine dioxide, 1,000 mg/L; the dosage of activated carbon-MnO₂ catalyst for catalytic oxidation, 6 g; reaction time, 60 min. The COD removal efficiencies of chemical oxidation and catalytic oxidation are 28.6% and 93.5%, respectively. The COD removal efficiency of catalytic oxidation is greater than that of chemical oxidation at the same treatment condition.

UV-Vis spectrophotometric analysis

In order to study the pollutant changes during the oxidation process, it is necessary to investigate the UV–Vis spectra before and after chlorine dioxide oxidation treatment. Figure 1 represents the UV–Vis spectra of water samples before and after

oxidation. As shown in Fig. 1, the simulated wastewater containing o-chlorophenol has strong absorption peaks at 227 nm and 261 nm (see curve 1), which belong to the characteristic absorption peak E_2 band and B band of phenol, respectively. The number of peaks increased after the simulated wastewater was treated by chemical oxidation (see curve 2). The peak at 333 nm was assigned to the product of p-quinone. The peaks at 234 and 287 nm were assigned to the benzene ring structure. The number of peaks decreased for the catalytic oxidation by comparison with the chemical oxidation. The absorption peak intensity at 287 and 333 nm weakened obviously (see curve 3). It indicates that the extent of COD removal efficiency by catalytic oxidation is greater than that of chemical oxidation. This evidence coincides with the data in "The wastewater treatment process".

FTIR analysis

In order to study the pollutant changes during the oxidation process, the FTIR spectra before and after chlorine dioxide oxidation treatment were further investigated. Figure 2 represents the FTIR spectra of *o*-chlorophenol samples before and after oxidation.

In the FTIR spectrum of *o*-chlorophenol (curve 1 in Fig. 2), the absorption near $3,520 \text{ cm}^{-1}$ is assigned to the O–H stretching. The absorptions near 3,076 and $3,040 \text{ cm}^{-1}$ are assigned to the aromatic Ar–H stretching. The absorptions near 1,588, 1,480, and $1,453 \text{ cm}^{-1}$ are assigned to the C=C framework vibration of benzene ring in aromatic compounds (sharp peak). The absorption near $1,198 \text{ cm}^{-1}$ is assigned to the C=O stretching in phenol. The absorption near $1,056 \text{ cm}^{-1}$ is assigned to the O–H deformation. The strong absorptions near 883, 832, and



Fig. 1 UV-Vis spectra of water samples before and after oxidation (curve 1: simulated *o*-chlorophenol wastewater; curve 2: chemical oxidation; curve 3: catalytic oxidation)



Fig. 2 Infrared spectra of *o*-chlorophenol wastewater before and after oxidation (curve 1: *o*-chlorophenol; curve 2: chemical oxidation; curve 3: catalytic oxidation)

 678 cm^{-1} are assigned to the Ar–H out-of-plane bending in phenyl. The absorption near 747 cm⁻¹ is assigned to the C–Cl stretching.

By comparing the spectra of chemical oxidation and catalytic oxidation with that of *o*-chlorophenol, the shapes of the curves changed a lot. This indicated that the pollutant's chemical structure changed a lot. In the FTIR spectrum of chemical oxidation (curve 2 in Fig. 2), the absorption near 3,450 cm⁻¹ is assigned to the O–H stretching in carboxylic acids. The absorption near 1,634 cm⁻¹ is assigned to the C=O stretching in *p*-quinone, which is conjugated with C=C double bond. The absorption near 1,121 cm⁻¹ is assigned to the C–O stretching. The absorption near 620–564 cm⁻¹ is assigned to the O–H out-of-plane deformation. The absorption near 2,968 cm⁻¹ and 2,934 cm⁻¹ are assigned to the C–H stretching of CH₂ group, which is formed from the degradation of benzene ring. The absorption near 1,405 cm⁻¹ is assigned to the aromatic C=C stretches in phenyl, which belongs to the unoxidized benzene ring. However, the peak intensity of 1,405 cm⁻¹ is greatly reduced.

In the FTIR spectrum of catalytic oxidation (curve 3 in Fig. 2), the absorption near $3,420 \text{ cm}^{-1}$ is assigned to the O–H stretching in carboxylic acids. The absorption near $1,628 \text{ cm}^{-1}$ is assigned to the C=O stretching in *p*-quinone, which is conjugated with C=C double bond. The absorption near $1,152-1,106 \text{ cm}^{-1}$ is assigned to the C–O stretching. The absorption near $620-564 \text{ cm}^{-1}$ is assigned to the O–H out-of-plane deformation. The absorptions near $3,076 \text{ cm}^{-1}$ and $3,040 \text{ cm}^{-1}$, which are assigned to the aromatic Ar–H stretching, and the absorption near $1,405 \text{ cm}^{-1}$, which is assigned to the aromatic C=C stretches in phenyl, are totally disappeared. This evidence

indicated that the benzene ring in o-chlorophenol had been totally oxidized by chlorine dioxide.

