Treatment of Chemical Wastewater by O₃-BAC Method

Le Luo
Chongqing Vocational Institute of Engineering Chongqing, China

Abstract. Aiming at the problem of lower biodegradability and higher chromaticity of two stage biochemical treatment of petrochemical industries wastewater treatment plant, O₃-BAC is used to treat the water outlet of sewage treatment plant and the COD Cr, and Ammonia-nitrogen and sewage chroma are analyzed as well. The results show that the treatment efficiency could be achieved through O₃-BAC method, that is, the COD Cr is 26.7mg/L, the Ammonia-nitrogen is 0.18mg/L and the sewage chroma is 5 times.

1. Introduction
O₃-BAC (O₃-Biological Activated Carbon) is a wastewater treatment based on organic matters in ozonation. This process integrates O₃ pre-oxidation, activated carbon adsorption, biological oxidation and activated carbon regeneration. The O₃ pre-oxidation means that the 0.002~0.08μm particles are oxidized into particles less than 0.002μm so that both of adsorption efficiency of activated carbon and degradation efficiency of microbe are improved. The absorption of activated carbon could easily lead to a enrichment of higher concentration pollutants in local area, which is beneficial to the diffusion of pollutants into cell membrane and improves the treatment efficiency of low concentration wastewater[1]. Activated carbon has developed internal pores which is beneficial to microbe reprodictions [2]. In addition, the unit area of activated carbon is too large to accumulate microbes, which is beneficial to improve the removal efficiency of organic matters [3]. At last, the microbial degradation of activated carbon could decompose organic pollutants into CO₂ and H₂O. When completing the degradation, the activated carbon could recover its adsorbability[4]. The former treatment of coagulation air is to remove pollutants larger than 0.08μm so that the oxidation efficiency of O₃ could be improved. The O₃-BAC method solve the problem of high cost of O₃ oxidation and the difficulty of activated carbon adsorption.

2. The Development of O₃-BAC
After 1960s, with the development of industry, the source water was generally polluted by organic matter, such as pesticides, insecticides, herbicides, various additives, endocrine interferons, etc.. In 1970s, chlorine disinfection was found to react with organic compounds to produce disinfection by-products, which is harmful to human health. At the same time, the conventional treatment process had no removal ability for these organic compounds, so that the impact of drinking water on human health has been a great concern, forcing people to seek new drinking water purification technology to make up for the shortcomings of conventional treatment processes. In this context, O₃-BAC has been developed and applied.

The first use of O₃-BAC was a water plant in Dusseldorf, Germany, in 1961 [5]. On the basis of the original ozone+filtration, the activated carbon adsorption was added, by which the effluent water quality was obviously improved. Its success has attracted the attention of the German and Western European water treatment engineering circles. In 1967, Parkhurst et al [6] affirmed the beneficial effect of microorganisms on activated carbon, and finally established the O₃-BAC Technology. Since the beginning of 1970s, O₃-BAC technology has been extensively studied and applied [7].
3. Case Study

3.1. Case description

The design scale of sewage treatment plant in Petrochemical Industry is $5.5 \times 10^4 \text{m}^3/\text{d}$, and the operating scale is $2.40 \times 10^4$–$3.36 \times 10^4 \text{m}^3/\text{d}$. The process of O$_3$-BAC includes oil separation, average adjustment, hydrolyzation, A/O and the treatment of aeration tank and clarifier. The sewage comes from refinery, additive plants, auxiliary plants and fine chemical plants. The composition of sewage could be divided into naphthalene, quinoline, pyridine, polyvinyl alchohol, styrene, acrylonitrile, nitrobenzene and two vinylichloride, which cause the two stage biochemical treatment effluent has lower biodegradability and higher chromaticity, and the sewage quality cannot meet the requirement of wastewater reuse pretreatment after the removal of COD$_{Cr}$. Therefore, the O$_3$-BAC method could treat the two stage biochemical effluent of sewage treatment plant properly.

3.2. The processing installation of O$_3$-BAC method

The processing installation of O$_3$-BAC includes floatation tank, O$_3$ contact oxidation tower, intermediate regulating tank, BAC reaction column and auxiliary equipments, the processing flow is shown in Fig.1.

