

INFLUENCE OF SULFATE AS AN ELECTRON ACCEPTOR ON THE ANAEROBIC HYDROLYSIS AND ACIDOGENESIS OF PARTICULATE ORGANICS

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Abstract : Influence of sulfate on the anaerobic hydrolysis and acidogenesis of particulate organics was studied in a completely mixed acidogenic reactor. The shattered food waste as a particulate organics was added into the reactor at a daily basis while dilution water containing various concentration of sulfate was continuously supplied. The efficiencies of hydrolysis and acidogenesis at control were 60.1% and 19.4%, respectively while they have increased up to 70.6% and 46.2% respectively at 350 mg/L of the sulfate level in the dilution water. The buffering capacity of the acidogenic system increased with the increase of the sulfate level. The efficiencies of hydrolysis and acidogenesis gradually decreased at over 350 mg/L of the sulfate level in the dilution water. It was caused by the increase of the acidogenesis product used as electron donor for sulfate reduction and inhibition effect of the hydrogen sulfide from sulfate reduction. It could be concluded that sulfate in acidogenesis of particulate organics was used as a useful electron acceptor to create a favorable condition thermodynamically and to produce additional alkalinity for the increase of buffering capacity.

Key Words : acidogenesis, electron acceptor, hydrolysis, particulate organics, sulfate

INTRODUCTION

Food waste in Korea has caused a lot of sanitary and aesthetical problems such as mal-odor, leachate, and hazardous gases during its collection and transportation.¹⁾ On the other hand, the food waste mainly consists of high biodegradable substances such as carbohydrate, lipid and protein. It means that the waste could be a good reusable resource.

In this point of view, a number of studies to produce a soil fertilizer by aerobic composting or earthworm and to make a stock feed from food waste have been conducted for the past

years.²⁾ However, some problems such as wide daily changes of the waste composition, high content of salts and difficulties in maintaining the freshness hindered the practical application of the reuse and recycling technologies. Then, it is reported³⁾ that anaerobic digestion make it easy to resolve the problems concerning food waste management. It includes the organic acids production through hydrolysis and acidogenesis and the methane production by methanogenesis of the acidified waste, or by co-digestion with sewage sludge in the existing digester.³⁾ Especially, the organic acids produced in anaerobic digestion process can be used as an external carbon source for denitrifying bacteria in biological nutrients removal process from a low C/N ratio wastewater. These applications of

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anaerobic technology have found to be more feasible for particulate organics including food waste if the stages of the hydrolysis and the acidogenesis are enhanced.

Generally, the hydrolysis is considered as a rate-limiting step in the anaerobic digestion of particulate organics like food waste.^{4,5)} The hydrolysis process depends on the activity of the hydrolytic enzyme which is produced by acidogens.⁶⁾ The production of hydrolytic enzyme is proportional to the rate of acidogenesis, but it can be inhibited by the acidogenic conditions such as pH, the levels of hydrolyzed organics and other products. As the acidogenic process is evaluated by thermodynamics, both the electron acceptors and the products of acidogenesis including VFAs and hydrogen have an influence on the performance of the acidogenesis,⁷⁾ which is expressed as the terms of the rate of acidogenesis, concentration and composition of the VFAs.

In this work, the influence of sulfate as an external electron acceptor on the anaerobic hydrolysis and acidogenesis of food waste was investigated to obtain a favorable condition and method for acidogenic fermentation for food waste in a completely mixed acidogenic reactor.

MATERIALS AND METHODS

Food Waste

The food waste as a particulate organics was obtained from a dining hall in KMU, and shattered after the removal of impurities such as plastic bags, chopsticks and others. The waste was screened with a sieve of 4 mm opening and the initial characteristics of the waste such as

solids, COD and pH was measured, and then the waste was stored in a refrigerator of 5°C to prevent the denaturation until it was added as the feed into the reactor. The seed sludge was obtained from an anaerobic digester of NG municipal wastewater treatment plant in B metro-city, and used as the inocula for the acidogenic reactor after the analysis of initial characteristics. Table 1 shows the average characteristics of the food waste and the seed sludge. The composition of the food waste changed daily, but the contents of vegetable and grain based on wet weight were generally higher than that of meat and fish.

