Treatment of high density tannery effluent by UASB process

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Abstract: The startup process of the laboratorial UASB reactor and the anaerobic degradation of the organic compounds were studied by treat density tannery effluent with UASB. Moreover, the shapes of anaerobic granular sludge were observed by the multimedia microscope, and the distributions of the organic acid were determined by the gas chromatographic instrument in tannery effluent. The result demonstrated that the laboratorial UASB reactor could be started up successfully within 50 days when using anaerobic sludge as seeds under mesospheric conditions. The COD removal rate became higher with the increase of influent COD, which reached 91.6% with influent COD of 5575mg/L. However, the removal rate decreases gradually as influent COD increasing over high, which reaches 85% with influent COD of 10000mg/L. The macromolecule organic compounds in tannery effluent were degraded into small molecular organic acids by the acid-producing bacteria at the bottom of UASB reactor, most of the degradation products were acetic acid, and then propanoic acid, isobutyric acid and isovalerate**.** The small molecular organic acids were degraded into CH_4 and CO_2 by the methanogenus through the entire sludgebeds.

Key words: tannery effluent; anaerobic process; UASB; granular sludge; startup process

1 Introduction

With the strict environmental protection laws and implying of water-saving craft, the pollution load of the tannery effluent was higher. For example, COD was up to 5000 ~ 8000mg/L, even up to several thousands, the concentration of S^{2-} was 400~500mg/L, and its maximum was700mg/L [1].The oxidation ditch [2-4] ,which was a more mature tannery effluent treatment, was no longer suitable for treating wastewater with so high loads. Anaerobic technology was an effective method to process high load organic wastewater. But it developed slowly in last one hundred years because of lack of understanding and research, and its limitation in implying had disappeared owe to the developed science and the improved technology as well as the birth of new crafts such as UASB、EGSB、SMPA、ABR、ASBR、LARAN. Especially, anaerobic technology which was energy saving and efficient had become a new hot research [5-8] along with serious energy crisis and more complex wastewater.

In view of its characteristics, tannery effluent was treated by anaerobic technology [9-11] in this paper. This method could not only reduce the sludge producing but also recovered part of resources.

2 Experimental sections

2.1 The main experimental material and instruments

Anaerobic sludge（VSS was 120.768g/L）which was from Henan Wastewater Treatment Plant of Shoes Union; vegetable tannin extract(FS);black dyes(2GB);fatting Agent(SE);chromium powder which was industrial product and another analytically pure chemicals.

Instruments including Agilent6890 Gas Chromatographic Instrument, DR/2010 COD Detector,

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Multimedia microscope and UASB（JK-020）

2.2 diagram of the experimental set-up

Schematic diagram of the experimental set-up was showed in Fig.1. UASB reactor used in experiment，which was made by Wastewater Treatment Experimental Instrument Plant attached Tongji University in Shanghai，was made of PMMA with a total effective volume of 28L. Its total height was 1.95m, in which the height of three-phase separator was 0.4m, the height of suspension layer and sludge bed were1.55mm in all. Wastewater was pumped in the reactor to the bottom and flowed out from the top. There were nine sampling places to observe the concentrations and properties of sludge. The gas produced went through water-tight seal bottle firstly and measured by Wet Gas Flowmeter.

