

Application of Ozone MBBR Process in Refinery Wastewater Treatment

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Abstract. Moving Bed Biofilm Reactor (MBBR) is a kind of sewage treatment technology based on fluidized bed. At the same time, it can also be regarded as an efficient new reactor between active sludge method and the biological membrane method. The application of ozone MBBR process in refinery wastewater treatment is mainly studied. The key point is to design the ozone +MBBR combined process based on MBBR process. The ozone +MBBR process is used to analyze the treatment of concentrated water COD discharged from the refinery wastewater treatment plant. The experimental results show that the average removal rate of COD is 46.0%~67.3% in the treatment of reverse osmosis concentrated water by ozone MBBR process, and the effluent can meet the relevant standard requirements. Compared with the traditional process, the ozone MBBR process is more flexible. The investment of this process is mainly ozone generator, blower and so on. The prices of these items are relatively inexpensive, and these costs can be offset by the excess investment in traditional activated sludge processes. At the same time, ozone MBBR process has obvious advantages in water quality, stability and other aspects.

1. Introduction

In recent years, the state has increased the intensity of environmental pollution management and pays more attention to environmental protection issue, which means that the country will increasingly strict sewage discharge standards for petroleum and petrochemical industries. With the progress of the times and the development of science and technology, the disadvantages of the traditional sewage treatment methods are becoming more and more obvious, and it has been unable to meet the current requirements of the relevant departments for the discharge of water quality. In order to solve this problem, the optimization of existing wastewater treatment processes and the development of new wastewater treatment processes have become a pressing matter of the moment for major petrochemical enterprises [1]. In this paper, the existing refinery wastewater treatment methods in a chemical enterprise are studied. When the refinery wastewater produced by the enterprise is treated by oil separation and biochemical treatment, the reverse osmosis process is used to further treat the wastewater [2]. However, in the advanced treatment, there will be a large number of reverse osmosis concentrated shrinkage which is not easy to degrade organic compounds. This part of reverse osmosis concentrated water contains more than 50mg/L of COD, which does not conform to the standards set by relevant parts [3]. At present, the methods to deal with concentrated water are very scarce, and



most companies have chosen reverse osmosis advanced treatment, that is, to inject fresh water into the water for dilution. Although this method can reduce the content of COD in the concentrated water to a certain extent and make it conform to the standard, this greatly consumes the water resources [4]. In view of this, in order to reduce environmental risks and ensure the discharge standards of enterprises, it is necessary to study the treatment technology of refinery wastewater, and build a set of devices that can effectively deal with concentrated water [5].

2. Methods

2.1. Experimental principle

The ozone MBBR process is based on the strong oxidation characteristics of ozone (O_3). The strong oxidation characteristics of O_3 can oxidize a variety of pollutants which are not easy to degrade, and decompose or dissociate them into small molecules which can be easily handled by microorganisms. The experiment designed in this paper mainly uses the strong oxidation of O_3 to reduce the content of COD in reverse osmosis concentrated water, so that it can reach the acceptable level without dilution of water. Then MBBR method is used to treat the concentrated water treated by O_3 deep oxidation process for two times, so as to reduce the content of COD, ensuring that the quality of the effluent meets the requirements. It is well known that O_3 is unstable in water, which is rapidly decomposed into oxygen in an aqueous solution with low purity. At the same time, hydroxyl (OH) with 2.8V oxidation-reduction potential and other small molecules with strong oxidation such as single atom oxygen (O) are formed. Although oxidation occurs when O_3 dissolves in water, the process is relatively long. However, it has high selectivity, and can react with ethanol and C_6H_5OH . At the same time, O_3 dissolves in water and causes hydrogen chain reaction by decomposing hydrogen radicals. The decomposition chemical reaction of O_3 can be expressed by formula (1) and the chemical reaction with water can be expressed by formula (2).



The carrier material used in the moving bed biofilm reactor is K3, which has the following advantages:

1) Biofilms grow on the inner surface of cells. Compared with the outer surface, the inner surface is more protected, and the biological content is relatively fixed. There will be no shrinkage of the surface area due to internal congestion.

2) Compared with the biofilm reactor filled with other fillers, the moving bed biofilm reactor selected in this paper has larger surface area and larger biofilm quantity. The basic amount is 10 to 14g/L, and the amount of VSS contained in the specific biofilm can be as high as 95%, which can guarantee the biological activity to some extent.

