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Degradation kinetics of azo dye by ozonation in water

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ABSTRACT：Decomposition of azo dye by ozonation was investigated. A methyl orange (MO) was used as a typical compound of azo dye. Concentration of MO in water was adjusted to 200 mg/L. 2.0% ozone in oxygen was introduced into the MO solution from the bottom of a bubble column reactor. The MO solution was decolorized rapidly by ozonation and the COD and TOC of MO solutions were also decreased with an increase in ozonation time. The color reduction rate of MO solution by ozonation was much faster than those of COD and TOC reduction. The decolorization and degradation were followed by pseudo-first-order kinetics independently

Keywords：Azo Dye, Ozonation, Degradation, Reaction Rate

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1. Introduction

There are about 8000 chemicals used as dyes and the commercial products containing azo dyes reached to about 10,000 items. Azo dyes currently represent around 60% of the world's market for dyes and are widely used in the dyeing of textile fabrics. Azo dyes are also used in the color solvent, ink, paint, varnish paper, plastic, food, drugs and cosmetics industries. The annual world production of textiles is about 30 million tons and the textile industry requires 0.7 million tons of different types of dyes per year. About 12% of the required dyes have been lost during manufacturing and processing operation. Azo dyes are hazardous materials to the environment due to their reactivity, toxicity and recalcitrance[1-7].

Azo dyes are the most commonly utilized reagents owing to the presence of azo group which confers to these chemicals a certain resistance to light, acids, bases and oxygen. The major limitation is determined by their resistance to conventional biological treatment process. Conventional methods including coagulation, activated carbon adsorption and membrane filtration have been used for decolorizing the waste water. However, these methods cannot completely destruct pollutant and need further disposal as well as increasing the treatment cost well. Although these methods resulted in a significant decolorization, there were either costly to apply in the actual field or enable to meet the discharge criteria of wastewater in term of chemical oxygen demand (COD). An affordable and easy-operated control technology without the formation of sludge is needed to comply with today's demanding legislation[1, 3, 8].

Ozone is a powerful oxygenized agent and it can oxygenate some organic and inorganic compounds. Ozonation for color removal is a promising process for the following reasons. No chemical sludge is left in the treated effluent. Ability of both color removal and organic compounds reduction are equipped in one step. A review of the literature shows that ozone cleaves the conjugated bonds of azo dyes and converts high molecular weight compounds of the dye into lower molecules of organic acids leading to color removal and enhancement in biodegradability[9]. The high oxidation potential is able to degrade many organic compounds. Ozone and hydroxyl radicals generated in aqueous solution are able to open the aromatic rings and oxidize inorganic and organic compounds to highest oxidation state[9-11]. In this study, degradation steps of azo dye in water by ozonation were investigated using some analytical methods and degradation kinetics.

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2. Experimental

2. 1 Preparation of sample solution.

Methyl orange (MO) was used as a raw material. MO solution was prepared by the dissolution of MO (0.2 g) in distilled water (1 L). MO has an azo functional group in its structure. The maximum visible wavelength of MO was 464 nm.

2. 2 Ozonation method

The ozone was generated by using a PHZ-12N ozone generator (Koflok). This generator operates based on corona discharge producing ozone from oxygen after separated from air by pressure swing adsorption method. The total flow rate of partially ozonized oxygen gas was 0.3 L min^{-1}. Ozonation was carried out in a bubble column reactor with an internal diameter of 2.5 cm and its height was 80 cm. 100 mL of the MO solution was put into the bubble column reactor. 0.2-2.0% of ozone diluted by oxygen were fed continuously from the bottom of the bubble column reactor through a micro pore diffuser (50 μm).

2. 3 Analytical method

The absorbance of the original and treated samples was measured by using a UV-1700 spectrophotometer (Shimadzu) with a quartz cell. The chemical oxygen demand (COD) of a sample was determined by commonly used potassium permanganate method. The average values were used in this study of three experimental results. Total organic carbon (TOC) was measured by using a TOC-800 (Yanaco).

3. Results and Discussion

3. 1 Effect of ozone concentration by decolorization

Orange color of MO solution was visibly disappeared completely by treatment of 0.2 and 2.0% of ozone in oxygen for 15 and 5 min, respectively. The changes of relative UV absorption intensities of all MO solutions (ln I/I_o) in the course of reaction time by ozonation are shown in Fig. 1. It was observed that the absorption strength of MO solution decreased with an increase in ozone concentration or ozonation time. It was suggested that the azo linkage in chromophore structure of MO was destroyed rapidly by that high concentration (2.0%) of ozone gas treatment. The rate constants (k min^{-1}) of decolorization by ozone (0.2-2.0%) treatment may be determined by the pseudo-first-order kinetics by the results shown in Fig. 1. The rate constants of decomposition of dye by ozonation were determined by the results at 5 min data under every ozone concentration. The rate constants of decolorization of MO were in proportion to the ozone concentration between 0.2 and 1.0% ozone concentration as shown in Fig. 2.

