

Pretreatment of anaerobic digestion effluent with ammonia stripping and biogas purification

Xiaohui Lei^{a,*}, Norio Sugiura^b, Chuanping Feng^c, Takaaki Maekawa^b

^a Doctor's Program in Life and Environmental Science, University of Tsukuba, 3050006, 31-207 Ichinoya, 2-1 Tennodai, Tsukuba, Ibaraki, Japan

^b Graduate School of Life and Environmental Science, University of Tsukuba, Japan

^c School of Water Resources & Environment, China University of Geosciences, Beijing, China

Received 14 June 2006; received in revised form 14 November 2006; accepted 14 November 2006

Available online 19 November 2006

Abstract

In this study, ammonia stripping was optimized for pretreating anaerobic digestion effluent from an anaerobic digestion plant, and the possibility of using CO₂ stripping and biogas injection for adjusting the pH of the effluent before and after the ammonia stripping process was also investigated. For ammonia stripping, the results showed that an overdose of calcium hydroxide, i.e., 27.5 g/L wastewater, achieved higher ammonia, phosphorus, chemical oxygen demand, suspended solids, and turbidity removal efficiency. An air flow rate of 5 L/min for 1 L of wastewater was thought as suitable for engineering application. The pH of the anaerobic digestion effluent can be increased from about 7 to about 9 by CO₂ stripping, however which is insufficient for ammonia stripping. For 1 L of wastewater treated after ammonia stripping, the pH can be neutralized to about 7 from greater than 11 through biogas injection at 1 L/min for less than 30 min, and continuous injection does not decrease the pH. It was roughly estimated that 43 m³ of biogas (CH₄:CO₂ ≈ 60%:40%) produced daily could be purified to CH₄:CO₂ ≈ 74%:26% by neutralizing the pH of the 5 m³ anaerobic digestion effluent pretreated by ammonia stripping.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Ammonia stripping; Anaerobic digestion effluent; Biogas purification; pH adjustment; CO₂ stripping

1. Introduction

Anaerobic digestion effluent typically contains high amounts of ammonium, phosphate, suspended solid (SS), and persistent organic substrate, which has been generally applied as a fertilizer for recycling the nutrients in agricultural field [1]. However, the excessive application of digested effluent in agricultural areas is the probable cause of nitrogen pollution in farming areas [2]. In addition, this method is unsuitable for urban areas because of the unpleasant odor of the effluent and limited agricultural area. A simple and effective process for removing nitrogen and residual organic substances is required for the post-treatment of the effluents from anaerobic digestion.

The high ammonia, phosphate and SS contents of anaerobic digestion effluent are generally difficult of access to conventional biological treatment processes such as activated sludge

process [3,4], soil trench system, etc. [5]. In addition, the relatively low chemical oxygen demand/total nitrogen (COD/TN) ratio (1–3) is insufficient to facilitate efficient TN removal. Meinhold et al. [6] suggested that the COD/TN ratio for efficient TN removal by nitrification and denitrification in an activated sludge process should be between 4 and 5. Hence, physico-chemical pretreatments such as ammonia stripping, ion exchange, membrane processes, and chemical precipitation are required to lower the concentration of ammonia, phosphate, and SS prior to application to biological treatment processes.

Ammonia stripping has been successfully applied in pretreating pig slurry [7,8], landfill leachate [9], urea fertilizer plant wastes [10], etc. However, researches on the application of ammonia stripping to anaerobic digested effluent are limited. Further, the optimal Ca(OH)₂ dosage must also be studied because of the different C, N, and P concentrations and pH buffer capacity of anaerobic digested effluent.

The biogas produced at the anaerobic digestion energy plant consists of 55–80% CH₄, 20–45% CO₂, 0–1.0% H₂S, and

* Corresponding author. Tel.: +81 8054121741; fax: +81 298537496.
E-mail address: rain_fields@hotmail.com (X. Lei).

0–0.05% NH_3 , and it is saturated with water [11]. There are three primary compounds that must be removed to improve the combustibility of biogas. Besides water vapor and H_2S , biogas typically contains a high percentage of CO_2 , which decreases its caloric value [12]. Although there are some physico-chemical [13] and biological methods [12,14] used to decrease the percentage of CO_2 in biogas, a method with a low cost and high efficiency is still required.

In this study, firstly, ammonia stripping will be optimized for pretreating anaerobic digestion effluent. The optimal dosage of calcium hydroxide will be determined systematically based on not only pH adjustment but also $\text{NH}_4^+\text{-N}$, $\text{PO}_4^{3-}\text{-P}$, COD, and SS removal efficiency. Then the effect of aeration rate on $\text{NH}_4^+\text{-N}$ removal will also be studied. Secondly, the possibility of using CO_2 stripping and biogas injection in the adjustment of the pH of the anaerobic digestion effluent before and after ammonia stripping will also be investigated by batch experiments.

