Advanced Treatment of Dry-Spun Acrylic Fiber Wastewater by O₃/UV-BAF Process

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Abstract: The dry-spun acrylic fiber wastewater is characterized by its complicated components and high volatility of water quality. Therefore, it is typically difficult to treat. In this paper, the advanced treatment of dry acrylic plant effluent was treated by the joint process of ozone/ultraviolet-biological aerated filter (O₃/UV-BAF). The effects of ozone dosage and pH on ozone to degrade COD were discussed, and under the condition of the process running steadily, the removal effect of each unit on COD was investigated. The results showed that with the increase of ozone dosage, the increase of COD removal was generally shown as a slow first, then a fast and then a steady trend. In the ozone dosage from 52.6 to 63.2 mg·L⁻¹, the COD removal rate reached 32.7% to 35.3%, and had the best economic feasibility. At pH 9 or so, the COD removal was the highest. The average removal of O₃/UV for COD was 32.0%, the average removal of BAF for COD was 32.6%, and the average COD concentration of effluent was 83.4 mg·L⁻¹, met its first class discharge standard.

1. Introduction

The dry-spun acrylic fiber wastewater is a typical industrial wastewater that is difficult to biodegrade. Its pollution composition is extremely complex, its water quality fluctuates greatly, and its toxic and harmful substances content is high. It is difficult to discharge within the standard, which severely restricts the development of acrylic fiber industry. Ozone oxidation (O₃) is a feasible method for the treatment of refractory wastewater[1-5]. Under the catalysis of ultraviolet light (UV), ozone decomposes to generate hydroxyl radical (·OH), which has very strong oxidation potential of 2.80 V, second only to fluorine's oxidation potential of 2.87 V. ·OH oxidizes organic substances that are difficult to biodegrade into small molecular substances with low toxicity and easy biodegradation through addition, bond breaking, electron transfer and other actions[6]. At the same time, ozone has the advantages of mild reaction conditions (normal temperature, normal pressure), no sludge, no secondary pollution, no transportation and storage of raw materials, etc. Biological Aerated Filter(BAF) packing has a large specific surface area. Dissolved oxygen in the packing gradually decreases from outside to inside, forming an aerobic-anoxic-anaerobic living environment for various microorganisms. The dissolved oxygen content is adjusted by controlling the aeration amount of each node, providing conditions for the growth and reproduction of various microorganisms and improving the pollutant removal efficiency[7-8]. At present, there are researches on advanced treatment of wastewater from oil refining, printing and dyeing, leather, landfill leachate and other wastewater by O₃-BAF combined process[9-12], but experimental researches on advanced treatment of acrylic fiber wastewater are rarely reported.

In this experiment, O₃/UV-BAF combined process was used to deeply treat the effluent of an acrylic fiber factory, aiming to verify the feasibility of this process to deeply treat dry acrylic fiber wastewater.
and to solve the effluent COD over-standard discharge, and to provide technical parameters for its later engineering reconstruction.

2. Experimental section

2.1. Source and quality of test water
The test water was taken from the effluent of the third sedimentation tank of a wastewater treatment plant of an acrylic fiber plant in Liaoning province. The COD concentration in the regulating tank of the sewage treatment plant is 600~1100 mg·L⁻¹, and contains a large amount of refractory organic matters, such as dimethylformamide (DMF) of about 100 mg·L⁻¹, acrylonitrile (AN) of about 30 mg·L⁻¹, CN of about 5 mg·L⁻¹. After treatment, the COD concentration has been effectively removed, but the COD in the effluent of the triple settling tank is still as high as 220~310 mg·L⁻¹, pH≈7.

2.2. Test instruments and analytical methods
Experimental instruments: ozone generator (3S-A10, Beijing Tonglin Gaoke technology co., ltd.), ultraviolet lamp tube (2W40D15W-851, Beijing electro-optic purple technology co., ltd.), gas-liquid mixing pump (20QY-1LD, Hangzhou south special pump industry co., ltd.), COD rapid monitoring instrument (5B-3C, Tianjin Lianhua), portable pH meter (HI98185, Hanna, Italy), biochemical incubator (SHP-250, Shanghai Jinghong Experimental Equipment Co., Ltd.), O₃ rapid analyzer (GDYS-101SC, Kyrgyzstan Swan), electronic analytical balance (AL204-IC, METTLER TOLEDO Instruments (Shanghai) Co., Ltd.), UV-Vis spectrophotometer (UV-6100, Shanghai Yuan-Jie Instrument Co., Ltd.).

