

Enhancing efficiency of biogas collection from industrial organic sludge

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ABSTRACT:

Industrial organic sludge is the concern of society and government levels since this kind of sludge will lead to the pollution of groundwater, surface water, air and the invasion of the food chain, increasing the disease and causing the bad effects on health without collecting and treating thoroughly. For high organic pollutants in sludge, appropriate treatment technology to recover biogas, supply energy for demand of production and living, is one of the current and priority solutions.

Research contents in this study were application of pretreatment by hydrolysis process and anaerobic sequencing batch reactor (ASBR) to enhance biogas recovery. The obtained experimental results by

hydrolysis through the alkalization process demonstrated that COD removal efficiency reached 62%, collected methane gas increased 4.9 times (360ml/L) compared to confronting sample (directly digestion, without hydrolyzed phase), at pH of 12, for 12 hours of hydrolysis time and after 20 digestion days at room temperature (30 - 35°C). Research results on anaerobic digestion reactor at organic loading rate of 1,6 kg VS/m³.day showed that COD and VS removal efficiencies can reach 61.59 – 62.24, 52.33 – 54.26%, respectively for 20 days. The methane yield obtained 0.343 – 0.402 m³CH₄/kgVS (corresponding to 0.523 – 0.628 m³CH₄/kg sludge).

Keywords: *Anaerobic digestion reactor; Hydrolysis process; Biogas recovery enhancement; Methane yield.*

1. INTRODUCTION

Currently, the sludge is one of the waste sources may cause environmental pollution and getting increasingly. According to Department of Natural Resources and Environment Ho Chi Minh City (2007), the average daily released sludge was approximately 3,000 tons including 2,000 tons from the dredging of canals and drainage network; 250 tons of sludge from

industrial zones; over 500 tons of sludge from septic tank...

However, sludge treatment technologies have not researched and applied appropriately yet in order to recover waste, increase economic efficiency, reduce loading for current landfills and incinerations. In last decades, there were several of methods to enhance sludge anaerobic

degradability by using pretreatment processes. The treatment may include mechanical, physical, biological, and chemical methods.. Financial feasibility in improving anaerobic digestion methods has been attention due to their application at industrial scale. Liu et al. (2008) carried out sludge hydrolysis by some different methods such as thermo-alkaline, thermo-acid, ultrasonic-alkaline, and ultrasonic-acid. The comparison results showed that alkaline treatment was more effect than other methods. Chulhwan Park et al. (2005) used either thermochemical or biological hydrolysis for waste activated sludge treatment. The research result determined thermochemical hydrolysis was better than biological hydrolysis in a bench-scale operation with the COD removal efficiency, volatile solid (VS) removal efficiency, methane yield and methane biogas content were 88.9%, 77.5%, $0.52\text{m}^3/\text{kg}$ VS and 79.5%, respectively.

Thermo-chemical pretreatment can be employed with different temperature ranges such as ambient temperature, moderate range ($60\text{-}100^\circ\text{C}$), medium temperature range ($100\text{-}175^\circ\text{C}$) or in high temperature range ($175\text{-}225^\circ\text{C}$) (Lin et al., 1997; Hiraoka, 1984; Li and Noike, 1992; Haug, 1983). Besides, it is necessary to add appropriate amounts of alkali agent with the purpose of keeping pH in the neutral region (Mukherjee and Levine, 1992).

In general, the pretreatment processes affected significantly to sludge treatment results. Therefore, in order to increase the efficiency of anaerobic digestion of industrial sludge and enhance the biogas production, it is necessary to carry out more researches to select appropriate conditions for industrial sludge treatment.

2. BIOREACTOR CONFIGURATION AND EXPERIMENTAL METHODS

2.1. Sludge Hydrolysis

Seed sludge and chemical

The seed sludge was taken from the concentrated wastewater treatment plant of Vinh Loc Industrial zone and the primary characteristic was as follows tCOD of $23,784 \pm 2,527$ mg/l; TS of $20,235 \pm 224$ mg/l; VSS of $8,744 \pm 351$ mg/l, TOC of 2.83 ± 0.03 ; pH of 6.42 ± 0.02 .

