Combined Alkaline and Recirculation Pretreatment on Waste Activated Sludge (Was) Stabilization

Patcharin Racho

***Abstract*—** Experiments were carried out via batch reactor that proposed to preliminary study and experimental on pilot scale of two stage anaerobic digestion with combined alkaline and recirculation as a pretreatment. The value of raw WAS biodegradability was about 0.08. After adjusted pH by $Ca(OH)_2$, the BOD20/COD ratios were increased where pH increase but the biodegradation was inhibited at pH 12. This can be explained by high concentrations of calcium ion was inhibited the activity of the microorganisms and interfere with their metabolism. The level of inhibition depends on the concentration found in the sludge. In order to inhibit the calcium ion toxicity during anaerobic digester. Recirculation of the anaerobic effluent supplied sufficient bicarbonate alkalinity for crystallization or calcium precipitation before methanogenic reactor. Consequently, the pilot scale of two stage anaerobic digester with the pretreatment were evaluated at hydraulic retention times of 10 days. The first-stage digesters were operated with proposes of sludge disintegration. The BOD5/COD ratios in reactors were higher than that of control reactor at the end of 100 days. These second-stage digester was conducted to methane production. Finally, in order to see the combined pretreatment effect in continuous operation, the sludge pretreated with high intensity alkaline (pH 12) and effluent recirculation for salt concentration toxicity reduction was fed to an anaerobic sequencing batch reactor (2nd stage). The production of methane increased by more than 35.3% and soluble COD (SCOD) removal also increased by more than 69.2% over the control. Therefore, it is recognized that higher digestion efficiencies of the WAS were obtained through alkaline and recirculation pretreatment.

***Keywords*—**Waste Activated Sludge (WAS); Sludge Stabilization; Alkaline and Recirculation Pretreatment; Biogas Production

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]. In the field of sludge treatment, the terms pretreatment, co-treatment, disintegration and hydrolysis usually refer to processes which are combined with the main biological sludge treatment process. The objectives of the overall treatment train is to remove organic material and water, hence reducing volume and mass, remove degradable material, which prevents subsequent odors and pathogen vectors, and remove pathogens. Anaerobic digestion is a favored stabilization method compared to aerobic digestion, due to its lower cost, lower energy footprint, and moderate performance, especially for stabilization. Co-treatment processes aim at enhancing the main anaerobic digestion processes by altering physical or chemical properties. The two basic properties that determine sludge behavior are degradation rate (often defined by a 1st order coefficient), and extent, or conversely, inert fraction. Co-treatment processes may change either property, and can be located in a number of places in the treatment plant. In the case of main treatment plant enhancement, the main process is manipulated to provide improved degradability. Changes in either kinetic degradation rate or degradability will enhance gas production and anaerobic digester performance. Improving rate can also allow process intensification, with the faster kinetics allowing for the same performance in a smaller digester, and thus decreasing hydraulic retention time (HRT) [2].

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 the particulate compounds contained in WAS into soluble compounds [1, 3, 4]. The chemical pretreatment is too efficient and cost-effective that capable in ambient temperature. 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 ionization of the hydroxyl groups lead to extensive swelling and subsequent solubilization gels in sludge [5]. Kim et al. [6] who used the alkaline pretreatment were performed at pH 12 and 30 minutes of contact time by various alkaline agents at ambient temperature. Those 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. As well as Chui et al. [7] reported that the percentages of SCOD to total COD (TCOD) were increased from 3.31% to 36.3% by alkaline pretreatment. $Ca(OH)_2$ pretreatment for WAS has an attractive because it lower cost than the other alkaline. However, the metabolism of microorganism were inhibited when high values of salt concentration in WAS. $Ca(OH)_2$ pretreatment for WAS causing of high calcium concentrations. Problems due to accumulation of calcium carbonate in anaerobic

Patcharin Racho is with the school of environmental engineering, Institute of Engineering, Suranaree University of Technology, Nakhon Ratchasima, 30000, Thailand (corresponding author's phone: 66044224565; e-mail: patcha@sut.ac.th).

reactors can be avoided by applying a crystallization reactor to remove calcium from the influent. The possibility of reusing the produced alkalinity by anaerobic effluent recirculation was investigated in this research. Calculations and experiments were carried out to investigate to what extent calcium could be removed from the alkaline pretreatment sludge before feed to anaerobic reactor. Also, this study has attractive to investigate the effect of $Ca(OH)_2$ pretreatment on WAS biodegradability. As well as, the solution for salt concentration toxicity reduction by carbonate recirculation.

