Catalytic oxidation and spectroscopic analysis of simulated wastewater containing acid chrome blue K by using chlorine dioxide as oxidant

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ABSTRACT

An activated carbon-MnO₂ catalyst was prepared by the dipping-calcination method using activated carbon as catalyst support. The catalyst was used for the catalytic oxidation of simulated acid chrome blue K wastewater. The COD removal efficiency and decolor efficiency by catalytic oxidation are 72.0% and 87.8%, respectively, at the condition of wastewater’s COD is 2,418 mg/L, the optimum pH value is 1.2, the dosage of chlorine dioxide is 1,200 mg/L, the dosage of activated carbon-MnO₂ catalyst is 4 g by reacting 50 min. The COD removal efficiency by catalytic oxidation is greater than that of chemical oxidation. The COD removal efficiency only decreased a little after the catalyst used 8 times. The FTIR spectra indicate that the active ingredient of manganese dioxide is linked with activated carbon by chemical bond, not merely mechanical blending. The intermediates during the degradation process were obtained by using online infrared spectrum analysis. The degradation reaction mechanism of acid chrome blue K by chlorine dioxide oxidation was proposed based upon the experiment evidence.

Key words | acid chrome blue K, catalytic oxidation, chlorine dioxide, online infrared spectrum, wastewater treatment

INTRODUCTION

The high colority and high COD of dyeing effluent cause serious environmental contamination nowadays. Nearly half of the dyes used in the textile industry are azo dyes. The dyeing effluent treatment is an urgent environmental problem that should be solved (Baiocchi et al. 2002; Hsueh et al. 2005). Otherwise, it can lead to extremely environmental pollution. Various treatment processes have been studied to remove or eliminate azo dyes from wastewaters, including biodegradation (Kim et al. 2008), sorption (Namasivayam & Arasai 1997; Cione et al. 1998; Mittal et al. 2007), electrochemical and oxidative degradation (Colonna et al. 1999; Salem & El-Maazawi 2000; Daneshvar et al. 2007; Mohan et al. 2007; Mounir et al. 2007) and so on. However, such processes usually involve complicated procedures and are not economically practical.

The catalytic oxidation process is an interesting technique to decompose toxic and/or non-biodegradable organic compounds in wastewaters (Luck 1999). The process is able to oxidize organic pollutants into other intermediate products, which can be eliminated by biological treatment. Ozone, oxygen, hydrogen peroxide or a combination of them are frequently used as oxidant. In fact, chlorine dioxide is an effective oxidant. However, there are few literatures about the use of chlorine dioxide in the catalytic oxidation processes (Jin et al. 2003; Bi et al. 2007, 2008, 2009). The chlorine dioxide catalytic oxidation of wastewaters containing phenol, p-chlorophenol, and p-nitrophenol was studied in recent years (Jin et al. 2003). The results showed that this method could decrease COD, with the COD removal efficiency up to 90%. The microwave-induced
ClO$_2$-CuO$_x$/Al$_2$O$_3$ process could effectively degrade phenol contaminant in a short reaction time with the COD removal efficiency of 79.1% (Bi et al. 2007). The catalyst of CuO$_x$/Al$_2$O$_3$ was prepared by the dipping-sedimentation method using γ-Al$_2$O$_3$ as a catalyst support. CuO and Cu$_2$O were loaded on the surface of Al$_2$O$_3$. The microwave assisted ClO$_2$ catalytic oxidation process with CuO$_x$/La$_2$O$_3$/γ-Al$_2$O$_3$ used as catalyst was also investigated (Bi et al. 2008). The results showed that the Al$_2$O$_3$ catalyst had an excellent catalytic activity in treating synthetic wastewater containing 100 mg/L phenol, and 91.66% of phenol and 50.35% of total organic carbon (TOC) could be removed under the optimum process conditions. Experiments were conducted to investigate the removal of remazol golden yellow dye in order to assess the effectiveness and feasibility of microwave enhanced chlorine dioxide catalytic oxidation process (Bi et al. 2009). The catalyst used in the process was CuO$_x$/La$_2$O$_3$/γ-Al$_2$O$_3$. The results showed that microwave enhanced catalytic oxidation process could effectively degrade remazol golden yellow dye with low oxidant dosage in a short reaction time and extensive pH range compared to the conventional wet catalytic oxidation. Under the optimal condition, the color removal efficiency was 94.03%, corresponding to 67.92% of total organic carbon removal efficiency.

