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# Comparison of degradation reactions of Acid Yellow 61 in both oxidation processes of $\text{H}_2\text{O}_2/\text{UV}$ and $\text{O}_3$

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**Abstract:** The comparison of degradation of Acid Yellow 61 as a model dye compound in both oxidation processes of  $\text{H}_2\text{O}_2/\text{UV}$  and  $\text{O}_3$  has been studied. When the decolorization rate of Acid Yellow 61 in both reactions presented similar, it was found there are some differences from the results of AOX removal and production of inorganic ions and organic acids. The results reveal that the  $\text{H}_2\text{O}_2/\text{UV}$  has beneficial effect on mineralization than  $\text{O}_3$  only for degradation of Acid Yellow 61 solution and it is possible for enhancement of method efficiency by taking longer reaction time and addition of high concentration of oxidants.

**Key words:** oxidation process;  $\text{H}_2\text{O}_2/\text{UV}$ ;  $\text{O}_3$ ; dye compound

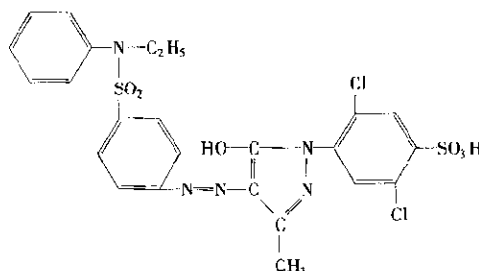
## Introduction

Color substances in dyeing effluents normally cause certain difficulties in traditional biological treatment processes due to the dye molecules are highly structured polymers and their toxicity (Hamza, 1980; Ginocchino, 1984; MaKay, 1980). It is necessary to improve the treatment efficiency with the help of some physical or chemical treatment processes (Li, 1996; Ikhal, 1996). It has been already proved that advanced oxidation processes (AOP) based on the generation of hydroxyl radicals OH may provide more effective treatment especially for the wastewater with nonbiodegradable nature. Hydrogen peroxide with UV irradiation and ozone are useful oxidation techniques and have been already applied widespread in the treatment of wastewater (Sheng, 1993; Susan, 1994; Gulyas, 1995; Jones, 1985; Cetoff, 1996). In most cases, the hydroxyl radical OH produced on different pathways which is responsible for the destruction of contaminants. The reaction mechanism has been previously demonstrated (Cetoff, 1996; Hoigne, 1976; Stachlin, 1976; Janssens, 1985). Strong color is the most notorious characteristic of dyeing waste effluents that would have a strongly negative impact on the aquatic environment. Hence decolorization has become a main part in the dyeing wastewater treatment process but it is not only goal. The purpose of the present paper is to make a comparative study for the differences in details of oxidation reaction of Acid Yellow 61 solution chosen as a model dye compound in both oxidation processes of  $\text{H}_2\text{O}_2/\text{UV}$  and  $\text{O}_3$ . Not only from the color removal, we also focused on the mineralization and degradation of dye compound. Therefore, as a case study, to consider the effort in an attempt to find the optimum reaction condition for enhance the method efficiency and decrease the treatment cost of dyeing wastewater.

## 1 Experimental section

### 1.1 Materials

Acid Yellow 61 (C. I. No: 18968) was obtained from a Company in German as a commercial dye without further purification. The purity was 73.6% calculated by the result of TOC measurement. The molecular structure of Acid Yellow 61 is as following:



The initial concentration of all test dye solutions was 0.22 mmol.

### 1.2 Oxidation experiment

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The oxidants used in the test were hydrogen peroxide and ozone. The hydrogen peroxide (30%, medical extra pure, Merck) was added in concentration of 97.94 mmol and ozone was continuously produced from ambient air by a laboratory scale ozone generator (Erwin Sander Elektroapparatebau GmbH Model 1992). Ozone inlet concentration in gas phase was  $2.6 \text{ g/m}^3$  detected on line by an ozone detector before it bubbled into the reactor. Ozonation run was conducted at a gas flow rate of  $0.75 \text{ L/min}$ . All experiments of hydrogen peroxide with UV irradiating and ozonation were carried out in a 1.5 liters cylindrical annular-type reactor with 50 cm height and 7.62 cm I.D. made of Pyrex glass. UV irradiation was accomplished by a 125 W middle pressure mercury lamp with emission spectrum of 254 nm located in the center of the reactor. Nitrogen with a flow rate of  $1.5 \text{ L/min}$  was used in  $H_2O_2/UV$  processes to improve the heterogeneous mixing condition. All the gas was bubbled through the solution from the bottom of reactor by a glass gas diffuser. During a run of 2h, a series of 20 ml samples were withdrawn at selected time intervals for analysis.