II. MATERIAL AND METHODS

A. Waste activated Sludge (WAS)

The waste activated sludge (WAS) samples were taken from the secondary sedimentation of activated sludge wastewater treatment in a food factory. The WAS samples and anaerobic effluents were stored at 4^oC for stabilization components before used in experiments. The WAS characteristics are shown in Table 1.

B. Batch Test of Alkaline and Carbonate Recirculation Pretreatment

Alkaline and carbonate recirculation pretreatment investigation were devised into two main parts study. Firstly, the experimental were performed by $Ca(OH)_2$ adjustment via pH value variation in ranges of 8, 9, 10, 11 and 12 for soluble fraction and biodegradability evaluation. Also, the contact times were varied by values of 0.25, 0.5, 1, 3, 6, and 12 h, respectively under anoxic condition and ambient temperature. Secondly, the influencing of recirculation on calcium precipitation and toxicity reduction were evaluated by WAS to anaerobic effluent ratio variation as details in Table 2.

TABLE I
WASTE ACTIVATED SLUDGE CHARACTERISTICS

Parameters	Unit	WAS
pH	-	5.1-6.9
TCOD	mg/L	7,157-9,566
SCOD	mg/L	94-296
BOD 20 days	mg/L	646-780
TS	mg/L	6,273-8,420
VS/TS	mg/L	0.46
TKN	mg/L	52-650
Total Alkalinity	mg/L as $CaCO_3$	119-564

TABLE II
PROCESS CONDITIONS FOR THE BATCH TEST REACTORS

Process conditions	Recirculation Ratios		pH adjustments
	WAS (mL)	Anaerobic Effluent (mL)	
R1	100	100	-
R2	150	50	-
R3	50	150	-
R4	100	100	pH 12
R5	150	50	pH 12
R6	50	150	pH 12
R7	200	-	pH 12

C. Hydrolysis Kinetics

At constant temperature and pH, the rate of hydrolysis is a first-order function for the conversion of particulate biomass to utilizable soluble substrate. In this study a first-order rate expression of the degradable particulate COD, was tested, according to the following expression [8]:

$$\frac{d(COD)}{dt} = k(COD_\infty - SCOD) \quad (1)$$

Where SCOD = soluble COD concentration, mg/L; PCOD = particulate COD concentration, mg/L; COD_{nh} = nonhydrolyzable COD_p concentration, mg/L; COD_∞ = maximum theoretical soluble COD, mg/L =P COD) COD_{nh}; k = first-order hydrolysis rate constant, h^{-1}.

In the above equation, the two unknown parameters, k and COD_∞ can be determined by the method of nonlinear curve fitting of experimental data especially for this type of differential equation. According to this method the experimental quantities of (t) and $(t/CODs^{1/3})$ have linear relationship: $(t/CODs^{1/3})$ = A+B(t). The constants A and B are determined from experimental data using a conventional linear regression method. After this, the COD_∞ and k are estimated according to the following equations: $COD_\infty = 1/(6A^2B)$ and k = 4.8387B/A.

D. Two stage anaerobic digester experimental set up

The two stage completed mixed anaerobic digester were operated at 10 days of retention time. The 1st stage of anaerobic digestion experiments were carried out in two stainless steel cylinders with an effective volume of 15 L each. The first stage reactor was filled with WAS sample, and the chemical pretreated sludge and adjusting the sludge pH to 12. Then the effluent of the 1st stage was fed to the 2nd stage of anaerobic digester and the 30% of 2nd stage effluent was recirculation to the 1st stage as the details was shown in Figure 1.

