Enhancement of biogas production from pineapple waste by acid-alkaline pretreatment

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Abstract. The present study examined the effect of acid-alkaline pretreatment on pineapple waste for the performance on the anaerobic digestion. The acid-alkaline pretreatment was carried out by varying pH values from 2 to 12 using HCl and NaOH, and the mixtures were agitated at 250 rpm with the contact time of 24 hrs. The overall result showed that SCOD concentrations increased when pH values were increased. The value of biodegradability of raw waste was about 0.304. The BOD/COD ratios increased to 0.439 and 0.473 for pH 7 and pH 9, respectively. However, the BOD/COD ratios decreased for adjusted pH 12. For BMP test at pH 7, the removal efficiencies were 76.34%, 91.69% and 84.69% for TS, VS and COD, respectively, which were the higher efficiency than other conditions. It was also the optimal condition for the gas production rate because the pretreated pine apple waste was hydrolyzed much the organic matter into the soluble forms that can be immediately consumed by the anaerobic digestion process.

1. Introduction
An industrial food processing, especially frozen and canned foods, is one of the main export products in Thailand. The processed pineapple is one of the high value products of the canned food. However, the manufacture process generally generates a large quantity of pineapple solid waste in the forms of peels and cores. On an average, one ton of fresh pineapple generates approximately 0.5 ton of solid waste. Each cannery normally disposes of 100-150 tons of solid waste per day [1], where it remains relatively untapped and often subjected to landfill. This situation has risen the concern on the environmental pollution issues. The pineapple waste contains high concentration of biodegradable organic material and suspended solid. The chemical composition appears to be a good nutrient for a cultivation of bacteria. It can potentially be used as a carbon source for organic acid fermentation. Pineapple wastes generally comprise of organic substances, and hence the disposal problem could be attenuated by an anaerobic digestion and composting. Anaerobic biogas production using this waste would reduce the aforementioned problems, and the process itself generates revenue. Moreover, this waste is a potential raw material for a biogas production, as it contains a high amount of fermentable sugar, and potentially hydrolysable cellulose and hemicellulose.
Pretreatment is an important tool for a cellulose conversion processes, and is essential to change the structure of cellulosic biomass to make cellulose more available to the enzymes that convert the carbohydrate polymers into fermentable sugars [2]. In general, the pretreatment methods can be classified into four different categories: physical, physio-chemical, chemical and biological processes. For the physio-chemical processes like steam explosion or liquid hot water pretreatment, the hemicellulose partially degrades and lignin can be depolymerised. Biological processes with fungi are also able to degrade hemicellulose and lignin. The addition of acidic or alkaline solutions causes lignin to dissolve and hemicellulose to degrade. All pre-treatment processes result in a better accessibility of the substrates for enzymes during a bio gas production. The separation of the hemicellulose from the lignocellulose complex can be affected during the pretreatment with chemicals (water, acid or alkaline solution) or/and by a high temperature. These conditions lead to splitting up the hemicellulose into oligomers and xylose by an auto hydrolysis. The oligomers and xylose are present in solution in the liquid fraction. Compared to other methods, the acid-alkaline pretreatment has several advantages, i.e. simple devices, easy to operate, and high efficiency. Most of the investigations exhibited an increase in methane production and decrease in volatile suspended solids [3]-[4]. The present study aimed to investigate the effect of acid-alkaline pretreatment on pineapple waste for the performance on the anaerobic digestion.

2. Material and methods
The pineapple peel samples were taken from the market and stored at 4 °C. The characteristics is shown in table 1. The acid-alkaline pretreatment was performed by varying pH values from 2 to 12, using HCl and NaOH solutions. The acid or alkaline-solid mixtures were agitated at 250 rpm with the contact time of 24 hrs under an anoxic condition at the ambient temperature. After the acid-alkaline pretreatment, the assay gas production by BMP tests was carried out following the procedure described by reference [5]. Biochemical methane potential (BMP) test was done to determine the biodegradability of the wastes before and after the alkaline pretreatment at the ambient temperature in the batch anaerobic digester for around 20 days.

Table 1 characteristic of pineapple waste in this studied

| Parameter          | Pineapple waste |
|--------------------|-----------------|
| pH                 | 3.89            |
| Moisture Content   | 96.44           |
| Dry matter content, DM (%) | 3.56          |
| Organic dry matter content, ODM (%) | 3.31          |
| Total solids, TS (mg/l) | 37890.00       |
| Total volatile solids, TVS (mg/l) | 34350.00       |
| Total suspended solids, TSS (mg/l) | 28490.00       |
| Total dissolved solids, TDS (mg/l) | 9400.00       |
| COD (mg/l)         | 52923.08        |
| SCOD (mg/l)        | 12923.08        |
| BOD (mg/l)         | 16090.00        |

The acid-alkaline pretreatment influent and effluent samples were analyzed for COD, SCOD, TS and VS following the standard methods for the examination of water and wastewater (APHA, 2005). SCOD was the measurement of COD in the soluble form. The supernatant was collected and filtered with the membrane filter (pore size of 0.45 μm). The filtrate was used to analyze SCOD. The BOD values were determined by an OxiTop®-C measuring pressure head instrument [6]. The SCOD/TCOD ratios were used as an indicator of the soluble capacity to reflect the extent of hydrolysis. Plus, TBOD<sub>20</sub>/TCOD ratios were used to evaluate the WAS biodegradability.

