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Effect of pH on Phase Separated Anaerobic Digestion

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Abstract A pilot scale experiment was performed for a year to develop a two-phase anaerobic process for piggery wastewater treatment (COD: 6,000 mg/L, BOD: 4,000 mg/L, SS: 500 mg/L, pH 8.4, alkalinity 6,000 mg/L). The acidogenic reactor had a total volume of 3 m^3, and the methanogenic reactor, an anaerobic up-flow sludge filter, combining a filter and a sludge bed, was also of total volume 3 m^3 (1.5 m^3 of upper packing material). Temperatures of the acidogenic and methanogenic reactors kept at 20°C and 35°C, respectively. When the pH of the acidogenic reactor was controlled at 6.0-7.0 with HCl, the COD removal efficiency increased from 50 to 80% over a period of six months, and as a result, the COD of the final effluent fell in the range of 1,000-1,500 mg/L. BOD removal efficiency over the same period was above 90%, and 300 to 400 mg/L was maintained in the final effluent. The average SS in the final effluent was 270 mg/L. The methane production was 0.32 m^3 CH_4/kg $COD_{removed}$ and methane content of the methanogenic reactor was high value at 80-90%. When the pH of the acidogenic reactor was not controlled over the final two months, the pH reached 8.2 and acid conversion decreased compared with that of pH controlled, while COD removal was similar to the pH controlled operation. Without pH control, the methane content in the gas from methanogenic reactor improved to 90% , compared to 80% with pH control.

Keywords: two-phase, anaerobic process, piggery wastewater, pH controlled, pH uncontrolled

INTRODUCTION

Three distinct bacterial groups (fermentative, acetogenic, and methanogenic) are involved in the anaerobic digestion process and these bacteria widely differ from one another in their physiology and nutritional requirements. In a stably operated process, these groups are well balanced. However, when easily hydrolysable substrates such as soluble starch are treated anaerobically, this process might have a problem at high loading rates because of the imbalance between acid and methane formation. In order to overcome these problems, many attempts have been tried to separate the process into two distinct phases; *i.e.* acidogenic and methanogenic phases [1-3]. In this phase separated system, methane formation is prevented in the acidogenic phase through kinetic control (short residence time), pH control (low pH values of 5-6), or a combination of both.

Piggery wastewater has high values of COD, ammonia nitrogen, and alkalinity. Depending upon the efficiency of solid separation, it also contains a high concentration of suspended solids (SS). Anaerobic treatment of piggery wastewater has been the subject of much research not only to reduce its pollution potential but to facilitate economic utilization by producing methane gas [4].

To treat the piggery wastewater, we selected the two-phase anaerobic treatment system. With a separate acidogenic reactor, we intended to hydrolyse and degrade SS components more efficiently than is possible in a single reactor system, since both acidogenesis and methanogenesis can be controlled independently. The piggery wastewater was collected after separation of the solid fraction. The characteristics were as follows: COD 6,000 mg/L, BOD 4,000 mg/L, alkalinity 6,000 mg/L, SS 500 mg/L. Since the alkalinity of this wastewater is relatively high, we investigated the effect of pH control in the acidogenic reactor on the performance of the entire treatment system.

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MATERIALS AND METHODS

Characteristics of Piggery Wastewater and Performance of Two-phase Anaerobic Reactor

The characteristics of the piggery wastewater used in this study are shown in Table 1. TCOD varied from 669 to 6,760 mg/L during the operation with a mean value of 3,830 mg/L. The value was the lowest during the rainy season. Biochemical oxygen demand (BOD) of the influent was about 60% of the COD. The concentration

Table 1. Characteristics of piggery wastewater

Item	Mean	Standard deviation	Size	Minimum value	Maximum value
TCOD (mg/L)	3,830	1,630	101	669	6,760
SCOD (mg/L)	3,410	1,650	102	382	6,250
TSS (mg/L)	424	139	90	167	931
TKN (mg/L)	1,760	395	32	736	2,307
NH_3-N (mg/L)	1,570	400	32	676	2,018
pH			8.0-8.5		
Alkalinity (mg/L)			6,000-7,000		

of ammonia nitrogen was in the range of 676 to 2,018 mg/L with a mean value of 1,570 mg/L. Although most of the suspended solids were separated before entering the pilot plant, the concentrations of organic carbon and ammonia nitrogen in piggery wastewater were so high that we found it difficult to treat piggery wastewater using conventional biological treatment processes.