Experimental Apparatus

In this study, two sets of the acidogenic systems with around 13 L of the effective volumes were used and each system was consisted of the acidogenic reactor made of transparent acryl, settling tank, dilution water tank, control box, and gas collector of water displacement type saturated with acidified salt as shown in Figure 1. On the upper plate of the reactor, an air sealed feeding port was placed to minimize the inflow of air during feeding of the waste. The content of the acidogenic reactor was completely mixed by the blade connected with motor vertically. During the acidogenic fermentation, the temperature of the acidogenic reactor content was maintained at 35±1°C by the thermostat that was connected with temperature sensor inserted in the reactor, and the heating material coiled around reactor. The shattered food waste was intermittently fed to the acidogenic reactors with a day time interval through the feeding port, and the organic loading rate was 15 g VS/L/day. The dilution water was

Table 1. Characteristics of the food waste and the seed sludge

Contents	pH	TS (mg/L)	VS (%)	TCOD (SCOD) (mg/L)	Alkalinity (mg/L)	TKN (mg/L)
Food waste	4.55	120,539	93.3	134,933 (37,287)	1,020	2,800
	Grain (37.5%), Vegetable (45.7%), Meat and fish (16.8%)					
Seed sludge	7.46	30,046	43.9	21,320 (14,573)	2,187	130.8

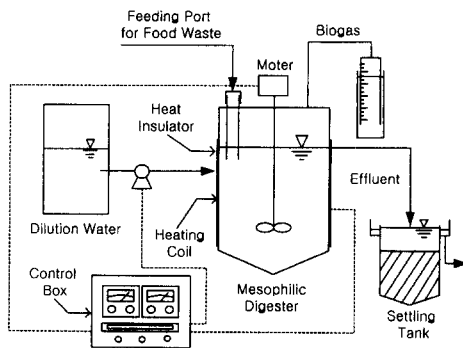


Figure 1. Schematic diagram of the lab-scale acidogenic system.

continuously injected into the acidogenic reactor with a peristaltic pump to supply the sulfate and to prevent the accumulation of the fermentation products such as VFAs, hydrogen and others and the rapid pH drop during the acidogenic fermentation. The flow rate of dilution water was maintained to 4.29 L/day throughout experiments. The alkalinity in the dilution water was controlled to 8,000 mg/L as CaCO_3 by adding sodium bicarbonate, and the concentration of sulfate was adjusted from control (50 mg/L) to 1,250 mg/L by adding of NaSO_4 according to the experimental schedule.

Sampling and Analyses

The fermented content was taken from the sampling port everyday and total VFA, pH and SCOD were measured to evaluate the stability of acidogenic reactors. As the system was approached to the steady state, the content was sampled several times by 2~3 hr of time intervals during a feeding cycle. The pH, solids, VFAs, alkalinity, nitrogen, phosphate and COD were determined according to Standard Methods⁸⁾ basically. The compositions of biogas were analyzed by a gas chromatography equipped with TCD detector.

Performance Estimation of the Hydrolysis and Acidogenesis

All components are expressed in grams of COD to evaluate the reactor efficiency for the hydrolysis and acidogenesis of food waste. As

the production of hydrogen and methane are relatively small, their contributions to the mass balances were neglected for the easy estimation. The percentage of hydrolysis (Hyd(%)) was defined by the ratio of the produced SCOD (g) and the added TCOD (g) for a feeding cycle by following Eq. (1).

