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Research Article

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Study on the treatment of high concentration organic waste water by ozone advanced chemical oxidation

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ABSTRACT

Ozone oxidation can remove the organics in wastewater effectively and be applied as advanced oxidation process for the treatment of wastewater, which has been developed as an independent field overseas and becomes research focus with broad prospect. Ozone oxidation has great advantages in aspects such as chromaticity removal, sterilization and biodegradability improvement of wastewater.

Keywords: Ozone; high concentration organic wastewater; advanced chemical oxidation

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INTRODUCTION

Ozone (O_3) , an allotrope of oxygen and called as rich oxygen, has a molecular weight about 48 and strong oxidative ability, whose redox potential (ORP) is 2.07 V, 0.43 V lower than that of the strongest F_2, but 0.72 V and 0.57 V higher than those of Cl_2 and ClO_2, individually. Ozone is extremely unstable in wastewater and can produce strong oxidative substances such as single oxygen radical (·O) and hydroxyl radical (OH) when decomposing into oxygen with relatively low oxidative ability. At temperature of 20 °C, the half-life period of O_3 in water is about 15～40 min[1]. Ozone can react with almost all metals except gold and platinum, and organics or groups such as —OH, —SH, =S, —NH_2 and —CHO[2]. Therefore, ozone oxidation technology can be used for the oxidative degradation of inorganic substances and organics in wastewater[3-6].

EXPERIMENTAL SECTION

2.1 Wastewater quality

The water quality indexes of wastewater samples in ozone oxidation reactor were as follows: COD 318 mg/L, BOD_5 6 mg/L, amino nitrogen (NH_3-N) 7mg/L, SS 124 mg/L, chromaticity 142 mg/L. To optimize those ozone oxidation conditions, ozone oxidation experiments were carried out to study the effects of initial system pH, flow rate of ozone, oxidation temperature and reaction time.

2.2 Methods

Those values of BOD_5, COD, pH, chromaticity and NH_3-N were determined according to corresponding national standards. The concentration of ozone was titrated by KI and $Na_2S_2O_3$ solvents.

RESULTS AND DISCUSSION

3.1 Effect of ozone concentration on the removal of COD, BOD_5 and chromaticity

3.1.1 Effect of ozone concentration on the removal of COD and BOD_5

Wastewater was cycled into the reactor through pumper and the flow rate of ozone was increased gradually to 262

mg/L according to the actual volume of reactor. When the flow rate reached stable, ozone was charged into the experimental reactor and the wastewater was sampled every period of time to detect items such as pH, COD, BOD_5 and chromaticity.

The change of COD and BOD_5 of wastewater output at different concentrations of ozone was shown in Figure 3-1.

According to those data in Figure 3-1, the drop of COD in wastewater increased with the consumption of ozone, as well as the increase of BOD_5. When the concentration of ozone was 235 mg/L, COD decreased from 318mg/L to 152mg/L, BOD_5 increased from 6mg/L to 72 mg/L and the value of BOD_5/COD was 0.37. While the concentration of ozone was 262mg/L, the value of wastewater COD dropped from 318 mg/L to 179 mg/L, BOD_5 increased from 6mg/L to 84mg /L and BOD_5 /COD was 0.5. Therefore, biodegradability of wastewater after ozone oxidation can be improved greatly through the increase of ozone consumption [7]. The reason for this is that organics with large molecules and uneasy to be oxidized tend to be decomposed into small molecules such as aldehyde, ketone and carboxyle acid through increasing ozone consumption, which are easy to be degraded further by microorganism.

The concentration of ozone used in this study was 1/20~1/10 of those reported in previous literatures. Hence, improvement of the ozone oxidation efficiency and biodegradability of wastewater can have influence on the practical engineering application to some extent in future.

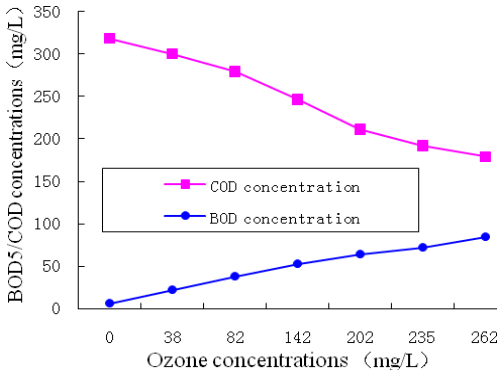

Figure 3-1 Changes of COD and BOD_5 at different concentrations of ozone

3.1.2 Effect of ozone concentration on the removal of chromaticity

The removal rates of chromaticity at different ozone concentrations were listed in Figure 3-2.

