Process Research on Advanced Treatment of Yeast Wastewater Through Enhanced Catalytic Ozonation

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ABSTRACT: After the secondary treatment of yeast wastewater, the chemical oxygen demand (COD) usually remains very high (approximately 800–1500mg/L) in this effluent, which contains various degradation-resistant substances. Because of the presence of bicarbonate ions, which are the inhibitor of ·OH free radical chain reaction, the direct ozonation of a secondary effluent treatment is limited. In this study, the addition of calcium hydroxide as a pretreatment not only eliminates adverse effects of bicarbonate ions on chain reaction of hydroxyl free radical's generation, but also enhances the indirect ozonation by increasing the pH value up to 11. At the same time, heterogeneous catalytic ozonation treatment is also conducted on the secondary effluent of yeast wastewater by the use of manganese sand (containing manganese dioxide as an effective constituent). The COD of the raw water is reduced to 389 mg/L from 853 mg/L, and the total removal rate reaches 54%. Process analysis is conducted on the pH value, Oxidation-Reduction Potential (ORP) value, and the concentration of dissolved ozone through an online monitoring system. A control method is also proposed to strengthen the catalytic ozonation technology by combining the ozone consumption and COD removal variation.

1. INTRODUCTION

Yeast industry is a new industry in China, with broad prospects for development. At the same time, yeast industry greatly reduces sugar molasses pollution, and the government vigorously supports the growth of yeast enterprises. China's current yeast has been produced by more than 10 enterprises, with an annual volume of about 129 thousand tons (dry yeast). Various volumes of wastewater from production processes are different among enterprises, and the amount of water is in the range of 80–130 m³ wastewater for each ton of yeast-production. At present, most of Chinese enterprises wastewater treatment processes are planned by Purac and other well-known international water treatment design and construction companies. But the treated sewage cannot be discharged directly to rivers or lakes. The sewage treatment is a continuous process, where the waste water is discharged into the centralized sewage treatment plant as well as the urban domestic sewage treatment plant.

Yeast wastewater has high pollutant concentration, high colors, high amounts of degradation-resistant substances, and high salt content, among others [1]. The main yeast wastewater treatment technology includes the combined biological treatments of anaerobic and aerobic treatments, and the advanced treatment technology of chemical precipitation [2,3]. The COD of the effluent in the biological treatment step is relatively high, (i.e. 800–1500 mg/L) [4,5]. Chemical coagulation process uses the iron salts, but the dosage of ferric salts has two problems: first, the operation cost of iron processing is too high; second, it causes serious corrosion on the storage tank and pipeline. Taking a yeast production enterprise as an example, the operating cost of the whole wastewater treatment process was 30.6 Yuan for each ton of wastewater, and the final effluent quality was COD 600~700 mg/L. At the biological treatment stage wastewater treatment costs average about 5 Yuan per ton, and chemical processing part costs for 25.6 Yuan per ton. (the cost of chemicals is 15.3 Yuan, the sludge treatment costs 6.6 Yuan, wear and tear equipment costs 3.7 Yuan). Economic pressure on corporate environmental protection, and in general, the amount of iron deficiency cause, the effluent COD to reach above 700 mg/L.

Extensive studies have been conducted on ozone, which is used as a strong oxidant in the field of wastewater treatment [6], including the removal of colors [7,8], improvement on biodegradability [9–10], disinfection [11,12], removal of particular pollutants
[13–15], and catalytic ozonation [16–18]. However, investigations on this complex system are rare because the oxidation process of the ozone is complex. Many intermediate products also exist, and the influence of the substances in water (such as accelerator and inhibitor) on the reaction cannot be controlled easily. Both the investment cost and operating cost of ozone equipment in practical application are extremely high. The water quality of real production wastewater is highly complex, and the efficient use of ozone is difficult. Therefore, the application of ozone is rare in the field of wastewater treatment in practical application.

