



DECOLORIZING DYE WASTEWATER WITH LOW TEMPERATURE CATALYTIC OXIDATION

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ABSTRACT

Novel oxidation technology to decolorize dye wastewater was discussed and the feasibility of color removal with Fe/MgO catalyst fluidizing in a reactor under continuous flow was demonstrated at room temperature. In batch tests, the oxidation reaction of reactive and disperse dye with an oxidizing agent, hydrogen peroxide, in the presence of Fe/MgO catalyst was performed. Through the catalytic oxidation, dyes were oxidized to molecules with lower molecular weight and then mineralized based on TOC analysis. The influence of hydrogen peroxide and catalyst dosage on the catalytic oxidation rate was verified. The catalytic oxidation rate increased with increasing hydrogen peroxide and catalyst dosage. Fe/MgO catalyst fluidizing in the reactor operated at room temperature was tested to decolorize the wastewater from a dye manufacturing industry. In the fluidized bed reactor, the wastewater was completely decolorized and about 30% of COD removal was obtained during 30 days of operation. Organic matters were degraded and part of them mineralized by the catalytic oxidation. BOD/COD ratio of the effluent from the fluidized bed reactor was increased compared to that of the influent. After 30 days of operation, the effluent from the fluidized bed reactor started becoming yellowish. COD and residual hydrogen peroxide concentration in the effluent started to increase due to the catalyst losing its activity. © 1999 IAWQ Published by Elsevier Science Ltd. All rights reserved

KEYWORDS

Color removal; dye wastewater treatment; Fe/MgO; fluidized bed reactor; hydrogen peroxide; low temperature catalytic oxidation.

INTRODUCTION

Dye stuff is widely employed in various industries and the wastewater generated from those industries are highly colored due to residual dyes (Nemerow, 1978). Until recently, color produced by residual dye in wastewater has not been dealt with effectively. However the color removal is required in effluent and has become an important issue in Korea.

There are several methods practiced to decolorize dye wastewater but they cannot be effectively used individually to deal with the wastewater containing soluble and insoluble dyes. For example, the coagulation process can effectively decolorize the wastewater containing insoluble dyes such as disperse dyes. However it does not work well for soluble dyes such as reactive dyes. Soluble dyes can be effectively decolorized by oxidation process such as ozonation (Perkins *et al.*, 1980). It, however, can not decolorize insoluble dyes. Fenton's reagent has shown to be effective in decolorizing both soluble and insoluble dyes

(Kuo, 1992). In the process, there is a large volume of sludge created during coagulation that is generated by ferrous ions.

A novel oxidation technology has been developed to effectively deal with wastewater difficult to treat by biological means (Pak *et al.*, 1997). In the novel oxidation technology, recalcitrant compounds in wastewater are oxidized by hydrogen peroxide at as low as room temperature in the presence of the heterogeneous catalyst. Transition metal-doped catalyst, prepared by impregnating MgO with a solution of transition metals, acts as a catalyst in the oxidation reaction. Other oxidizing agents such as oxygen, air, or ozone can be used as an oxidizing agent.

In this study, batch and continuous tests were conducted to demonstrate the feasibility of color removal from dye wastewater by the novel oxidation technology. In batch tests, the simulated dye wastewater prepared with soluble or insoluble dye was tested to demonstrate that the novel oxidation technology was able to deal with two different types of dye. In continuous tests, the fluidized bed reactor was designed and operated. The wastewater obtained from a dye manufacturing industry in Korea was fed to the fluidized bed reactor. Decolorization of the dye wastewater by catalytic oxidation and performance of the fluidized bed were discussed.

METHODS

Catalyst preparation

MgO and ferric chloride were purchased from Sigma Chemical Co.. The iron-doped catalysts were prepared by impregnating 1g MgO with a solution of 0.11g ferric chloride. The impregnated mass was dried at 60°C and 100°C for 12 hours in a rotary vacuum evaporator (EYELA N-1N) and calcined at 450°C in a furnace for 4 hours.

Batch test

Batch tests were performed with the simulated dye wastewater prepared with reactive dye yellow H-E4R or disperse dye navy blue S-GL. The simulated dye wastewater contains 6 g of sodium sulfate, 0.8 g of sodium carbonate, 0.1 g of sodium hydroxide and 0.6 g of dye. Experiments were performed in 500 ml Erlenmeyer flasks containing 200 ml of the simulated dye wastewater. The flasks were open to the air and mounted on bottle holders in a shaker equipped with temperature controller. The shaker was run at 150 rpm and 25°C. The oxidation reaction was started by adding hydrogen peroxide to the simulated wastewater containing Fe/MgO catalysts. As a control, the simulated wastewater without the catalyst was added with hydrogen peroxide.

