CHEMICAL ENGINEERING TRANSACTIONS

VOL. 89, 2021

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Jeng Shiun Lim, Nor Alafiza Yunus, Jiří Jaromír Klemeš

ISBN 978-88-95608-87-7; **ISSN** 2283-9216

DOI: 10.3303/CET2189063

Performance of Oyster Shell Powder Size on Methane Gas Generation in Two-Stage Anaerobic Digestion System

Peni Astrini Notodarmojo[a,*], Takeshi Fujiwara[a], Habuer[a], Mochammad Chaerul[b]

[a] Okayama University, 3-1-1 Tsushima Naka Kita-Ku, Okayama 700-8530, Japan
[b] Bandung Institute of Technology, Ganesa No.10, Bandung, Jawa Barat 40132, Indonesia
pgk975b4@s.okayama-u.ac.jp

An anaerobic digester system is a sequence of process to digest biodegradable waste into biogas in the absence of oxygen. In two-stage anaerobic digestion system acid-forming steps or hydrolysis stage are separated from the methane forming steps. Although hydrolysis stage tends to get too acidic, addition of alkali substance can prevent pH from dropping too low so as to maintain good decomposition condition for microorganism. Oyster shell powder is a useful pH control additive containing $CaCO_3$ at high percentage that can neutralize acid. In this study, the performances between industry-made fine oyster shell (IOS) powder (size 10.5 μm) and manually ground oyster shell (OS) powder (size < 1 mm) in methane generation yield were compared. NaOH, which is an alkali reagent for controlling pH, also used in comparison. The result showed that at the end of the hydrolysis stage, IOS powder increased pH up to 6.63, NaOH did almost the same (6.72), and OS powder was the lowest (6.1). In liquid residue, ratio of inorganic ash content with IOS treatment was the highest (2.1 %), but OS was the lowest (1.4 %). In the methanogenesis stage, CH_4 concentration with NaOH treatment was the highest (80 %) compared to oyster shell powders: 74.33 % in IOS and 74.24 % in OS. Average methane yield over observation period of IOS treatment was the highest (533.9 mL/gVS), followed by alkali (487.3 mL/gVS) and OS (413.7 mL/gVS). Total CH_4 from IOS treatment was 37 % and 8 % higher than OS and alkali treatment. Powder size of oyster shell greatly affected pH control, methane yield, and solid-liquid separation, but not methane concentration. Using IOS powder as pH control in hydrolysis of two-stage anaerobic system resulted in 78 % less cost than using NaOH.

1. Introduction

Anaerobic digestion (AD) is a process by which microorganisms break down biodegradable material without oxygen. This process is suitable as waste treatment to produce fuel (methane gas) for industrial/domestic waste or any biodegradable waste that have high water content. Domestic waste such as kitchen waste, food leftover, agriculture waste, and livestock manure are used as AD material. The usual treatment is either dumped together to be incinerated or piled up in sanitary landfill. Incineration may reduce the volume of the waste, but it also removes the valuable nutrients and chemical substance from incinerated substrate (Paritosh et al., 2017).

The AD process can be divided into 4 steps: hydrolysis, acidogenesis, acetogenesis and methanogenesis. In hydrolysis and acidogenesis phase, pH tends to drop because of VFA (volatile fatty acid) production. Microbes in these phases are more tolerant to acidic condition, but if the pH drops to lower than 4, it will affect and stop the hydrolysis process (Bajpai, 2017). This shows the necessity of pH control in acid phase (hydrolysis and acidogenesis) to avoid digester failure. Especially considering that the next stage, methanogenesis, is very sensitive to VFA in acidic pH (Horn et al., 2003). One way to overcome this problem is to control the pH using alkaline chemical. NaOH and KOH are the chemicals commonly used in anaerobic digester to increase the reactor pH and avoid reactor failure from acidic condition. Addition of such chemicals means an increase of operating cost, and so a cheaper alternative is required. One of materials having potential to function as pH control with cheaper price is oyster shell waste.

