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Study on Biological Treatment of Limestone-gypsum Wet Desulfurization Wastewater

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Abstract. The limestone-gypsum wet desulfurization wastewater was studied in this paper, and the biological treatment method was proposed for the problem that the water quality of the desulfurization wastewater after the physicochemical treatment was still not up to standard. In this experiment, the domestic sewage of a power plant was added into the desulfurization wastewater to make the desulfurization wastewater biodegradable, then SBR biological treatment was carried out to make the effluent water quality met the relevant requirements of *Sewage Discharge Standard (GB8978-1998)* and *Water Quality Control Index of Limestone - gypsum Wet Desulfurization Wastewater of Thermal Power Plant* (DL/T 997-2006).

1. The introduction

The limestone - gypsum wet flue gas desulfurization technology was currently the most widely used in the world with high reliability, high desulfurization efficiency, suitable types of wide scope, high utilization rate of absorbent, high operation rate and absorbent cheap, and many other advantages. It was the most mature technology of SO_2 removal, and about 90% of the installed desulfurization units use the technology[1].However, the water quality of wet desulfurization wastewater was generally characterized by low pH value, high suspended matter content, various heavy metal ions, high salt content and unstable water quality, which seriously pollutes the environment and endangers human health. So the water could only be discharged after treatment[2]. After the biological treatment of desulfurization wastewater, the content of pH, fluoride and suspended matter decreased a lot and the water quality of wastewater improved greatly [3]. But the water quality of desulfurization wastewater was not fully up to standard, especially the ammonia nitrogen, COD and nitrate nitrogen could completely meet the relevant requirements of *Sewage Discharge Standard* (GB 8978-1998) and *Water Quality Control Index of Limestone-gypsum Wet Desulfurization Wastewater of Thermal Power Plant* (DL/T 997-2006) after biological treatment.

2. Test materials and methods

2.1 Test materials

Experimental instruments: 721 visible spectrophotometer, phs-3c precision pH meter, electronic balance, general aerator, small electromagnetic air compressor, oven, etc. The experimental equipment was a transparent plexiglass single-cell SBR reactor, with an inner diameter of 5.5cm, a height of 15.5cm, and an effective volume of 1.5l. The device was shown in figure 1.Marks 1-8 in the figure were air pump, aerator, mixing motor, agitator, reactor, sludge tank, collecting tank and flow valve.

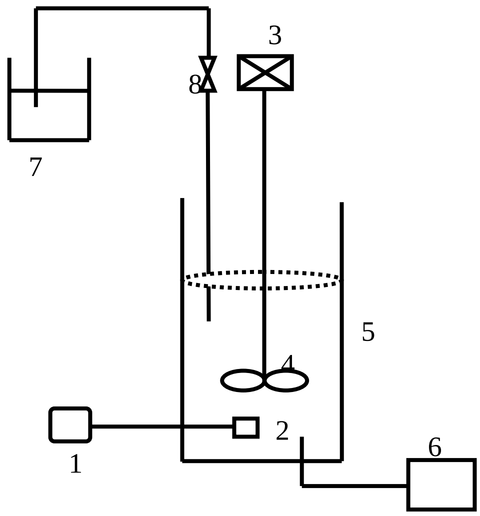

Figure 1. The system diagram of experimental apparatus

2.2 Methods for the determination of water quality parameters

Desulfurization wastewater had a variety of harmful substances, including ammonia nitrogen, COD, nitrate nitrogen, etc., and the determination of water quality parameters was shown in table 1.

Table 1. The determination of water quality parameters

The water quality parameters	Determination method	Refer to the national standard
NH_3-N	Nascar reagent colorimetry	GB7479
COD	Potassium dichromate oxidation process	GB11914
NO_3-N	Phenol disulfonic acid spectrophotometry	GB7480

3. Acclimation of activated sludge

3.1 Domestication and culture of microorganisms

The activated sludge used in the test was taken from the aeration tank of the sewage treatment plant in Baoding City. We domesticated and cultivated the active sludge with different proportion of the power plant sewage sludge and physico-chemical treatment of desulfurization wastewater. Then let the sludge aerate 3 days after inoculation, and gave the sludge water once a day. We domesticated the sludge in different influent load by adjusting the proportion of waste water, and gradually increased the proportion of desulfurization wastewater into water. Let it aerate continuously during domestication, so the dissolved oxygen in SBR pool was enough. We kept the water temperature at 17℃-24℃, and adjusted mixture pH between 8.0 ~ 9.0.The result of microscopic examination of activated sludge was showed in table 2.