Continuous test

In continuous tests, the fluidized bed reactor was designed as illustrated schematically in Figure 1. The fluidized bed reactor consists of a Pyrex column having a height of 40 cm and an ID of 2.2 cm. The measured internal liquid volume of the reactor was 150 ml. Volume of the catalyst added to the reactor was 70 ml. Reactor effluent was drawn from near the top and recycled into the bottom assembly to achieve a 100% expansion of catalyst bed. The resulting height of fluidized catalyst bed was 30 cm. Hydrogen peroxide and the wastewater obtained from a dye manufacturing industry in Korea were fed into the recycle line. The catalyst used in the fluidized bed reactor was Fe/MgO with a median particle size of 0.8 mm, based on a sieve analysis. Temperature was maintained at 25°C and pH was monitored. The sample was taken from the effluent reservoir.

Analytical methods

COD and BOD were according to Standard Methods (1995). TOC was analyzed by using a TOC analyzer (Shimadzu 5000A). To quantify the residual hydrogen peroxide, the iodimetric method was used (Schumb, 1955). A typical procedure for the iodimetric method consists of the addition of a sample to 50 ml of a 1% KI solution, acidified with 1 ml of 1:4 H₂SO₄ solution and warmed to 40°C. After stirring and allowing to

stand for 5 minutes, the iodine liberated is titrated with thiosulfate solution. The absorbance of each sample was determined with a spectrophotometer (Shimazu UV-1601). The maximum wavelength for absorbance of reactive dye yellow H-E4R or disperse dye navy blue S-GL were determined experimentally at 410 nm and 303 nm, respectively. Gel permeation chromatographic samples were analyzed at room temperature on a column (Shodex GF-310 HQ) in a chromatograph (Spectra System P2000) equipped with a detector (Shodex RI-71). The solvent was distilled water and its flow rate was 0.6 ml/min.

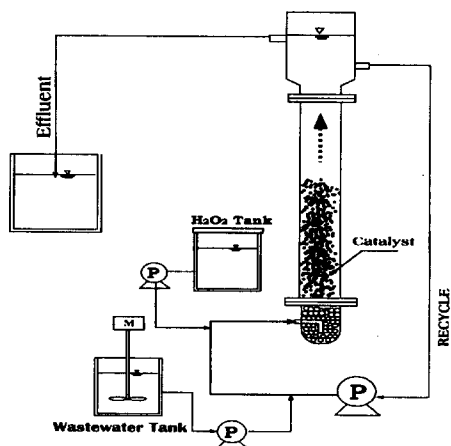


Figure 1. Schematic diagram of lab-scale fluidized bed reactor.

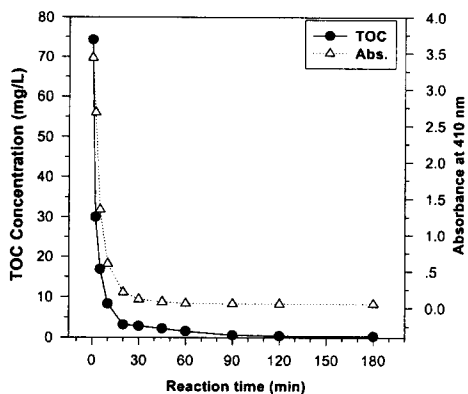


Figure 2. Color and TOC reduction of the simulated dye wastewater containing reactive dye yellow H-E4R in batch reactor.

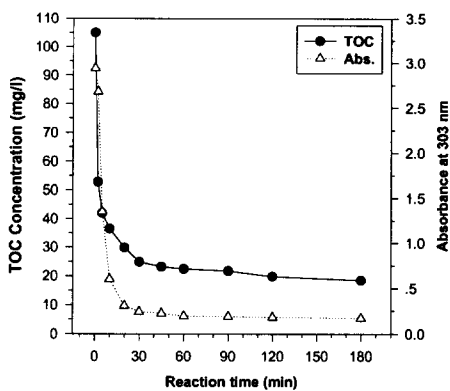


Figure 3. Color and TOC reduction of the simulated dye wastewater containing disperse dye navy blue S-GL in batch reactor.