$$\text{Hyd}(\%) = \left[\frac{\sum_{i=1}^n Q_i S_{si} \Delta t_i}{FS_{S_0}} \right] \times 100 \quad (1)$$

where, S_{si} and Q_i are the SCOD in the effluent and the flow rate of dilution water at time t_i and F , and S_0 indicate the volume and the TCOD of the feeding waste. The percentage of acidification (Ac(%)) was estimated by the VFA fraction of the amount of SCOD in the discharged dilution water like below Eq. (2).

$$\text{Ac}(\%) = \left[\frac{\left(\sum_{i=1}^n Q_i S_{ai} \Delta t_i - FS_{S_0} \right)}{\left(\sum_{i=1}^n Q_i S_{si} \Delta t_i - FS_{S_0} \right)} \right] \times 100 \quad (2)$$

where, S_{ai} and S_{S_0} are the total VFA in the effluent at time t_i and the VFA of the feeding waste.

RESULTS

After 3 weeks of the start-up, the characteristics of the acidogenic effluent such as VFA, SCOD, and pH were stable and any perceivable methane gas production was not observed, indicating the steady state and the successful start-up of the system. It took around 3 weeks to approach a steady state after changes of the operation conditions through the experimental period. Figure 2 shows the behavior of soluble COD according to the concentration of sulfate in the dilution water during feeding cycle. The SCOD were increased from 31,000 to 57,000 mg/L, depending on the level of sulfate, up to around 3 hr from the feeding of food waste, and then rapidly dropped to 26,000 ~ 28,000 mg COD/L. However, from 6 hr to the end of the feeding cycle, the SCOD slowly decreased. The

peak levels of SCOD were observed to be the highest at 350 mg/L of the sulfate of dilution water, and followed by 750 mg/L, 150 mg/L, 1,250 mg/L and the control. In the behavior of total VFA (Figure 3), the peak values were observed as 4,000~13,600 mg HAc/L between 3 and 6 hr after feeding of the food waste. The maximum peak value of total VFA was the highest as 13,600 mg HAc/L at 350 mg/L of sulfate and the order of the levels at other concentrations of sulfate was similar with that of the SCOD. However, unlike the case of SCOD, the peaks depending on the sulfate level were not clear except for 350 mg/L of the sulfate level.

The reduction efficiencies of the sulfate were around 80% at 1,250 mg/L of the sulfate, but around 40~60% at the other sulfate concentrations.

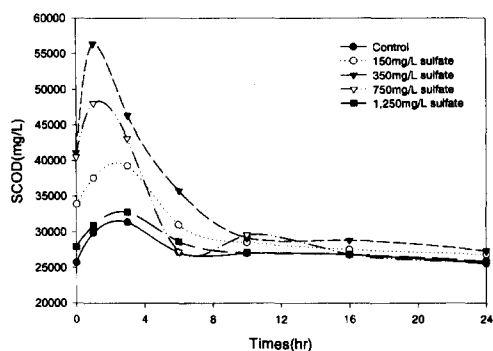


Figure 2. Behaviors of SCOD in the acidogenic reactor according to the sulfate concentration during a feeding cycle.

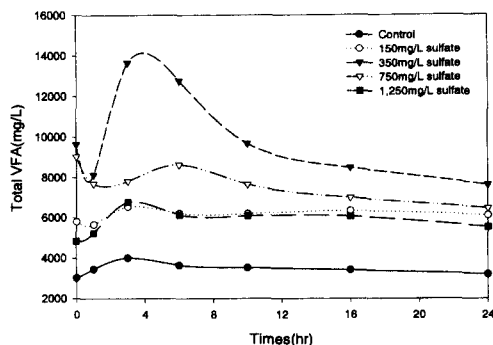


Figure 3. Behaviors of total VFA in the acidogenic reactor according to the sulfate concentration during a feeding cycle.

The amount of reduced sulfate during the feeding cycle was the order of the concentration of sulfate in dilution water (Figure 4).