2. Materials and methods

The temperature during all experiments was about 15 °C.

2.1. Anaerobic digestion plant

In 2005, an anaerobic digestion energy plant using pig excreta and kitchen garbage as the substrate was built in Sanwa city, Japan. The plant produced 43 m^3 of biogas and 5 m^3 of digested effluent daily from a two-phase plug flow anaerobic digestion reactor. The anaerobic digestion effluent obtained from the anaerobic digestion energy plant was taken to laboratory and stored at 4 °C prior to the experiments. And all experiments using biogas were accomplished in the plant.

2.2. Ammonia stripping

2.2.1. Optimal $\text{Ca}(\text{OH})_2$ dosage

Different dosages of calcium hydroxide – 3, 5, 7, 9, 11, 13, and 15 g – were added to 400 mL anaerobic digestion effluent in 500 mL beakers, respectively. The mixtures were stirred for 30 min to dissolve the calcium hydroxide and facilitate the reaction between calcium and phosphate. The resulting mixtures were then allowed to precipitate, and the pH, $\text{NH}_4^+\text{-N}$, $\text{PO}_4^{3-}\text{-P}$, and COD of the supernatants were measured over 2 days. The precipitation (% v/v) – sludge volume to total volume of wastewater – was also measured in order to determine the settling rate of sludge.

2.2.2. Optimal air flow rate

After adding an optimal dosage of calcium hydroxide to the anaerobic digestion effluent, the sludge was allowed to settle for 8 h. The supernatants were used in air stripping.

Air stripping experiments were carried out in 500 mL beakers. Supernatants of 200 mL were added to the beakers, and ammonia stripping was started by aeration using diffusers at different rates—0, 0.6, 1, and 2 L/min. The ammonium

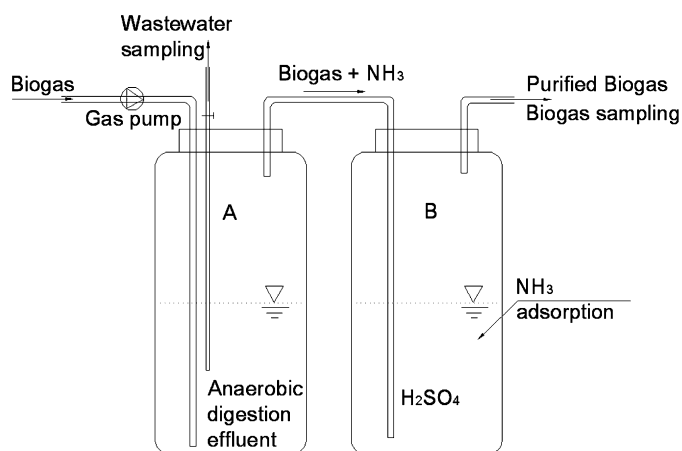


Fig. 1. Device of biogas purification and pH decreasing of wastewater.

nitrogen contents in the supernatant were analyzed during 1 day.

2.3. Biogas purification and pH adjustment

2.3.1. pH increase by CO_2 stripping

Air was blown into 400 mL anaerobic digestion effluent in a 500 mL beaker at flow rate of 1 L/min. The pH variations with time were monitored during 1 day.

2.3.2. pH decrease by biogas injection

The CO_2 injection experiment device (Fig. 1) was composed of two 2-L plastic bottles—one for biogas injection (bottle A) and the other containing H_2SO_4 (70%) for ammonia adsorption (bottle B). Ammonia reacts with H_2SO_4 to produce $(\text{NH}_4)_2\text{SO}_4$ that can be used as a fertilizer. The batch experiments were carried out at the anaerobic digestion energy plant because of the easy access to biogas. Biogas was collected by using a 100 L Tedlar Bag (Tokyo Deodorant Co., Ltd., Japan), which was measured for CH_4 , CO_2 , and H_2S percentages before experiments. The biogas was blown into 1 L anaerobic digestion effluent pretreated after ammonia stripping at different flow rates of 0.5, 1, and 2 L/min in bottle A. And the purified biogas was discharged to atmosphere after sampling with 1 L Tedlar Bags (Tokyo Deodorant Co., Ltd., Japan) at 5, 15, 25, 35, and 60 min after the beginning of biogas injection.

