

Study on Ozone/Fenton Reagent Co-processing of Wheat Straw Pulp Hypochlorite Bleaching Wastewater

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Abstract. This experiment explores to pre ozone used for wheat straw pulp hypochlorite bleaching wastewater treatment of optimum oxidation time, initial pH of Fenton reaction water, H₂O₂/FeSO₄ dosing ratio, reaction time on Fenton method depth treatment effect of bleaching effluent. The bleaching wastewater is pretreated with the ozone concentration 2.9mg/l. The experimental results show that the best pretreatment time of ozone is 30min. The removal rates of COD_{Cr}, TOC_{Cr} and chroma were 53.9%, 82.8% and 68% respectively with ozone pretreatment. The ozone oxidation process has a good effect on the removal of organic substances in wastewater. Treatment of straw pulp hypochlorite bleaching wastewater by Fenton reagent, the experimental results show that COD_{Cr} removal rate of wastewater is about 74%, the chroma is above 87.5%, and the supernatant is colorless under the initial pH 5.6, H₂O₂ of 1ml, n (H₂O₂): n (Fe²⁺)=4, FeSO₄ dosage 2ml, reaction temperature 20°C, reaction time 40min, 0.1%PAM.

Introduction

With the international community's attention to environmental issues, as well as the improvement of people's living standards, people pay more and more attention to the environment of their lives. Papermaking enterprises is a major wastewater production. Researching and developing a good treatment effect and low cost of wastewater treatment method is particularly important from the perspective of the future development and survival. The research and development of new wastewater treatment technology has opened up a new way for the treatment of papermaking wastewater.

Ozone wastewater treatment technology is a new technology. No two pollution is produced in the process, it is a more and more popular wastewater treatment technology. But the technology is not mature enough in the practical application. Fenton oxidation treatment technology has many advantages, but its own processing cost is higher and the Fe²⁺ content is higher in the treated wastewater process. So it is of great practical significance to find a kind of low cost and good effect of wastewater treatment and to study the reactive mechanism of Fenton and other processes. This paper mainly studies of ozone and Fenton reagent co-treatment process of wheat straw pulp hypochlorite bleaching wastewater.

Experimental

Materials. The wastewater from a paper mill wheat straw pulp hypochlorite bleaching wastewater, laboratory stored for 3months, water is dark brown and smell.

Instruments and Chemicals. Oxyhydroxide harmless handler (Qingdao ODO Environmental Technology Development Co., Ltd. China); Ozone Generator (Fujian Hui Wei Environmental Protection Technology Co., Ltd. HW-OW-50,China);Oven(Shanghai SHULI instrument and Meter Co., Ltd., china); Electronicbalance PTF-A100, Fuzhou Hua Zhi Science Co., Ltd., China; PH acidity meter PHS-25C(Shanghai Peng Shun Scientific Instrument Co., Ltd., China); COD determinator: DRB200 DR1010 (Qingdao Hash company, China); Total organic carbon analyzer: TOC-LCPH

(SHIMADZU analysis instrument division, China); BOD determinator (Germany WTW China Technical Service Center, Germany).

H₂O₂ (30%), AR, 8.8mol/L; FeSO₄ solution, 10%, 0.359mol/L; 5% H₂SO₄ solution; NaOH(5%) solution; PAM solution: Anion type, molecular weight 12 million, industrial grade, formulated into 0.1% solution (the drugs were for Tianjin Kernel Chemical Reagent Co., Ltd, prepare by oneself).

Experimental Method. Determination of the concentration of ozone water produced by ozone generator. Determination of iodine content, the ozone concentration of ozone generator is 2.9mg/l.

Wastewater Pretreatment. The wastewater was filtered by 150 mesh filtering net, and the following experiments were carried out with the pretreated wastewater.

Ozone Pre-Oxidation. After the filtration, the wastewater was treated with ozone generator, and then the waste water was used for the detection of the indicators in the fixed time period.

