

STUDY ON THE HYDROLYTIC ABILITY OF ORGANIC COMPONENTS IN MUNICIPAL SOLID WASTE SERVING FOR METHANE RECOVERY TECHNOLOGY

Nguyen Van Phuoc*, Nguyen Thi Thanh Phuong

Institute for Environment and Resources, Vietnam National University Ho Chi Minh City

Received 23 August 2012

Abstract

The organic component in municipal solid waste has been considered as a valuable resource. Recent experimental data showed that organic components in municipal solid waste of Vietnam in general and Ho Chi Minh City in particular produced during anaerobic process are more than 65 %, which is advantage condition for methane recovery in anaerobic reactors. This research focused on the hydrolytic ability of organic components in municipal solid waste in laboratory scale at ambient temperature under anaerobic condition. Research results showed that appropriate pH for hydrolysis process is 10, additional NaOH dose is 10 g/L and hydrolysis time is 6 days. After hydrolysis process, soluble COD can reach $63,078 \pm 277$ mg/L to $83,782 \pm 582$ mg/L and hydrolysis efficiencies are in the range of 47-63 %. Hydrolysis efficiency with NaOH agent is 95 %, higher than that of when using $\text{Ca}(\text{OH})_2$, 74 %. This study aims to devise a comprehensive approach for selecting appropriate waste treatment technology, meeting energy reuse and biogas recovery targets.

Keywords: Methane recovery, hydrolysis, domestic waste, household waste, biogas recovery.

1. INTRODUCTION

Household or domestic waste is solid waste, composed of garbage and rubbish, which normally originates from residential, private households, or apartment buildings. According to Department of Natural Resources and Environment of Ho Chi Minh City's report (2010), the total amount of municipal solid waste (MSW) was estimated to be approximately 7,500 to 8,000 tons per day. In particular, the amount of waste was collected and transported to landfill was about 6,500 to 6,700 tons per day in which the organic component was 65-70 %.

The organic waste components have been considered as a valuable resource that can generate useful products with mediated microbial impact [1]. Nowadays, anaerobic digestion has been considered as a promising method, it not only can be alternative method for incineration and composting, but also has the ability to produce biogas and renewable energy [2]. In addition, biosolid stabilization can be used to improve soil quality [3]. This technology has been applied successfully to reduce the amount of waste to be buried in landfills and greenhouse gas emissions [4-6].

Anaerobic biodegradation methods have been studied and applied widely in the world for high organic content wastes. Anaerobic process contains many metabolic stages such as hydrolysis/liquefaction, acidogenesis and methano-genesis [7, 8] which require long retention time and have low removal organic compound efficiencies [7]. Recent studies showed that hydrolysis is recognized as rate-limiting step in the complex digestive process, in which lignocellulose with special chemical structure has restrained the biodegradation rate of organic components of municipal solid waste [9, 10].

To overcome these disadvantages, solid waste pre-treatment systems such as mechanical [11, 12], chemical and biological methods [13] have been proposed to promote substrate solubility and accelerate the biodegradability of organic waste, based on the principle of breaking down the structure of complicated organic matter into simpler elements [14-16].

Among the solutions listed above, alkaline hydrolysis using sodium hydroxide (NaOH) or potassium hydroxide (KOH) to catalyze the hydrolysis of biological material has been considered as an appropriate technology for waste pre-treatment process [17].

In this study, the authors focused on hydrolysis of organic compounds in domestic waste. The main purpose is determination of optimal operational parameters for the hydrolysis process such as pH, hydrolysis time, optimal chemical dosage (NaOH; Ca(OH)₂) and hydrolysis efficiencies. Research results are the bases for selecting appropriate waste treatment technology, meeting energy reuse and biogas recovery targets.

2. MATERIALS AND METHODS

2.1. Materials

The object of the study is domestic waste (mostly food waste) with the main components including banana, tomato, broccoli, cabbage, Chinese pea, water spinach, carrot. Rubbish was collected from Cho Lon (Ho Chi Minh City).