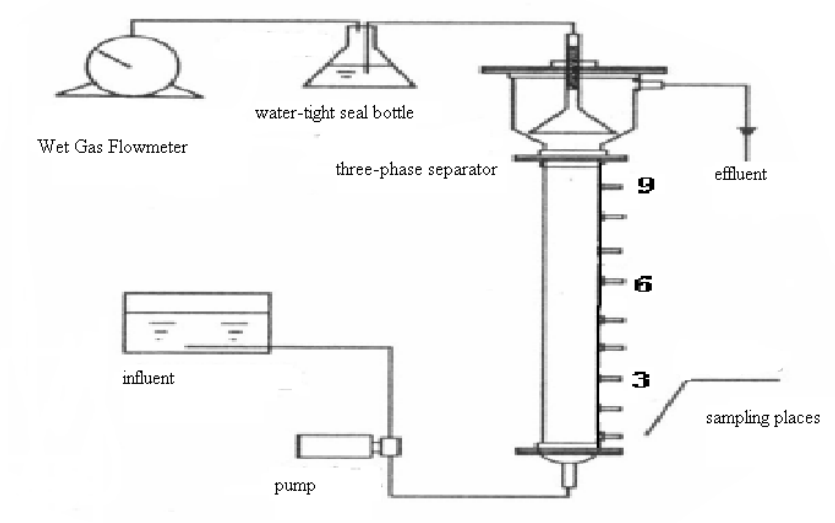

Fig.1 Schematic diagram of the experimental set-up

2.3 Experiment contents

2.3.1 Preparation of simulative tannery wastewater

5g lime and 60g Na_2S were dissolved in 2L water, then 100 g wool were added, elevating temperature to 40℃ to hydrolyze it slowly. When all the wool was dissolved completely, added successively 2g KH_2PO_4, 2g $(NH_4)_2SO_4$, 0.2g vegetable tannin extracts(FS), 0.15g black dyes(2GB), 0.73g fatting Agent(SE), 0.5g chromium powder and 2g NaCl into the solution. Finally pH was adjusted to 7.2 with CH_3COOH, and then COD was measured. According to the experimental needs，simulative tannery wastewater needed to be diluted.

2.3.2 Startup and control

（1）Loading and activation of the sludge seed

About 14L anaerobic granular sludge and a little of starch were added to UASB which was full of running water, elevating temperature gradually after soaking several days to revive the activation of anaerobic microorganism. The next step could be operated when the temperature was up to 36℃.

（2）The adjustment of temperature

Medium temperature, about 35~38℃, was better for UASB reactor, which was based on the former experimental results and the related date. After loading, open the constant temperature water circulating system which heats ones outside automatically to increase temperature at 1℃/4h continuously, then pay attention to it carefully in order to remain the inside temperature of UASB at 36±1℃.

（3）Influent modes

Interval influent were as follows: the pump was started for two hours every time then stopped for a

hour to influent several times per day firstly, and then prolonged the pump starting time and shorted the interval time with the length of cultivating time and improvement of COD so as to transition to continuous influent. In the stage of cultivating, the quantity of influent was 1752 ml/ at the beginning, increased gradually until the full load operation. According to the experiment need, the influent COD was gradually increased, ranging from 764.05mg/L to 10033.6 mg/L, at the same time the biogas volume needed to be recorded until the goal COD. The uniformity could be obtained by the agitation of water flow and biogas flow in UASB reactor.

2.3.3 The changes of COD, CH_4 production and pH in startup

COD and pH of influent and effluent needed to be determined per day. However, the determinations of sulfide and the physical properties of anaerobic granular sludge were none scheduled.

2.3.3The preparation of microscope sample

There were two ways to prepare the microscope samples. One was that one drop sludge-water mixture diluted with distilled water in the ratio of 1：10 was covered by cover glass. This step must be careful. The mixture was touched by one side of cover glass firstly and then the entire was lower lightly lest produce bubbles which affected observation. The other was that bubbles were run off by gradually light compression-extrusion of cover glass before covering. The observation was needed in the moment of preparation.

2.3.4 The observation of organic acid in startup

The organic acids needed to be determined by Gas Chromatographic Instrument in the startup of UASB reactor to study the degradation of tannery effluent.

Gas chromatographic instrument adopt Agilent 6890. Auto Injection Gas Chromatographic Instrument was used with SUPELCOWAX10 analytical column (30m×0.53mm, 0.5μm) and flame ionization detector. The rate of gas through the analytical column was 3.5mL/min.The initial temperature of SUPELCOWAX10 analytical column was at 105℃ for 2min,and finally it was elevated to 180℃ for 7min with the rate of 10℃/min, retention for 5min.

1μL of each kind of organic acid were added to a 5mL volumetric flask which was diluted the final volume with ultrapure water, and was measured by Gas chromatographic instrument adopt.