In previous papers, we studied the chlorine dioxide catalytic oxidation of simulated wastewater containing naphthol green B or eriochrome black T (Shi et al. 2006, 2007; Li et al. 2008). The catalysts used in the processes were MnO$_2$-silica gel or TiO$_2$. The COD removal efficiency and decolor efficiency were improved comparing with that of chemical oxidation. The ability to biological treatment of the wastewater was improved.

In this paper, in order to improve the COD removal efficiency and to investigate the inherent essence of contaminant degradation mechanism, the activated carbon-MnO$_2$ catalyst was prepared by dipping-calcination method and used in the ClO$_2$ catalytic oxidation process to treat simulated wastewater containing acid chrome blue K. The optimum treatment condition was obtained. We further investigated the reaction system by UV-vis, FTIR and online FTIR spectroscopy. The intermediates were detected by online FTIR spectroscopy during the chlorine dioxide catalytic oxidation. The degradation reaction mechanism of acid chrome blue K by chlorine dioxide oxidation was proposed based upon the experiment evidence.

**MATERIALS AND METHODS**

**Materials**

All the reagents used were analytical grade. The ClO$_2$ solution was prepared by mixing a hydrochloric acid solution and a sodium chlorite solution before using. The chlorine dioxide concentration of the solution was 9.38 g/L.

Acid chrome blue K, which is a complexing indicator and dye, was chosen as the target compound, and its chemical structure was shown in Figure 1.

Simulated wastewater containing acid chrome blue K was prepared by dissolving 6.000 grams acid chrome blue K in water in a 2,000 ml volumetric flask. The COD of the wastewater was 2,418 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.

**Wastewater treatment procedure**

100 ml of simulated wastewater containing acid chrome blue K was added in a 250 ml flask. The pH value was adjusted by hydrochloric acid solution to certain value, e.g. 1.2. Then, 4 grams of the activated carbon-MnO$_2$ catalyst for catalytic oxidation was added. For chemical oxidation, the dosage of the activated carbon-MnO$_2$ catalyst was zero. Finally, the different amount of ClO$_2$ solution was added according to the pre-designed procedure.

**Figure 1** Chemical structure of acid chrome blue K.
The treatment was carried out at room temperature for certain reaction 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 analysis
UV-vis spectrophotometric measurements were performed on 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 nm–1,000 nm. The simulated wastewater containing acid chrome blue K, the effluent by chemical oxidation, and the effluent by catalytic oxidation were diluted by 40 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 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. 100 ml simulated wastewater containing acid chrome blue K was added into a 250 ml flask. The pH value was adjusted to 1.2 by hydrochloric acid solution. Then, chlorine dioxide solution containing 120 mg chlorine dioxide, and 4 grams of activated carbon-MnO₂ catalyst were added. In addition, using a magnetic stirrer allows for effective mixing in flask during the online FTIR measurement.

RESULTS AND DISCUSSION
Factors affecting the COD removal efficiency
The dosage of chlorine dioxide
The reaction conditions were as follows: the simulated wastewater containing acid chrome blue K, 100 ml; pH value, 1.2; reaction time, 50 min; the dosage of activated carbon-MnO₂ catalyst for catalytic oxidation, 4 grams. Figure 2 represents the COD removal efficiency versus the dosage of chlorine dioxide for the simulated wastewater treatment. As shown in Figure 2, the COD removal efficiency increases with the dosage of chlorine dioxide. The COD removal efficiency is 30.3% when the dosage of chlorine dioxide is 1,400 mg/L for the chemical oxidation. The COD removal efficiency levels off when the dosage of chlorine dioxide exceeds 1,400 mg/L for the chemical oxidation. The COD removal efficiency is 72.0% when the dosage of chlorine dioxide is 1,200 mg/L for the catalytic oxidation. The COD removal efficiency levels off when the dosage of chlorine dioxide exceeds 1,200 mg/L for the catalytic oxidation. Therefore, considering the economic reason, the optimum dosage of chlorine dioxide is 1,400 mg/L for the catalytic oxidation. Furthermore, the COD removal efficiency of catalytic oxidation is greater than that of chemical oxidation at the same treatment condition.