![Figure 1: The processing flow of O$_3$-BAC](image)

3.3. Sewage quality

The sewage comes from sewage treatment plant in Lanzhou Petrochemical Industry. The sewage quality and effluent design index are shown in Tab.1.

| Items               | Sewage quality | Effluent design index |
|---------------------|----------------|-----------------------|
| COD$_{Cr}$/mg/L     | $60$–$70$      | $\leq 30$             |
| Ammonia-nitrogen/mg/L | $\leq 10$     | $\leq 3$              |
| Petroleum/mg/L      | $\leq 5$       | $\leq 1$              |
| SS/mg/L             | $\leq 20$      | $\leq 5$              |
| PH                  | $6$–$9$        | $6$–$9$               |
| BOD$_5$/mg/L        | $\leq 10$      | $\leq 3$              |

3.4. Analytical method

COD$_{Cr}$ is measured by the dichromate titration, and BOD$_5$ is measured by tacheometer, then the sewage chroma is measured by a dilution multiple method, besides Ammonia-nitrogen is measured by reagent spectrophotometer, at last, the biological phase is photographed by microscope.
3.5. **Processing parameters**

The processing parameters of O$_3$-BAC is shown in Tab.2.

| Items                      | Parameters                         |
|----------------------------|------------------------------------|
| Sewage loads/kgCOD/m$^3$   | 1.3~1.5                            |
| Aeration                   | Gas-water ratio is (2~3):1          |
| Agent addition/mg/L        | 10~15                              |
| O$_3$ concentration/mg/L   | 4.2~4.5                            |
| Temperature/℃              | 18~25                              |
| PH                         | 7~9                                |

4. **BAC Hanging and Domestication**

Cultivation of biological membrane: the sewage temperature is about 30℃, which is beneficial to microbe cultivation. Before the operation of BAC column, it is essential to conduct the microbiological inoculation. After a week of cultivation and domestication, efficient microbe, selected from ordinary microbe, is full of BAC column with 72h aeration. Afterwards, 1/3 sewage in the column is discharged and new sewage is added to conduct the aeration again. At the beginning of aeration, the sewage is muddy. After 3-week treatment,

5. **Results Analysis**

5.1. **The analysis of COD$_{Cr}$ treatment efficiency**

The influent COD$_{Cr}$ is not stable and fluctuates between 50~80mg/L. The treatment efficiency of COD$_{Cr}$ by O$_3$-BAC is shown in Fig.2.

As shown in Fig.2, when the process runs continuously, the average COD$_{Cr}$ removal is above 50%. When the influent pollutant concentration changes, the concentration of pollutants in the effluent is slightly increased and is below 30mg/L, indicating that the O$_3$-BAC has a strong impact load resistance. Comparing the contribution of each unit to the COD$_{Cr}$ removal, the contribution of O$_3$ contact oxidation tower is about 10% and average effluent COD$_{Cr}$ concentration is about 56mg/L. it is seen that O$_3$ oxidation is not complete oxidation, which reduces the cost of sewage treatment. In addition, the BAC is main unit for degrading COD$_{Cr}$ and the average COD$_{Cr}$ concentration and removal respectively are 26.7mg/L and 56%, and then the BAC could continuously operate 3~4 months without washing. If the total amount of COD$_{Cr}$ removal in each washing cycle is about 60 times more that the theory removal, it shows that the biodegradation of microbe contributes to the
COD$_{cr}$ removal and the BAC plays a key role during the whole process. At last, it takes about 3~4 weeks from the beginning of BAC hanging to the stable operation.

5.2. The analysis of Ammonia-nitrogen treatment efficiency
The fluctuation of influent Ammonia-nitrogen concentration is between 0.2mg/L and 1.0mg/L, but its total content is low. After the O$_3$-BAC, the Ammonia-nitrogen concentration is 0.18mg/L and removal is 75%, which could be detected in Fig.3.

5.3. The analysis of chroma treatment efficiency
The influent chroma changes between 12~16 times. The effluent chroma is about 5 times. The chroma removal by O$_3$-BAC is shown in Fig.4.
Figure 4. The chroma removal efficiency by O$_3$-BAC

As shown in Fig.4, BAC is the main unit of chroma removal, which accounting for more than 90% of the total removal. However, the contribution of O$_3$ is relatively low and about 5%~10%, due to the chromophoric groups in sewage is hard to remove by O$_3$.