3 Results and discussion

3.1 The changes of COD, methane production and pH in startup

The UASB reactor used anaerobic sludge as seed at medium temperature was started successfully in 50days under appropriate condition. Fig. 2 indicates that when the COD of influent came to about 10000mg/l, its removal rate is maximal, but if the COD of influent was improved continuously, the COD of effluent would be prominently increased, its removal rate is significantly decreased. However fig.3 demonstrates that with the improving of the COD of influent, methane production is gradually increased. So methane production would be stable after UASB reactor is started successfully. But temperature greatly affects methane production. Fig. 4 implicates the stability of system is not affected greatly with little changes of pH of influent because of the obvious buffer action of microorganism.

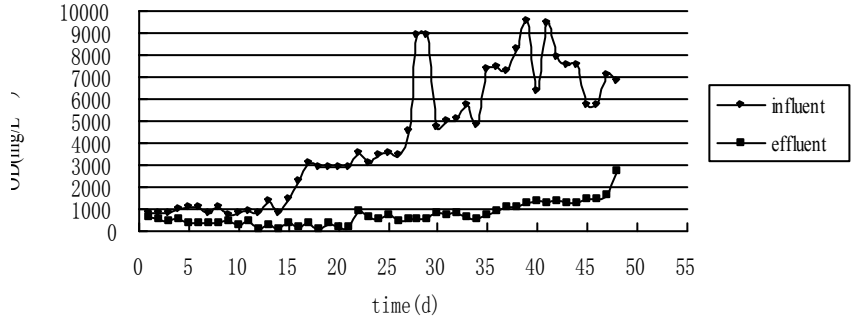

Fig.2 changes of COD of influent and effluent

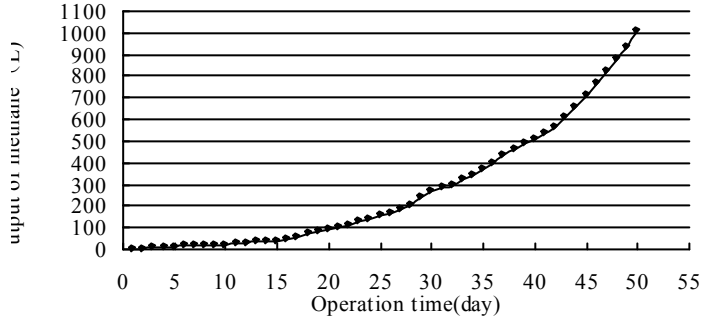

Fig.3 methane production

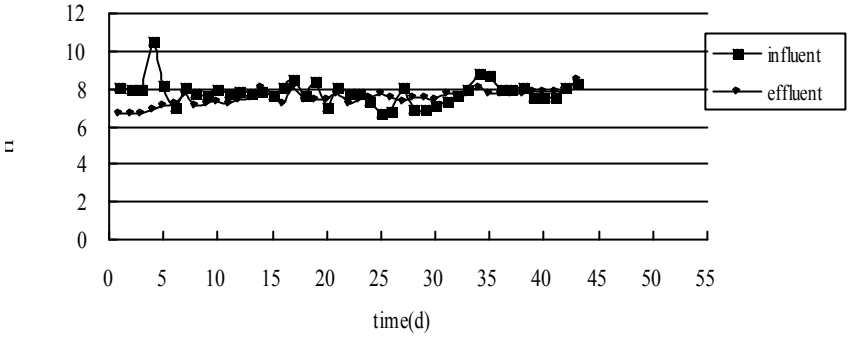

Fig.4 changes of pH of influent and effluent

3.2 The morphology of anaerobic granular sludge and microorganism in UASB reactor

What were needed to observed by Multimedia microscope during entire starting were the shapes and sizes of anaerobic granular, the kinds of microorganism and the distributions of flora. The results are as follows:

Fig.5 shows that anaerobic sludge which would be about to become granular still uses activated sludge to enlarge its size, and its boundaries is unconsolidated. But the black anaerobic granular sludge's boundaries is clear, its shape is regular ellipse and its diameter is beyond 1.55mm mostly (generally 0.2~3.0mm, maximally 4mm).

