Application of Ozone-BAC process in advanced treatment of drinking water and sewage

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Abstract. With the increasing pollution of water sources and the improvement of Drinking Water Regulations, the conventional treatment technology can no longer meet the needs of the people. It is increasingly necessary to adopt advanced drinking water treatment technologies. Ozone-BAC process (O$_3$-BAC) is a new type of process to treat slightly-polluted source water efficiently, catalysts and oxidants preparation of which are simple and efficient. It can remove turbidity, odor and color from the water, to improve the effect of flocculation as well as the taste; it can also remove hard-to-degrade and soluble organics; can achieve the indicators of circulating water, with good application prospects. This article analyzes the operation status of ozone-BAC process in water treatment process, proposes the problems of the technology in water treatment process and discusses its future development.

1. Introduction

Water is essential for sustaining biological life and maintaining biological health, and it is an irreplaceable resource for the survival and sustainable development of human society. The “2016 China Water Resources Bulletin” shows that in 2016, the total amount of water supply in the country was 604.02 billion cubic meters. Compared with 2015, the water supply of surface water sources decreased by 5.71 billion cubic meters, and the water supply of groundwater sources decreased by 1.22 billion cubic meters. The water supply of other water source increased by 630 million cubic meters, and the government supplemented the environment with 14.26 billion cubic meters water artificially, occupying 2.4% of the total water[1].

At the same time as water resources are in short supply, water pollution in China is serious. Among the 1940 surface water national examination sections that were inspected in 2016, 47 were class I, accounting for 2.4%; 728 were class II, accounting for 37.5%; 541 were class III, accounting for 27.9%; iv class 325, accounting for 16.8%; v class 133, accounting for 6.9%; inferior v class 166, accounting for 8.6%. Ministry of Land and Resources carried out monitoring of groundwater quality of 6124 monitoring sites (including 1,000 national monitoring sites) in 225 prefecture-level administrative regions of 31 provinces (regions, cities) across the country. The results showed that: the water quality was excellent, good, fair, poor and very bad monitored sites were 10.1%, 25.4 %, 4.4%, 45.4% and 14.7%[2]. With the increasing pollution of drinking water sources, in order to meet the ever-increasing drinking water quality standards, the use of advanced drinking water treatment technology has become increasingly necessary. Due to the complexity of water source pollutants, conventional water purification processes such as activated sludge process and A/O process have been unable to meet the water quality requirements of drinking water. In order to effectively remove various organic pollutants in the drinking water source, advanced treatment technologies such as ozonation and biological activated carbon technology and membrane treatment technology have emerged. Compared to the chlorine disinfection used at this stage commonly, the equipment required for the O$_3$-BAC process is
simple, and the treatment effect is good. The \( \text{O}_3 \) produced by itself is non-toxic, and the \( \text{O}_2 \) formed by decomposition does not pollute the environment. The process forms relatively less disinfection by-products. In recent years, it has been widely used in various places and has been an excellent technology for water treatment.

2. Ozonation and biological activated carbon technology and its mechanism
Ozone has been used in water treatment for a long history. It can be used to decolorize, eliminate algae, remove odors, and remove petroleum products. It can also reduce COD and color in water, which has been applied to many aspects. The reaction between ozone and organic pollutants is mainly divided into two aspects. On the one hand, ozone and organic matter react directly, that is, ozone molecules directly oxidize organic pollutants; on the other hand, ozone generates hydroxyl radicals, and chain reactions occur in water[3]. Ozone oxidation process is simple and takes less time, but the oxygen molecules limits oxidizing ability and have strong selectivity. The excessive energy consumption of the ozone preparation system hinders the wide application of this technology. In recent years, the combination of ozone and other technologies has been yielding good results at various pilot sites. The application of ozone is gradually gaining new vitality in the field of water treatment.

The first combined use of the O\(_3\)-BAC process was at the Amstaaad water plant in Dusseldorf, Germany, in 1961. The success attracted the attention of the water treatment engineering communities in German and Western European, and was introduced to China in the 1970s, also has been applied since 80s in the 20\(^{th}\) century.

