The Methanogenic Treatment of Tannery Wastewater

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Abstract: Anaerobic treatment by methanogenesis is widely used for the stabilization of municipal wastewater sludges and municipal solid wastes. Methane fermentation of high-strength industrial wastewaters is also widely practiced. But as yet the applications are far below the potential that actually exists in the leather industry. The reasons for the underuse for leather industrial wastewaters include lack of experience with use of the process, lack of adequate understanding of process chemistry and microbiology, and the presence of toxic compounds. Tanning, in particular chrome leather production, is still characterized by an inefficient use of raw materials, the production of highly polluted wastewater, solid wastes and odor. CLFI has collaborated to develop anaerobic treatment technologies to treat the wastewater from tanneries. The anaerobic treatment system of tannery wastewater and a sulfur recovery process have been developed and successfully implemented in tannery. The tannery wastewater treatment plant is based on the anaerobic treatment of wastewater in a UASB (Up-flow Anaerobic Sludge Blanket) and sulfur recovery process. In this plant, 240 m^3 capacity of reactor (500 m^3 wastewater/day) is treated in a demonstration project. This paper describes the design, operation and management of the tannery anaerobic treatment system of the wastewater and sulfur recovery system in detail, which will be helpful for the tannery to select and apply the wastewater treatment technologies.

Key words: leather industry; wastewater treatment; methanogenesis; sulfur recovery

1 Introduction

Industrial effluent treatment is considered an effective way to control costs, improve efficiencies and to comply with industry standards and effluent discharge limits. Restrictions related to lack of space (like the south and east part of China) or to other factors.

Anaerobic wastewater treatment is the biological treatment of wastewater in the absence air or oxygen to breakdown of the organic pollutants to gas (methane and carbon dioxide). Many applications [1]are directed towards the removal of organic pollution in wastewater, slurries and sludges. The organic pollutants are converted by anaerobic microorganisms to a gas, known as "biogas", see Fig. 1 below.

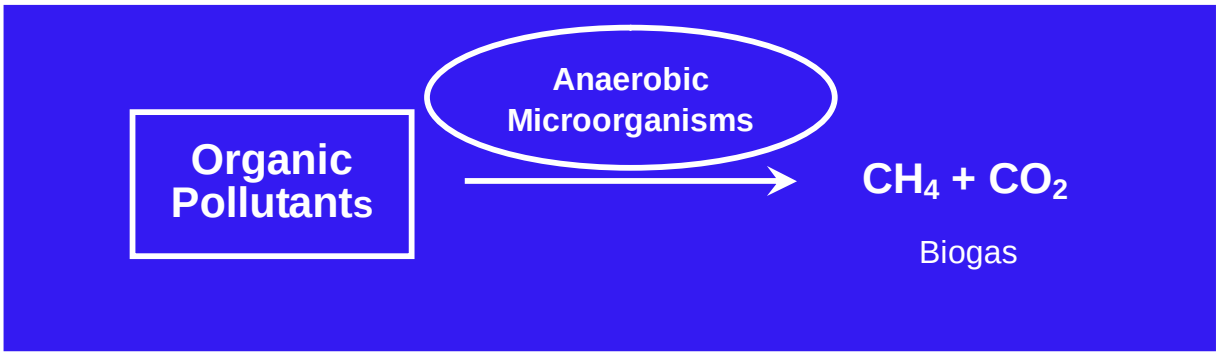

Fig. 1 Conversion of Organic Pollutants to Biogas by Anaerobic Microorganisms

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Although the process kinetics and material balances are similar to those of aerobic systems, certain basic differences require special consideration. The conversion of organic pollutants to methane gas yield little energy; hence the rate of growth is slow and the yield of organisms by synthesis is low. The kinetic rate of removal and the sludge yield are both considerably less than in the activated sludge process.

The quantity of organic matter converted to gas will vary from 80 to 90 percent. Since there is less cell synthesis in the anaerobic process, the nutrient requirements and bacteria growth are correspondingly less than in the aerobic system. High process efficiency require elevated temperatures and the use of heated (keep warmly) reaction tanks.