Fig.6 displays that winding filamentous adhered to the seed sludge to become anaerobic zoogloea which is about to formatting big granular sludge when its concentration was high enough.

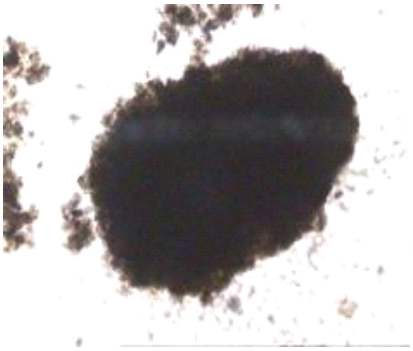

Fig.5 the anaerobic granular sludge（400x ）

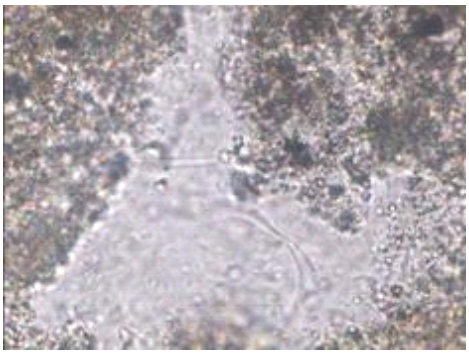

Fig.6 the shape of filamentous（1000x）

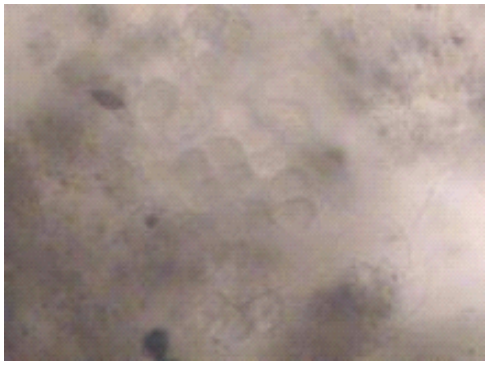

Fig.7 the classical methanosarcina（4000x）

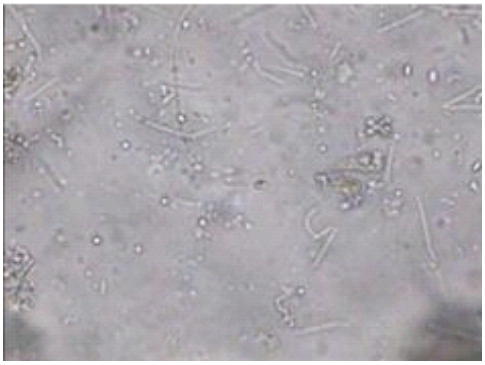

Fig.8 the main kinds of microorganism（1000x）

What can be obtained in fig.7 is that classical methanosarcina and methane bacteria can be observed under 4000 magnifications times and it is worth paying attention to a population composed of aggregated methanosarcina.

There is abundant anaerobic microorganism such as the number of cocci, short Streptococcus composed of a couple of cocci and bacillus by the observation of fig.8.

3.3The distribution of organic acids in UASB reactor

The quality of organic acid which is basically decreased with the increase of height from the bottom to the top of UASB , presenting gradient variation, which means that organic acids produced by acidate bacteria degradation organic substances are used gradually by methanogen to produce methane through the entire sludge bed. During degradation, organic acids including acetic ccid, propionic acid, isobutyric acid, butyric acid and caproic acid are gradually decreased, and caproic acid can not be determined finally which demonstrates that the degradation is over basically. But there is an exception that the quality of isovaleric acid in effluent is as same as the quality in the sixth sampling place. The reason is that isovaleric acid might be produced by the other acids such as caproic acid degraded completely.

The experimental results indicates that the macromolecule organic compounds in tannery effluent are degraded into the small molecular organic acid by the acidate bacteria at the bottom of UASB reactor, among which acetic acid is the most，and then propionic acid、isobutyric acid and isovaleric acid, while butyric acid, valeric acid and caproic acid are very little. And then the small molecular organic acids are degraded into CH_4 and CO_2 by the methanogenus finally.