Table 2. The situation of sludge culture (20℃)

	Microbial growth	Sludge structure condition
Target wastewater≤20%	There were many kinds of microorganism (bellworms, mantella, cladularia, rambler), and the community structure was stable.	Sludge flocculation state was very good

20%<Target wastewater<40%	The microbial species gradually decreased (including paramecium, etc.), and the activity decreased. The previously existing nematode and rotifer were dead, and the stability of community structure also decreased	The sludge flocculates well
40%<Target wastewater<50%	Microbial species decreased again, activity decreased, and community structure stability was poor.	Sludge flocculation state (not very good)
50%≤Target wastewater	The large microorganisms have died, and only a small living body was left, and the species was single, and the community structure was not healthy.	The sludge dissolved and the growing emblems were in a free state

3.2 Biodegradability test of desulfurization wastewater

After a period of acclimation and cultivation of activated sludge, power plant domestic sewage and desulfurization wastewater were put into SBR reactor in different proportions. Under the conditions of $0.2m^3/h$ aeration and 2000mg/l MLSS, the removal rates of nitrate nitrogen under different Cl^- concentrations were shown in table 3.

Table 3. The removal efficiency nitrate nitrogen in different Cl- concentration

The serial number	Waste water addition ratio /%	Concentration of Cl^- /mgl^{-1}	Nitrate nitrogen removal rate /%
1	20	2856	96.42
2	40	5714	86.56
3	45	6428	75.51
4	50	7142	28.32
5	55	7856	15.68

As shown in table 3, the proportion of desulfurization wastewater and the removal effect of nitrate nitrogen were taken into account. The proportion of desulfurization wastewater was controlled at 40% ~ 45%, and the concentration of Cl^- was controlled at about 6000mg/l.

4. Test on treatment of desulfurization wastewater by SBR

After sludge acclimation was completed, according to the biodegradability test of the desulfurization wastewater mentioned above, the domestic sewage and desulfurization wastewater of power plant were added to the SBR reactor in a ratio of 6:4. After 20 hours of continuous aeration, the reactor was oxygenated and stirred for 10 hours. The concentrations of COD, ammonia nitrogen and nitrate nitrogen were sampled every 2 hours[5].

4.1 The influence of aeration time

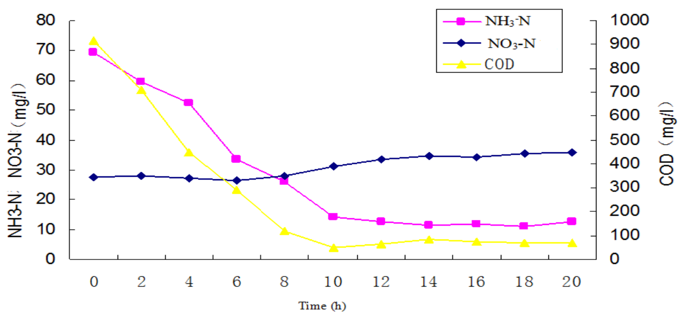

Figure 2. The curve of changes in water quality in the aeration process

The curve of water quality changing with aeration time was shown in figure 2. As can be seen from figure 2, the removal rate of COD and ammonia nitrogen within 6 hours of aeration was 68.10% and

52.01% respectively. The removal rate of COD and ammonia nitrogen was 86.98% and 62.83% respectively after 8 hours of aeration. After 10 hours of aeration, COD decreased to 49.01mg/l, reaching the first-level discharge standard of sewage discharge standard. At this time, COD removal rate was as high as 94.66%. Ammonia nitrogen concentration was 14.30mg/l, which also meets the first-level discharge standard of sewage discharge standard, and the removal rate reaches 79.42%, indicating that whether the aeration time was sufficient was an important factor affecting the removal effect.

4.2 The influence of hypoxia time

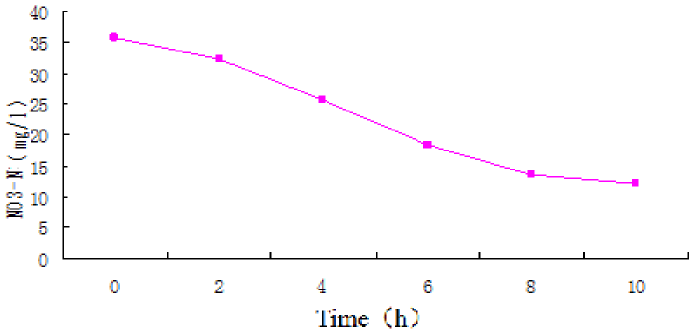

Figure 3. The curve of water quality with the hypoxia time

The curve of water quality changing with aeration time was shown in figure 3. As can be seen from figure 3, the intracellular storage was used as a carbon source for denitrification, and the denitrification rate was low. Therefore, carbon sources need to be added in the denitrification process, and the time should not be too short. However, if the denitrification time was too long, the denitrifying bacteria would conduct endogenous respiration due to the lack of carbon source, resulting in a decrease in the number of bacteria and a decrease in sludge concentration.

