Efficacy of Anaerobic Treatment of Fur Wastewater under Different Pre-Acidification Degrees

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Abstract. In this research, we studied fur processing wastewater and examined the effect of acidification degree on the treatment performance of internal circulation anaerobic reactor (IC). The results showed that the acidification degree had significant effects on the removal rate of CODcr, effluent volatile fatty acid content (VFA), stability of the system and the microbial biomass of granule sludge in IC. When the acidification degree of wastewater is about 45%, the removal rate of CODcr is more than 70% in the anaerobic system. Although the effluent VFA is higher, there was no inhibition in aciditation, the effluent ALK/VFA maintained at about 1.3, the anaerobic system run stably and well, granule sludge microbial biomass maintained at about 80% as well as in good activity. In practical engineering applications, controlling the acidification degree at about 45% can maintain the anaerobic system stable, efficient CODcr removal and the steady growth of microbial in granule sludge.

1. Introduction

In the process of wastewater anaerobic treatment, hydrolysis acidification can hydrolyze the macromolecule organic matter in fur wastewater into easy-to-use small molecule organic matter, thus improving the biochemicality of wastewater. At this stage, the acidity of wastewater plays an extremely important role in the methane phase in anaerobic reactor, and if the polymer organic matter is not complete, it will be difficult to remove the methane-producing phase [1], if the acidity degree is too high, it may cause the wastewater pH to plummet, the reactor acidification or even collapse. A large number of synthetic dyes and additives are added to the multi-process dyeing process of fur processing [2-3], and the hydrolysis of protein in the processing process, resulting in complex waste water composition, containing a large number of organic matter, volatile fatty acids (VFA) content after acidification is high, in the process of anaerobic treatment, although there are certain advantages, but very easy to exceed the processing capacity of methane bacteria, the risk of acidification of the reactor is greater.
The judgment of the degree of acidification of wastewater is often characterized by evaluation indexes such as "acidification rate" [4-6], that is, the ratio of VFA to CODcr in the water discharge. However, with the in-depth understanding of the process of hydrolysis of wastewater, it is found that the removal of some CODcr before and after the acidification of wastewater is accompanied. Therefore, this study from the point of view of material migration and transformation to measure the role of acid production, the "acidity degree" index of the calculation of reference mu Jun and other research results [7-8], that is, when the total amount of acid is calculated, add edgto cr remove s.of the form of VFA in V/C. This index can truly reflect the degree of acidification of wastewater, and can guide the relevant engineering design.

In the early stage of the project, the waste water of a sheep shear processing enterprise in Hebei was the research object, and the experimental study of the IC reactor to treat different concentrations of fur wastewater was carried out, and the operating conditions and engineering parameters of the IC reactor for the treatment of fur wastewater were explored. On this basis, this paper focuses on the operation effect of THE IC inner circulatory reactor to treat fur wastewater under different acidity conditions, which is of guiding significance to improve the operation effect of anaerobic reactor treatment of fur wastewater in practical engineering applications.

2. Materials and Methods

2.1. Experimental wastewater and particulate sludge.

The existing comprehensive wastewater treatment process of the test ingress enterprise is "aeration regulation , coagulation precipitation, hydrolysis acidification, aerobics and A/O", and the wastewater used in the experiment is taken from the adjustment pool, the main nature of which is shown in Table 1. The sludge used in the experiment was domesticated and stable grain sludge in the process of pre-treatment of fur wastewater, which was well grainy and black, with a particle size range of 0.8 to 3 mm, MLVSS/MLSS 0.78, 93% water content, and an auxiliary enzyme F420 content of 0.331 smol/g VSS.

| Table 1. The characteristics of the fur wastewater |
|-----------------|--------|--------|--------|
| CODcr (mg · L-1) | pH     | VFA (mmol · L-1) | Oil (mg · L-1) |
| 1900~3100       | 7.8~9.5| 9~23.7 | 150~260 |