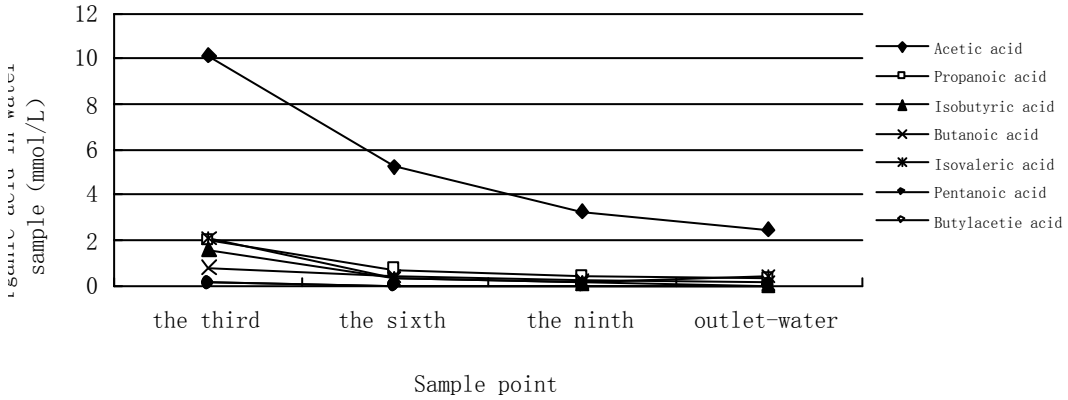

Fig.9 organic acid in each of height of USAB reactor（COD=10033.6mg/L）

4 Conclusions

The conclusions are as follows: (1) UASB reactor can be started in 50days successfully by which tannery effluent is treated. (2)The anaerobic granular sludge is cultivated finally. (3) The maximal removal rate of COD is 91.6%, and 85% is stable one.(4) The macromolecule organic compounds are degraded into the small molecular organic acid by the acidate bacteria firstly ,among which acetic acid is the most and then the small molecular organic acids are degraded into CH_4 and CO_2 by the methanogenus, realizing the transformation from waste to resource.

References

[1] Hating Wu; Ming Chen; Jianming Jing. Problems and counter measure in tannery wastewater treatment in China.China Leather. 2005, 34(5): 35-36.

[2] Tusuo Geng. The new process of tannery wastewater treatment. Guizhou Environmental Protection Science and Technology, 2004, 10(1): 21-23.

[3] Xiudong Ma. Treatment of tannery wastewater with biological oxidation process [J]. Shanxi Chemical Industry, 2003, 23(1): 51-52.

[4] Andre Bachman; Virbinia L Beard; Perry L Mc-Carty. Performance characteristics of the anaerobic baffled reactor. Water Res, 1985.

[5] Xiaoxing Li; CongZheng Yu; Xingyuan Ma. Progress of study on treatment of tannery effluent from. China Leather, 2003, 32(19): 31-36.

[6] William P Barber; David C Stuckey. Startup strategies for anaerobic baffled reactors treating synthetic sucrose feed. Proc 8th International Conf on Anaerobic Digestion, 1997.

[7] Grobicki A; Stuckey D C. Performance of the anaerobic baffled reactor under steady-state and shock loading conditions. Biotech. and Bioeng., 1991: 344-355.

[8] Nachaiyasit S; Stuckey D C. Effect of low temperatures on the performance of an anaerobic baffled reactor(ABR). Journal Chem. Tech. Biotech., 1997, 69: 276-284.

[9] Zhongbai Gao. Operation and management of tannery wastewater anaerobic treatment system. The 6th Asian International Conference of Leather Science and Technology. October 19-21, 2004, Himji, Japan.

[10] Xingyuan Ma; CongZheng Yu; Xiaoxing Li. Some important factors influencing tannery wastewater treatment with UASB system. Technology of Water Treatment, 2005, 31(7): 66-68.

[11] Xingyuan Ma; CongZheng Yu; Xiaoxing Li. Study on the toxicity of sodium chloride and chrome tanning agent on anaerobic microbe. China Leather, 2005, 34(5):38- 41.