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Treatment of acid rose dye containing wastewater by ozonizing – biological aerated filter

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Abstract

The ozonizing – biological aerated filter process was used to treat the acid rose dye containing wastewater. The most suitable conditions were identified as follows: the mass ratio of ozone to dye = 4.5, temperature $t = 18–25$ °C, HRT = 3 h and gas/liquid = 4:1. Experimental results showed that ozonizing process had an excellent de-color efficiency and could improve the biodegradability of wastewater. With ozonizing the BOD/COD ratio increased from 0.18 to 0.36, and as a result, the subsequent biological aerated filter could be more effective for further reducing COD and SS concentrations, especially for wastewater with low concentration of SS and COD. After treatment the effluent COD was less than 40 mg/L, SS about 50 mg/L and color less than 20°. It can meet the water quality standards of the treated water reused for industry cooling water.

Keywords: Dyeing wastewater; Acid rose dye; Ozone; Biological aerated filter; Refractory wastewater

1. Introduction

Some dye wastewater, containing various refractory organic pollutants from residual dye, is often discharged into the water environment without appropriate treatments. In order to remove refractory organic pollutants effectively from this kind of wastewater, the optimal treatment process with high quality effluent and low operating cost must be selected, and moreover appropriate operating conditions of the wastewater treatment process are required.

The acid rose dye belongs to xanthene dye which is nonbiodegradable both in aerobic and anaerobic processes [1], and because of its high solubility in water, it is impossible to remove by coagulation. So when a dyeing process mainly used acid rose dye, the wastewater was refractory. At present, the most common treatment for this kind of wastewater is using chloros to de-color via oxidation, but chloros oxidation reduces chemical oxygen demand (COD) only slightly. As a result, it is not able to reach the discharge standard of water pollutants for dye industry. At the same time chloros oxidation produce Trihalomethanes (THMs) which may pose cancer risk [2].

It was found that refractory organic pollutants could become biodegradable after appropriate chemical oxidation [3,4]. The biological treatment unit was followed to reduce COD in order to reach the standard of wastewater discharge or gray water utilization. Due to the characteristic of acid rose red dye containing wastewater which is deep in color and refractory, a combination process of ozonizing – biological aerated filter (BAF) was used. Ozone has outstanding performance in removing the organic pollutants, algae, taste, color and control mutagenic matters. This oxidizer is highly efficient, decomposes quickly and causes no secondary pollution. It is a very promising advanced oxidation process in wastewater treatment. Biological aerated filter (BAF), which incorporates an inert medium to support biomass and filter out suspended solids, is an alternative to the traditional activated sludge process, has the excellent character in removal

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Table 1
The model wastewater quality

pH	Color°	COD (mg/L)	BOD (mg/L)
7	4000	300	60

of suspended solids (SS), chemical oxygen demand (COD), biochemical oxygen demand (BOD), and ammonia nitrogen, especially for low SS and COD wastewater. The key of the process was ozone for oxidizing pretreatment, which increased the biodegradability of the wastewater, and most of the organic matter was removed in the next step by BAF.

2. Experimental

2.1. Model wastewater preparation

The acid rose dye is widely used for polyamide fabric dyeing. It is estimated that producing 1 ton of this kind of fabric will consume 2 kg of dye, 2.5 kg of degreasing agent and dye leveler, and discharge about 10 tons of wastewater. Ten percent of dye is wasted and discharged into the wastewater, and this kind of wastewater contains many pollutants such as residual acid rose dye, auxiliaries, and chemical impurities which are left in the fabric. The model wastewater was confected in the laboratory according to the main pollutants found in practical wastewater, i.e., acid rose dye of mass concentration 30 mg/L, degreasing agent and dye leveler of concentration 200 mg/L. The model wastewater quality is shown in Table 1.

2.2. Apparatus and operation

The experimental apparatus mainly composed of two parts; one part was the ozone oxidation equipment, while another part was biological aerated filter treatment apparatus. Fig. 1 shows the schematic of the process. All equipments are tabulated in Table 2.

The ozonizer flow rate was measured by the air flowmeter and with the concentration of ozone which was surveyed in advance, and so the ozone dosage can be calculated. There was a pore bubbler in the bottom of the ozone reactor which made the ozone dissolve into the wastewater quickly.

