International Journal of Technology 12(2) 320-328 (2021)
Received Month June 2019 / Revised October 2019 / Accepted March 2021

International Journal of Technology

http://ijtech.eng.ui.ac.id

The Simulation and Experimental Study of COD Removal from Rubber Industrial Wastewater using Anaerobic Fixed Bed Reactors

Chandra Wahyu Purnomo[1,2*], Marisah el Mawaddah[1], Silwina Bayonita[1]

[1]*Chemical Engineering Department, Universitas Gadjah Mada, Jl. Grafika No.2, Yogyakarta 55281, Indonesia*
[2]*Agrotechnology Innovation Center PIAT UGM, Kalitirto Tanjungtirto, Berbah, Sleman 55573, Indonesia*

Abstract. Industrial wastewater from natural rubber factories has a strong odor due to its high organic content of mostly protein compounds. An anaerobic fixed bed reactor (AFBR) can be used in treating rubber wastewater due to the reactor's ease of operation and short residence time. However, the reactor's design parameters need to be modeled and tested for use in a laboratory before it can be used industrially. This study aims to examine the effect of immobilization media and the presence of trace element, Fe(II), in AFBR for the treatment of natural rubber wastewater. The reactor was operated in two modes: batch and semicontinuous modes. The removal of soluble chemical oxygen demand (sCOD) and methane production during the process were monitored, and the kinetics of COD decomposition were simulated. A high reaction rate constant and high COD removal rate of more than 90% was observed when the reactor was operated using immobilized media and Fe(II).

Keywords: Anaerobic fix bed reactor; Biogas; Immobilized media; Rubber wastewater

1. Introduction

Natural rubber industries produce wastewater with the following characteristics: a pH of 4.2–4.8, Chemical Oxygen Demand (COD) of 2,000–6,000 mg/L, Biological Oxygen Demand (BOD5) of 1,000–3,500 mg/L, 250–400 mg/L of suspended solids, and a Total Kjeldahl Nitrogen (TKN) of 250–700 mg/L (Vijayaraghavan et al., 2008). The disposal of these effluents into public water bodies can cause severe pollution problems. However, in some small-scale rubber processing factories, the effluent is discharged into surroundings without sufficient treatment.

In general, Indonesia's rubber industries adopt conventional lagoon wastewater treatment systems that require extensive areas of land due to prolonged natural degradation processes. The low digestion efficiency of the anaerobic pond digestion method warrants several reaction stages to produce biogas, which requires an extensive residence time. Moreover, uncontrolled waste accumulations release methane into the atmosphere, and this accelerates global warming (Ariyanto et al., 2017). Many efforts have been made to improve conventional lagoon digester performance; for instance, high flow rate anaerobic reactors, such as anaerobic fixed bed reactors (AFBRs) and up-flow anaerobic sludge blankets (UASBs), have been developed.

*Corresponding author's email: chandra.purnomo@ugm.ac.id, Tel.: +62-274-6492171; Fax: +62-274-6492170
doi: 10.14716/ijtech.v12i2.3261

In general, an AFBR is easier to operate than a UASB, even though it has a lower COD removal rate (Sarono et al., 2016). An AFBR consists of a vertical column packed with a solid material with a high surface area, which wastewater is passed through; thus, it is also called an anaerobic filter reactor (AFR). Various packing media materials for supporting biofilm formation have been studied, such as zeolite rocks, pebbles, plastic rings, granulated activated carbon, wooden blocks, and rubber sheets (Loupasaki and Diamadopoulus, 2013). A packed bed serves as a support for biofilm; it is attached on the surface or retained within the pore spaces of the biofilm for faster growth. Joung et al. (2009) confirmed that the anaerobic filter with packed bed (honeycomb type) immobilization media from polystyrene had a 79% COD removal efficiency. Jo et al. (2016) used a downflow anaerobic filter packed with blast furnace slag (BFS) grains to treat cheese whey, and there was an 80% COD removal efficiency and a high loading rate (OLR) with an increasing methane production rate.

An optimum substrate for supporting microorganism growth should be rich in nutrients containing various elements, such as energy sources, electron acceptors, cell buildings blocks, and micronutrients (Schurer and Jarvis, 2009). In terms of microelements, Takashima et al. (2011) suggested that there is a minimum concentration of metallic elements needed to affect biogas production. For instance, the minimum concentrations of Fe, Ni, Co, and Zn are 3.5, 0.40, 0.45, and 2.0 mg/L, respectively. These micronutrients, together with sulfide, are essential for methanogen bacteria to convert acetic acids into methane (Gerardi, 2003). As stated earlier, the amount of Fe required is larger than the needed amounts of the other metals. The significant requirement of Fe ions shows that these ions become various building blocks of cell structure and microorganism metabolism systems.

