Research Progress on Biochemical Process Treatment of Coking Wastewater

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Abstract: Coking wastewater, as one kind of industrial wastewater, was discharged in the process of coking, which is polluted by organic matter and metal ions. The wastewater was highly polluting and difficult to treat, so an efficient method is needed to treat the coking wastewater. At present, coking wastewater is mainly treated by biochemical technology. This study first briefly describes the source, composition and harm of the coking wastewater. Then introduces the common treatment methods and processes of coking wastewater, reviews the application of different biochemical treatment technologies in coking wastewater treatment, compares and summarizes the different processes of biochemical technology (including A/O, $A_1/A_2/O$, A/O/O process), and finally discusses the research direction of biochemical technology treatment of coking wastewater. This paper can provide reference for future biochemical treatment of coking wastewater.

Keywords: coking wastewater, biochemical technology, A/O, $A_1/A_2/O$, A/O/O

1. Introduction

Coking wastewater is produced from the initial cooling of coke oven gas and coking production process and the steam condensing wastewater [1].It is a typical kind of industrial wastewater containing refractory organic compounds. If treated improperly, it will cause great harm to the environment.

At present, the treatment process of coking wastewater mainly includes three parts: pretreatment, biochemical treatment and advanced treatment. In the pretreatment step [2], some technologies are often used, such as homogeneous precipitation, air flotation, oxidation, oil isolation and reverse osmosis. The pretreatment process can remove part of the pollutants that are easy to be removed and reduce the difficulty of treatment for subsequent treatment. And biochemical treatment technology mainly adopts anoxic/oxic (A/O) biological treatment, after biochemical treatment, the wastewater cannot meet the discharge standard, and need further depth treatment, depth treatment technology includes advanced oxidation, coagulation precipitation and immobilization biotechnology and reverse osmosis membrane treatment technology.

Coking wastewater can be recycled after reasonable treatment. In the above three treatment steps, biochemical treatment is the biggest improvement of the water quality of coking wastewater, and it is also the most important part of sewage treatment. At present, the main biochemical technology for the treatment of coking wastewater is A/O series process. The

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A/O series process is developed in the general biochemical treatment technology, combining aerobic treatment with anaerobic and hypoxia treatment, and using some obligate bacteria to achieve the transformation of different nitrogen forms into harmless nitrogen[3]. This series of processes is very effective in treating coking wastewater with high COD and high ammonia nitrogen. A/O series process including technologies like A/O, A1/A2/O, A/O O,etc. [4].

This paper first describes the source, composition and harm of coking sewage, summarizes the application progress of the above several processes in coking wastewater treatment, analyzes the A/O series biochemical treatment technology, and introduces the advantages and disadvantages of several A/O series processes in the treatment of coking wastewater. This paper can provide reference for future biochemical treatment of coking wastewater.

2. Characteristics of Coking Wasterwater

2.1 Composition of coking wastewater

Coking wastewater contains suspended particulate matter, nitrogen, oxygen, phosphate, sulfide, phenols, benzene, multi-cyclic aromatic compounds and heavy metals [5], which is a typical industrial wastewater containing refractory organic compounds. From the perspective of water quality characteristics, coking wastewater is characterized by low pH value, high chemical oxygen demand (COD), biochemical oxygen demand (BOD), solid suspended matter concentration (Table 1).

Table 1. Comparison of the composition and discharge standards of coking wastewater

	CODcr(mg/L)	Phenol (mg/L)	Ammonia nitrogen(mg/L)	Prussiate(mg/L)	pH	Reference
Coking wastewater	4000-8000	5000-7000	1500-2500	5-15	9±0.2	[6-9]
Effluent standard	100	0.5	10	0.5	6-9	

2.2 Hazards of coking wastewater

Coking wastewater contains high concentration of organic matter, suspended matter and pollutants, these substances will cause irreversible impact on the environment [10]. Among them, organic matter mainly includes benzene, toluene, etc., with toxic and carcinogenic [11]. Certain phenolics can also cause protein denaturation and precipitate [12]. The accumulation and deposition of suspended matter, phosphate and sulfide in coking wastewater lead to excessive eutrophication of water, causing the proliferation of algae, and finally forming the bloom phenomenon [13]. In addition, the coking wastewater also contains ammonia nitrogen, cyanide and other pollutants, which will not only cause pollution to the water body, but also have a negative impact on the air and soil [14]. The heavy metals in coking wastewater not only affect the growth and development of aquatic animals, but also threaten human life and health through the biological enrichment of the food chain [15]. Therefore, a series of effective measures should be taken to treat the coking wastewater to ensure the people's health and the integrity of the ecosystem.