3) There are more species of bacteria on K3 carrier. At the same time, the environment on the K3 carrier is more suitable for the growth of microorganisms which can degrade and decompose non-degradable materials. Therefore, the effluent quality of K3 treated with MBBR is better. In addition, in view of the biological growth mode of K3 matched with the environmental requirements of nitrifying bacteria growth, the number of nitrifying bacteria is relatively heavy, which makes the nitrification efficiency more ideal. It can reach 1 kgNH₃-N/m³ D, and the nitrification efficiency is increased by nearly 5 times compared with activated sludge.

4) The ratio of K3 carrier is close to 1, so it tends to flow when it is in the reactor, which can effectively promote mass transfer, reduce congestion and energy consumption.

5) K3 can rotate freely in the reactor, which can effectively promote the splitting and collision times of bubbles in water. In addition, it can prolong the time length of the bubbles to stay in water,

which promotes the use efficiency of O₂ and reduces the energy consumption of aeration to some extent.

2.2. Equipment and materials

1) Experimental raw water

The pretreatment for waste water can adjust the production of sediment by pH, and the strong oxidation of O₃ can mineralize the harmful organic compounds in sewage, so as to remove the COD in reverse osmosis concentrated water. At the same time, it can transform harmful substances and COD which cannot be decomposed by microorganisms into organic compounds which can be degraded by microorganisms, so as to improve their biological characteristics. After O₃ oxidation, the concentration of COD in concentrated water will be reduced to some extent. At this time, the use of activated carbon, aeration, coagulation and other treatment methods to re-care can be clearly reduce the concentration of COD in concentrated water.

The raw water is obtained from reverse osmosis concentrated water, which is produced by oil separation and biochemical treatment of refinery wastewater. The unique nature of this water is that it contains a small amount of heavy metals and difficult (non) biochemical degradation substances. At the same time, it has the characteristics of low biodegradability and toxicity to microorganisms. The amount of water to be treated is about 0.5m³/h. The content of COD is not more than 200mg/L, the content of ammonia nitrogen is not more than 8mg/L, and the suspended matter is not more than 20mg/L.

2) Major drugs

The drugs used in this experiment and their purity requirements are shown in table 1.

Table 1 Experimental drugs

Reagent	Purity	Manufacturer
NaOH	Analytical reagent	Tianjin Standard Technology Co., Ltd.
K ₂ Cr ₂ O ₇	Analytical reagent	Tianjin Tianda Chemical Reagent Factory
HgSO ₄	Analytical reagent	Jiangyan Huanqiu Reagent Factory
Ag ₂ SO ₄	Analytical reagent	Tianjin Standard Technology Co., Ltd.
H ₂ SO ₄	98%	Jinzhou Gucheng Chemical Reagent Factory
(NH ₄) ₂ Fe(SO ₄) ₂ ·6H ₂ O	Analytical reagent	Tianjin Standard Technology Co., Ltd.
FeSO ₄ ·7H ₂ O	Analytical reagent	Tianjin North-Tianyi Chemical Reagent Factory
phenanthroline	Analytical reagent	Shanghai Reagent Factory
Distilled water	—	Self-made
H ₂ O ₂	30%	Shenyang Federal Reagent Factory

The equipment needed by the experiment is assembled and assembled by the research unit and a chemical enterprise, mainly including catalytic oxidation tower, tail gas destruction tank and MBBR biochemical tank. Specific equipment parameters are shown in table 2.

Table 2 Parameters of the main unit device

Main unit	Clearance size (m)	Active area (m ³)	Filler content (m ³)
Catalytic oxidation tower	Φ0.5×4.0	0.7232	Catalytic packing 0.45
Tail gas destruction tank	1.2×0.5×3.0	1.8	
MBBR biochemical tank	1.2×1.2×3.0	3.8	K3 biological vector 1.5
Drain trap	1.2×1.2	Superficial area 1.6m ²	

2.3. Experiment process

1) Experimental flow

The specific process of this experiment is shown in figure 1. First of all, we need to start the test and run the water, then access to tap water after determining that the device function is normal. The tap water is filled into the device until it is full, and then the sludge is connected to the MBBR pool. Nutrients, such as P and sugar, are added for microbial growth according to the setting time. At the same time, aeration should be carried out according to the actual situation. After the biofilm is added, the raw water is injected into it, which is about 1/5 of the total raw water. Then, the amount of water is slowly increased and the number of nutrients injected is reduced, ensuring that the microorganisms in the MBBR pool can survive normally in the pool.