2.3. Analytical method

Standard methods of P.R. China was used for measuring color degrees, pH, COD and BOD_5 of the wastewater. The concentration of ozone was measured by iodimetry [5]. In addition, the experiment had drawn the biodegradation curve of COD to estimate the aerobic biodegradability of wastewater [6].

2.3.1. Definitions and units of biodegradation curve

The amount of degradation attained at the end of the test is reported as the Biodegradability in the Zahn–Wellens test:

$$D_T = \left[1 - \frac{(C_T - C_B)}{(C_A - C_{BA})}\right] \times 100$$

where:

D_T = biodegradation (%) at time T,
C_A = COD values in the test mixture measured 3 h after the beginning of the test (mg/L),
C_T = COD values in the test mixture at time T of sampling (mg/L),
C_B = COD value of the blank at time T of sampling (mg/L),

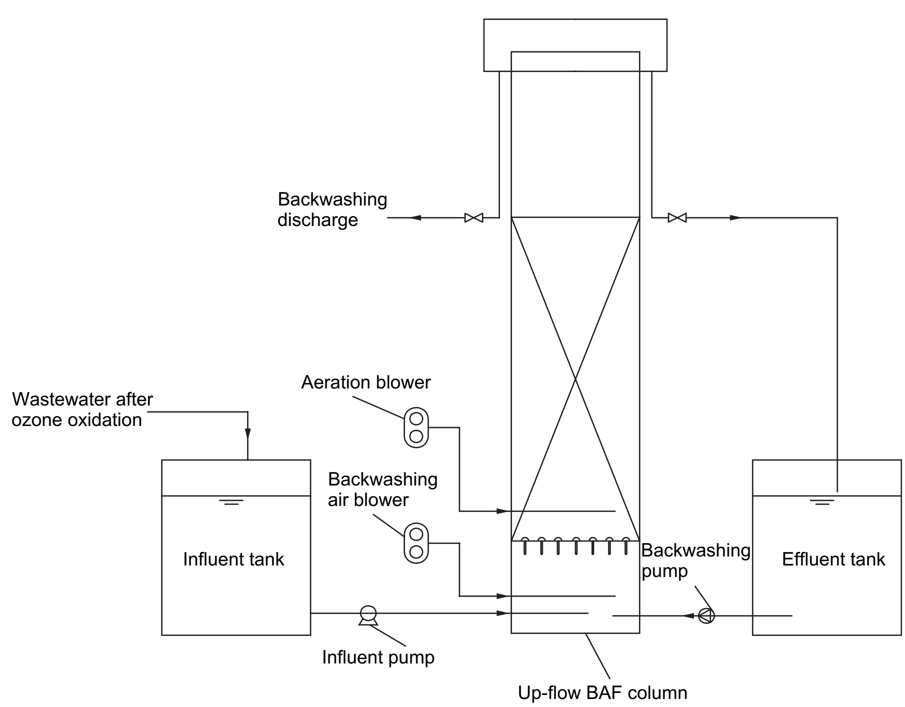

Fig. 1. Flowsheet of biological aerated filter process.

Table 2
Main equipments for the experiment

Sequence number	Appellation	Specification and type
1	Ozonizer	2 mg/L × 4
2	Air flowmeter	0–0.16 m^3/h
3	Ozone reactor	Φ 115 mm × 1200 mm
4	Influent tank	35 cm × 30 cm × 50 cm
5	Influent pump	LPH6 $Q_{max} = 18.9$ L/h
6	Up-flow BAF column	Φ 150 mm × 1200 mm
7	Aeration blower	ACO328 $Q = 75$ L/min
8	Backwashing air blower	ACO500 $Q = 470$ L/min
9	Backwashing pump	WZ10-10 $Q = 10$ L/min
10	Effluent tank	20 cm × 30 cm × 50 cm

C_{BA} = COD value of the blank, measured 3 h after the beginning of the test (mg/L).

The extent of degradation is rounded to the nearest full percent.

Percentage degradation is stated as the percentage COD removal of the tested substance.

