Effect Of pH On Liquid-Phase Mass Transfer And Diffusivity Coefficient At Leachate Treatment Of Municipal Waste Landfill In Anaerobic Bioreactor

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Artikel histori:

Diterima 9 Juli 2018 Diterima dalam revisi 31 Juli 2018 Diterima 15 September 2018 Online 31 Oktober 2018 ABSTRAK: Leachate is a liquid waste resulted from physical, biological and chemical decomposition of landfill waste. Leachate contains complex dissolved organic and inorganic substrate which are biodegradable and non-biodegradable. Anaerobic treatment principally utilizes anaerobic bacteria in order to degrade the dissolved organic substance into biogas. Anaerobic treatment is very sensitive towards the substrate concentration, temperature, and pH. This research used anaerobic bioreactor with the volume of 160 L, the ratio of the leachate:biogas is 70:30. Seeding and acclimatization steps were done, respectively for 10 days, leachate treatment was done in 21 days. Seeding, acclimatization, and leachate treatment were done on the pH ambience of 7.2 and 8.0 and ambient temperature. COD and VFA analysis were done every two days. The objective of this research is to decide the pH effect on the coefficient of liquid-phase mass transfer: k_L , and the diffusivity of the dissolved substance, D_L pH affects the degradation of the concentration of dissolved organic substrate in the leachate. The higher the pH is, the higher the obtained VFA concentration is. VFA concentration is affected by pH; however, it still considers the optimal pH condition of the substrate biodegradation. pH affects the average rate of mass transfer, r_{kl} and diffusivity of the dissolved substance, D_L in the anaerobic treatment of leachate. pH affect the concentration of dissolved organic substrate which subsequently influences the coefficient of liquid-phase mass transfer of the leachate, k_L and the diffusivity of the dissolved substance, D_L . The higher the pH is, the more increasing the k_L is and the more decreasing the D_L is.

Keywords: anaerobic bioreactor; diffusivity leachate; mass transfer

1. Introduction

1.1. Leachate

Leachate is a liquid waste resulted from the influx of external water into the landfill waste. It either dissolves and washes away dissolved organic and inorganic materials or is suspended within the waste, including complex organic material resulted from physical, biological, and chemical decomposition (Kumaret al., 2013). Therefore, leachate becomes a complex mixture organic material and dissolved contaminants. Leachate contains: VFA, LCFA, fulvic and humic compounds, ammonia-nitrogen, phosphate, sulfate, heavy metal, organic xenobiotic (XOCs); aromatic phenols, and chlorinated aliphatics, hydrocarbons, inorganic salts and microorganism (Christensen et al., 2001; Renou et al., 2008; Zainol et al., 2012; Hassan and Xie, 2014); and biorefactory contaminants (Tatsi et al., 2003). Therefore, leachate contains complex dissolved organic and inorganic substrates which are biodegradable and non-biodegradable (Christensen et al., 2001).

Such characteristics make leachate very dangerous for the environment with the contamination potential transcends some industrial waste (Zainol et al., 2012; Hassan and Xie, 2014). Characteristics and quality of leachate are influenced by: characteristics and composition of waste, type of soil covering the landfill, season, pH and humid; and the age of landfill (Zainol et al., 2012; Hassan and Xie, 2014). The variation of leachate composition depends on several factors, such as composition and age of landfill, design and operation and the condition of landfill, climate and hydrogeological condition, humidity, temperature, and level of stabilization (Renou et al., 2008). The mass transfer may occur during liquid phase, gas phase, or to both phases simultaneously. It may occur during multi-phase system or one phase system (Thibodeaux, 1996; Geankoplis, 2003). With concentration gradient, there will be a movement of mass transfer from higher concentrated area to the lower concentrated area. This movement is used so that the intensive contact occurs between the dissolved material and microorganism, that it enables more mass transfer (Geankoplis, 2003; Welty et al., 2007). In the case of

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ISSN: 1410-394X

complex organic substrate, which is generally expressed as Biological Oxygen Demand (BOD); Volatile Fatty Acid (VFA) or Chemical Oxygen Demand (COD), a part of substrate which is difficult to degrade (Zaiat et al., 2000; Christensen et al., 2001; Hassan and Xie, 2014).

The essential problem of the technical scale in the development of bioreactor is hydrodynamics, the phenomenon of mass transfer between phases, kinetics, and the thermal transfer (Leib et al., 2001). Despite the fact that it is not the main factor on bioprocess, mass transfer is crucial in anaerobic bioreactor (Leib et al., 2001; Doble, 2006; Benz, 2011). Many factors influencing the mass transfer on bioprocess such as: temperature, pressure, concentration, diffusivity, viscosity, density, pH, fluid flow rate, bioreactor geometry, surface tension (Monit, 2009).

1.2. Anaerobic Bioreactor

Anaerobic treatment principally utilizes the anaerobic bacteria in order to degrade dissolved organic materials or soluble chemical oxygen demand (SCOD) to become biogas (Abdelgadir et al., 2014). The process of anaerobic decomposition degrades natural polymer, such as polysaccharides, proteins, nucleic acids, and lipids into methane and carbon dioxide. It occurs in gradual and parallel reaction. The efficiency of anaerobic bioreactor treatment is sensitive towards the composition of wastewater, temperature, and pH (Merlin et al., 2012).

Anaerobic treatment of organic material is a complex and specific biochemical reaction. Biodegradation of dissolved organic material undergoes reaction stages: hydrolysis, acidogenesis, acetogenesis and methanogenesis that happen simultaneously, either in serial or parallel ways (Zinatizadeh et al., 2006; van Lier et al., 2008; Deublein and Steinhauser, 2008; Appels et al., 2008; Abdelgadir et al., 2014). Bacteria that plays the role on the four stages works specifically and has mutual dependence (Hossain et al., 2009).