In addition to being a nutrient, iron has been proven to be effective in controlling H_2S formation and increasing the microbial population in the solution (Choi et al., 2018) and in anaerobic reactors with packed media (Purnomo et al., 2017; Mawaddah et al., 2019). Qiang et al. (2012) demonstrated the importance of the Fe ion over other ions during enzyme synthesis in the growth of methanogenic bacteria. A current review noted three major roles of Fe ions: for synthesizing cellular components, such as metalloenzymes, for controlling major microbial reactions, such as methanogenesis, and improving the granulation process in anaerobic digesters for the successful operation of high flowrate digesters and preventing the accumulation of methanogen inhibitors (sulfides) in digesters (Baek, 2019).

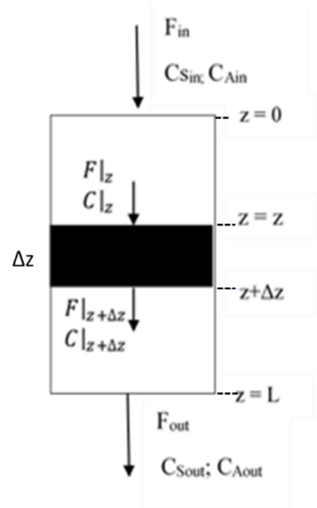
The papers on AFBRs are mostly focused on experimental results on a laboratory scale. It is necessary to operate AFBRs on a larger scale to obtain some parameters for designing an industrial scale treatment. Unlike other common wastewater, such as palm oil mill effluent (POME), rubber wastewater has not been sufficiently explored as a substrate for biogas production. Although it has a lower organic content, latex wastewater has a lower pH and higher nitrogen content than POME. Substrates with low pH pose a challenge in the Anaerobic Digestion (AD) system (Hendroko et al., 2013). Thus, this study focuses on using industrial rubber waste for biogas production using a high flow rate fixed bed reactor. Plastic bio balls were used for reactor packing to ensure a low weight of the reactor. Trace metal (Fe^{2+}) addition in biogas production was also investigated to improve the performance of the AFBR and ensure stable methane formation.

2. Material and Methods

Natural rubber wastewater with a maximum COD of 37,300 mg/L and a pH of 5, was obtained from PT. REMCO, Jambi, Indonesia. This wastewater was mixed with inoculum from an active digester effluent located in the Agrotechnology Innovation Center at

Universitas Gadjah Mada (UGM) before being loaded into the AFBR reactors. The inoculum had an sCOD level of 3,400 mg/L and a pH of 7. For displacing air inside AFBR, Nitrogen (N_2) No. CAS 7727-37-9 from PT. Samator Yogyakarta was flushed before use. Fe ions were required for trace element addition, and bio balls with diameters of 2.5 cm were used as packing media inside the reactor. The chemicals used for analysis were H_2SO4 (EMRE, 95–98%), NaOH pellets (Merck KgaA), $K_2Cr_2O_7$ (EMSURE), Ag_2SO_4 (Merck), $HgSO_4$ (EMSURE), $Na_2B_4O_7.10H_2O$ (Merck KgaA, 99.5 purity), and HCl (Merck KgaA, 37%).

This research was carried out at Pusat Inovasi Agroteknologi (PIAT) UGM (the Agrotechnology Innovation Center) Berbah, Sleman, Yogyakarta. AFBRs were made from a transparent acrylic column with a 63 cm internal diameter and height of 200 cm. The reactor had a working volume of 40 L and an inoculum/wastewater volumetric ratio of 1:2. The AFBR reactor was equipped with side sampling ports and a line for wastewater input and output. The reactor model for a mass balance simulation with element volume is represented in Figure 1.