Waste characteristic are shown in table 1.

Table 1: Characteristics of food waste

Parameters	Unit	Result
pH	-	4.64-5.04
Humidity	(%)	90.3-90.7
TCOD	mg/kg	120,121-120,872
VS/TS	(%)	91.09-91.45

2.2. Experimental models

The experimental setup of hydrolysis models was arranged as shown in figure 1.

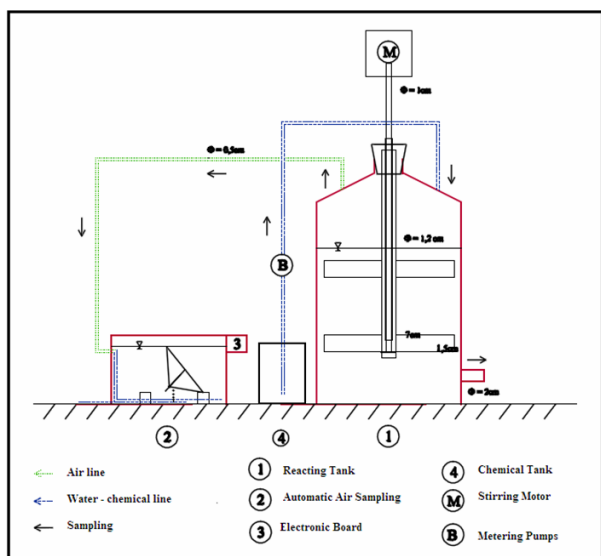


Figure 1: Organic solid waste hydrolysis model

Five operating models include A1 model (pH of 5); A2 model (pH of 8); A3 model (pH of 10); A4 model (pH of 12) and C1 model (pH of 10). In A models, pH values were adjusted by NaOH while C1 model, pH value was adjusted by Ca(OH)₂.

Five experimental models are made from acrylic material with the volume of 14 L (D × H = 0.15 m × 0.5 m) (figure 1).

2.3. Research Methodology

Experimental study was carried out at room temperature (27-35 °C). Initial volume of waste was 10 kg. The size of waste was 5 mm. Here, the mixture waste is hydrolyzed at different pH (pH of 5, 8, 10, 12), in anaerobic conditions with agitation (stirring velocity of 150 rpm/min). Temperature was adjusted automatically by a pH controller.

40 ml sample was taken every day (9AM) and was analyzed pH, sCOD for three times.

2.4. Analytical methods

SS, TS, VS, COD were analysed according to Standard Method for examination of water and wastewater treatment, 20th edition, 2005.

Hydrolysis efficiency was evaluated through the changes of the sCOD values (mg/L), according to operation time in comparison with the tCOD (mg/kg) of the initial waste.

Decomposing efficiency is described by the following equation

$$\mu_1(\%) = \frac{sCOD \times V}{tCOD \times M} \times 100\%$$

Where, μ_1 : Hydrolysis efficiency (%); $sCOD$: soluble COD of mixture waste (mgO₂/L); $tCOD$: total COD in the initial waste (mgO₂/L); V : Volume of waste in the model (L); M : amount of waste in the model (kg).

Hydrolysis efficiency according to time t is described by the following equation:

$$\mu_2(\%) = \frac{(sCOD_\tau - sCOD_0) \times V}{tCOD \times M - sCOD_0 \times V} \times 100\%$$

Where, μ_2 : Hydrolysis efficiency (%); $sCOD_\tau$: soluble COD of mixture waste at τ (mgO₂/L); $sCOD_0$: soluble COD of the initial mixture waste (mgO₂/L).

3. RESULTS AND DISCUSSION

Research results for determination of appropriate pH for hydrolysis process are shown in table 2.