Two-phase Anaerobic Process

The schematic diagram of the overall process is shown in Fig. 1. The acidogenic reactor had total volume of 3 m^3. When the hydraulic retention time (HRT) of the acidogenic reactor was changed from 4.0 to 0.7 days, the organic loading rate (OLR) increased varied from 1.0 to 4.0 kg COD m^{-3} day^{-1} depending on the COD concentration of the influent. The methanogenic reactor, an anaerobic up-flow sludge filter combining a filter, and a sludge bed, had a total volume of 3 m^3 (1.5 m^3 of upper packing material). When the HRT of the metha-nogenic reactor was changed from 5.5 to 0.7 days, the OLR increased from 1.0 to 5.0 kg COD $m^{-3}day^{-1}$ depending on the COD concentration of the acidified effluent. Temperatures of the acidogenic and methanogenic reactor were maintained at 20°C and 35°C, respectively, with a heating coil.

In order to investigate the effects of pH control on phase separation, the pH of the acidogenic reactor was controlled at 6.0-7.0 with HCl during the initial operating period. When the system stabilized, HCl addition was discontinued and the performance of the system was investigated.

Analytical Methods

Three kinds of samples (raw wastewater, acidified effluent, and final effluent) were taken from the pilot plant. Gas production and the composition of gas were monitored three times per week. The pH, COD, volatile fatty acids (VFAs), SS, and alkalinity were also recorded. SCOD was analyzed using a closed reflux method after centrifugation (3000 g, 10 min) and filtration (GF/C). For volatile fatty acid analysis, filtered samples were acidified to pH 2.0 and analyzed by gas chromatography (HP 5880) equipped with a flame ionization detector (FID). A 30 m long, 0.53 mm id, and 0.52 μm film thickness capillary column (HP-FFAP) was used for the separation. Butanol was used as an internal standard. Other parameters, such as SS and alkalinity, were analyzed using the Standard Methods [5].

Gas composition was determined with an infra-red gas analyzer (GA 94A) and gas detector (GASTEC, Japan); concentrations of CH_4, CO_2, and H_2S were monitored.

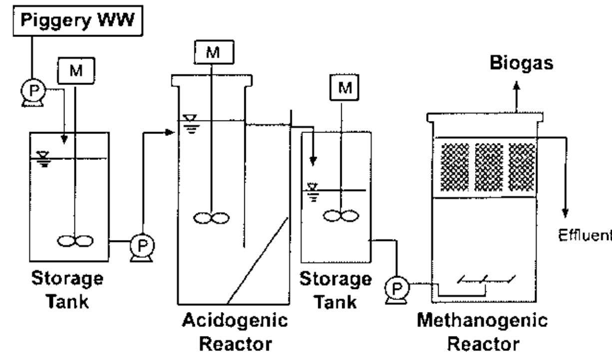

Fig. 1. Schematic diagram of the two-phase anaerobic process for piggery wastewater treatment.

Calculation of the Acid Conversion Percentage

The acid conversion percentage in the acidogenic reactor was determined by Eq. (1) as follows:

$$\text{Acid conversion percentage (\%)} = \frac{\text{COD equivalent of the volatile fatty acids after acidification (mg/L)}}{\text{COD of the influent (mg/L)}} \times 100 \quad (1)$$

RESULTS AND DISCUSSION

Effect of Microorganism Seeding on the Start-up of the Two-phase Anaerobic Digestion

Although anaerobic microorganisms acclimatized to piggery wastewater can be good inoculums for a fast start-up of the operation at the initial stage, the waste sludge of the activated sludge process was used as a seeding inoculum to avoid possible infection by pathogenic microorganisms from other piggery wastewater treatment plants. During the start-up period, the organic loading rates of both acidogenic and methanogenic reactors were 2.6 kg COD $m^{-3}day^{-1}$ with 2 days hydraulic retention. The acid conversion in the acidogenic reactor was 60% of the influent organic matter, as

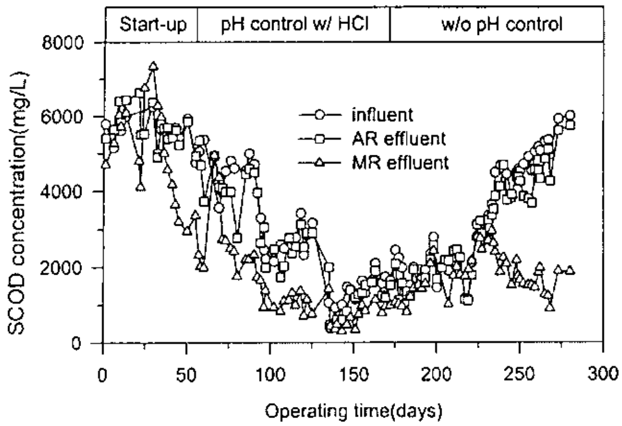

Fig. 2. Variation of SCOD of the influent and effluent of the acidogenic (AR) and methanogenic (MR) reactors.