F: flowrate, in L/day
C: concentration, in ppm
z: distance from the top
Δz: length of element volume

subscripts:
S: soluble chemical oxygen demand (sCOD)
A: volatile fatty acids (VFA) concentration
in: input
out: output
Δz: length of element volume in m

Figure 1 Schematic diagram of AFBR modeling with element volume

In Figure 1, the reactor is represented by a simple tube reactor for ease of model development. Since the solution's flowrate due to natural gravitation is very slow (5–8 L/day), it is expected that the gradual decrease of organic content concentration (sCOD) throughout the length of the reactor will follow the plug flow pattern. Based on this assumption, the mathematical model of concentration degradation that corresponds to the reactor's height can be developed via a simple cylindrical element volume, as shown in Figure 1. The volume of wastewater in the element volume can be determined by multiplying the total element volume with a void fraction (ε) of the bed, as some fraction of the volume is occupied by the bio ball.

Experimental data was obtained in the two operating modes in sequence. The first mode was the batch stage, and this stage was necessary for preparing the reactor for daily wastewater loading during the semicontinuous mode. The 40L AFBR reactor was filled with the latex wastewater and inoculum mixture substrate with an initial COD of 24,000 ppm in the batch mode. This step was necessary to allow the growth of microorganisms, and stabilization was done for 22 days or until there was no significant change in sCOD inside the reactor. The next stage was the normal operation of the flow reactor (i.e., semicontinuous operation). It was done by introducing fresh wastewater daily from the top and removing the same volume of treated wastewater from the bottom effluent by gravitational flow. Two flowrate variations (5 and 8 liters per day) were used with the same COD of 24,000 ppm from fresh latex wastewater without added inoculum. During this stage, the loading and unloading times of fresh substrate to the reactors was about 5 min beginning at 09.00 am every morning. A reactor without a bio ball (hollow tube) was operated to understand the impact of bio ball addition on the anaerobic process.

A small sample volume was taken three times a week for the batch stage from the outlet line, while during the semicontinuous stage, a sample volume was taken every day from the outlet flow to measure sCOD and VFA concentration. During the semicontinuous operating mode, the sample from the side effluent port was also collected. Soluble COD and VFA were measured using a standard method to examine water and waste American Public Health Association (APHA)5220-D (APHA, 1980). The gas volume was measured using the water replacement gas meter method (Walker et al., 2009). For ease of identification, the samples from each different reaction condition and their sampling ports are listed in Table 1. For example, the effluent sample from the reactor to which trace metal and bio balls were added, was named B-Me, and the sample effluent from the reactor without packing or Fe(II) addition was identified as NB-NMe.

Table 1 Sample identification

Sample name	Bio ball	Fe^{2+} addition	Sampling port
B-Me	Yes	Yes	Effluent
B-NMe	Yes	No	Effluent
NB-Me	No	Yes	Effluent
NB-NMe	No	No	Effluent
B-Ms	Yes	Yes	Side Effluent
B-NMs	Yes	No	Side Effluent
NB-Ms	No	Yes	Side Effluent
NB-NMs	No	No	Side Effluent

The model's governing equations were formulated based on Momodu et al. (2017) with some modifications for a continuous flow digester. A simplified bioprocess reaction in biogas production is represented by Equation 1.

$$\mathrm{S} \overset{k_1}{\rightarrow} \mathrm{A} \overset{k_2}{\rightarrow} \mathrm{G} \quad (1)$$

All organic compounds or substrates were designated as S. The conversion of these organic compounds into simple volatile acids or VFA (A) results from microorganism activity. Methane (G) formation from the intermediate product of A is achieved via the anaerobic process using methanogenic microbes. In Equation 1, the rates of formation of VFA and methane are determined by the rate constants k_1 and k_2. The rate constants' values are highly affected by the concentrations of nutrients, the population of microorganisms, temperature, and pH.

A component mass balance of decomposition of sCOD in the AFBR with a semicontinuous mode (no accumulation) as shown in Figure 1, is represented in Equation 2.

$$(F.C_S)|_{z} - (F.C_S)|_{z+\Delta z} - k_1 . C_S{}^{n} . \Delta V . \varepsilon = 0 \quad (2)$$

VFA mass balance in the continuous mode of the AFBR is shown in Equation 3.

$$(F.C_A)|_{z} - (F.C_A)|_{z+\Delta z} + k_1 . C_S{}^{n} . \Delta V . \varepsilon - k_2 . C_A{}^{m} . \Delta V . \varepsilon = 0 \quad (3)$$

Substituting *F* with *Us.A* and the element volume, *ΔV*, with *A.Δz.ε* (*ε* is a void fraction of the bed) followed by some manipulations of the above equations, the final differential equations can be obtained and are represented by Equation 4 and Equation 5.

$$\frac{dC_s}{dz} = -\frac{1}{U_s}.\varepsilon.k_1 . {C_s}^n \quad (4)$$

$$\frac{dC_A}{dz} = -\frac{1}{U_s}.\varepsilon.(k_1 . {C_s}^n - k_2 . {C_A}^m) \quad (5)$$

Us is the linear mass flow rate of materials in the digester (m/day), while k_1 and k_2 are the constant rates of COD and VFA decomposition (l/day), respectively.