The advantages of anaerobic decomposition are:

- Higher reactors, lower land requirement;
- Without oxygen, lower power requirement and running cost;
- Higher efficiency process;
- Lower sludge production;
- Lower nutrition requirement;
- Energy produced out (methane used as fuel).

The COD balance during aerobic and anaerobic treatment of wastewater, see Fig. 2 below.

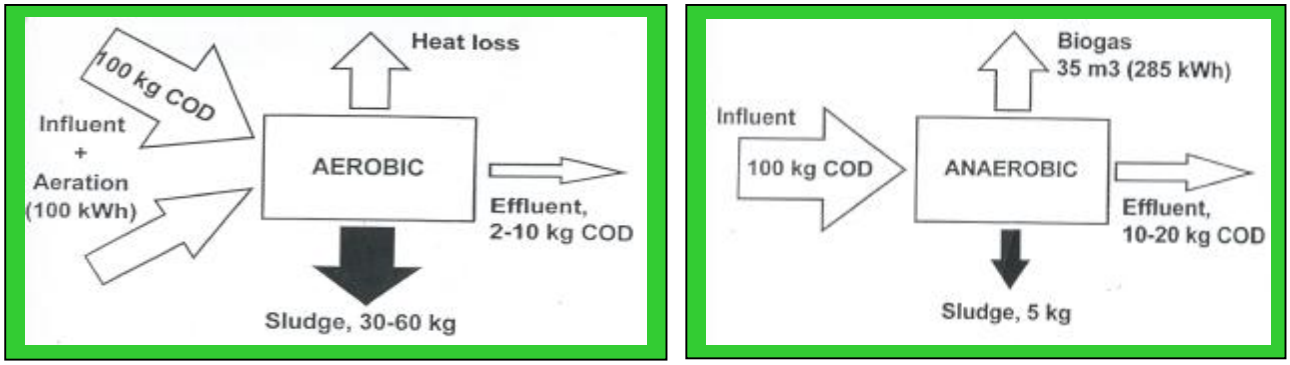


Fig. 2 Comparison of the COD balance during aerobic and anaerobic treatment

An anaerobic treatment system is a complex three-step process (see Fig. 3 below) that produces methane gas (in addition to other products) from the biological decomposition of tannery wastewater. The first stage is the hydrolysis of fats or grease and proteins. Extracellular enzymes produced by the inhabiting bacteria breakdown these macromolecules into smaller digestible forms. Next, these molecules are decomposed into fatty acids such as acetic, propionic, and butyric acid. This decomposition is performed by several anaerobic bacteria such as Clostridium, Bifidobacterium, Desulphovibrio, Actinomyces, and Staphylococcus. Finally, methanogenic bacteria such as Methanobacterium, Methanobacillus, Methanococcus, and Methanosarcina digest these fatty acids, resulting in the formation of methane gas.

Anaerobic treatment process removes a large part of the COD and has the higher efficiency for the high concentration of organic pollutants and no-degradation organic pollutants of industrial wastewater. The effluent standard cannot be reached by anaerobic treatment process only which is implemented as pre-treatment process. In most cases, post-treatment process, like aerobic treatment process or another form of treatment, also is required before its disposal.

