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Analysis on the operating characteristics of improved UASB to treat the thermal dehydration wastewater of sludge

Li Huili¹, Pei Yuanmei¹ and Long Zhiqiang^{1,2}

¹School of Civil Engineering, Lanzhou University of Technology, Lanzhou730050 ²Kev Lab of Urban Environment and Health, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021

379063403@qq.com; 3422177453@qq.com; 969370482@qq.com.

Abstract In order to investigate COD removal efficiency and production capacity of energy, the anaerobic sludge bed reactor with high diameter ratio of 10 was used to treat the thermal dehydration wastewater (TDW) of sludge. The experiment was divided into 7 stage, the results showed that on the condition of the acclimated sludge, the reactor would be stable after 25 days; then the maximum removal rate of COD was up to 68%, the maximum amount of Nissan CH₄ was 575.53 ml/L, and methane production ratio was 104.05ml/ (g COD d). The concentration of ammonia nitrogen (NH4+-N) was the main factor affected the stable operation of the reactor. When the concentration of NH4+-N reached 1.5g/L, the inhibition phenomenon to methanogenic bacteria appeared. And when it was up to 2.4g/L, the methanogenic bacteria were seriously inhibited. The optimal sludge loading of the experiment was $0.10 \sim 0.24$ kg COD/ (kg Sludge d), and the optimal volume load was $5 \sim 13 \text{ kg COD}/(\text{m}^3 \text{ d})$.

1. Introduction

With the improvement of emission standards and industrial development level in China, the Sewage quantity of the urban sewage treatment plant has increased greatly, and the byproduct- the surplus sludge, has also increased. Main components in excess sludge are persistent organic pollutants including protein, polysaccharide, fat and humic substances, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and two (PCDD/Fs), and so on[1-2]. In 2015, the sludge production in Chinese urban sewage is about 35 million tons. Therefore, sludge reduction, recycling and harmless are particularly important for protecting environment, sludge dewatering is an important technical method to achieve those objectives. The technology of sludge hydrothermal carbonization treatment may effectively reduce the sludge, at the same time, the residual sludge can be produced used to activated carbon [3-4]. The process of sludge hydrothermal carbonization treatment will produce a large number of sludge thermal dehydration liquid, which is the production of the processes of a hydrothermal carbonization treatment $(130 \sim 250^{\circ}\text{C})$ and high pressure mechanical filter dehydration. The composition of the TDW is complex, containing various kinds of organic matters, they are high in concentration, especially high nitrogen. Therefore, it is difficult to degrade.

At present, there are few researches on the treatment of the TDW of the sludge (TDWS) in China, and the mainly methods was advanced oxidation, dilution treatment and anaerobic SBR. According to the research of Wang D et al. [5], they used the methods of Fenton and UV-Fenton to treat the TDWS, only part of COD was being removal. The experimental conclusion showed the removal rate of COD were 40%, 85%, respectively, but the removal rate of NH4+-N and total nitrogen were very low. In the

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experiment of Zhu W et al.[6], the mixed liquid of the simulated domestic sewage and the TDW was been deal with the SBR reactor. The experiment found that when the ratio of the TDW was 0.05% of the simulated domestic sewage, the operation of SBR system would not be impact, and the indexes of the effluent could achieve the A level of GB18918-2002 (China). But, the huge dilution ratio is less operational in practical applications. According to the results of treating the TDW with the sequencing batch anaerobic digestion (ASBR)[7-8], the removal rate of the COD, NH4+-N, chroma and other indicators were more than 90%. This means the anaerobic treatment method was effective on sludge thermal dehydration. However, the process of treating 200mL wastewater was a period of 26 days. The hydraulic load is too low for practical application.

Summarizing of the above research results, in this experience, the TDWS was treated with the anaerobic sludge bed reactor (UASB) on the condition of the temperature of (52.5 ± 2.5) °C, for studying the removal capacity of various pollutants, the influence factors of the reactor operation and production prospects. The result would be provided a reference for the treatment method of theTDW.