3. Results and Discussion

The effect of immobilization media and Fe ion addition on anaerobic digestion performance is shown in Figure 2. These experiments were carried out in a semicontinuous mode using various reactor configurations.

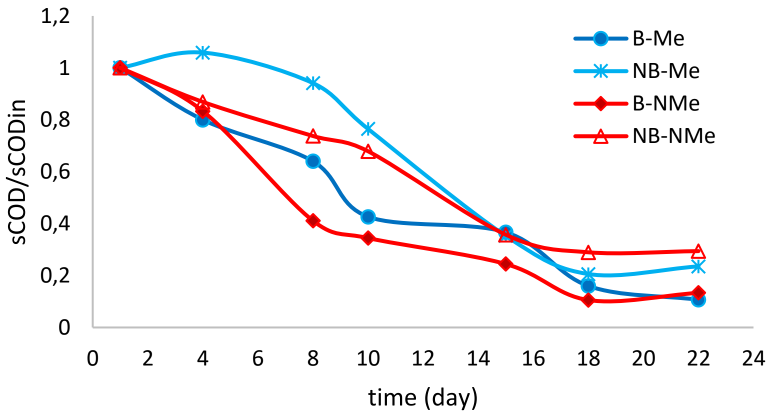


Figure 2 sCOD concentration profile of the AFBR reactor in batch mode

Figure 2 shows that the reactor with immobilized media (bio balls) had a higher sCOD reduction rate than the hollow tube reactor. In the batch mode, the reactors with a packed bed (B-Me and B-NMe) showed a fast and steady decrease of sCOD while the tube reactor had a slightly fluctuating sCOD profile. The sCOD removal rate of the packed bed reactor was larger than that of the tube reactor, indicating an enhancement in performance due to the presence of immobilized media. The addition of Fe can further increase sCOD removal. For instance, after 22 days of operation, the sCOD removal rate for the reactor with media to which Fe was added (B-Me), was 90.7% and that of the reactor without media (NB-Me) was 86.7%. In contrast, with the same residence time, the sCOD removal rates of the reactors with no metal addition (B-NMe and NB-NMe) were 76.5% and 70.5%, respectively.

The role of immobilized media in anaerobic digestion was also significant during the semicontinuous process (Figure 3). The introduction of fresh substrate during the transition time from the batch to the semicontinuous mode produced a sudden rise in sCOD content. This could have been due to an instantaneous mixing of the high organic content substrate with the remaining treated substrate in the AFBR, leading to a sudden increase of organic concentration in the reactor and the effluent.

Figure 3 shows the sCOD profiles of the semicontinuous mode after the batch mode. The sample from the side reactor effluent had a higher sCOD level than the final effluent since it was drawn before the final effluent so its residence time was lower.