RESULTS AND DISCUSSION

Decolorizing the simulated dye wastewater in the batch reactor

Figure 2 shows that soluble dye such as reactive dye yellow H-E4R is decolorized in the presence of Fe/MgO catalyst and 1000 mg/l of H_2O_2 in a batch reactor. Absorbance at 410 nm was reduced from 3.4 down to 0.05. TOC concentration also decreased rapidly from 75 mg/l to 5 mg/l and then slowly reduced to 0.1 mg/l. This indicates that almost all of the reactive dye is mineralized through the catalytic oxidation

reaction. Insoluble dye such as disperse dye was also decolorized in the presence of Fe/MgO catalyst and 1000 mg/l of H_2O_2 in a batch reactor. Figure 3 shows that the oxidation of a disperse dye of navy blue S-GL proceeds rapidly and TOC concentration is reduced from 105 mg/l down to 20 mg/l. Absorbance at 303 nm was also decreased rapidly from 3 to 0.2.

Figure 4 shows the results of GPC (Gel Permeation Chromatograph) analysis of the simulated dye wastewater containing disperse dye navy S-GL before and after the catalytic oxidation reaction. According to the chromatogram, the dispersed dye molecule was degraded to a molecule with lower molecular weight in the presence of hydrogen peroxide only (Figure 4 B). However, in the presence of the Fe/MgO catalyst and hydrogen peroxide, dye molecules were degraded to molecules with lower molecular weight and then mineralized to CO_2 (Figure 4 C). A similar chromatogram was obtained for the reactive dye.

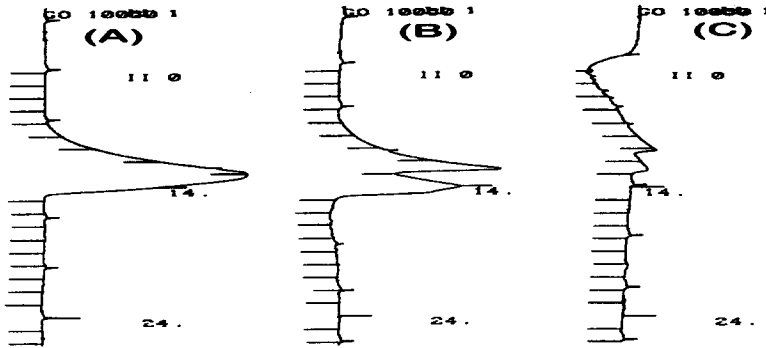


Figure 4. The results of GPC analysis (A: the simulated dye wastewater before the catalytic oxidation, B: the simulated dye wastewater added with hydrogen peroxide, C: the simulated dye wastewater after the catalytic oxidation)

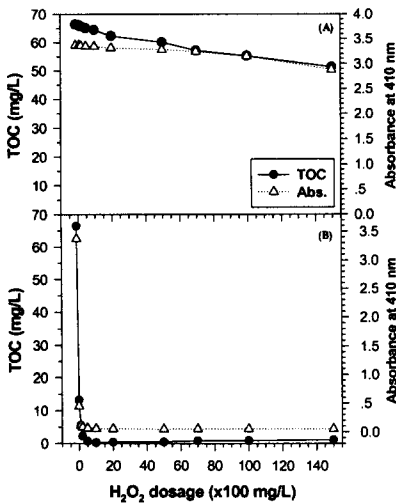


Figure 5. Absorbance and TOC concentration of reactive dye yellow H-E4R after 30 minutes of catalytic oxidation when hydrogen peroxide dosage varies (A: without catalyst, B: with catalyst).

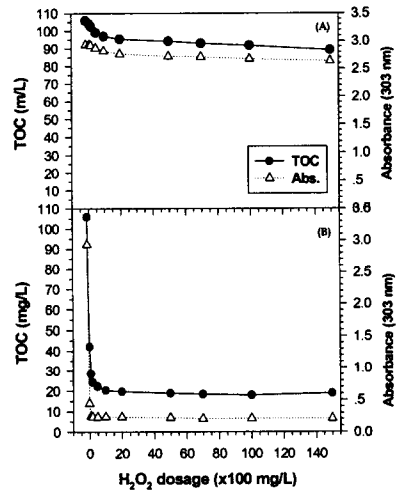


Figure 6. Absorbance and TOC concentration of disperse dye navy blue S-GL after 30 minutes of catalytic oxidation when hydrogen peroxide dosage varies (A: without catalyst, B: with catalyst)

Figure 5 shows that hydrogen peroxide dosage affects the catalytic oxidation rate of reactive dye. In the presence of 5 g/l of Fe/MgO catalyst in batch reactor, hydrogen peroxide dosage was varied from 100 mg/l to 15,000 mg/l. After 30 minutes of catalytic oxidation, absorbance and TOC concentration in the simulated dye wastewater were analyzed. Color was completely removed from the simulated dye wastewater. TOC and color removal rate increased as hydrogen peroxide dosage increased. In the control where only hydrogen peroxide was added, color and TOC reduction were not observed. In Figure 6, the oxidation rate of disperse dye is also shown to depend on hydrogen peroxide dosage. In the presence of 4 g/l of Fe/MgO catalyst in a batch reactor, hydrogen peroxide dosage was varied from 100 mg/l to 15,000 mg/l. TOC concentration in the simulated dye wastewater after 30 minutes of catalytic oxidation was reduced from 105 mg/l to 20 mg/l and color removal was obtained based on absorbance at 303 nm.

