Pilot-scale Study on Removal of Pollutants in Tannery Wastewater and Sludge Reduction by Biological Synergist Effect

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Abstract. The characteristics of tannery wastewater are complex composition, high suspended substance (SS) and heavy sludge load. Adding the functional bacteria agent into the Aerobic system and Sludge digestion tank can improve the biological system activity and reduce sludge discharge. The pilot-scale study results show that: The removal of CODCr and NH3-N was improved after biological synergy. The average removal rate of CODCr was 90.1% and the average removal rate of NH3-N was 97.4%, both of which were higher than the control group. The excess sludge reduction of the system could reach 75.16%, and the effect of sludge reduction was obvious in the experimental group. After biological synergy, the number of bacteria in aerobic pool increased significantly, and the microbial flora migrated in a better direction.

1. Introduction
Tannery wastewater is a kind of wastewater with complex composition, large fluctuations in water quality, high chromium content in heavy metals, deep color, high suspended matter, and easy biochemical. Because the main pollutants in wastewater are protein and grease, there are many problems in tannery wastewater treatment process, such as heavy sludge load, high oxygen consumption, and heavy odor in biochemical system.

The Global and China Sludge Treatment and Disposal Industry Development Research Report (2018) released by GEP Research shows that in 2017-2018, China produced about 55 million tons of sludge in 2017-2018. According to statistics, about 150 kg of sludge is produced per 1t of raw hide, and tannery sludge accounts for about One-tenth of the country's total sludge output. With China's increasingly strict requirements on wastewater discharge standards and sludge disposal, the issues of tannery wastewater treatment and sludge reduction have gradually received attention.

Based on the principle of microbiology, this study aimed at the poor biochemical capacity and high sludge production of tannery wastewater in Xinji, Hebei Province.

The biological synergistic technology of Shandong environmental engineering Co. Ltd was used to carry out bio-augmentation pilot study on biochemical system.

The removal efficiency of pollutants in the biochemical system was improved by adding microbial strains to the aerobic tank, and at the same time, the lysozyme produced by Lysobacter ruishenii was added to the sludge digestion tank to reduce the sludge of the tannery wastewater.
2. Materials and methods

2.1 Experimental water and inoculation sludge
The experimental wastewater was taken from the regulation tank of a tannery enterprise in Xinji, Hebei Province. The inoculated activated sludge was taken from the biochemical aeration tank of the wastewater treatment system. The water-quality index and the activated sludge index are shown in Table 1.

| Pollutant index | COD mg/L  | NH$_3$-N mg/L | Nitrogen mg/L | SS mg/L | MLSS mg/L | Chroma Value | PH |
|-----------------|-----------|----------------|---------------|---------|-----------|--------------|----|
| Value           | 1600-1900 | 290-350        | 340-420       | ≤1000   | 9000      | ≤100         | 6-9|

2.2 Experimental material
The bacteria agent was provided by Shandong environmental engineering Co.Ltd. 1# bacteria agent is a mixed strain of high-efficiency pollutant-degrading bacteria, which can improve the degradation rate of difficult-to-degrade pollutants in wastewater. 2# bacteria agent is Lysobacter ruishenii, which has the effect of digesting sludge.

2.3 Experimental process
The pilot process control group was consistent with the field wastewater treatment process, and the process flow is shown in the figure 1.

Figure 1. The pilot-scale process map

2.4 Experimental methods
In this experiment, two A/O systems were synchronized for three months. The average amount of wastewater treated was 1m$^3$/h. After two weeks of stable operation, added 1# bacteria agent to the O1 pool of the experimental group, and the daily dosage was 50mg/L. And added 2# bacteria agent to the sludge digestion tank, and the daily dosage was 50mg/L. Both of two bacterial agents were added after on-site activation, and the control group was not added.

After the system operation was stable for two weeks, recorded effluent datas and sludge discharge. At the same time, the sludge samples were taken from two aerobic tanks. The microbial flora of the two systems were analyzed after high-throughput sequencing. The control group of the whole experiment period was the same as the test group except that no bacteria agents was added.
2.5 Experimental method
The water-quality index such as COD$_{Cr}$, NH$_3$-N and MLSS were all determined by the national standard method, and high-throughput sequencing tested by Shanghai Shengong.

3. Results and discussion

3.1 Comparison of effluent COD$_{Cr}$ in the pilot-scale
The effluent of the system was stable after a week of adding bacteria agents. And then determined the effluent of COD$_{Cr}$. The results are shown in the figure 2.