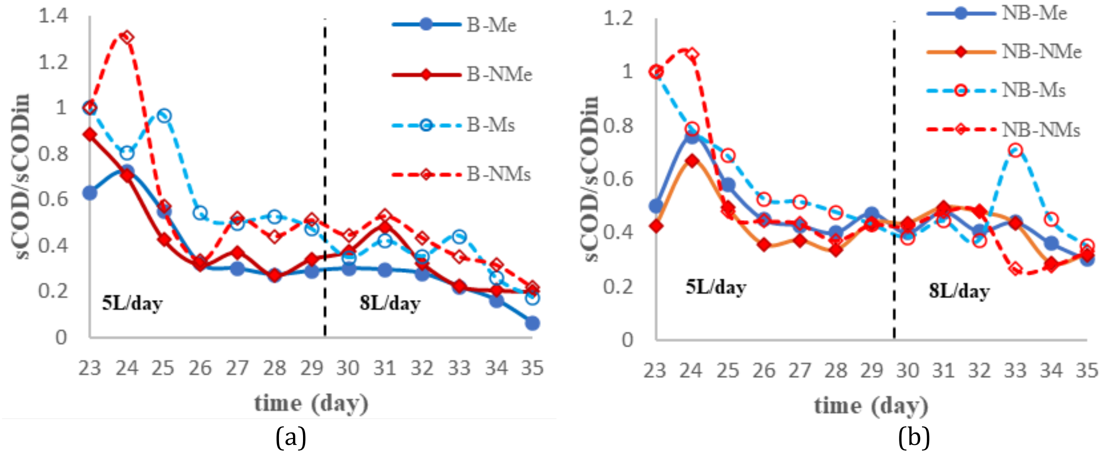


Figure 3 sCOD concentration profile of the AFBR reactor in the semicontinuous mode: (a) with bio ball; and (b) without bio ball

These differences could indicate a concentration gradient along the length of the reactor or the AFBRcould be considered a plug flow reactor. After eight days of the continuous process, the loading rate was increased from 5L/d to 8L/d, and a surge in COD level was observed although it was not as high as the first shock at the beginning of the continuous batch process. With the increase in flow rate, the reactor's residence time decreased from eight to five days. It is interesting to note that after three days of semicontinuous mode operation, the sCOD level dropped, which indicated that the reactor with immobilized media, which had a flow rate of 8 L/day, could achieve a relatively high sCOD removal rate. The reactors with immobilized media could accomplish this removal faster and even further reduced sCOD by around 80–90.7% within 13 days of operation compared to other reactor types.

Figure 3a shows an interesting result of Fe addition in the semicontinuous stage for the reactor with immobilized media; there was no significant sCOD level shock during the initial fresh loading period. It seemed that the Fe addition had enhanced the effect of the media. Even when loading was done at 8 L/day, the sCOD level could be kept low for B-Me and B-NMe samples. For the reactor without media, the addition of Fe(II) did not have a significant effect for dealing with operation mode changes. The longer the residence time, the more substrate needed by the bacteria, and insufficient nutrient availability with high COD can be a barrier to anaerobic digestion (Jo et al., 2015). At optimum conditions, AFRs can reduce organic matter concentration quickly or remove COD at a high rate (Sarono et al., 2016).

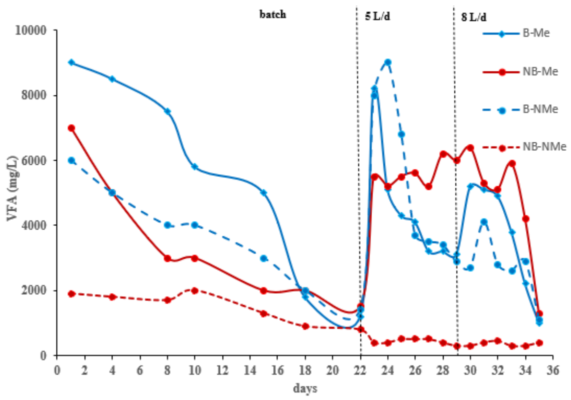


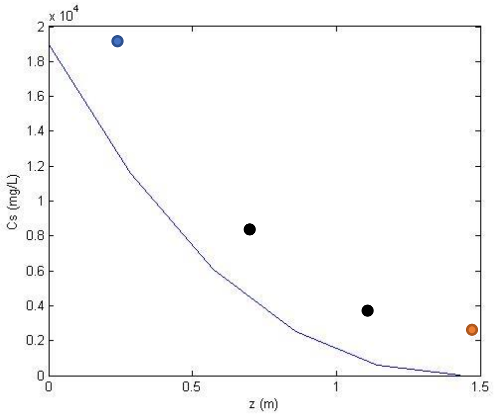
Figure 4 VFA concentration in effluent of fixed bed reactor in batch and continuous mode

Figure 4 shows the VFA concentration of a combined batch-continuous process. VFA is the intermediate product of methane generation, and the concentration is preferably low. A high acid concentration can impede methanogenic bacteria metabolism. The concentration of VFA in the effluent of the reactor with immobilized media (B-Me) was lower than that in the effluent from the hollow tube reactor (NB-Me). In the presence of bio balls, both acidogenic and methanogenic microorganisms will stick and grow on the surface of the bio balls to form a biofilm layer to promote the vast organic content conversion to methane. As a result of the twice shock loading from the batch to semicontinuous mode and the increasing loading rate, the media can suppress the VFA surge better than the non-packed bed reactor. The best reactor performance in controlling VFA concentration, especially in semicontinuous mode with loading rate fluctuation, is the reactor with a packed bed and added Fe(II), shown by the VFA profile of the B-Me sample. The concentration of VFA began to decline, so the production of methane gas increased sharply, indicating the growth of methanogenic bacteria. The addition of Fe(II) contributes to better bio-film growth and microorganism attachment to bio balls since Fe(II) will be accumulated in the extracellular membrane (EPS) that enables the microorganisms to form microbial aggregates. Divalent cations like Fe(II) can bridge negatively charged polysaccharides and proteins in the EPS matrix and stabilize the aggregate structure to create a stable biofilm on the surface of the solid (Baek et al., 2019).

