Nitrogen Removal of Tannery Wastewater with High-concentration Ammonia

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Abstract: High-concentration ammonia has seriously prevented tannery wastewater to meet its relative discharge standards. To solve this problem, cleaner production is adopted in the liming-deliming process which decreases influent ammonia content from source, thus reducing the amount of ammonia flowing into the following comprehensive wastewater treatment system. In some enterprises, secondary denitrification processes, especially bio-film processes should be added to the other existing biological treatment systems. This paper describes two denitrification treatment schemes based on bio-film processes which have already been put into use and investigates the main influencing factors affecting the nitrogen removal efficiency of the secondary denitrification processes.

Keywords: tannery wastewater; deashing and softening; secondary biological denitrification

1 Introduction

In recent years, as the power of environmental treatment and supervision increasing, tannery wastewater, especially ammonia nitrogen whether can reach the discharge standards, which needs to be solved urgently, relates to the survival and sustainable development of our tannery industry. In general, physical and chemical pretreatment combined aerobic biological treatment are adopted to treat tannery wastewater, which can efficiently remove COD, BOD₅, S², Cr, color and so on. The wastewater quality after treatment can basically reach the first and second class standards of comprehensive wastewater discharge standard (GB8978-1996). However, the ammonia concentration of tannery wastewater is high up to hundreds mg/L per liter, it is harder to treat than any other industrial wastewater. This paper preliminarily studies the high concentration of ammonia nitrogen and its relative denitrification technologies.

2 Decreasing Ammonia Concentration of Tannery Influent

High concentration ammonia nitrogen in tannery wastewater is mainly from large amount of ammonium and enzyme used in deashing and softening processes, as well as other chemical materials in neutralization, dyeing and fat-liquoring. At the same time, in soaking and liming of raw hide, organic nitrogen is generated after protein hydrolyzes. Ammonia nitrogen and COD distribution in each section is listed in Tab.1.

<table>
<thead>
<tr>
<th>season</th>
<th>Adjusting tank</th>
<th>1st sedimentation tank</th>
<th>2nd sedimentation tank</th>
<th>constructed wetland</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NH₃-N</td>
<td>COD</td>
<td>NH₃-N</td>
<td>COD</td>
</tr>
<tr>
<td>spring</td>
<td>130~176.8</td>
<td>5700</td>
<td>37~73</td>
<td>89</td>
</tr>
<tr>
<td>autumn</td>
<td>101.6~189.7</td>
<td>5550</td>
<td>10.8~39.9</td>
<td>91</td>
</tr>
<tr>
<td>winter</td>
<td>104.3~124.8</td>
<td>5200</td>
<td>24.8~68.8</td>
<td>99.5</td>
</tr>
</tbody>
</table>
According to the above analysis, it is advised that ammonia-free cleaner production should be adopted i.e. ammonium sulfate is substituted by ammonia-free deliming agent. The production cost is higher than the conventional (almost 200～250%), but it will greatly save the cost for ammonia nitrogen treatment, which is worthwhile through overall accounting.

The other measure to decrease the ammonia nitrogen concentration is to treat wastewater from processes of deliming and softening singly, of which process flow chart (Fig.1) is as follows:

![Fig. 1 Treatment process of deliming and softening wastewater](image)

The pH value of the deliming and softening wastewater is almost between 8 and 9, and ammonia nitrogen concentration is high up to 2000～3000mg/L. If pH value is adjusted between 10 and 11 and air lifting is adopted with the air amount of 2000～3000m³ per ton, the ammonia nitrogen removal efficiency can reach 70～80%.

3 The mechanism and process of the double biological denitrification technology

Many practice shows that single biological denitrification technology can not remove both organics and ammonia nitrogen at the same time, so double biological denitrification technology must be adopted, in which the primary is mainly to remove organics, while the secondary to remove ammonia nitrogen. In the processes of double biological denitrification technology, organics is greatly removed during the primary process, so the C/N of the wastewater flowing into the secondary is lower, and the ratio of nitrobacteria to the active microorganism is relatively higher, so the oxidizing rate of ammonia nitrogen is higher. The organics concentration of wastewater flowing into the secondary is relatively lower, and the amount of heterotrophic bacteria decreases, so the flocculating function of active sludge decrease, which is not good to separation of solids and liquid. The secondary biological denitrification should adopt biological membrane technology, which weakens the competition for adhesion surface of 异养菌 and is beneficial for heterotrophic bacteria to adhesively grow, thus improving the removal efficiency of ammonia nitrogen. The process flow chart (Fig.2) of double biological denitrification technology is as follows:

![Process flow chart of double biological denitrification technology](image)
Fig. 2 Two-step biological denitrification

For the tannery wastewater treatments which have already had oxidation ditch or other biological treatment technologies, of which the secondary biological denitrification technologies are recommended as follows:

3.1 Step-feed A/O contact oxidation technology

The process flow diagram of step-feed A/O contact oxidation technology is shown in Fig.3. Its principal is that partial influent and returned sludge inflow to the first section of anoxic zone, while other parts of influent separately inflow to each section of anoxic zone, thus forming concentration gradient in the reactor, and along with the sludge retention time (SRT) prolongs, the variation of MLSS concentration gradient increases. Besides, nitrification liquor generated from each section of aerobic zone directly flows into its next section for denitrification, so that the inner recycling facilities will are never needed.

![Fig. 3 Step-feed A/O denitrification technology](image)

The effluent of the secondary sedimentation tank after the primary biological treatment directly flows into step-feed A/O contact oxidation. Organics and ammonia nitrogen in the effluent of contact oxidation tank will be greatly removed. In the end, it will be discharged after coagulation and sedimentation. Take the wastewater treatment project of a leather limited company in Jiangsu for example, the scale of this treatment design is 5000m$^3$/d, four step-feed A/O contact oxidation technology is adopted, designed retention time is 24h, the volume ratio of A/O is 1:3, and the nitrification rate is 0.15kgNH$_4^+$-N/m$^3$-d.

3.2 Biological aerated filter

Biological aerated filter is mainly applied to advanced treatment of wastewater and domestic sewage. Biological aerated filter is fitted with spherical, rough and porous ceramicsites with high specific surface area. When the wastewater flows through the filter bed, the suspended substances and colloids are intercepted on the surface and internal pores of the filter materials. At the same time, microorganism attaches on the surface of the filter materials as bio-film, which can efficiently remove organics, ammonia nitrogen and SS through biological oxidation and nitrification.

In recent years, this technology has been applied to advanced treatment of tannery wastewater, e.g., a leather company in Henan adopted it. The effluent of oxidation ditch flows to two-stage biological aerated filters for advanced treatment. The volume loading is 0.5 ~ 0.6kgNH$_3$-N /m$^3$-d, the hydraulic retention
time is 4h, and the COD and ammonia nitrogen of effluent both basically reach the discharge standards.

4 Conclusion

To solve the problem of high ammonia nitrogen concentration in tannery wastewater, priority should be given to ammonia-free deliming cleaner production, i.e. ammonia-free deliming agent is used to substitute ammonium sulfate, thus ammonia nitrogen concentration is reduced from source. Pretreatment of alkaliifying and air stripping to deliming and softening wastewater can also reduce ammonia nitrogen concentration flowing into comprehensive wastewater treatment system. To those tannery wastewater treatment systems, which have already built biological technologies, the secondary bio-film biological denitrification system should be added, so that the primary sludge A/O is mainly to remove COD and partial ammonia nitrogen, while the secondary bio-film A/O is mainly to remove ammonia nitrogen.

References