2.4. Analytical procedures

The analytical procedures for the determination of pH, ammonia, *ortho*-P, COD, and SS of wastewater were conducted according to Standard Methods [15]. The turbidity was assayed at 860 nm by using Attenuated Radiation Method [16] with a Hach DR4000 spectrophotometer. The component gases in biogas – CH_4 , CO_2 , and H_2S – were measured with a gas analyzer model GA94A (Geotechnical instruments (UK) Ltd.). The total organic carbon (TOC) and inorganic carbon (IC) of the wastewater were measured with a Shimadzu TOC5000A.

Table 1
Characteristics of anaerobic digestion effluent

Parameters	Anaerobic digestion effluent
pH	7.50
Temperature (°C)	15
Total suspended solid (mg/L)	20,000
Turbidity (FAU)	51,700
COD (mg/L)	2,290
TOC (mg/L)	2,032
IC (mg/L)	1,014
TN (mg/L)	1,770
NH ₄ ⁺ -N (mg/L)	1,510
NH ₃ ⁻ -N (mg/L)	34
TP (mg/L)	432
ortho-P (mg/L)	227

3. Results and discussion

3.1. Characteristics of anaerobic digestion effluent and biogas

Characteristics of the effluent were analyzed before the experiments, and the results were shown in Table 1. The CH₄:CO₂:H₂S volumetric ratio of the biogas used in the experiment was 58.1:41.4:0.5.

3.2. Ammonia stripping

3.2.1. Optimal Ca(OH)₂ dosage

The pH of wastewater showed irregular variations with the dissolution of calcium hydroxide; however, it became stable after 30 min, and the effect of different dosages on the pH is shown in Fig. 2. It is evident that the pH became greater than 12 when 12.5 g/L calcium hydroxide was added, and no further increase was found for higher dosages. To evaluate the settling rate of the sludge (HAP and CaCO₃ flocs), the sludge volumes were measured after 24 h, and the result is also shown in Fig. 2. The sludge for the dosages of 22.5 and 37.5 g/L settled very slowly; however, for the dosages of 7 and 27.5 g/L, the sludge settled very quickly, and the sludge volumes were almost stable in 1 h. The sludge for the dosages of 7.5, 12.5, 17.5, and 22.5 g/L were almost black in color; however those for the over-dosages

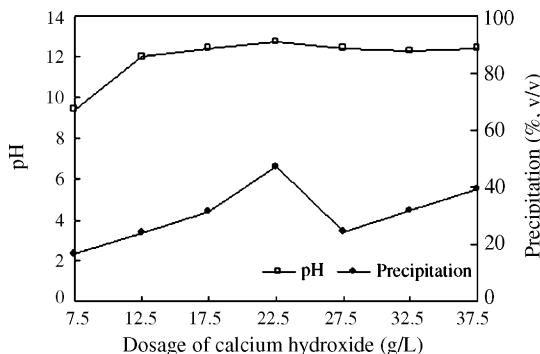


Fig. 2. Effect of calcium hydroxide dosages on pH and precipitation (% v/v) after settlement for 24 h.

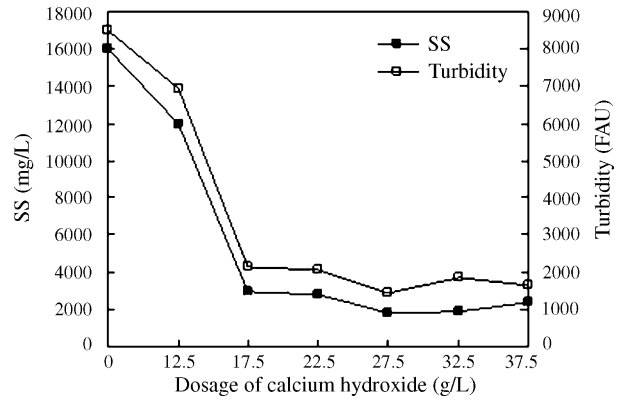


Fig. 3. Effect of calcium hydroxide dosages on SS and turbidity in supernatant after settlement for 24 h.

of 27.5, 32.5, and 37.5 g/L were light black. Many small white points were also observed, which might indicate the saturation of calcium hydroxide.

After settlement of sludge for 1 day, the SS and turbidity variations of different calcium hydroxide dosages in the supernatant were measured and are depicted in Fig. 3. It can be seen that all the dosages had very good turbidity removal efficiency, decreasing from the original 51,700 FAU to lower than 9000 FAU. Further, when the dosage was increased from 7.5 to 17.5 g/L, the SS and turbidity decreased sharply. On the other hand, when the dosages were greater than or equal to 27.5 g, the SS and turbidity reached an almost stable value for additional increase in the dosage.