2. Experimental equipment and analytical method

2.1. The reactor of experiment

An improved upflow anaerobic sludge blanket reactor (UASB) was used in this study, of which the ratio of height to diameter was 10. This reactor was similar to the expanded granular sludge bed (EGSB) without reflow, in order to improve the rising velocity, promote the formation of granular sludge, and reduce sludge loss in reactor.

The basic dimensions of the reactor were shown in Table 1; the structure of the reactor was shown in figure 1.

	Reaction	Three-phase separation	Setting	The
	area	area	area	reactor
high(dm)	7	0.77	0.73	
internal diameter (dm)	0.7	0.5	1.5	
volume(L)	2.69	0.15	1.29	5





2.2 Experimental wastewater and inoculated sludge

In this experiment, the TDWS was taken from a wastewater treatment plant in Xiamen, their wastewater was from the food industry park wastewater nearby.

As a result, the characteristics of the TDWS had high concentration of organic matter, complex and biodegradable components. The basic parameters of waste water quality were shown in table 2:

Table 2. Original quality of wastewater without diluting

COD	BOD_5	pН	alkalinity	Nitrite nitrogen

(mg/L)	(mg/L)		(mgCaCO ₃ /L)	(mg/L)
50107.5	27175	7.4	8658.65	0.66
NH4+-N (mg/L)	Nitrate nitrogen	total nitrogen	phosphate	total phosphorus
	(mg/L)	(mg/L)	(mg/L)	(mg/L)
3011.17	176.1	3192.7	115.56	152.26

2.3. Experiment analysis project and method

The main test items were monitored by standard methods, such as: COD, BOD₅, pH, alkalinity, gas production and gas composition, acidity and acid composition, ORP, SS, and VSS, and so on. Testing equipment were such as the fast COD measuring instrument of the Lian Hua 5B-3C, a type BOD apparatus of the LH-BOD601, the gas chromatograph of Zhejiang Fuli 9790-II, the wet gas flowmeter, and the pH meter of the Ohaus ST3100, respectively. The experimental analysis methods of other test items was mainly from "water and wastewater monitoring and analysis methods", China Environmental Science Press, 2002 edition.

2.4. Operating conditions

The temperature of the reactor was controlled at (52.5 ± 2.5) °C, making the normal operation of UASB in the high temperature range. The pH value was greater than 5 (there was the alkalinity in the TDWS, which can avoid the low pH to the impact of methanogenic activity). To form granular sludge and maintain the high sludge concentration in the reactor, the rising velocity of the anaerobic reactor was 0.5m/h~0.655m/h. Hydraulic retention time (HRT) was 69.5h. The concentrations of the influent COD and other pollutants were controlled by dilution method. The experiment divided into 7 stages. The influent COD concentration was 5000mg/L, 7000mg/L, 1000mg/L, 12000mg/L, 15000mg/L, 20000mg/L, and 23000mg/L, respectively.

3. Experimental results and analysis

3.1. Reactor operation analysis

3.1.1. The removal efficiency of COD

As the acclimated pilot test sludge was inoculated with sludge on the start-up of reactor, the influent COD concentration was 5000mg/L. From figure 2, during 1~15th day, the COD concentration of effluent increased gradually, and the COD removal rate decreased continuously. On 16th day, the COD removal rate was only 11.78%, which indicated the microbial activity decreased in the reactor because the living environment changed. The COD removal rate increased gradually from the seventeenth day. On 25th day, under the condition of the same influent COD concentration, the COD removal rate reached 49.69%, which indicated that the microorganism gradually adapted to the environment and the activity was recovered.