3. A/O Series Process

There are many organic substances in coking wastewater that are difficult to be degraded by microorganisms alone. Only when they coexist with easily degradable organic substances, can they be degraded into degradable organic substances through the common metabolic action of microorganisms [10]. Therefore, the wastewater treatment plants simply use aerobic or anaerobic technology to treat the coking sewage is difficult to reach the standard of discharge [5]. The main biochemical technology for the treatment of coking wastewater is A/O series process. The A/O series process is developed in the general biochemical treatment technology, combining aerobic treatment with anaerobic and hypoxia treatment, and using some obligate bacteria to achieve the transformation of nitrogen form, and finally into harmless nitrogen[3]. A/O series process includes A/O, A1/A2/O, A/O/O etc. [4]

3.1 Anaerobic-aerobic (A/O) process

wastewater first flows into A section (denitrification) and then experience the aeration treatment of O section (aerobic) , organic compounds in wastewater serve as carbon source in denitrification reaction, cooking wastewater should be proceed denitrification in the hypoxia pool, denitrification produced in the nitrification reaction consumption reduce about 50% [16], organic compound in wastewater which is difficult to be aerobic degraded can be degrade into simple fats and organic matter , thus improve the biochemical feasibility of wastewater [17]. The nitrogen removal process is simple and used widely. This process uses the organic matter in water as the carbon source to removal denitrification, and the alkali produced in the denitrification process can be used in the nitrification reaction stage, which makes full use of the carbon source and saves the alkali [18]. After treatment of A/O process, the NH4+ in the wastewater was quickly oxidized to NO3-N, NH3-N and NO2-N [19], the removal rate of COD, ammonia nitrogen and other pollution indexes in wastewater can reach 95% (Table 2).

Table 2. Comparison of wastewater before and after treated by A/O process

	COD (mg/L)	Ammonia nitrogen (mg/L)	Volatile phenol (mg/L)	Cyanide (mg/L)	pH	Reference
Original coking wastewater	2981	125	130	11	9.33	[9]
Coking wastewater after treated	95	2.261	0.46	0.462	7.67	
Removal rate%	96.81	98.19	99.65	95.8	-	

The pH, reflux ratio, temperature and quality of wastewater are important parameters which affecting the treatment effect of coking wastewater in A/O process. The pH value of the aerobic tank is not easy to control which will affect the stable operation of the whole system. The pH of general nitrification process is controlled at 7.5-8.0, and the pH of denitrification process is controlled at 6.5-7.0. When the reflux ratio is too low, the concentration of nitrate nitrogen which flow into the denitrification pool is low, resulting in a low level of C/N at denitrification pool, and the denitrification reaction cannot proceed normally. If the reflux

ratio is too high, the concentration of nitrate nitrogen which flow into the denitrification pool is high, carbon source is insufficient and need adding carbon source; in addition, A high reflux ratio will lead to the high dissolved oxygen content in the denitrification pool and inhibit the denitrification. The reflux ratio of 2-4 is appropriate. The temperature of wastewater is also one of the important factors affecting the growth of microorganisms. Too high temperature leads to the death of microorganisms, while too low temperature will inhibit or even stop microbial growth. The appropriate temperature for nitrification was 25-35℃ and that for denitrification was 32-34℃. The content of organic matter in the wastewater is closely related to the operation stability of the system. When the COD is about 3000 mg/L, the A/O system is running normally, the effluent index is relatively stable and could attain the standard of discharged; when the COD is between 4500 and 6000 mg / L, the A/O system stability is poor, the effluent COD increases, and the indexes of volatile phenol and cyanide are abnormal[20]. So A/O process needs controlling the quality of wastewater with an inlet COD <4500 mg/L to ensure stable operation of the system and outlet water quality.