Reactor operation

The experiments were carried out at room temperature of $30 - 34^\circ\text{C}$ and separated into three parts including alkaline hydrolyse, thermal hydrolyse and anaerobic digestion. In which, alkaline hydrolyse using NaOH was conducted at adjusted pH of 7, 8, 9, 10, 11 and 12 with controled moisture of 90%. While thermal hydrolyse was carried out at initial pH of 12. A wide range of temperatures has been studied at 55, 70, 100, 125, 150 and 170°C . After reaction times of 30 minutes, the mixture was shaken and sampled then centrifuged at 4000 rpm/min for 20 minutes before analyzing selected parameters.

Alkaline hydrolysis study was conducted in a batch reactor of 1 liter, which placed on a shaker to stir the mixture of sludge and water. While, thermal hydrolysis study was carried out on the special tube that resistant to heat as well as pressure, besides reaction tube was covered with the lid to prevent evaporation. The basic parameters such as pH, alkalinity, sCOD, TS, VS, VFA were periodical analyzed after 2 hours.

The study of anaerobic digestion was conducted with alkaline hydrolysed sludge with and without adding Aqua Clean/ACF32.

Basically, AquaClean/ACF 32 is a community of microorganisms are cultured in liquid form, are specially selected for use in all industrial wastewater treatment systems. AquaClean/ACF 32 contains a mixture of 12 microorganisms were selected with density $387/450$ million bacteria/mL. Therefore, with addition of probiotics, the system was supported groups of high activity microorganisms, digested quickly and efficiently compounds of cellulose; starch;

proteins, lipids... cause to increase the COD removal efficiency and destroy pathogenic microorganisms. Aqua Clean/ACF32 enhances the biological oxidation of slow to degrade organic compounds significantly improving overall system performance and stability.

VS loading rate was changed from 1,6gVS/m³.day to 8gVS/m³/day, and a hydraulic retention time (HRT) varying 30, 20, 10, 6 days. Added AquaClean/ACF32 concentration was 10 ppm.

At each loading rate, sampling and analyzing main parameters included sCOD, pH, alkalinity, VFA, VS. Particular, methane was measured daily by gas accounted clock.

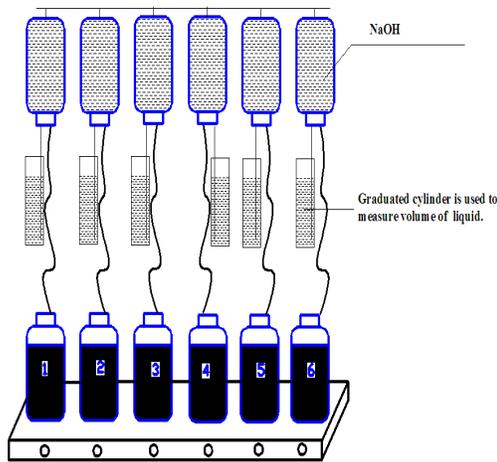


Fig. 1: Anaerobic sequencing batch reactor (ASBR)

2.2. Analytical method

Mixture samples were taken every day. pH, alkalinity, COD, VS, TS, VFA were analyzed according to standard method for the examination of water and wastewater (APHA 2005).

3. RESULTS AND DISCUSSION

3.1. Chemical pretreatment by using NaOH

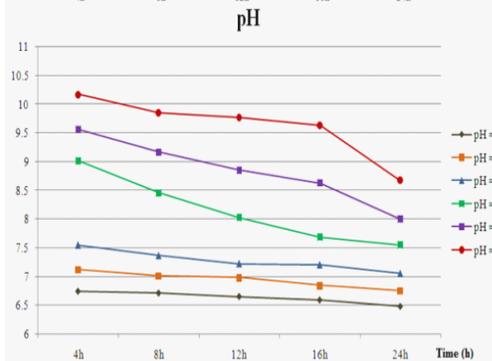
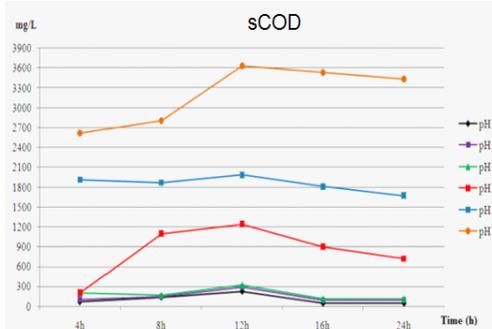
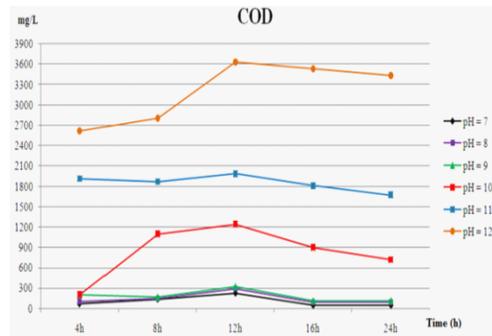


