Study on the Pretreatment of COD in Brewing Wastewater Based on the Ozone Oxidation Technology

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Abstract. The high content of COD has always been a difficult problem for the efficient treatment of brewing wastewater. Pretreatment of brewing wastewater to reduce the content of COD was considered as a better solution. In this paper, ozone oxidation technology was used to pretreat brewing wastewater to preliminarily reduce the COD content, so as to provide beneficial conditions for further efficient treatment. The results showed that the reaction temperature (A), ozone intake (B), pH value of reaction solution (C) and reaction time (D) were the main factors affecting the removal of COD from brewing wastewater by ozone oxidation. Combined with the orthogonal test method, the optimum process conditions were A_2B_3C_2D_2. It was that the reaction temperature was 50 ℃, the ozone intake flow was 7 L/min, the pH value of reaction solution was 7 and the reaction time was 1 h, which made the removal rate of COD reach 40.5%, and realized the goal of pre-removal of COD in brewing wastewater.

1. Introduction

Brewing wastewater was referred to the general name of all wastewater generated in the brewing process of alcoholic drinks, mainly including pit bottom water, pot bottom water and production cleaning water. Brewing wastewater had the characteristics of high acidity, high organic matter content, high suspended matter content and high chromaticity [1], which made it difficult to treat and could not be solved by conventional domestic sewage treatment. With the implementation of national standard "GB 27631-2011 fermentation of Alcohol and Baijiu industry water pollutants discharge", the liquor making industry was facing the major problem of reducing sewage discharge and improving the quality of sewage discharged. The efficient treatment of brewing wastewater had become a major obstacle to the sustainable development of liquor making industry [2].

At present, the treatment methods of brewing wastewater mainly include three categories, namely physical adsorption method, chemical oxidation method and biochemical treatment method [3]. Physical adsorption method had high requirements for adsorption medium and poor desorption effect which was mostly used in the treatment of small-scale brewing wastewater. For example, Guo [4] used a variety of adsorption materials to adsorb organic amines in wastewater and the research results showed that the removal rate of activated carbon adsorption in the treatment of organic wastewater could reach 90%, while the desorption rate was about 70%. Chemical oxidation required high selection of oxidants and was easy to cause secondary pollution. For example, Pan et al. [5] used fenton method to treat alcohol wastewater, the removal rate reached 90%, however trace Fe impurities were also introduced. Although biochemical treatment method had become the mainstream treatment method of brewing wastewater because of its simple treatment process and low cost, it was also greatly affected by water quality, especially the higher requirements for organic content. For
example, Harada [6] put brewing wastewater with high organic matter in UASB reactor for 430 days, and the results showed that high organic matter concentration greatly reduced the COD removal rate, about 39-67%.

Therefore, we propose to use ozone oxidation technology to pretreat brewing wastewater, reduce the content of COD, and create conditions for further treatment of subsequent brewing wastewater. Ozone has strong oxidation capacity, which can directly or indirectly react with organics in sewage to degrade refractory organics [7], and has been widely used in sewage treatment [8]. Firstly, we studied the effects of reaction temperature, ozone intake, pH value of reaction solution and reaction time on the COD removal rate of brewing wastewater by single factor experimental method, and then optimized the optimal removal process conditions combined with orthogonal experimental method. The research results could be conducive to improving the treatment efficiency of brewing wastewater.

2. Materials and Methods

2.1. Main Experimental Reagents and Equipment
Brewing wastewater (a brewery in Guizhou), concentrated sulfuric acid (Chengdu Jinshan), ozone generator (Nanjing elevation), magnetic heating mixer (Japan, IKA), pH meter (Shanghai Instrument and electricity), etc.

2.2. Experimental Method
Take a certain amount of brewing wastewater, used the ozone generated by ozone generator to oxidize and remove the COD content in brewing wastewater under certain reaction conditions. After the experiment, calculated the COD removal rate by analyzing the COD value in brewing wastewater before and after oxidation. The reaction conditions included reaction temperature, ozone intake, pH value of reaction solution and reaction time. The optimum process conditions were optimized by single factor test and orthogonal test respectively.

2.3. Test Method
The content of COD in the sample was determined by potassium permanganate method. Take an appropriate amount of water sample into a 250 ml conical flask, dilute it to 100 ml with distilled water, add 10 ml of sulfuric acid, shake it well, add $V_1$ ml of excess potassium permanganate solution, heat the conical flask in a boiling water bath for 0.5 h, cool it, add 0.01 mol/L sodium oxalate standard solution, shake it well, place it in a water bath at 75-80 ℃, and titrate it with 0.01 mol/L potassium permanganate solution until it is slightly red, the end point of titration is that it does not fade for 30 s and record the dosage $V_2$ of potassium permanganate solution.