Oyster shells are composed mostly of $CaCO_3$ (Yoon et al., 2003), an alkaline source that can neutralize acid and act as buffer. In previous study, addition of oyster shell powder in AD can increase and keep the pH from being too acidic (Notodarmojo et al., 2021). In this study two different-sized oyster shell powder were used to

Paper Received: 15 July 2021; Revised: 16 September 2021; Accepted: 31 October 2021
Please cite this article as: Notodarmojo P.A., Fujiwara T., Habuer ., Chaerul M., 2021, Performance of Oyster Shell Powder Size on Methane Gas Generation in Two-Stage Anaerobic Digestion System, Chemical Engineering Transactions, 89, 373-378 DOI:10.3303/CET2189063

investigate the effects on two-stage anaerobic digester. Different size of lime powder can have different effects in the increase of soil pH value even months after application (Crozier and Hardy, 2017). Finer particles of lime powder can increase soil pH higher than bigger particles. In AD system or bioreactor, Rugele et al. (2014) used alkaline activated material (AAM) that leached NaOH gradually to control pH. They concluded that bigger AAM particle leach the base chemical more gradually than smaller particles and that smaller particles of AAM are more suitable for shorter fermentation. The mentioned AD is single batch system, while the system used in this study is two-stage anaerobic digestion system, in which only used the oyster shell in first stage. Nevertheless, the effects of different sized oyster shell powders were examined in both stages and in longer period of observation than previous experiment. The cost of coarse and fine oyster shell powders were also compared with commercial NaOH, all of which were used in anaerobic digester.

2. Materials and Methods

2.1 Materials

Raw materials for AD are kitchen waste (KW), agriculture waste (AW) and horse dung (HD). AW composed of post-harvested waste taken from agriculture faculty field of Tsushima Campus, Okayama University. Fresh horse dung collected from horse stable in the same campus. KW is a simulated waste composed of commercial rice, vegetable, and fish bought from a local food market in the same ratio of household waste composition data from Kyoto city survey (2012). KW and AW were chopped into small pieces before being mixed in anaerobic digester so that the ratio of total solid (TS) of each material may be 6:3:2 (KW: AW: HD). TS (total solid) and VS (volatile solid) of each raw material can be seen in Table 1 below.

Table 1: Total solid and volatile solid properties of raw material

Raw material	TS % (w/w)	VS % (w/w)
Kitchen waste	15.6	14.82
Agriculture waste	22.01	17.62
Horse dung	18.26	16.56

There are two types of oyster shell powder used, oyster shell (OS) powder ground by hand using mortar and pestle until the size is less than 1 mm. On the other hand, industrial oyster shell (IOS) powder was produced by Sanyou Clay Industry Co., Ltd and ground by industrial milling machine with particle size 10.5 µm. The properties of industrial oyster shell powder and typical oyster shell chemical composition are shown in Table 2.

Table 2: Properties of industrial oyster shell and typical oyster shell

Industrial Oyster Shell						Oyster Shell (Yoon et al., 2003)		
Parameter	Value	Unit	Parameter	Value	Unit	Parameter	Value	Unit
Moisture	<1.0	%	Mn	32	mg/kg	$CaCO_3$	95.99	%
pH	8	-	Fe	59	mg/kg	SiO_2	0.69	%
$CaCO_3$	94	%	Br	8	mg/kg	MgO	0.65	%
N	0.08	%	Mo	<1	mg/kg	Al_2O_3	0.42	%
H_3PO4	<0.2	%	Na	4600	mg/kg	SrO	0.33	%
K	0.04	%	Zn	3.40	mg/kg	P_2O_5	0.20	%
Mg	0.17	%	Humic acid	18	mg/kg	NaO	0.98	%
Organic matter	3	%				SO_3	0.72	%