Fig. 2: The variation of sCOD and pH at different pH

pH is an important parameter, affecting the sludge treatment efficiency. The higher the pH is, the higher sludge hydrolysis ability increases, leading to increase in sCOD. At pH of 7, 8, 9, sCOD was very low, fluctuated from 50 to 300 mg/L after 24 hours operation. sCOD increased slightly as pH stepped up from 7 to 9. When pH changed from 10 to 12, compared to neutral pH (pH = 7), sCOD increased dramatically. As a results, sCOD was 3 to 4 times higher at pH of

10; 5 to 7 times higher at pH of 11 and 9 to 12 times higher at pH of 12. The final sCOD achieved 12000 mg/l, 20000 mg/l and 36000 mg/l, respectively.

sCOD was not only affected by pH but also depended on hydrolysis time. At the first 8 to 12 hours, sCOD increased rapidly with maximum COD concentration of 3600 mg/l for alkaline hydrolysis at pH of 12, also in the next 12 hours, sCOD only reduced to 300 mg /L. Obviously, the alkaline hydrolysis can disrupt flocs and cells, release inner organic matters and accelerate sludge hydrolysis (Novelli et al., 1995; Lin et al., 1997)

To sum up, pretreatment period gained optimum efficiency at pH of 10 to pH of 12, and hydrolysis time of 12 hours. NaOH 6N was considered as an appropriate chemical for pH adjustment. From the above research results, sludge hydrolysis process was tested again at 3 pH levels of 10, 11 and 12. Table 1 showed the chemical characterization of sludge as follow.

Table 1: Chemical characterization of primary sludge

Parameter	Unit	pH = 10	pH = 11	pH = 12
tCOD	mg/L	24963 ±314	25017 ± 338	25164 ± 213
sCOD	mg/L	494 – 898	1387 – 2156	868 – 3650
VFA	meq/L	64	96	118
TDS	g/L	1.665	3.687	5.463
VDS	g/L	0.888	1.375	3.008

(Sources: Environmental Technology Laboratory - Institute for Environment and Resources)

Research results showed that VFA after alkalization at pH of 12 was 1.9 times higher than VFA value after alkalization at pH of 10. Datta's

research (1991) also included alkali pretreatment process can increase VFA by using NaOH 1%.

Advantages of alkalization process are cross-linked destructibility, cellulose hydrolysis, release acid led to increase VFA.

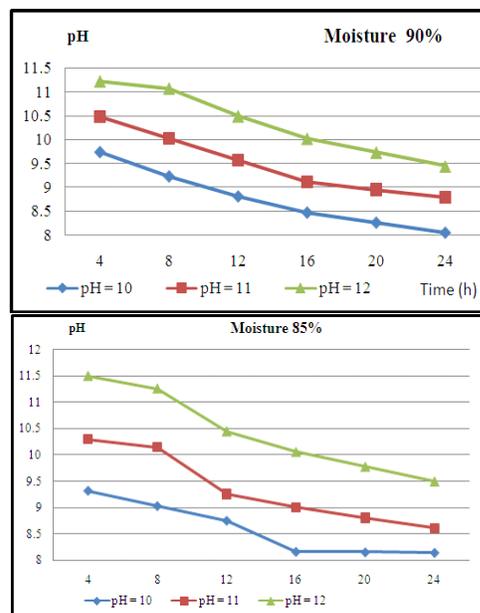


Fig. 3: pH variation with time at different pH

The pH curves of the experiments were almost similar to each other, as indicated by the pH decrease over time. With sludge humidity of 90%, pH tends to decrease rapidly in the first 16 minutes and reduce slower in the next 8 hours. The pH's reduction rate is greater when the pH is higher. pH decreased 2.09 – 2.25 unit, 2.38 – 2.4 unit; and 2.84 – 3.19 unit respectively at pH of 10, 11 and 12, respectively.