Fenton Reagent Oxidation. Get the Waste water after ozonation, dosage of cylinder volume 100ml to the beaker, adding proper amount of FeSO₄ solution, rapid mixing, and then adding an appropriate amount of H₂O₂ solution, rapid mixing and at the same time pay attention to the change of pH, available configuration of dilute sulfuric acid to adjust, after 30 minutes, with prepared sodium hydroxide solution to adjust pH to 7, then add a certain amount of PAM flocculation, standing about 5 minutes and the supernatant were detected. From the economic cost and oxidation effect of consideration, investigation system in different Fenton reagent addition COD_{Cr} changes, and to determine the Fenton reagent reaction of the best initial pH.

Results and Discussion

Wastewater Pretreatment. After pretreatment of wastewater, the water quality of the supernatant was detected, and the results of the effluent were shown in Table 1.

Table 1. The water indicators of the supernatant after pretreatment.

| COD _{Cr} / (mg/l) | TOC _{Cr} / (mg/l) | pH | suspended solid/ (mg/L) | chroma/ times |
|----------------------------|----------------------------|------|-------------------------|---------------|
| 1063 | 912.30 | 6.19 | 126 | 200 |

Ozone Pretreatment. The effects of O₃ oxidation time on COD_{Cr}, TOC_{Cr} and chroma of wastewater, as shown in Fig. 1.

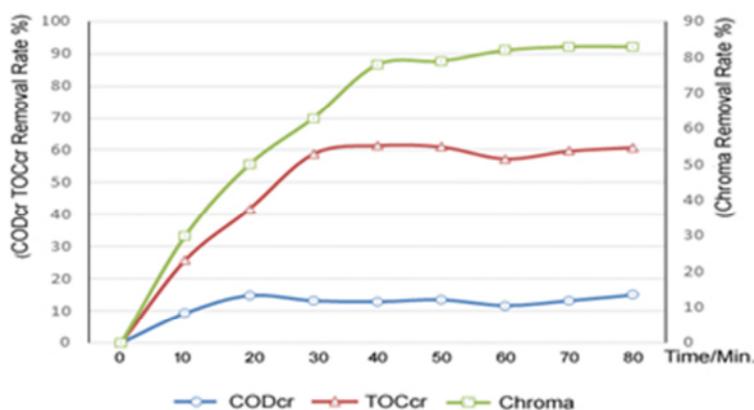


Fig. 1 The effects of O₃ oxidation time on COD_{Cr}, TOC_{Cr} and chroma of wastewater.

Can be seen from Fig. 1, the removal rate of TOC_{Cr}, COD_{Cr} and chroma of wastewater are increasing with the increase of ozone oxidation reaction time in the reaction time of 40 minutes. However, after 40min, the removal rate remained essentially unchanged. The removal rate of COD_{Cr} remained at about 15%, TOC_{Cr} 63%, chroma 80%. The reasons can be summarized as follows: Ozone and hydroxyl radicals generated in the reaction of ozone has strong oxidation. At the beginning of the reaction, the concentration of organic pollutants in wastewater is large, so the reaction is fast. With

extension of reaction time, the concentration of the organic matter in the wastewater continue to decline, but with limited processing capability of ozone reaction to a certain degree, the wastewater of COD_{Cr} and TOC_{Cr} will no longer occur change. Therefore, the ozone pre-oxidation time is more suitable for 40min.

Treatment of Wastewater with Fenton Reagent. Take 100ml ozone pretreatment 90min wastewater 4, add 6 ml prepared FeSO₄ solution, and then add 0.15 ml of 30% H₂O₂ solution. The initial pH of wastewater is regulated by dilute sulfuric acid. The effects of different initial pH on the treatment of wastewater are investigated. The results are shown in Fig. 2.

