# Alkaline Pretreatment of Waste Activated Sludge in Anaerobic Digestion

Watcharapol Wonglertarak and Boonchai Wichitsathian

*Abstract*—**Slow degradation of waste activated sludge (WAS) is a disadvantage of anaerobic digestion leading to high sludge retention time in conventional digesters. So, this study was proposed to increase biodegradability of WAS by alkaline pretreatment, and effect of pretreatment on the performance of anaerobic digestion and treatment efficiency was evaluated under both ambient and thermophilic condition. The soluble chemical oxygen demand (SCOD) and biochemical oxygen demand (BOD) fractions increased when pH values were increased. The solubilization had the highest increase in the pH range of 11 to 12 and gradually increased in the pH range of 8-11. However, the $BOD_{20}$/COD ratios decreased for adjusted pH 10 and pH 11, and biodegradation was limited at pH 12. And pH 8 was the optimal value this alkaline pretreatment on anaerobic digestion. In alkaline pretreatment thermophilic anaerobic condition (PTAN), the result remove were 42.16%, 43.15% and 50.64% for TS, VS and COD removal, respectively, which are higher efficiency and gas production when compared to other conditions.**

*Index Terms*—**Waste activated sludge, alkaline pretreatment, anaerobic digestion, thermophilic.**

## I. Introduction

The activated sludge treatment process is one of the most common methods used in a sewage and industry wastewater treatment plant to remove organic contaminants. The large amount of waste sludge, constituting of refractory and non-biodegradable cellulose compounds which is produced by this process, leads to the difficulty of sludge disposal [1]. Anaerobic digestion is a conventional sludge treatment process used to stabilize organic matter. Mass reduction, methane production, and improved dewatering properties of the treated sludge are the main features of the process. Slow degradation of sewage sludge is a disadvantage of anaerobic digestion leading to have a retention time in conventional digesters of about 20-30 days. In order to destroy the refractory structure of waste activated sludge (WAS) and increase its biodegradability, a physio-chemical pretreatment method is commonly carried out to transform particulate compounds contained in WAS into soluble compounds [1]-[3]. Compared with other methods, 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 (VSS), especially during low-dose alkaline treatment [4], [5]. Alkaline destroys floc structures and cell walls by hydroxyl anions. Extremely high pH causes natural shape losing of proteins, saponification of lipid, and hydrolysis of RNA. Chemical degradation of the hydroxyl groups leads to extensive swelling and subsequent solubilization gels in sludge [6]. The preferred reagent, in most cases, is sodium hydroxide (NaOH), which is reported to yield greater solubilization efficiency than calcium hydroxide ($Ca(OH)_2$). Reference [7] used the alkaline pretreatment performed at pH 12 and 30 minutes of contact time by various alkaline agents at ambient temperature. The results showed the soluble COD values were increased about 39.8%, 36.6%, 10.8% and 15.3% for NaOH, KOH, $Mg(OH)_2$ and $Ca(OH)_2$, respectively after added alkaline. Reference [8] reported that the percentages of SCOD to total COD (TCOD) were increased from 3.31% to 36.3% by alkaline pretreatment. Moreover, reference [9] reported the wet electrolytic oxidation pretreatment can be improved biodegradability of WAS. After pretreatment, the BOD/COD ratios were increased to >50% from 6-15% of raw WAS that caused to increase methane yield.

Temperature is one of the most important environmental parameters for anaerobic digestion. With better understanding of the basic mechanisms occurring in the anaerobic process and conducting the process at thermophilic temperatures, many advantages such as higher conversion rate, better pathogen reduction effect, and shorter retention time can be obtained than when it is carried out at mesophilic temperature. This work focused on alkaline pretreatment for anaerobic digestion. The sludge used in the experiments was a waste activated sludge. The process of alkaline sludge disintegration was first examined using NaOH. The variation in sludge pH was investigated during alkaline pretreatment. Based on these data, the parameters of alkaline pretreatment were optimized. Under the proposed conditions, the effect of pretreatment on the performance of anaerobic digestion and treatment efficiency was evaluated under both ambient and thermophilic condition.

## II. Materials and Method

### A. Sludge Samples

The waste activated sludge (WAS) samples were taken from the oxidation ditch wastewater treatment of the Health promoting hospital, a regional health promotion centre 5, Nakhon Ratchasima municipality, Thailand. The WAS samples were stored at 4°C for stabilization components before used in experiments. The WAS characteristics are shown in Table I.