2.2 Anaerobic system

The anaerobic digester used in this study is two-stage anaerobic digester system, separating hydrolysis stage (acid phase) with methanogenesis stage (alkaline phase). The hydrolysis stage, the former, is a batch system in 5 L tank with stirrer and adjusted to TS 8 %. During fermentation period, temperature was kept at 35 °C. 100 g of OS or IOS were mixed with the raw materials at the start of fermentation. NaOH 10 M was added in the other reactor once in a day to keep a certain pH level. After 5 d, this stage was terminated, and liquid residue was separated from solid residue manually by using non-woven kitchen filter mesh. Longer retention time for hydrolysis stage allows for more material to be hydrolyzed, but it might start methanogenesis process earlier. Minimum retention time for hydrolysis microorganism was around 1-2 d, while methanogen was 8-20 d (Wikandari and Taherzadeh, 2019). This is due to CH_4 producing microorganism need longer doubling time (5-15 d) than acid producing microorganism (1-1.5 d). Methane production also started to increase on the 4th and

5th day in the previous experiment using a single stage batch reactor. Based on these references, retention time for first stage was set for 5 d.
The methanogenesis stage is an up-flow anaerobic sludge blanket (UASB) reactor with a heater to keep the temperature at around 35 °C. The liquid residue was fed to the reactor from hydrolysis stage with the same organic loading rate (1.5 gVS/l/d) and 9 d of hydraulic retention time. The methanogenesis process was continuously observed for 21-30 d.

2.3 Analytical Method

TS and VS properties of raw material at the start of hydrolysis stage, and solid and liquid residue at the end of the stage were analysed. The samples were collected and dried in an oven at 105 °C (DV340S, Yamato Science Co., Ltd.). The weight difference indicated moisture loss and showed the TS ratio. Dry samples then burned in a muffle furnace at 550 °C (FO300, Yamato Science Co., Ltd.). Ash weight obtained and VS can be calculated from the weight lost after burning the samples. The liquid residue was also analysed for its COD value using the tintometer (MD600 Photometer, Lovibond ® Water Testing). For soluble COD (sCOD) analysis, we used 45 µm filter to separate the particulate within the sample before analysis. Biogas is collected in gas bag, measured, and analysed using Shimadzu GC-2014. Cost comparison between IOS and NaOH was done by calculating the amount of materials used during experiment and the price as well. The price of IOS acquired from the producer and the price for commercial NaOH was acquired from the price in website market.

3. Results and Discussions

3.1 Hydrolysis stage

Fermentative bacteria for hydrolysis and acidogenesis quite tolerant to wide pH range between 4 to 8.5 (Appels et al., 2008), but the optimum pH for hydrolysis digester is close to neutral. It is recommended to operate at a neutral pH range of 6-7 to maximize acetate production (Yu and Fang, 2003) and avoid inhibition from undissociated acid in lower pH (Babel et al., 2004). Zhang et al. (2005) managed to get the highest concentration of VFA and high percentage of dissolved total organic carbon and COD from hydrolysis of kitchen waste at pH 7. IOS treatment was able to maintain the reactor pH in the closest to optimum pH on the second day while OS treatment was not able to reach within the range until the end of fermentation period. As shown in Figure 1, the pH of alkali treatment dropped to 3.92 one day after the beginning of fermentation. It was required to add alkali (NaOH) constantly to keep the reactor pH at around 7. Both IOS and OS treatments had similar fluctuation pattern of pH unlike alkaline treatments. At the beginning of the reaction, the pH dropped to the bottom and then gradually rose without the addition of oyster shell powder. A remarkable point is that the powder size affected the ability to raise pH of the reactor. At the beginning, initial pH of IOS treatments was 6.84 that was higher than pH 5.77 of OS treatment and the difference did not change a lot until the end of hydrolysis stage.