Table 2 Simulation results of rate constants in various types of reactor

Constants	B-Me	B-NMe	NB-Me	NB-NMe
k_1 (1/day)	1.768	0.162	1.150	0.121
k_2 (1/day)	3.080	0.003	0.001	0.022
Error %	7.617	7.420	7.621	3.864

The simulation results of the rate constants (k_1 and k_2) are listed in Table 2. The value of the constant was affected by the type of reactor and the addition of trace nutrients. AFBRs always have higher constant values. The high value indicates the raid conversion of substrate to VFA and then to biogas. A high k_2 was observed only in the AFR with added Fe (B-Me); the k_2 values in other reactor configurations were relatively low. This indicates a synergetic effect between the biofilm and the added nutrients. Figure 5 shows some fitting of experimental data with simulation for sCOD and VFA decomposition of sCOD concentration (a) and the decomposition of VFA concentration (b) for B-Me.



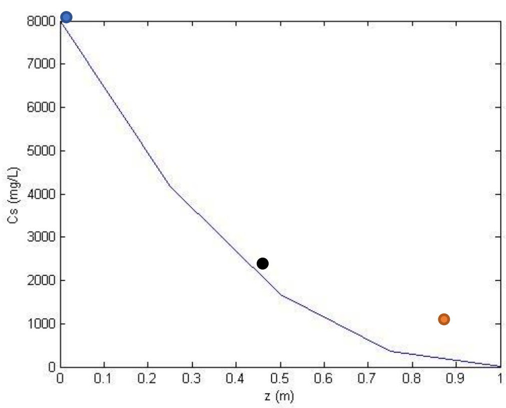


Figure 5 Fitting curves of: (a) COD; and (b) VFA

4. Conclusions

The results showed that bio balls in packed bed reactors increased sCOD removal compared to those in hollow tube reactors. The addition of Fe accelerates the rate of VFA conversion to methane. Reactors with bio balls and added Fe(II) are optimal, shown by their COD removal rates of 90.7%, which was the highest measured rate. The combination of packed media and Fe addition will provide a robust AFR due to fast degradation performance and the ability to withstand the organic loading fluctuation. This effort can increase the performance of AFBR to a level that is similar to that of the more expensive UASB reactor. This finding is supported by the simulation result of the high value of rate constants for AFBRs with added Fe(II). Other essential trace metal additives should be studied in the future, along with the possibility of metal recovery or recycling to reduce the operational cost and avoid the environmental impact of excess ions.

Acknowledgements

This study was supported by Rekognisi Tugas Akhir (RTA) grant UGM no. 488/UN1.P.III/DIT-LIT/PT/2020 and Penelitian Terapan Unggulan Perguruan Tinggi (PTUPT) no. 1860/UN1/DITLIT/DIT-LIT/PT/2020 Ministry of Research and Higher Education grants. We would like to express sincere gratitude to Dr. Mohd. Razif bin Harun from UPM for his contribution during the preparation of this manuscript.

References

American Public Health Association (APHA), 1980. *Standard Methods for the Examination of Water and Effluents Water*. 15th edition, American Public Health Association, New York, USA

Ariyanto, T., Cahyono R.B., Vente, A., Mattheij, S., Millati, R., Sarto., Taherzadeh, M.J., Syamsiah, S., 2017. Utilization of Fruit Waste as Biogas Plant Feed and its Superiority Compared to Landfill. *International Journal of Technology*, Volume 8(8), pp. 1385–1392

Baek, G., Kim, J., Lee, C., 2019. A Review of the Effects of Iron Compounds on Methanogenesis in Anaerobic Environments. *Renewable and Sustainable Energy Reviews*, Volume 113, doi.org/10.1016/j.rser.2019.109282