During 25~40th days, the removal rate of COD increased slightly to 55%. From 41th day, when the influent COD increased to 7000mg/L, the treatment efficiency of the reactor began to increase slowly. On 66th day, the effluent COD was 2302mg/L, the removal rate was up to 66%, the volume load was $5.22 \text{kgCOD}/(\text{m}^3.\text{d})$, and the sludge load was 0.1 kgCOD/ (kg sludge d), respectively. When the influent COD increased to 12000mg/L, the removal rate of COD shown a large fluctuation, which had a great impact on microorganisms. At this time, the volume load was 13.29kgCOD/ (m3.d), the sludge load was 0.24 kg COD/ (kg sludge d), and the removal rate of COD was up to 65%. According to the 107 day's operation, with the increase of influent COD concentration (from 5000~12000mg/L), the removal rate of COD showed an upward trend, reached more than 65% after the stable operation.

The removal rate of COD was lower than that of similar wastewater by using batch anaerobic treatment method (ASBR) on the temperature of 35° C[7]. The reason may lie on the wastewater quality and HRT. In the experiment of ASBR, The TDW's quality parameters: COD concentration was 8650 mg/L, pH was 7, chroma was 96 and NH₃-N was 125 mg/L, the COD removal rate was

more than 89%. The acid dehydration wastewater's COD concentration was 28225 mg/L, pH was 5.1, chroma was 192, and NH₃-N was 286mg/L, the COD removal rate was more than 97.5%. But the HRT of ASBR was 26 days, which is much larger than that of the present experiment (69.5h).

To improve the removal rate of pollutants, a batch of acclimated anaerobic sludge was added in to the reactor on 108th day. The COD removal rate dropped sharply to 12%, which indicated that the ecological environment of the reactor suffered a serious impact. After a week, the COD removal rate was recovered to 50%. From 117th day, when the influent COD concentration increased to around 15000mg/L, the COD removal rate of this stage was 59~68%. When the influent COD concentration was 18000mg/L~23000mg/L, the sludge load was 0.43kgCOD/ (kg sludge d), and the COD removal rate gradual declined from 58% to 35%. The results of adding sludge showed that COD removal efficiency of the reactor was about 65%, and the influent COD should be controlled below 15000mg/L.



3.1.2. The concentration of Volatile fatty acid (VFA)

In anaerobic fermentation process, variety of organic acids will be produced. The state of the main bacteria in the anaerobic fermentation process, the operation efficiency and the acidification trend of the reactor can be obtained by monitoring the changes of organic acids in the reactor.

From Figure 3, the Graphical of influent VFA concentration was similar with the change of the effluent VFA concentration. At the beginning, volatile acid accumulation and the removal rate of VFA was 0. This meant methanogens did not use the organic acids, the activity was very low. During 17 ~ 30th days, the COD removal rate increased from 12% to 51.5%, the VFA removal rate was unchanged. The results showed bacteria producing acid recovered gradually after a period of 17 days of adaptation, and the adaptation period of methanogens was more than 30 days. During 31~66th days, the removal rate of organic acids was about 30%, and the COD removal rate increased from 56% to 66%. During 67~107th days, the removal rate of organic acids increased gradually, which indicated the activity of methanogenic bacteria was enhanced, and the COD removal rate was above 60%. On 97th day, the removal rate of VFA reached to 98.19%, and the corresponding COD removal rate was about 65.59%, which showed that the COD removal efficiency was directly related to the VFA degradation. When the influent COD concentration was 12000 mg/L, the removal rate of VFA reached more than 85%.

After the addition of new mud on 107th day, the VFA concentration of effluent increased sharply, indicated methanogenic bacteria were been a serious impact. After the adaptation period of 10 days, the removal rate of VFA reached to 98.5%, and the removal rate of COD increased to more than 55%.