Figure 7 shows that catalyst dosage also determines the oxidation rate of reactive dyes. Catalyst dosage was varied from 0.5 g/l to 10 g/l. After 30 minutes of oxidation, residual TOC and absorbance at 410 nm are plotted against catalyst dosage. TOC and color removal rates were dependent on the catalyst dosage. In the case of disperse dye, TOC and color removal rates were also determined by catalyst dosage (Figure 8). The oxidation rate of disperse dye was observed to be lower than that of reactive dye.

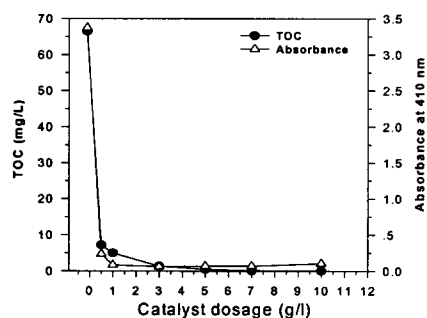


Figure 7. Absorbance and TOC concentration of reactive dye yellow H-E4R in batch reactor after 30 minutes of catalytic oxidation when catalyst dosage varies.

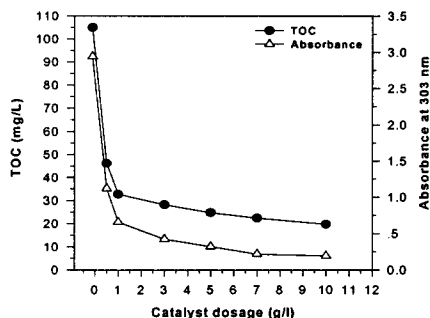


Figure 8. Absorbance and TOC concentration of disperse dye navy blue S-GL after 30 minutes of catalytic oxidation when catalyst dosage varies.

Mechanism

The readiness with which hydrogen peroxide may be decomposed is a characteristic that has been familiar. In the presence of metal ions or metals, hydrogen peroxide can be easily decomposed. Through the decomposition of hydrogen peroxide, the highly reactive hydroxyl radicals ($^{\circ}\text{OH}$) may be produced. The hydroxyl radical generated via the reaction of Fe^{3+} and hydrogen peroxide is well known and reported in the literature. This hydroxyl radical has been shown to partly degrade or mineralize dye molecules (Spadaro *et al.* 1994; Solozhenko *et al.* 1995).

In this study, heterogeneous catalyst Fe/MgO was used to catalyze the oxidation reaction of dye with hydrogen peroxide. When only hydrogen peroxide was added to the simulated dye wastewater, there was no significant reduction in TOC or absorbance. This indicates that there was no adsorption of dye on the catalyst. After hydrogen peroxide is added to the simulated dye wastewater containing Fe/MgO catalysts, it may be first decomposed to produce the hydroxyl radicals as shown in Figure 9. The hydroxyl radicals will mediate the degradation of dyes. Water-soluble dye is degraded more easily than water-insoluble dye. Water-insoluble dyes have been reported to be degraded to water-soluble products which will be degraded further to CO_2 by hydroxyl radicals (Spadaro *et al.*, 1994).

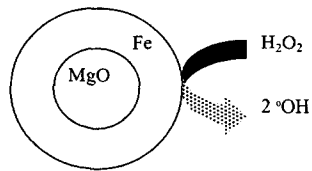


Figure 9. The mechanism of hydroxyl radical production in the presence of Fe/MgO catalyst.

Decolorizing the wastewater from dye manufacturing industry

The wastewater from a dye manufacturing industry was tested to know if Fe/MgO catalyst was able to decolorize dye wastewater containing soluble and insoluble dyes. Figure 10 shows that, in the fluidized bed reactor, organic matters are oxidized and part of them mineralized based on COD analysis. About 30% of COD was removed, however, BOD concentration was slightly increased. Thus BOD/COD ratio was increased from 0.4 to 0.65. This illustrates that biodegradability of the wastewater is increased by the catalytic oxidation reaction (Yu *et al.*, 1994; Mantzavinos and Livingston, 1996). As a control, hydrogen peroxide was added to a batch reactor without catalyst. After 30 minutes, COD concentration was increased due to the residual hydrogen peroxide (Talinli and Anderson, 1992). The presence of residual hydrogen peroxide made BOD/COD ratio decrease to 0.15.

