Study on the efficacy of anaerobic biological treatment of industrial wastewater

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Abstract: In this research, we examined the internal circulation (IC) reactor performance on fur processing wastewater and explored the optimum operation parameters of IC reactor with high concentration volatile fatty acids (VFA) by a 60d field test in middle temperature. The results showed that the wastewater can be adapted to the IC reactor and start rapidly. In steady operation stage, when the influent CODcr concentration stabilises at under 3000 mg·L⁻¹ and the acidibility is at around 45%, there is no apparent VFA accumulation and the effluent CODcr removal rate remained stable at about 55%. When the concentration of influent CODcr exceeds 3000 mg·L⁻¹ and fluctuations obviously, the average removal rate of CODcr is about 50%. The average removal rate of grease is 61.3%, and the HRT is 6 h. Compared with the existing hydrolysis acidification and aerobic treatment, IC reactor treatment has improved the efficiency of VFA degradation significantly, which indicates that IC reactor has great engineering applicability for treating fur processing wastewater.

1. Introduction
Fur production wastewater composition is complex, containing a large number of organic matter, of which the grease content is high, and due to the use of a large number of chemical materials in the processing process, so that the wastewater is difficult to degrade increased, resulting in aerobic biochemical treatment process is long, difficult, high energy consumption. At present, the application of anaerobic in fur wastewater treatment is limited to hydrolysis, with the actual water treatment project in the demand for high efficiency and economical technology, the anaerobic technology into the existing process, has become an urgent need of the industry. The content of volatile fatty acids (VFA) in fur wastewater is high, the sulphide concentration is low, and it is more suitable for the application of anaerobic technology than tanning wastewater. Up to now, IC reactor steaming in fur wastewater treatment is still lack of large-scale engineering applications, and systematic research and guidance data are relatively lacking.
Sheep shearing process wastewater mainly comes from the production process of skin washing, immersion, degreasing, acid softening, tanning and dyeing and other processes, this study uses IC reactor in medium temperature conditions for a sheep shear processing enterprises in Hebei from different sources of wastewater pilot experiments, and combined with laboratory data analysis, The working conditions and engineering parameters of The IC reactor treatment of fur wastewater are explored in order to provide technical basis for anaerobic technology in the application of fur wastewater engineering.

2. Materials and methods

2.1. Experimental wastewater and anaerobic sludge

The existing comprehensive wastewater treatment process of the test enterprise is "aeration regulation and coagulation precipitation, hydrolysis and aerobic acidification, aerobics and A/O", the wastewater sample used in the experiment 1 is taken from the hydrolysis acidification pool, as the IC reactor start-up phase water, the water sample 2 is taken from the adjustment pool, used for the continuous water flow after the stable operation of the reactor, water sample 3 is taken from the adjustment pool, For continuous water inlet after the reactor is stable. The main properties of the three wastewaters are shown in table 1.

The inoculated particulate sludge used in the experiment came from the grain sludge in UASB, a sewage treatment plant in a starch processing enterprise in Hebei Province, which had good granularity, with a particle size range of 0.7 ~ 2 mm, and MLVSS/MLSS is 80%, with a water content of 95%. Before the reactor is activated, the inoculated sludge of 0.25 m³ is connected, which accounts for about 1/2 of the total volume of the reactor.

| Table 1 Water quality |
|-----------------------|
| Index | CODcr(mg·L⁻¹) | NH₃-N(mg·L⁻¹) | pH | Chroma(times) | Grease(mg·L⁻¹) |
|-------|---------------|---------------|----|---------------|---------------|
| Sample 1 | 684~792 | 70~110 | 7.5~8.2 | 290~320 | 98~170 |
| Sample 2 | 1900~3100 | 90~130 | 7.8~9.5 | 400~800 | 150~260 |
| Sample 3 | 3000~4775 | 110~150 | 8.3~9.7 | 400~800 | 140~210 |