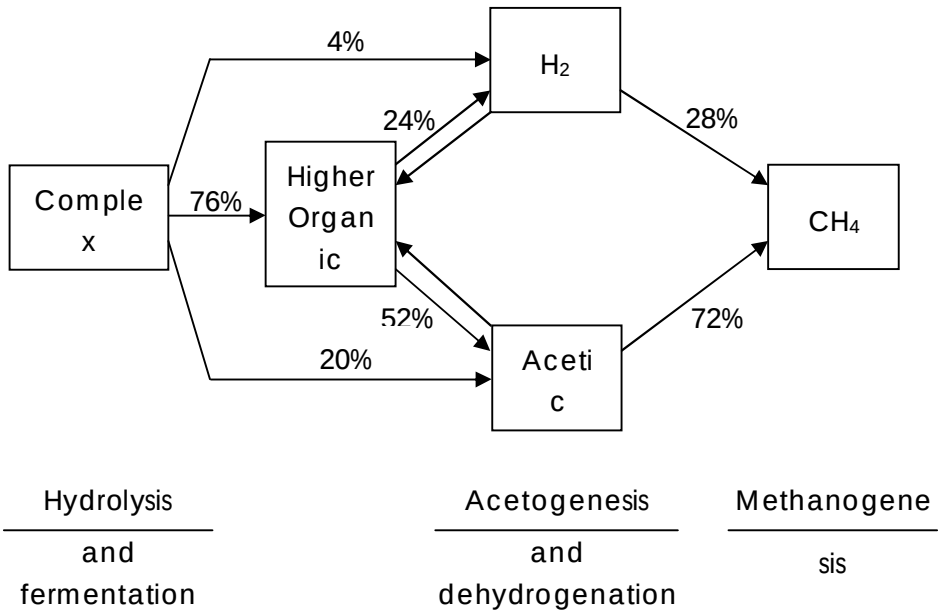


Fig.3 Three of methane fermentation

2 Anaerobic Treatment Process

2.1 The Process Flow of Anaerobic Treatment

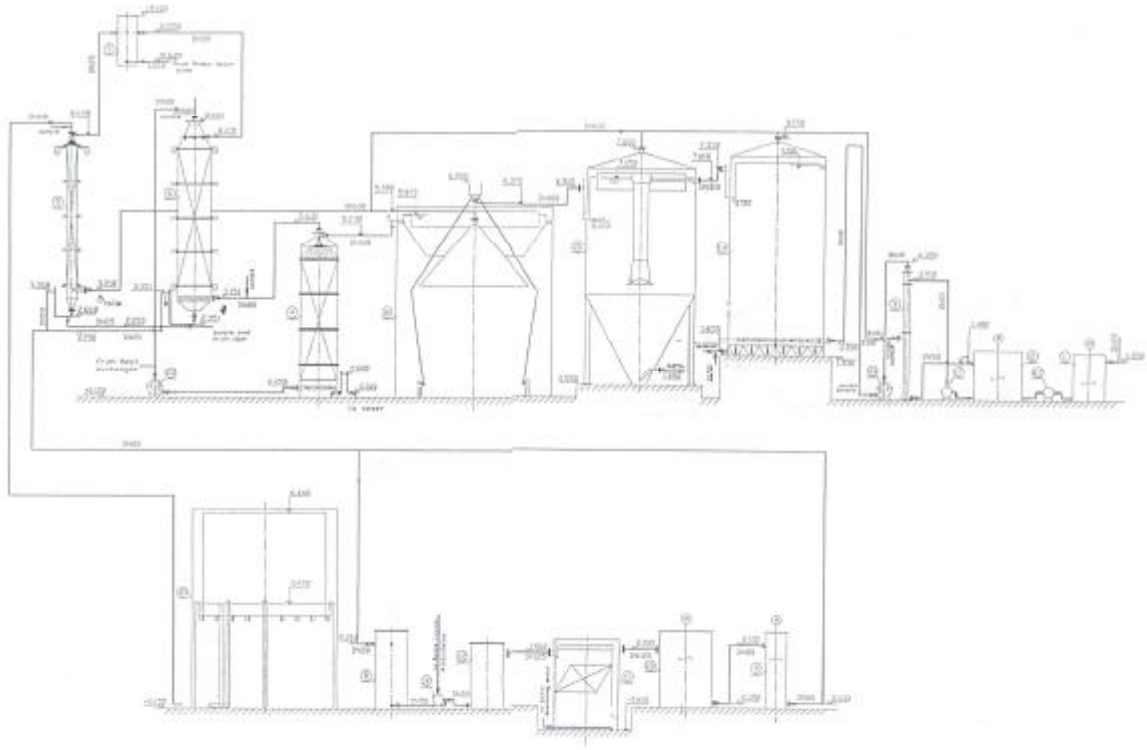


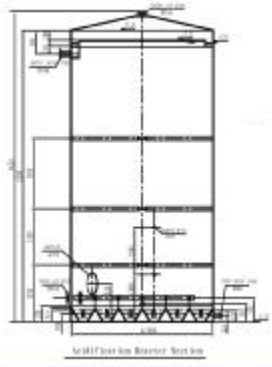
Fig. 4 The process flow of anaerobic treatment demonstration plant