In this study, a real yeast wastewater is used as a treatment object. Adding Calcium hydroxide as a pre-treatment is used to remove bicarbonate ions in wastewater, thereby eliminating its disadvantageous effect on indirect ozone oxidation, enabling the pH value to be within the alkaline range at the same time, strengthening the treatment effect of catalytic ozonation. Heterogeneous catalytic ozonation technology is applied to the complex system to remove COD. The reaction processes of direct ozone oxidation and enhanced catalytic ozonation are also studied by comparing the online monitoring process parameters. A basis for ozone oxidation process control in the complex system is provided while studying COD removal and ozone consumption through advanced treatment on real wastewater using ozone catalytic oxidation technology.

2. EXPERIMENT PART

2.1. Introduction to Experimental Apparatuses

In the experiment, yeast wastewater is treated by using apparatuses (Figure 1). The contact oxidation tower used is a bubbling type reactor that is 150 cm in height, has an internal diameter of 5 cm, has an effective volume of 2 L, and is made of organic glass. Three electrodes are installed in a constant current device, i.e., a pH value electrode, a liquid-phase ozone concentration electrode and an oxidation-reduction potential electrode. These three electrodes correspond to the three parameters for monitoring the operation parameters in the ozone contact oxidation tower.

The online monitoring system mainly comprises the following parameters and devices: a gas-phase ozone concentration meter with a measurement range of 0–200 mg/L; a liquid-phase ozone concentration meter with a measurement range of 0 (model pH7685); pH measurement range of 0–14.00; ORP measurement range of –1000 mV to +1000 mV; a constant current device for pH, ORP, and liquid-phase ozone simultaneously; a data collection module with a model of FS-1208 and a software kit of TraceDAQ.

2.2. Experimental Water Quality and Material

The water used for the experiment is taken from the

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effluent of a secondary sedimentation tank at a waste water treatment plant (Hebei Mali Food Co., Ltd.), and the water quality indexes are shown in the following table in detail.

Manganese sand is used as a catalyst. The effective constituent of this catalyst is manganese dioxide. The content of manganese sand is more than 35%, and its density is 2.8 g/cm³. Calcium hydroxide is used as a pretreating agent. This pretreating agent is of analytical purity. COD determination is conducted by using the HACH fast method (HACH reagent HR1500) in cooperation with a spectrophotometer DR6000.

### 2.3. Experimental Method

Direct ozone oxidation and ozone catalytic oxidation are both conducted intermittently in the batch reactor. The raw water enters the ozone contact oxidation tower through the water pump. The ozone used in the experiment takes oxygen as a gas source. The oxygen enters the ozone generator to generate ozone. Then, the ozone enters from the micro porous aeration plate at the bottom of the ozone contact oxidation tower. At the upper part of the ozone contact oxidation tower, the tail gas is collected and then discharged into the tail gas absorption bottle containing a potassium iodide solution.

The catalyst used in the experimental process of catalytic ozonation is manganese sand; the effective constituent is manganese dioxide. Manganese sand is placed in the reactor and participates in the reaction in the form of a fixed bed. The system consists of an ozone contact oxidation tower and a loop circuit to form a continuous bubbling column reactor. In the reaction process, a water sample is pumped from the upper part of the contact tower to the constant current device. Thereafter, the water sample is returned to the bottom of the contact tower by backflow to achieve a uniformly mixed state of liquid in the contact tower. This is a continuous cycle and the quality of water sample is almost the same, whether in the contact tower or in the constant current device.

Bicarbonate ions are removed by adding calcium hydroxide. The pretreatment process of calcium hydroxide dosage is conducted in the beaker. The reaction between calcium hydroxide and bicarbonate ions in the solution is shown in the following Equation (1).

$$\text{Ca(OH)}_2 + \text{HCO}_3^- \rightarrow \text{CaCO}_3 \downarrow + \text{H}_2\text{O} + \text{OH}^-$$

The concentration of the bicarbonate ions in raw water is 187 mg/L and is calculated accordingly (227 mg/L of calcium hydroxide is added). A total of 400 mg calcium hydroxide is added to remove the bicarbonate ions in water. After the calcium hydroxide is added, a precipitation appears in the solution. After the precipitation caused by calcium hydroxide, the COD in the supernatant is 792 mg/L, and the pH value is 11.35.