After settlement of sludge for 2 days, the concentrations of NH₄⁺-N, PO₄³⁻-P, and COD in the supernatants were measured; the final concentrations are shown in Fig. 4. The ammonium nitrogen removal efficiency remained at almost the same level when the pH became greater than 12, while, for a dosage of 7.5 g/L (pH 9.4), it was relatively low. Because the proportion of free [NH₃] of total ammonia–nitrogen [NH₃] + [NH₄⁺] is a function of pH and temperature, as given by the following equation [17]:

$$[\text{NH}_3] = \frac{[\text{NH}_3] + [\text{NH}_4^+]}{1 + [\text{H}^+]/K_a} \tag{1}$$

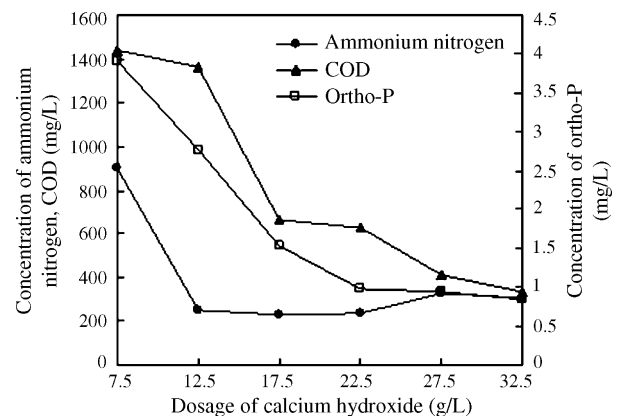


Fig. 4. Effect of calcium hydroxide on NH₄⁺-N, PO₄³⁻-P, and COD removal after settlement for 48 h.

Here $[\text{NH}_3]$ represents the free ammonia concentration (mol/L), $[\text{NH}_4^+]$ the ammonium concentration (mol/L), $[\text{H}^+]$ the hydrogen ion concentration (mol/L) and K_a is the acid ionization constant of ammonia (mol/L). Using this formula, it can be calculated that for a pH of 12 and temperature of 15 °C, the ratio of ammonia to total ammonia–nitrogen reaches 99.6%; however, it reaches only 21.49% for a pH of 9.

ortho-Phosphorus reached a relatively low level (lower than 5 mg/L) for all dosages (Fig. 4) after the calcium phosphate precipitation formed and settled for about 8 h. And during the settling of sludge, the concentration of $\text{NH}_4^+\text{-N}$ and $\text{PO}_4^{3-}\text{-P}$ in the supernatant decreased continuously (data not shown). The COD removal efficiency increased with the increase in the $\text{Ca}(\text{OH})_2$ dosage (Fig. 4); however, the COD level remained almost stable during the settling of the sludge (data not shown).

From these results, it is evident that the limiting factor in obtaining optimal dosage of calcium hydroxide is not phosphorus, but pH adjustment (higher than 12), COD, SS and turbidity removal, and the settlement of sludge. And the dosage of calcium hydroxide, 27.5 g/L, was optimal for $\text{NH}_4^+\text{-N}$, $\text{PO}_4^{3-}\text{-P}$, COD, SS, and turbidity removal, which is greater than the value of 8 g/L for landfill leachates obtained by Ozturk et al. [18]. Compared with our result, 8 g/L of calcium hydroxide is even insufficient to bring the pH close to 12 that may be a result of the higher pH buffer capacity of anaerobic digestion effluent as compared with landfill leachates, and then a good ammonia stripping efficiency could not be achieved. Moreover, even a dosage greater than 8 g is just sufficient for increasing the pH to 12, and a good ammonia removal efficiency can then be obtained. However, the COD, SS, and turbidity removal will remain inferior and the settling rate of sludge will be slow. The $\text{NH}_4^+\text{-N}$, $\text{PO}_4^{3-}\text{-P}$, COD, SS, and the turbidity removal rate for the optimal dosage of calcium hydroxide after sludge formed and settled for 48 h was 78%, 99.9%, 82.1%, 91%, and 97.2%, respectively.

Calcium hydroxide $\text{Ca}(\text{OH})_2$ is usually selected for pH adjustment before air stripping because of the low cost and other advantages for phosphorus and SS removal. In addition, due to the high Ca, N, and P contents of produced sludge, it can be easily transformed into compost to improve soil fertility and quality. Phosphorus removal is achieved by the direct precipitation of calcium phosphate (hydroxyapatite (HAP) $\text{Ca}_5(\text{PO}_4)_3\text{OH}$) [19]. Further, CaCO_3 precipitation, which occurs due to the reaction between calcium hydroxide and CO_2 absorbed from the ambient air, induces a sweep coagulation process and larger particles can be entrapped [20].