![Figure 2](https://iwaponline.com/wst/article-pdf/61/8/1931/448482/1931.pdf)
pH value

The reaction conditions were as follows: the simulated wastewater containing acid chrome blue K, 100 ml; the reaction time, 50 min; the dosage of activated carbon-MnO₂ catalyst for catalytic oxidation, 4 grams. The dosage of chlorine dioxide is 1,400 mg/L for the chemical oxidation, 1,200 mg/L for the catalytic oxidation, respectively. Figure 3 represents the COD removal efficiency versus the pH value for the simulated wastewater treatment. As shown in Figure 3, the COD removal efficiency decreases with the increase of pH value. This changing trend agrees with the property of chlorine dioxide having higher oxidative ability at lower pH value. Therefore, the optimum pH value is 1.2. It has also been found that the COD removal efficiency of catalytic oxidation is greater than that of chemical oxidation at the same treatment condition.

The reaction time

The reaction conditions were as follows: the simulated wastewater containing acid chrome blue K, 100 ml; pH value, 1.2; the dosage of activated carbon-MnO₂ catalyst for catalytic oxidation, 4 grams. The dosage of chlorine dioxide is 1,400 mg/L for the chemical oxidation, 1,200 mg/L for the catalytic oxidation, respectively. Figure 4 represents the COD removal efficiency versus reaction time (t) for the simulated wastewater treatment. As shown in Figure 4, the COD removal efficiency increases with reaction time. The COD removal efficiency levels off when the reaction time exceeds 50 min. Therefore, the optimum reaction time is 50 min for the chemical oxidation and catalytic oxidation. The fact that the COD removal efficiency of catalytic oxidation is greater than that of chemical oxidation at the same treatment condition can also be seen.

The lifetime of the catalyst

In order to study the lifetime of the catalyst, the activated carbon-MnO₂ catalyst was used for 8 times. Figure 5 gives the influence of catalyst used times to the COD removal efficiency.
efficiency. As shown in Figure 5, the COD removal efficiency is high within the used times. The COD removal efficiency only decreases a little, which is because of the active ingredient MnO₂ coming off from the surface of the activated carbon. Therefore, the activated carbon-MnO₂ catalyst can be used for 8 times, and without changing the catalyst.

Spectrophotometric analysis and characterization

UV-vis spectrophotometric analysis of pollutant changes

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 6 represents the UV-vis spectra of water samples before and after oxidation.

As shown in Figure 6, the simulated wastewater containing acid chrome blue K has a strong absorption peak at 525 nm (see curve 1), which is belong to the characteristic absorption peak of azo bond. The absorption peak at 525 nm disappeared after chemical oxidation or catalytic oxidation (see curve 2 and 3). It indicates that azo bond can be easily oxidized by chlorine dioxide. The simulated wastewater containing acid chrome blue K also has a strong absorption peak at 306 nm (see curve 1), which is belong to the characteristic absorption peak of naphthalene ring. The absorption peak at 306 nm also disappeared after chemical oxidation or catalytic oxidation (see curve 2 and 3). It indicates that naphthalene ring can also be easily oxidized by chlorine dioxide.

The simulated wastewater containing acid chrome blue K has a strong absorption peak at 226 nm (see curve 1), which is belong to the characteristic absorption peak of benzene ring. The absorption intensity at 226 nm decreased after chemical oxidation (see curve 2). We could find that the absorption intensity at 226 nm further decreased after catalytic oxidation (see curve 3). This evidence indicated that the simulated wastewater treated by chemical oxidation or catalytic oxidation still contained some benzene ring compounds. The chlorine dioxide chemical oxidation or catalytic oxidation has the degradative ability to benzene ring compounds to some extent.