Choi, G., Kim, J., Lee, S., Lee, C., 2018. Anaerobic Co-digestion of High-strength Organic Wastes Pretreated by Thermal Hydrolysis. *Bioresource Technology*, Volume 257, pp. 238–248

Gerardi, M.H., 2003. *The Microbiology of an Anaerobic Digesters*. Hoboken, New Jersey, USA: John Wiley & Sons, Inc

Hendroko, R., Wahyudi, A., Wahono, S.K., Praptiningsih, G.A., Salafudin, S., Liwang, T., 2013. Bio-Refinery Study in the Crude Jatropha Oil Process: Co-Digestion Sludge of Crude Jatropha Oil and Capsule Husk Jatropha Curcas Linn as Biogas Feedstocks. *International Journal of Technology*, Volume 4(3), pp. 202–208

Jo, Y., Kim, J., Hwang, S., Lee, C., 2015. Anaerobic Treatment of Rice Winery Wastewater in an Upflow Filter Packed with Steel Slag under Different Hydraulic Loading Conditions. *Bioresource Technology,* Volume 193, pp. 53–61

Jo, Y., Kim, J., Lee, C., 2016. Continuous Treatment of Dairy Effluent in a Downflow Anaerobic Filter Packed with Slag Grains: Reactor Performance and Kinetics. *Journal of the Taiwan Institute of Chemical Engineers*, Volume 68, pp. 147–152

Joung, J.Y., Lee, H.W., Choi, H., Lee, M.W., Park, J.M., 2009. Influences of Organic Loading Disturbances on the Performance of Anaerobic Filter Process to Treat Purified

Terephthalic Acid Wastewater. *Bioresource Technology*, Volume 100(8), pp. 2457–2461

Loupasaki, E., Diamaldopoulus, E., 2013. Attached Growth Systems for Wastewater Treatment in Small and Rural Communities. *Journal of Chemical Technology and Biotechnology*, Volume 88, pp. 190–204

Mawaddah, M.E., Purnomo, C.W, Yuliansyah, T., 2019. The Effect of Packing Media Addition on Biogas Production from Rubber Industrial Wastewater. *AIP Conference Proceedings* 2085, 020029

Ministry of Agriculture, 2015. Pusat Data dan Sistem Informasi Pertanian (*Center for Agricultural Data and Information Systems*), Sekretariat Jenderal-Kementerian Pertanian (*General Secretary Ministry of Agriculture*), Jakarta, Indonesia

Momodu, O., Ekundayo, O.A., Ogiehor, I.S., Iyayi, A.F., Ohaga, S., Momoh, D., 2017. Pollution Monitoring and Control in Rubber Industry in Nigeria. *Direct Research Journal of Agriculture and Food Science*, Volume 5(7), pp. 278–283

Purnomo, C.W., Mellyanawati, M., Budhijanto, W., 2017. Simulation and Experimental Study on Iron Impregnated Microbial Immobilization in Zeolit for Production of Biogas. *Waste and Biomass Valorization*, Volume 8(7), pp. 2413–2421

Qiang, H., Lang, D.L., Li, Y.Y., 2012. High-solid Mesophilic Methane Fermentation of Food Waste with an Emphasis on Iron, Cobalt, and Nickel Requirements. *Bioresource Technology*, Volume 103(1), pp. 21–27

Sarono., Suparno, O., Suprihatin., Hasanudin, U., 2016, The Performance of Biogas Production from Pome at Different Temperatures. *International Journal of Technology*, Volume 7(8), pp. 1413–1421

Schurer, A., Jarvis, A., 2009. *Microbiological Handbook for Biogas Plants*. Swedish Waste Management U2009:03 Swedish Gas Centre Report 207, Svenkt Gastekniskt Center AB, Sweden

Takashima, M., Shimada, K., Speece, R.E., 2011. Minimum Requirements for Trace Metals Fe, Ni, Co, and Zn in Thermophilic Methane Fermentation from Glucose. *Water Environment Research*, Volume 83(4), pp. 339–346

Vijayaraghavan, K., Ahmad, D., Yazid, A.Y.A., 2008. Electrolytic Treatment of Latex Wastewater. *Desalination*, Volume 219(1-3), pp. 214–221

Walker, M., Zhang, Y., Heaven, S., Bank, C., 2009. Potential Errors in the Quantitative Evaluation of Biogas Production in Anaerobic Digestion Process. *Bioresource Technology,* Volume 100(24), pp. 6339–6346