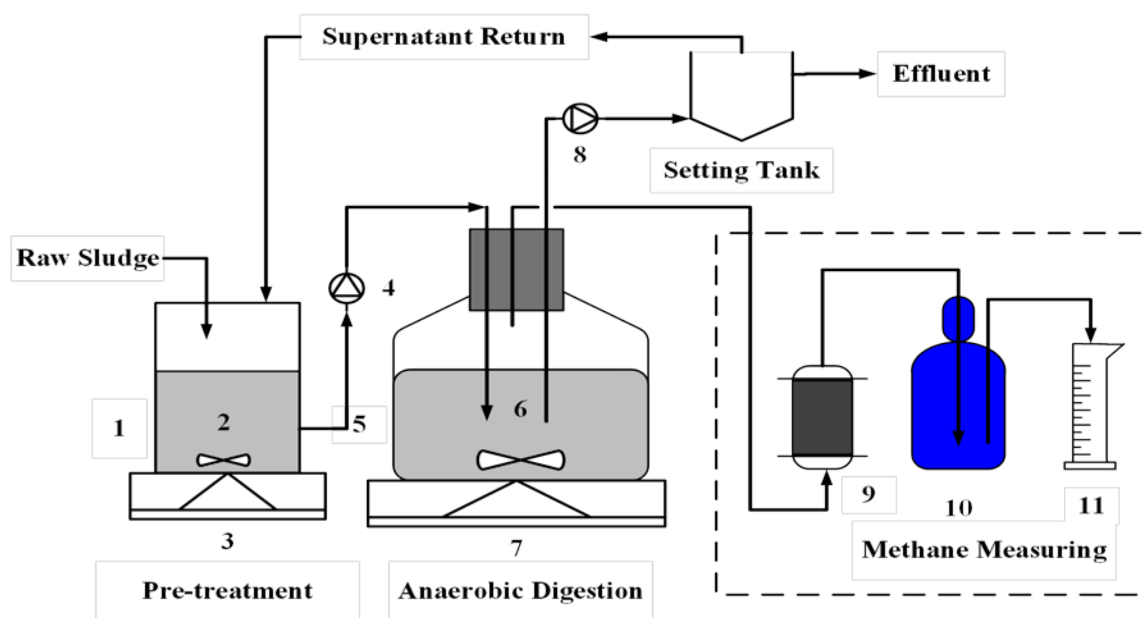

Fig. 1. Two stage anaerobic digester experimental set up

E. Analytical methods

The influent and effluent samples of alkaline and carbonate recirculation pretreatment were analyzed following the standard methods [9] for the examination of water and wastewater including of COD, SCOD, TS, VS, TKN and total alkalinity. The BOD values were determined by an OxiTop®-C measuring pressure head instrument [10]. The SCOD/TCOD ratios were indicating parameter for capable of solubility that to reflect the extent of hydrolysis. As well as, $TBOD_{20}$/TCOD ratios were used to evaluated the WAS biodegradability.

III. BATCH TEST EXPERIMENTS

A. $Ca(OH)_2$ Enhanced SCOD Fractionations

Alkaline pretreatment were performed under various pH values and contact times. The overall results of this study are illustrated in Table 3. That showed SCOD increased during pH values and contact times were increase. $Ca(OH)_2$ can disintegrate the sludge. After 30 min $Ca(OH)_2$ treatment, sludge SCOD increased from 296 mg/L to 573 mg/L, 613 mg/L, 773 mg/L, 981 and 1,240 mg/L with the pH values of 8, 9, 10, 11 and 12, respectively. The results showed that soluble organic matters decreased gradually when $Ca(OH)_2$ increase. Similar results were also reported. The effect of $Ca(OH)_2$ treatment duration on sludge disinteAgration is also shown in Figure 2. The increase of SCOD can be divided into two stages: an initial rapid stage of 30 minutes and a subsequent slow stage. The similar duration of the first stage can also be found in other papers [1, 2, 5, 6]. In first 30 min, the solubilization quantity was 70–85% of total solubilized organic matters in 12 h. So most efficient treatment duration was 30 min.

B. Hydrolysis Kinetics

Experimental data related to SCOD concentrations and pH values during hydrolysis process are given in Figure 3. An increase of soluble COD concentration as well as a increase of the pH values. For all the hydrolysis conditions, a rapid increase of SCOD was observed during the first hour. Then a decreasing rate on the SCOD production was observed until the maximum value was reached. However, for more intensive hydrolysis conditions (pH ≥ 10) the COD solubilization increased significantly until the 5th hour of hydrolysis, where about >80% of the solubilization had been achieved.

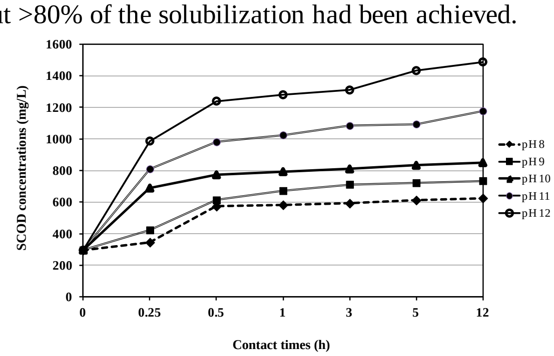

Fig. 2 Variation of sludge SCOD with duration time during $Ca(OH)_2$ treatment.