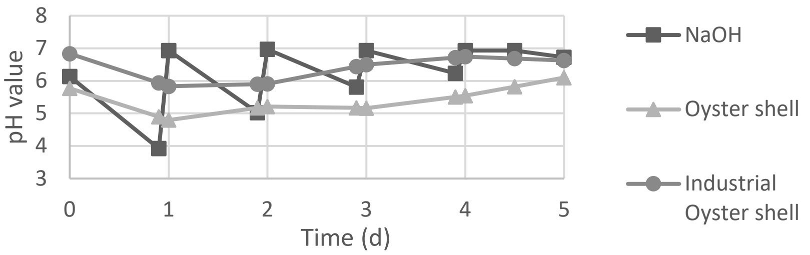

Figure 1: pH of hydrolysis reactor

In oyster shell treatments, even though $CaCO_3$ can neutralize VFA, the reaction produces CO_2 gas that can lower the pH. CO_2 gas can be released to the atmosphere to reduce CO_2 saturation. The liquid-gas transfer rate is not fast enough to keep up with neutralizing reaction and high concentration of CO_2 end up decreasing the reactor pH at the beginning of fermentation (Salek et al., 2015).
The size of oyster shell powder also affects generation of CO_2. OS treatment released 23,798 mL CO_2 gas, twice as much as alkali treatment (10.136 mL) and IOS released around thrice higher (33,645 mL). Since smaller powder has larger surface to volume ratio, the reaction rate with acids become faster. As a result of higher neutralization effect of smaller powder, the pH was increased higher, and more CO_2 was released.
The difference by selection of pH control additive can also be recognized in hydrolysis residue. Properties of solid and liquid residue are shown in Table 3. Oyster shell treatment increased the liquid residue TS than alkali treatment: the reason is higher VS in OS treatment and higher inorganic ash content in IOS treatment. Solid

residue from OS treatment had the highest inorganic ash content due to insoluble oyster shell powder deposited in residue. On the other hand, the oyster shell powder in IOS treatment was too small and able to pass the filter and accumulated into the liquid residue.

VS percentage and COD level in liquid residue indicated organic matter solubilization from raw materials (Saragih et al., 2019). sCOD level itself showed concentration of soluble organic matter that is more readily biodegradable (Płuciennik-Koropczuk and Myszograj, 2019). With reactor pH that best meets the optimum pH condition for hydrolysis, IOS treatment was able to hydrolyze the raw material well and produced liquid residue with the highest COD, sCOD, and percentage of VS transferred to liquid residue.

Table 3: Liquid and solid residue properties

Residue sample		TS (w/w)	VS (%TS)	Inorganic Ash (%TS)	% VS transferred to residue (%)	COD (g/L)	sCOD (g/L)
Alkali	Liquid	4.49 ± 0.16	61.54 ± 0.3	38.46 ± 0.3	34.05 ± 1.92	59.08 ± 4.92	38.44 ± 1.92
	Solid	23.2 ± 0.92	88.44 ± 1.1	11.56 ± 1.1	35.48 ± 0.99		
Oyster shell	Liquid	4.71 ± 0.31	69.05 ± 0.85	30.95 ± 0.85	33.75 ± 2.49	56.77 ± 11.04	42.8 ± 2.11
	Solid	23.14 ± 1.36	80.97 ± 2.41	19.03 ± 2.41	47.86 ± 0.29		
Industrial oyster shell	Liquid	5.21 ± 0.24	59.51 ± 1.11	40.49 ± 1.11	42.22 ± 2.92	69 ± 5.26	46.45 ± 3.269
	Solid	23.61 ± 0.31	86.03 ± 1.54	13.97 ± 1.54	31.73 ± 1.22		

3.2 Methanogenesis stage

Methanogenesis stage was observed for 21-30 d to investigate the trend of biogas production. Figure 2a and 2b shows that the OS treatment produced the least biogas, both CH_4 and CO_2, and IOS treatment produced the most biogas by 21st day. The difference in the accumulated CH_4 gas between IOS treatment and alkali treatment is less than the difference between accumulated CH_4 gas in OS and IOS treatment. This difference can be attributed to the similar end pH of liquid residue of IOS and alkali treatment at the end of first stage.