2.2. Reactor device and operating flow.

The IC reactor unit used in the experiment is 2.3 m high, 0.6 m in diameter and 0.5 m3 in effective volume. The experiment used the running mode of continuous water intake, and the timing of the reactor after the steady operation of 6 d at each acidity level was taken out of the water, and the indexes of CODcr, VFA, ALK, pH, MLSS, MLVSS and sludge coenzyme F420 were measured. When entering water, the pipe pump pumps the waste water from the reservoir into the heating pot for heating up and then pumping into the IC reactor, the external insulation jacket is provided by the external reactor, and the medium temperature (30~40℃) condition strapped to the reaction needs is maintained through the heating pot water flow cycle. Before anaerobic treatment of wastewater, the processing industry hydrochloric acid regulation test wastewater pH to 6.8 to 7.4, at the same time to ensure that the system has sufficient buffer capacity, before entering the water to supplement NaHCO3 to improve the alkalinity of wastewater.

2.3. Analysis of detection methods.

In the experiment, CODcr was measured by rapid digestion method, the industry standard HJ/T399-2007 《Water quality chemical oxygen demand rapid delysiolation speclumity method》. VFA and ALK use joint titration method [9], and oil content is extracted [10],pH and temperature was measured
quickly by pH instrument and thermometer, MLSS and MLVSS were measured by weight method, and the coenzyme F420 in sludge was measured by ultraviolet spectrophotosis [11].

3. Results and discussions

3.1. Effect of acidity on CODcr removal rate.
Different types of wastewater have their own appropriate acidity degree, in the course of this experiment, the test fur wastewater V/C and CODcr removal rate was monitored, at different acidification degree, the IC circulating anaerobic reactor on high VFA fur wastewater CODcr removal rate is shown in Figure 1.

As can be seen from Figure 1, with the increase of the acidity of wastewater, the removal rate of wastewater CODcr shows the tendency of rising first and then plummeting. When the degree of acidification is 30.21 %, the removal rate of wastewater CODcr is 40 %, and then with the increase of acidity, the removal rate of wastewater CODcr increases to about 70 %, at which time the degree of acidification of wastewater is 45.30 %. When the acidity level continued to rise to 74.59 % and 86.94 %, the removal rate of CODcr in wastewater was less than 20 %. It is speculated that when the acidity of wastewater is about 45.3 %, the amount of CODcr that can be degraded by anaerobic degradation is close to the limit, and then the degree of acidification of wastewater continues to increase, which inhibits the microbial activity in the reactor, destroys the dynamic balance of acid and methane-producing bacteria in the reactor, and leads to poor CODcr removal. Therefore, in the IC reactor treatment of fur wastewater in the actual project, control the acidity of wastewater in about 45%, can ensure an efficient and stable CODcr removal rate.

![Image](image_url)

**Figure 1.** Relationship between influent V/C and CODcr removal rate

3.2. Effect of acidity on VFA value of water
The VFA concentration of water out is considered to be the most important parameter in anaerobic reactor control [13]. Monitoring the concentration of the water-out VFA can quickly respond to the operation of the reactor and facilitate timely adjustment in the actual operation [14]. Figure 3 shows changes in the water VFA of anaerobic reactors at different acidity levels.

As can be seen from Figure 2, with the increase in the acidity of wastewater from 30.21 % to 45.20 %, the water-out VFA was relatively stable and maintained at 15mmol/L or so, after the acidification level increased to 74.59 % and 86.94 %, respectively, the trend of water VFA increase, reaching 20 mmol/L or more. Overall, with the increase of the acidity of wastewater, anaerobic reactor water VFA into an elevated trend, water VFA is too high to indicate that there is a large number of VFA accumulation in the reactor, high VFA may inhibit the activity of methane-producing bacteria, at this time the growth rate of acid-producing bacteria is much larger than the production of methane bacteria.
However, in the experimental process, with the increase of the degree of acidification of wastewater, the reactor did not appear pH reduction and other acidification, the reason may be that the wastewater in the VFA content is high, but mainly from oil and other easy-to-degradable organic matter, in a certain degree of acidification easy to degrade, but also shows that the IC reactor itself has a good acid-base buffer system. This is consistent with the results of Liu Bing's study, Tang Yuan, etc. [15]. In addition, the high protein content in fur wastewater, in the process of anaerobic degradation will produce a large number of ammonium bicarbonate, produce a certain alkalinity can buffer the corresponding VFA, is also one of the reasons for the good operation of the reactor.