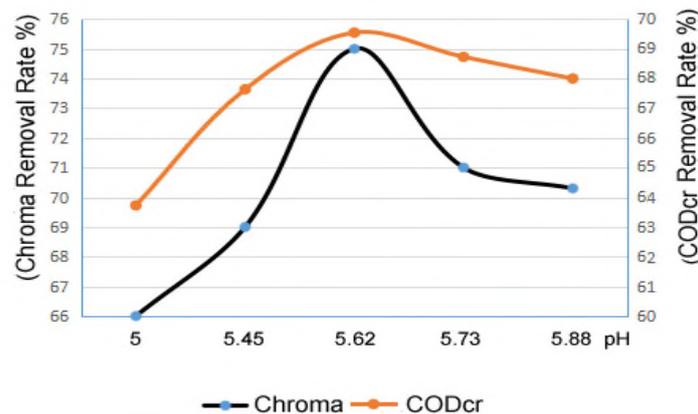


Fig. 2 The Effect of different initial pH changes on COD_{Cr} and chroma of wastewater.

Can be seen from Fig. 2 and Fig. 3, the initial pH has a great influence on the oxidation treatment of Fenton wastewater. Experimental results show that the removal rates of COD_{Cr} and chroma were 69.6% and 75% respectively when pH was close to 5.6 and the removal rate decreased when the pH was higher than 5.6. This shows that the treatment effect of wastewater is the best when pH 5.6. Comprehensive analysis is as follows, Fenton oxidation reaction is generally in the acidic pH 4-6 environment is the most suitable conditions. The reaction rate of Fenton was relatively fast under the acid condition. When pH was 5.6, the reaction rate was the fastest, and the generation rate of hydroxyl radical was the highest. The reaction rate becomes slow with the increase of pH value. This is because of the occurrence of two side effects: first, there will be part of the Fe²⁺ is oxidized to Fe³⁺ with the progress of the reaction. The catalytic effect of Fe³⁺ generated is far less Fe²⁺. This decrease the reaction rate; secondly, H₂O₂ is not stable and easy to be decomposed into water and oxygen under higher pH conditions. So we chose pH as 5.6 in this experiment.

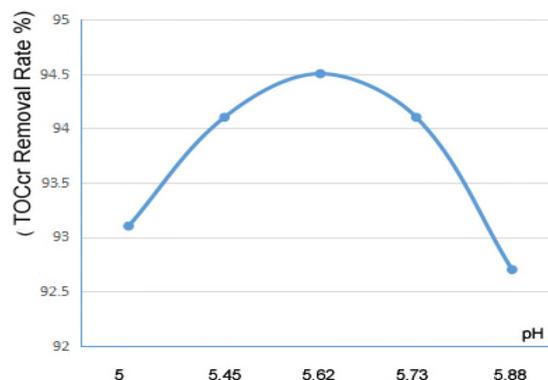


Fig. 3 The effect of different initial pH change on TOC_{Cr} of wastewater.

The Effect of H₂O₂/FeSO₄ addition Ratio on Wastewater Treatment. Take ozone pretreatment 90min wastewater, and then divided it in five, each take 100ml, determination of wastewater pH, with dilute sulfuric acid to adjust to the best pH 5.6, to add different doses of H₂O₂ and Fe²⁺ respectively. To

join the Fe^{2+} stirring 5min to uniform, then add to 30% H_2O_2 to react for 40min. At the end of the reaction, join NaOH solution to adjust the effluent pH to 7 directly, then add to 0.1% PAM and mixing flocculation and static precipitation for 30min, the supernatant was determined.