### B. Alkaline Pretreatments

The experiment was performed by varying pH values in

Manuscript received April 13, 2013; revised July 11, 2013.

W. Wonglertarak and B. Wichitsathian are with School of Environmental Engineering, Institute of Engineering, Suranaree University of Technology, Nakhon Ratchasima, Thailand (e-mail: w_watcharapol@hotmail.com, boonchai@sut.ac.th).

ranges of 8 to 14, and using NaOH adjusted as the semi-concentration, detailed in Table II. Then, the WAS and NaOH mixtures were agitated at 250 rpm with contact times 24 hr under anoxic condition at ambient temperature. The solubilization of the organic substances in the WAS was measured using soluble chemical oxygen demand (SCOD). The degree of sludge disintegration was calculated as the ratio of increase in SCOD. And $TBOD_{20}/TCOD$ ratios were used to evaluate the WAS biodegradability.

### C. Anaerobic Digestions

The experimental set up consisted of four continuous stirred tank reactors (CSTR) with 20L working volume for each, two of which were under thermophilic condition and the other two were under ambient conditions. The temperature was controlled by circulating hot water inside the reactor water jacket from water bath maintained at 55 $^{o}C$ for thermophilic reactor. The hydraulic retention time was set at 21 days. Reactors were fed and withdrawn once a day. The influent and effluent samples of alkaline pretreatment analyzed following the standard methods [10] for the examination of water and wastewater included COD, SCOD, TS and VS. The BOD was determined by an OxiTop®-C measuring pressure head instrument [11]. Biogas production was measured by water displacement method.

TABLE I: WASTE ACTIVATED SLUDGE (WAS) CHARACTERISTICS

| Parameters | Values |
|---|---|
| pH | 7.8 ± 0.2 |
| COD (mg/l) | 10615 ± 1020 |
| $BOD_{20}$ (mg/l) | 2050 ± 640 |
| TS (mg/l) | 11720 ± 2273 |
| VS/TS | 0.52 |
| TKN (mg/l as N) | 450 ± 52 |
| Total alkalinity (mg/l as $CaCO_3$) | 470.4 ± 17 |

TABLE II: THE ADJUSTED NAOH CONCENTRATIONS FOR SUFFICIENT THE PH VALUES

| Condition at pH | g NaOH/$m^3$ wet sludge | Condition at pH | g NaOH/$m^3$ wet sludge |
|---|---|---|---|
| Untreated | 0 | 11.0 | 472 |
| 8.0 | 8 | 12.0 | 1,576 |
| 9.0 | 88 | 13.0 | 11,000 |
| 10.0 | 232 | 14.0 | 31,000 |

## III. RESULTS AND DISCUSSION

### A. The Effect of Alkaline Pretreatment on WAS

Alkaline pretreatment was performed under various pH values. The overall result of this study is illustrated in Fig. 1. For experiments with various pH values, the overall result showed that SCOD concentrations increased when pH values were increased. This can be explained by SCOD expressing various reactions when being adjusted pH values such as saponification of uronic acid and acetyl ester, the reactions occurring with free carboxylic groups and neutralization of various acid formed from the degradation. Moreover, the SCOD were about 1.99%, 2.28%, 2.58%, 3.23%, 16.35%, 32.34% and 33.29% for pH values of 8, 9, 10, 11, 12, 13 and 14, respectively. As same as, the result of several researches such as, reference [7] improved the WAS solubility to increase in 39.8% of SCOD by NaOH adjusted treatment for 3.8 % of TS of raw WAS; reference [12] improved the WAS solubility to >65% of SCOD by NaOH adjusted treatment for 5.6% of TS of raw WAS and reference [4] reported the soluble fraction increased to >50% of TS for WAS 1.2 % of TS that pretreated by NaOH 40 meq/L. It can be concluded that the soluble fraction decreased when TSS concentration of WAS and NaOH concentrations were increased [1].

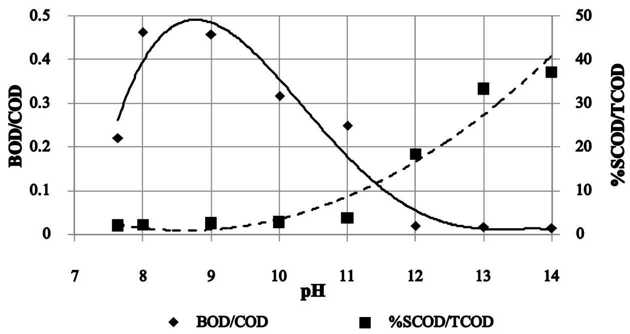


Fig. 1. Biodegradability performances by alkaline pretreatment.