Analytical methods: COD was determined by COD rapid analyzer, BOD₅ was determined by dilution and inoculation method, pH was determined by portable pH analyzer, O₃ was determined by ozone rapid analyzer, and O₃ concentration (gas) was determined by iodometric method.

2.3. Pilot plant and process
The test device is mainly composed of advanced oxidation unit and biological aerated filter unit (see fig. 1). The reactor is made of white steel and has good corrosion resistance.

![Schematic diagram of pilot-scale system of O₃/UV-BAF](image)

In the advanced oxidation unit, pure oxygen was used as the gas source in the experiment. The ozone generated by the ozone generator and the effluent from the three-stage sedimentation tank were quickly mixed by a gas-liquid mixing pump, then pumped into the ozone oxidation tower and then into the ozone contact residence tank equipped with an ultraviolet lamp. The flow rate of the reflux oxidation tower in the residence tank was controlled to 900 L·h⁻¹. The spilled ozone was collected at the top of the oxidation tower and dissolved, absorbed and purified with 20% potassium iodide. In the biological aerated filter unit, the filler was porous volcanic rock with a particle size of 1~2 cm, the effluent from the advanced oxidation unit and the effluent from the pool B enter the bottom of the pool A together, the bottom of the pool A was not aerated, and the nitrate nitrogen returned from the pool B was denitrified by denitrifying bacteria using the effluent organic matter from the retention pool as an electron acceptor.
The upper part of pool A and pool B were both in aerobic state with a gas-water ratio of 5~10: 1. According to the actual operation situation, backwashing shall be conducted once every 2~3 weeks.

3. Results and discussion

3.1. Effect of ozone dosage on COD removal

It was used to evaluate the effectiveness of ozone degrading organic matter using the ozone quality required for every unit mass of COD removal (O_3/COD). The removal effect was not good when the ozone dosage was insufficient, and the economic feasibility decreased when the ozone dosage was excessive. The temperature of the test wastewater was normal temperature, the pH was not adjusted and was about 7, and the dosage of ozone was 6.66 g·h^{-1}. With the passage of time, ozone was continuously added to the reactor. Water samples were taken every 3 hours to determine COD value, and the effect of different dosage on COD removal effect was investigated. The results are shown in Figure 2.

![Figure 2](image)

Fig.2 The removal of COD by different ozone dosage

As can be seen from fig. 2, with the continuous addition of ozone to the reactor, the increase rate of COD removal generally showed a slow first, then a fast and then a steady trend. When the ozone dosage was 10.5 mg·L^{-1}, the COD removal rate was 2.9%, and the O_3/COD value was 1.4. When the ozone dosages were 21.0, 31.6, 42.1, 52.6 and 63.2 mg·L^{-1} respectively, the COD removal rate and O_3/COD values were (13.3%, 0.4), (20.3%, 0.6), (27.8%, 0.6), (32.7%, 0.8), and (35.3%, 1.6) respectively. When the concentration of ozone was 73.7 ~ 94.7 mg·L^{-1}, the increase of COD removal rate became smaller and tended to be stable. The COD removal rate was 36.1% ~ 38.1%, and the O_3/COD value was 2.7 ~ 8.8. It was analyzed that the low O_3/COD value may be due to the generation of ·OH and continuous mineralization of some organics in the wastewater irradiated by ultraviolet light within a long reaction time[6]. When the dosage of ozone was greater than 63.2 mg·L^{-1}, O_3/COD rose rapidly, which indicated that if the dosage of ozone is further increased, the degradation efficiency of ozone will decline rapidly, which is not desirable in economic feasibility. According to the above analysis, when the optimal ozone dosage was 52.6 ~ 63.2 mg·L^{-1}, the COD removal rate can reach 32.7% ~ 35.3%, and the O_3/COD value in each interval is 0.4~1.6. At the same time, it has higher COD removal rate and ozone degradation efficiency.

3.2. Effect of pH on COD removal

pH affects the mechanism of action of ozone degradation of organic matter. When the pH is lower than 4, the direct interaction plays a dominant role between ozone molecules and organic matters. When the pH is higher, the indirect oxidation of hydroxyl radicals generated by ozone decomposition dominates[13]. The initial COD concentration of wastewater in this test was 255.8 mg·L^{-1}, 1L of tail water was added to each beaker. The pH value was adjusted to 4 to 11 with sodium hydroxide or sulfuric acid solution. The ozone intake was 3 L·min^{-1} and the reaction time was 10 min. The effect of different initial pH values on the degradation of COD by ozone was investigated. The results are shown in Figure 3.
Fig. 3 Effects of different initial pH on COD removal

As can be seen from fig. 3, with the increase of pH, COD endpoint concentration showed a trend of decreasing first and then increasing. When pH = 4 ~ 6, COD removal rate was 16.3% ~ 22.2%. When pH = 7 ~ 8, COD removal rate was 26.7% ~ 27.6%. When pH = 9, COD removal rate was 29.9%. When pH = 10 ~ 11, COD removal rate was 25.6% ~ 27.0%. According to the test results, weakly alkaline conditions were conducive to carbonization of organic substances by O₃. The COD removal rate was the highest when pH=9, but it was not much different from that when pH=7. Therefore, the pH value of pilot-scale wastewater ranges from 6.96 to 7.19, and good removal effect can be obtained without adjusting the pH value.