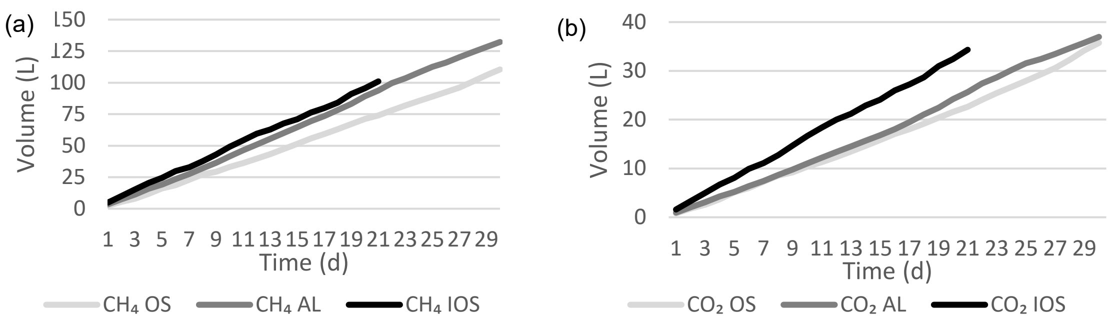

Figure 2: CH_4 (a) and CO_2 (b) gas accumulation in methanogenesis stage.

The typical CH_4 concentration in biogas is 55-70 % (EPA, 2006). Both OS and IOS treatment produced biogas with no significant difference in CH_4 concentration (74.24 % ± 1.69 and 74.33 % ± 2.33), while alkali treatment had the highest CH_4 concentration (80 % ± 2.52). It seems that particle size did not affect the concentration of CH_4 in biogas, but addition of oyster shell did. Even though lower than alkali treatment, CH_4 concentrations in OS and IOS treatments were still higher than typical CH_4 concentration in biogas.

After weeks of observation, we recognized that oyster shell treatment (Figure 3a for OS and 3c for IOS) had high variation in their methane yield compared to the alkali treatment (Figure 3b). Coarser oyster shell powder did not mix well with liquid residue unlike alkaline solution. The solid particle of oyster shell powder has size variant, even more so in OS treatment, that affect the reaction rate (Cho and Sohn, 2016). The affected reaction rate making the reactions uneven and influenced the stability of CH_4 production in reactor fed with liquid residue from oyster shell treatment (OS and IOS).

Another observation from weekly average is the increase of OS treatment methane yield until the end of experiment period. Meanwhile, alkali treatment yield was increasing up to third week. At the end of third week of alkali treatment, excess sludge had to be removed from the reactor to keep it operational, and this removal changed the methane yield to be lower than previous week. IOS treatment methane yield increased up to second week and go down again at the third week even without interference, yet average methane yield is still relatively high.

Methanogen is active at pH 6.2-8 and the optimum pH is 7-7.2 (Liu et al., 2008). OS treatment had the lowest pH and it was lower than the active range of methanogen. IOS and alkali treatments had the same pH and caused the methane yield to not differ significantly, unlike with OS treatment. The lower CH_4 concentration in both oyster shell treatments shows that addition of oyster shell or $CaCO_3$ in the liquid residue will release CO_2 and reduce CH_4 concentration in biogas. Mayumi et al. (2013) mentioned that high CO_2 concentration can shift methanogenesis pathway to acetoclastic methanogen pathway and accelerates methanogenesis. This acceleration of methanogenesis could be the cause of the high methane yield in the IOS treatment. Micronutrients from oyster shell can also affect the methanogen growth and increase CH_4 production (Chen et al., 2015). Looking at the difference between OS and IOS, it seems like pH have bigger effect on methane yield.

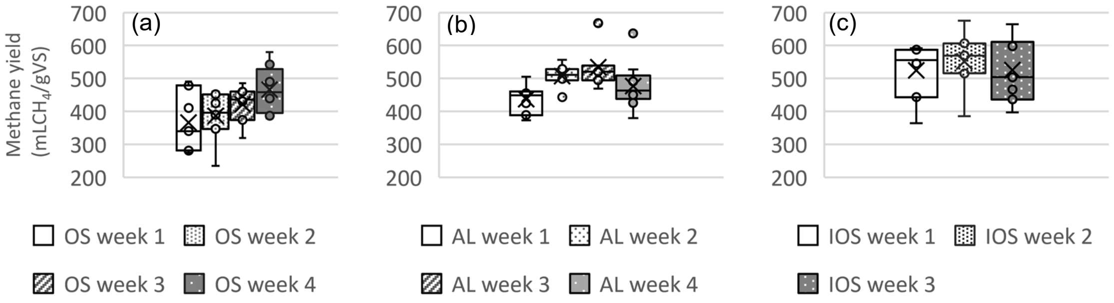

Figure 3: Weekly average of methane yields of (a) oyster shell (OS), (b) alkali (AL), and (b) industrial oyster shell (IOS) treatment.