3.1. Determination of appropriate pH for hydrolysis process

Table 2: Research results of alkaline hydrolysis process

Parameters	Models				
	A1	A2	A3	A4	C1
pH	5	8	10	12	10
HRT μ_{max} (ngày)	11	6	6	5	6
TCOD ₀ (mgO ₂ /kg)	120.872	120.748	121.121	120.125	120.748
sCOD _i (mgO ₂ /L)	63.078	69.179	83.782	81.119	67.792
NaOH (g/L)	0	4	10	12	0
Ca(OH) ₂ (g/L)	0	0	0	0	45
$\mu_{1\ max}$ (%)	73	80	97	94	86
$\mu_{2\ max}$ (%)	56	68	95	90	74

Ghi chú: μ_1 - hydrolysis efficiency at the time of observation; μ_2 - hydrolysis efficiency according to time τ .

Evaluation of hydrolysis efficiency of the control model (A1 model - pH = 5)

Evaluation of hydrolysis efficiency of the A2 model (pH = 8)

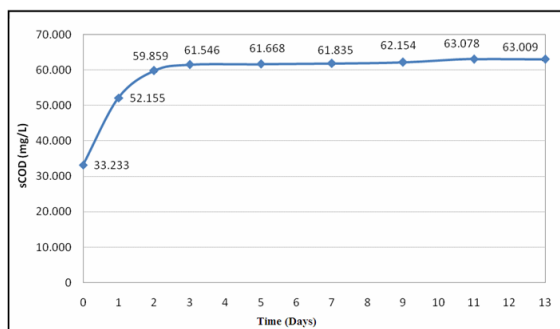


Figure 2: Hydrolysis result of the control model A1 (pH = 5)

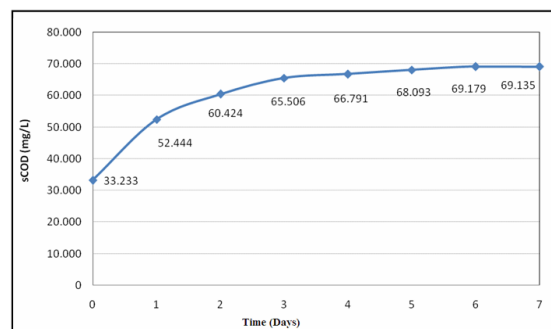


Figure 3: Hydrolysis result of the A2 model

In the control model (A1), soluble COD (sCOD) increased rapidly to 59,859 mg/L in the first two days, then increased slightly and maintained from 61,546 mg/L to 62,154 mg/L. After 11 days of operation, sCOD can reach 63,078 mg/L.

In the A2 model, sCOD was improved compared to the control model. sCOD increased 60,424 mg/L after two days. From the third day, sCOD continued to increase slowly to reach 68,093mg/L until fifth day.

These results are compatible with the studies of Sans et al (1995) [18] and Traverso et al (1995) [19]. The increasing COD phenomenon proved that the predominated phase is acidogenesis in the control model where hydrolysis and acidification processes take place at the same time. The low pH value causes to high VFA content in the system and inhibits the activity of methane bacteria. As a result, sCOD does not tend to decrease after 15 days.

Clearly, causticizing process has caused the swelling, breaking of cross-linking and increasing the pore size for enzyme-substrate interaction and soluble substrates increase. In fact, acidogenic bacteria can carry out immediately alkaline fermentation without hydrolysis stage [20].

Evaluation of hydrolysis efficiency of the A3 model (pH = 10)

In model of A3, sCOD also increased sharply to 66,226 mg/L after two operation days. From third

day, sCOD increased gradually until reaching 83,782 mg/L at sixth day.