4.3 The influence of precipitation time

SBR was static precipitation, the precipitation performance was good, so the need for static precipitation time was short. If the precipitation time was too long, the denitrification reaction would cause the ammonia gas generated to escape and make the sludge float, causing the floating mud to affect the effluent water quality.

4.4 The orthogonal test of desulfurization wastewater treatment with SBR

This experiment mainly discusses the factors influencing the removal effect of COD, ammonia nitrogen and nitrate nitrogen and the determination of the optimal operation combination mode in the process of SBR process treating desulfurization wastewater after physicochemical treatment. According to the single factor test above, anaerobic time, aeration time, anoxic agitation and precipitation time were selected as the main factors affecting the treatment of desulfurization wastewater by SBR. Orthogonal tests were conducted on various influencing factors, and the results were shown in table 4.

Table 4. The results of orthogonal test

Remove the object	Optimal operating parameter (h)			
	Anaerobic time	Aeration time	A lack of oxygen time	Settling time
COD	0.5	10.0	4.0	0.5
NH_3-N	1.0	10.0	2.0	1.0
NO_3-N	0.5	6.0	4.0	1.5

Through the analysis of the above factors, it could be seen that the removal rate of nitrate nitrogen by predenitrification was greatly improved, so the anaerobic time was 0.5h. The longer the aeration time was, the higher the removal rate of COD and ammonia nitrogen would be. However, excessive consumption of organic matter in water would seriously affect the denitrification and denitrification effect in the anoxic section. Therefore, the aeration time was 8.0h. Hypoxia time was 4.0h and precipitation time was 1.0h. Therefore, after comprehensive consideration, the optimal combination conditions of the experiment were preliminarily determined as follows: anaerobic time 0.5h, aeration time 8.0h, hypoxia time 4.0h, and precipitation time 1.0h.

Considering the influence of aeration amount and MISS on the removal efficiency of COD, ammonia nitrogen and nitrate nitrogen[6], the aeration amount in SBR reactor was selected as $0.2m^3/h$, and the sludge concentration was determined as 2000mg /l.

4.5 The test under the best operating conditions

According to the above experiments, the optimal operating parameters of desulfurization wastewater treated by SBR reactor after chemical treatment were determined as follows: anaerobic time was 0.5h, aeration time was 8.0h, hypoxia time was 4.0h, precipitation time was 1h, aeration volume was $0.2m^3/h$, MLSS volume was 2000mg/l. Under this operating condition, COD, NH_3-N and NO_3-N contents in the wastewater treated by SBR reactor were measured every 2.0 hours at the aeration stage, and the degradation curves of COD, NH_3-N and NO_3-N were drawn, as shown in figure 4, figure 5 and figure 6.

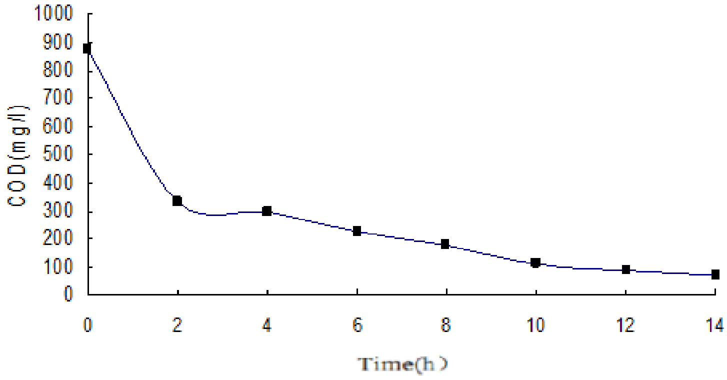

Figure 4. The curve of COD degradation

As can be seen from figure 4, the COD of raw water was 873.42mg/l, and the wastewater entered the anaerobic stirring stage. After the biological adsorption in the anaerobic stage, part of the COD in the wastewater was removed, and the COD in the wastewater dropped to 651.05mg/l. When the wastewater entered the aeration process, the COD decreased to 296.45mg/l in the first 4 hours. In the following 4.0 hours, the COD decreased slightly. The COD at the end of aeration was 176.89mg/l and it provided carbon source for denitrification. In the anoxic stage and the precipitation stage, the denitrification consumed COD, so COD decreased slowly.