3.2 A1/A2/O (anaerobic, aerobic and oxic) process

A1/A2/ O method is composed of three sections of biological treatment device, adding anaerobic section on the basis of A/O process, the order is anaerobic, hypoxia and anaerobic, the anaerobic section can hydrolyze acidification wastewater better, in order to improve the efficiency of subsequent treatment (hydrolysis acidification promotes the biochemical feasibility of coking wastewater) [10].A1/A2/ O process improves the oxidative decomposition capacity of carbon source on the basis of A/O process [21], and has the characteristics of strong impact load resistance and stable operation, but there are still deficiencies in some indicators, such as low sulfide removal rate and NH3-N is also more difficult to stabilize below 15mg/L [22]. Show in table 3.

Table 3. Comparison of inlet and outlet coking water through $A_1/A_2/O$ process

	COD (mg/L)	Volatil (mg/L)	Prussiate (mg/L)	Sulfide (mg/L)	Ammonia nitrogen (mg/L)	pH	Reference
Inlet coking water	2000-3000	400-600	10-20	30-100	200-300	7-10	[23]
Outlet coking water	120-180	0.01-0.5	0.01-0.5	0.3-1	5-25	7-8	
Removal rate (%)	94	99.9	99.9-97.5	99	97.5-91.7		

A1/A2/O process will be affected by factors such as pH, reflux ratio, temperature and wastewater quality. The water's temperature for anaerobic and hypoxia stage of A1/A2/O process is about 55℃. The dissolved oxygen in aerobic tank should be controlled above 2 mg/L. Too high dissolved oxygen content can cause sludge swelling; with too low content, bacterial death and loss will occur, so the dissolved oxygen in hypoxic tank should be control below 0.5mg/L [23]. The removal rate of TN can increase under the C/N value, reduce the sludge production and alkali injection, shorten the reaction time and reduce the reactor volume [16].The oxic pool needs to control the pH value at about 8.0-8.4. And the aerobic pool controls the pH value at 6.5-8.0. Ammonia nitrogen releases H＋ during nitrification which

resulted in the decrease of pH value, the pH value of the aerobic pool can be guaranteed basically by reflow effect. But the the aerobic pool must be modulated pH value to guarantee by adding Na2CO3[23]. The change of climate causes the change of wastewater temperature and affects the treatment results in the system obviously. The suitable treatment's temperature is 20℃ -30℃. When the water temperature is less than 18℃, the bacterial vitality decreases and the concentration of COD and NH3-N in coking wastewater rise. The active of bacteria which process cyanide will be inhibited when the water's temperature was higher than 35℃, and then the concentration of cyanide increased significantly. The water quality of the system may also lead to the effluent COD to exceed [24], and the mass concentration after ammonia is NH3-N is controlled below 300 mg/L; COD should be controlled below 3500 mg/L; and sulfide is controlled below 80 mg/L [23]. The change of the incoming water mass concentration will also affect the nitrification and denitrification process, and the bacterial vitality will be inhibited, especially the ammonia nitrogen index of the effluent.

3.3 A/O/O process

Section A of the A/O/O process is the anoxic denitrification section, the first O is the nitrosating section, and the second O is the nitrification section. In the traditional nitrification and denitrification process, the nitrogen in the coking wastewater is composed of nitrite nitrogen (NO2-), which needs to consume a certain amount of dissolved oxygen when converted to nitrate nitrogen (NO3-). When reconverting NO3- into NO2-, more organic carbon sources will be consumed. A/O/O process can achieve the denitrification directly rather than converting NO2 to NO3-. A/O/O process improves the activity of the microorganisms system and the impact resistance and load capacity of the system , better solve the phenomenon of high dissolved oxygen, improve the denitrification ability of A section, a part of nitrite root water flow back to A Section, with nitrite nitrogen removal method, can reduce the amount of alkali add about 20% [25]. The efficiency of removal COD and ammonia nitrogen is high. For A/O/O process, the removal rate of COD in coking wastewater can attain more than 95%, ammonia nitrogen and sulfide removal rate can attain more than 97%, and volatile phenol removal rate can reach more than 99% (Table 4).

Table 4. Comparison of inlet and outlet coking water through A/O/O process

	COD (mg/L)	Ammonia nitrogen (mg/L)	Volatil (mg/L)	Sulfide (mg/L)	Prussiate (mg/L)	SS(mg/L)	pH	Reference
Inlet coking water	2243.1	99.3	455	27.2	1.78	214.2	8.276	[26]
Outlet coking water	100.4	2.82	0.037	0.69	0.13	0.13	6.701	
Removal rate%	95.52	97.16	99.99	97.47	92.7	78.52		

Note: The coking wastewater in this table has been pretreated, so the water intake value is low.