5.4. The analysis of biodegradability of sewage
The biodegradability of effluent from Lanzhou Petroleum Industry is low. Before entering the O$_3$ contact oxidation tower, the sewage BOD$_5$/COD$_{Cr}$ ratio is about 0.08, which is difficult to degrade. In the pilot test, the O$_3$ additive is about 4.0~4.5mg/L, and the BOD$_5$/COD$_{Cr}$ ratio of effluent is about 0.21 due to incomplete oxidation between O$_3$ and organic pollutants in sewage.

5.5. The analysis of microbe in BAC tower
Biodegradation of BAC degradation are the main mechanism of activated carbon adsorption and biofilm, and microbial degradation of pollutants test plays a direct role in the process of test. Through the examination, the operating state of system could be marked in accordance with the species and activity of microbe. During the pilot test, the biological observation of BAC was conducted irregularly so as to better understand the operation of the system and make appropriate adjustment.

The observation of the biological phase was carried out by 100 times optical microscope. Before the observation, the carbon samples in the BAC reaction tower were placed in the beaker, and then the carbon particles were broken with tweezers. Through the observation, didinium, rotifers, nematodes, insects roaming, dun pelionella, caterpillar and other protozoa and metazoan daphnia are detected, which means there are lots of species on the microbial membrane in BAC tower. At the same time, The emergence of protozoa and metazoan showed good effluent quality and stable system operation.

6. Conclusion
The O$_3$-BAC process can be used for a stable treatment of the two grade biochemical effluent of Lanzhou Petrochemical Industry wastewater treatment plant. The influent COD$_{Cr}$ concentration is fluctuated between 50mg/L and 80mg/L, and the average effluent COD$_{Cr}$ concentration is 26.7mg/L. The influent Ammonia-nitrogen concentration is 0.2~1.0mg/L, and the average Ammonia-nitrogen concentration is 0.18mg/L. The influent chroma is about 12~16 times, and the effluent chroma is nearly 5 times. About analysis shows that O$_3$-BAC has a strong impact load resistance. O$_3$ contact oxidation tower can not only degrade some pollutants, but also improve the biodegradability of sewage. The BOD$_5$/COD$_{Cr}$ ratio of sewage before entering O$_3$ contact oxidation tower is about 0.08, and the effluent BOD$_5$/COD$_{Cr}$ ratio is about 0.21. Through the observation, the biological composition of the activated carbon filler is complete and the microbial population is abundant, indicating the stable operation of the system.

7. References
[1] Benitez F J, Acero J L, Real F J, “Comparison of different chemical oxidation treatments for the removal of selected pharmaceuticals in water matrices,” Chemical Engineering Journal, vol.168, Mar. 2011, pp. 1149-1156.
[2] D. He, N. Gao, W. Zeng, “Biofilm Colonization in Advanced Treatment of Drinking Water using Biological Activated Carbon Process,” Industrial Water & Wastewater, vol.37, May. 2006, pp. 16-19.

[3] H. Yao, F. Ma, G. Li, “Treatment of Petrochemical Wastewater by O3-BAC,” China Water & Wastewater, vol. 19, 2003, pp. 39-41.

[4] J. Zhang. “Study on the Removal of Micro Pollution by O3-BAC,” Water & Wastewater Engineering, vol. 22, Apr. 1996, pp. 57.

[5] Li L, Zhang P, Zhu W, “Comparison of O 3 -BAC, UV/O 3 -BAC and TiO 2 /UV/O 3 -BAC processes for removing organic pollutants in secondary effluents,” Journal of Photochemistry & Photobiology A Chemistry, vol.171, Feb. 2005, pp. 145-151.

[6] Li L, Zhu W, Zhang P, “Comparison of AC/O3-BAC and O3-BAC processes for removing organic pollutants in secondary effluent,” Chemosphere, vol. 62, Sep. 2006, pp. 1514-1522.

[7] Zhu J P, Peng Y Z, Li X L, et al., State Environmental Protection Administration of China, Monitoring and analysis method of water and wastewater. Beijing: China Environmental Science Press, 1997.