As can be seen from Fig. 4, the removal rate of COD_{Cr} and TOC_{Cr} varies with the change of $\text{H}_2\text{O}_2/\text{FeSO}_4$ ratio. There is a wave of the COD_{Cr} removal rate with the $\text{H}_2\text{O}_2/\text{FeSO}_4$ ratio, the first increase and then decrease and in the final pH reached 4.1 to reach the maximum. At the same time, the removal rate of TOC_{Cr} is the same point pH 4.1. when the ratio to about 4, the removal rate of COD_{Cr} reached about 72% and TOC_{Cr} 77%. The reasons are as follows, when the amount of H_2O_2 is too low to produce sufficient amounts of $\cdot\text{OH}$ to participate in the reaction. The generation of $\cdot\text{OH}$ gradually increased with the amount of H_2O_2 added, so that the removal rate of COD_{Cr} gradually increased. When continue to increase of H_2O_2 dosage, the organic matter oxidation has been completed of the system, then the H_2O_2 will be Invalid decomposed and there will be reaction $\text{R} + \cdot\text{OH} = \text{ROH}$ (R is organic groups). The first-OH production occurred is devoid of. Not only an excess of H_2O_2 will cause the remnants of the COD_{Cr} increase, but also lead to the H_2O_2 's own invalid decomposition. Therefore, it is very necessary to control the amount of H_2O_2 in order to save processing costs and to achieve wastewater reuse standards. The optimum dosage of H_2O_2 is 88mmol/l.

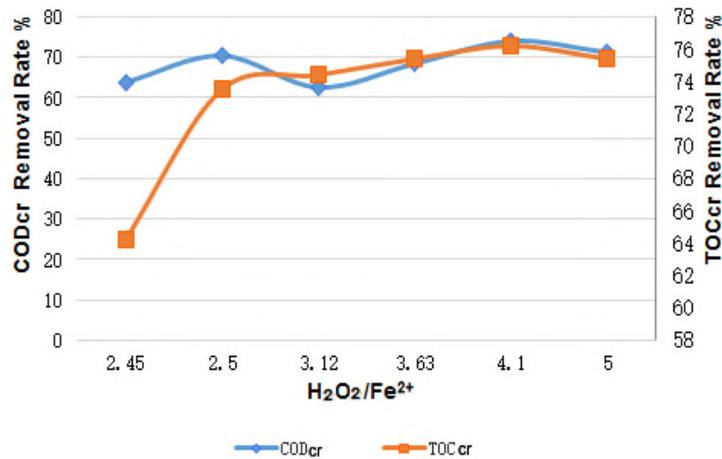


Fig. 4 The effect on the COD_{Cr} and TOC_{Cr} removal rate of the $\text{H}_2\text{O}_2/\text{FeSO}_4$ ratio.

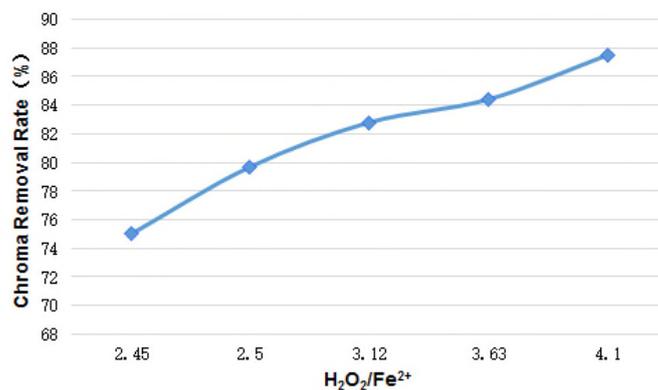


Fig. 5 The effect on the chroma removal rate of the $\text{H}_2\text{O}_2/\text{FeSO}_4$ ratio.

As can be seen from Fig. 5, the dosage of Fe^{2+} has a great influence on the oxidation treatment effect of Fenton. The removal rate of chroma increases with the ratio of $\text{H}_2\text{O}_2/\text{FeSO}_4$.

In the Fenton treatment system, Fe^{2+} is a necessary condition for the production of free OH radicals. H_2O_2 is difficult to break down to product $\cdot\text{OH}$ without Fe^{2+} . When the concentration of Fe^{2+} is relatively low, the reaction OH is very low, and the speed is slow, which limits the reaction speed of the system. Therefore, the removal rate of COD_{Cr} is relatively low. The number of OH generated is also increasing with the concentration of Fe^{2+} , and the removal rate of COD_{Cr} is increasing. When the amount of Fe^{2+} added is too high, a large number of Fe^{2+} make H_2O_2 decompose fast and produce a

large number of $\cdot\text{OH}$. OH can not react with the organic pollutants in the system and aggregate and mutual react and come into being water and O_2 . A part of the initial production of the OH is consumed and reduced the utilization of H_2O_2 . Therefore the choice of $\text{H}_2\text{O}_2 / \text{Fe}^{2+}$ ratio equal to 4 is more appropriate.