From the UV-vis spectra before and after chlorine dioxide oxidation treatment, the degradative ability of chlorine dioxide to benzene ring, naphthalene ring, and azo bond has the following change trend.

azo bond > naphthalene ring > benzene ring

By comparing the peak intensity in the UV-vis spectra of chemical oxidation and catalytic oxidation, 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 Figure 2–4.

According to the UV-vis spectra before and after chlorine dioxide oxidation treatment, the decolor efficiency could be calculated. The formula is as follows.

\[S = \left(\frac{A_1}{A_0}\right)^2 + A_2 + A_3 + \ldots + A_{n-1}\]

deolor efficiency (%) = \left[1 - \left(\frac{S}{S_0}\right)\right] \times 100\%

where \(S_0\) is the area of absorption curve of original wastewater, \(S\) is the area of absorption curve of treated wastewater sample, \(A_1\) is the absorbency value at the first wavelength of 200 nm, \(A_n\) is the absorbency value at the last wavelength of 1,000 nm.

The decolor efficiencies were 77.1% and 87.8% for chemical oxidation and catalytic oxidation, respectively. The process had excellent decoloring effect.

FTIR analysis of pollutant changes

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 7
represents the FTIR spectra of acid chrome blue K samples before and after oxidation.

In the FTIR spectrum of acid chrome blue K (curve 1 in Figure 7), the absorption near 3,428 cm\(^{-1}\) is assigned to the O-H stretching. The absorptions near 3,065 cm\(^{-1}\), 2,916 cm\(^{-1}\) and 2,843 cm\(^{-1}\) are assigned to the aromatic Ar-H stretching. The absorptions near 1,576 cm\(^{-1}\) and 1,514 cm\(^{-1}\) are assigned to the benzene ring stretching in aromatic compounds (sharp peak). The absorption near 1,397 cm\(^{-1}\) is assigned to the N=N stretches in azo. The absorptions near 1,201 cm\(^{-1}\) and 1,045 cm\(^{-1}\) are assigned to the sulfate in acid chrome blue K.

In the FTIR spectrum of chemical oxidation (curve 2 in Figure 7), the absorption near 3,428 cm\(^{-1}\) is assigned to the O-H stretching in carboxylic acids. The absorptions near 3,065 cm\(^{-1}\), 2,916 cm\(^{-1}\) and 2,843 cm\(^{-1}\) are assigned to the aromatic Ar-H stretching, which indicates that the benzene ring has not been totally oxidized by chlorine dioxide. The absorptions near 1,576 cm\(^{-1}\) and 1,514 cm\(^{-1}\) are assigned to the benzene ring stretching in aromatic compounds, which also indicates that the benzene ring has not been totally oxidized by chlorine dioxide. The absorptions near 1,201 cm\(^{-1}\) and 1,045 cm\(^{-1}\), which are assigned to the sulfate in acid chrome blue K, still existed. It can be deduced that the sulfate in acid chrome blue K changes into sodium sulfate. The absorption near 1,397 cm\(^{-1}\), which is assigned to the N=N stretches in azo, disappeared. At the same time, a new absorption near 1,429 cm\(^{-1}\), which is assigned to the nitrate, appeared. It indicated that theazo bond was oxidized by chlorine dioxide, and changed into nitrate. There is no C=O stretching absorption peak in the FTIR spectrum of acid chrome blue K. However, there is a new strong absorption near 1,735 cm\(^{-1}\), which is assigned to the C=O stretching in carboxylic acids, after treated by chemical oxidation. Also, there is a new strong absorption near 1,631 cm\(^{-1}\), which is assigned to the C=O stretching in quinone or conjugated carboxylic acids, after treated by chemical oxidation. That is to say, the benzene ring and naphthalene ring in acid chrome blue K was degraded into carboxylic acids, quinone or conjugated carboxylic acids.