The oxygen flow is kept constant in the experimental process. The ozone generator has an ozone output of 60–80 mg/L and a reaction time of 30 minutes. The amount of ozone entering or exiting from the ozone contact oxidation tower can be monitored by a gas flow meter and a gas-phase ozone concentration meter. This amount can also be obtained via calculations. The total amount of ozone added into the ozone contact oxidation tower increases with time extension.

In the reaction process, the inlet flow (mixed gas, with main components of oxygen and ozone) is stably controlled at 1 L/min and the volume of the liquid that participates in the reaction is constant at 1L. The concentrations of gas-phase ozone and liquid-phase ozone entering or exiting from the reactor are determined by online monitoring meters. Because the concentration of dissolved ozone is very low, the instantaneous variation of dissolved ozone could be negligible. The instantaneous ozone consumption is obtained by the following Equation (2).

$$C = \frac{(C_{G1} - C_{G2}) \times Q_G}{V_L}$$

where

- $C = \text{instantaneous ozone consumption (mg/(L\cdot min))}$
- $C_{G1} = \text{value of ozone concentration at a gas inlet end (mg/L)}$
- $C_{G2} = \text{value of ozone concentration at a gas outlet end (mg/L)}$
- $Q_G = \text{gas flow (L/min)}$
3. RESULT AND DISCUSSION

This study aims to distinguish the process of the advanced treatment of yeast wastewater by strengthening catalytic ozonation. Thus the direct ozone oxidation is selected as a contrast experiment to compare the variations of process parameters, such as pH values, ORP values, and liquid-phase ozone concentration values; the situations in COD removal; the situations in effective utilization of ozone at the two experimental processes.

3.1. The Effect of Pretreatment

The experimental wastewater contains bicarbonate ions, which are an inhibitor of indirect ozone reaction. The indirect reaction involves hydroxyl radicals, which are highly unstable and undergo an immediate reaction with another molecule, in order to obtain the missing electron. In losing an electron, the molecule itself becomes a radical, which will react further, continuing the chain reaction. But bicarbonate radical is a kind of secondary free radical. These free radicals can terminate the chain reaction, inhibit the decomposition of ozone. This reaction is shown in the following Equation (3).

\[ \text{OH}^- + \text{HCO}_3^- \rightarrow \text{OH}^- + \text{HCO}_3^- \]  (3)

At the same time, the pH value can also be adjusted to the alkaline range by adding calcium hydroxide. Improving pH values is a method to enhance the effect of ozonation, and the dissociation degree of pollutants in water is improved [19]. To sum up, the pretreatment has two effects: One is the adverse effect of shielding bicarbonate on indirect oxidation, the other is to improve the decomposition of ozone, promoting indirect oxidation.

3.2. Changes of pH Value in the Reaction Process

The activity of ozone reacting with some inorganic substances and dissociative organic substances varies significantly with the variation of pH [19]. The ozonation rate is related to both direct and indirect reaction with the increasing pH value. On one hand, hydroxide ions can catalyze the decomposition of ozone, which is beneficial to indirect reaction. On the other hand, a high pH value can promote the dissociation of pollutants; thus, the direct reaction of ozone becomes a key factor in removing pollutants [20,21]. In the complex system, the influence of a pH value is highly complex.