### 1.3 Analytical methods

Color removal of dye solution was determined by monitoring the maximum absorption spectra at 421 nm with a spectrophotometer of Varian Cary 1/3. TOC (total organic carbon) was analyzed by means of a carbon analyzer DC-180 of DOHRMANN Company. The degree of mineralization of samples during the oxidation process was also determined by measurement of the ions production from the degradation of substitute groups such as chloride, sulfate, nitrate and some smaller molecular weight organic acids by an Ion Chromatography (Dioncx-DX500). The analysis condition was with a column of Dioncx AS-11, the conductivity detector and the eluent of carbonate solution. Meanwhile the cleavage of organic structure could be determined by reduce of adsorbable organic chloride compound in solution measured by a total organic halogen analyzer (TOX-10) of AOX ABIMED (Analysen-Technic GmbH).

## 2 Results and discussion

### 2.1 The result of color removal

From the results of color removal of Acid Yellow 61 solution in both oxidation reactions shown in Fig. 1, it was observed that the reaction rates of color removal in both reactions are similar although the amount of oxidants really involved in both oxidation systems were hardly to calculate and compare quantitatively. On the base of this consider other experimental results of both reactions were compared each other in order to reveal their differences in details.

### 2.2 The result of degradation of molecular structure

From the result of AOX removal in both oxidation processes shown in Fig. 2, the reaction rate of AOX removal of Acid Yellow 61 solution in  $H_2O_2/UV$  process is faster than that in  $O_3$  process. It is consistent with the result of chloride ion production shown in Fig. 3. The results demonstrated that it is more advantageous for the degradation of molecule structure in  $H_2O_2/UV$  process than in  $O_3$  only process.

Moreover, it was been found that the amount of chloride production was always lower than that produced directly from AOX removal. Although they increased at similar rate in both reactions, it reveals that not all of the organic chloride compound were oxidized directly to chloride ion during the molecular degradation process and there are still some other middle products before it change to chloride ion. Which either escaped out with the bubbling of carry gas or were not detected in this analytical system.

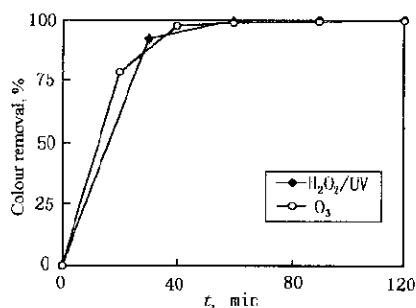


Fig.1 Comparison of color removal of AY61 in both oxidation processes

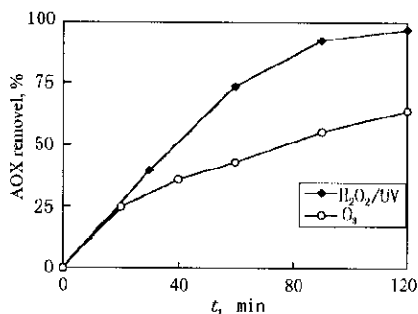


Fig.2 Comparison of AOX removal of AY61 in both oxidation processes

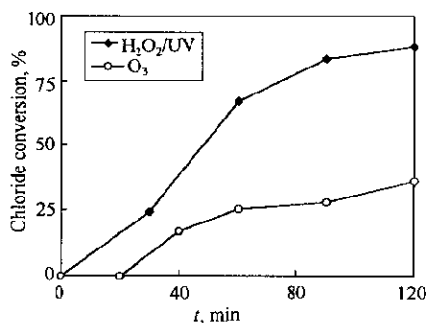


Fig.3 Comparison of chloride ion production of AY61 in both oxidation processes

The results of sulfate and nitrate production shown in Fig.4 and Fig.5 confirmed the conclusion from the result of AOX again. There is also no significant difference tendency between nitrate production with the results above. The amount of nitrate production is much smaller than chloride and sulfate. It indicates that organic nitrogen compounds were still the most final products during the oxidation. Which is more difficult for oxidized mainly the organic nitrogen structure to nitrate or nitrite in  $O_3$  or  $H_2O_2/UV$  process. From the result of organic acids production shown in Fig.6, which is the sum of formic acid, acetic acid and oxalic acid, it revealed the same regulation of degradation in both oxidation processes.