Hydrolysis is a liquifaction of organic materials using extra-celular enzyme produced by hydrolytic bacteria (Zinatizadeh et al., 2006; Deublein and Steinhauser, 2008; Appels et al., 2008). Celulolytic bacteria holds the role in hydrolisis stage, works in the pH rate of 6-7. In this process, the likelihood of pH degradation may happen due to the formation of organic acids. Hydrolisis depends on the parameter such as: particle size, pH, enzyme production, diffusion and adsorption of enzyme on the waste particle that undergoes decomposition process (Ziemiński and Frac, 2012), the substrate concentration and temperature (Gerber and Roland, 2008). Another research reported that the rate of hydrolysis constant depends on pH but not coefficient with the total and concentration of VFA (Veeken et al., 2000). And the best pH range to reach maximum biogas result in anaerobic bioreactor is 6.5-7.5 (Liu et al., 2008; Khalid et al., 2011) and 6.8-7.2 (Ward et al., 2008).

Acidogenesis is a step of the recast of organic materials resulted from hydrolysis to become amino acid, simple

sugar and VFA, including format acid, acetic, propionic, butyric, lactic, succinic, ethanol, and CO₂, H₂, NH₃, H₂S by acid-forming bacteria (van Lier et al., 2008; Ziemiński and Frac, 2012). For batch system experiment, the range of pH on stage thermophilic acidogenesis is 6-7 (Park et al., 2008). VFA is an intermediate product which is very important in anaerobic treatment (Appels et al., 2008). Acetogenesis is a stage of forming acetic compound, carbondioxyde and hydrogen (Ziemiński and Frac, 2012). It is reported that methanogenesis in anaerobic bioreactor is efficient on the pH of 6.5-8.2 (Lee et al., 2009), while hydrolysis and acidogenesis respectively on the pH of 5.5 and 6.5 (Kim et al., 2009). The last step in anaerobic biodegradation is methanogenesis. Most methanogens bacteria is mesophilic with the range of temperature between 28-42°C and thermophilic temperature with the range of 55-72°C (Ziemiński and Frac, 2012). Optimum methanogens bacteria on the pH range of 7.2-8.0 (Suryawanshi et al., 2013).

1.3. Mass Transfer and Diffusion of Dissolved Material

The coefficient of liquid-phase mass transfer is a function of liquid physical characteristic and the liquid superficial velocity (Zaiat et al., 2000; Abdelgadir et al., 2014). If the liquid-phase mass transfer becomes the limitation of the whole process rate, then k_L can be estimated with Equation 1 (Zaiat et al., 2000; Cho and Young, 2001).

$$N_L = k_L (S_b - S_i) \tag{1}$$

Where N_L is the flux of liquid-phase mass transfer, (mg/cm².h); k_L is the coefficient of liquid-phase mass transfer; S_b is the substrate concentration on the bulk liquid, (mg COD/L); and S_i is the substrate concentration on the solid-liquid interface, (mg COD/L).

Mass transfer depends on the diffusion of dissolved materials and the variables controlling the character of fluid flow such as; flow rate, viscosity, density, and a linear dimension. Diffusion based on empirical modification reported by Wilke-Chang (Geankoplis, 2003), where the solution diffusion can be calculated using Equation 2.

$$D_{L} = 7,4x10^{-8} \frac{\left(\psi_{B}.M_{B}\right)^{1/2} T}{\mu_{L}.V_{A}^{0.6}}$$
(2)

Where, D_L is liquid-phase diffusion of the dissolved materials and the solvent, cm²/s; T is temperature, K; μ_L is viscosity of the solution, cP; V_A is the molar volume of the dissolved material in normal boiled point, cm³/gmol; Ψ_B is the parameter of solvent association (water = 2.6) and M_B is the weight of solution molecule (18 g/gmol).

Several studies reported that bioreactor failures or deficient performance due to pH degradation is caused by the accumulation VFA within the system of anaerobic treatment (Visser et al., 1993; Fabián dan Gordon, 1999; Poh and Chong, 2009; Thabathaba'i et al., 2011). The increase of VFA concentration in batch system bioreactor

gives different influence towards hydrolysis, acidogenesis, and methanogenesis stages (Appels et al., 2008). The high VFA concentration will obstruct hydrolysis, acidogenesis, and methanogeneis that the adequate process of mass transfer and microorganism seeding become important things in anaerobic bioreactor (Vabilin et al., 2002).

The objectives of this research is to decide the pH influence towards the coefficient of liquid-phase mass transfer; k_L , and the diffusion of dissolved material, D_L on the leachate treatment in anaerobic bioreactor.

2. Method

Leachate used was from Sambutan Landfill, Samarinda, East Borneo, Indonesia. The anaerobic bioreactor used was featured with heater, leachate recirculation pump, leachate recirculation flowmeter, manometer, leachate entrance inlet, biogas thermometer, pressure gauge, leachate thermomeer, sampling port, leachate recirculation entrance faucet, leachate recirculation exit faucet and leachate effluent faucet. The type of this research is pilot scale experiment with semi-batch system.

This research uses anaerobic bioreactor with the total volume \pm 160 L. After doing characterization and analysis of leachate quality, subsequently the designing of anaerobic bioreactor with the design according to the need of the research was done. Then the test of leakage and calibration from the system of anaerobic bioreactor was done.

Seeding and acclimatization were done, respectively for 10 days. Then it was continued by anaerobic treatment for 21 days. Seeding and acclimatization were done in the anaerobic bioreactor on the ambient temperature with pH variation: ambient, 7.2 and 8.0, where the ratio of leachate volume: biogas was 70:30. Microorganism used was from cow rumen and leachate with the ratio of 1:3 and filtered for the extract. Analysis and parameter test of COD and VFA were done once in two days. The process of leachate treatment was stopped if the decreasing percentage of COD (COD removal) reached 60-80%.