2.3.2. Plot of biodegradation curve

Activated sludge, mineral nutrients and the test material as the sole carbon source in an aqueous solution are placed together in a glass vessel equipped with an agitator and an aerator. The mixture is agitated and aerated at 20–25 °C under diffuse for up to 28 days. The degradation process is monitored by determination of the COD values in the filtered solution daily or at other appropriate regular time intervals. The ratio of eliminated COD after each interval to the value 3 h after the start is expressed as percentage biodegradation which serves as the measure of the extent of degradation at this time. The result is plotted versus time to give the biodegradation curve.

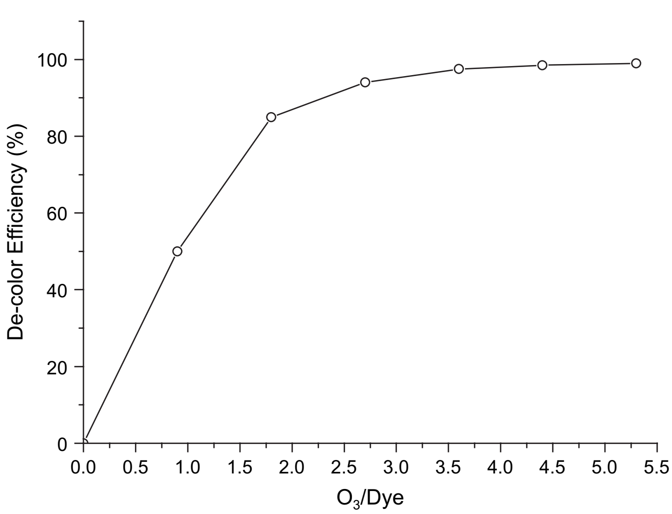

Fig. 2. Effect of ozonizing oxidation on de-color.

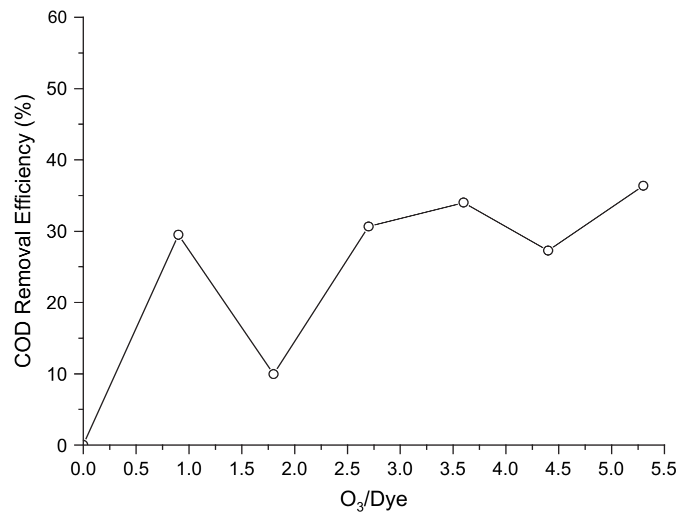

Fig. 3. Effect of ozonizing oxidation on COD removal.

3. Results and discussion

3.1. Effect of ozonizing oxidation on de-color efficiency

Fig. 2 shows the effect of O_3/dye ratios on the de-color efficiency in the oxidation of the model wastewater by ozone. The de-color ratio increased with increase in the ozone dosage. When the mass ratio of ozone to dye was 4.5, the de-color efficiency was up to more than 99%, and the color degree of the resulting model wastewater was less than 20 after oxidation. When the ratio of ozone to dye was 3.6, the color degree of model wastewater was about 40 after ozone oxidation. The results thus indicated that ozone oxidation had excellent de-color efficiency.