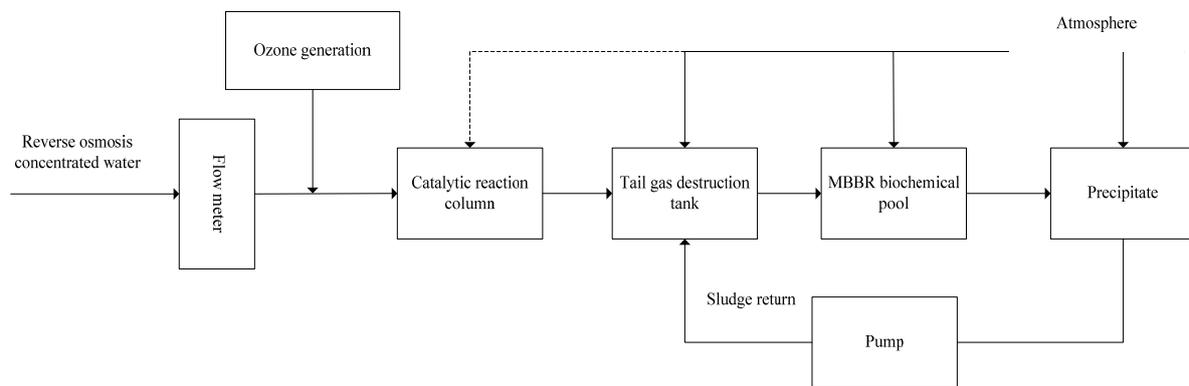


Figure 1 Test process flow chart

After the culture of microorganisms for a period of time, the index data of biochemical effluent can be measured. It is confirmed that the removal effect is ideal and the removal effect is stable. The raw water, catalytic oxidation influent, effluent, biochemical influent and effluent data are collected and arranged. After the successful culture of microorganisms, the experiment is carried out according to the experimental process. Once the experiment can be carried out stably, the process is adjusted according to the experimental results. That is, under the condition that the process conditions are not changed, the amount of water is adjusted and the raw water is continuously injected until the amount of water reaches the predesigned quantity. At the same time, the input amount of O_3 should be adjusted so as to save the input resources. O_3 is adjusted to the appropriate dose that can meet the process requirements. Then, the DO, temperature and other adjustable conditions are adjusted based on the actual test results to ensure that these conditions can guarantee the best experimental results. After meeting the design requirements, the impact test can be used to find the maximum operating point. In order to supplement the nutrients needed for microbial growth in MBBR, the industrial grade KH_2PO_4 must be continuously added after the system is stable. Every treatment of 1t wastewater requires the addition of 1.5g KH_2PO_4 .

2) Parameter control

(1) Temperature: about $25^\circ C$.

(2) Sludge volume: In the initial stage of the system, nutrients should be increased to improve the sludge concentration. After the system runs stably, the water can be increased and the nutrient solution is reduced until the nutrient is stopped completely.

(3) pH value and alkalinity: The pH value of waste water is determined by pH on-line monitor. Dosing pump is used to automatically add Na_2CO_3 to control pH value of wastewater, and pH value is set between 6~7.

(4) Aeration rate: The system dissolved oxygen is maintained at 1~2mg/L during the initial start-up and biofilm formation. When the influent load is increased to the design load, the dissolved oxygen is maintained at 2~5mg/L.

(5) Ozone control: According to the experimental data, the amount of O₃ is adjusted and the dosage of O₃ is reduced as much as possible to ensure the removal rate.

3) Analysis method

The water quality indexes of this experiment are measured by national standard analysis method. Specifically, the potassium dichromate method is used to determine COD; the mass concentration of NH₃⁺-N is measured by the dichromate titration method of sodium reagent; the pH is measured by glass electrode method; and the content of DO is measured by a dissolved oxygen meter.

2.4. Treatment effect

After the completion of biochemical microorganism domestication and biofilm formation on MBBR filler, sampling analysis began in June 1, 2017, and the analysis data were shown in table 3.