The Effect of Reaction Time on the Treatment of Wastewater. The initial pH of water sample after ozone treatment was 5.8. Fixed $n(\text{H}_2\text{O}_2):n(\text{Fe}^{2+})=4$, FeSO_4 dosage was 6ml, H_2O_2 dosage was 1ml. The reaction temperature is room temperature. The reaction time was set to 10, 20, 30, 40, 50min for the experiment, and the reaction results were shown in Fig. 6.

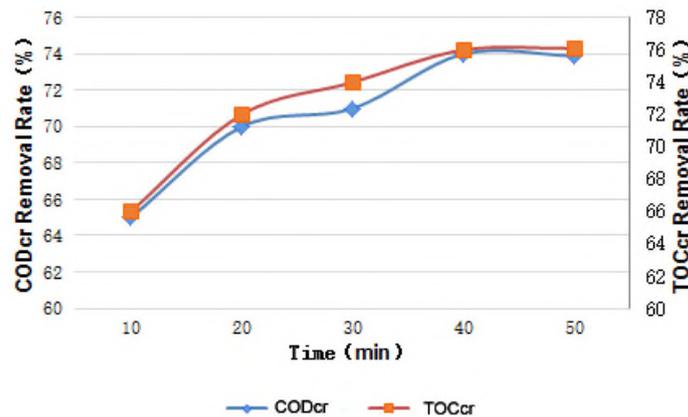


Fig. 6 The effect on the removal rate of CODcr and TOCcr of different reaction time.

As can be seen from Fig. 6, the removal rates of CODcr and TOCcr are increasing with the increasing reaction time. The removal rate reached 73.7% and 76.2% respectively when the reaction time was 40 minutes. CODcr and TOCcr removal rate changes little with the reaction time increase continued. Moreover, the slope of the initial stage of the reaction is larger. This is because of the higher concentration of organic matter in the early stage of the reaction, the reaction rate is the fastest. As the reaction is carried out, the concentration of organic matter in the waste water is reduced, and the reaction speed is slowed down. When the reaction was carried out to about 40min, the reaction rate of the system was obviously slowed down, which showed that the oxidation reaction of the system was very good, and the increase of reaction time had no effect.

Reaction time reflects the reaction process. The reaction time is insufficient to cause the oxidation of incomplete. The reaction time is too long will cause the reduction of processing efficiency. In the actual engineering operation, the equipment cost and operation cost will be increased, which makes the system lack of maneuverability. So to determine the most appropriate response time should be controlled at about 40min.

Conclusion

This experiment explores to pre ozone used for wheat straw pulp hypochlorite bleaching wastewater treatment of optimum oxidation time, initial pH of Fenton reaction water, $\text{H}_2\text{O}_2/\text{FeSO}_4$ dosing ratio, reaction time on Fenton method depth treatment effect of bleaching effluent. The bleaching wastewater is pretreated with the ozone concentration 2.9mg/l. The experimental results show that the best pretreatment time of ozone is 30min. The removal rates of CODcr, TOCcr and chroma were 53.9%, 82.8% and 68% respectively with ozone pretreatment. The ozone oxidation process has a good effect on the removal of organic substances in wastewater. Treatment of straw pulp hypochlorite bleaching wastewater by Fenton reagent, the experimental results show that CODcr removal rate of wastewater is about 74%, the chroma is above 87.5%, and the supernatant is colorless under the initial pH5.6, H_2O_2 of 1ml, $n(\text{H}_2\text{O}_2):n(\text{Fe}^{2+})=4$, FeSO_4 dosage 2ml, reaction temperature 20°C, reaction time 40min, 0.1% PAM.

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