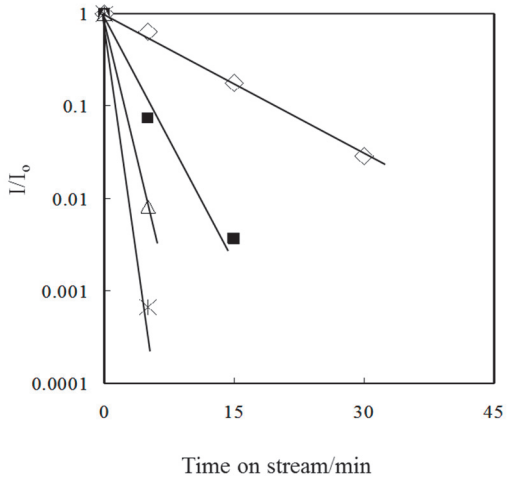

Fig. 1 Changes in absorption strength of MO solutions after treatment by ozone bubbling at 0.2% (◇), 0.5% (■), 1.0% (△) and 2.0% (＊) of ozone in oxygen.

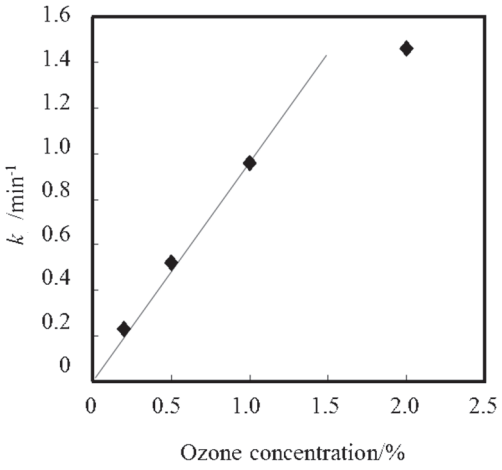

Fig. 2 The average rate constants of decolorization reactions of MO by ozone bubbling in MO solutions for the first 5 min.

3. 2 Change of COD and TOC by ozonation

Generally, many organic chemicals such as dyes, carriers, biocides, ionic and non-ionic surfactants, sizing agents are contained in industrial wastewaters. Therefore, it is hard to determine the degradation degree of every organic compound contained in the wastewater separately. Thus, some global

wastewater parameters such as COD and TOC are used for degradation kinetics of organic compounds by ozonation. Figures 3 and 4 indicate the change of COD, TOC and pH values of MO solutions after treatment of ozone. The large amount of COD and pH values decreased immediately after the beginning of reaction for the first 15 min. The changes of first 5 min are caused by the decomposition of chromophore groups as shown in Fig. 1. It is expected that the changes of first 15 min might be caused by the decomposition of azo bond (-N=N-) in MO and formation of nitric acid by ozonation. On the other hand, the TOC values reduced gradually with an increase in reaction time. The decrease of TOC values for the first 5 min was nearly corresponded with the theoretical value of decomposition of two methyl groups in MO structure.

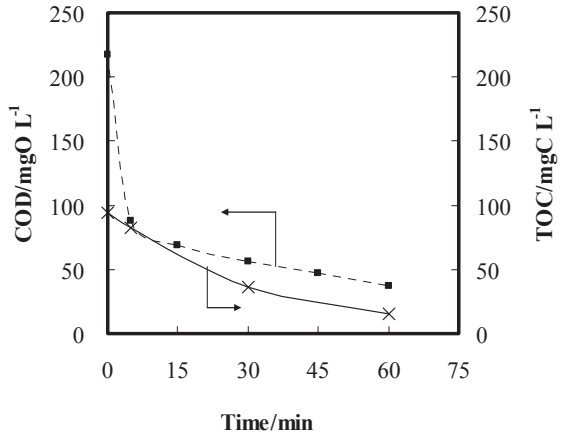

Fig. 3 Changes in COD (■) and TOC (×) of MO solutions treated by ozone at 2.0%.