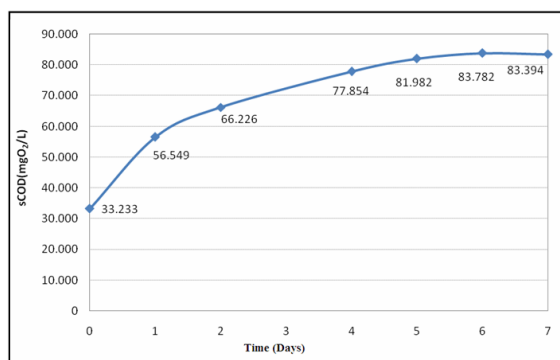


Figure 4: Hydrolysis result of the A3 model

Clearly, the higher the pH, the more increasing the solubility of substrate, the persistent compounds are easily transformed into biodegradable compounds [21]. At pH of 10, the solubility of substrate was higher than the others. This result is compatible with the study of [22] for sludge treatment.

1.1.1. Evaluation of hydrolysis efficiency of the A4 model (pH = 12)

With A4 model, sCOD also increased sharply in the first two days, then increased slowly in the next days (from second day to sixth day), reached 81.119 mg/L at fifth day.

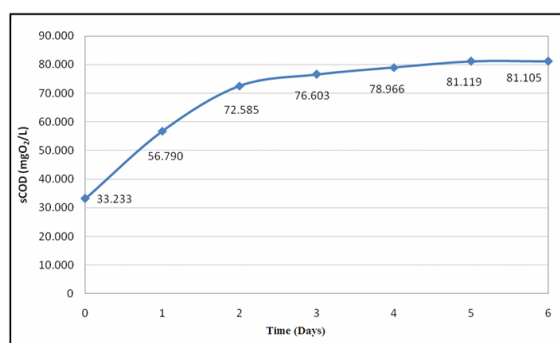


Figure 5: Hydrolysis result of the A4 model

The cells lose the ability to exist independently at high pH value. They cannot achieve the appropriate swelling capability and they will be difficult to break. When adding more alkaline, the chemical agents interact with the cell wall by the following mechanism. That is saponification of lipids at the cell wall to dissolve substances. The higher the concentration of alkaline is, the more increasing of the biodegradability is.

The disruption of the cell membrane caused the leaking of intracellular cellulose. On the other hand, when pH increases, the compounds including proteins, carbohydrates, etc, are dissolved and act as the electrolytes [23].

Compared with the control model, in the model with pH control by NaOH agent, hydrolysis efficiency was significantly improved. As adding alkaline agent, soluble COD increased by a number of specific chemical reactions namely neutralization reaction between NaOH with the free carboxylic group, the intermediate acid, fatty acid, The hydrolysis reaction includes the chain disconnected process, converting the original compounds into simpler compounds, smaller structures which are easy to dissolve.

The hydrolysis efficiency increases according to the increasing of pH [24]. However, if NaOH concentration is too high, it can be counterproductive and limit the hydrolysis process. Statistics results of hydrolysis efficiency in the models are shown in figure 6.

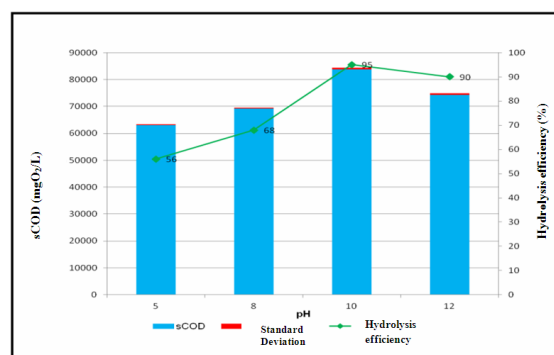


Figure 6: sCOD and hydrolysis efficiencies at different hydrolysis pH

Figure 6 showed that pH of 10 is the optimal pH for hydrolysis. This result is compatible with the study of Chen Y. et al. (2007) when hydrolyzed activated sludge at different pH levels.

Determination of hydrolysis time

Appropriate hydrolysis time of the model of A1, A2, A3, A4 were 11 days, 6 days, 6 days and 5 days, respectively and the higher the pH is, the shorter the hydrolysis time is. With the experimental results, the optimal hydrolysis time was 6 days in the model of A3 with hydrolysis efficiency of 62 %.