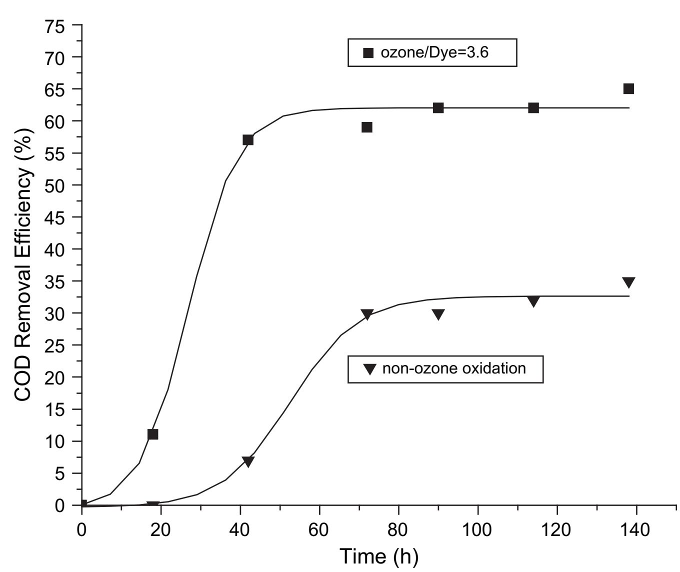

Fig. 4. Biodegradation curve of influent and effluent at the ratio of ozone to dye at 3.6.

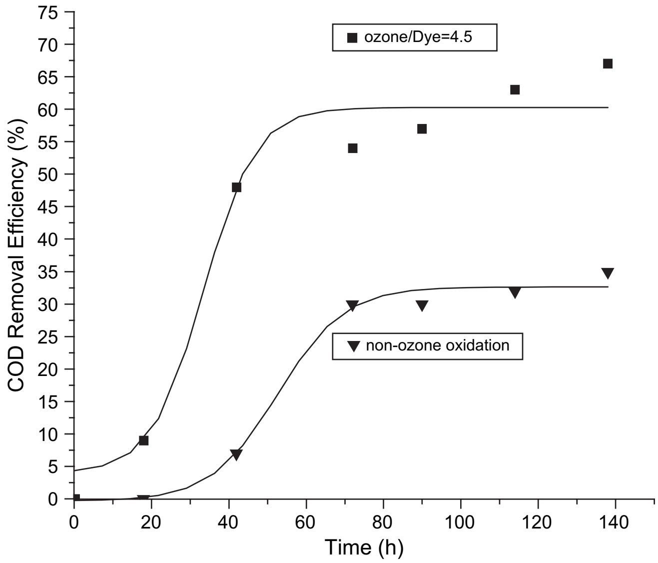

Fig. 5. Biodegradation curve of influent and effluent at the ratio of ozone to dye at 4.5.

3.2. Effect of ozonizing oxidation on COD removal

The COD removal from the model wastewater by ozonizing oxidation is shown in Fig. 3. When the ratio of ozone to dye was increased from 3.6 to 4.5, the COD removal efficiency of the model wastewater achieved was about 30%, and continuous increase of ozone dosage had not increased the efficiency in COD removal quickly.

3.3. Effect of ozonizing oxidation on biodegradability of wastewater

In general, chemical oxidation can change the molecular structure of compounds which are nonbiodegradable and rupture them into smaller molecules, the intermediate products usually have better aerobic biodegradability than original compounds [7]. This experiment studied the biodegradation curve of the model wastewater which had been subjected to ozone oxidation treatment in the ratio of ozone to dye 3.6 and 4.5, respectively. The biodegradation curves of oxidation influent and effluent are shown in Figs. 4 and 5.

A significant increase in the biodegradability (Figs. 4 and 5) shown in the experiment with ozone oxidation not only shortened the adaptive period of the microbe greatly, but also increased the value of COD_B/COD from 0.3 to 0.6 (COD_B was the total COD which can be biodegraded at the end of the Zahn–Wellens test). According to the conversion relation of COD_B and BOD, the value of BOD/COD, achieved as 0.36 after ozone oxidation, shows that the model wastewater had become biodegradable.

3.4. Wastewater treatment by ozonizing – biological aerated filter process

3.4.1. Effect of ozone dosage on COD removal

The model wastewater was treated by the ozonizing – biological aerated filter process in which the hydraulic retention time (HRT) of BAF was fixed at 5 h, the ratio of gas to liquid was 4 and the temperature of wastewater was 18–25 °C, and change in the addition of ozone dosage was carried out. The experimental results are shown in Table 3. The COD removal ratio of the non-ozone process was only 30% and the color degrees even had slight rise. On the other hand, when the process added ozone to pre-oxidation, the removal rate of COD and color degrees had increased significantly; when the ratio of ozone to dye was 4.5, COD removal rate of the model wastewater was 91.5% and the color of effluent was reduced to about 20°.