### 2.3 The result of TOC removal

It was observed from the result of Fig.7 that the TOC removal in  $H_2O_2/UV$  process is a little higher than that in  $O_3$  process finally. It is worth noting that there is a different TOC removal rate for both oxidation reaction. In  $O_3$  process, the rate of TOC removal increase rapidly at beginning period and achieved up to 41% (near the maximum value) in 40 min. On the contrary, in  $H_2O_2/UV$  process it increased slowly but always at the same speed in whole period. It reveals that it is not useful to take longer time for further oxidation of smaller molecular products by  $O_3$  process. But in  $H_2O_2/UV$  process, it is possible to last the further oxidation by means of increasing of longer time or addition of more  $H_2O_2$  amount.

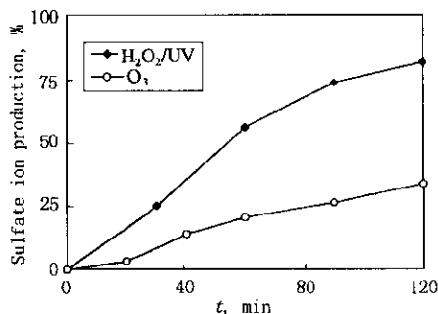


Fig.4 Comparison of sulfate ion production of AY61 in both oxidation processes

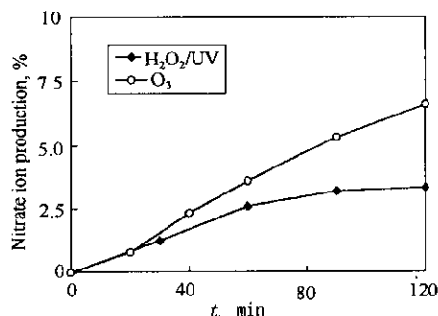


Fig.5 Comparison of nitrate ion production of AY61 in both oxidation process

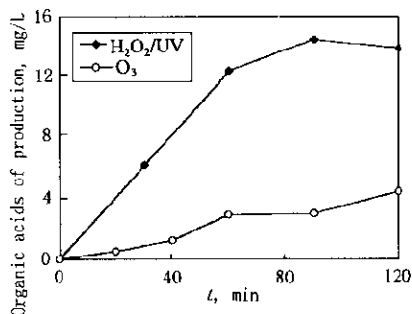


Fig.6 Comparison of organic acids production of AY61 in both oxidation processes

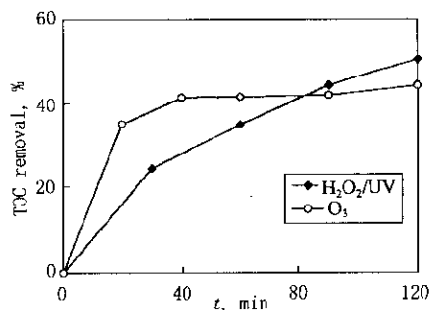


Fig.7 Comparison of TOC removal of AY61 in both oxidation processes

## 3 Conclusions

It is found that there are some differences in details between the degradation rates of molecular structure of Acid Yellow 61 in both oxidation processes of  $H_2O_2/UV$  and  $O_3$  only although the decolorization rate are very similar. From the results of AOX removal and the production of chloride, sulfate, nitrate and several organic acids with smaller molecular weight, it was indicated that  $H_2O_2/UV$  process has beneficial effect than that of  $O_3$  only on the mineralization of Acid Yellow 61. From the result of TOC removal rate, it could be concluded that the rate of TOC removal in  $H_2O_2/UV$  is faster than that in  $O_3$  especially at the beginning stage. On the other hand, from the economical point of view, it should be finished in short period in  $O_3$  process. But in  $H_2O_2/UV$  process it still has a possibility for enhancement of method efficiency by addition of high concentration of oxidants and taking the longer time.

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