3.2.2. Optimal air flow rate

Based on previous result, after adding an optimal dosage of calcium hydroxide, 27.5 g/L wastewater, to the anaerobic digestion effluent and mixing for 30 min, the sludge was allowed to settle for 8 h. The supernatants were used in air stripping.

During the first 30 min, a large amount of foam was produced, especially for the rate of 2 L/min, and it was broken manually by a glass stick. Subsequently, however, the production of foam decreased very quickly. Since only 200 mL of supernatants was used in 500 mL beakers, the loss of solution caused by the foam

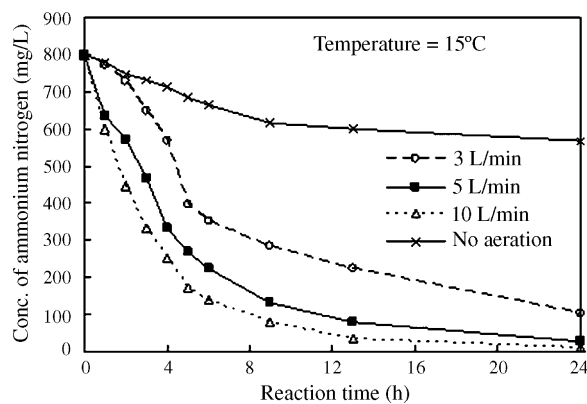


Fig. 5. Effect of aeration rate on $\text{NH}_4^+\text{-N}$ removal.

can be neglected. The ammonium removals for different aeration rates over 24 h are shown in Fig. 5.

The ammonia stripping performance is highly dependent on the air/water ratios. From the results of the air stripping, it is clear that for 1 L of wastewater, the ammonia removal rate reached a maximum of almost 95.3% after 12 h at an air flow rate of 10 L/min, which is very close to the ratio of free ammonia to total ammonium–nitrogen (99.6%) calculated previously. Further, after air stripping for 12 h at an air flow rate of 5 L/min for 1 L of wastewater, the ammonia removal rate also reached 89.9%. This result is similar to that obtained by Ozturk et al. [18] for landfill leachates. However at an air flow rate of 3 L/min for 1 L of wastewater, the ammonia removal rate was only 72.1% even after 24 h. In the case of no aeration, the concentration of $\text{NH}_4^+\text{-N}$ was over 600 mg/L and the ammonia removal rate was only 25.1%. This result is because an increase of the air flow rate increases the gas–liquid surface area, which in turn controls the amount of NH_3 diffused from water [17]. However, from the viewpoint of engineering applications, an air flow rate of 5 L/min for 1 L of wastewater should be optimal because the significantly more expensive method of using an air flow rate of 10 L/min for 1 L of wastewater increases the ammonia removal efficiency only about 5% compared with that of 5 L/min.

Further, the temperature of 15 °C was used in the experiments, it can be expected that higher temperature would greatly increase the ammonia stripping efficiency [8,21], and the air stripping time would greatly reduced.

3.3. pH increase by CO_2 stripping

The most important step in ammonia stripping is to increase the pH of treated wastewater by adding alkali. Considering the significant relationship between CO_2 and pH (pH of water increases as the amount of CO_2 dissolved in water decreases, vice versa), it is possible to decrease the alkali quantity by CO_2 stripping of the digested effluent (forcibly removing CO_2 from the digested effluent) for pH increasing.

CO_2 dissolves according to the following reactions:



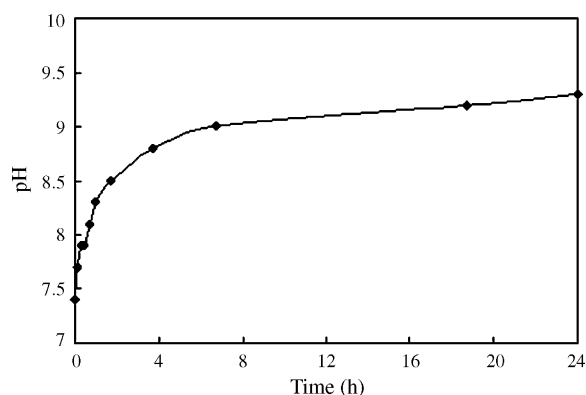
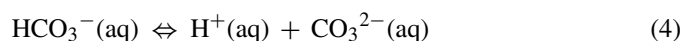
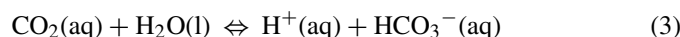


Fig. 6. Effect of CO₂ stripping on pH of anaerobic digestion effluent.