After screened, the influent from the tannery will be collected into the collection tank firstly, and then pumped into the acidification reactor. This is an anaerobic contact process. The reactor is completely mixed and contains hydrolysis and acidification sludge flocs. The mixed liquor passed a gastight settling

tank in which the primary sludge from tannery and the anaerobic sludge settles. A large part of the settled sludge will be returned back to the acidification reactor and a smaller part will be discharged only. The gas from acidification reactor with more concentration of H_2S will be removed by alkali scrubber as NaHS which will be reused in tannery during unhairing. The supernatant liquid of the settler will be transported to the second anaerobic reactor, the methanogenic reactor (UASB reactor). The outlet liquid of UASB reactor will be going into stripper to remove the H_2S in liquid phase further. The mixed gas from UASB reactor will be cleaned by absorbers and cleaned biogas will be kept in the gas holder. The process flow is seen from Fig. 4.

2.2 The Design of the Anaerobic Treatment Process

The Acidification Reactor:



A tank with a water height of 6 m and 0.5 m head space. Total height: 6.5 m.

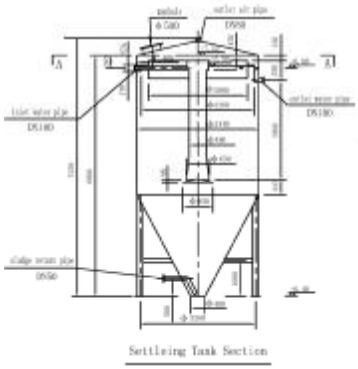
Volume of the water: 42 m^3. Total volume: 45 m^3.

Diameter is 3 m

HRT (hydraulic retention time is 4.2 h).

The reactor is closed at the top, an inspection lid at the top is necessary. At the bottom section a stripping gas distributor has to be placed. The stripping gas flow rate is 120 m^3/h.

The Settling Tank



The mixed liquor from the acidification reactor passes the settling tank. The sludge will be settled down in the settling tank and supernatant liquor will goes to the UASB reactor under gravity flow. The settling tank is closed Dortmund type of settling tank with a top diameter of 3 m. The sludge concentration in the acidification reactor will amount of 3 kg dry material/m^3, the return sludge is to contain 10 kg/m^3.

The following flows are recommended:

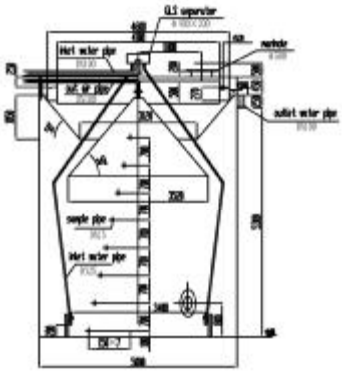
Return sludge flow rate: 3 m^3/h

Sludge discharge flow rate: 0.3 m^3/h

Settler influent (= reactor effluent + return sludge) = 10 + 3 = 13 m^3/h

The settler is closed at the top and connected to the biogas transport pipe: gases produced in the settler will be cleaned in the srubber to prevent odour nuisance.

The UASB reactor:



UASB Reactor Section

Hydraulic height of the water: 6 m

Total volume: 120 m^3

Diameter: 5 m

HRT: 12 hours

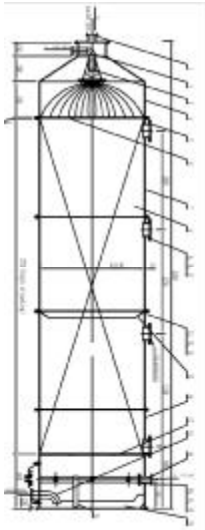
No packing material in the reactor.

Connections: top section: biogas outlet, effluent outlet

Bottom section: influent inlet, draining pipe with valve (for total drainage).
The drainage outlet is connected with a pipe to the sewer system of the tannery.
The effluent goes by free hydraulic flow to the distributor of the stripper column.
Water sample ports on different heights.