COD calculation formula was as follows:

$$\text{COD(Mn)} = \frac{[(V_1 + V_2 - V_4) \times f - 10] \times 0.01 \times 16 \times 1000}{10}$$

$f = (V_3 - V_4)/10$ —— each ml of potassium permanganate is equivalent to $f$ ml of sodium oxalate standard solution;
$V_3$: Dosage of standard solution for titration of sodium oxalate with potassium permanganate solution;
$V_4$: Dosage of blank sample in potassium permanganate titration.

3. Results & Discussion

3.1. Analysis of Single Factor Experimental Results
Figure 1a showed the experimental results of the effect of pH value of reaction solution on COD removal rate of brewing wastewater. It could be seen from the figure that when the pH of the reaction
solution changed between 4-10, the COD removal rate increased first and then decreased. When the pH value was 4, the removal rate of COD in wastewater was 29.2%; when the pH value was 7, the COD removal rate reached the maximum, which was 34.7%; When the pH value was 7-10, the COD removal rate decreased rapidly with the increase of pH. When the pH value was 10, the COD removal rate was 25.4%. This was because when the pH value of the reaction solution was acidic, ozone oxidation was dominated by direct oxidation reaction; When the pH of the reaction solution was 7, the oxidation reaction process was mainly an indirect reaction to produce hydroxyl radical; With the further increased of pH value, when pH was 10, due to the strong alkalinity, the collision probability between hydroxyl radicals increased and H\(_2\)O\(_2\) was generated, resulting in the obstruction of free radical chain reaction [9], resulting in the decrease of COD removal rate. The main reaction equation were:

1. \(O_3 + 2H^+ + 2e \rightarrow H_2O + O_2\)
2. \(O_3 + OH \rightarrow HO_2 + O_2\)
3. \(O_3 + HO_2 \rightarrow OH + O_2 + O_2\)
4. \(\cdot OH + OH \rightarrow H_2O_2\)

Figure 1b showed the experimental results of the effect of reaction temperature on the COD removal rate of brewing wastewater. It could be seen from the figure that the COD removal rate increased slowly with the increase of reaction temperature. When the temperature was 30 ℃, the COD removal rate was low, which was 26.1%; When the temperature continued to rise to 70 ℃, the COD removal rate was 34.7%. This was because the increase of temperature was conducive to accelerate the molecular thermal movement, increased the collision probability between reaction molecules, improved the oxidation reaction rate, and then improved the COD removal rate.

Figure 1c showed the experimental results of the effect of ozone intake on the COD removal rate of brewing wastewater. It can be seen from the figure that the COD removal rate increased slowly with the increase of ozone intake. When the ozone inlet flow was 3 L/min, the COD removal rate in wastewater was 29.9%; When the ozone inlet flow was 7 and 8 L/min, the COD removal rate was higher, and the COD removal rates were 35.8% and 36.1% respectively. The results showed that there was a positive correlation between COD removal rate and intake O\(_3\) flow, because the increase of ozone intake O\(_3\) flow increased the ozone flow and concentration, which could produce more ozone and oxidize organic matter in wastewater.

Figure 1d showed the experimental results of the effect of reaction time on the COD removal rate of brewing wastewater. It could be seen from the figure that the COD removal rate increased with the extension of reaction time. When the reaction time increased from 0.5 h to 1 h, the COD removal rate increased rapidly; With the extension of reaction time, the highest COD removal rate reached 41.3%, but the increased currency slowed down. This was because ozone could quickly oxidize with small molecular organics in the early stage of the reaction, and directly oxidized most of the small molecular organics in the wastewater into CO\(_2\) and H\(_2\)O; With the extension of reaction time, the rate of hydroxyl radical produced by ozone began to decrease, and the degradation rate of macromolecular organics decreased, resulting in the slow rise of COD removal rate.
Based on the above experimental results, taking the COD removal rate in brewing wastewater as the target index, the better process conditions for the treatment of organic matter in brewing wastewater based on ozone oxidation were preliminarily obtained by single factor experimental method. The results showed that when the initial pH value of the reaction solution was 7, the reaction temperature was 60 °C, the ozone intake was 7 L/min and the reaction time was 1 h, the COD removal effect in the wastewater could reach 39.1%.