The pH value of the raw water is 8.1. The pH value in the process of direct ozone oxidation is slightly decreased, and the pH value is decreased to 7.8 when the reaction is stopped. The reduction of the pH value within a small range indicates that the reaction of hydroxide ions catalyzing the decomposition of ozone is conducted in water simultaneously. The ozone dissolved in the wastewater reacts with the pollutants mainly through the direct reaction due to the scavenging action of bicarbonate ions [see Equation (3)]. In the process of strengthening catalytic ozonation via calcium hydroxide to conduct pretreatment, the pH value has a large variation range and is decreased from the initial value of 11.35 to a final value of 7.64. After adding the calcium hydroxide, the concentration of the hydroxide ions in the solution during the strengthening process is increased, whereas the bicarbonate ions are converted into the calcium bicarbonate. In alkaline solution, the reaction is generated during the process of adding ozone, as shown in the following Equation (4).

\[ \text{O}_3 + \text{OH}^- \rightarrow \text{O}_2^- + \text{HO}_2^- \]  (4)

This process shows a chain reaction of ozone decomposition production and hydroxyl free radical generation. The hydroxide ions in water are consumed continually with the reaction, and the pH value of the solution is rapidly reduced. The solution is within the neutral range after the concentration of the hydroxide ions is decreased. Therefore the decomposition reaction of ozone is weakened.
3.3. Changes of ORP Value in the Reaction Process

Every substance in water has oxidation-reduction properties. However, the mutual influence between these different substances forms the macroscopic oxidation-reduction properties. The organic pollutants in water, which can be oxidized with an oxidizer, have reducibility. The higher the concentration of the organic pollutants is, the smaller the value of the oxidation-reduction potential in water is. By contrast, the increase of the concentration of oxidizers, such as dissolved oxygen and dissolved ozone, etc. may cause the oxidation-reduction potential in water to increase. In the field of wastewater treatment, the oxidation-reduction potential is generally used to measure the anaerobic environment and oxygen deficient environment of microorganisms. The oxidation-reduction potential is used to study an advanced oxidation process with Fenton, however, this method is rarely used to study ozonation in the field of wastewater treatment.

The initial ORP value of the raw water is –257 mV. The ORP value is slowly increased with the addition of ozone, and the ORP value is –168 mV until the reaction is finished. The higher the concentration of the pollutants in the raw water is, the higher the concentration of the substances having reducibility is. The reaction of the ozone in the wastewater is mainly a direct reaction. The concentration of the pollutants is gradually decreased with the reaction, and the oxidation-reduction potential is increased to a small extent.

In the process of strengthening catalytic ozonation, the ORP value generates a large fluctuation. After being decreased from 110 mV to 30 mV at the early stage of the reaction, the ORP value is slowly increased to 106 mV. Then, the ORP is suddenly increased to 900 mV and stabilized to 919 mV. This process matches the research process of Chiang et al. [24]. In the process of strengthening catalytic ozonation, the direct reaction between the ozone and pollutants, the catalytic reaction between the ozone and the catalyst, and the decomposition reaction between the ozone and the hydroxyl ions exist in the wastewater. The concentration of pollutants, which can conduct the direct reaction with the ozone, is decreased with the consumption of the hydroxyl ions, and the reaction is gradually transitioned to a slow reaction stage from a fast reaction stage. Dissolved ozone appears in the solution. At this moment, the ORP value of the system is the comprehensive reflection of the liquid-phase ozone [25]; the hydroxyl free radicals and pollutants are in a reduction state in water. The ORP value obviously increases at the later stage because of the existence of the liquid-phase ozone.

3.4. Changes of Dissolved Ozone Value in the Reaction Process

The composition of wastewater in the process of ozonation is changed, and its reactivity with ozone is also changed. The process of waste waste ozonation can be divided into two phases. The first phase is at the beginning of the ozonation of efficient stage, whereas the second phase is at the inefficient ozonation rate of declining stage. The presence of ozone solubility in water is an important indication to distinguish the two phases [19,21,26].

In the process of directly adding ozone into the yeast wastewater, the liquid-phase ozone concentra-
tion is always zero. The system is also the fast reaction system of the ozone; the substances can react immediately with the ozone existing in water. Finally, the ozone dissolved in water is rapidly decomposed. No liquid-phase ozone is monitored within the time period of reaction.