Similarly to pH, VFA also has a significant change with the time. In 4 – 12 hours, VFA increased up to the peak then decreased. After the hydrolysis reaction, at pH < 10, acidogenic bacteria were provided favorable conditions to develop. This can be explained that lipid, amino acid degradation process convert to formic acid (HCOOH), acetic acid (CH₃COOH), propionic

acid ($\text{CH}_3\text{CH}_2\text{COOH}$), iso-butylic acid ($(\text{CH}_3)_2\text{CHCH}_2\text{COOH}$), VFA and bi-products.
 $((\text{CH}_3)_2\text{CHCOOH})$, iso valeric acid

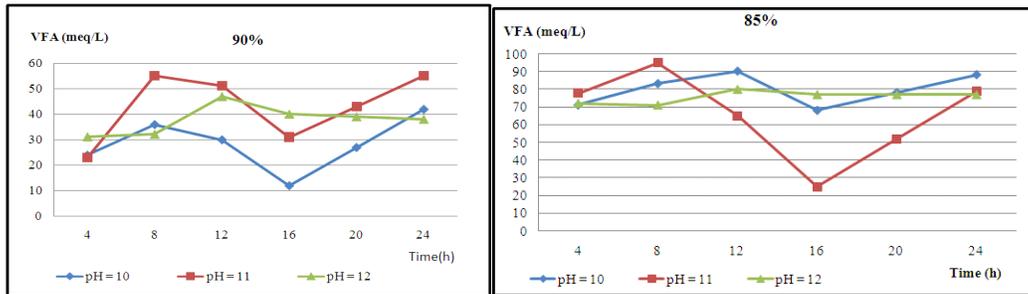


Fig.4: VFA changes by different pH of 10, 11, 12

On the contrary, alkalinity increased during the hydrolysis time from 4 to 16 hours at all moisture levels, then reduced steadily from 16 to

24 hours. The higher pH is, the higher alkalinity is. The peak of alkalinity reached 12000 mgCaCO_3/L at pH of 12 after 24 hours.

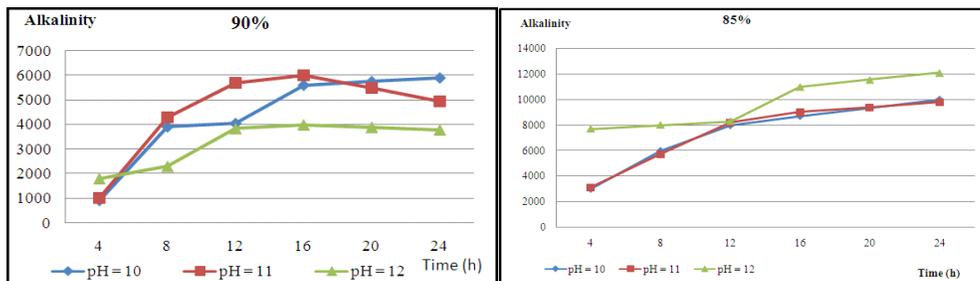


Fig.5: Alkalinity changes by different pH of 10, 11, 12

The alkalinity increase can be explained by hydrolysis reaction of organic compound, releasing HCO_3^- and NH_3 . According to Ripley (1986), alkalinity changes depend on transform ability substrate to HCO_3^- (specified alkalinity) and VFA (indirect alkalinity). Total alkalinity is the sum of two above alkalinities. Therefore, VFA/alkalinity ratio is the most important parameter to evaluate organic components digestion process in the model.

At the beginning of the process, solubilization and hydrolysis were dominated cause to increase of alkalinity. After 12 hours, dissolved substrate

rate reduced, acidification reaction was dominated lead to decrease of alkalinity.

In generally, optimal condition for sludge digestion process was pH of 12, sCOD of 3600 mg/L after 12 hour operation at room temperature. At pH of 12, after 20 digestion days, COD removal efficiency reached 62%. Methane productivity when alkali/NaOH was employed as a pretreatment was 4.9 times higher than sample without hydrolysis.