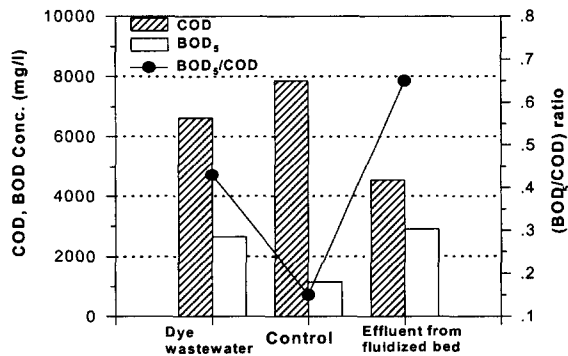


Figure 10. COD and BOD concentration of the wastewater from a dye manufacturing industry before and after catalytic oxidation (control: wastewater added with hydrogen peroxide in the absence of the catalyst).

Figures 11 and 12 show the results obtained from the operation of a lab-scale fluidized bed reactor during 2 months. Figure 11 illustrates that the dye wastewater containing soluble and insoluble dyes is decolorized through catalytic oxidation in the fluidized bed reactor. The effluent from the fluidized bed was too clear to distinguish any color during 30 days of operation. Absorbance of effluent was maintained at lower than 0.1. After 30 days of operation, the effluent became slightly yellowish. The catalysts seemed to lose their activity. Biodegradability of the dye wastewater was enhanced significantly based on BOD/COD ratio during the initial phase of operation and then BOD/COD ratio was maintained at about 0.7. Figure 12 shows that organic matter in the dye wastewater is also degraded and mineralized by the catalytic oxidation. More than 60% of COD removal was obtained during 30 days of operation. During the same period residual hydrogen peroxide remained below 1000 mg/l. After 30 days, COD and hydrogen peroxide concentrations in the effluent from the fluidized bed reactor started to increase. Due to increasing residual hydrogen peroxide, BOD concentration started to decrease.

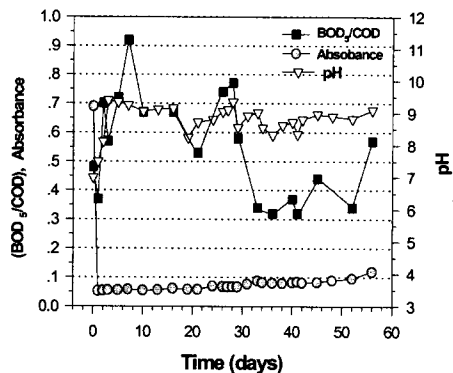


Figure 11. BOD/COD ratio, absorbance and pH of the effluent from fluidized bed reactor fed with the wastewater from a dye manufacturing industry.

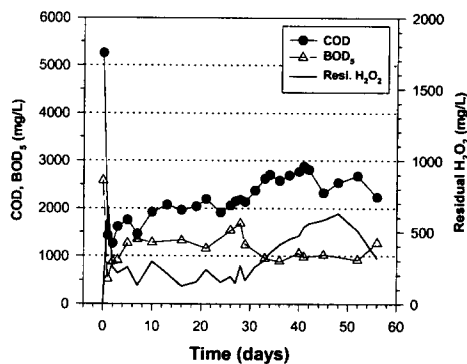


Figure 12. COD, BOD and residual H_2O_2 in the effluent from fluidized bed reactor fed with wastewater from a dye manufacturing industry.

CONCLUSIONS

A novel oxidation technology has been developed to decolorize dye wastewater. Soluble and insoluble dyes in dye wastewater can be decolorized rapidly at room temperature by the catalytic oxidation using Fe/MgO catalyst and hydrogen peroxide as an oxidizing agent. Through the catalytic oxidation those dyes can be degraded to molecules with lower molecular weight and then a part of them can be mineralized based on TOC analysis. The catalytic oxidation rate is dependent on hydrogen peroxide and catalyst dosage. The catalytic oxidation rate increases with increasing hydrogen peroxide and catalyst dosage.

The wastewater from a dye manufacturing industry can be decolorized by the catalytic oxidation using Fe/MgO catalyst fluidizing in a reactor. COD and BOD removal from the dye wastewater can also be possible with the catalytic oxidation. Biodegradability of dye wastewater can be enhanced through the catalytic oxidation. Activity of the catalyst in lab-scale fluidized bed reactor lasts longer than 30 days.

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