3. Result and Discussion

3.1. Results

The condition of seeding and acclimatization was done on pH ambient. On seeding, the leachate temperature started from 27.4-29 °C, biogas temperature of 26-27.5 °C, pH decreased from 7.5-7.3, and the biogas pressure started to increase on the 9th day, for 1-1.5 mm H₂O. Meanwhile on acclimatization, the leachate temperature started for 28.2-28.5 °C, biogas temperature of 27-27.9 °C, pH increased from 7.2-7.7, and biogas pressure increased from 4-21 mm H₂O, with the average value of BOD/COD 0.58.

The condition of seeding and acclimatization was done on pH of 7.2. On seeding, the leachate temperature started from 28.2-29 °C, biogas temperature of 27.5–28.5 °C, and the biogas pressure started to increase on the 6^{th} day, with the up and down fluctuation between 1 up to 5 mm H_2O . Meanwhile on acclimatization, the leachate temperature started for 27-27.5 °C, biogas temperature of 26-27.5 °C,

and biogas pressure increased from 7-29 mm H₂O, with the average value of BOD/COD 0.70.

The condition of seeding and acclimatization was done on pH of 8.0. On seeding, the leachate temperature started from 27–28.5 °C, biogas temperature of 26–27.9 °C, and the biogas pressure started to increase on the 8^{th} day, with the up and down fluctuation between 1–2 mm H₂O. Meanwhile on acclimatization, the leachate temperature started for 27-28.5 °C, biogas temperature of 26-27.9 °C, and biogas pressure increased from 3-17 mm H₂O, with the average value of BOD/COD 0.65.

3.2. Mass Transfer Rate, r_{kL} and Diffusion Rate of Dissolved Material, r_{DL}

On pH ambient, the average mass transfer rate per day was the lowest of 0.00407 mg/L.day and the highest on the 27th day which was 0.14134 mg/L.day. The rate of dissolved material diffusion ranged between 5.57442x10⁻⁵ - 1.40034×10^{-4} cm²/s. On the pH of 7.2, the average rate of mass transfer per day was the lowest of 0.00227 mg/L.day and the highest on the 25th day was 0.16953 mg/L.day. The rate of dissolved material diffusion initially decreased and then increased, with the range between 5.96009x10⁻⁵ -1.44715x10⁻⁴ cm²/s. Meanwhile on the leachate treatment within anaerobic bioreactor with the pH of 8.0, the average rate of mass transfer per day was the lowest of 0.02957 mg/L.day and the highest on the 37th day was 0.13090 mg/L.day. The rate of dissolved material diffusion went up and down, with the range between 5.54146x10⁻⁵ - $1.2416 \times 10^{-4} \text{ cm}^2/\text{s}.$

A research about pH influence on two-phased anaerobic bioreactor reported that acidogenic bioreactor preserved on the pH of 6.0-7.0; resulted in the decrease of SCOD from 6000 mg/L to 1000-1500 mg/L, that the efficiency of COD removal increased from 50% to 80%. And the methane production of 0.32 m 3 CH $_4$ /kg COD removed with methane contents on the methanogenic bioreactor of 80-90%. Meanwhile, without the pH control, the pH condition on acidogenic bioreactor increased up to 8.2; the acid conversion decreased yet the COD degradation was almost similar to the pH controlled on 6.0-7.0. Only without the pH control, methane contents from methanogenic bioreactor increases more for 90% (Jung et al., 2000).

3.3. Discussion

3.3.1. pH

pH in seeding and acclimatization steps, went up and down from the lowest of 6.3 and increased up to 7.9. As seen in Figure 1, where seeding and acclimatization steps were done on the first day until the 20th day. It can be seen that seeding step on pH ambient ranged between 6.2 up to 7.8. Meanwhile, acclimatization step on pH ambient ranged between 6.3 up to 8.0.

ISSN: 1410-394X

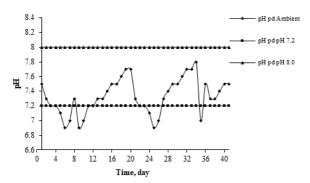


Figure 1. pH on multiple variations

pH is one of important parameters on anaerobic treatment because methanogenic bacteria is very sensitive towards the change of pH. Methane-forming bacteria live well on neutral to a little alkali condition. pH in bioreactor is directly dependent on the retention time (Kigozi et al., 2014).

pH on both stages, seeding-acclimatization steps and anaerobic treatment, showed the difference of pH range. Where pH of seeding-acclimatization was on a little acid pH while pH of anaerobic treatment was on a little alkali pH. It occurred due to the fact that biodegradation stage involved hydrolysis bacteria which produced extra-cellular enzyme (Abdelgadir et al., 2014). This group of cellulolytic bacteria optimally played the role on the pH ranging between 6-7. Dihydrolisis protein became amino acid by the protease functioning as exo-enzyme. Hydrolysis lipid became glycerol and fat acid. Hydrolysis hydrocarbon became glucose and other simple sugars. Hydrolysis was done by facultative anaerobic bacteria through exo-enzyme (Wiesmann et al., 2007). In this process, the likelihood of pH decrease may happen due to the formation of organic acids.

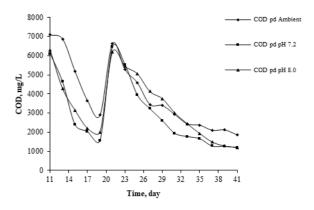
In initial stage, a large number of VFA is produced by acid-forming bacteria, pH in bioreactor may decrease up to below 5. This condition can obstruct or stop the process within bioreactor. Methanogenic bacteria is very sensitive towards the change of pH and cannot develop on the pH below 6.5 despite the fact that the process can still run within pH range between 6.0-8.0 (Kigozi et al., 2014).