IOS treatment has the highest overall average of specific methane yield at 533.9 mL CH_4/gVS. The second highest methane yield is alkali treatment (487.3 mL CH_4/gVS) and the last is OS treatment (413.7 mL CH_4/gVS). Lehtomaki and Bjornsson (2006) used two stage anaerobic digester and obtained specific methane yield 0.39 m^3/kgVS from grass silage. For co-digestion, methane yield from mixture of food waste and straw reached 0.392 m^3/kgVS (Yong et al., 2015) and mixture of fruit vegetable waste and food waste reached 0.49 m^3/kgVS (Ike et al., 2010). Rodriguez-Pimentel et al. (2015) used two stage system composed of batch hydrolysis reactor and UASB to digest organic fraction of municipal solid waste and obtained 279 mL CH_4/gVS. Compared to previous studies, the methane yield in IOS treatment can be considered as high. Alkali and OS treatment also obtained relatively high specific methane yield result.

3.3 Cost comparison

NaOH is a commercialized chemical alkali that is easy to acquire and commonly used to maintain pH from going acidic. Raw materials needed to produce the chemical, while using oyster shell can help in reducing oyster shell waste and reduce the cost for chemical. In Table 4, comparison of cost between IOS powder and NaOH described. OS was not included because of its minimal processing and cost. From the Table 4, more IOS powder are needed per waste material than using NaOH. The price for IOS powder is significantly lower than NaOH making the cost 78 % less than using alkali.

Table 4: Cost comparison between industrial oyster shell and chemical NaOH

Parameter	IOS (Sanyo Clay Industries Ltd.)	NaOH (Hayashi Junyaku, Co. Ltd)
g material/g waste	0.044	0.019
price (JPY/kg material)	150	1,598
Cost (JPY/kg waste)	6.6	30.26
Cost difference %	78 %	-

4. Conclusions

Performance of three kinds of pH control additives, NaOH, OS and IOS, were evaluated in terms of pH controllability, yields of CH_4 and CO_2 gas, properties of liquid and solid residue, and cost as well, by using two-stage anaerobic digester system. The following remarkable results ere obtained. IOS with smaller particle size can increase hydrolysis reactor pH higher than OS with rougher particle size and the same dosage. Due to higher pH, IOS treatment could hydrolyze more effectively, produced better quality of liquid residue, and higher methane yield than OS. Addition of oyster shell increased CO_2 release from both stages of hydrolysis and methanogenesis and decreased CH_4 percentage in biogas. More CO_2 was released from treatment with smaller oyster shell particles (IOS). The methane concentration of oyster shell treatments is more or less the same regardless the oyster shell powder size and still higher than typical biogas. The insoluble oyster shell particle in liquid residue also causes the methane production in oyster shell treatment to fluctuate. From cost perspective, using IOS is 78 % cheaper than using NaOH. Besides buffering ability of oyster shell addition, using oyster shell was also more practical than NaOH that needs continuous addition and monitoring.

References

Babel, S., Fukushi, K., Sitanrassamee, B., 2004, Effect of acid speciation on solid waste liquefaction in an anaerobic acid digester, Water Research, 38(9), 2417-2423.

Bajpai, P., 2017, Basics of anaerobic digestion process, Anaerobic Technology in Pulp and Paper Industry, 7-12, Springer, Singapore.

Chen, S., Zhang, J., Wang, X., 2015, Effects of alkalinity sources on the stability of anaerobic digestion from food waste, Waste Management & Research, 33(11), 1033-1040.

Cho, J., Sohn, H.Y., 2016, Effects of particle shape and size distribution on the overall fluid-solid reaction rates of particle assemblages, The Canadian Journal of Chemical Engineering, 94(8), 1516-1523.

