Advanced Treatment Experiment of Brewing Wastewater

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Abstract. The decolorization of wastewater treated by biochemical treatment with Fenton catalytic oxidation technology was studied by using Dashaba sauce-flavored brewing wastewater in Erhe Town of Guizhou city as the research object. The results of single factor and orthogonal test show that the dosages of pH, FeSO₄ and H₂O₂ in wastewater mainly affect the chromaticity of wastewater, while the dosages of pH, quartz sand in wastewater mainly affect the effect of flocculation and sedimentation. When the initial chromaticity and UV₂₅₄ of the wastewater are 179 degrees and 1.51 cm⁻¹ respectively, the optimum process parameters are pH 6.5, FeSO₄ 2.5 mmol/L, H₂O₂ 25.0 mmol/L and quartz sand 3.0 g/L. The effluent chromaticity and UV₂₅₄ removal rate are 68.06% and 31.78%, and the chromaticity reached the emission limit value required in Table 3 of GB 27631–2011 “Emission Standards for Water Pollutants in Fermented Alcohol and Liquor Industry". Moreover, and the flocculation and sedimentation effect of iron mud is better and the treatment drug consumption is less.

1. Introduction
Renhuai City is the main production area of sauce-flavor liquor in China. In recent years, with the improvement of people's health care awareness, the market demand of sauce-flavor liquor is growing, the production scale of sauce-flavor liquor is expanding, and the corresponding amount of wastewater is also increasing. The Dashaba wastewater treatment plant uses an IC anaerobic reactor to treat brewing wastewater in Renhuai City, Guizhou province. However its effluent chromaticity is difficult to reach the standard of discharge, so other methods need to be used for collaborative treatment⁴⁻⁹. In 1894, French scientist H. Fenton⁵ first discovered that Fe⁷⁺/H₂O₂ could effectively oxidize tartaric acid in acidic aqueous solution, which is used for the field of water treatment. Later generations named this reaction as Fenton reagent. Fenton reagent has a strong oxidative hydroxyl radical (•OH), which is a simple and efficient oxidation technology without secondary pollution. To a certain extent, the decomposition and removal of organic pollutants that cannot be directly treated or treated effectively by biochemical methods⁶⁻⁹. In this paper, we would explore the feasibility of Fenton's reagent for the advanced treatment of anaerobic-biological contact oxidation and aerobic treatment of the sauce-flavored white wine brewing wastewater by single factor experiment and orthogonal experiment.

2. Single factor experimental study
The Fenton process treats wastewater by using H₂O₂ to form a strong oxidizing hydroxyl radical (•OH) under the catalysis of Fe⁷⁺. Through the redox reaction, the refractory organic matter in brewing wastewater is oxidized and decomposed. The reaction mechanism is as follows:

Fe⁷⁺ + H₂O₂ → Fe⁶⁺ +•OH + OH⁻ (1)
Fe⁷⁺ + H₂O₂ → Fe⁶⁺ +•HO₂ + H⁺ (2)
Fe⁵⁺ +•OH → Fe⁶⁺ + OH⁻ (3)
Fe⁵⁺ +•HO₂ → Fe⁶⁺ + O₂ + H⁺ (4)
2.1. Effect of pH on removal of main pollutants such as chromaticity in brewery wastewater treatment

The experimental control of FeSO₄ and H₂O₂ was 2.5 mmol/L and 25.0 mmol/L, and the initial pH of regulating brewing wastewater was 5.5~8.0. 1.5mg/L quartz sand and 3.0g/L quartz sand were added at the same time respectively, and the results are shown in figure 1.

1. When the initial reaction pH is 5.5 and 6.0, after the reaction pH is about 3.00, when the initial pH condition is 6.5, the pH is basically balanced before and after the reaction. When the initial pH of the reaction is between 6.5 and 8.0, the pH after the reaction will slightly increase to weakly basic. When the initial pH is greater than 9.0, Fenton reaction is inhibited, and the pH is basically unchanged after the reaction.

2. With the increase of influent pH, the chromaticity removal rate rise first and then fall, reached the maximum removal rate of 69.46% at pH is 6.5. According to research[10-12], the chromaticity of sauce-flavor liquor wastewater mainly depends on the conjugation of unsaturated groups (chromophones) and -OH, -NH₂ and -ORN (chromophones) containing π bond in aromatic hydrocarbon and amide organic compounds, such as C = C, C = O, N = N, N = O, and the delocalization of electrons makes π electrons excited and chromogenic. When pH is 6.5 or so, the Fenton reaction is in the most favorable environment. Under the strong oxidation effect of •OH, the Fenton reaction is oxidized and decomposed to reduce the chromaticity, while the overacid or overbase will inhibit (2) (4) and the main reaction (1), respectively, resulting in a reduced chromaticity removal rate.