Meanwhile, on anaerobic treatment stage, where anaerobic biodegradation that played the role was methanogenesis bacteria; hydrogenophilic or hydrogenotrophic, that formed methane from ${\rm CO_2}$ and ${\rm H_2}$ and methanogens acetoclastic or acetotrophic, resulting in methane by acetate decarbonization manner (Sekiguchi dan Kamagata, 2004). The group of methanogens bacteria utilized the result from three biogas. Methanogens bacteria is optimally mesophilic within the temperature range of 28-42 °C (Ziemiński and Frac, 2012) and optimum on the pH range of 7.2-8.0 (Suryawanshi et al., 2013).

3.3.2. COD and BOD

The indicator of microorganism success in biodegradation is the decrease of substrate concentration (COD and BOD) in the leachate, as shown in Figure 2.

The substrate concentration (COD and BOD) on acclimatization stage, 11th day up to 21st day, decreased, as shown on figure 4.10 and 4.11. The minimal decrease of COD was 40.42% and maximal of 75.07%. Meanwhile the minimal decrease of BOD was 41.97% and maximal of 72.78%.



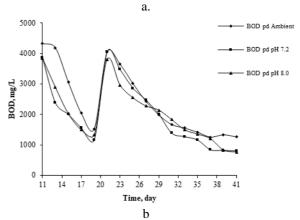


Figure 2. a. COD and b. BOD on pH variations

The decrease of COD and BOD on acclimatization stage was caused by the decrease of dissolved substrate concentration utilized by microorganism to grow, reproduce, and adapt within the leachate. Therefore, in this stage, the hydrolysis undissolved complex organic molecules become simple molecules dissolved in the leachate. It indicates that the growth of bacteria goes well. It can also be seen that the value of biodegradability ratio BOD/COD ranges between 0.43-0.70. The process of anaerobic treatment is effective enough for leachate with the high BOD:COD ratio resulted from the landfill initial stage (Li et al., 2010).

After the acclimatization stage entered the anaerobic treatment stage, leachate was added on the 21st day, COD and BOD increased again, as seen in figure 2. Such increase occurred due to the addition of organic and inorganic materials dissolved in the leachate within the bioreactor. Therefore, COD and BOD increased due to the addition of substrate concentration to the leachate.

The pH also affects the decrease of substrate concentration in anaerobic treatment stage, the 21st until 41st days. The percentage of COD decrease on pH ambient,

pH 7.2 and pH 8.0 respectively were 71.84%, 81.43% and 80.55%. Therefore, COD removal on pH 7.2> pH 8.0 > pH ambient. Meanwhile BOD removal obtained ranged between 68.91% and 80.29%. With average COD and BOD removal respectively were 77.94% and 76.37%.

On overall stages, seeding-acclimatization and anaerobic treatment, the COD and BOD removal were on pH 7.2 > pH 8.0 > pH ambient. The bigger COD reduction was, the bigger the organic material degraded to organic acids. Organic acids were subsequently converted to methane gas. Therefore, the bigger reduction of COD was, the bigger the rate of methane gas formation was.

3.3.3. VFAs

VFA is an intermediate product (Appels et al., 2008) that will be converted on acetogenesis stage to become acetate acid (Gerardi, 2003; Ganidi et al., 2009), CO₂ and H₂ (Ziemiński and Frac, 2012). The VFA concentration is determined as a parameter in order to figure out how far the acidogenesis and acetogenesis stages go. Where VFA concentration becomes one of the good parameters to monitor in deciding the stability of anaerobic bioreactor.

The higher the pH is, the higher the obtained VFA concentration is. The VFA concentration is influenced by pH. On pH influence, it is obtained that the VFA concentration ranges between 83.33–370.63 mg/L. However, it still considers the optimum pH condition of the microorganism involved in such biodegradation. Where

VFA and pH ambient > pH 7.2 > pH 8.0 as seen in Figure 3.

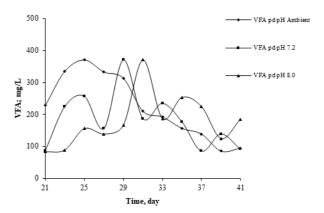


Figure 3. VFA from pH variation

As seen in figure 4, in the initial treatment, VFA increase is accompanied by the decrease of substrate concentration (COD and BOD). As time goes by, the bigger the COD and BOD removal are, the more decreasing VFA is. It is an undeniable fact that the exponential increase of VFA decreases again; it shows that the dependence of VFA towards the limited substrate concentration in the leachate (Reid *et al.*, 1991). It can also be seen that the highest VFA concentration in all operation condition was on the 25th - 31st days.

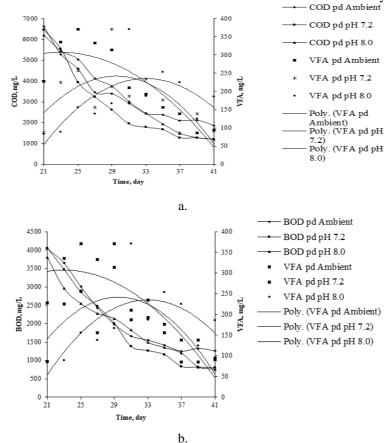


Figure 4. a. COD vs VFA and b. BOD vs. VFA

ISSN: 1410-394X

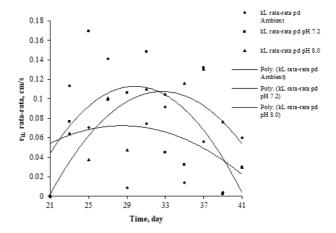
The VFA accumulation within anaerobic bioreactor represented imbalance between acid produced and consumed by bacteria. If the bioreactor overloads and the content of VFA concentration is high, bigger than what the methane-producing bacteria consumes (slow-growers), then the biogas production will increase. This increase potentially improves the foaming in anaerobic bioreactor (Baber, 2005). The higher the biodegraded COD is, the higher VFA concentration is. The more decreasing the substrate concentration is, the more decreasing the VFA concentration is. It is in line with the statement that the higher reduced substrate concentration is, the bigger the biodegraded dissolved organic material to become organic acids is. This VFA is subsequently converted into methane gas. Therefore, if the decrease of COD gets bigger, then the rate of biogas formation becomes higher.