3.2. Analysis Of Orthogonal Test Results
On the basis of the above single factor experimental research results, the reaction temperature (°C), intake O₃ flow (L/min), pH value of reaction solution and reaction time (min) were selected as the factors. Three levels were selected for each factor, and the orthogonal test was designed according to the standard orthogonal table L₉(3⁴). Table 1 was the orthogonal test design. The experimental results were shown in table 2.

Table 1. Orthogonal experimental design.

|   | A: Temperature (°C) | B: Intake flow (L/min) | C: pH | D: Time (min) |
|---|---------------------|------------------------|-------|---------------|
| 1 | 40                  | 3                      | 4     | 30            |
| 2 | 50                  | 5                      | 7     | 60            |
| 3 | 60                  | 7                      | 10    | 90            |
Table 2. Analysis of COD removal rate range.

| Number | A  | B  | C  | D  | COD removal rate (%) |
|--------|----|----|----|----|-----------------------|
| 1      | 1  | 1  | 1  | 1  | 28.4                  |
| 2      | 1  | 2  | 2  | 2  | 31.4                  |
| 3      | 1  | 3  | 3  | 3  | 28.7                  |
| 4      | 2  | 1  | 2  | 3  | 35.1                  |
| 5      | 2  | 2  | 3  | 1  | 28.2                  |
| 6      | 2  | 3  | 1  | 2  | 34.2                  |
| 7      | 3  | 1  | 3  | 2  | 19.4                  |
| 8      | 3  | 2  | 1  | 3  | 23.5                  |
| 9      | 3  | 3  | 2  | 1  | 32.6                  |
| K₁     | 88.5| 82.9| 86.1| 76 |                       |
| K₂     | 97.5| 83.1| 99.1| 92.2|                      |
| K₃     | 75.5| 95.5| 76.3| 87.3|                      |
| k₁     | 29.5|27.63|28.7| 25.33|                   |
| k₂     | 32.5|27.7|33.03|30.73|                   |
| k₃     | 25.17|31.83|25.43|29.1|                   |
| R      | 7.33| 4.2 | 7.6 | 5.4 |                   |

In the above orthogonal experimental results table, k₁, k₂ and k₃ were the average values of the total COD removal rate of wastewater obtained under the first, second and third levels of factors A, B, C and D respectively, which reflected the influence of various factors on the COD removal rate of wastewater at different levels. The factor level corresponding to the maximum value of k₁, k₂ and k₃ was the best level of this factor in the orthogonal table. R was the difference between the maximum value and the minimum value in k₁, k₂ and k₃, which represented the influence of different factors on the COD removal rate of wastewater. The larger value in R meant that this factor had a greater influence on the COD removal rate of wastewater. The reaction conditions obtained from the best combination of various factors were the best process conditions.

It could be seen from the results in table 2 that the R values of factor C and A (reaction solution pH and reaction temperature) were larger than that of factor B and D, reaching 7.6 and 7.33 respectively, which were significantly higher than the R values of other factors, indicating that the pH and reaction temperature of reaction solution had a significant impact on the COD content of wastewater removed by ozone oxidation, followed by factors D and B, i.e. reaction time and ozone inlet flow. According to the range analysis results, taking the COD removal rate as the target index, the influence degree of four factors on the COD removal rate of wastewater were as follows: pH value of reaction solution (C) > reaction temperature (A) > reaction time (D) > ozone inlet flow (B).

The influence of each factor level on the COD removal rate of wastewater was plotted according to the data in table 1 and 2, as shown in figure 2A, B, C and D. It can be seen from the figure that if the COD removal rate was to be the highest, the best process condition should be A₂B₃C₂D₂, that meant the best reaction condition should be controlled as the reaction temperature of 50 °C, ozone inlet flow of 7 L/min, pH of reaction solution of 7 and reaction time of 1 h. under this process condition, the COD removal rate in wastewater reached 40.5%.
4. Conclusions
In this paper, the ozonation technology was used to pretreat brewing wastewater to reduce the COD content. Combined with the orthogonal test method, the optimal process conditions for removing the COD content of brewing wastewater based on ozonation technology were obtained. The results showed that the reaction temperature (A), ozone intake (B), reaction solution pH (C) and reaction time (D) were the main factors affecting the removal of COD from brewing wastewater by ozone oxidation. The optimal process conditions were A₂B₃C₂D₂, that meant the reaction temperature was 50 ℃, the ozone inlet flow is 7L/min, the pH of the reaction solution was 7, and the reaction time was 1 h. under these optimal process conditions, the removal rate of COD in wastewater reached 40.5%, realizing the goal of pre-removing COD content in brewing wastewater.

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