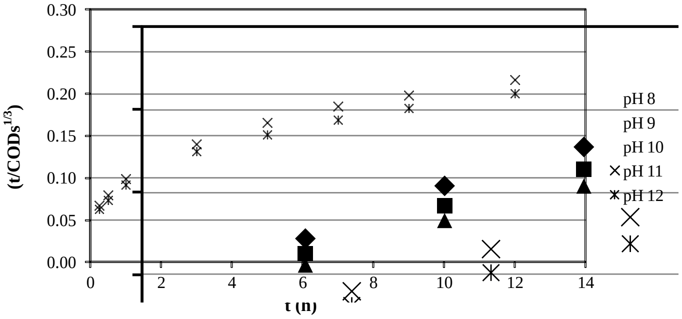

Fig. 3 The experimental quantities of (t) and ($t/CODs^{1/3}$)

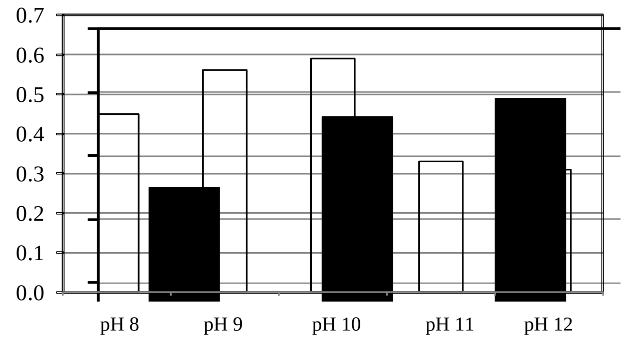

Fig. 4 The BOD_{20}/COD profiles of WAS after adjusted pH

TABLE III
CALCULATION OF THE HYDROLYSIS RATE CONSTANT K AND THE THEORETICAL UPPER LIMIT OF SOLUBLE COD

pH	A	B	Maximum theoretical soluble COD ($COD\infty$; mg/L)	Hydrolysis rate, k (h^{-1})	r^2
8	0.0987	0.0140	1,222.04	0.6863	0.9266
9	0.0987	0.0140	1,222.04	0.6863	0.9266
10	0.0908	0.0138	1,464.87	0.7353	0.9106
11	0.0843	0.0121	1,938.24	0.6945	0.9075
12	0.0785	0.0111	2,436.61	0.6841	0.9075

D. Biodegradability Performances

The BOD_{20}/COD ratios were evaluated during pH values varying and 5 h of contact time as the results shown in Figure 4. The BOD_{20}/COD ratio of raw WAS was about 0.08. After adjusted pH, the BOD_{20}/COD ratios were increased to 0.52 and 0.59 of pH 8 and pH 9, respectively. However, the BOD_{20}/COD ratios were decreased during adjusted pH 10 and pH 11 and biodegradation was inhibited at pH 12. This can be explained by the metabolism of microorganism were inhibited at the higher values than pH 9 [1, 11].

Hydrolysis of organic matter was limited at high calcium hydroxide concentration [11]. As results of BOD_{20}/COD ratios were less than 0.05 when adjusted pH values in ranges of 12 to14. Calcium 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 concentrations of calcium ion was inhibited the activity of the microorganisms and interfere with their metabolism. The level of inhibition depends on the concentration found in the sludge. Very little is known about the toxicity of Ca2+ in the anaerobic system. Jackson-Moss et al. [12] observed that Ca^{2+} concentrations of up to 7,000 mg/L had no inhibitory effect on anaerobic digestion. A large proportion of the Ca^{2+} passed through the digester and was present in the effluent. Theses reported a much lower toxicity threshold. They showed that the optimum Ca^{2+} concentration for methanation of acetic acid was 200 mg/L. Ca^{2+} was moderately inhibitory at a concentration of 2,500–4,000 mg/L, but was strongly inhibitory at a concentration of 8,000 mg/L [2, 11, 12].

C. Calcium Precipitation and Alkaline Toxicity Reduction Potential

Calcium hydroxide can be improved the SCOD fraction but high calcium ion can be inhibited the microorganism activity. In this study, the possibility of reusing the produced alkalinity by recirculation anaerobic effluent was investigated. Calculations and experiments were carried out to investigate to what extent calcium could be removed from the influent. Experiments were carried out in batch test study. The influent contained up to 2,815 mg/L as $CaCO_3$ during the adjusted pH to 12, condition. Removal of calcium from the influent could be successfully accomplished as the result results showed in Table 4. Recirculation of the anaerobic effluent supplied sufficient bicarbonate alkalinity for crystallization. Consequently, no extra chemicals (i.e. Na_2CO_3 and/or NaOH) were needed. A chemical equilibrium model, with adapted pseudo solubility products, is a very useful tool to determine the proper recycle ratio of effluent for optimal performance.