3.2. Thermal pretreatment method

pH of sludge samples decreased with reaction time; the higher temperature is, the faster pH

decreases. After 2 hours, pH reduced 1.1 – 1.96 unit at temperature of 55⁰C and decreased 3.6 – 3.66 unit at temperature of 170⁰C. This indicated that at high temperature, organic compounds dissolved more easily, especially long-chain fatty acids. VFA and intermediary acids cause to the amount of consumed OH⁻ was high, then lead to decrease pH after 2 hours. As a result, alkalinity was increased; the faster pH reduces, the more alkalinity increases since hydrolysis process and acidification were occurred to form HCO₃⁻ and NH₃.

The higher the temperature is, the greater solubility is. Concentration of sCOD in effluent sludge sample increased with increasing temperature. At humidity of 85%, temperature of 170⁰C, the sCOD content peaked at 21,644 mg/L. According to research by Vlyssides and Karlis (2004) in the hydrolysis at a temperature of about 50 - 90⁰C, pH of 11 with reaction times from 1 to 10 hours, sCOD content increased after an hour treatment.

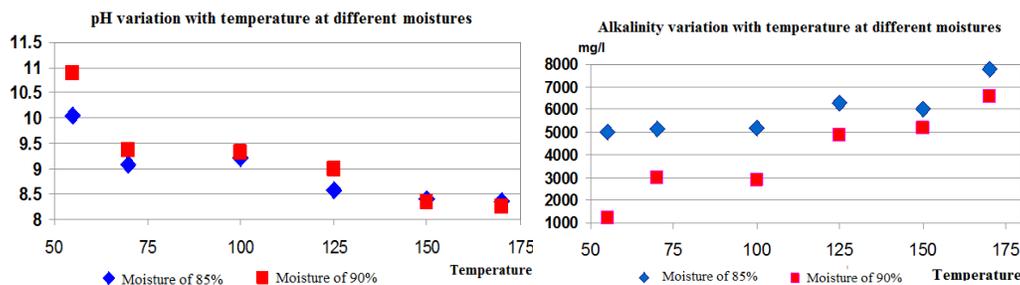


Fig.6: Effect of temperature to pH and alkalinity

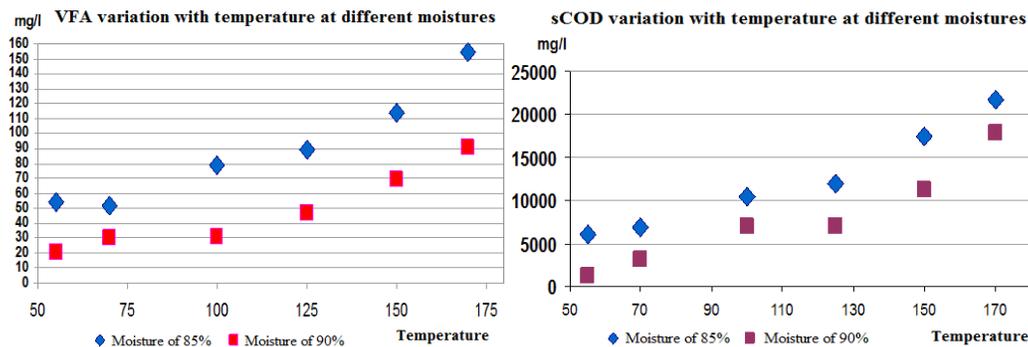


Fig.7: Effect of temperature to sCOD, VFA of sludge decomposition process

When temperature increased, the reaction occurred as quickly as, solubility COD, along with alkalinity and VFA content increased, shortened the sludge retention time, accelerated decomposition of sludge, created favorable conditions for the production of biogas in the next stage.

Concentration of VFA in temperature of 170⁰C was 3 times higher than the amount of VFA produced at 55⁰C, it is easily to recognize that temperature was important impact on the process of anaerobic sludge decomposition in the bioreactor. At high temperature (170⁰C), solubility COD of sludge increased and the

amount of volatile fatty acids also increased. With high humidity, the produced VFA decreased (VFA at humidity of 90% was less than at humidity of 85%). The ratio of VFA/alkalinity of the system was in the range of 0.01 - 0.02; these values were lower than 0.4, in accordance with the requirements of the stability conditions for the sludge decomposition process according to R. Roberts et al. after 2 hours of reaction.