It is shown that the pH of the anaerobic digestion effluent can be increased by CO₂ stripping (Fig. 6). The pH of a 400 mL solution of the anaerobic digestion effluent can be increased from 7.4 to 9.3 by CO₂ stripping at the rate of 1 L/min for 1 day.

During anaerobic digestion, a large amount of CO₂ was produced, so the anaerobic digestion effluent had a high concentrated dissolved IC (Table 1). And CO₂ is a main component of IC. As CO₂ is removed by CO₂ stripping from the anaerobic digestion effluent, reactions (2)–(4) proceed to the left direction; as a result, more H⁺ is reacted and the pH increases.

Based on the previous results (Fig. 2), the pH is not sufficient for efficient ammonia stripping. However, CO₂ stripping could be a very good method for the pH adjustment of MAP precipitation (magnesium ammonium phosphate hexahydrate MgNH₄PO₄·6H₂O). Because the optimal pH range of this reaction is from 8.5 to 9.5 [22–24], and the pH of the anaerobic digestion effluent can be increased to the optimal range in a short time (2–4 h), and maintains below 9.5 even in the case of over-aeration. In fact, this method has already been successfully applied in pH adjustment for treating swine wastewater by MAP precipitation [25].

3.4. pH decrease by biogas injection

Further, after ammonia stripping, it is necessary to decrease the pH of treated wastewater for subsequent biological treatment or for discharge to a water body. A large amount of biogas is readily available for use in the plant. So it is also possible to decrease the acid quantity and purify biogas by injecting the CO₂ in biogas into the ammonia stripping pretreated digested effluent for pH decreasing.

Biogas (CH₄:CO₂ = 58.1%:41.4%) was used for decreasing the pH of anaerobic digestion effluent pretreated after ammonia stripping. The variations of the CH₄ and CO₂ concentrations in the effluent biogas are shown in Fig. 7. The CH₄ and CO₂ concentrations of the purified biogas decreased and increased with time, respectively, and finally recovered to the original concentrations. At the beginning of the biogas injection, reactions (2)–(4) would proceed to the right direction at a high rate, leading

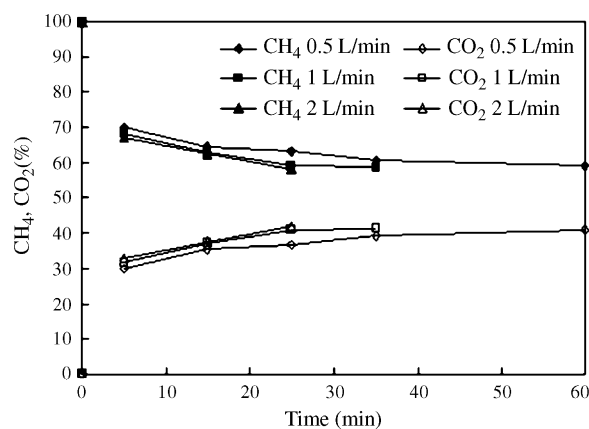


Fig. 7. Variation in CH₄ and CO₂ percentage in the biogas effluent.

to greater adsorption of CO₂ per unit time under alkaline condition, as a result, more H⁺ was produced and the pH decreased (Fig. 8). Further, the reaction rates decreased gradually with the pH of the anaerobic digestion effluent decreased; hence, less CO₂ could be adsorbed per unit time. Finally, almost no CO₂ could be adsorbed, and the CH₄ and CO₂ concentrations of the effluent biogas recovered to the original concentrations.

Fig. 8 shows that as the biogas flow rate increased, the recovery process of the biogas concentrations developed quickly, and the time required for decreasing the pH to 7 also greatly decreased. It is also observed that the pH and IC of the treated wastewater remained at relatively stable levels of about 7 and 920 mg/L, respectively, with continuous biogas injection.

In conclusion, as the pH of the wastewater decreased to about 7, the IC of wastewater increased from 28 to about 900 mg/L. It means CO₂ of about 3.2 g (or 1.6 L, ρ_{CO₂} = 1.9769 g/L) was absorbed from biogas for pH decreasing of

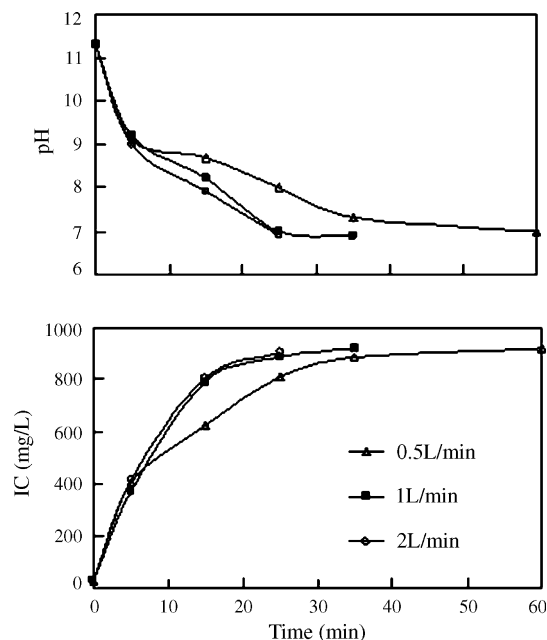


Fig. 8. Variation of pH and IC in the treated wastewater after injected with biogas.