IV. TWO STAGE ANAEROBIC DIGESTION EXPERIMENTS

The ability of chemical and recirculation pre-treatment to solubilize or remove particulate organic matter has been demonstrated by the experiments in the first part of the paper, the comparison and analysis of the treated sludge anaerobic biodegradability were required to optimize the coupling process of alkaline and recirculation pre-treatment and biodegradation.

A. COD and VSS Removal

The alkaline and recirculation pre-treatment was carried out in the following conditions: sludge concentration were about 7.0-9.0 g/L, pH 12.0 fed into the 1st anaerobic digester (1st AD). Results of the first stage of experiments on COD degradation and VSS removal are shown in Table 5, where the residual COD and VSS are represented. Table 5 shows the changes in characteristics of sludge samples after alkaline and recirculation pre-treatment. Since a small portion of the organic solids was degraded or solubilized into the supernatant after the pre-treatment, the initial TS and TCOD concentrations of sludge samples after the pre-treatment were slightly lower than the control samples but different, and their reduction percentages were 32-39% and 12-15%, respectively. These shows higher performances when compared to the control unit of two stage anaerobic digester without alkaline and recirculation pre-treatment (Control AD) [13, 14, 15, 16, 17].

B. Biogas generation

Biogas production from WAS by 2nd stage anaerobic digestion with alkaline and recirculation pre-treatment was investigated. The results showed that the methane yield of 2nd AD with alkaline and recirculation pre-treatment higher than the control AD about 2 times during operation periods of 100 days. These can be concludes of alkaline can be improved the chemical hydrolysis efficiency and reducing that toxic by supernatant recirculation.

V. Conclusions

Adjusted pH by $Ca(OH)_2$, the BOD20/COD ratios were increased where pH increase but the biodegradation was inhibited at pH 12. This can be explained by high concentrations of calcium ion was inhibited the activity of the microorganisms and interfere with their metabolism. The level of inhibition depends on the concentration found in the sludge. In order to inhibit the calcium ion toxicity during anaerobic digester. Recirculation of the anaerobic effluent supplied sufficient bicarbonate alkalinity for crystallization or calcium precipitation before methanogenic reactor. Consequently, of 2nd AD operation with alkaline and recirculation pre-treatment can improved the biogas yield more 2 times than the control AD.

TABLE IV
COD FRACTIONATION AND CALCIUM PRECIPITATION PERFORMANCES

Process conditions	Concentrations (mg/L)					Concentrations (mg/L as $CaCO_3$)	
	TS	TSS	TDS	TCOD	SCOD	Alkalinity	Ca-Hardness
R1	9,945	8,280	1,665	469	88	2,565	360
R2	9,280	8,110	1,170	352	205	2,270	400
R3	10,825	8,270	2,555	352	205	2,955	580
R4	14,525	10,090	4,435	2,053	1,906	2,600	455
R5	13,340	9,630	3,710	3,520	2,346	3,480	790
R6	14,605	11,410	3,195	3,285	2,053	1,850	245
R7	12,355	8,450	3,905	4,106	2,698	2,680	2,815

TABLE V
CHARACTERISTICS OF SLUDGE AFTER TWO STAGE ANAEROBIC DIGESTION (AD)

Parameter	Unit	Influent	Effluent		
			Control AD	1st AD	2nd AD
pH	-	5.1-6.9	5.6-7.0	11-12	7.6-8.4
TCOD	mg/L	7,157-9,566	6,440-8,418	6,080-7,418	4,294-5,165
SCOD	mg/L	94-296	125-350	567-750	234-456
TS	mg/L	6,273-8,420	5,520-7,409	4,205-5,109	3,261-4,041
TDS	mg/L	410-820	356-765	1,356-2,765	1,244-1,840
TKN	mg/L	52-650	123-567	223-467	183-367
VFA	mg/L	45	150-186	50-300	200-300
TP	mg/L	10-19	6-13	10-14	8-12
Methane Yield	(L/kg-VS)	-	143-150		245-284

Consequently, 2nd Stage anaerobic digester (2nd AD) showed higher removal efficiency from the very beginning of digestion. During 100 days of digestion operation, TS and TCOD removed about 48-52% and 40-46%, respectively at 10 days of retention time. Therefore, alkaline and recirculation pre-treatment could significantly enhance sludge biodegradability and anaerobic digestion efficiency.