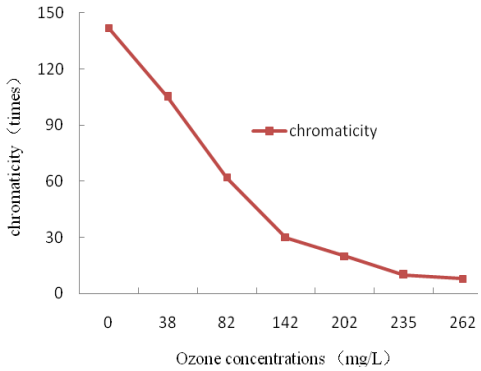

Figure 3-2 Effect of ozone concentration on chromaticity removal

According to Figure 3-2, the removal rate of chromaticity was increased with ozone consumption. When the concentration of ozone was 136 mg/L, the chromaticity of wastewater was about 40 (dilution times), reaching the requirement in the national standard for the pollution control of municipal solid waste landfill (GB16889-2008). In case of ozone concentration 235 mg/L, the chromaticity of water was about 10 (dilution times). When the concentration of ozone was 136 mg/L, the chromaticity of water was about 8 (dilution times). Subsequently, the removal rate of chromaticity remained almost stable with further increase of ozone consumption. Judging from the decrease of chromaticity removal, it seems that ozone oxidation process has a higher efficiency than coagulation process, which is similar to those results of some researchers.

3.2 Effects of oxidation time on the removal rates of COD and chromaticity

3.2.1 Effect of reaction time on the treatment of COD

Under conditions of ozone concentration 262 mg/L and pH 7.51, COD of output wastewater after ozone oxidation for different periods of time was detected to study the effect of oxidation time. The result was shown in Figure 3-3.

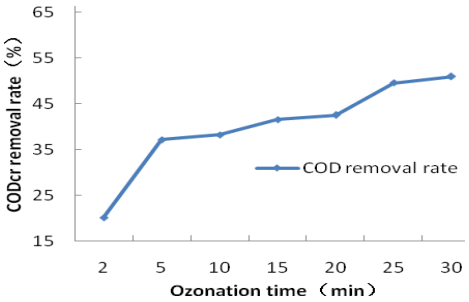

Figure 3-3 Effect of ozone oxidation time on the removal of COD of wastewater

As shown in Figure 3-3, COD of wastewater decreased gradually with oxidation time, especially in the original stages, the decrease of COD was significant, while the decrease rate turned out to be slow subsequently. The decrease of COD was due to the decomposition of organics caused by ozone oxidation, but there are still other organics in wastewater, which are not easy to be oxidized by ozone. Therefore, COD varied little in the later treatment stages. This proves that there exists an optimum oxidation time for the best oxidation efficiency during removal of organics by ozone oxidation. Since the COD removal rate reached 43.71 %, it is obvious that the optimum oxidation time was 30 min.

3.2.2 Effect of oxidation time on the removal of chromaticity

Under conditions of ozone consumption 262 mg/L and solvent pH 7.51, removal rates of chromaticity of wastewater after treatment for different periods of time were detected and the result was shown in 3-4.

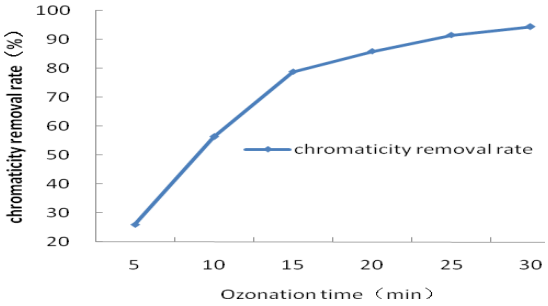

Figure 3-4 Effect of ozone oxidation time on the removal of chromaticity

It can be seen in Figure 3-4 that the chromaticity of water reduced with oxidation time. Especially in early ozone oxidation stages, this decrease was significant. Afterwards, the rate became slow. The reason for this is that ozone degraded some organics in the wastewater, however, there were other un-degradable organics, leading the variation of chromaticity became smaller and smaller. It can be concluded that there is an optimum oxidation time for the treatment of wastewater using ozone. According to the data and Figure 3-4, this optimum oxidation time is 30min. In this case, the value of chromaticity dropped from 142 mg/L to 8 mg/L and the removal rate of chromaticity reached 94.37%.