3.3.4. Liquid-Phase Mass Transfer and Diffusion of Dissolved Material

The mass transfer and dissolved material diffusion in the leachate also depends on the change of dissolved substrate concentration within the leachate. The average of mass transfer per day is the number dissolved material substrate biodegraded in each day. COD degradation is accompanied by the increase of mass transfer rate, average r_{kL} per day. Diffusion of dissolved material, D_L decreases by the increase of the pressure. As seen in figure 5, figure 6, and figure 7.

On pH ambient, it is obtained that the average lowest r_{kL} per day is 0.00407 mg/L.day and the highest on the 27th day is 0.14134 mg/L.day. r_{DL} of the dissolved material ranges between 5.57442 x 10^{-5} - 1.40034 x 10^{-4} cm²/s. On pH of 7.2, the average lowest r_{kL} per day is 0.00227 mg/L.day and the highest on the 25th day is 0.16953 mg/L.day. The coefficient of liquid-phase mass transfer is 0.08400 cm/s. r_{DL} of the dissolved material initially decreases and then increases, with the range between 5.96009 x 10^{-5} - 1.44715 x 10^{-4} cm²/s. Meanwhile with the pH of 8.0, the obtained lowest average r_{kL} per day is 0.02958 mg/L.day and the highest on the 37th day is 0.13090 mg/L.day. The

coefficient of liquid-phase mass transfer is 0.09200 cm/s. r_{DL} of the dissolved material initially decreases and then increases, with the range between 5.54146 x $10^{-5} - 1.2416$ x 10^{-4} cm²/s.



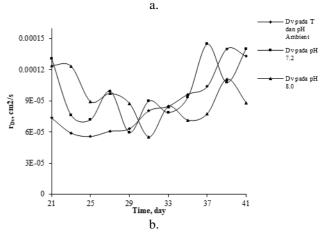
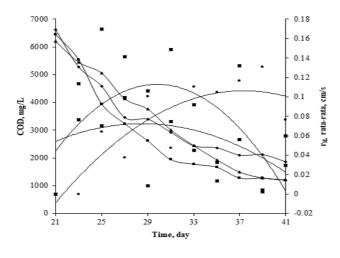
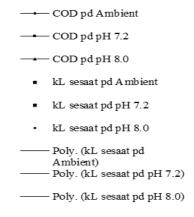
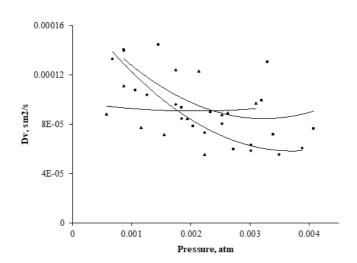


Figure 5. r_{kL} and r_{DL} on pH variations

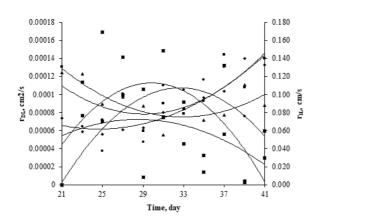






- Tekanan vs Difusivitas pd pH Ambient
- Tekanan vs difusivitas pd pH
 7.2
- Tekanan vs difusivitas pd pH
 8 0
- Poly. (Tekanan vs Difusivitas pd pH Ambient)
- —— Poly. (Tekanan vs difusivitas pd pH 7.2)
- Poly. (Tekanan vs difusivitas pd pH 8.0)

 $\label{eq:b.b.} \textbf{Figure 6}. \ a. \ COD \ vs \ r_{kL} \ on \ pH \ variation; \ b. \ Diffusivity \ vs \ Biogas \ Pressure \ on \ pH \ variation$



- Dv pd Ambient
- Dv pd pH 7.2
- ▲ Dv pd pH 8.0
- kL pd Ambient
- kL pd pH 7.2
- kL pd pH 8.0
 Poly. (Dv pd Ambient)
- Poly. (Dv pd pH 7.2)
- Poly. (kL pd Ambient)
 Poly. (kL pd pH 7.2)

Figure 7. r_{DL} vs r_{kL} on pH variation

The k_L and D_L of leachate treatment within the anaerobic bioreactor done on pH ambient, pH 7.2 and pH 8.0. Where the coefficient of liquid-phase mass transfer increases from 0.056 - 0.092 cm/s, while the diffusivity of dissolved materials decreases from 4.10 x 10^{-6} to 1.10 x 10^{-6} cm²/s, as seen from Table 1.