2.1 Mechanism
The O\(_3\)-BAC process combines ozone chemical oxidation with activated carbon physics, chemical adsorption, and bio-oxidation degradation technologies to oxidize and adsorb pollutants in water to purify water. After the combination of ozone catalytic oxidation and the activated carbon, the quality of treated sewage water can be significantly improved, and the treatment cost is greatly reduced. Ozone and biological activated carbon show their complementarity in the process of water treatment. Ozone oxidizes macromolecule organics into small-molecule organics and improves the biodegradability of water, at the same time the left small-molecule organics are degraded by biological activated carbon. Due to the full supply of oxygen from the ozone, large amounts of aerobic microorganisms grow and multiply in the carbon bed. They further degrade and remove the adsorbed organic matter with the dissolved oxygen in the water. The activated carbon can be continuously regenerated and the adsorption of organic matter and dissolved oxygen can be continuous. In this way, the dual role of bio-adsorption and bio-oxidation of the biofilm is gradually formed in the carbon bed[4]. Ozone catalytic oxidation and its combination technologies have obvious advantages in the organic matter removal and the control of oxidation by-products, also can improve the adsorption performance of activated carbon nearly twice. After the combination with biological activated carbon, after integrated with organic compounds, the removal capacity of system increased by 10%[5].

2.2 Advantages
Simply put, this technology is based on the traditional water treatment process. Pre-ozonification was used instead of pre-chlorination and biological activated carbon filter was set up after the fast filter tank[6]. The mechanism of action mainly includes the following aspects: (1) Ozone has a high oxidation-reduction potential (E\(_v\)=2.07V); (2) For non-biodegradable organic substances, ozone oxidation can partially increase its biodegradability and adsorption performance, making it be easily adsorbed on activated carbon; (3) Ozone will be decomposed into oxygen, providing beneficial growth condition for aerobic microorganisms on activated carbon; (4) The pore structure of activated carbon provides a habitat for the growth of microorganisms[7].

3. The application of O\(_3\)-BAC process in drinking water treatment
Due to its economic and operational advantages, the O\(_3\)-BAC process has been widely used at home and abroad. It has been confirmed through experiments in China that this process has a good removal effect on toxic substances such as light petroleum-polluted groundwater, pharmaceutical wastewater, and excessive antibiotics in water bodies. It can reduce pollutants and toxicity, as well as increase the biodegradability of wastewater, but it is too costly to achieve wastewater discharge standards only depends on ozone catalysis[4,
The cost of water treatment is a fundamental problem in the application of various technologies. There is a large amount of sewage in China, the treatment costs and maintenance costs of various technologies must be taken into account.

The O₃-BAC process is more commonly used to treat secondary sedimentation tanks and further improve water quality. Shi et al. used intermediate high density sedimentation tank sinking water as influent, indicating that the O₃-BAC process has a good removal effect on water turbidity, CODₘᵢ, and ammonia nitrogen during the period of film formation[10]. However, in their experiments, biofilms did not mature until about 82 days later in the experiment, and the long film formation period was also one of the defects of the process. Wang et al. reported on the application of O₃-BAC technology in the advanced treatment of drinking water in Kunshan Luanhe Water Plant and Kunshan No. 3 Water Plant (Phase II), indicating that the removal rate of NH₃-N is 27.9% higher than that of conventional treatment processes, which is up to 77.2%; the removal rate of CODₘᵢ increased by 32.8% and the highest was 74.6%. CODₘᵢ of the effluent was less than 3.0 mg/L[11]. The process removes ammonia nitrogen by biotransformation, replacing the chlorination method at the breakpoint and avoiding the formation of large amounts of organic chlorides[6, 12-15]. The total amount of ozone is less than that used alone, the cost is lower than that of single use of ozone or activated carbon and the effect is better; the water quality after treatment is fully improved, more stable and easier to manage. Li and others introduced two advanced treatment plants that used III-IV lake water as the source of water. After the operation of more than one year, they found that COD of the effluent dropped from 3.51 mg/L to 2.27 mg/L; the turbidity dropped from 0.45 NTU to 0.28 NTU; the trihalomethane content of the chlorination disinfection by-product was also reduced by 79%; the sensory index of drinking water was significantly improved[16].

The original intention of the process is to remove turbidity and color, according to experimental data, the effect is significant. Liu et al. found that the O₃-BAC process has a good effect on the purification of micro-polluted source water. Through the analysis of the water quality of the water plant, the overall removal rate of the color was 80%; the turbidity was nearly 100%, and the iron ions was 98%; the manganese ions was 90%[17]. Long et al. found that the O₃-BAC process made the effluent water biologically stable and inhibited the growth of E. coli and other microorganisms. The removal of the precursor of the trihalomethane, a chlorination disinfectant by-product in water, had a removal rate of 49.3%[18]. Gao et al. took Jialingjiang water treatment plant filtered water as the research object, and studied the removal effect of ozone-biological activated carbon process on the trace phthalates in drinking water (also known as phthalates, phthalate) esters, PAEs), and found that the removal rate of PAEs gradually leveled off after 100 cm charcoal column, the removal rate of low molecular weight PAEs was higher than that of high molecular weight[19]. Subsequent research should explore the removal of some increasing pollutants in recent years, such as surfactants, printing and dyeing wastewater.