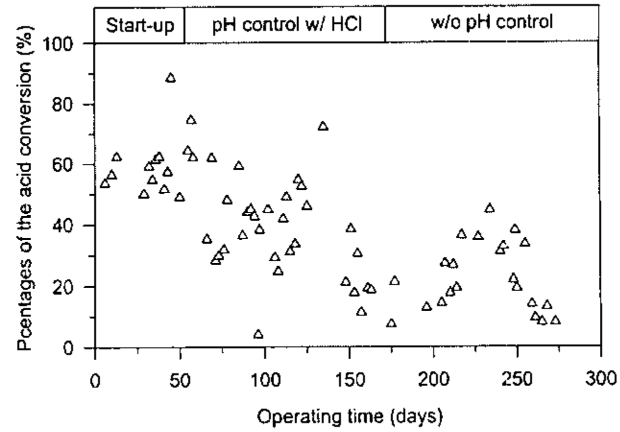

Fig. 4. Variation of acid conversion in the acidogenic reactor.

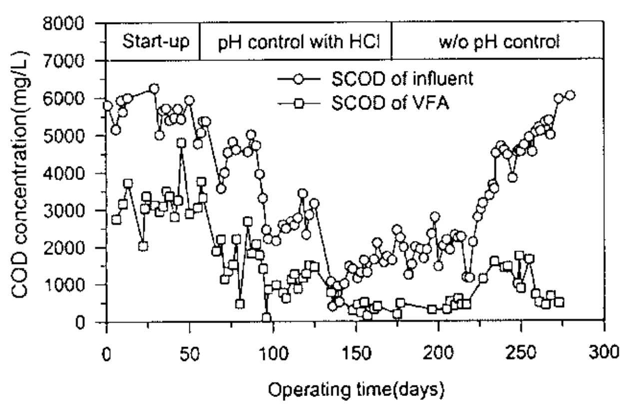

Fig. 3. Comparison of SCOD of influent and SCOD of volatile fatty acids (VFA) in the acidogenic reactor.

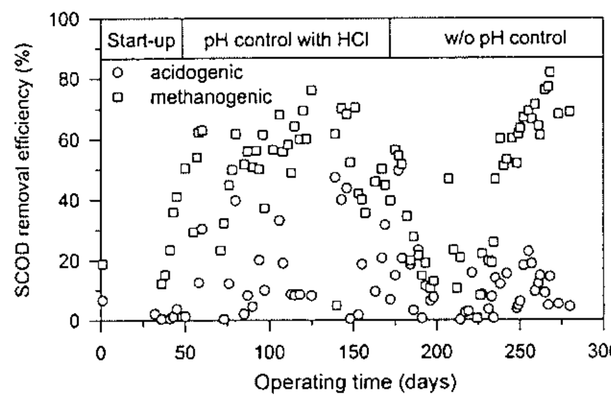

Fig. 5. SCOD removal efficiency in the acidogenic and methanogenic reactors.

shown in Fig. 4. However, the methanogenic activity remained very low for the first 30 days of operation. Therefore, we seeded with sediment sludge, which had been taken from the lower part of the piggery wastewater storage tank. After an additional seeding to the methanogenic reactor, the COD removal efficiency gradually increased to 60% as shown in Fig. 5.

Operation with pH Control

The variations of SCOD in the influent and effluent of both acidogenic and methanogenic reactors were shown in Fig. 2. SCOD was varied significantly from 6,500 mg/L to less than 1,000 mg/L throughout the operating period. Day 130 marked the start of the rainy season, the SCOD of influent dropped to 1,000-1,500 mg/L for 20 days and then increased steadily to 6,000 mg/L. HCl was added to the acidogenic reactor for the first 170 days to maintain the pH at 6.0–7.0, since pH in the reactor did not reduce on its own accord to the acidic region. When we controlled the pH at 6.0–7.0, the production of VFA in the acidogenic reactor was quite active (Fig. 3). The amount of VFA produced was estimated to be about 40 to 60% of SCOD (Fig. 4), which means that acidogenesis was relatively successful with pH control. Since the alkalinity of the wastewater was very high (6,000 mg/L), the pH of the acidogenic reactor could not decrease to the acidic region although the VFA concentration was high. With pH control, the SCOD removal in the acidogenic reactor remained at about 10%, while that in the methanogenic reactor increased significantly after 30 days and varied between 50 and 70% for the next 100 days (Fig. 5)