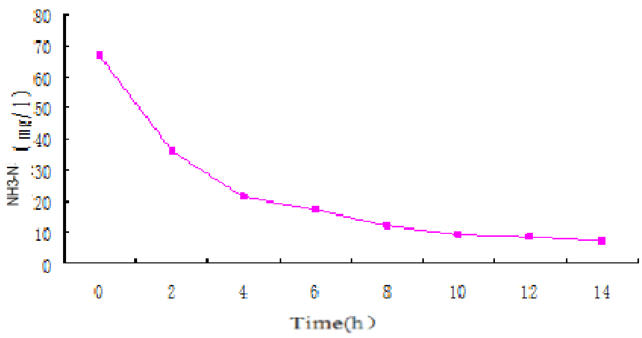

Figure 5. The curve of ammonia degradation

As can be seen from figure 5, the concentration of ammonia nitrogen in raw water was 66.74mg/l. In the first 4.0h of the aeration stage, ammonia nitrogen was rapidly nitrified by microorganisms in the SBR reactor, and more than half of ammonia nitrogen in the wastewater was removed with a large degradation range. At the end of aeration, the ammonia concentration was only 12.05 mg/l, and the removal rate reached the maximum value (81.94%). In the subsequent stages of hypoxia and precipitation, ammonia nitrogen content decreased but the degradation rate was slow.

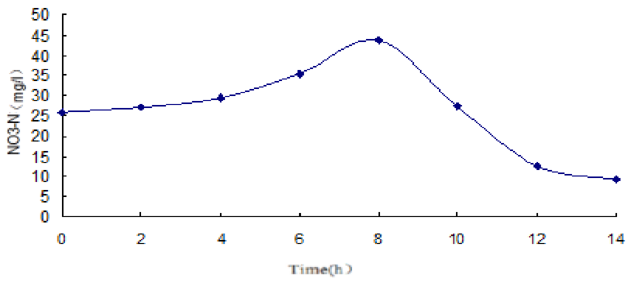

Figure 6. The degradation curve of nitrate nitrogen

As can be seen from figure 6, the first half of the aeration process of nitrate nitrogen increased a little. The main reason was that the high COD concentration made the heterotrophic bacteria with a high growth rate rapidly. The heterotrophic bacteria competed for dissolved oxygen, thus making the aerobic nitrifying bacteria grew slowly. In the half stage after aeration, with the gradual decrease of organic matter concentration, nitrifying bacteria took the advantage and realized the high conversion rate from ammonia nitrogen to nitrate nitrogen. The more completed the transformation from ammonia nitrogen to nitrate nitrogen, the more denitrification was carried out.

5. Conclusion

The desulfurization wastewater was mixed with domestic wastewater and put into SBR reactor. The addition proportion of desulfurization wastewater was controlled at 40%-45%, and the concentration of Cl^- was controlled at about 6000 mg/l. The desulfurization wastewater had biodegradability.

The biochemical treatment of desulfurization wastewater was carried out in a SBR reactor. The optimal process conditions for SBR were: anaerobic time was 0.5h, aeration time was 8h, hypoxia time was 4.0h, and precipitation time was 1.0h. Under the optimal process conditions, the effluent concentrations of COD, NH_3-N and NO_3-N were 73.41mg /l, 7.19mg /l and 9.34mg/l. The removal rates of COD, NH_3-N and NO_3-N were 91.60%, 89.23% and 63.90%. The effluent concentrations reached the requirements of *Sewage Discharge Standard* (GB 8978-1998) and *Water Quality Control Index of Limestone-gypsum Wet Desulfurization Wastewater of Thermal Power Plant* (DL/T 997-2006).

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References

[1] Liang Z X, Zhang L,Yang Z Q, et al.Evaporation and crystallization of a droplet of desulfurization wastewater from a coal-fired power plant[J].Applied Thermal Engineering,2017, 119:52-62.
[2] MA Shuangchen, YU Weijing, JIA Shaoguang, CHAI Feng, ZHANG Runpan. Research and application progresses of flue gas desulfurization (FGD) wastewater treatment technologies in coal-fired plants[J].CHEMICAL INDUSTRY AND ENGINEERING PROGRESS, 2016, 35(1):255-262.
[3] Lianqing YIN, Shanshan ZHANG, Peng KANG. Physico chemical Pilot Study Of Wet Limestone-gypsum Method For Flue Gas Desulfurization Wastewater. Environmental Pollution and Public Health(EPPH) Special Track within iCBBE.2012.
[4] Zheng Huaili, Liu Kewan. Research progress and development trend of the inorganic polymer composite flocculants[J]. Technology of water treatment, 2004 30 (6): 315-317.
[5] Chen Yongxiang, Cheng Xiaoru, Shao Qing. Progress in researches of inorganic polymer composite flocculants and developing trend [J]. Journal of civil engineering college of Wuhan university, 2001, 6 (3) :55-57.
[6] Yu Tingkang. The new best practical environmental options of sewage treatment[J]. Techniques and equipment for environmental pollution control [J]. 2000, 1 (5): 54-59.