The Stripper for UASB effluent

Stripper tower with packing. The water from the UASB reactor is trickled over the packing.
Volume of the packing (the filter bed): 3.8 m^3
Height of the filter bed: 4 m
Head space: 0.4 m
Height of bottom section under the filter bed: 0.6 m
Diameter: 1.1 m
Total height: 5 m
Total volume: 4.7 m^3
Type of packing material: plastic, about 100 m^2/m^3.
Top section: outlet for stripping gas and inlet for effluent from UASB reactor.
Bottom section: inlet for stripping gas and outlet for water. The outlet for water is situated lower than the gas inlet and to prevent gas is going through the water outlet, this outlet is under water. The effluent produced by the stripper is discharged in the sewer (effluent collection channel).



2.3 Operation of the Anaerobic Treatment System

Granular Sludge

Granular sludge is at the core of anaerobic technology. A granular sludge is an aggregate of microorganisms forming during anaerobic wastewater treatment. Those microorganisms are capable of attaching to each other and form into compact bio-films referred to as "granular" (see Fig. 5 to Fig. 8 below, observed by the media microscope). Since their large particle size (generally from 0.5 to 2 mm in diameter), the granular sludge resist washout from the anaerobic reactor. Additionally, the granular sludge has the fine sedimentation performance in anaerobic process (see Fig. 9 below).

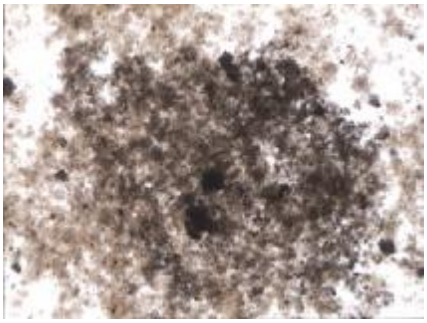


Fig. 5 15 days (with 400x)

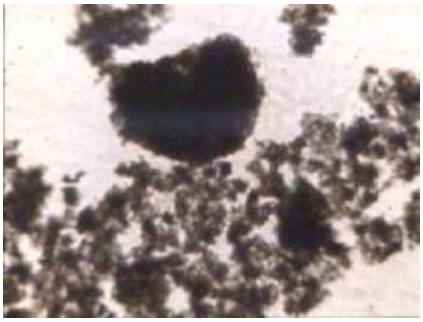


Fig. 6 36 days (with 400x)

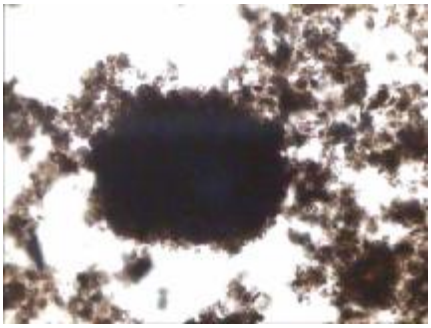


Fig. 7 50 days (with 400x)

Fig. 8 150 days (with 400x)

Fig. 9 Granular sludge and sedimentation performance

System Start Up

The production of methane gas is the slow and more sensitive step of the anaerobic process due to it requires specific environmental conditions for the methanogenic bacteria growth.

- These bacteria can only work effectively at a pH of 6.5-7.5 (the optimum near pH7.0), and also be limited by temperature [usually the mesophilic range of 85 – 100 ℉(29 to 38 ℃)].
- The toxic concentration of soluble sulfide in the anaerobic system is more than 200 mg/l. Acidification process (reactor) is able to avoid toxicity of sulfide which is present as H_2S (gaseous), HS^- (liquid), and precipitated sulfide. The loss of sulfide in the gas could also permit higher concentration of sulfide in the influent feed to the process.
- The heavy metal, such as chrome in the tannery wastewater, is toxic at low concentration. It must be removed before treatment below the toxic level.