When the VFA concentration reached 9000mgHAC/L (corresponding to 20000mg/L COD of the influent), the VFA removal rate was fluctuation (max 81%, min 65%), it meant that the pollutants concentration of the influent caused effect on methanogenic activity. However, the COD removal rate was still above 51%, which showed the concentration of pollutants had no significant effect on the bacteria producing acid. After 20 days, the VFA and COD removal rate were all increased. When the VFA concentration of the influent reached 12000mgHAC/L (corresponding to 23000mg/L COD of the

influent), the VFA removal rate and COD removal rate continued to decline, indicating the pollutant concentration of the influent were causing serious impact on the two main bacteria in the anaerobic reactor. Increasing the influent COD concentration to 24000mg/L, the removal rate of VFA continue to decline. On the 186th day, the VFA concentration of the effluent reached 6243mgHAC/L, the removal rate of VFA and the removal rate of COD were only 48% and 41.89%. At this time, a large number of VFA has been accumulated in the reactor, and the removal rate of COD was decreased and the gas production efficiency was reduced. This state indicated that acidification had occurred in the reactor. Therefore, the influent VFA concentration should be controlled lower than 5000 mgHAC/L of, which was helpful to ensure the stable operation of the reactor.



3.1.3. Gas production and CH₄ production

The output of CH_4 is an important factor to measure the feasibility and efficiency of UASB reactor to treat the TDWS. From figure 4, After 23 days of experiment, the reactor had a relatively stable gas production rate. On 23th day, the gas production rate was 115.2mL/L (the ratio of the volume of gas produced to the effective volume of the reactor in the same day), and the methane production was 14.58 ml/L. With the increase of influent COD concentration, the gas production increased. When the influent COD concentration was 10000mg/L, the daily output of CH_4 and the methane production ratio increased continuously. On 87th days, the daily output of CH_4 reached the maximum of 575.53 mL/L, the methane production ratio was 104.05ml/ (g COD.d). On 88th day, when the influent COD increased to 12000mg/L, the high COD concentration impacted on microorganisms, gas production began to decline. The methane production decreased from 548.58 mL/L to 342.76mL/L, and the methane production rate decreased from 95.32ml/ (g COD.d) to 60.75ml/ (g COD.d). It showed that the activity of methanogenic bacteria decreased, and 12000mg/L COD was the controlling concentration for maintaining a good operation of the reactor. After adding the new mud, gas production was not measured due to equipment commissioning.

During 147~161th days, when the influent concentration of COD was 20000~23000 mg/L, the average daily production of CH₄ was about 550ml/L. However, the gas production efficiency continued to decline, and the methane production rate decreased from 60.61 ml/ (g COD.d) to about 41.22 ml/ (g COD.d). The average methane production ratio was 58.95ml/ (g COD.d). The results showed that the activity of methanogenic bacteria decreased obviously.



3.1.4. The change of ammonia nitrogen (NH_4^+-N) concentration

 NH_4^+ -N is the one of the nutritional sources of anaerobic microorganisms, suitable concentration of NH_4^+ -N can improve the activity of methanogenic; in addition, NH_4^+ -N can enhance the alkalinity of the reaction system and increase the ratio of VFAs to ALK, thereby improving the buffer capacity of the system for volatile fatty acids. On the other hand, with the increase of NH_4^+ -N concentration, the concentration of free ammonia in the system will increase, which will strongly inhibition the production of methane[9].

From figure 5, NH_4^+ -N was monitored from the 40th day. With the increase of influent COD concentration, the influent NH4+-N concentration increased from 684.5mg/L to 2826.5mg/L. As can be seen from figure 5, the overall trend of NH4+-N concentration of the effluent was increased with the influent. However, the removal rate of NH4+-N, the removal rate of COD and the influent and effluent concentration of NH4+-N were not significant relevance. This showed that the change of NH4+-N concentration was not a single factor.