Table 1. Liquid-phase Mass Transfer Coefficient, k_L , and Coefficient of Dissolved Materials Diffusion; D_L

Treatment, pH	k_{L_s} cm/s	D_L , cm ² /s
Ambient	0.056	4.10^{-06}
7.2	0.084	2.10^{-06}
8.0	0.092	1.10^{-06}

On the treatment of pH variation, it can be seen that the higher pH is, the more increasing k_L is and the more increasing the D_Lis. k_L pH $8.0 > k_L$ pH $7.2 > k_L$ pH ambient. Meanwhile D_L pH ambient D_L pH ambient D_L pH D_L p

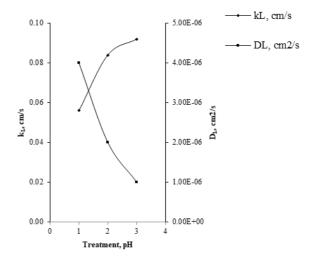


Figure 8. D_L vs k_L on pH variations

ISSN: 1410-394X

Table 2. Research on Mass Transfer

Bioreactor	Wastewater	V _R , L	HRT(days)	Temp.	COD _{Inf.} (mg/L)	COD _{Rem.}	Mass Transfer Coefficient, k _L	References
HAIB (pilot-scale)	Glucose-based synthetic substrate	237	8 h	30	2.090-41	98	3.40.10 ⁻² cm/h	Zaiatet al., 2000
	Domestic Sewage		8 h	30	341-71	79.2	2.23.10 ⁻¹ cm/h	Zaiatet al., 2000
Two-stage Anaerobic Filter	Brewery wastewater	7.45 and 6.55	0.5-6 d	35	1500-2500 (OLR 0.5-20 g SCOD/L.d	98.2	1.4-2.2 d ⁻¹	Cho and Young, 2001
Fixed-Bed ASBR	Synthetic Wastewater (Polyurethane Foam)	1.2	8 h	30	500-68	72-87	1.98-1.85 h ⁻¹	Ramos et al., 2003
UASB	Synthetic Wastewater (phenol)	3.78	0.97-1.03 d	35	10.53-12.61 kg COD/m ³ .d	99.3- 96.3	19.2 mg phenol/L	Chou and Huang, 2005
SASBR	Synthetic Wastewater (Polyurethane Foam)	5		30	285-333	84-89	0.48-0.60 h ⁻¹	Cubas et al., 2007
Anaerobic Batch Bioreactor (pilot-scale)	Leachate	160	1 d	Ambient (27-30)	6200-6625.4	71.84- 81.43	0.056, 0.084 and 0.092 cm/s	This research

Annotation:

HAIB: Horizontal-Flow Anaerobic Immobilized Biomass UASB: Upflow Anaerobic Sludge Bed Reactors ASBR: anaerobic sequencing batch Reactor SASBR: Stirred Anaerobic Sequencing Batch Reactor

The large number of wastewater used in the research on mass transfer is synthetic wastewater (Zaiat et al., 2000; Ramos et al., 2003; Chou and Huang, 2005; Cubas et al., 2007) and on laboratory scale (Cho and Young, 2001; Ramos et al., 2003; Chou and Huang, 2005; Cubas et al., 2007). The research done by Souza et al. (2014) aims at finding out the density and viscosity of leachate on different temperatures. Meanwhile, the research done by Vavilin et al. (2002), on anaerobic bioreactor of solid waste on the influence of leachate recirculation and pH aims at analyzing the balance between hydrolysis rate/organic polymer acidogenesis and methanogenesis. comparison of the research done in this research is shown in Table 2.

4. Conclusion

The pH affects the decrease of concentration of dissolved organic substrate (COD and BOD) of the leachate. The higher the pH is, the higher the obtained VFA concentration is. VFA concentration is influenced by pH, but still considering the optimum pH condition of the biodegraded substrate. pH affects the average mass transfer rate, r_{kL} on the anaerobic treatment of leachate. pH affects the concentration of dissolved organic substrate which subsequently influences the coefficient of liquid-phase mass transfer of leachate, k_L and diffusivity of dissolved material, D_L . The higher the pH is, the more increasing the k_L is and the more decreasing the D_L is. The k_L pH $8.0 > k_L$

pH 7.2 > k_L pH ambient. Meanwhile, D_L pH ambient > D_L pH 7.2 > D_L pH 8.0. The coefficient of liquid-phase mass transfer increases from 0.056–0.092 cm/s, while the diffusivity of dissolved material decreases from 4.10 x 10^{-6} to 1.10×10^{-6} cm²/s.

Acknowledgement

We thank the Directorate of Research and Community Service (DP2M) Dikti that have funded this research, with the letter of agreement No: No: 416/UN17.41/KL/2017.

Nomenclature

 N_L is flux of liquid-phase mass transfer, (mg/cm².h)

 k_L is coefficient of liquid-phase mass transfer

 S_b is substrate concentration on bulk liquid, (mg COD/L)

Si is substrate concentration on solid-liquid interface, (mg COD/L)

 D_L is liquid-phase diffusion of dissolved material and solvent, (cm²/s)

T is temperature, (K)

 μ_L is viscosity of solvent, (cP)

 V_A is molar volume of dissolved material in normal boiling point, (cm³/gmol)

 Ψ_B is the parameter of solvent association (air = 2.6)

 M_B is the weight of solvent molecule (18 g/gmol)