Table 3 Experimental data

Date	Inlet flow(m ³ /h)	Ozone (g/h)	Oxidation influent COD (mg/L)	Oxidation effluent COD (mg/L)	Biochemical effluent COD (mg/L)
1	0.4	0	162		133
2	0.4	0	192		147
3	0.4	0	168		164
4	0.4	0	165		148
5	0.4	0	183		175
6	0.4	0	129		112
7	0.4	0	207		181
8	0.4	0	149		125
9	0.4	68.8	175	138	120
10	0.4	68.8	186	143	122
11	0.4	68.8	152	120	98.3
12	0.4	68.8	168	123	81.8
13	0.4	68.8	164	119	73.8
14	0.4	68.8	122	77.6	65.3
15	0.5	85	114	81.8	49.1
16	0.5	85	94	90	65.4
17	0.5	85	102	94	61.3
18	0.6	85	135	131	69
19	0.6	101.3	126	94	61.5
20	0.6	101.3	123	77.7	85.8
21	0.8	101.3	137	80	45
22	0.8	101.3	105	55	31
23	0.8	101.3	119	75	39
24	0.8	101.3	136	73.7	44.2
25	0.8	101.3	120	63.4	38.7
26	0.8	90.8	127	69.8	41.5
27	0.8	90.8	152	80.6	48.7
28	0.5	60.8	165	80.6	37.2
29	0.5	60.8	168	85.7	43.5
30	0.5	60.8	167	79.5	39.4
31	0.5	60.8	175	82.6	43.8
32	0.5	45	127	65.4	40
33	0.5	45	126	68	42
34	0.5	45	136	78.9	36
35	0.5	45	144	74	44

36	0.5	45	152	82.3	48
37	0.5	45	146	84	44
28	0.5	45	140	78	38
29	0.5	45	134	70.2	40.9
30	0.5	45	136	76.4	40

Through the analysis for table 3, it can be found that when the influent is normal, the influent COD is about 141mg/L. Through the catalytic effect of O₃, the effluent is about 77.2mg/L, and the removal rate of catalytic oxidation is about 43.9%. The biochemical effluent is about 41 mg/L, and the biochemical removal rate is about 46.3%. When the high pressure pump is opened, the influent COD is about 170.6mg/L, and the catalytic oxidation effluent is about 83.7mg/L. The removal rate of catalytic oxidation is about 50.9%, the biochemical effluent is about 41.9mg/L, and the biochemical removal rate was about 49.9%. The effluent COD is less than 60mg/L, which meets the national emission standard.

The basic reason for this result is that the amount of O₃ dissolved in water increases substantially because of the addition of O₃. When the catalyst is added, the oxidation of O₃ will result in the decomposition of many hydroxyl radicals [6]. The higher the content of the molecule is, and, the more organic matter it touches, which means that the amount of organic matter that can be treated increases with the removal rate [7]. In addition, increasing the amount of O₃ can degrade the intermediate products accumulated in the process to inhibit the degradation of pollutants and produce CO₂ and H₂O. The degradation of these intermediate products will be more beneficial to the decomposition of harmful substances by microorganisms, that is, to promote the reaction. This can also improve the removal rate to a certain extent [8].

After the treatment of MBBR process, using the advantages of K3 carrier filler, the wastewater COD can be further treated until it reaches the standard [9]. At the same time, ozone dosage is 45 g/h, and the power of ozone generator SKW is adjusted to 13%, that is, the power consumption of 0.65KW tons of water is about 1 yuan. There is no blower in power consumption equipment. Relative to the engineering design, the operation cost is 0.11 yuan /t.H₂O. This shows that the cost of dealing with a ton of water is relatively cheap, and the operating cost is relatively low [10].

3. Conclusion

In order to solve the problem that COD is not up to standard in the concentrated wastewater discharged from some petrochemical refinery wastewater treatment plants, the ozone MBBR process is adopted to treat the wastewater in depth, and the effect of the process on the treatment of reverse osmosis concentrated water is investigated. The experimental results show that the process has a significant effect on the degradation of COD. Under normal influent conditions, the removal rate of catalytic oxidation is about 43.9%, and the biochemical removal rate is about 46.3%. When the high pressure pump is opened, the removal rate of catalytic oxidation is about 50.9%, and the biochemical removal rate is about 49.9%. O₃ can oxidize this kind of sewage. After MBBR treatment, the effluent quality is up to standard, and it tends to stable. The effluent COD is less than 60mg/L, which meets the national emission standard. At the same time, through the calculation of the equipment loss and investment cost in the process of wastewater treatment, it is concluded that the investment cost of dealing with a ton of water is relatively cheap, and the operation cost is relatively low.

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