2.2. Reactor and experimental methods

The IC reactor device used in the experiment, which is 2.3 m high, 0.6 m in diameter and 0.5 m³ in effective volume. The experimental process is divided into three stages, (1) start-up stage: water sample 1 intake, according to intermittent water intake cycle experiment, cycle flow of 50%, internal cycle 4 h after the reactor water for CODcr, NH₃-N, VFA, ALK, Chroma, pH, grease and other indicators, the start-up phase of a total cycle experiment 16 times, the total test time is 64 h; (2) the stable operation phase (64 h ~ 678 h): this stage of water intake sample 2 intake, operating intermittently to 304 h, the continuous water intake method, At this time, the processing industry hydrochloric acid regulation test wastewater pH to 7.5 or so, in order to ensure that the system has sufficient buffer capacity, in the water to add the appropriate amount of NaHCO₃ (1.6kg/1000L) to improve alkalinity, the experimental process regularly take the reactor out of water for CODcr, NH₃-N, VFA, ALK, Chroma, pH, grease and other indicators to determine; (3) high load fluctuation stage: run to 678 h, water sample 3 intake, intake flow, sampling time and monitoring parameters in the same stage. When entering water, the pipe pump will pump the waste water from the reservoir into the heating pot for heating insulation measures, the water from another pipe pump from the bottom pump into the IC reactor, the external reactor is equipped with a heat-proof jacket, through the heating pot water flow cycle to maintain the reaction needs of the medium temperature (30~40°C) conditions. The total duration of the experimental operation monitoring is 1002 h.
2.3. Analysis methods
In the experiment, CODcr was measured by rapid delysiation, the industry standard HJ/T 399-2007 "Water quality chemical oxygen demand rapid deprecataion speculmity method", VFA and ALK using joint titration method, NH₃-N measurement using Nashi reagent speculmity method, national standard HJ 535-2009. The grease content is measured by weight method, the chroma is measured by the platinum cobalt chroma ratio, the pH and temperature are measured by pH instrument and thermometer respectively.

3. Results and discussions
3.1. Changes of CODcr and VFA values and their relationship in the experimental process
VFA, as an intermediate product of anaerobic processes, can be used to reflect whether the anaerobic digestion process is thorough and the reactor is stable. Since some unacidized contaminants are converted into VFA during anaerobic process, when acidic or alkaline intermediates accumulate, it is easy to cause a sharp change in the pH of the anaerobic system, which often lags behind the VFA value of 2 to 3 d performance. The acidity balance in the VFA and the time control reactor should be closely monitored during the operation of the experiment.Due to the high content of VFA in fur wastewater, VFA value fluctuations are very important to judge the operation of the IC reactor in fur wastewater.

Figure 1 shows the change of CODcr and VFA values in and out of the water during the entire operation phase of the IC reactor. The figure shows that in the initial stage of start-up, the concentration of inlet CODcr is low, due to the good activity of methane bacteria in the inoculated sludge, the water VFA value is always lower than the inlet water, basically maintained at 4 mmol/L or so. Numerous studies have shown that when anaerobic reactors come out of water VFA 5 mmol. The experimental results show that the test wastewater is more suitable for the start-up of the IC reactor and can operate quickly and steadily. During the stable operation phase, during the period of 64 h~304 h, with the increase of the incoming water load, the water VFA gradually increased, at 3~10.5 mmol/L range fluctuations are obvious, 304 h~678 h period, the water CODcr concentration is stable, the incoming water VFA is stable to maintain at 18~22.3 mmol. In the higher range, 1mmol is raised by 1mmol/L~1.2 mmol/L, there was a temporary build-up, but at this point the water CODcr remained stable at 1200 mg/L.

In order to examine the operation of The IC reactor under high load and large fluctuations, the water was directly adjusted by the field adjustment pool after 678 h, and the CODcr concentration was in 3000~4775 mg/L between and unstable, this stage out of the water CODcr fluctuations, at this time in and out of the water VFA value are large fluctuations, acid accumulation led to the system VFA began to accumulate, at this time, water CODcr in 890~2200 mg/L range changes, but CODcr removal rate can still reach 50% average, fur wastewater VFA mainly comes from grease, is a easily degradable organic matter, its good biochemicality may be the reason why IC reactor sadapts well to fur wastewater.
3.2. Changes of ALK/VFA and alkalinity

The operation of IC reactor has more stringent requirements for the alkalinity of wastewater, while pH and its acid-base balance in anaerobic system is the balance of the concentration of substances such as VFA and ALK in the system. The total alkalinity of the system is divided into VFA alkalinity and bicarbonate alkalinity, and the study of the change of alkalinity can analyze the operating state of the reactor, but the total alkalinity does not reflect the buffer capacity of the whole system[1]. As a common electron receptor in anaerobic system, bicarbonate can accelerate the consumption of H₂ when the concentration increases, which in turn accelerates the rate of degradation of VFA[2,3]. Therefore, bicarbonate alkalinity can effectively monitor the accumulation of VFA, is commonly used pH buffer in anaerobic system, the system has enough bicarbonate alkalinity to ensure a stable pH environment.