![Figure 2. The comparison of COD$_{Cr}$ removal rate between two systems](image)

It can be seen from the figure 2: When the influent COD$_{Cr}$ was the same, after adding bacteria agent, the average COD$_{Cr}$ of the test group was 178 mg/L, which was obviously lower than the 254 mg/L in the control group. The average COD$_{Cr}$ removal rate of the test group was 90.1%, which was higher than that of the control group (85.9%).

3.2 Comparison of effluent NH$_3$-N in the pilot-scale

![Figure 3. The comparison of NH$_3$-N removal rate between two systems](image)

It can be seen from the figure 3: When the average value of the influent NH$_3$-N is 323.7 mg/L, the average effluent NH$_3$-N of the test group is 8.4 mg/L, which is obviously lower than the 13.4 mg/L in the control group.

The average NH$_3$-N removal rate of the test group is up to 97.4%, which is higher than that of the control group (95.9%).
3.3 Discharge of the excess sludge during pilot-scale

Figure 4. The cumulative discharge of the excess sludge during operation of the two systems

It can be seen from the figure 4: The excess sludge discharge of the test group with the addition of 2# bacteria agent was significantly lower than that of the control group. From the first day to the seventh day, the amount of excess sludge in the test group decreases gradually, and tends to be stable in the later period. The average amount of excess sludge discharged is 349g/d, which is significantly lower than the control group's 1405g/d. That is to say, after adding 2# bacteria agent with lysozyme production, the excess sludge reduction of the system reaches 75.16%.

3.4 OTU abundance of aerobic system during pilot-scale

The abundance information of microbial OTU in the aerobic sludge of the experimental group (PGEG) and the control group (PGCK) was analyzed. The abundance of OTU indicated the species richness. The OTU statistical results of each sample are shown in Table 2-1

Table 2. Sample data and OTU statistics

| Sample_name | Amplicon_type | Clean_tags | Effective_tags | Singleton | Singleton (%) | Chimeras | Chimeras (%) | otus |
|-------------|---------------|------------|----------------|-----------|---------------|----------|--------------|-----|
| PGCK        | 16S           | 100594     | 87555          | 10559    | 10.4966       | 2480     | 2.4654       | 480 |
| PGEG        | 16S           | 103850     | 89225          | 12130    | 11.6803       | 2495     | 2.4025       | 499 |

Two samples produced a total of 535 OUT. After clustering multiple sequences according to the distance between the sequences, the PGCK sample has a total of 480 OTUs, while the PGEG sample has a total of 499 OTUs, indicating that the bacterial species in the micelles have increased after biological enhancement.

3.5 Genus-level distribution

It can be seen from the figure 5: The active sludge bacteria mainly consist of Comamonas, Unclassified, Alicyciphilus, Rheinheimera, Proteus and Acinetobacter in coal chemical industry.

After biological synergy, the number of bacteria in aerobic pool increased significantly, and the microbial flora migrated in a better direction. The number of Alicyciphilus and Rheinheimera in PEG samples was significantly higher than that in PGCK samples. Among them, Alicyciphilus has been reported to degrade hydrophobic organic pollutants[4], while the Rheinheimera has been reported to produce lipase. Biological efficiency has increased the number of effective functional bacteria in the biochemical system of the tannery wastewater[5].

Figure 5. Distribution of microbial flora of samples in genus level

4. Conclusions
During the operation of tannery wastewater, because of the complex wastewater composition and high SS, the effluent CODCr and NH3-N are unstable and the sludge output is high.

The biological activity of the biochemical system of tannery wastewater was improved by using the biological synergy technology without changing the process and facilities of the original biochemical system. The CODCr and NH3-N of the effluent are relatively stable, ensuring the total discharge water qualification rate of 100%.

1) The removal rate of CODcr and NH3-N in the biochemical system of tannery wastewater was significantly increased by biological synergy. The average removal rate of CODCr in the biochemical system after biological synergy was 90.1%, higher than 85.9% in the control group; the average removal rate after synergy was 97.4%, which was 1.5% higher than the control group;

2) By adding lysozyme produced by the Lysobacter ruishenii to the sludge digestion tank, the excess sludge sludge in the test group could be reduced by 75.16% compared to the control group.

3) After biological synergy, the number of bacteria in aerobic pool increased significantly, and the microbial flora migrated in a better direction.

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