3. 3 Effects of pH on the removals of COD and chromaticity

3.3.1 Effect of pH on the removal of COD

The effect of pH on the removal of COD under conditions of ozone consumption 262 mg/L and oxidation time 30min was shown in Figure 3-5.

In Figure 3-6, the efficiency of COD removal was improved with pH of wastewater. The possible reason for this is that ozone can produce stronger oxidative substance hydroxyl radical (·OH) in basic environment, which can accelerate the oxidation of un-biodegradation organics. Therefore, quick lime was applied and added into the wastewater to adjust pH value and study the effect of pH on the removal of COD. However, the difference between COD removal rates at pH 10.2 and pH 7.51 was within 15 %. Furthermore, the oxidation efficiency is usually high

at the beginning and has small difference no matter pH high or slow. Hence, pH was kept 7.51 during the treatment of wastewater.

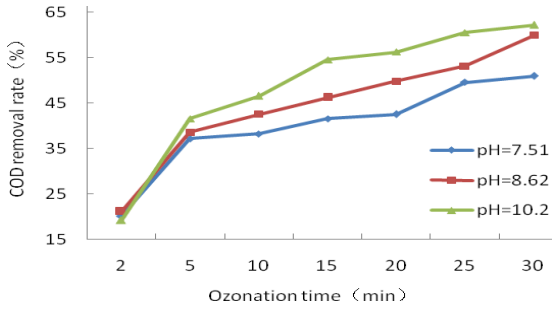

Figure 3-5 Effect of pH on the removal rate of COD

3.3.2 Effect of pH on the removal of chromaticity

The effect of pH on the removal of chromaticity was studied under conditions of ozone consumption 262 mg/L, oxidation time 30min and the result was shown in Figure 3-6.

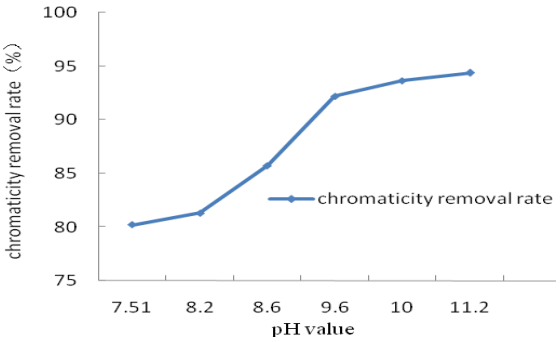

Figure 3-6 Effect of pH on the removal rate of chromaticity

According to Figure 3-6, the efficiency of chromaticity removal was improved with pH. The reason for this is that ozone can produce stronger oxidative substance hydroxyl radical (OH) in basic environment, which can accelerate the oxidation of un-biodegradation organics. Therefore, to study the effect of pH on the removal of chromaticity, quick lime was applied and added into the wastewater to adjust the pH value. However, the difference between chromaticity removal rates at pH 10.2 and pH 7.51 was within 15%. Furthermore, no matter how much the solvent pH is, the oxidation efficiency is usually high at the beginning and the difference is small. So, pH was kept 7.51 during the treatment of wastewater.

3.4 Effects of temperature on the removal of COD and chromaticity

Under conditions of ozone intake flow rate 262mg/L, pH 7.51 and oxidation time 30 min, the removal rates of COD and chromaticity at 5 °C, 15 °C, 25 °C, 35 °C and 45 °C were detected individually to study the effect of temperature.

3.4.1 Effect of temperature on the removal of COD

The removal rates of COD at different temperatures were shown in Figure 3-7.