3.3. Research and evaluation of results of the batch anaerobic digestion process

Operating mode without probiotics

Initial loading was 1.6 kgVS/m³/day then gradually increased to 8 kgVS/m³/day, with hydraulic retention time changes of 30, 20, 10, 6 days.

Research results showed that COD and VS removal efficiencies at loading of 1.6 kgVS/m³/day were the highest values, indicating long sludge retention time had the effect of increasing treatment efficiency. Meanwhile, the slow growth of bacteria were involved in substrate processing treatment, helped process more thoroughly.

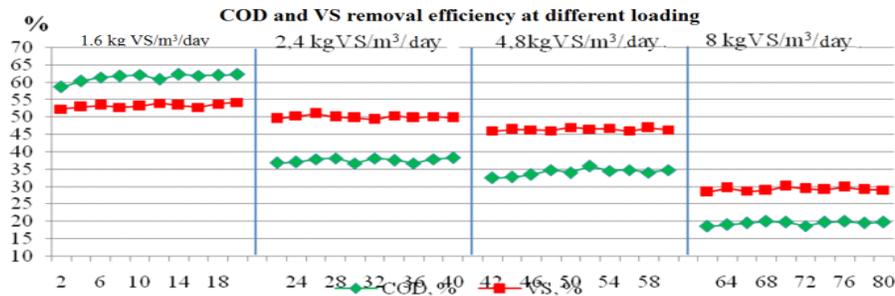


Fig.8: COD and VS removal efficiency at different loading

Production of biogas ranged from 0.523 to 2.36 m³ CH₄/m³.day. When the operation loading increased, the production of biogas also increased. This means that the treated amount of

organic matter increased. However, the amount of produced CH₄ per unit volatile solids mass decreased as the loading increased.

Table 2: Production of biogas variation with loadings

Loading	m ³ CH ₄ /m ³ day	LCH ₄ /kgVS
1.6 kgVS/m ³ /day	0.523 – 0.628	343 – 402
2.4 kgVs/m ³ / day	0.9 – 0.96	344 – 400
4.8 kgVS/m ³ / day	1.27 – 1.36	318 – 330
8 kgVS/m ³ / day	1.98 – 2.36	219 – 231

Thus, at the loading of 1.6 - 2.4 kgVS/m³/day, generated the biogas was rather high (about 343 - 402 LCH₄/kgVS) compared to the remaining loadings.

Produced biogas is inversely proportional to the sludge retention time. This result is consistent with studies of Kiyohara et.al. in the sludge treatment from urban sludge treatment plant. In

fact, microorganisms in the anaerobic sludge treatment process used organic matter to convert and did not occur overload or loss of sludge from the system.

The figure 10 showed the relationship between production of biogas and VFA with loadings. Production of biogas depends on the

loading or in other words, depends on the sludge retention time.

Research results showed that loading of 1.6 kgVS/m³/day can reach the highest COD and VS removal efficiency compared to the remaining loading. Therefore, the loading of 1.6 kgVS/m³/day is optimal loading with sludge retention time of 30 days.

