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Study on Ozone Treatment Technology of Waste Paper Pulping Wastewater

Zhengshun Wang[1, a]*, Tongcai Yang[1]

[1]Key Laboratory of Pulp and Paper Science & Technology of Ministry of Education, Qilu University of Technology, Jinan, China, 250353

[a]wzsylq@aliyun.com

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Abstract. This study is a factory waste paper pulping wastewater of Shandong Zibo as treatment object, with ozone generator homemade ozone water, hydrogen peroxide, activated carbon, aluminum sulfate, polyacrylamide, manganese dioxide co-processing, combined with flocculation and sedimentation, adsorption, filtration, sewage after treatment fully meet the standard recycling. Experimental findings show that the ozone-water continuous separate treatment wastewater at temperature (20°C) and pH 6.91 for 70min, COD, BOD, TOC, SS, and chroma of wastewater is respectively from the original 2660mg/l, 1962mg/l, 1165mg/l, 707mg/l and 120 times reduced to 1308mg/l, 1108mg/l, 142mg/l, 80mg/l and 50 times. The ozone-water with ozone-catalytic oxidation - activated carbon - hydrogen peroxide- flocculants – filtration to co-treatment wastewater at temperature (20°C) and pH 6.65 condition for 70min, COD, BOD, TOC, SS and chroma of wastewater respectively from the original 2660mg/l, 1962mg/l, 1165mg/l, 707mg/l and 120 times reduced to 384mg/l, 401mg/l, 74mg/l, 39mg/l and 30 times by method of using hydrogen peroxide 60mmol/l, activated carbon 220mg/l, aluminum sulfate 25mg/l, PAM 15mg/l, manganese dioxide 10mg/l of wastewater.

Introduction

From the beginning of the 19th century, ozone treatment technology of water has been used. It has hundreds of years history up to now. The technology is more and more mature. But looking at home and abroad, ozone treatment of sewage application rate is low. The purpose of this study is on the ozone treatment technology of waste paper pulping effluent. To change the original single processing method by making use of the characteristics of strong oxidation of ozone and develop new technology, It can reduce wastewater treatment cost greatly, increase the processing speed and ability of wastewater. So it has important practical significance.

Experimental

Materials and Chemicals. The wastewater from a waste paper pulp mill; H_2O_2 (30%)，AR, 8.8mol/L; $FeSO_4$ solution, 10%, 0.359mol/L; 5% H_2SO_4 solution; NaOH (5%) solution; PAM solution：Anion type, molecular weight 12 million, industrial grade, formulated into 0.1% solution; Activated carbon (AC); Manganese dioxide (MnO_2); Aluminum sulfate (Al_2SO_4) (the chemicals were for Tianjin Kermel Chemical Reagent Co., Ltd, prepare by oneself).

Experimental Instruments. 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); Electronic balance 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) .

Determination of the Concentration of Ozone Water. The ozone water produced by ozone

generator. Using iodine method to determine the ozone concentration of the ozone water. The ozone concentration of the ozone water is 2.9mg/l.

Experimental Program. Waste water ozone treatment process as shown in Fig. 1.

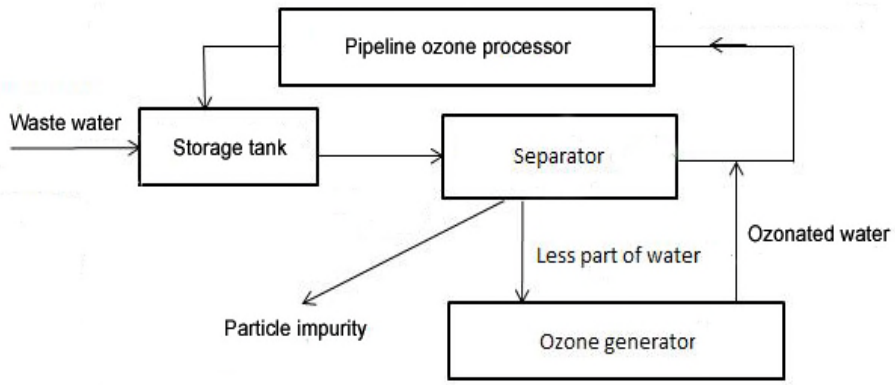

Fig. 1 Wastewater ozone treatment process.