3.3. COD removal by continuous operation of O₃/UV-BAF process

Bacteria in the biological aerated filter came from the factory's returned sludge, which contains a large number of bacteria specifically degrading characteristic pollutants, and was conducive to the rapid start-up and operation of the biological aerated filter. The lower half of BAF pool A was in an anoxic state. Denitrifying bacteria use organics in advanced oxidation effluent as carbon source to remove nitrate nitrogen refluxed from pool B, while COD in wastewater is degraded. The upper part of pool A and pool B were aerobic. The effluent from the third sedimentation tank of acrylic fiber plant was used as the test wastewater. After the O₃/UV-BAF process was started and stabilized, the pilot plant was continuously operated. the dosage of ozone was 38 ~ 44 mg·L⁻¹, the hydraulic retention time of the advanced oxidation pond water was 12 h, and the hydraulic retention time of the biological aerated filter was 20 h. the test results are shown in fig. 4.

Fig. 4 COD removal of each unit of the O₃/UV-BAF process during the stable operation stage
As can be seen from fig. 4, the influent COD concentration of the ozone oxidation tower ranged from 156.0 to 316.5 mg·L\(^{-1}\), with an average value of 245.7 mg·L\(^{-1}\). The concentration of BOD\(_5\) ranged from 3.0 to 13.4 mg·L\(^{-1}\), with an average value of 9.4 mg·L\(^{-1}\). The influent B/C was almost zero, which indicates that it was not feasible to further remove COD from tail water by biological method, and physical and chemical methods should be adopted first. After the combined action of ozone and ultraviolet, the effluent COD concentration dropped to 111.2 ~ 208.6 mg·L\(^{-1}\), with an average value of 165.8 mg·L\(^{-1}\). The concentration of effluent BOD\(_5\) ranged from 17.8 to 33.7 mg·L\(^{-1}\), with an average value of 24.6 mg·L\(^{-1}\), and the B/C was increased to about 0.15, thus improving the nutritional conditions for the subsequent biological aerated filter. The removal rate of COD by ozone ultraviolet treatment was 22.4%~40.2%, and the average removal rate was 32.0%. After the wastewater was treated by the biological aerated filter, the effluent COD concentration was reduced to 70.8-108.7 mg·L\(^{-1}\), with an average value of 83.4 mg·L\(^{-1}\), and the removal rate of COD by the biological aerated filter was 19.7%~40.9%, with an average value of 32.6%. The effluent COD met the requirements of the first-level discharge standard in the Notice on Issuing the Comprehensive Wastewater Discharge Standard (GB 8978-1996) Notice on Modifying Industrial COD Standard Values of Sinopec.

4. Conclusion
(1) COD removal rate is positively correlated with ozone dosage. With the increase of ozone dosage, COD concentration decreased continuously. In each time period (3h), the O\(_3\)/COD value generally showed a small increase first, then a rapid decrease and kept lower level. When the ozone dosage was greater than 63.2 mg·L\(^{-1}\), the O\(_3\)/COD value rapidly increased. When the dosage of ozone was 52.6 ~ 63.2 mg·L\(^{-1}\), the removal rate of COD can reach 32.7% ~ 35.3%, and it had good economic feasibility.

(2) When pH = 9, the COD removal rate was the highest, with little difference (>3.1%) from the COD removal rate when pH=7. The pH value of the effluent from the third sedimentation tank of acrylic fiber factory was in the range of 6.96 ~ 7.19, and good COD removal effect can be obtained without adjusting pH.

(3) O\(_3\)/UV-BAF process was feasible to solve the problem that COD in the effluent of dry acrylic fiber plant did not meet the standard. The average COD removal rate of O\(_3\)/UV unit was 32.0%, the average COD removal rate of BAF unit was 32.6%, and the average COD concentration of effluent was 83.4 mg·L\(^{-1}\), which met the requirements of the first-level discharge standard in the Notice on Issuing the Comprehensive Wastewater Discharge Standard (GB 8978-1996) Notice on Modifying Industrial COD Standard Value of Sinopec.

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