**4. Application of O₃-BAC process in sewage treatment**
The O₃-BAC process is not only used in water purification technology, but also plays an important role in the wastewater treatment process. It is mainly used for the advanced treatment of effluent from secondary sedimentation tanks. The typical urban sewage treatment process includes mechanical (primary) treatment, biochemical (secondary) treatment, and sludge treatment. The characteristics of secondary effluent from urban sewage treatment plants in China are: large overall emissions, high TN content, low organic pollution, and poor biodegradability[20]. The commonly used treatment methods for tailwater at the municipal sewage treatment plants include: ozone/ultraviolet light, ozone/hydrogen peroxide, and ozone/activated carbon. The most commonly used method is ozone/activated carbon at this stage. Zhou et al. studied the wastewater treated with ozone/activated carbon, and its effluent index values were all lower than the water quality standards required for the reuse of reclaimed water, fully satisfying the requirements of various reuse water[22]. Zheng et al. performed optimization of conditions for ozone oxidation and ozone/activated carbon oxidation by orthogonal experiments and single-factor experiments, and screened out the ozone/activated carbon oxidation
method as a pretreatment method of the follow-up biological treatment from the perspective of economic and technical effects[23].

In the application of the ozone oxidation process, researchers added catalysts for catalytic ozone oxidation to further improve the processing results. Liu and others studied the treatment effect of ozone activated/carbon technology on printing and dyeing wastewater, added ferric salt as a catalyst, and found that the more ferric salt added, the better the pollutant removal effect, and the effect of divalent iron catalyst is better than that of trivalent[24]. Zou et al. found that the combination process of oxygen catalytic oxidation process and activated carbon adsorption process has obvious advantages over sewage oxidation process alone or activated carbon adsorption process. The COD removal of hard-degradable wastewater in chemical industry park can reach up to 82%[3]. Jia and others used the combined process of biological filter-ozone oxidation-biological activated carbon to treat the slightly contaminated river water of the Baoding Moat deeply, and found that the removal of COD$_{Mn}$, NH$_3$ -N, color, and turbidity reached higher than 80%[25].

5. **Deficiency**

5.1 Defection of technology

Although the O$_3$-BAC process has been widely used in water plants worldwide, the following problems still exist in current operation: (1) high investment and operating costs impede the large-scale operation of the process; (2) it is almost impossible to establish a system model to identify the relationship of influent water quality, residence time of bio-activated carbon devices, filtration rate, ozone dosage, and ozone concentration; (3) the granularity of activated carbon, its surface chemical and electronic status, and the mechanism of its attachment to bacteria, etc. still need further study; (4) It is impossible for the added ozone to oxidize organic substances in the micro-polluted water source into inorganic substances completely, but generated various intermediate products; (5) The effect of the operation is affected by various conditions, such as water temperature, pH, and bacterial species, and the effect is not stable; (6) The degradation products in the process of microbial metabolism, and the microorganisms themselves enter the water body, there are no reports in the literature about whether they will harm human, and further research is needed[26, 27].

5.2 Defection of activated carbon

The performance of activated carbon is a key factor of the process, it affects the treatment directly, so it is necessary to pay attention to its maintenance and regeneration. The deactivation of activated carbon is a problem that should be thoroughly studied in terms of the attenuation of the adsorption capacity of selected activated carbon. The feasibility and operating costs of activated carbon rejuvenation must be further considered, and detailed economic costs for the overall process should be estimated[3, 28]. Biological activated carbon is only suitable for deep purification of low-temperature, low-turbidity, and micro-polluted water sources. The initial investment of equipment is large, the natural film coating takes a long time, the application range of influent pH is narrow, and the impact load is poor, all the factor hinder the O$_3$-BAC process’s further development[29].

6. **Improvement**

Studies have found that chlorine, temperature, pH, and dissolved oxygen all have a certain influence on the biofilm formation. In the subsequent process of activated carbon adsorption, the appropriate aeration of the inlet water of carbon column increase the dissolved oxygen concentration in the water, which is conducive to maintaining the aerobic environment in the carbon column and shortening the film-forming time[10]. The ozone treatment effect is good because it is more oxidizing than liquid chlorine, destroys the dehydrogenase of the bacteria, interferes with the respiration and leads to the death of the bacteria. The disadvantage is that the chemical nature of ozone is unstable, which easily decomposed into O$_2$ in water and cannot be retained for a long time, unable to play the "residual chlorine" effect. In order to ensure that the water is not contaminated during transportation, a small amount of organic substances such as liquid chlorine or chloramine should be added in the last step of effluent to avoid water quality problems due to pipeline’s leakage and other problems. As the organic pollutants have been basically removed during the ozone oxidation process, less mutagenic substances are finally generated, which at the same time can reduce the dosage of disinfectant and save cost and reduce the process[27].
The effect of activated carbon in the O₃-BAC process is excellent as it forms biofilm in its pore structure and on its surface, and adsorbs and decomposes organic matters. However, Tang et al. found that the amount of bacteria in the factory water after biological activated carbon treatment may not meet the standards. In addition to strengthen the management of the conventional process, the water plant should also perform the soaking treatment of the activated carbon filter regularly[30]. For the status of survival and metabolites of microorganisms in O₃-BAC process, further researches are needed.