Crozier, C., Hardy, D., 2003, Soil acidity and liming for agricultural soils, Soil Facts, N.C. Cooperative Extension, North Carolina, USA.

Environmental Protection Agency, 2006, Biosolids technology fact sheet: multi-stage anaerobic digestion, National Service Center or Environmental Publications (NSCEP),US EPA Office of Water, Washington, DC, USA.

Horn, M.A., Matthies, C., Küsel, K., Schramm, A., Drake, H.L., 2003, Hydrogenotrophic methanogenesis by moderately acid-tolerant methanogens of a methane-emitting acidic peat, Applied and Environmental Microbiology, 69(1), 74-83.

Ike, M., Inoue, D., Miyano, T., Liu, T.T., Sei, K., Soda, S., Kadoshin, S., 2010, Microbial population dynamics during startup of a full-scale anaerobic digester treating industrial food waste in Kyoto eco-energy project, Bioresource Technology, 101(11), 3952-3957.

Lehtomäki, A., Björnsson, L., 2006, Two-stage anaerobic digestion of energy crops: methane production, nitrogen mineralisation and heavy metal mobilisation, Environmental technology, 27(2), 209-218.

Liu, C.F., Yuan, X.Z., Zeng, G.M., Li, W.W., Li, J. 2008, Prediction of methane yield at optimum pH for anaerobic digestion of organic fraction of municipal solid waste, Bioresource technology, 99(4), 882-888.

Mayumi, D., Dolfing, J., Sakata, S., Maeda, H., Miyagawa, Y., Ikarashi, M., Tamaki, H., Takeuchi, M., Nakatsu, C.H., Kamagata, Y., 2013, Carbon dioxide concentration dictates alternative methanogenic pathways in oil reservoirs, Nature communications, 4(1), 1-6.

Notodarmojo. P.A., Fujiwara, T., Habuer, 2021, Oyster Shell as pH Control Substitute for Two Stage Anaerobic Co-Digestion System, Chemical Engineering Transactions, 83, 481-486.

Paritosh, K., Kushwaha, S. K., Yadav, M., Pareek, N., Chawade, A., Vivekanand, V., 2017, Food waste to energy: an overview of sustainable approaches for food waste management and nutrient recycling, BioMed Research International, 2017.

Płuciennik-Koropczuk, E., Myszograj, S., 2019, New approach in COD fractionation methods, Water, 11(7), 1484.

Rodríguez-Pimentel, R. I., Rodríguez-Pérez, S., Monroy-Hermosillo, O., Ramírez-Vives, F., 2015, Effect of organic loading rate on the performance of two-stage anaerobic digestion of the organic fraction of municipal solid waste (OFMSW), Water Science and Technology, 72(3), 384-390.

Rugele, K., Bumanis, G., Bajare, D., Lakevics, V., Rubulis, J., 2014, Alkaline activated materials for pH control in biotechnologies. InKey Engineering Materials, 604, 223-226.

Salek, S. S., van Turnhout, A. G., Kleerebezem, R., van Loosdrecht, M. C. M., 2015, pH control in biological systems using calcium carbonate, Biotechnology and Bioengineering, 112(5), 905–913.

Saragih, F.N.A., Priadi, C.R., Adityosulindro, S., Abdillah, A., Islami, B.B., 2019, The effectiveness of anaerobic digestion process by thermal pre-treatment on food waste as a substrate, IOP Conference Series: Earth and Environmental Science, 251(1), 012014.

Wikandari, R., Taherzadeh, M. J., 2019, Rapid anaerobic digestion of organic solid residuals for biogas production using flocculating bacteria and membrane bioreactors–a critical review. Biofuels, Bioproducts and Biorefining, 13(4), 1119-1132.

Yong, Z., Dong, Y., Zhang, X., Tan, T., 2015, Anaerobic co-digestion of food waste and straw for biogas production, Renewable energy, 78, 527-530.

Yu, H.Q., Fang, H.H., 2003, Acidogenesis of gelatin-rich wastewater in an upflow anaerobic reactor: influence of pH and temperature, Water research, 37(1), 55-66.