In the FTIR spectrum of catalytic oxidation (curve 3 in Figure 7), the absorption near 3,443 cm\(^{-1}\) is assigned to the O-H stretching in carboxylic acids. The absorptions near 3,065 cm\(^{-1}\), 2,916 cm\(^{-1}\) and 2,843 cm\(^{-1}\), which are assigned to the aromatic Ar-H stretching, disappeared almost. It indicates that the benzene ring is totally oxidized by chlorine dioxide. The absorptions near 1,576 cm\(^{-1}\) and 1,514 cm\(^{-1}\), which are assigned to the benzene ring stretching in aromatic compounds, also disappeared almost. It also indicates that the benzene ring is totally oxidized by chlorine dioxide. The absorption near 1,397 cm\(^{-1}\), which is assigned to the N=N stretches in azo, disappeared. At the same time, a new absorption near 1,402 cm\(^{-1}\), which is assigned to the nitrate, appeared. It indicated that theazo bond was oxidized by chlorine dioxide, and changed into nitrate. There is no C=O stretching absorption peak in the FTIR spectrum of acid chrome blue K. However, there is a new strong absorption near 1,633 cm\(^{-1}\), which is assigned to the C=O stretching in quinone or conjugated carboxylic acids, after treated by catalytic oxidation. That is to say, the benzene ring and naphthalene ring in acid chrome blue K was degraded into quinone or conjugated carboxylic acids.

**FTIR analysis of catalysts**

In order to study the function of the catalyst during the chlorine dioxide oxidation reaction, the FTIR spectra of the catalysts were further investigated. Figure 8 represents the FTIR spectra of the catalysts.

In the FTIR spectrum of activated carbon (curve 1 in Figure 8), the absorption near 3,406 cm\(^{-1}\) is assigned to the O-H stretching of water, which is absorbed by the activated carbon. The absorption near 1,621 cm\(^{-1}\) is assigned to the C=O stretching absorption peak in the FTIR spectrum of acid chrome blue K. However, there is a new strong absorption near 1,631 cm\(^{-1}\), which is assigned to the C=O stretching in quinone or conjugated carboxylic acids, after treated by catalytic oxidation. That is to say, the benzene ring and naphthalene ring in acid chrome blue K was degraded into carboxylic acids, quinone or conjugated carboxylic acids.
assigned to the C-C stretching. In the FTIR spectrum of MnO₂ (curve 2 in Figure 8), the absorption near 3,407 cm⁻¹ is assigned to the O-H stretching of water, which is absorbed by MnO₂. The absorption near 1,631 cm⁻¹ is assigned to the H-O-H bending of water. The absorption near 1,384 cm⁻¹ is assigned to the Mn-O stretching. The absorptions near 716 cm⁻¹ and 531 cm⁻¹ are assigned to the O-Mn-O bending.

The activated carbon-MnO₂ catalyst was prepared by the dipping-calcination method using activated carbon as catalyst support. In the FTIR spectrum of activated carbon-MnO₂ catalyst (curve 3 in Figure 8), the absorption near 3,422 cm⁻¹ is assigned to the O-H stretching of water, which is absorbed by the activated carbon. The absorption near 1,573 cm⁻¹ is assigned to the H-O-H bending of water. The absorption near 1,082 cm⁻¹ is assigned to the C-C stretching. The absorption near 488 cm⁻¹ is assigned to the O-Mn-O bending. It was found that the wavenumber of C-C stretching changed from 1,117 cm⁻¹ of activated carbon to 1,082 cm⁻¹ of the activated carbon-MnO₂ catalyst. The wavenumber of the absorption peak decreased 35 cm⁻¹. It was also found that the wavenumber of O-Mn-O bending changed from 531 cm⁻¹ of MnO₂ to 488 cm⁻¹ of the activated carbon-MnO₂ catalyst. The wavenumber of the absorption peak decreased 43 cm⁻¹. The wavenumber decrease of the absorption peaks indicated that the intensity of C-C bond or Mn-O bond decreased. It could be explained by the fact that the new C-O-Mn bond was formed during the activated carbon-MnO₂ catalyst synthesis process by the reaction of activated carbon with Mn(NO₃)₂ at the temperature of 300°C. The new C-O-Mn bond weakened the C-C bond in
activated carbon and Mn-O bond in MnO₂. In the waste-water catalytic oxidation, it is favorable to the absorption of chlorine dioxide and organic compounds to the surface of catalyst, and therefore increases the catalytic activity of the catalysts. The fact that the activated carbon-MnO₂ catalyst could be used for 8 times indicated that the active ingredient of manganese dioxide was linked with the activated carbon by chemical bond, not merely mechanical blending.