O_3 treatment Alone. Experimental procedure： First detection of the original water COD, BOD, SS, TOC, chroma and other indicators before ozone treatment. The wastewater injection equipment, first open the power transfer pump, and then open the ozone generator. The wastewater has been circulating oxidation in the equipment, 20min began sampling, every 10min to take a sample.

Co-processing of O_3 and H_2O_2. Similarly, first detection of the original water COD, BOD, SS, TOC, chroma and other indicators before ozone treatment. The wastewater injection equipment, first open the power transfer pump, and then open the ozone generator. Pours into the prepared hydrogen peroxide in advance when the wastewater circulation is stable. The wastewater has been circulating oxidation in the equipment, 20min began sampling, every 10min to take a sample. Detect the indicators of water samples.

Co-processing of O_3-AC- flocculants (AP). As mentioned above, first detect the wastewater indicators, and then add to flocculants after ozonizing 20min, then add to activated carbon after ozonize 20min. The experiment is stop after five minutes.

Co-processing of O_3 and MnO_2. As mentioned above, the catalyst is added to after ozonizing 10min. The wastewater in the equipment has been circulating oxidation. Detect the indicators of water samples after 30min.

Co-processing of O_3 - MnO_2 - H_2O_2 - AC-AP- Filter. As mentioned above, add to catalyst after ozonizing 5min, to hydrogen peroxide after 10min, to flocculants after 15min, to activated carbon after 10min. Detect the indicators of water samples after 10min.

Results and Discussion

Ozone Treatment Alone. The changes of wastewater BOD and COD with the time of wastewater and ozone reaction as shown in Fig. 2. Can be seen from Fig. 2, COD and BOD decreased faster in 0-40min. The COD of wastewater decreased significantly slowed down after 40min. Time to reach 70min, the reduction rate of wastewater BOD is also significantly slowed down. As can be seen, the reaction time of ozone and wastewater is better for 70min from the point of reducing the wastewater COD and BOD.

As shown in Fig. 3, the wastewater TOC reduction is very obvious when the ozone is passed into. TOC is from the original 1165mg/l down to about 150mg/l for the reaction 20 minutes. The removal rate reached 87%. The value of TOC will not change significantly when the ozone reaction time is more than 50min. SS is from the original 707mg/l down to about 80mg/l for the reaction 70 minutes. The removal rate reached 88.7%. Obviously, ozone treatment of waste paper pulping wastewater is very effective for reducing SS and TOC.

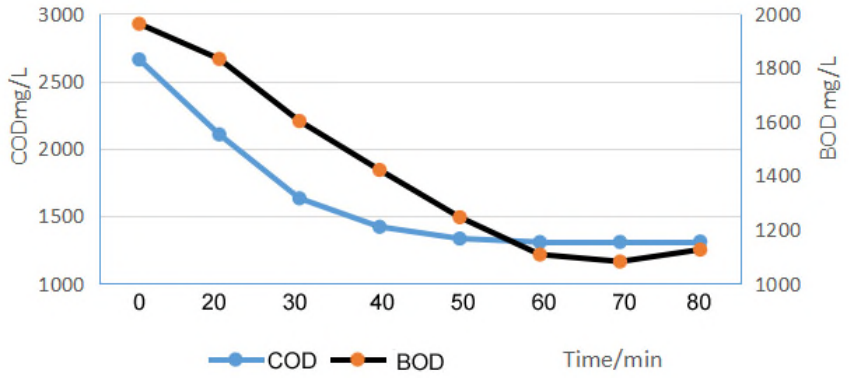

Fig. 2 The change of COD and BOD of wastewater with ozone reaction time.

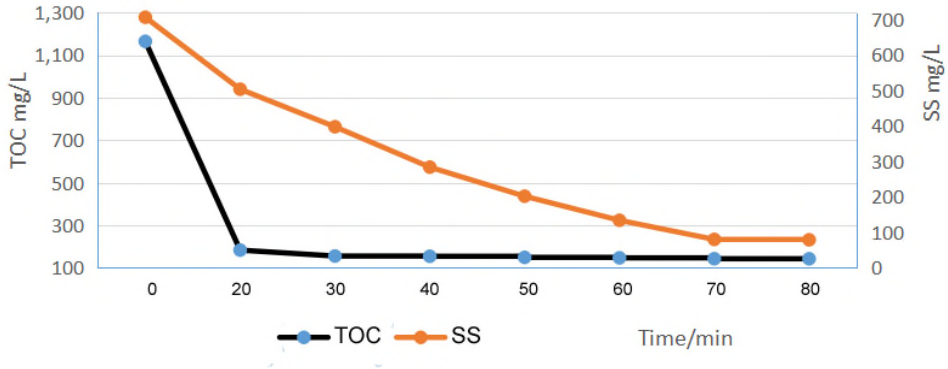

Fig. 3 The change of TOC and SS of wastewater with ozone reaction time.