This result is compatible with the study of Traverso et al (2000) [19], the authors proved that most of the soluble organic compounds are converted into organic acid when they are treated by

chemical at room temperature and appropriate hydrolysis time of 6 days.

Determination of appropriate agent for hydrolysis process

Ca(OH)₂ significantly improved the hydrolysis efficiency. However, at pH of 10, hydrolysis efficiencies using NaOH and Ca(OH)₂ were 63 % and 50 % respectively. In general, Hydrolysis efficiency using Ca(OH)₂ was low since Ca(OH)₂ connects with the bicarbonate presented in the model to create insoluble compounds which affect the hydrolysis efficiency [26]. Actually observing in the experiments showed that the formation of insoluble complexes and compounds deposited at the bottom of the model. Research of Kim Jeongsik., Et al, 2003 [27] about activated sludge hydrolysis with NaOH, KOH, Mg(OH)₂, Ca(OH)₂ also proved that hydrolysis efficiency using NaOH is higher than using Ca(OH)₂.

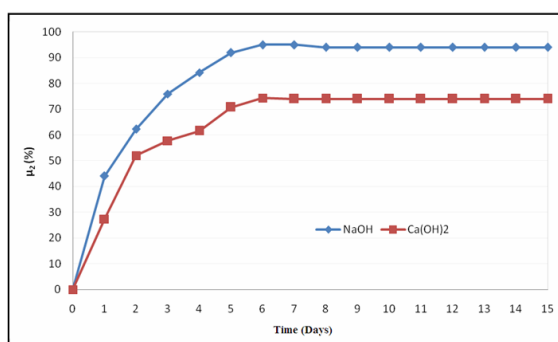


Figure 7: Hydrolysis efficiency when using NaOH and Ca(OH)₂

In addition, Penaud et al. (1999) [16]; Jeongsik Kim et al. (2003) [27] concluded that univalent alkali agents (e.g. NaOH) led to high COD solubilization's hydrolysis efficiency compared to various alkaline agent (Mg(OH)₂, Ca(OH)₂).

Experimental results to determine the appropriate solid-liquid ratio for hydrolysis process

Experiments to determine the rate of waste - water were carried out with two cases:

- A1 model was not adjusted the rate of solid-liquid, corresponding to the real humidity of waste of 91 %.
- C model was increased the solid - liquid ratio by adding water, corresponding to the real humidity of waste of 95 %.

Hydrolysis efficiency of waste at 91 % and 95 % of humidity are shown in figure 8.

In general, the both models are hydrolyzed rapidly from the first day. Soluble COD in model of A1 (humidity of 91 %) and model of C (humidity of 95 %) are 42 % và 16 % compared to initial COD, respectively. In the following days, the solubility of organic components in A1 model is higher than in C model. sCOD from the second day to the 12th day were 60 % (model of A1) and 18 % (model of C) compared to the initial COD.

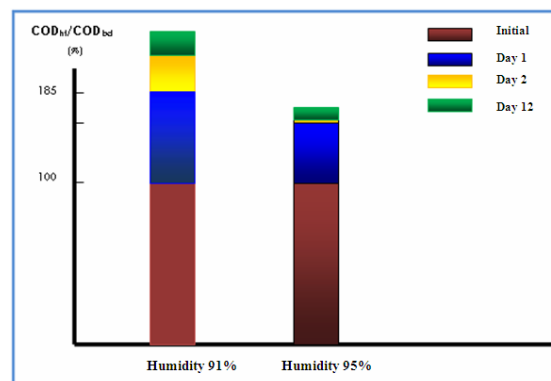


Figure 8: Hydrolysis efficiency of waste at humidity of 91 % and 95 %

At the appropriate moisture content (more than 90%), addition of water, increasing humidity will improve the dissolved substrates process. If humidity exceeds the real humidity of waste, the hydrolysis efficiency will not increase.