When COD concentration of the influent was 5000~7000 mg/L and the average concentration of the influent NH4+-N was 700 mg/L, the average concentration of the effluent NH4+-N was about 536 mg/L, and the average NH4+-N removal rate was about 22.7%. Due to the demand of anaerobic process for nitrogen, some NH4+-N was consumed. At this time, from the removal rate of NH4+-N, indicated that the dominant bacteria group has not been formed to converse ammonia effectively. When COD concentration of the influent was 10000~12000 mg/L and the average concentration of the influent NH4+-N was 1100 mg/L, the average concentration of the effluent NH4+-N was about 611mg/L, and the average NH4+-N removal rate was about 40.7%. Meanwhile, the removal rate of COD was higher (the average removal rate was 63.4%), and the methane ratio of producing gas was about 50%. It indicated that the concentration of NH4+-N had no inhibition action on the microorganisms in the reactor, and the bacteria group conversing ammonia was formed in the reactor. When COD concentration of the influent was 15000 mg/L and the average concentration of the influent NH4+-N was 1600 mg/L, the average concentration of the effluent NH4+-N was about 1150mg/L, and the average NH4+-N removal rate and the average COD removal rate dropped down to 29% and 60%, respectively. Compared the concentration and removal rate of VFA, the NH4+-N concentration became affected to methanogens; however, NH4+-N had no significant inhibitory action to methanogenesis process. When COD concentration of the influent was 20000 ~ 23000 mg/L and the average concentration of the influent NH4+-N was 2400 mg/L, the average concentration of the effluent NH4+-N was about 1800mg/L, and the average NH4+-N removal rate and the average COD removal rate gradually decreased to 15% and 45%, respectively. In this stage, the VFA in the reactor was greatly accumulated, and the gas daily output decreased from 7.4L to 4.8L. Indicated that methanogens had were seriously affected by the concentration of NH4+-N.

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Figure 5. The removal rate of the NH_4^+ -N and COD, the NH_4^+ -N concentration of influent and effluent

In this experiment, the results of NH4+-N restraining methanogenic bacteria was different from that of He SJ et al. [10] and Borja R et al.[11], Sossa K et al. [12], Gerardi M H et al.[13]. The inhibition concentration of NH4+-N in the experiment was 1.5g/L, which was much larger than that of other experiments (0.8g/L). Analyzing the reasons, an acclimated inoculated sludge was the key, of which microbial adapted to the toxicity of ammonia. The significant inhibitory concentration of NH4+-N was 2.4g/L, which was less than that of He SJ et al. (4g/L)[10], indicated that under the high pH value, the high concentration of NH4+-N was greater toxicity to the methanogens than others.

3.2. The affecting factors of the reactor operation

3.2.1. Alkalinity and pH value

Alkalinity is an important index to monitor the running state of the reactor, and to some extent, it can also reflect the accumulation of organic acids in the reactor. Usually, on the condition of the good operation and non-acidification in the internal reactor, the alkalinity change of influent and effluent wastewater remained the same trend.

From figure 6, when the influent COD concentration was 5000~15000mg/L, the change trend of the alkalinity was the same and the alkalinity of effluent had been greater than influent. It indicated that NH4+-N coming from the decomposition of organic nitrogen may lead to the increase of alkalinity in anaerobic system. When the influent COD concentration was greater than 20000mg/L, the effluent alkalinity was close to the influent alkalinity, which indicated that there were a lot of substances consumed alkalinity.

Comparing with the VFA concentration in the same period, it was found that, VFA in this stage was accumulated in a large amount. This meant that the methanogenic bacteria were not able to metabolize it in time; meanwhile, the alkalinity of the reactor was consumed by organic acids so that the alkalinity decreased. The time period was corresponded with the sudden decline of the COD removal rate due to acidification.



Figure 6. The relationship of influent/effluent alkalinity and COD removal rate in UASB

The optimum growth pH range of the bacteria producing acid and methanogens are 5.00-6.50 and 6.60-7.50 [14]. It can be seen that the pH value can intuitively reflect the survival status of two main bacteria in the reactor. From the figure 7, When the influent COD concentration less than 7000 mg/L, the pH value was higher and the wastewater was not acidified because of the high dilution multiple. At this time, the organic acids of anaerobic digestion in the reactor decreased pH value of effluent.

When the influent COD concentration was 10000~23000mg/L, the partly influent was acidified and the influent pH decreased because of the dilution ratio reduced. After the anaerobic digestion process, the decomposition of nitrogen content and the production of methane would increase the alkalinity, leading to the effluent pH value higher than that of influent. In the whole operation period, the pH value in the reactor was maintained between 7.0~8.0.