References

- Abdelgadir, A., Xiaoguang Chen, Jianshe Liu, XuehuiXie, Jian Zhang, Kai Zhang, Heng Wang, and Na Liu., 2014. Characteristics, Process Parameters, and Inner Components of Anaerobic Bioreactors. BioMed Research International Volume 2014, Article ID 841573, http://dx.doi.org/10.1155/2014/841573, pp. 1-10.
- Appels, L., Jan Baeyens., Jan Degre've., Raf Dewil., 2008. Principles and potential of the anaerobic digestion of waste-activated sludge. Progress in Energy and Combustion Science 34 (2008) 755–781.
- Barber, W.P., 2005. Anaerobic Digester Foaming: Causes and Solutions. Water 21 (FEB), 45-49.
- Benz, G.T., 2011. Bioreactor Design for Chemical Engineers. American Institute of Chemical Engineers (AIChE), August 2011. www.aiche.org/cep.p.21-26.
- Cho, Y.T., and Young, J.C., 2001. Prediction of Gas Production and COD Removal of Two-Stage Cyclic Anaerobic Filters by Mass Transfer Models. Environ. Eng. Res. Vol. 6, No. 4, 2001, pp. 211-222.
- Chou, H.H., and Ju-Sheng Huang., 2005. Role of Mass Transfer Resistance in Overall Substrate Removal Rate in Upflow Anaerobic Sludge Bed Reactors. Journal of Environmental Engineering, Vol. 131, No. 4, April 1, 2005. ISSN 0733-9372/2005/4-548-556 DOI:10.1061/(ASCE)0733-9372(2005) 131:4(548).
- Christensen, T.H., Peter Kjeldsen, Poul L. Bjerg, Dorthe L. Jensen, Jette B. Christensen, Anders Baun, Hans-Jorgen Albrechtsen, Gorm Heron., 2001. Review: Biogeochemistry of Landfill Leachate Plumes. Apllied Geochemistry 16 (2001) 659-718.
- Cubas, S.A., E. Foresti, J.A.D. Rodrigues, S.M. Ratusznei, M. Zaiat., 2007. Effects of solid-phase mass transfer on the performance of a stirred anaerobic sequencing batch reactor containing immobilized biomass. Bioresource Technology 98 (2007), p. 1411-1417.
- Deublein, D., and Steinhauser, A., 2008. Biogas from waste and renewable resources. Weinheim, Willey-VCH Verlag GmbH & Co. KGaA.
- Doble, M., 2006. Avoid the Pitfalls of Bioprocess Development. Bioprocessing, August 2006. www.cepmagazine.org. p.34-41.
- Ganidi, N., Sean Tyrrel., Elise Cartmell., 2009. Anaerobic Digestion Foaming Causes A review. Bioresource Technology, Volume 100, Issue 23, December 2009, p. 5546-5554.
- Geankoplis, C.J., 2003. Transport Processes and Separation Process Principles. Fourth Edition. International Edition Pearson Prantice Hall, NJ.
- Gerardi, M.H., 2003. The microbiology of anaerobic Digesters. 1st ed. Somerset NJ: Wiley.
- Gerber, M., and Roland Span., 2008. An Analysis of Available Mathematical Models for Anaerobic

- Digestion of Organic Substances for Production of Biogas. International Gas Union Research Conference IGRC, Paris.
- Hassan, M., and Xie, B., 2014. Use of aged refuse-based bioreactor/biofilter for landfill leachate treatment. Appl. Microbiol. Biotechnol (2014) 98:6543–6553, DOI 10.1007/s00253-014-5813-5
- Hossain, Sk.M., N. Anantharaman, and Manas Das., 2009. Anaerobis Biogas Generation from Sugar Industry Wastewater in Three-phase Fluidized-Bed Bioreactor. Indian Journal of Chemical Technology, Vol. 16, January 2009, pp.58-64.
- Khalid, A., Muhammad Arshad, Muzammil Anjum, Tariq Mahmood, and Lorna Dawson, 2011. Review: The anaerobic digestion of solid organic waste. Waste Management 31 (2011).1737–1744.
- Kigozi, R., A. Aboyade and E. Muzenda., 2014. Biogas Production Using the Organic Fraction of Municipal Solid Waste as Feedstock. Int'l Journal of Research in Chemical, Metallurgical and Civil Engg. (IJRCMCE) Vol. 1, Issue 1(2014) ISSN 2349-1442 EISSN 2349-1450, p. 107–114, http://dx.doi.org/10.15242/IJRCMCE.E1113563.
- Kim, J., Park, C., Kim, T.H., Lee, M., Kim, S., Kim, S.W., Lee, J., 2003. Effects of various pretreatments for enhanced anaerobic digestion with waste activated sludge. J.Biosci. Bioeng. 95, p.271–275.
- Kumar, S., DhruvKatoria and Gaurav Singh. 2013. Leachate Treatment Technologies. International Journal of Environmental Engineering and Management. ISSN 2231-1319, Volume 4, Number 5 (2013), pp. 439-444.
- Lee, D.H., Behera, S.K., Kim, J., Park, H.S., 2009.

 Methane production potential of leachate generated from Korean food waste recycling facilities: a lab scale study. Waste Manage. 29, p.876–882.
- Lee, W.S., Adeline Seak May Chua, Hak Koon Yeoh, Gek Cheng Ngoh., 2014. A review of the production and applications of waste-derived volatile fatty acids. Chemical Engineering Journal 235 (2014) 83–99.
- Leib, T.M., Carmo J. Pereira, and John Villadsen., 2001. Bioreactors: a chemical engineering perspective. Chemical Engineering Science 56 (2001) 5485–5497.
- Li, W., Zhou, Q., and Hua1, T., 2010. Review ArticleRemoval of Organic Matter from Landfill Leachate by Advanced Oxidation Processes: A Review. International Journal of Chemical Engineering Vol. 2010, Article ID 270532, 10 pages doi:10.1155/2010/270532.
- Liu, C., Yuan, X., Zeng, G., Li, W., Li, J., 2008. Prediction of methane yield at optimum pH for anaerobic digestion of organic fraction of municipal solid waste. Bioresour. Technol. 99, p.882–888.
- Liu, H., J. Wang, X. Liu, B. Fu, J. Chen, H. Yu., 2012. Acidogenic fermentation of proteinaceous sewage