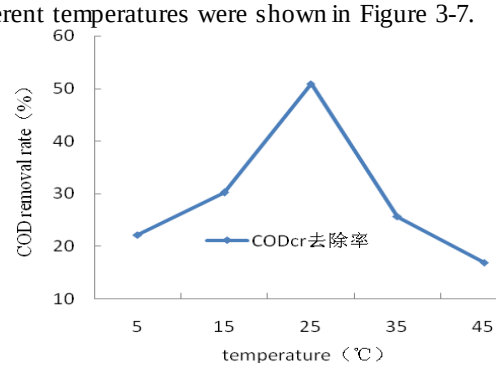

Figure 3-7 Effect of oxidation temperature on the removal of COD

The removal rate was 22.16 % at 5 °C and increased to 50.86 % at 25 °C. With further increase of temperature, the removal rate of COD reduced and reached 16.87 % at 45 °C, which proves that temperature has significant influence on the removal of COD. Therefore, the temperature was controlled within a range from 15 °C to 25 °C in this study.

3.4.2 Effect of temperature on the remove of chromaticity

The results of chromaticity removal rates at different temperatures were presented in Figure 3-8.

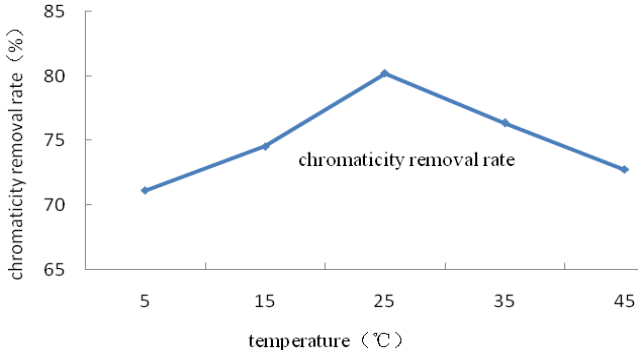

Figure 3-8 Effect of temperature on the removal of chromaticity

The removal rates of chromaticity were 77.13 % and 80.21 % at temperatures 5 °C and 25 °C, respectively. With further increase of temperature, the removal rate reduced and reached 72.75 % at 45 °C. Hence, oxidation temperature was selected at around 25 °C.

RESULTS AND DISCUSSION

4.1 Effect of ozone oxidation on the biodegradability of wastewater

Since ozone can destruct structures of large molecule organics into small molecules which can be further degraded by biodegradation, the biodegradability of wastewater can be improved effectively. The variation of biodegradability with oxidation time was recorded under conditions of wastewater pH 7.51 and ozone concentration 262 mg/L to effect of ozone oxidation.

As shown in Figure 3-9, the biodegradability of wastewater was improved significantly and reached the highest value when oxidation time was 30 min.

Due to the amount increase of substances easy for biochemical degradation and the decrease of toxicity caused by ozone oxidation，the value of BOD_5/COD (B/C) increased gradually from 0.02 to 0.47 with the time, reaching the maximum value after 30 min ozone oxidation. The reason for the decrease of B/C after 30 min was that oxidation time was too long and ozone degraded those substances easy for biodegradation.

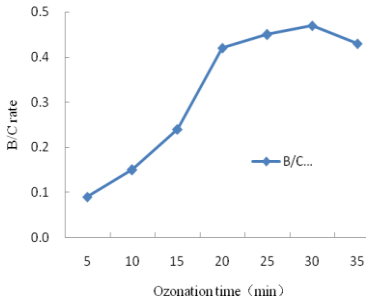

Figure 3-9 Effect of ozone o the biodegradability of wastewater

4.2 Analysis of water quality after ozone oxidation

Water quality indexes of wastewater after ozone oxidation were listed in Table1.

Table1 Characteristics of wastewater after treatment by ozone oxidation

Quality index	COD (mg/L)	BOD_5 (mg/L)	NH_3-N (mg/L)	TP (mg/L)	SS (mg/L)	pH	Chromaticity (dilution times)
Value	179	84	6	not detected	18	6.92	8
Limit value	100	30	25	3	30	--	40

It can be seen in Table1 that the value of NH_3-N in wastewater after oxidation was 6 mg/L, low enough to eliminate the mistrust that amino nitrogen would inhibit biodegradation. Furthermore, TP was not detected and pH was 6.92，which was beneficial to the growth of microorganism. Chromaticity was 8 and lower than the limit value 40 in the new national standard. Although COD was 179 mg/L and higher than the limit value in national standard, the ratio of BOD_5 to COD was about 0.47, which means wastewater has good biodegradability and can be treated subsequently by biodegradation using SBR process.

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