3.4.2. Effect of hydraulic retention time of BAF on COD removal

On the other hand, in determining the effect of hydraulic retention time, we fixed the ratio of ozone to dye at 4.5, the ratio of gas to liquid was 4 and the temperature of wastewater was 18–25 °C, and changed the hydraulic retention time of BAF. The treatment efficiency of this process is shown in Fig. 6. In the experiment performed with the hydraulic retention time of BAF at 3 h, the average COD of effluent was about 33 mg/L and the COD average removal rate of the process reached about 88%. In the case of 5 h, the average COD was reduced to 25 mg/L and the average removal rate was 91.5%. In the case of 7 h, the average COD was decreased further to 16 mg/L and the average COD removal rate went up to 95%. The process showed excellent treatment efficiency for the model wastewater.

4. Conclusions

(1) The ozone oxidation showed excellent performance in the decolorization of acid rose red dye containing wastewater.

Table 3
Effect of ozone dosage in wastewater treatment by ozonizing – biological aerated filter process

Ozone/dye	COD (mg/L)			COD removal rate (%)			Color (°)		
	Influent	Ozone	Effluent	Ozone	BAF	Total	Influent	Ozone	Effluent
0	297.81	297.81	210.80	0	29.22	29.22	4000	4000	4500
1.8	297.81	261.98	47.62	12.03	81.82	84.01	4000	800	800
2.7	297.81	230.30	33.30	22.67	85.54	88.82	4000	200	200
3.6	297.81	207.10	30.46	30.46	85.29	89.77	4000	40	40
4.5	297.81	203.05	25.25	31.82	87.56	91.52	4000	20	20

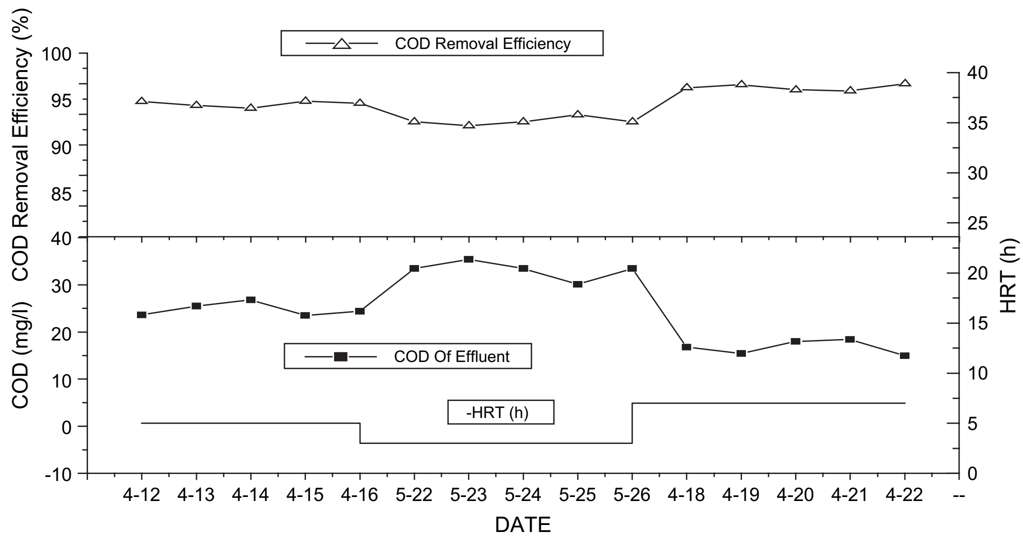

Fig. 6. Effect of retention time of BAF on wastewater treatment.

When added at the ratio, of ozone to dye, of 4.5, the decolor efficiency of the model wastewater was more than 99% and the color of effluent reduced to 20°.

(2) The ozone oxidation could significantly improve the biodegradability of the model wastewater. When used at the ratio, of ozone to dye, of 4.5, the value of BOD/COD increased from 0.18 to 0.36.

(3) The ozonizing − biological aerated filter process is a promising technology for refractory wastewater treatment. In the treatment of the model wastewater, the color of effluent obtained was 20°, COD less than 40 mg/L and SS about 50 mg/L. The treatment cost was about 2 yuan RMB per ton wastewater, suggesting that the ozonizing − biological aerated filter is an effective process for this kind of wastewater treatment in terms of its high quality effluent and low operating cost.

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