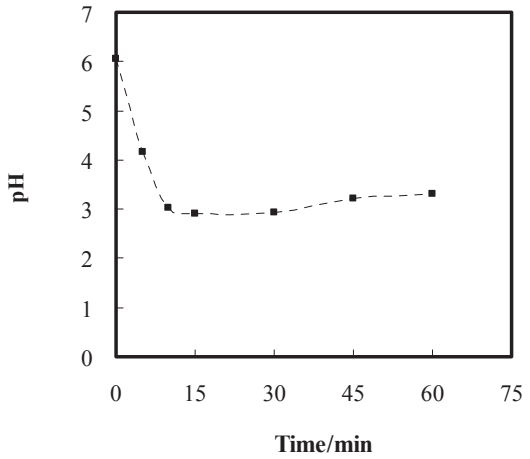

Fig. 4 Change in pH values of MO solutions treated by ozone at 2.0%

Gradual decreases of both the COD and TOC values were observed in Fig. 3 after 15 min reaction. The changes of COD and TOC values after 15 min are caused by the decomposition of aromatic rings in MO structure. On the other hand, the pH values of MO solution after treatment of ozone for 15 min increased gradually as shown in Fig. 4. It might be thought that carbon dioxide (CO_2) was formed from the decomposition of aromatic rings in MO structure and the CO_2 was removed from the solutions. Therefore, the decomposition of MO by ozone was occurred by two consecutive steps. The first degradation step of MO ozonation is the decomposition of chromophore groups (-N=N-, -N-$(CH_3)_2$) and the second degradation step is the decomposition of aromatic rings.

3. 3 Degradation kinetics

The reaction kinetics of decomposition of dye by ozonation was studied. Figure 5 shows the change of relative COD values (ln COD_t/COD_0) of MO solutions after treatment of ozone at 2.0%. When the amount of ozone is in excess or when the ozone concentration is assumed to reach a stationary state at the interface, the oxidation rate follows a pseudo-first-order kinetics with respect to the concentration of the organic compounds in terms of degradation and the rate equation is as follows[1, 12].

$$-\frac{dCa}{dt} = kCa$$

The pseudo-first-order rate constant shows as k and the concentration of organic compound shows as Ca. The rate equation in this study is as follows due to the concentration of organic compounds in MO solution after treated by ozone is represented as [COD]:

$$-\frac{dCOD_t}{dt} = k[COD_0]$$

On integration, the above equation is as follows:

$$\ln(\frac{COD_t}{COD_0}) = -kt$$

In this study, it seems that the results do not fit the simple pseudo-first-order kinetics. Since the decomposition process of MO by ozone was occurred by the two consecutive steps as mentioned above paragraph, it might be thought that the rate constants of degradation were consisted of two reaction steps. The rate constant of first reaction step was determined to k_1 = 0.18 min^{-1} by the beginning 5 min reaction. The rate constant of second reaction step was determined to k_2 = 0.014 min^{-1} by the after 15 min reaction.

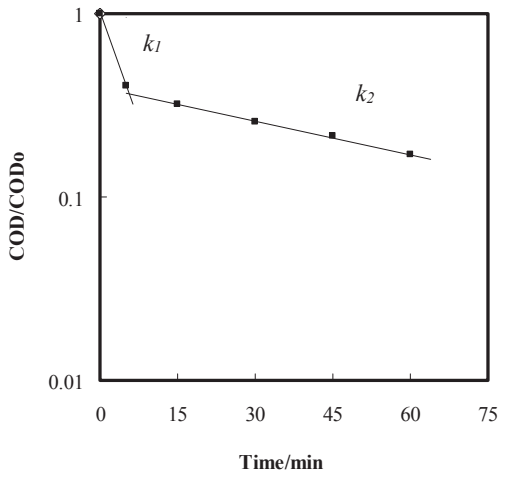

Fig.5 Change in COD_t/COD_0 of MO solutions treated by ozone at 2.0%.

4. Conclusion

Ozonation was effective for reduction of color, COD and TOC of the original MO solution. It was observed that the color, COD and TOC of MO solution decreased with an increase in the reaction time. The MO solution was completely decolorized for 15 min ozonation. COD and TOC reduction ratio of the MO solution reached to 90% and 80%, respectively, for 60 min ozonation. The color reduction rate of MO solution by ozonation was faster than those of COD and TOC reduction. The chromophoric group, such as nitrogen double bonds (-N=N-), was easily decomposed to some compounds having lower molecular weights such as organic and inorganic acid by ozonation. The decolorization and degradation were followed by pseudo-first-order kinetics independently.

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