Practice has proved that [27], at the same total reaction time, the removal of COD and ammonia nitrogen, A/O/O has higher efficiency than A1/A2/O. Both the effluent COD and ammonia nitrogen are guaranteed to meet the standards. But the removal rate of cyanide and SS is not very high.

3.4 Comparison of the advantages and disadvantages of the biochemical process

A/O method of biological treatment system has poor ability to resist impact and require high quality of water [20]. Compared with A/O/O process and A/O process, A/O/O process saved carbon source about 40%, under the same ratio of carbon to nitrogen, ammonia nitrogen removal rate increased, oxygen demand reduced about 25%, alkali consumption reduced about 20%, time of staying has been shortened, the sludge of production is greatly reduced, the process of ammonia nitrogen load impact capacity is stronger than A/O [28].

Denitrification and detoxification capacity of A1/A2/O system is greater than that of the A/O system [29]. At the aerobic unit with DO <0.5 mg/L and pH <6.5, The load of anaerobic treatment COD of A1/A2/O2 process can be increased by 20-30 times compared with A/O process [10], A1/A /O process is more suitable for the treatment of high concentration of refractory coking wastewater [30].

A1/A2/O and A/O/O process, and more aerobic tank of A/O/O than A1/A2/O, A/O/O process is more difficult to manage than A1/A2/ O process[31]. Moreover, anaerobic conditions are more conducive to microbial degradation, and the microbial ring-opening enzyme system is not strong, which prevents the degradation of polycyclic aromatic meridian and heterocyclic compounds [27]. Anaerobic conditions are more able to degrade toxic and refractory substances, and the number of aerobic units located after anaerobic conditions has little effect, so from the perspective of microbial degradation A1/A2/O process is superior to the A/O/O process [32]. In addition, in the above three processes, A/O/O has the highest energy consumption, the total hydraulic residence time is the longest in the process of low-concentration coking wastewater treatment, the area is large and the operation difficulty is high [31], so A1/A2/O process is more suitable for the treatment of coking wastewater.

4. Conclusion

Coking wastewater contains a variety of organic compounds and heavy metals, which is a typical kind of industrial wastewater containing refractory organic compounds. Biochemical treatment can significantly improve the water quality of coking wastewater. A1/A2/O process, as a kind of biochemical processing techniques has better treatment effect in removing the COD content of coking wastewater and harmful substances such as ammonia nitrogen, and the cost, footprint and energy consumption of A1/A2/O process are relatively reasonable, so A1/A2/O process is the most suitable for treating coking wastewater in the current A/O series biochemical technology.

5. Outlook

Although A/O series biochemical technology has made some achievements in the treatment of coking wastewater, the single A/O technology is not complete to treat coking wastewater currently, the technology still needs to be further developed and improved in the future. With the strengthening of environmental governance and the improvement of environmental protection awareness, coking industry are more and more inclined to choose composite process to treat coking wastewater. For instance, A1/A2/ O process and MBR process, A/O

process and air flotation, A/O and coagulation process, The combination of A1/A2/ O process and three-dimensional electrode electrocatalytic technology has achieved good results in the treatment of coking wastewater. In addition, it is necessary to do a good job in wastewater pretreatment and deepening treatment, strengthen the scientific management of each link, and strive to make the indicators of water to reach the first level of water discharge, and further improve and optimize the wastewater treatment process, and reduce the operation cost. Under the premise of the effluent quality standard discharge, explore the wastewater reuse method and attain "zero pollution and zero discharge", and finally to achieve the harmonious coexistence of natural and unity.

References

[1] He Li, the new ideas and new measures of coking sewage treatment.

[2] Xu Yunchuan, shallow discussion of coal chemical industry sewage characteristics and treatment technology. Chemical Industry Management, 2019 (23): Pages 112-113.

[3] Zhang Jianguo and Yang Fei, the research on the deep treatment of nanofiltration membrane in coking sewage. Fuel and Chemical Industry, 2011.42 (2): page 35-37.

[4] Jin, X., et al., Coking wastewater treatment for industrial reuse purpose: combining biological processes with ultrafiltration, nanofiltration and reverse osmosis.J Environ Sci (China), 2013. 25(8): p.1565-74.