Biodegradability performance is indicated by the results of biodegradability test by $BOD_{20}/COD$ ratio evaluation with varying pH values and 24 hr of contact time. The value of biodegradability of raw WAS was about 0.22. The $BOD_{20}/COD$ ratios increased to 0.46 and 0.45 for pH 8 and pH 9, respectively. However, the $BOD_{20}/COD$ ratios decreased for adjusted pH 10 and 11, and biodegradation was inhibited at pH 12. This can be explained by the metabolism of microorganism, which was inhibited at pH higher than 9 [12], [13]. Hydrolysis of organic matter is limited at high sodium hydroxide concentration [12]. As the result, $BOD_{20}/COD$ ratios were less than 0.05 when adjusted pH values were in the range of 12 to14. Sodium hydroxide at low concentration is essential for the methanogenic bacteria presumably because it is important for the formation of ATP or oxidation of NADH. However, high concentration of sodium ion was inhibits the activity of the microorganisms and interferes with their metabolism. The level of inhibition depends on the concentration found in the sludge. The optimal growth condition of hydrogenotrophic methanogens occurs at concentration of 350 mg $Na^{+}$/L. Moderate inhibition is at the concentrations between 3,500 and 5,500 mg/L, whereas the concentration about 8,800 mg/l is strongly inhibitory to methanogenic bacteria during mesophilic digestion [2], [13].

In conclusion, the waste activated sludge (WAS) with highly slowly degradation is a disadvantage of anaerobic digestion or conventional digesters. Alkaline pretreatment is capable of improving WAS biodegradability by increasing organic solubility fraction or soluble chemical oxygen demand (SCOD). The SCOD increased when pH was increased. However, the $BOD_{20}/COD$ ratios decreased for adjusted pH 10 and pH 11, and biodegradation was limited at pH 12. This caused by inhibition of the metabolism of microorganism at pH higher than 11. And, the result indicated that 8 was the optimal value for alkaline pretreatment on anaerobic digestion.

### *B. The Effect of Alkaline Pretreatment on Anaerobic Digestion*

To verify the effectiveness of alkaline pretreatment process, the percent removal of TS, VS and COD were used as the indicator of the biodegradability enhancement. In past thermophilic temperature condition, alkaline pretreatment thermophilic anaerobic condition (PTAN) removed 42.16%, 43.15% and 50.64% for TS, VS and COD, respectively. In thermophilic anaerobic condition (TAN), it removed 38.42%, 38.71% and 42.88% for TS, VS and COD, respectively, which indicated that it had lower efficiency than PTAN.

In past ambient temperature condition, alkaline pretreatment anaerobic condition (PAN) had higher removal efficiency for TS, VS and COD than anaerobic condition (AN) with the same past thermophilic temperature condition. PAN had removal efficiency of 36.92%, 35.94% and 38.41% for TS, VS and COD, respectively. For AN reactor, it removed 33.61%, 32.11% and 36.51% for TS, VS and COD, respectively. The overall result of this study is illustrated in Fig. 2.

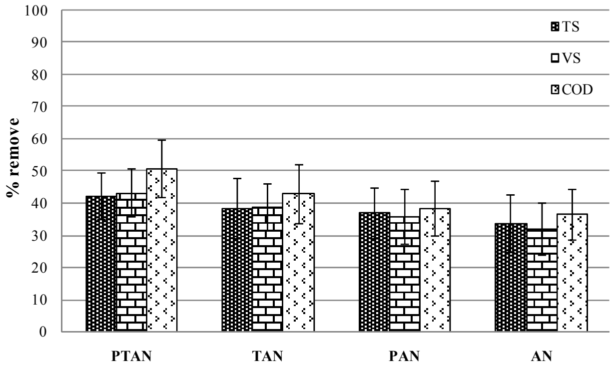


Fig. 2. Variations of efficiency remove organic matter on anaerobic condition.