The initial values of the pH ranged from 5.4 to 6.6 depending on the initial VFA concentration. During the fermentation, the values of pH were dropped with the increase of VFA concentration, and then gradually recovered up to the end of the feeding cycle. However, the recovery rate was affected by the sulfate concentration, and was a little faster in the cases of 750 mg/L and 1,250 mg/L of the sulfate in dilution water (Figure 5).

DISCUSSION

The peak levels of SCOD were depended on the sulfate level of dilution water and the highest

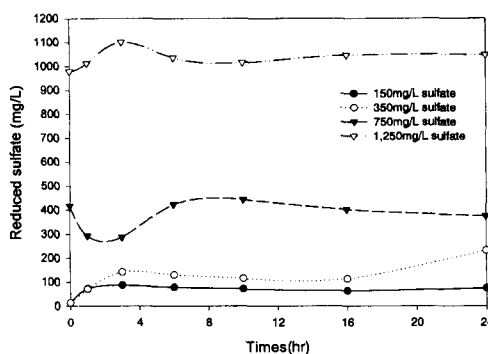


Figure 4. Amount of the reduced sulfate according to the sulfate concentrations during a feeding cycle.

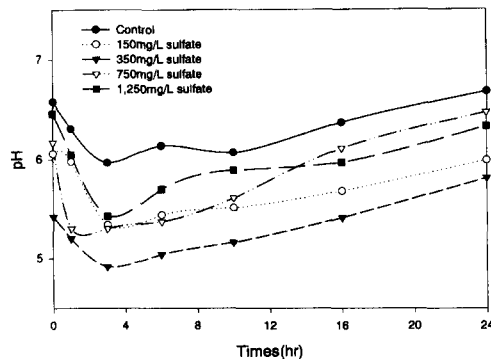


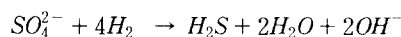
Figure 5. Variation of pH level according to the sulfate concentrations during a feeding cycle.

value was observed at 350mg/L as shown in Figure 2. The percentage of hydrolysis at 350 mg/L of the sulfate level was higher as 70.1% than 60.1% of the control (Table 2). These values are in agreement with the work by Henze et al. describing that the synthesis of the hydrolytic enzyme was affected under electron acceptor conditions.⁴⁾ However, the levels of monomer COD, differences with SCOD and VFA as COD, were several times higher than the VFA level as COD, and the influences of the sulfate level on the SCOD was not so much except for their peak times. Besides, the hydrolyzed monomer to be fermented by acidogens was affected by the sulfate and was lower than that of the control. This indicates that the monomer products from the hydrolysis could inhibit the synthesis of the hydrolytic enzyme, and the excretion of the enzyme might be induced by the shortage of the hydrolyzed product to be fermented by acidogens.³⁾ Therefore, the apparent effect of electron acceptor on the hydrolysis might be obtained at the lower organic loading rate than 15 g VS/L/day or at the higher dilution rate the 0.33 day.

The performance of acidogenic reactor can be generally expressed by the terms of the acidification percentage and the concentration and composition of VFAs. In the study, the percentage of acidification of the food waste was only 19.4% in control, but increased to 46.2% at 350 mg/L of sulfate. The maximum concentration of total VFA was affected by the sulfate level in dilution water, and was 13,600 mg HAC/L at 350 mg/L of the sulfate (Figure 3). This indicates that the performance of acidogenesis of food waste could be enhanced by the shift of electron flow through the addition of external electron acceptor. According to Mizuno et al.,⁹⁾ the sulfate reducing bacteria

(SRB) plays an important role to create a thermodynamically favorable condition in an acidogenic reactor by the consumption of hydrogen produced from acidogenesis as a main electron donor.⁷⁾ However, both the concentration of total VFA and the percentage of acidification decreased a little in the sulfate range of over 350mg/L as presented at Table 2. It can be concluded that the some portion of produced VFA was used as an electron donor for SRB or the activity of acidogenic bacteria was inhibited by the hydrogen sulfide from the sulfate reduction.⁹⁻¹¹⁾

In Figures 3 and 5, the trends of pH changes according to the sulfate were mainly affected by the behavior of VFA concentration, but did not directly depend on only the concentration of total VFA. The dropped pH per a mole of total VFA and the recovery rate depended on the amount of reduced sulfate (Figure 4). The following stoichiometry of the sulfate reduction shows that the 2 moles of alkalinity as CaCO₃ are produced from a mole of sulfate reduction.