ISSN: 1410-394X

- sludge: effect of pH. Water Res. 46 (2012) 799-807.
- Merlin, G., François Kohler., Maele Bouvier., Thierry Lissolo., Hervé Boileau., 2012. Importance of heat transfer in an anaerobic digestion plant in a continental climate context. Bioresource Technology 124 (2012), p.59–67.
- Monit, M., 2009. Bioprocess Design: The Geogas Project:
 Bioremediation of geothermal gases and SCP
 production with HOX/SOX bacteria. A Master's
 thesis done at RES the School for Renewable
 Energy Science. in affiliation with University of
 Iceland & the University of Akureyri Akureyri,
 February 2009. www.res.is.
- Park, Y., Tsuno, H., Hidaka, T., Cheon, J., 2008. Evaluation of operational parameters in thermophilic acid fermentation of kitchen waste. J. Mater. Cycl. Waste Manage. 10, p.46–52.
- Poh, P.E., Chong, M.F., 2009. Development of anaerobic digestion methods for palm oil mill effluent (POME) treatment. Bioresour. Technol. 100, p. 1–9.
- Ramos, A.C.T., Suzana M. Ratusznei, José A.D. Rodrigues, Marcelo Zaiat, 2003. Mass transfer improvement of a fixed-bed anaerobic sequencing batch reactor with liquid-phase circulation. Interciencia, vol. 28, no. 4, April, 2003, 0378-1844/03/04/214-06, pp. 214-219.
- Renou, S., J.G. Givaudan, S. Poulain, F. Dirassouyan and P. Moulin., 2008. Landfill leachate treatment: Review and opportunity. Journal of Hazardous Materials 150 (2008), 0304-3894, doi:10.1016/j.jhazmat.2007.09.077, p. 468–493.
- Souza, M.A.B.B., Oliveira, M.B., Araújo, A.S.F., de Castro J.A., 2014. Analyze of the Density and Viscosity of Landfill Leachate in Different Temperatures. American Journal of Environmental Engineering 2014, 4(4): 71-74. DOI: 10.5923/j.ajee.20140404.01
- Suryawanshi, P.C., Chaudhari A.B., Bhardwaj S., and Yeole T.Y., 2013. Operating Procedures for Efficient Anaerobic Digester Operation. Research Journal of Animal, Veterinary and Fishery Sciences, ISSN 2320 6535, Vol. 1(2), March (2013),12-15.
- Tabatabaei, M., Alawi Sulaiman, Ali M. Nikbakht., NorjanYusof., GhasemNajafpour. 2011. Influential Parameters on Biomethane Generation in Anaerobic Wastewater Treatment Plants. ISBN: 978-953-307-372-9, InTech, Available from: http://www.intechopen.com
- Tatsi, A.A., A.I. Zouboulis, K.A. Matis, P. Samaras., 2003. Coagulation–flocculation pretreatment of sanitary landfill leachates. Chemosphere 53 (2003) 737–744. doi:10.1016/S0045-6535(03)00513-7.
- Thibodeaux, L.J., 1996. Environmental Chemodynamics: Movement of Chemical in Air, Water, and Soil.

- Second Edition. Awiley-Interscience Publication. John Wiley & Sons, Inc. NY.
- Van Lier, J.B., Mahmoud, N., and Zeeman, G., 2008.

 Anaerobic Wastewater Treatment: Biological
 Wastewater Treatment: Principles Modelling and
 Design. Edited by M. Henze, M.C.M. van
 Loosdrecht, G.A. Ekama, and D. Brdjanovic.
 ISBN: 9781843391883. IWA Publishing, London,
 UK. p. 401-441.
- Vavilin, V.A., Rytov, S.V., Lokshina. L.Y., Pavlostathis, S.G., Barlaz, M.A., 2002. Distributed model of solid waste digestion-effects of leachate recirculation and pH adjustment. Biotechnol Bioeng 2002;81:66-73.
- Veeken, A., Sergey Kalyuzhnyi, Heijo Scharff, and Bert Hamelers., 2000. Effect of pH and VFA on hydrolysis of organic solid waste. Journal of Environmental Engineering, Vol. 126, No. 12, December, 2000, ISSN 0733-9372/00/0012, p.1076-1081.
- Ward, A.J., Hobbs, P.J., Holliman, P.J., Jones, D.L., 2008.
 Optimization of the anaerobic digestion of agricultural resources. Bioresour. Technol. 99, p.7928–7940.
- Welty, J.R., Charles E. Wicks, Robert E. Wilson, and Gregory L. Rorrer. 2007. Fundamentals of Momentum, Heat, and Mass Transfer. 5th Edition. John Wiley & Sons, Inc.
- Wiesmann, U., In Su Choi., Eva-Maria Dombrowski., 2007. Fundamentals ofBiological Wastewater Treatment. WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, ISBN: 978-3-527-31219-1.
- Zaiat, M., Jose´ Alberto Domingues Rodrigues, Eugenio Foresti., 2000. External and internal mass transfer effects in an anaerobic fixed-bed reactor for wastewater treatment. Process Biochemistry 35 (2000), p.943-949.
- Zainol, N.A., Hamidi Abdul Aziz and Mohd Suffian Yusoff., 2012. Characterization of Leachate from Kuala Sepetang and Kulim Landfills: A Comparative Study. Energy and Environment Research; E-ISSN 1927-0577, Vol. 2, No. 2; 2012, doi:10.5539/eer.v2n2p45, p.45-52.
- Ziemiński, K., and Frąc, M., 2012. Review: Methane Fermentation Process As Anaerobic Digestion Of Biomass: Transformations, Stages And Microorganisms. African Journal of Biotechnology, ISSN 1684–5315, Vol. 11(18), pp. 4127-4139.
- Zinatizadeh, A.A.L., A.R. Mohamed, G.D. Najafpour, M. Hasnain Isa, H. Nasrollahzadeh., 2006. Kinetic Evaluation Of Palm Oil Mill Effluent Digestion In A High Rate Up-Flow Anaerobic Sludge Fixed Film Bioreactor. Process Biochemistry 41 (2006) 1038–1046.