The absorption near 747 cm⁻¹, which is assigned to the C–Cl stretching, had totally disappeared after *o*-chlorophenol was oxidized by chemical oxidation or catalytic oxidation. At the same time, the benzene ring was also greatly degraded. There is no C=O stretching absorption peak in the FTIR spectrum of *o*-chlorophenol. However, the new absorption peaks of C=O stretching in *p*-quinone and carboxylic acids appeared. That is to say, *o*-chlorophenol maybe degraded into *p*-quinone and carboxylic acids in the chlorine dioxide oxidation process.

Online FTIR analysis

Figure 3 gives the 3D online infrared spectrum of wastewater treatment by the catalytic oxidation method. In Fig. 3, the strong absorption near 3,346 cm⁻¹ is assigned to the O–H stretching of water. The strong absorption near 1,656 cm⁻¹ is assigned to the H–O–H bending of water. Figure 4 represents the peak height (*H*) versus reaction time. As shown in Fig. 4, the two peak heights increased greatly in the beginning of the 5-min reaction time, and then increased slowly with the reaction time.

Four intermediates were detected automatically during the online FTIR analysis. Its FTIR spectra were obtained. In the FTIR spectrum of intermediate 1 (Fig. 5), the absorption near 1,698 cm⁻¹ is assigned to the C=O stretching in carboxylic acids, which should be product (d) in the degradation reaction mechanism. The absorption near 1,652 cm⁻¹ is assigned to the C=O stretching in *p*-quinone or carboxylic acids, which is conjugated with C=C double bond. It should be product (a), (b), or (c) in the degradation reaction mechanism. The absorptions near 1,559, 1,544, 1,524, and 1,520 cm⁻¹ are assigned to the C=C stretching in ethylene, which is conjugated with C=O bond. It should be product (a), (b), or (c) in the degradation reaction mechanism.



Fig. 3 3D online infrared spectrum of wastewater treatment by catalytic oxidation method



Fig. 4 Curve of peak height versus reaction time (curve A: $3,346 \text{ cm}^{-1}$ absorption peak; curve B: $1,656 \text{ cm}^{-1}$ absorption peak)



Fig. 5 Infrared spectrum of intermediate 1 during the reaction process

mechanism. Therefore, intermediate 1 should be one of the *p*-quinone, butenedioic acid, chloro-butenedioic acid, and ethanedioic acid.

In the FTIR spectrum of intermediate 2 (the figure is omitted), the absorption near 1,644 cm⁻¹ is assigned to the C=O stretching in *p*-quinone or carboxylic acids, which is conjugated with C=C double bond. It should be product (a), (b), or (c) in the degradation reaction mechanism. It indicated that *o*-chlorophenol was oxidized by chlorine dioxide to *p*-quinone, butenedioic acid, chloro-butenedioic acid.

Therefore, intermediate 2 should be one of the p-quinone, butenedioic acid, and chloro-butenedioic acid.

In the FTIR spectrum of intermediate 3 (the figure is also omitted), the absorption near 1,636 cm⁻¹ is assigned to the C=O stretching in *p*-quinone or carboxylic acids, which is conjugated with C=C double bond. It should be product (a), (b), or (c) in the degradation reaction mechanism. Therefore, intermediate 3 should be one of the *p*-quinone, butenedioic acid, and chloro-butenedioic acid.

In the FTIR spectrum of intermediate 4 (the figure is also omitted), the absorption near 1,640 cm⁻¹ is assigned to the C=O stretching in *p*-quinone or carboxylic acids, which is conjugated with C=C double bond. It should be product (a), (b), or (c) in the degradation reaction mechanism. Therefore, intermediate 4 should be one of the *p*-quinone, butenedioic acid, and chloro-butenedioic acid.

Figure 6 gives the intermediate 1-4's relative concentration (*c*) versus reaction time. As shown in Fig. 6, the relative concentration of intermediate 1 and 2 decreases slightly with the prolonging of reaction time. The relative concentration of intermediate 3 increases with the extension of reaction time. The relative concentration of intermediate 4 decreases with the increase of reaction time. Therefore, intermediate 4 should be *p*-quinone.

O-chlorophenol was oxidized by chlorine dioxide into *p*-quinone and carboxylic acids during the chemical oxidation or the catalytic oxidation. Finally, it was changed into carbon dioxide and water. Therefore, the degradation reaction mechanism of *o*-chlorophenol by chlorine dioxide oxidation was proposed based upon the experiment evidence. The mechanism was presented in Fig. 7.



Fig. 6 Curve of intermediate 1–4's relative concentration versus reaction time (curve 1: intermediate 1; curve 2: intermediate 2; curve 3: intermediate 3; curve 4: intermediate 4)



Fig. 7 Degradation reaction mechanism of o-chlorophenol

Conclusions

- (1) The chlorine dioxide catalytic oxidation process is an interesting technique for the treatment of wastewater. The COD removal efficiencies of chemical oxidation and catalytic oxidation are 28.6 and 93.5%, respectively. The COD removal efficiency of catalytic oxidation is greater than that of chemical oxidation at the same treatment condition. It has great practical significance for the design of actual wastewater treatment process.
- (2) By using UV–Vis and an online FTIR analysis technique, the intermediates during the degradation process were obtained. It was useful to investigate the degradation reaction mechanism of the pollutants. The result has important theoretical significance.

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