Using the sequencing batch anaerobic reactor to treat the TDWS in the research of Dong H et al.[7], the low concentration of ammonia (286mg/L) did not affect the operation of reactors, when the influent pH value was 6.7~7.2, the effluent pH value was about 7. Compared with the experimental results, the pH value of the effluent in this study was about 7.7 after the stable operation of the reactor. Under the high pH conditions, the toxic effects of NH4+-N would increase.



3.2.2. ORP

In the initial stage of the reactor, the value of Oxidation-Reduction Potential in the reactor was relatively volatile. Frome the figure 8, After seventy-first days, the ORP showed a steady downward trend. After stable operation, the ORP value was always less than -320 mV, which could ensure the normal metabolism of methanogens.



Table.3 Reactor loading and COD removal rate				
operation time	Influent COD	Sludge load	volume load	The COD removal
d	mg/L	gCOD/(gVSS d)	$kgCOD/(m^3 d)$	after stable %
28~106	5000~10000	0.1	5.22	51~68
108~142	12000~15000	0.24	13.29	50~68
143~186	20000~23000	0.42	15.08	41~61
187~189	23000	0.35	24.68	35~41

3.2.3. Sludge load and volume load

According to the sludge quality in each stage of the experiment, the reactor load in different operation stages was calculated. As shown in the table3, when the sludge load was less than 0.24 g COD/ (g VSS d) and the volume load was less than 13.29 kg COD/ (m^3 d), the reactor could be stable operation. When the sludge load reached 0.42 g COD/ (g VSS d), the treatment efficiency of the reactor decreased continuously. Even if the sludge load was reduced in the later stage, the operation state of the reactor could not be recovered, which showed this load exceeded the load requirement of the stable reactor. In contrast to similar experiments, the sludge organic load was 0.9gCOD/ (g VSS d) ~3.0gCOD/ (g VSS d) in the experiment of Ohtsuki T et al. [15] to treat acidified sucrose wastewater; The maximum load of mature granular sludge was 3.7g COD/ (g VSS d) at the temperature of 55 °C, which was studied by Syutsubo et al.[16]. In this study, the capacity of the sludge was lower than that of the similar studies, which may be related to the high concentration of NH4+-N in wastewater and the complex and difficult degradation of water quality.

Compared with the volumetric loading, such as the research of Zhang ZJ et al.[17], when the corn alcohol wastewater was deal with the UASB reactor and anaerobic biofilter under the condition of $55(\pm 2)$ °C, the volume load of the reactor was 3 kg COD/(m³ d)~20 kg COD/(m³ d); Under the same conditions to deal with, the actual volume load was more than 10 kg COD/ (m³ d) in the process of treating the brewery wastewater[18]. The results of previous experiments showed that the volume load used in this study was appropriate.

4. Conclusions

The TDWS was treated by the UASB reactor with the high ratio of height to diameter. After 7 operation stages, the following conclusions were obtained:

1. On the condition of the temperature of $52.5(\pm 2.5)^{\circ}$ C, the influent COD concentration of the TDW should be controlled below 15000mg/L for the stable operation of UASB. After the stable operation, the COD removal rate could reach 65%, the daily output of CH₄ was more than 550 ml/L, and the methane production ratio was up to 100 ml/ (g COD d).

2. Because of the high pH value of the TDW, the ammonia toxicity to methanogens was increased. Therefore, in order to ensure the stable operation and the efficiency of the reactor should control the influent NH4+-N concentration, making it less than 1000 mg/L. When the concentration of influent NH4+-N reached 1500 mg/L, the inhibition of anaerobic digestion began to appear.

3. The optimal sludge loading of the UASB reactor was 0.10~0.24 kg COD/ (kg sludge d), and the optimal volume load was $5\sim13$ kg COD/ (m³ d) for the treatment of the TDWS.

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