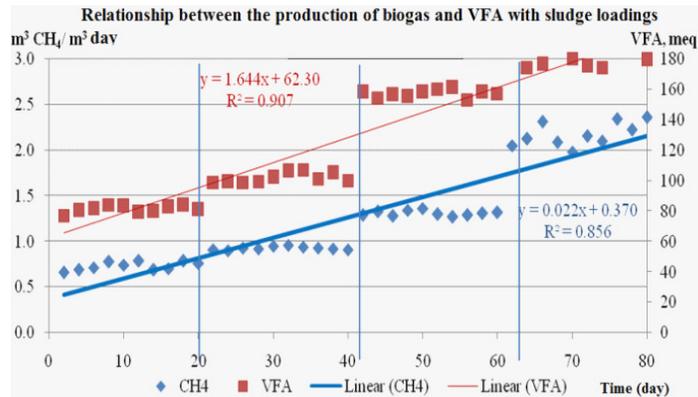
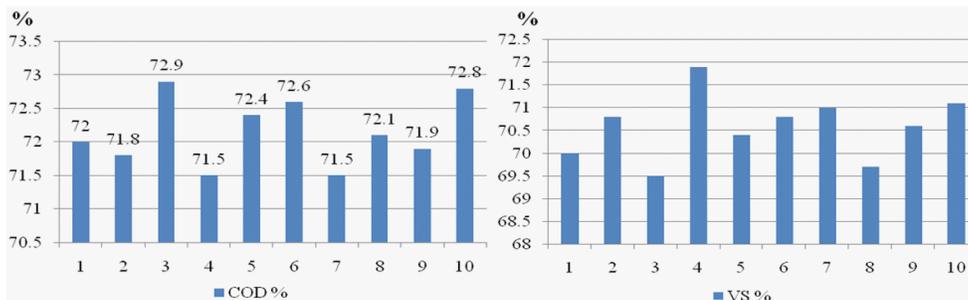


Fig.9: Relationship between the biogas production and VFA with sludge loadings

Operating mode with probiotics

The loading of 1.6 kgVS/m³/day was chosen for the research in the direction of adding probiotics of AquaClean/ACF 32 in order to

assess the catalytic efficiency to sludge treatment. Amount of microbial preparations in a dose of 10 ppm.



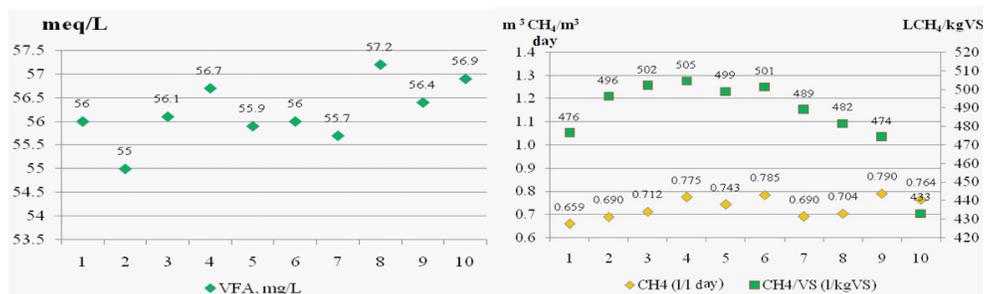


Fig.10: COD, VS, VFA removal efficiency and the biogas production with AquaClean/ACF 32

COD removal efficiency with adding preparations ranged from 71.5 to 72.9%, an increase of 10.66% compared to without adding preparations.

Protein and carbohydrates are two main components that form to COD in sludge. Additional microbial preparations makes quantity and activity of microorganisms increase. The addition of microbial products promote metabolic process, increase efficient decomposition of organic matter in the sludge. Microbial preparations to help metabolize proteins into

polypeptides, dipeptit, amino acids ... The amino acid further converted to ammonia, CO₂ and organic acids with a less molecular weight.

Meanwhile, the carbohydrates are hydrolyzed polysaccharide, even metabolized to sugars (Ji and Brune, 2005). Thus, the rate of hydrolysis, acetogens and methanogens increase. Amount of production biogas was higher, more stable process.

Thus, adding microbial preparations was positive effects to organic digestion process and increased biogas production in the system.

Table 3: Comparison of treatment efficiencies and biogas production in two operation modes

Parameters	Without adding AquaClean/ACF 32	With adding AquaClean/ACF 32
COD removal efficiency, %	61.37 - 62.48	71.5 - 72.9
VS removal efficiency, %	52.33 - 54.26	69.5 - 71.9
m ³ CH ₄ /m ³ /day	0.523 - 0.628	0.66 - 0.79
LCH ₄ /kgVS	343 - 402	433 - 505

Similarity to COD removal efficiency, VS removal efficiency and biogas production also increased 17%, 20 – 34% with adding microbial preparations, respectively, compared to without adding microbial preparations. VFA in the bioreactor with using microbial preparations was lower than without additional preparations. Effluent VFA was low, ranging from 55 to 57.2 mg/L. The rate of VFA/alkalinity was in the range of 0.007 - 0.008, consistent with the process of anaerobic digestion. This ratio was

used to observe the stability of the process. When the process is not stable, the concentration of VFA increased, alkalinity reduced leads to increase this rate.