7. Conclusion
Research shows that the O₃-BAC process can effectively remove organic matter and other impurities in the secondary effluent of the sewage treatment plant, improve the quality of the effluent, and have advantages over the traditional water treatment methods in the treatment of effluent and wastewater. O₃-BAC process is a new type of highly efficient micro-polluted water treatment process which has broad application prospects. We should research and develop new technologies actively, improve level of its operational control, reduce investment and operating costs, make full use of effectiveness of the process in removing pollution, reflect the superiority of this technology, and promote its wide application in engineering fields.

References
[1] Xiaohu Qi, China Financial and Economic News, 003 (2016)
[2] China Environmental Status Bulletin 2016 (Excerpt), 35-47 (2017)
[3] Zhan Zou, University of Chemical Technology (2016)
[4] Xiaoyan Qu, Jianguang Liu, Ding Li, Ailian Shen, water science and engineering, 33-35 (2010)
[5] Renguang Cha, Bangjun Han, Jun Ma, Liping Shen, China Water & Wastewater, 1-5+10 (2007)
[6] Yuequn Xu, Qiaoli Zhao, Journal of Shijiazhuang Institute of Railway Technology, 34-37 (2010)
[7] Yanning Chen, Qiangshen Ning, Yichun Zhu, Guangming Zhang, water&wastewater engineering, 57-62 (2010)
[8] Minghao Kong, Chinese Research Academy of Environmental Sciences (2016)
[9] Yong Yue, Hao Deng, Guangquan Liu, Xiaohui Liu, Journal of Northeast Normal University(Natural Science Edition), 177-181 (2009)
[10] Rui Shi, Qi Wei, Heping Liu, Water Technology, 10-12 (2012)
[11] M. Wesseler, Jian Wang, General Machinery, 32-33 (2009)
[12] U.v. Gunten, Water Research. 37 (2003)
[13] Jongsheng Yang, Dongxing Yuan, Tsuzaop Weng, Desalination. 263 (2010)
[14] Naiyun Gao, Yan Ma, Wenhui Chu, Wenlei Rong, water&wastewater engineering, 13-16 (2013)
[15] Dong Zhang, Jie Dai, Hanwei Ren, Jianwei Yu, Jun Tong, Hongbin Chen, water&wastewater engineering, 21-24 (2013)
[16] Shuyuan Li, Yuhong Wu, Haiyan Liu, China Water & Wastewater, 36-38 (2008)
[17] Bocai Liu, Hebei University of Technology (2015)
[18] Yutao Long, JLU (2016)
[19] Xu Gao, Zhongxun Yu, Jingsong Guo, Huaimao Li, Sheng Guo, Fengqing Wang, Lei Lu, Qing Hu, Chinese Journal of Environmental Engineering, 1773-1778 (2011)
[20] Jiejun Hu, Lanzhou Jiaotong University (2017)
[21] Xuemin Xiang, Hao Tang, Environmental Science & Technology, 91-92+114-115 (2005)
[22] Chunqiao Zhou, Li Li, Tingting Nih, Jingyu Zhao, Guangzhou Chemical Industry, 127-128+141 (2013)
[23] Zhiyang Zheng, Hebei University of Science & Technology (2017)
[24] Qing Liu, Nanjing Normal University (2014)
[25] Ding Jia, Yuanyuan Gao, Zhiyuan Niu, Zhenchen Li, Technology of Water Treatment, 73-77 (2016)
[26] Liyi Liu, Yinyin Xie, Jianming Huang, Fujian Analysis & Testing, 57-62 (2014)
[27] Yunfeng Xiong, Wei Sun, Science & Technology Information, 45-46 (2012)
[28] Jabo Liu, Hebei University of Engineering (2013)
[29] Feng Guo, Xia Wang, Qiang Xiao, He Xiao, Industrial Water Treatment, 19-23 (2011)
[30] Liwen Tang, Baiming Zhou, Guangdong industry chemistry, 136+135 (2016)