ACKNOWLEDGMENT

The authors would like to express their sincere gratitude to the National Research Council of Thailand (NRCT) and Suranaree University of Technology for funding this research.

REFERENCES

[1] Chang, C.N., Ma, Y.S. and Lo, C.W. (2002). Appication of oxidation-reduction potential as a controlling parameter in waste activated sludge hydrolysis. Chemical Engineering Journal 90: 273-281. http://dx.doi.org/10.1016/S1385-8947(02)00015-3

[2] Appels, L., Baeyens, J., Degreve, J., Dewil, R. (2008). Principles and potential of the anaerobic digestion of waste-activated sludge. Progress in Energy and Combustion Science 34: 755–781. http://dx.doi.org/10.1016/j.pecs.2008.06.002

[3] Lin, J.G., Chang, C.N. and Chang, S.C. (1997). Enhancement of anaerobic digestion of waste activated sludge by alkaline solubilization. Bioresource Technology 62: 85-90. http://dx.doi.org/10.1016/S0960-8524(97)00121-1

[4] Lin, J.G., Ma, Y.S., Chao, A.C. and Huang, C.L. (1999). BMP test on chemically pretreated sludge. Bioresource Technology 68: 187-192. http://dx.doi.org/10.1016/S0960-8524(98)00126-6

[5] Yinying, J., Huan, L., Bux, M. P., Zhiyu, W. and Youngfeng, N. (2009). Combined alkaline and ultrasonic pretreatment of sludge before aerobic digestion. Journal of Envirnmental Science 21: 279-284.

[6] Kim, J., Park, C., Kim, T.H., Lee, M., Kim, S., Kim, S.W. and Leej, J. (2003). Effects of Various Pretreatments for Enhanced Anaerobic Digestion with Waste Activated Sludge. Journal of Bioscince and Bioengineering 95: 271-275. http://dx.doi.org/10.1016/S1389-1723(03)80028-2

[7] Chu, Y.C., Chang C.N., Lin, J.G. and Huang, S.J. (1997). Alkaline and ultrasonic pretreatment of sludge before anaerobic digestion. Water science and technology 36: 155-162. http://dx.doi.org/10.1016/S0273-1223(97)00681-1

[8] Vlyssides, A.G.., P.K. Karlis. (2004). Thermal-alkaline solubilization of waste activated sludge as a pre-treatment stage for anaerobic digestion. Bioresource Technology 91: 201-206. http://dx.doi.org/10.1016/S0960-8524(03)00176-7

[9] APHA, AWWA, and WEF. (2005). Standard methods for the examination of the water and wastewater. Washington D.C.: American Public Health Association.

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

[11] Chen, Y., Cheng, J.J., Creamer, K.S.(2008). Inhibition of anaerobic digestion process: A review. Bioresource Technology 99: 4044–4064. http://dx.doi.org/10.1016/j.biortech.2007.01.057

[12] Jackson-Moss, C.A., Duncan, J.R., Cooper, D.R., 1989. The effect of calcium on anaerobic digestion. Biotechnol. Lett. 11 (3), 219–224. http://dx.doi.org/10.1007/BF01026064

[13] Kugelman, I.J., McCarty, P.L., 1964. Cation toxicity and stimulation in anaerobic waste treatment. J. Water Pollut. Control Fed. 37, 97–116.

[14] Nges, I.A., and Liu, J. (2009). Effects of anaerobic pre-treatment on the degradation of dewatered-sewage sludge. Renewable Energy 34: 1795–1800. http://dx.doi.org/10.1016/j.renene.2008.12.001

[15] Penaud, V., Delgene`s, J.P., Moletta, R. (1999). Thermo-chemical pretreatment of a microbial biomass: influence of sodium hydroxide addition on solubilization and anaerobic biodegradability. Enzyme and Microbial Technology 25: 258–263. http://dx.doi.org/10.1016/S0141-0229(99)00037-X

[16] Serikawa, R. M. (2007). Wet electrolytic oxidation of organic sludge. Journal of Hazardous Materials 146: 646–651. http://dx.doi.org/10.1016/j.jhazmat.2007.04.107

[17] Zhang, L., Jahng, D. (2010). Enhanced anaerobic digestion of piggery wastewater by ammonia stripping: Effects of alkali types. Journal of Hazardous Materials 182: 536-543.biaxial anisotropy," in *1987 Proc. INTERMAG Conf.*, pp. 2.2-1–2.2-6.