Similar to the SS, after 70 minutes of ozone treatment, the chroma of the wastewater decreased by 120 times to 50 times, the removal rate of 58.3%.

Co-processing of O_3 and H_2O_2. The synergistic effect of ozone and hydrogen peroxide can produce hydroxyl groups with strong oxidation, which can effectively remove the organic pollutants in wastewater. The experimental facility capacity is larger and there is large amount of wastewater in it. It is impossible to directly add hydrogen peroxide in the facility. So the experiment was carried out by sampling. First make the pulping wastewater and ozone react 70min, and then take a certain amount of water samples to the experimental bag quickly, adjust the pH to appropriate, join the prepared hydrogen peroxide in and closed the experimental bag immediately. Reaction time is 40min. The experimental data are as follows.

Table 1. The effects on the wastewater index of O3 and H2O2 co-processing.

Indicator	Before treatment	After treatment	Removal rate
COD	2660mg/l	782mg/l	70.6%
TOC	1165mg/l	118mg/l	89.9%
BOD	1962mg/l	684mg/l	65.1%
SS	707mg/l	112mg/l	84.2%
Chroma	120times	50times	
Remarks: O_3:70min; PH: 9.03; H_2O_2： 60mmol/l			

Through Table 1 can be clearly seen, with the treatment of hydrogen peroxide ozone treatment of waste paper pulping effluent, in the access to ozone 70min, pH is 9.03, the amount of hydrogen peroxide of 60mmol/l under the conditions, the removal rate of COD and TOC was higher, reached

70.6% and 89.9% respectively, and chroma also drops a lot. Although the COD removal rate is higher, the COD of water is still higher. This is because very long fibers in the water were oxidized to much many fine fibrils that not easy to be oxidation. These tiny fibers increased the COD of water greatly. And the TOC of experimental measured is soluble, so that the TOC value is small. Suspended solids numerical is also larger because of the fiber fines.

In summary, ozone treatment of waste paper pulping wastewater, the effect is better. The indicators decreased significantly, especially TOC and color.

Co-processing of O_3 -Flocculants (AP: Al_2SO_4 and PAM) – AC. After adding flocculants in wastewater, suspended particles will lose the original stability. The particle shaped material cohesion between particles leads to increase and form flocs and alum. When the flocs grow to a certain volume, it will precipitate from the water phase under the action of gravity.

Activated carbon is widely used in the field of wastewater treatment. Because it contains a large number of pores, has great specific surface area. Not only can absorb fine fiber, but also reduce the water odor and color. It has high processing efficiency to some substance difficult to remove in the sewage. Activated carbon adsorption method has the advantages of wide application range, good treatment effect, recycling of useful materials, and can be reused. It is widely used in the advanced treatment of sewage.

Using the adsorption of activated carbon and the flocculation of the flocculants, the small fiber and impurity in wastewater which is not easy to be oxidized flocculate and subside and adsorb and then filtrate out, so as to achieve the desired treatment effect. The experimental data are shown in Table 2

Table 2. The effects on the wastewater index of O3- AP- AC co-processing.

Indicator	Before treatment	After treatment	Removal rate
COD	2660mg/l	525mg/l	80.3%
TOC	1165mg/l	98mg/l	91.6%
BOD	1962mg/l	432mg/l	78.0%
SS	707mg/l	48mg/l	93.2%
Chroma	120times	30times	
Remarks: O_3:70min; PH： 6.65; Al_2SO_4:25mg/l; PAM:15mg/l; AC:220mg/l			

The above scheme is used to deal with the waste paper pulping effluent by the ozone – flocculants - activated carbon (O_3- AP- AC) method. As can be seen from Table 2, the removal rate of TOC and SS was higher, reaching 91.6% and 93.2% respectively. Other indicators are also significantly reduced, the removal rate is basically between 75% and 80%. But from the COD and BOD numerical point of view, it has not yet reached the emission standards.