1.2. Expense calculations for the alkaline hydrolysis process

Costs for hydrolysis chemical are shown in table 3.

Table 3: Costs for hydrolysis process

Adding chemical	Chemical cost (VND/kg COD)
NaOH	1,413
Ca(OH) ₂	930

Calculation results show that, to hydrolyze 1 kg COD, consumed chemical costs for NaOH and Ca(OH)₂ are 1,413 VND and 930 VND, respectively.

The amount of COD in 1 kg of waste is 120,722 mgCOD/kg waste, the chemical cost is 1,413 VND/kg COD. So, chemical cost to hydrolyze 1 ton of waste is 170,588 VND/ton (equivalent to \$8.5/ton of waste, with the exchange rate of 1 USD = 20,000 VND).

4. CONCLUSIONS

Result of hydrolysis of organic components in domestic waste with laboratory scale showed that: appropriate pH for hydrolysis process is 10. Optimal additional doses of NaOH are 10 g/L and hydrolysis time is 6 days. sCOD after hydrolysis process was up to 83,782 mg/l.

Hydrolysis efficiency with NaOH agent (63 %) is higher than that with Ca(OH)₂ (50%) at pH of 10.

REFERENCES

1. M. Lesteur, V. Bellon-Maurel, C. Gonzalez, E. Latrille, J. M. Roger, G. Junqua, J. P. Steyer. *Alternative methods for determining anaerobic biodegradability: a review*, Process Biochem., **45**, 431-440 (2010).
2. D. H. Lee, S. K. Behera, J. Kim, H. S. Park. *Methane production potential of leachate generated from Korean food waste recycling facilities: a lab scale study*, Waste Manage, **29**, 876-882 (2009).
3. H. Bouallagui, Y. Touhami, R. Ben Cheikh, M. Hamdia. *Bioreactor performance in anaerobic digestion of fruit and vegetable wastes: review*, Process Biochem., **40**, 989-995 (2005).
4. J. Mata-Alvarez, S. Macé, P. Llabrés. *Anaerobic digestion of organic solid wastes. An overview of research achievement and perspectives*, Bioresource Technology, **74**, 3-16 (2000).
5. T. Forster-Carneiro, M. Perez, L. I. Romero. *Thermophilic anaerobic digestion of source-sorted organic fraction of municipal solid waste*, Bioresource Technology, **99(15)**, 6763-6770 (2008).
6. H. Bouallagui, H. Lahdheb, R. E. Ben, B. Rachdi, M. Hamdi. *Improvement of fruit and vegetable waste anaerobic digestion performance and stability with co-substrates addition*, Journal of Environmental Management, **90(5)**, 1844-1849 (2009).
7. Jeongsik Kim, Chulhwan Park, Tak-hyun Kim, Myunggu Lee, Sangyong Kim, S Eung-wook Kim, and Jinwon Lee. *Effects of Various Pretreatments for Enhanced Anaerobic Digestion with Waste Activated Sludge*. Journal of Bioscience and Bioengineering Vol. 95, No. 3, 271-275. 2003.
8. W. Charles, L. Walker, R. Cord-Ruwisch. *Effect of pre-aeration and inoculum on the start-up of batch thermophilic anaerobic digestion of municipal solid waste*, Bioresource Technology, **100**, 2329-2335 (2009).
9. Chulhwan Park, Chunyeon Lee, Sangyong Kim, Yu Chen, and Howard A. Chase. *Upgrading of Anaerobic Digestion by Incorporating Two Different Hydrolysis Processes*, Journal of Bioscience and Bioengineering, **100(2)**, 164-167 (2005).
10. J. Mumme, B. Linke, R. Tölle. *Novel upflow anaerobic solid-state (UASS) reactor*, Bioresour. Technol., **101**, 592-599 (2010).