3. The removal rate of UV₂₅₄ also rise first and then fall, but reached the highest removal rate of 54.55% at pH is 6.0. According to research[13], sauce-flavor liquor wastewater UV₂₅₄ is mainly a conjugated system of aromatic compounds, double bonds or carboxyl groups containing C=C and C=O double bonds. Under acidic conditions, aromatic compounds are acidified and chain dissociated. Under alkaline conditions, acidic groups such as carboxyl groups can also be decomposed and neutralized. At the same time, since the neutral acid condition is suitable for the Fenton reaction, the organic molecules are oxidized, decomposed and recombined, so that UV₂₅₄ is the best effect when pH is 6.0.

4. The COD content increases with the increase of pH, in the determination of COD by potassium dichromate method, the process of Fe²⁺ being oxidized into Fe³⁺ and the content of extremely strong oxidizing •OH made COD increase. When the pH is 7.0 or less, the reaction (1) and (3) is positive, but with the increase of pH gradually inhibited, the COD content gradually increases and the rate is fast. Under alkaline conditions, reaction (1) is inhibited, Fe²⁺ cannot be converted into Fe³⁺, and COD is mainly affected by Fe²⁺, with a slow change rate.

Figure 1. The removal effect of chromaticity and UV₂₅₄ in brewing wastewater and changes of pH and COD after reaction under different pH

Figure 2. The removal effect of chromaticity and UV₂₅₄ in brewing wastewater and changes of pH and COD after reaction under different pH
The experiment also shows that when the flocculation is in an acidic environment with the pH of 3.0, floating mud appeared in the reaction. After that, the experiment pH is adjusted back to the pH under different influent conditions to carry out the above experiment, and quartz sand is added. The experimental effect is shown in figure 2. Compared with Figure 1, 1. The maximum removal rate of chromaticity reach 84.51% at pH is 6.0. 2. The removal rate of UV$_{254}$ decrease from 85.19% at the beginning to 26.94% as pH increase. 3. The COD content is still increase with the increase of pH.

The redox reaction of aromatic hydrocarbons and amides occurs under acidic condition, when the pH value is returned to the initial state by the acid, the Fenton reaction is carried out in the forward direction of the reaction (1) (3), and conducive to aromatic hydrocarbon in the brewery wastewater and oxidative decomposition of chromophores and auxochrome organics in amides, the chromaticity removal well in figure 1; the removal of UV$_{254}$ is also related to the above process.

The experimental flocculation particle size laser particle size meter detection display (figure 3), when pH is 6.0 or less, the flocculation particle size distribution below 100m, and the flocs are finely dispersed, with the increase of pH, the particle size of flocs increase gradually and the stability is enhanced, and the flocculation effect is improved under neutral alkaline condition. Therefore, when the influent pH is 6.5 and the pH is about 7.00 after the reaction, it is under suitable flocculation conditions, and the removal effect of outlet water chromaticity is good.

2.2. Effect of FeSO$_4$ addition on wastewater treatment efficiency

Based on the effect of the aforementioned pH on the chromaticity, using experimental water pH 6.5, H$_2$O$_2$ and quartz sand with 25.0 mmol/L and 3.0g/L respectively was used to control the addition of FeSO$_4$ with 0~2.75 mmol/L, and the experimental results are shown in Figure 4. 1. Under the condition of weak acid, the removal rates of both chroma and UV$_{254}$ increase with the addition of FeSO$_4$, but with the increase of reaction (1), the organic matter in brewing wastewater is rapidly oxidized and decomposed and the total amount of organic matter decrease. After the reaction, pH and COD show a downward trend. When Fe$^{2+}$ addition is low, the main reaction is in the form (1) and forward. With the increase of Fe$^{2+}$ addition, the amount of •OH and OH$^-$ increase rapidly, and the reaction (3) proceed, and the COD content gradually decrease. 2. With the continuous increase of Fe$^{3+}$, the reaction gradually to (2) (4), the pH after the reaction gradually decrease, but still a neutral base, and continue to form flocculation deposition, chromaticity and UV$_{254}$ removal rate is increasing. When the addition amount of FeSO$_4$ is greater or equal to 2.5mmol /L, the chroma of effluent is less than 10 times, meeting the discharge standard.
2.3. Effect of $\text{H}_2\text{O}_2$ Addition on Wastewater Treatment

Based on the above pH effect on chromaticity, the control wastewater pH was 6.5 and the addition amounts of FeSO$_4$ and quartz sand were 2.5 mmol/L and 3.0g/L respectively, to change the addition amount of H$_2$O$_2$ (0–27.5 mmol/L), as shown in figure 5. Under acidic conditions, with the increase of H$_2$O$_2$ content, the content of •OH formed in the main reaction (1) increase, the oxidability increase, the removal rate of chromaticity increase, from 55.42% to 68.46%, the chromaticity of effluent can meet the corresponding emission standards; At the same time, the formation of hydrogen superoxide with double bonds by reaction (2) gradually increase, resulting in a decrease in the removal rate of UV$_{254}$, 37.59% to 25.17%. 2. With the reaction, the reaction gradually from (1), (3) reaction to (2), (4) reaction, the content of •OH increase, COD show a rising trend; Meanwhile the pH value decrease gradually from 7.81 to 7.10.