In the course of the experiment, the pH and bicarbonate alkalinity of the water in and out were controlled and determined, and the results were shown in Figure 2. In the actual operation process, the water pH is stable, basically maintained above 8.0, the reactor has been in a stable acid-base balance system, the inner pH of the particulate sludge is maintained between 7.0~7.5, can provide and cultivate a suitable pH environment for the metabolism of microorganisms inside the particulate sludge. At the same time, attention was paid to the change of water-out ALK/VFA, and the results showed that the 304 h forward water alkalinity value was low, i.e. the alkalinity of the wastewater for the test fur was basically maintained at 5 mmol. So the alkalinity of the water is significantly increased, at this time the ALK/VFA value fluctuations in 0.5 to 5 mmol. At 304 h after artificial addition of sodium bicarbonate to improve the alkalinity of the system, maintained at an average of 18 mmol/L, the water out ingress alk also increased accordingly, but due to the increase of the inlet VFA caused by the increase of the water VFA, the whole operation stage ALK/VFA stable at 1.2 mmol/L. In the stage of high load fluctuation, the reactor also did not see any acidification and inhibition during the experiment, which showed that the IC reactor itself had a good acid-base buffer system, which was suitable for the treatment of fur wastewater.
3.3. Changes of grease
In the traditional anaerobic treatment process, the presence of grease-based substances will lead to slow anaerobic degradation, but also affect the stability of the system, in general, the treatment of this type of wastewater lipids is usually first removed by physical methods, increasing the treatment process and energy consumption. In the experiment, the content of water and grease in and out during continuous water intake was measured, and the results showed in Figure 3, the grease content in fur wastewater was high, with an average value of 198.78 mg/L, after the IC reactor anaerobic treatment, the grease content is significantly reduced, the average value is 76.95 mg/L, the average grease removal rate is as high as 61.3%.

**Fig. 2** Change of Influent/effluent pH (a)、ALK & effluent ALK/VFA (b)

**Fig. 3** Change of Influent/effluent lipid
3.4. Changes of sludge concentration

The sludge concentration in the IC reactor is mainly related to the water quality and the operating state of the reactor, so the regular determination of sludge concentration in the reactor has a guiding effect on its operational efficiency [4]. Volatile suspended solid (MLVSS) contain volatile organic and cellular bodies, and the measurement of this parameter reflects to some extent the amount of microorganisms in anaerobic systems. The sludge concentration under different running times was measured in this experiment, and the relative value of microorganisms in anaerobic sludge (MLVSS/MLSS) was expressed, and the results of the measurement are shown in Table 2. With the increase in running time, MLVSS/MLSS is on the rise after first. At the beginning of the start-up, the inoculated particulate sludge is in the adaptation period, while the high hydraulic load leads to more loose sludge that can not adapt to the water quality of the new wastewater is washed out, at which time the MLVSS/MLSS ratio begins to decline. With the increase of running time, the activity of grain sludge is gradually restored after it is adapted to the water quality of fur wastewater.

| Table 2. Concentration of granular sludge with time |
|------------------------------------------------------|
| Time       | 0h         | 280h       | 424h       | 768h       | 972h       |
| MLVSS/MLSS | 80.78%     | 80.19%     | 77%        | 79.32%     | 80.44%     |

4. Conclusion

(1) IC reactor in the operation of fur wastewater, VFA easy accumulation, alkalinity and pH buffer is good, so it is important to control alkalinity and pH, this test IC water to maintain about 8.0, can ensure the survival of acid-producing methane bacteria need pH range. It is suggested that the acid-adjusting wastewater is weakly alkaline, so that pH 8 and the microscopic pH of the sludge is maintained between 7.0–7.5, while the sodium bicarbonate is appropriately supplemented to improve the alkalinity of the wastewater, ALK/VFA 1 can keep the IC reactor running well.

(2) IC reactor in the operation of fur wastewater, VFA easy accumulation, alkalinity and pH buffer is good, so it is important to control alkalinity and pH, this test IC water to maintain about 8.0, can ensure the survival of acid-producing methane bacteria need pH range. It is suggested that the acid-adjusting wastewater is weakly alkaline, so that pH 8 and the microscopic pH of the sludge is maintained between 7.0–7.5, while the sodium bicarbonate is appropriately supplemented to improve the alkalinity of the wastewater, ALK/VFA 1 can keep the IC reactor running well.

(3) The research shows that the treatment of fur wastewater in IC reactor is significantly improved compared with the current hydrolysis acidification or aerobic treatment efficiency, while the IC reactor is convenient to operate, saves a lot of human resources, reduces energy consumption and has certain economic benefits, has good engineering adaptability in the field of fur wastewater, which is worth promoting.

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