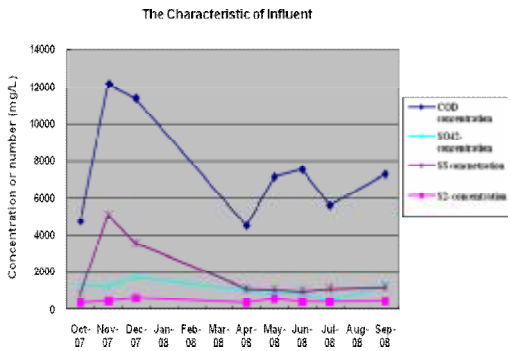
The acidification reactor is started up firstly. When you are convinced the pH of effluent of acidification reactor can be controlled between 7.0 to 7.5 (it maybe take 3 to 4 weeks), then UASB reactor can be filled with the granular sludge and started up. The biogas will be produced out within 24h after started up the UASB reactor.

3 Results and Discussion

3.1 The Influent of Anaerobic Treatment Process

The average quality of the influent from tannery is:

- total COD – 7.98 g/l;
- sulfate – 1.26 g/l;



- sulfide – 0.045 g/l.

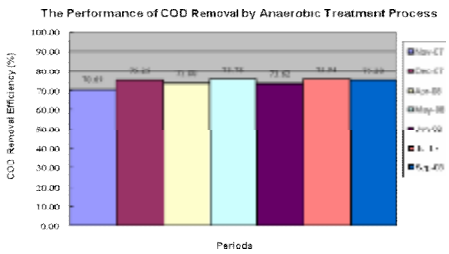
see right figure.

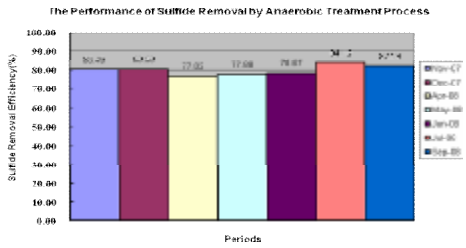
3.2 The Results of Demonstration Plant

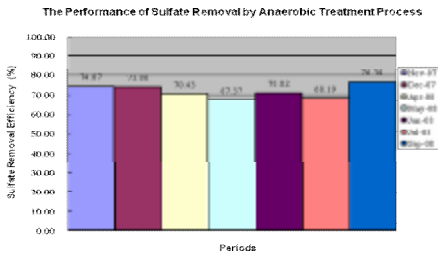
After a year running, the results of anaerobic treatment process are:

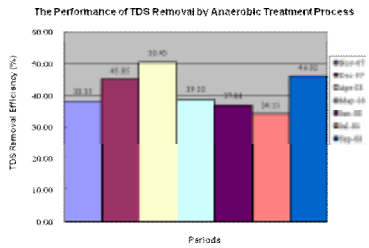
- 70 to 80 percent of COD is removed;
- 80 percent of sulfide is removed;
- 70 percent of sulfate is removed;
- 40 to 45 percent of TDS is removed;
- 85 to 95 percent of SS is removed;
- 45 percent of TKN is removed.

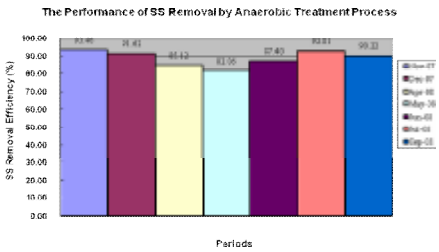
See the figures as below.

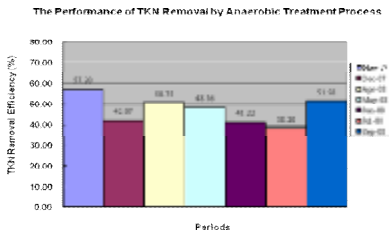












4 Conclusions

Anaerobic treatment can be considered as one of the most cost-effective and environmentally technologies for the treatment of the tannery wastewaters. Not only does this greatly reduce the final volume of sludge appeared from the plant which need to be disposed, it also creates enough energy and materials, in the form of methane gas and sulfur elements or sulfur compounds, which can be used as fuel or chemical raw materials.

Acknowledgements

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