3. Result and discussion
3.1. Effect of acid-alkaline pretreatment on the solubilization and biodegradability

Acid-alkaline pretreatment was performed under various pH values. The overall result of this study is illustrated in Figure 1. The experiments showed that SCOD concentrations increased when pH values were increased. Moreover, the SCOD were about 53.73%, 63.41%, 59.34%, 65.15%, and 67.07% for pH values of 2, 4, 7, 9, and 12, respectively. Compared to a non-pretreatment condition, acid-alkaline pretreatment condition has a higher value of SCOD solubilization. This can be explained by the reason that the acid-alkaline pretreatment condition can improve the characteristics of pineapple waste by transforming the particulate organic fraction to the soluble organic fraction.

Biodegradability performance is indicated by the BOD/COD ratio evaluation. If BOD/COD > 0.45 indicates that the biodegradability is very good; BOD/COD=0.45, the biodegradability is good; BOD/COD = 0.2–0.3, the biodegradability is poor; BOD/COD < 0.2, the biological treatment is unsuitable [7]. The value of biodegradability of raw waste was about 0.304. The BOD/COD ratios increased to 0.439 and 0.473 for pH 7 and pH 9, respectively. However, the BOD/COD ratios decreased for adjusted pH 12.

![Figure 1. Biodegradability performances by acid-alkaline pretreatment](image-url)

3.2. Effect of acid-alkaline pretreatment on solid fraction

Acid-alkaline pretreatment possibly improve the hydrolysis step in the anaerobic process, which can be indicated in the part of solid fraction. The total dissolve solid (TDS) and suspended solid (SS) contents of pineapple waste before and after pretreatment condition are shown in figure 2. In the present research, the solid content was defined on the fraction (%). TDS ratio is often used to represent the transformation of the particulate organic fraction to the soluble organic fraction. A comparison of TDS/TS ratios generally reveals the extent of hydrolysis. The TDS/TS ratios of raw waste increased from 24.8% to 51.4%, 35.7%, 61.2%, 63.7%, and 72.1% for the pH 2, 4, 7, 9, and 12, respectively.

3.3. Effect of acid-alkaline pretreatment on COD fraction

The COD fractionations were evaluated and the results are illustrated in Figure 3. It showed that the slowly biodegradable organic matter was hydrolyzed to the readily biodegradable organic matter and inert soluble organic matter. Readily biodegradable organic substrate (S_R) increased, and the hydrolysis from X_S into S_R and S_I after acid-alkaline pretreatment was observed. For the pretreatment at pH 7 and 9, the readily biodegradable (S_R) increased to 32.0% and 29.0%, respectively, and the slowly biodegradable hydrolysis into the readily biodegradable also increased.
3.4. BMP test
Biochemical methane potential (BMP) test was carried out to determine the biodegradability before and after the acid-alkaline pretreatment under the ambient temperature in the batch anaerobic digester for around 20 days. The removal percentage of TS, VS and COD were used as the indicators of the biodegradability enhancement. It clearly showed that the organic compound removal efficiency
increased when the waste went through the acid-alkaline pretreatment. In figure 4, at pH 7, the removal efficiencies were found to be 76.34%, 91.69% and 84.69% for TS, VS and COD, respectively, which is higher than those of other pH conditions. The acid-alkaline pretreatment has proved to improve the removal efficiency compared to a non-pretreatment. Reference [8] used a municipal waste activated sludge (WAS) for being treated with NaOH to solubilize the particulate organic matter in order to improve its digestibility. The improvement in VS removal for the sludge treated with 40 meq/l of NaOH was as high as 41% over the non-pretreated sample, and the COD removal was improved by 30% over the control.

Due to the pretreatment by HCl and NaOH addition, BMP test was the assay performance of anaerobic digesters. Biochemical methane potential formation from the pretreated waste was evaluated based on BMP test about 20 days. The specific gas production rate increased from 132.05 L/kg of VS for non-pretreatment to 866.75 and 258.82 L/kg of VS for the acid-alkaline pretreatment at pH 7 and 9, respectively shown in figure 5. Increasing gas production at pH 7 could be explained by the fact that the pretreated pine apple waste was hydrolysed the most of organic matter into soluble forms that can be consumed easily and immediately.

![Figure 4. Summaries of efficiency on BMP test](image)

![Figure 5. Gas production rate on BMP test](image)

4. Conclusion

Acid-alkaline pretreatment was performed under various pH values. SCOD concentrations increased when pH values were increased. The value of biodegradability of raw waste was about 0.304. The
BOD/COD ratios increased to 0.439 and 0.473 for pH 7 and pH 9, respectively. However, the BOD/COD ratios decreased for adjusted pH 12. BMP test at pH 7 provided the removal efficiencies of 76.34%, 91.69% and 84.69% for TS, VS and COD, respectively, indicating that the higher efficiency and gas production rate could be achieved at the neutral pH because the pretreated pine apple waste was hydrolysed to produce the soluble forms of organic matter that can be easily and immediately consumed in the anaerobic digestion process.

5. References

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