4. CONCLUSIONS

Research and evaluation of the sludge hydrolysis process by alkaline pretreatment and thermal pretreatment methods showed that the optimal condition of sludge hydrolysis was pH of 12 (sCOD of 3600 mg/l), after 12 hours at room temperature. After 20 days of decomposition, at

pH of 12, the amount of methane generated 4.9 times higher than methane production in sludge samples without alkaline pretreatment. VS removal efficiency was over 40% and COD removal efficiency reached 62%. Besides, study the influence of temperature on the sludge decomposition process at temperature of 55⁰; 70⁰, 100⁰; 125⁰; 150⁰ and 170⁰C with two sludge samples with 85% and 90% humidity indicated that the higher temperature, the greater solubility of organic matter, content of sCOD, VFA, alkalinity in the effluent sludge sample increased with increasing temperature. As temperature increases, the reaction takes place as quickly, shortens decomposed time. Moreover, the research results indicated that ASBR model was appropriate for industrial sludge treatment by anaerobic digestion process, oriented simple and

effective can be apply in Vietnamese conditions. At once, a combination of anaerobic biological and bioproducts to increase treatment efficiency of organic matter can be also used.

In case of using biological products, after 10 days of anaerobic digestion, COD and VS removal efficiency ranged from 61.92% ± 1% 52.33% ± 0.05%, respectively; Production of methane was 372 ± 58 LCH₄/kgVS (corresponding to 0.5760.1 m³CH₄/kg sludge). In case of using biological products, after 10 days of anaerobic digestion, COD and VS removal efficiency were 71.8 ± 1% and 70.7 ± 1.2%, respectively. COD removal efficiency increased by 10.66% and VS removal efficiency increased by 17% compared to without preparation. Production of methane ranged from 0.659 to 0.79 m³ CH₄/ kg sludge.

Nâng cao hiệu quả thu hồi khí sinh học từ bùn thải công nghiệp

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TÓM TẮT:

Bùn thải công nghiệp đang được quan tâm của xã hội và chính quyền các cấp. Đây là loại nguồn thải có khả năng gây ô nhiễm nước ngầm, nước mặt, không khí, thâm nhập vào chuỗi thực phẩm, gia tăng bệnh tật và gây ảnh hưởng nghiêm trọng đến sức khỏe con người nếu không được thu gom và xử lý hiệu quả. Do đặc điểm là bùn thải công nghiệp chứa thành phần hữu cơ cao

nên công nghệ xử lý theo phương pháp sinh học kỵ khí, thu hồi khí sinh học cung cấp năng lượng phục vụ cho nhu cầu cuộc sống được đánh giá là giải pháp ưu tiên và hữu hiệu.

Nội dung của nghiên cứu bao gồm thủy phân bùn ở giai đoạn tiền xử lý, sau đó phân hủy dịch thủy phân trong môi trường kỵ

khí tại mô hình kỵ khí dạng mẻ (ASBR) để khảo sát khả năng nâng cao hiệu quả thu hồi khí sinh học. Kết quả nghiên cứu trong điều kiện PTN đã xác định hiệu quả xử lý COD đạt đến 60%, hàm lượng khí metan tăng 4,9 lần (360ml/l) so với các nghiên cứu trước đây (không thủy phân trước khi phân hủy kỵ khí), pH thủy phân 12, thời gian thủy

phân 12 giờ và thời gian phân hủy kỵ khí sau 20 ngày ở nhiệt độ phòng (30-35oC). Kết quả phân hủy bùn sau 20 ngày ở tải trọng 1,6 kg VS/m³. ngày cho thấy hiệu quả loại bỏ COD, VS lần lượt là 61.59 - 62.24, 52.33 - 54.26%. Lượng khí metan thu hồi khoảng 0.343 - 0.402 m³CH₄/kgVS (tương ứng với 0.523 - 0.628 m³CH₄/kg bùn).

Từ khóa: Bể phân hủy kỵ khí, quá trình thủy phân, nâng cao thu hồi khí sinh học, hàm lượng metan.

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