Gas production shown in Fig. 3 was 84.22, 78.24, 72.46 and 61.09 ml/d for PTAN, TAN, PAN and AN, respectively. Alkaline pretreatment condition had an increase in gas production because that pretreated WAS hydrolyzed much organic matter into soluble forms, and the anaerobic digestion process use it immediately consumed. Alkaline pretreatment could make organic matter release from inner fractions to outer fractions, thus increase the hydrolysis rate of granular organics and improve digestion efficiency [14]. PTAN and PAN reactors had greater rate of gas production than TAN and AN reactors. The fractional increase in gas production of PTAN and PAN was 7.64% and 18.61% when compared to TAN and AN, respectively.

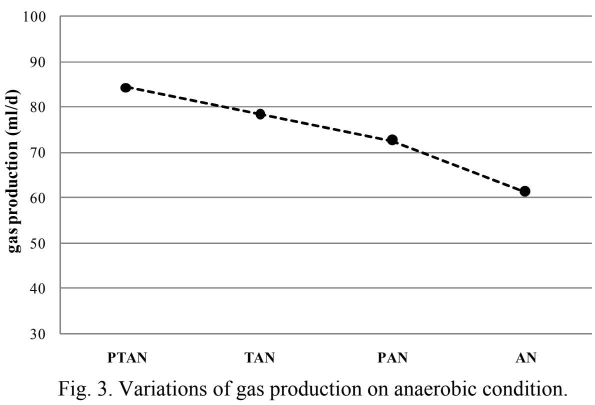


Fig. 3. Variations of gas production on anaerobic condition.

From data, fractional increase in gas production of comparison between PTAN and TAN was less than that of comparison between PAN and AN, but removal efficiency for remove COD in PTAN compared to TAN was increase by 18.09%, which was more than that (5.20%) in PAN compared to AN. So, in past thermophilic condition, alkaline pretreatment increased removal efficiency for organic matter and slightly increased in gas production. For ambient temperature condition, alkaline pretreatment showed increase of removal efficiency for organic matter and gas production. Reference [4] showed that alkaline pretreatment, an improvement of digester to have high performance compared to that without alkaline pretreatment at ambient temperature and HRT 20 days, can remove 36% of VS and produce gas production by 113 $l/m^3_{reactor}$. Reference [15] reported that adjusting pH values (9-12) of WAS with comparison to the control (without adjusting pH), provided an increase in removal of TSS and VSS following pretreatment at pH 9-11, and improved gas production by 7.2-15.4%. Reference [16] showed that NaOH was used to disintegrate a mixture composed mainly of primary sludge with biofilm sludge before anaerobic digestion in batch experiments, NaOH pretreatment dissolved some organic substance, and with dose 0.1 mol/l of NaOH, the oganic degradation rate was 38.3% and the gas production was 0.65 $l/g_{VSS}$.

For the effect of temperature on anaerobic digestion, thermophilic and mesophilic condition, it was found that thermophilic anaerobic digestion was much faster than mesophilic anaerobic digestion. Two conditions on pretreatment and non-pretreatment in this study showed that PTAN and TAN had higher removal efficiency for organic matter, and gas production. In thermophilic anaerobic digestion, waste activated sludge with thermal lysis of microbial cell was the dominant mechanism resulting in high degradation rate. Reference [17] showed that performance of the reactor improved with increases in temperature and with HRT 20 days. The COD removal increased from 35% in mesophilic condition to 45% in thermophilic condition, and gas production were 0.33 to 0.45 $m^3/kg_{VSfed}$ at mesophilic and thermophilic condition, respectively.

## IV. Conclusion

Alkaline pretreatment has capability to improve WAS biodegradability by increasing organic solubility fraction or soluble chemical oxygen demand (SCOD). The SCOD increased when pH values were increased. However, the $BOD_{20}$/COD ratios were decreased for adjusted pH 10 and pH 11. Adjusted pH 8 showed the optimization for alkaline pretreatment with increasing SCOD and maximizing $BOD_{20}$/COD ratios.

In alkaline pretreatment, thermophilic anaerobic condition (PTAN) removed 42.16%, 43.15% and 50.64% for TS, VS and COD, respectively, and provided higher efficiency and gas production when compared to other conditions. Regarding the effect of temperature on anaerobic digestion, thermophilic and ambient condition, and alkaline pretreatment and non-alkaline pretreatment, it showed that PTAN and TAN reactors had higher removal efficiency for organic matter and gas production compared to PAN and AN reactors.

## ACKNOWLEDGMENT

This work was supported by National Research Council of Thailand and Suranaree University of Technology and Thailand Institute of Scientific. We would like to thank the staff for their continual assistance in preparing and carrying out this research in the Institute of Environmental Engineering, Suranaree University of Technology.