![Figure 5. The removal effect of chromaticity and UV$_{254}$ in brewing wastewater and changes of pH and COD after reaction under different H$_2$O$_2$ dosage](image)

3. Orthogonal experimental study

According to the single-factor experimental results, the addition amount of fixed quartz sand was 3g/L, and the addition amount of pH value, FeSO$_4$ and H$_2$O$_2$ were selected as orthogonal experimental factors. Three levels were set for each factor, and the influencing factors and levels of the experiment are shown in table 1.

| Level | pH | FeSO$_4$ dosages (mmol/L) | H$_2$O$_2$ dosages (mmol/L) |
|-------|----|--------------------------|-----------------------------|
| 1     | 6.5| 2.25                     | 22.5                        |
| 2     | 7.0| 2.50                     | 25.0                        |
| 3     | 7.5| 2.75                     | 27.5                        |

The experiment aimed at the removal effect of chromaticity, designed a 4-factor 3-level orthogonal experiment, and carried out the experiment according to the conditions of L$_9$(3$^4$) orthogonal table. Three sets of parallel experiments were carried out under the same condition, and the average value was taken for analysis. The orthogonal experiment results and range analysis results of brewing
wastewater treatment are shown in table 2, and the influence of various factors on the chromaticity removal rate is shown in figure 6.

Table 2. Orthogonal test design and chromaticity removal results

| Serial number | A  | B  | C  | Chromaticity | Chroma removal rate (%) |
|---------------|----|----|----|--------------|-------------------------|
| 1             | 1  | 1  | 1  | 64.998       | 63.850                  |
| 2             | 1  | 2  | 2  | 59.658       | 66.820                  |
| 3             | 1  | 3  | 3  | 51.649       | 71.274                  |
| 4             | 2  | 1  | 2  | 75.677       | 57.910                  |
| 5             | 2  | 2  | 3  | 70.337       | 60.880                  |
| 6             | 2  | 3  | 1  | 73.007       | 59.395                  |
| 7             | 3  | 1  | 3  | 78.347       | 56.425                  |
| 8             | 3  | 2  | 1  | 83.686       | 53.456                  |
| 9             | 3  | 3  | 2  | 81.016       | 54.941                  |
| I             | 67.438 | 59.395 | 58.900 |
| II            | 59.395 | 60.509 | 60.014 |
| III           | 54.941 | 61.870 | 62.860 |
| R             | 8.043 | 2.475 | 3.96    |

According to the size of the mean range in the table, it can be seen intuitively that the order of the factors affecting the chromaticity removal rate is as follows pH > H₂O₂ dosages > FeSO₄ addition amount, and the influence of each factor on the mean chromaticity removal rate (figure 6), the pH value is the largest for chromatic removal, followed by H₂O₂ and the FeSO₄ is less affected. The optimal parameters of orthogonal experimental results are A₁B₃C₃ with a pH of 6.5 and the addition amounts of FeSO₄ and H₂O₂ are 2.75mmol/L and 27.5mmol/L respectively. Orthogonal test results also show that under A₁B₂C₂ condition, the effluent from brewing wastewater can meet the corresponding discharge standard of chromaticity. at this time, it is proved that the dosages of each drug are less and the economic benefits are better.

Figure 6. Effect of various factors on chromaticity removal rate
4. Conclusion
(1) The single factor and the orthogonal experimental studies show that Fenton reagent oxidation method is feasible for the treatment of major pollutants in brewing wastewater, but the formed Fe(OH)$_3$ is slow to precipitate, quartz sand should be added to improve the sedimentation performance. Quartz sand should be about 3.0g/L.

(2) The orthogonal test show that the order of the factors influencing the removal rate of chromaticity is pH > H$_2$O$_2$ > FeSO$_4$, and the appropriate process parameters are pH 6.5, H$_2$O$_2$ and FeSO$_4$ are 2.5 mmol/L and 25.0 mmol/L respectively.

(3) When the pH of wastewater is adjusted to acidic, the phenomenon of nitrogen-containing organic matter denaturation and precipitation will occur, and the removal effect of chromaticity and UV$_{254}$ by Fenton reagent oxidation method can be improved.

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