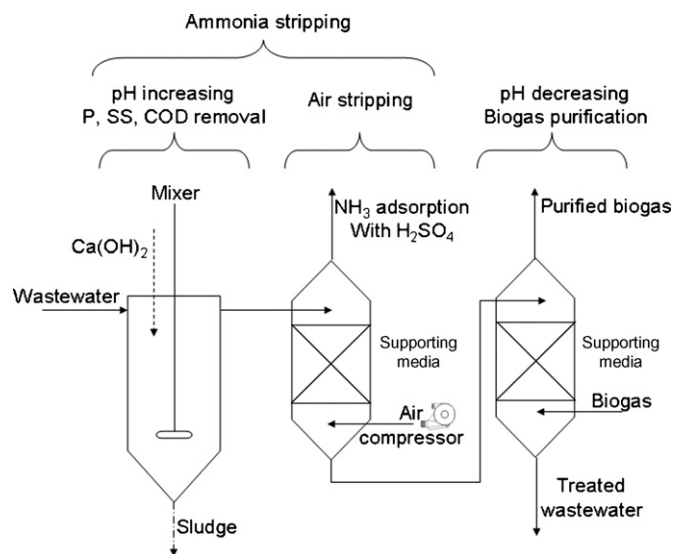


Fig. 9. Design of anaerobic digestion effluent pretreatment system.

1 L wastewater, if there are no losses in the biogas injection process. For the anaerobic digestion energy plant, 43 m³ of biogas (CH₄:CO₂ ≈ 60%:40%) produced daily can be purified to CH₄:CO₂ ≈ 74%:26% by neutralizing the pH of the 5 m³ anaerobic digestion effluent pretreated after ammonia stripping.

3.5. Design of anaerobic digestion effluent pretreatment system

Based on previous results, an anaerobic digestion effluent pretreatment system was designed for future field application as shown in Fig. 9. Firstly, the effluent is treated with calcium hydroxide, after mixture and settlement, phosphorus, COD, SS, turbidity and a part of ammonia could be removed from wastewater besides the increasing of pH in wastewater. The sludge could be made into compost, and the supernatant will be treated in following steps. Secondly, ammonia is stripped out from the supernatant by air stripping, which is adsorbed by H₂SO₄ to produce (NH₄)₂SO₄. Finally, pH of treated wastewater is neutralized to about 7 by biogas injection (CO₂ injection), biogas is also purified simultaneously.

4. Conclusion

Ammonia stripping was optimized for pretreating anaerobic digestion effluent, and the possibility of using CO₂ stripping and biogas injection for adjusting the pH of the effluent before and after the ammonia stripping process was also investigated in this study. The following conclusions can be drawn:

(1) For 1 L anaerobic digestion effluent, by adding an optimal quantity of 27.5 g of calcium hydroxide and aerating at an aeration rate of 5 L/min for 12 h, NH₄⁺-N, PO₄³⁻-P, COD, SS, and turbidity can be effectively removed. Further, the treated wastewater can be directly applied to biological treatment processes, and no further physico-chemical NH₄⁺-N

and PO₄³⁻-P treatments are required, except for the pH adjustment.

(2) The high pH of the ammonia stripping treated wastewater can be neutralized to about 7 through biogas injection in a short time, and continuous injection does not decrease the pH.

Acknowledgement

This research was supported by the Strategic International Cooperative Program, JST.