[5] Bishayee, B., et al., End-of-pipe-treatment-of-secondary-treated-coke-oven-waste_2023_Chemical-Eng.2023.

[6] Gan Xiushi, analysis and research of coking sewage treatment technology.2008.

[7] Wang, Y., et al., From pollutant to valuable phenolic resin: a novel reutilization strategy of industrial semi-coking wastewater.Journal of Cleaner Production, 2022. 377: p.134477.

[8] Zhu Qingchun, the influence of coking sewage quality on biochemical A / O depth treatment system. Fujian Analysis test, 2010.19 (04): p. 39-41 + 45.

[9] Zan Kunjing, A_1-A_2-O process application in coking sewage treatment. Tianjin Metallurgy, 2006 (05): p. 62-64 + 76.

[10] Sun, W., et al., Carbon dot-based molecularly imprinted fluorescent nanopomegranate for selective detection of quinoline in coking wastewater.Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2023. 284: p.121770.

[11] Hu, Y., et al., Preparation of Fe-loaded needle coke particle electrodes and utilisation in three-dimensional electro-Fenton oxidation of coking wastewater.Chemosphere, 2022. 308: p.136544.

[12] Mishra, L., K.K.Paul and S.Jena, Coke wastewater treatment methods: Mini review.Journal of the Indian Chemical Society, 2021. 98(10): p.100133.

[13] Wang, C., et al., Distribution characteristics, air-water exchange, ozone formation potential and health risk assessments of VOCs emitted from typical coking wastewater treatment process.Science of The Total Environment, 2023. 862: p.160845.

[14] Wu Kun et al., the integrated analysis of the heavy metal chromium, cadmium, and lead enrichment ability of constructed wetland plants in sewage. Jiangsu Journal of Agriculture, 2022.38 (06): pp. 1532-1540.

[15] Xing Xiangjun, coking wastewater A-A_O process operation... Deep treatment of repolarity 3 D electrode technology.2005.

[16] Li Jianfeng, Yankuang coking plant wastewater treatment by A / O method successfully. Coal chemical industry, 2003 (05): page 29.
[17] Dong Lizhu, air flotation, A / O biological nitrogen removal process in the treatment of coking sewage application. Environmental Engineering, 2011.29 (06): Page 58-60 + 78.
[18] Liu Huan, a brief talk about coking sewage treatment process. Metallurgical Management, 2019 (1): Page 93.
[19] Tong Bin and Zhang Jianmin, A-O biological nitrogen removal method in coking sewage treatment. Chemical Engineering and Equipment, 2015 (06): Pages 241-242.
[20] Kingdom, the development trend and research of coking sewage control and treatment technology, 2006: Beijing. Pages 609-614.
[21] Xu Rui, A / A / O biological nitrogen removal process in coking wastewater treatment. Baotou Steel Technology, 2007 (06): p. 68-70.
[22] Ni Ningfeng, A~2 / O sewage treatment process in coking wastewater treatment. Shanxi Chemical Industry, 2006 (06): p. 60-61.
[23] Chen Yi, A2O method treatment of coking wastewater start operation practice.2005.
[24] Li Rongbo, the status quo and prospect of coking wastewater treatment.2001.
[25] Du, Z., et al., Coagulation performance and floc characteristics of poly-ferric-titanium-silicate-chloride in coking wastewater treatment.Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2022. 642: p.128413.
[26] Niu Jiyong, et al., A-O-O sewage treatment technology in coking wastewater application. Metallurgical Power Force, 2009 (1): pp. 71-71,77.
[27] Guo Lihong, the application of coking sewage system treatment and water treatment process.
[28] Jiang Chengfu, Li Liu and Li Guobao, AOO biological treatment process in Shaogang coking wastewater treatment.2010.
[29] Li Yongmei et al., the role of anaerobic acidification in nitrogen removal and toxicity reduction in coking wastewater. Environmental Science, 2001.22 (4): page 86-90.
[30] Effect of Yao Jun and He Miao on aerobic biodegradation performance after anaerobic acidification in coking wastewater. Environmental Science, China, 1998.18 (3): p. 276.
[31] Fan Dan, research on biochemical treatment process of coking wastewater and energy consumption of engineering operation.2016.
[32] He Miao et al., anaerobic-hypoxia / aerobic process and conventional activated sludge treatment of coking wastewater. Water supply and drainage, 1997 (06): page 31-33.