Operation without pH Control

During the rainy season (days 130 to 150), because the SCOD concentration in the influent dropped to 1,000-1,500 mg/L, the acidogenesis seemed to experience a shock. VFA production decreased significantly compared to production prior to day 120 (Fig. 3). Without pH control, the acid conversion in the acidogenic reactor varied between 15 and 30% of SCOD (Fig. 4), while SCOD removal efficiency in the methanogenic reactor decreased slightly (Fig. 5). At this time (day 180), although it seemed that the acidogenesis did not recover from the shock, the HCl addition was stopped,

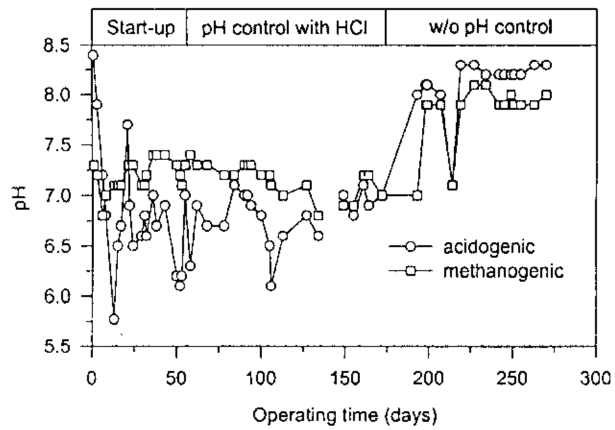

Fig. 6. Variation of pH in the acidogenic and methanogenic reactors during the operating period.

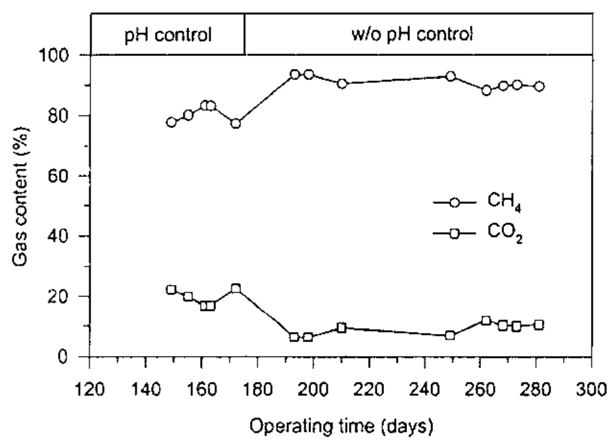

Fig. 7. Variation of gas content in the methanogenic reactor.

that is, the pH was no longer controlled. As soon as the pH control was stopped, the SCOD removal in the methanogenic reactor dropped below 20% immediately and remained there for 50 days (Fig. 5). After day 200, the SCOD of the influent increased gradually from 2,000 mg/L, while SCOD removal efficiency recovered only after day 225. Acidogenesis also seemed to recover, for a while, from days 225 to 255, but VFA production dropped again on day 260. Although VFA production was not fully recovered, the SCOD removal efficiency increased continuously and reached over 70%. This suggests that methanogenic activity in the methanogenic reactor had fully recovered. Since VFA production was recovered somewhat between days 230 and 260, it is curious why acidogenesis was inhibited again after day 260. It is postulated that in the absence of pH control the major reaction in the acidogenic reactor was hydrolysis rather than acid formation. The reason for this phenomenon is now under investigation.

During operation without pH control, the pH in both reactors increased to around 8.0 and reached up to 8.3 (Fig. 6). Although the overall methanogenic performance decreased without pH control, the gas content in the methanogenic reactor was improved in a positive way. That is, the methane content increased from 80 to 90% after pH control was stopped at day 180 (Fig. 7). Since the pH of the methanogenic reactor was maintained at above 8, more carbon dioxide was dissolved in the medium and as a result, the methane content in the gas phase increased [6]. In this two-phase anaerobic digestion of piggery wastewaer, average methane production was 0.32 m^3 CH_4/kg $COD_{removed}$.

CONCLUSION

This pilot scale experiment was performed for a period of a year to develop a two-phase anaerobic process for piggery wastewater treatment. The reactor was fed with piggery wastewater (COD: 6,000 mg/L, BOD: 4,000 mg/L, SS: 500 mg/L, pH 8.4, alkalinity 6,000 mg/L) and temperatures of the acidogenic and methanogenic reactor were maintained at 20°C and 35°C, respectively, using a heating coil. During operation period for its initial six months, SCOD removal increased from 50 to 80% and the pH of the acidogenic reactor was controlled at 6.0-7.0 with HCl, as a result, the SCOD of the final effluent fell in the range 1,000-1,500 mg/L. Methane production through this period was 0.32 m^3 CH_4/kg $COD_{removed}$ and the methane content of the methanogenic reactor was high value at 80-90%. When the pH of the acidogenic reactor was not controlled with HCl addition during the final two months, the pH reached 8.2 and acid conversion decreased, while the final COD removal was similar to the pH-controlled operation.

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