## REFERENCES


[1] C. N. Chang, Y. S. Ma, and C. W. Lo, "Appication of oxidation-reduction potential as a controlling parameter in waste activated sludge hydrolysis," *Chemical Engineering Journal*, vol. 90, pp. 273-281, 2002.

[2] I. A. Nges and J. Liu, "Effects of anaerobic pre-treatment on the degradation of dewatered-sewage sludge," *Renewable Energy*, vol. 34, pp. 1795-1800, 2009.

[3] J. G. Lin, Y. S. Ma, A. C. Chao, and C. L. "Huang, BMP test on chemically pretreated sludge," *Bioresource Technology*, vol. 68, pp. 187-192, 1999.

[4] J. G. Lin, C. N. Chang, and S. C. Chang, "Enhancement of anaerobic digestion of waste activated sludge by alkaline solubilization," *Bioresource Technology*, vol. 62, pp. 85-90, 1997.

[5] L. Appels, J. Baeyens, J. Degreve, and R. Dewil, "Principles and potential of the anaerobic digestion of waste-activated sludge," *Progress in Energy and Combustion Science*, vol. 34 pp. 755-781, 2008.

[6] J. Yinying, L. Huan, M. P. Bux, W. Zhiyu, and N. Youngfeng, "Combined alkaline and ultrasonic pretreatment of sludge before aerobic digestion," *Journal of Envirnmental Science*, vol. 21, pp. 279-284, 2009.

[7] J. Kim, C. Park, T. H. Kim, M. Lee, S. Kim, S. W. Kim, and J. Leej, "Effects of Various Pretreatments for Enhanced Anaerobic Digestion with Waste Activated Sludge," *Journal of Bioscince and Bioengineering*, vol. 95, pp. 271-275, 2003.

[8] Y. C. Chu, C. N. Chang, J. G. Lin, and S. J. "Huang, Alkaline and ultrasonic pretreatment of sludge before anaerobic digestion," *Water science and technology*, vol. 36, pp. 155-162, 1997.

[9] R. M. Serikawa, "Wet electrolytic oxidation of organic sludge," *Journal of Hazardous Materials*, vol. 146, pp. 646-651, 2007.

[10] A. P. H. A, A. W. W. A., and W. E. F., "Standard methods for the examination of the water and wastewater," *Washington D.C.: American Public Health Association*, 2005.

[11] M. N. Gatti, F. G. Usach, A. Seco, J. Ferrer, "Wastewater COD characterization: analysis of respirometric and hysical-chemical methods for determining biodegradable organicmatter fractions," *J Chem Technol Biotechnol,* vol. 85, pp. 536-544, 2010.

[12] V. Penaud, J. P. Delgene`s, and R. Moletta, "Thermo-chemical pretreatment of a microbial biomass: influence of sodium hydroxide addition on solubilization and anaerobic biodegradability," *Enzyme and Microbial Technology*, vol. 25, pp. 258-263, 1999.

[13] Y. Chen, J. J Cheng, and K. S. Creamer, "Inhibition of anaerobic digestion process: A review," *Bioresource Technology*, vol. 99, pp. 4044-4064, 2008.

[14] L. Zhang and D. Jahng, "Enhanced anaerobic digestion of piggery wastewater by ammonia stripping: Effects of alkali types," *Journal of Hazardous Materials*, vol. 182, pp. 536-543, 2010.

[15] L. Shao, X. Wang, H. Xu, and P. He, "Enhanced anaerobic digestion and sludge dewaterability by alkaline pretreatment and its mechanism," *Journal of Environmental Sciences*, vol. 24, pp. 1731-1738. 2012.

[16] H. Li, C. Li, W. Liu, and S. Zou, "Optimized alkaline pretreatment of sludge before anaerobic digestion," *Bioresource Technology*, vol. 123, pp. 189-194, 2012.

[17] D. Bolzonella, C. Cavinato, F. Fatone, P. Pavan, and F. Cecchi, "High rate mesophilic, thermophilic, and temperature phased anaerobic digestion of waste activated sludge: A pilot scale study," *Waste Management*, vol. 32, pp. 1196-1201, 2012



**Watcharapol Wonglertarak** follows a Bachelor's Degree in Environmental Engineering. And now is a graduate student in Environmental Engineering of Suranaree University of Technology, Nakhon Ratchasima, Thailand. My researches interested are in biological wastewater treatment.