In the process of strengthening catalytic ozonation, the dissolved ozone appears in the system when the reaction is conducted in 20 minutes. The concentration is also rapidly increased to 1.4 mg/L, and is then kept stable. The appearance of the dissolved ozone in the solution indicates that the reaction between the ozone and the pollutants is transitioned from the fast reaction to the slow reaction. The bicarbonate ions are removed in the system, thereby eliminating the capturing effect on the hydroxyl free radicals. Substances containing free radicals, which are generated through catalysis, rapidly react with pollutants in water, thereby rapidly consuming the pollutants that can conduct direct reaction with the ozone via the ozone and the nonselective hydroxyl free radicals. Thus, the substances that can conduct the fast reaction with the ozone are consumed. At this moment, the system is transitioned from the fast reaction system to the slow reaction system, and the dissolved ozone appears.

3.5. Changes of Ozone Consumption in the Reaction Process

The ozone consumption curve reflects the consumption of ozone through the system in the reaction process. Although the ozone inflow can be stably controlled, the reduction of the concentration of pollutants in water results in the occurrence of the overflow and dissolution of ozone in the reaction process. The ozone consumption can be accurately calculated with the online monitoring system, thereby making an assessment basis for the utilization effect of the ozone.

In the process of direct ozone oxidation, ozone consumption via wastewater is rapidly increased to 58 mg/L. Then, it is slowly reduced to 47 mg/L and is kept stable. In the process of enhanced catalytic ozonation, ozone consumption via wastewater is rapidly increased to 78 mg/L from the beginning of reaction. Then, ozone consumption is slowly reduced to 39 mg/L and is kept stable. The common point of the two processes is that after reaching the maximum value, the ozone consumption is gradually decreased. But in the first 20 minutes of the reaction, the ozone consumption in the enhanced catalytic ozonation process was higher than that of the direct ozonation process. And after 20 minutes, the ozone consumption of the catalytic ozonation process was lower than that of the direct ozonation process.

The direct ozonation reaction mainly includes fast reaction between ozone and pollutants in water. The amount of ozone consumed by the wastewater is gradually decreased with the reaction, which is caused by the gradual decrease of the pollutant concentration. The analysis conducted on the dissolved ozone indicates that the early stage of the process of strengthening catalytic ozonation includes the decomposition reaction of ozone and the direct reaction of ozone. The later stage mainly includes indirect reaction. The ozone consumption indicates that at the early stage of reaction, the amount of ozone consumed by wastewater is obviously increased because of the presence of catalyst and hydroxide ions. At the later stage of reaction, the ozone consumption is less than that in the direct ozonation process, thus indicating that the content of substances capable of consuming ozone in wastewater
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is decreased at the later stage of reaction. At the same time, given the transition to a slow reaction stage, the ozone in the system is mainly consumed by catalyst decomposition because a catalyst exists in this process. The ozone consumption is also less than that in the direct oxidation process.

The above figure shows a diagram of COD variation in wastewater and stage ozone consumption in a process of direct ozone oxidation. COD is gradually decreased to 663 mg/L from 853 mg/L, and the total removal rate is 22%. The integral calculation is conducted by taking every 5 minutes as a time unit in the reaction process in obtaining the ozone consumption within the time unit to measure the effective utilization rate of ozone for COD removal at each stage. The effective utilization rate of directly oxidized ozone is not high, which is 5.5 gO³/gCOD at the initial stage of reaction, and a maximum value of 8.8 gO³/gCOD is reached in the reaction process. The effective COD removal through the ozone in the reaction process is not ideal, and this process has no constant COD removal efficiency.