11. K. Leikam, R. Stegmann. *Influence of mechanical-biological pretreatment of municipal solid waste on landfill behavior*, Waste Management and Research, **17(8)**, 424-429 (1999).
12. S. Sawayama, S. Inoue, K. Tsukahara, T. and Ogi. *Thermochemical liquidization of anaerobically digested and dewatered sludge, and anaerobic retreatment*, Bioresource Technology, **55(2)**, 141-144 (1997).
13. M. Pichler, and Kogel-Knabner. *Organic Matter of Mechanical Biological Pretreated Waste in Landfill Simulation Experiments*, Proceedings SARDINIA 99, 7th International Landfill Symposium, Environmental Sanitary Engineering Centre Cagliari, Italy (1999).
14. M. Lo'pez Torres and Ma. del C. Espinosa Llore'ns. *Effect of alkaline pretreatment on anaerobic digestion of solid wastes*, Waste Management 28: 2229-2234 (2008).
15. W. Charles, L. Walker, R. Cord-Ruwisch. *Effect of pre-aeration and inoculum on the start-up of batch thermophilic anaerobic digestion of municipal solid waste*, Bioresource Technology, **100**, 2329-2335 (2009).
16. V. Penaud, J. P. Delgenes, R. Moletta. *Thermochemical pretreatment of a microbial biomass: influence of sodium hydroxide addition on solubilisation and anaerobic biodegradability*, Enzyme and Microbial Technology, **25(3-5)**, 258-263 (1999).
17. I. Dogan, and F. D. Sanin. *Alkaline solubilization and microwave irradiation as a combined sludge disintegration and minimization method*, Water Research, **43**, 2139-2148 (2009).
18. C. Sans, J. Mata-Alvarez, F. Cecchi, P. Pavan, A. Bassetti. *Acidogenic fermentation of organic urban wastes in a plug-flow reactor under thermophilic conditions*, Bioresour. Technol. (1995).
19. P. Traverso, P. Pavan, D. Bolzonella, L. Innocenti, F. Cecchi, J. Mata-Alvarez. *Acidogenic fermentation of source separated mixtures of vegetables and fruit waste from supermarket*, Biodegradation, **11**, 407-414 (2000).
20. J. Mata-Alvarez. *Biomethanization of the organic fraction of municipal solid wastes*, IWA Publishing (2003).
21. E. Neyens, J. Baeyens, and C. Creemers. *Alkaline thermal sludge hydrolysis*, Journal of Hazardous Materials B 97 (2003).
22. D. Zhang, Y. Chen, Y. Zhao, and V. Zhu. *New sludge pretreatment method to improve methane production in waste activated sludge digestion*, Environ. Sci Technol., **44**, 4802-4808 (2010).
23. Vallom and McLoughlin. *Lysis as a factor in sludge flocculation*, Wat. Res, **18**, 1523-1528 (1984).
24. Jih-Gaw Lin et al. *Enhancement of anaerobic digestion of waste activated sludge by alkaline solubilization*, Bioresource Technology, **62**, 85-90 (1997).

25. Y. Chen, et al. *Hydrolysis and acidification of waste activated sludge at different pHs*, Water Research, **41(3)**, 683-689 (2007).
26. M. Lo'pez Torres và Ma. del C. Espinosa Llore'ns. *Effect of alkaline pretreatment on anaerobic*

- digestion of solid wastes*. Waste Management, **28**, 2229-2234 (2008).
27. Jeongsil Kim, et al. *Effect of various pretreatment for enhanced anaerobic digestion with waste activated sludge*, Bioscience and bioengineering, **95(3)**, 271-275 (2003).

Corresponding author: **Nguyen Van Phuoc**

Institute for Environment and Resources
142 To Hien Thanh, District 10, Ho Chi Minh City, Vietnam
Email: nvphuoc1960@gmail.com.