Co-processing of O_3 and Catalytic (MnO_2). Ozone catalytic oxidation technology belongs to the category of advanced oxidation technology. It is the pursuit of ozone has strong oxidation ability more intermediate product in the presence of catalyst to improve the ozone oxidation ability. According to the phase of catalyst, Ozone catalytic oxidation divided into homogeneous catalytic oxidation and heterogeneous catalytic oxidation in two categories. In homogeneous catalysis, the catalyst mix water soluble and catalyst loss or oxidizing agent not easy to recover and easy to produce two pollution. The higher cost of operation and maintenance which increase the cost of water treatment. Heterogeneous catalytic ozonation using solid catalyst to accelerate the liquid phase under atmospheric pressure (or vapor phase) oxidation catalyst in solid state, it is easy to separate from water, twice pollution is less, and simplify the treatment process.

The experiment use MmO_2 as catalyst to carry out multi-phase catalytic oxidation. MmO_2 is as a solid catalyst in the experiment. At the end of the experiment, it can be filtered through the method of extraction from water samples, water samples will not produce metal ions pollution.

The experimental data are as follows.

Table 3. The effects on the wastewater indicators of catalytic and ozone co-processing.

Indicator	Before treatment	After treatment	Removal rate
COD	2660mg/l	642mg/l	75.9%
TOC	1165mg/l	82mg/l	93.0%
BOD	1962mg/l	408mg/l	79.2%
SS	707mg/l	80mg/l	88.7%
Chroma	120times	50times	
Remarks: O_3:70min; PH:6.42; MnO_2:10mg/l; H_2O_2:60mmol/l			

This plan is mainly through the catalytic effect of ozone and hydrogen peroxide to enhance the oxidation capacity and make the organic matter in the sewage oxidation off, so as to achieve the effect of clean wastewater. Data from the table 3 can be seen, SS and TOC removal rate is the highest in the sewage, reaching 93.0% and 88.7% respectively, COD and BOD removal rate is 75.9% and 79.2%. These data can prove that the effect is better by using ozone catalytic oxidation treatment of sewage than using ozone alone.

Co-processing of O_3 - H_2O_2- MnO_2- AC-AP- Filter. Three schemes have been used to deal with the waste water of waste paper pulp. Through the data comparison, it is found that different methods have different effects on the treatment of sewage. Combined optimization of these programs, the following program is developed. The wastewater was treated by the method of ozone-hydrogen peroxide-catalytic oxidation –flocculants- activated carbon- filtration (O_3 - H_2O_2- MnO_2- AC-AP-filter). The results of the experiments are shown in Table

Table 4. The effects on the wastewater index of O3 - H2O2- MnO2- AC-AP- filter co-processing.

Indicator	Before treatment	After treatment	Removal rate
COD	2660mg/l	384mg/l	85.6%
TOC	1165mg/l	74mg/l	93.6%
BOD	1962mg/l	401mg/l	79.6%
SS	707mg/l	39mg/l	94.4%
Chroma	120times	30times	
Remarks: O_3:70min; PH:6.65; H_2O_2:60mmol/l; MnO_2:10mg/l; Al_2SO_4：25mmol/l; PAM:15mmol/l; AC:220mg/l			

Through the Table 4 can be seen that the indicators of wastewater are very obvious improvement. The removal rate of TOC and SS reached about 94%, the removal rate of COD and BOD were 85.6% and 79.6% respectively. It is also good to reduce the chroma of wastewater. The reason of the color can not continue to reduce is that the circulatory system of metals, such as iron, are oxidized to a colored substance. It can be concluded that the method is very effective for the treatment of wastewater.

Conclusion

Experimental findings show that the ozone-water continuous separate treatment wastewater at temperature (20°C) and pH 6.91 for 70min, COD, BOD, TOC, SS, and chroma of wastewater is respectively from the original 2660mg/l, 1962mg/l, 1165mg/l, 707mg/l and 120 times reduced to 1308mg/l, 1108mg/l, 142mg/l, 80mg/l and 50 times. The ozone-water with ozone-catalytic oxidation - activated carbon - hydrogen peroxide- flocculants – filtration to co-treatment wastewater at temperature (20°C) and pH 6.65 condition for 70min, COD, BOD, TOC, SS and chroma of wastewater respectively from the original 2660mg/l, 1962mg/l, 1165mg/l, 707mg/l and 120 times reduced to 384mg/l, 401mg/l, 74mg/l, 39mg/l and 30 times by method of using hydrogen peroxide

60mmol/l, activated carbon 220mg/l, aluminum sulfate 25mg/l, PAM 15mg/l, manganese dioxide 10mg/l of wastewater.

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