COD in the process of enhanced catalytic ozonation is reduced to 389 mg/L from 792 mg/L, and the removal rate reaches 47%. The ozone utilization rate is relatively stable at the early stage of reaction. It is also decreased to approximately 2.9 gO³/gCOD from the initial 4.4 gO³/gCOD, changing in a small range. The ozone utilization rate is also increased to 10.9 gO³/gCOD at the last 5 minutes. At the first 25 minutes during reaction, the efficiency of COD removal through ozone is the highest. The ozone is decomposed, when the system enters the slow reaction stage because of the catalytic action. However, this process does not directly result in COD removal.

3.6. Study on Control Process

The study on the control process of ozone oxidation reaction in the complex system aims to use ozone effectively in providing a reliable control method for the application of the enhanced catalytic ozonation technology to the advanced treatment of yeast wastewater. The enhanced catalytic ozonation obtains a relatively good treatment effect in the advanced treatment of yeast wastewater. The variation of each process parameter in the reaction process is consistent with the reaction of ozone in water, and the measured values of each parameter at different stages are shown in the following table in detail:

According to the characteristics of different ozone reaction stages, which are obtained by judging the appearance of the dissolved ozone, the pH value is decreased at the fast reaction stage. The ORP value is also increased from a low value; the ozone consumption of wastewater is large; the removal effect of COD is obvious; COD is reduced to 405 mg/L from 792 mg/L (during the first 25 minutes of reaction); and the average utilization rate of ozone is 4.0 gCOD/gO³. At the slow reaction stage, the pH value is stabilized at approximately 7.6; the ORP value is kept at a high level; the ozone consumption of the system is low, which is approximately 37.5 mg/L; and the removal effect of COD is poor, which is only 3.7%.

The process of the advanced treatment of yeast wastewater by strengthening catalytic ozonation indicates that both the pH and the ORP values generate large fluctuations in the reaction process, which can indicate the variation of the wastewater state with the reaction. The appearance of the dissolved ozone indicates that the reaction type of the ozone is converted by stages. Adding the ozone before the dissolved ozone appears is efficient for COD removal in water. However, continuing to add the ozone after the stable state is maintained following the appearance of the dissolved ozone is uneconomical. Therefore, a monitoring system for the pH value, ORP value, and dissolved ozone shall be established in actual production, to guide an effective use of ozone.

4. CONCLUSION

The effective advanced treatment can be conducted on the effluent of the secondary settling tank for yeast wastewater through enhanced catalytic ozonation technology. Bicarbonate ions in raw water can be removed through calcium hydroxide to conduct pre-
treatment, thereby eliminating the inhibition effect of these ions on indirect ozone oxidation, while adjusting the pH value of the solution to the alkaline range, and strengthening the indirect oxidation function of ozone oxidation. The COD of the effluent is reduced to 389 mg/L from 853 mg/L with manganese sand as a catalyst to conduct a catalytic ozonation reaction and with the calcium hydroxide added for pretreatment; the total removal rate reaches 54%. This technology can reach the COD requirement in the discharge standard of water pollutants for yeast industry (Chinese standard GB25462-2010).

The experimental design of the on-line monitoring system can accurately calculate each moment of the consumption of ozone. The enhanced catalytic ozonation reaction can be divided into two stages by comparing this reaction with COD removal and the consumption of ozone. In this reaction, the average utilization rate of ozone at the high-efficiency stage is 3.8 gO\(_3^{-}\)/gCOD, and the removal rate of COD is 48% during the first 25 minutes of reaction. The average utilization rate of ozone at the low-efficiency stage is 10.9 gO\(_3^{-}\)/gCOD, and the removal rate of COD is only 4.0%.

The state variation of the solution during the reaction can be reflected by the pH value and the ORP value. The different stages of the enhanced catalytic ozonation reaction process can be obviously distinguished by the concentration of dissolved ozone. The reaction process can be effectively monitored with the online monitoring system. Considering the point of view of economy, adding ozone can be stopped when the reaction enters the slow reaction stage, thereby providing a control method reference for the application of the enhanced catalytic ozonation technology in the advanced treatment of yeast wastewater.

5. REFERENCE