![Figure 2. Relationship between influent V/C and effluent VFA](image)

3.3. Effect of acidity on microbial quantity and activity of sludge
Coenzyme F420 in anaerobic treatment device sludge generally contains a considerable concentration, especially in the sludge with high methane bacteria activity, its concentration is higher [16], because of the presence of coenzyme F420 in various methane-producing bacteria, it is generally believed that it has a certain relationship with methane-producing activity, so this indicator can be used to measure anaerobic sludge [11]. The reactor was stably operated at different acidity levels to determine the content of the particulate sludge coenzyme F420 at this stage. Anaerobic particulate sludge is composed of acid-producing bacteria and methane-producing bacteria, Sun Fuxuan and other research found that anaerobic particulate sludge hydrolysis bacteria are distributed outside the particulate sludge [17], particulate sludge is produced in the interior of methane bacteria. By determining the relative value of sludge microorganism (MLVSS/MLSS), the amount of microorganisms such as volatile organic matter and cell body in anaerobic system can be reflected to a certain extent, and the results of the sludge microbial mass determination under different acidity degree are shown in Figure 3.

When the acidity of wastewater increased from 30.21 % to 45.20 %, MLVSS/MLSS increased to about 80 %, indicating that the increase of acidity in a certain range can lead to an increase in sludge microbes in anaerobic reactors. As acidity continued to increase to 86.94 %, MLVSS/MLSS decreased to 77 %. It is speculated that the reason may be that with the increase of acidity, the proportion of non-degradable organic matter in the wastewater entering anaerobic reactor is decreasing, the growth rate of acid-producing bacteria is reduced due to the reduction of the matrix required for reproduction, resulting in a decrease in the growth rate of sludge and a decrease in the amount of sludge microorganisms. In the actual anaerobic operation process, taking into account economic factors, it is recommended to control the acidity of fur wastewater at about 45%, which can ensure a high amount of sludge microorganisms, but also maintain a stable and efficient COD removal rate.

The content of coenzyme F420 shows the regular trend of increasing and then decreasing with the increase of the acidity of fur wastewater, although anaerobic particulate sludge has some adaptability.
to fur wastewater after domestication in the early subject, the experimental initial sludge coenzyme F420 is 0.331 μmol/g VSS, but because the organic matter in fur wastewater is more complex, the degree of acidification is 30.21. When % of its coenzyme F420 is 0.263 μmol/g VSS, with the acidity increased to 45.30%, at this time the sludge coenzyme F420 reached a maximum of 0.309 μmol/g VSS, but as the acidity continued to increase, the sludge activity dropped sharply, coenzyme F420 decreased to 0.072 μmol/g VSS. It can be seen that with the change of acidity, the variation law of Coenzyme F420 content is consistent with the law of CODcr removal rate in the same period, which indicates that in the same reactor, the CODcr removal rate can be used as a reference index for methane bacteria activity in particulate sludge.

![Figure 3. Relationship between influent V/C and the content of coenzyme F420 & MLVSS/MLSS in sludge](image)

4. Conclusion

The results of this experiment show that the use of IC reactor to treat fur wastewater, acidity on the system's CODcr removal rate, water VFA, system ALK/VFA, particle sludge microbial production and methane bacteria activity have a significant impact.

(1) After the acidification of fur wastewater itself, VFA content is high, in the process of anaerobic treatment, although there are certain advantages, but VFA is easy to accumulate, it is recommended to add acid to adjust the water pH between 7 to 8, at the same time appropriate lybiad sodium to improve the alkalinity of the wastewater. According to the prior exploration to obtain the supplemented bicarbonate condition of 1.6g/L, or the wastewater ALK/VFA 1, can keep the IC reactor running well.

(2) The degree of acidification has a significant effect on the removal rate of CODcr, but the higher the degree of acidity, the higher the removal rate of CODcr. When the acidity degree reaches about 45 %, the CODcr removal rate and the methane activity in sludge show a stable and good state, and anaerobic reactor water VFA becomes elevated. When the acidity is about 45%, the sludge MLVSS/MLSS is about 80%, and then the sludge MLVSS/MLSS value decreases as the acidity increases.

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