**Online FTIR analysis of degradation mechanism**

Figure 9 gives the 3D online infrared spectrum of waste-water treatment by catalytic oxidation method. The 3D is
absorbance, wavenumber and reaction time. In Figure 9, 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.

Three intermediates were detected automatically during the online FTIR analysis. Its FTIR spectra were obtained. In the FTIR spectrum of intermediate 1 (Figure 10), the absorption near 1,107 cm\(^{-1}\) is assigned to the O-H in-plane deformation in carboxylic acids. The absorption near 1,702 cm\(^{-1}\) is assigned to the C=O stretching in carboxylic acids, which should be the product of ethanedioic acid 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 the product of p-quinone, naphthoquinone, or butenedioic acid in the degradation reaction mechanism. The absorptions near 1,540 cm\(^{-1}\), 1,520 cm\(^{-1}\), and 1,509 cm\(^{-1}\) are assigned to the C=C stretching in ethylene, which is conjugated with C=O bond. It should be the product of p-quinone, naphthoquinone, or butenedioic acid in the degradation reaction mechanism. Therefore, intermediate 1 should be one of the p-quinone, naphthoquinone, butenedioic acid, and ethanedioic acid.

In the FTIR spectrum of intermediate 2 (the figure is omitted), 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 the product of p-quinone, naphthoquinone, or butenedioic acid in the degradation reaction mechanism. Therefore, intermediate 2 should be one of the p-quinone, naphthoquinone, and butenedioic acid.

In the FTIR spectrum of intermediate 3 (the figure is also omitted), the absorption near 1,107 cm\(^{-1}\) is assigned to the O-H in-plane deformation in carboxylic acids. The absorptions near 1,717 cm\(^{-1}\) and 1,702 cm\(^{-1}\) are assigned to the C=O stretching in carboxylic acids, which should be the product of ethanedioic acid 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 the product of p-quinone, naphthoquinone, or butenedioic acid in the degradation reaction mechanism. The absorptions near 1,540 cm\(^{-1}\), 1,520 cm\(^{-1}\), and 1,509 cm\(^{-1}\) are assigned to the C=C stretching in ethylene, which is conjugated with C=O bond. It should be the product of p-quinone, naphthoquinone, butenedioic acid, and ethanedioic acid.

In Figure 11 gives the intermediate 1–3’s relative concentration versus reaction time. As shown in Figure 11, the relative concentration of intermediate 1 increases slowly at first, then decreases slightly with reaction time. The relative concentrations of intermediate 2 and 3 increase with reaction time. Therefore, intermediate 1 should be p-quinone or naphthoquinone.

Acid chrome blue K 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 acid chrome blue K by chlorine dioxide oxidation was proposed based upon the experiment evidence. The mechanism was presented in Figure 12.

CONCLUSIONS

The chlorine dioxide catalytic oxidation process is an interesting technique for the treatment of wastewater. The COD removal efficiency by catalytic oxidation is 72.0% at the condition of wastewater’s COD is 2,418 mg/L, the optimum pH value is 1.2, the dosage of chlorine dioxide is 1,200 mg/L, the dosage of activated carbon-MnO\(_2\) catalyst is 4 g by reacting 50 min. The COD removal efficiency by catalytic oxidation is great than that of chemical oxidation. The decolor efficiencies are 77.1% and 87.8% for chemical oxidation and catalytic oxidation, respectively.

The activated carbon-MnO\(_2\) catalyst was prepared by the dipping-calcination method using activated carbon as catalyst support. The research on the catalysts by FTIR analysis showed that the active ingredient of manganese dioxide was linked with activated carbon by chemical bond, not merely mechanical blending.

By using the advanced 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. Also, it has great practical significance for the design of actual wastewater treatment process. This process can be used in the dyeing effluent treatment after further investigation.

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