References

- [1] E. Salminen, J. Rintala, J. Härkönen, M. Kuitunen, H. Högmander, A. Oikari, Anaerobically digested poultry slaughterhouse wastes as fertilizer in agriculture, *Bioresour. Technol.* 78 (2001) 81–88.
- [2] K.R. Woli, T. Nagumo, K. Kuramochi, R. Hatano, Evaluating river water quality through land use analysis and N budget approaches in livestock farming areas, *Sci. Total Environ.* 329 (2004) 61–74.
- [3] X.Z. Li, Q.L. Zhao, Inhibition of microbial activity of activated sludge by ammonia in leachate, *Environ. Int.* 25 (1999) 961–968.
- [4] P. Battistoni, G. Fava, P. Pavan, A. Musacco, F. Cecchi, Phosphate removal in anaerobic liquors by struvite crystallization without addition of chemicals: preliminary results, *Water Res.* 31 (1997) 2925–2929.
- [5] H. Bouwer, R.L. Chaney, Land treatment of wastewater, *Adv. Agron.* 26 (1974) 133–176.
- [6] J. Meinhold, H. Pedersen, E. Arnold, S. Issacs, M. Henze, Effect of continuous addition of an organic substrate to the anoxic phase on biological phosphate removal, *Water Sci. Technol.* 38 (1998) 97–105.
- [7] A. Bonmati, X. Flotats, Air stripping of ammonia from pig slurry: characterisation and feasibility as a pre- or post-treatment to mesophilic anaerobic digestion, *Waste Manage.* 23 (2003) 261–272.
- [8] P.H. Liao, A. Chen, K.V. Lo, Removal of nitrogen from swine manure wastewaters by ammonia stripping, *Bioresour. Technol.* 54 (1995) 17–20.
- [9] K.C. Cheung, L.M. Chu, M.H. Wong, Ammonia stripping as a pretreatment for landfill leachate, *Water Air Soil Pollut.* 94 (1997) 209–220.
- [10] V.K. Minocha, A.V.S. Prabhakar, Ammonia removal and recovery from urea fertilizer plant waste, *Environ. Technol. Lett.* 9 (1988) 655–664.
- [11] L.V.-A. Truong, N. Abatzoglou, A H₂S reactive adsorption process for the purification of biogas prior to its use as a bioenergy vector, *Biomass Bioener.* 29 (2005) 142–151.
- [12] K.A. Strevett, R.F. Vieth, D. Grasso, Chemo-autotrophic biogas purification for methane enrichment: mechanism and kinetics, *Chem. Eng. J. Biochem. Eng. J.* 58 (1995) 71–79.
- [13] M. Constant, H. Naveau, G. Ferrero, E. Nyns, *Biogas End-use in European Community*, Elsevier, New York, USA, 1989.
- [14] S. Ghosh, D.K. Klass, *Two Phase Anaerobic Digestion*, US Patent No: 4,022,665, USA, 1977.
- [15] AAPHA, *Standard Methods for the Examination of Water and Wastewater*, 20th ed., American Public Health Association, Washington, DC, USA, 1998.
- [16] HACH, DR/4000 Spectrophotometer Procedures Manual, http://www.hach.com/hc/view.file.categories.invoker/FILCAT_MAN_PHOTOMETERS-DR4000/.
- [17] E.G. Srinath, R.C. Loehr, Ammonia desorption by diffused aeration, *Res. J. Water Pollut. Control Federation* 46 (1974) 1939–1957.
- [18] I. Ozturk, M. Altinbas, I. Koyuncu, O. Arikian, C. Gomec-Yangin, Advanced physico-chemical treatment experiences on young municipal landfill leachates, *Waste Manage.* 23 (2003) 441–446.
- [19] W.G. Yi, K.V. Lo, Phosphate recovery from greenhouse wastewater, *J. Environ. Sci. Health Part B: Pesticides Food Contam. Agric. Wastes* 38 (2003) 501–509.

- [20] S. Elmaleh, H. Yahi, J. Coma, Suspended solids abatement by pH increase—upgrading of an oxidation pond effluent, *Water Res.* 30 (1996) 2357–2362.
- [21] USEPA, Nitrogen Removal by Ammonia Stripping, US Environmental Protection Agency, Washington, DC, 1973.
- [22] T. Maekawa, C.-M. Liao, X.-D. Feng, Nitrogen and phosphorus removal for swine wastewater using intermittent aeration batch reactor followed by ammonium crystallization process, *Water Res.* 29 (1995) 2643–2650.
- [23] X.Z. Li, Q.L. Zhao, X.D. Hao, Ammonium removal from landfill leachate by chemical precipitation, *Waste Manage.* 19 (1999) 409–415.
- [24] N.O. Nelson, R.L. Mikkelsen, D.L. Hesterberg, Struvite precipitation in anaerobic swine lagoon liquid: effect of pH and Mg:P ratio and determination of rate constant, *Bioresour. Technol.* 89 (2003) 229–236.
- [25] K. Suzuki, Y. Tanaka, T. Osada, M. Waki, Removal of phosphate, magnesium and calcium from swine wastewater through crystallization enhanced by aeration, *Water Res.* 36 (2002) 2991–2998.