This indicates that the addition of sulfate as an external electron acceptor can increase the buffering capacity during the acidogenesis, leading to the reduction of alkalinity requirement to maintain pH in the acidogenic reactor.

CONCLUSION

The addition of sulfate as an external electron acceptor was effective to enhance the performance of hydrolysis and acidogenesis of particulate organic. The proper concentration of sulfate in the dilution water was 350 mg/L at 15 g VS/L/day of food waste loading rate and 0.33/day of dilution rate. The synthesis of hydrolytic enzyme might be inhibited by the monomer hydrolyzed from particulate organics. The sulfate in acidogenic reactor might be used as an electron acceptor to create a favorable condition thermodynamically and to produce additional alkalinity to increase

Table 2. Percentages of hydrolysis and acidification according to the sulfate

Sulfate conc. (mg/L)	Control	150	350	750	1,250
Hydrolysis (%)	60.1	65.2	70.6	65.1	61.1
Acidification (%)	19.4	32.1	46.2	41.5	31.9

buffering capacity.

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REFERENCES

1. DOE, '97 Current Status of Production and Treatment of Waste in Korea (1998).
2. Koh, S. C., Song, Y. C., and Kim, I. S., "Efficient Treatment of Food Waste by EM (Effective Microorganisms) and Their Recycling," *J. of Korea Solid Wastes Engineers Society*, **14**(7), 729~740 (1997).
3. Song, Y. C., Kim, M. K., Shin, H. S., Paik, B. C., and Kim, J. O., "Environmental Conditions on the Acidogenesis of Food Waste," *Proceeding of the 2000 KSWES Autumn Conference*, Taegu, Korea, pp. 156~259 (2000).
4. Henze, M. and Mladenovski, C., "Hydrolysis of Particulate Substrate by Activated Sludge under Aerobic, Anoxic and Anaerobic Conditions," *Water Res.*, **25**(1), 61~64 (1991).
5. Veeken, A., Kalyuzhnyi, S., Scharff, H., and Hamelers, B., "Effect of pH and VFA on Hydrolysis of Organic Solid Waste," *J. Environ. Engineer.*, **126**(12), 1076~1081 (2000).
6. Jain, S., Lala, A. K., Bhatia, S. K., and Kudchadker, A. P., "Modelling of Hydrolysis Controlled Anaerobic Digestion," *J. of Chem. Tech. Biotech.*, **53**, 337~344 (1992).
7. Ruzicka, M., "The Effect of Hydrogen on Acidogenic Glucose Cleavage," *Water Res.*, **30**(10), 2447~2451 (1996).
8. APHA, AWWA, and WPCF, Standard Methods for the examination of water and wastewater, 18th ed., American Public Health Association, Washington, DC (1987).
9. Mizuno, O., Li, Y. Y., and Noike, T., "The Behavior of Sulfate-reducing Bacteria in Acidogenic Phase of Anaerobic Digestion," *Water Res.*, **32**(5), 1626~1634 (1998).
10. Lin, C. Y. and Hsiu, M. W., "Effects of sulfide, sulfite and sulfate on acidogenesis in upflow anaerobic sludge blanket process," *J. Environ. Sci. Health*, **A32**(4), 1171~1184 (1997).
11. Manilal, V. B., Litvin-scramm, S. B., and Suidan, M. T., "Effect of Sulphidogenesis on Acid-Phase Digestion of Waste Activated Sludge," *Bioprocess Eng.*, **23**, 595~597 (2000).