EFFECTS OF TEMPERATURE-pH ON LIQUID PHASE MASS TRANSFER AND DIFFUSION COEFFICIENTS AT LEACHATE TREATMENT IN ANAEROBIC BIOREACTOR

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ABSTRACT

Leachate contains complex dissolved organic and inorganic substrates that are biodegradable and non-biodegradable. Principally, anaerobic treatment utilizes anaerobic bacteria to degrade the dissolved organic matters. Anaerobic treatment is very sensitive towards the change of temperature and pH. This research used an anaerobic bioreactor with volume of 160L, with a ratio of leachate:biogas was 70:30. Seeding, acclimatization and leachate treatment were executed at temperature 35°C; pH ambient, temperature 45°C; pH ambient, temperature 35°C; pH 7.2 and temperature 45°C; pH 8.0. Based on this research, that there is dependency on mass of solutes organic substrate (COD) in the leachate, at all operating conditions of leachate treatment in anaerobic bioreactor. Hence, the organic substrate concentration (COD) will affect the VFA, the liquid phase mass transfer and diffusion of solute organic. Consequently, the higher the temperature-pH, the higher the liquid-phase mass transfer, but lower diffusion coefficients is.

INTRODUCTION

Leachate

Leachate is liquid waste arising as a result of external water, which enters into a trash heap, then it dissolves and rinses the dissolved and suspended organic and inorganic matter in the garbage, including complex organic matter as a result of the process of physical, biological, and chemical decomposition (Kumar et al., 2013). Therefore, the leachate is a complex mixture consisting of dissolved organic matters and inorganic contaminants. Leachate contains: VFA, LCFA, fulvic and humic substance, ammonia-nitrogen, phosphate, sulphate, heavy metals, organic xenobiotics (XOCs); aromatic hydrocarbons, phenols and chlorinated aliphatics, inorganic salts and microorganisms (Christensen et al., 2001; Renou et al., 2008; Zainol et al., 2012; Kawai et al., 2012; Hassan and Xie, 2014); as well as biorefractory contaminants (Tatsi et al., 2003). Consequently, the leachate contains complex dissolved organic and inorganic substrate, which are biodegradable and non-biodegradable (Christensen et al., 2001).

The characteristics make leachate to be very dangerous matters for environment and it has more potential contamination than other industrial wastes (Zainol et al., 2012; Hassan and Xie, 2014). Variation of leachate composition of municipal landfill depends on several factors, among others: the composition and age of the landfill, design and operation of the landfill, as well as conditions of landfill, climate, hydrogeological conditions, humidity, temperature, and stabilization level (Renou et al., 2008).

Anaerobic bioreactors

Anaerobic treatment of organic matter constitutes a complex and specific biochemical reactions. Biodegradation of organic matter is dissolved through reaction stages: hydrolysis, acidogenesis, acetogenesis and methanogenesis occurring simultaneously, either serial or parallel (Zinatizadeh et al., 2006; van Lier et al., 2008; Deublein and Steinhauser, 2008; Appels et al., 2008; Abdelgadir et al., 2014, Kahar et al., 2017). The bacteria that have role in the four mechanism work specifically and interdependence (Hossain et al., 2009).
Hydrolysis is a liquefaction of organic matter using extra-cellular enzymes produced by hydrolytic bacteria (Zintaizadeh et al., 2006; Deublein and Steinhauser, 2008; Appels et al., 2008). Cellulolytic bacteria plays a role in the hydrolysis stage, it works in a pH range of 6-7. Other studies report that the hydrolysis rate constant depends on pH but not related to total and the concentration of VFA (Veeken et al., 2000). The best pH ranges to achieve maximum biogas resulting 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 the stage where organic matter as a result of hydrolysis mechanism is converted into amino acids, simple sugars and volatile fatty acids (VFA), including formic acid, acetic, propionic, butyric, lactic, succinic, ethanol, and CO2, H2, NH3, H2S by acid-forming bacteria (Batstone et al., 2002; van Lier et al., 2008; Ziemiński and Frac, 2012). For experimental batch system, the pH range at acidogenesis thermophilic mechanism is 6-7 (Park et al., 2008). Volatile fatty acids (VFA) is an intermediate product, which is very important in anaerobic treatment (Appels et al., 2008). Acetogenesis is a mechanism to form acetates, carbon dioxide and hydrogen (Ziemiński and Frac, 2012).

It is reported that methanogenesis in anaerobic bioreactor is efficient at pH 6.5-8.2 (Lee et al., 2009), while hydrolysis and acidogenesis at pH 5.5 and 6.5 (Kim et al., 2003). The last mechanism in the anaerobic biodegradation is methanogenesis. Most of methanogens bacteria are mesophilic with a temperature range of 28-42 °C, while at a thermophilic temperature is in range of 55-72 °C (Ziemiński and Frac, 2012). Methanogens bacteria are optimum in pH range of 7.2-8.0 (Suryawanshi et al., 2013).

**Mass Transfer**

Mass transfer may occur in liquid phase, gas phase, or in both phases simultaneously. And it may occur with a multi-phase or single-phase system (Thibodeaux, 1996; Geankoplis, 2003). In the case of complex organic substrates, which is generally expressed as COD, a substrate that is degraded hard (Zaiat et al., 2000; Christensen et al., 2001; Hassan and Xie, 2014)). Even though mass transfer is not the main factor in, it is crucial in anaerobic bioreactor (Leib et al., 2001; Doble, 2006; Benz, 2011).

Liquid phase mass transfer coefficient is a function of the properties of liquid physic and liquid superficial velocity (Zaiat et al., 2000; Abdelgadir et al., 2014). If the liquid phase mass transfer is as a constraint of the overall process rate, then $k_L$ can be estimated by equation 1 (Zaiat et al., 2000; Cho and Young, 2001).

$$N_L = k_L (S_b - S)$$ (1)

Where, $N_L$ is the liquid phase mass transfer fluxes, (mg/cm²/h); $k_L$ is the liquid phase mass transfer coefficient; $S_b$ is substrate concentration in bulk liquid, (mg COD/L); and $S$ is the substrate concentration in the solid-liquid interface, (mg COD/L).

**Diffusion Coefficients**

Mass transfer depends on solute diffusion and variable controlling the characteristics of fluid flow, which are: mass transfer depends on solute diffusion and variables controlling the characters of fluid flow, which are: flow rate, viscosity, density, and a linear dimension. Diffusion based on empirical modifications was reported by Wilke-Chang (Geankoplis, 2003), where the solute diffusion can be calculated by the equation 2.

$$D_L = 7.4 \times 10^{-8} \left( \frac{\Psi_b M_B}{\mu_L V_b} \right)^{1/2} T^{1/2}$$ (2)

Where, $D_L$ is solute and solvent liquid phase diffusion, cm²/s; $T$ is temperature, K; $\mu_L$ is solvent viscosity, cP; $V_b$ solute molar volume in normal boiling point, cm³/gmol; $\Psi_b$ is solvent association parameter (water = 2.6) and $M_B$ is molecular weight of solven (18 g/gmol).

Several studies have reported bioreactor failure or poor performance due to a decrease in pH caused by the accumulation of VFA in the anaerobic treatment system (Visser et al., 1993; Fabián and Gourdon, 1999; Poh and Chong, 2009; Tabataba’i et al., 2011). High VFA concentration will inhibit hydrolysis, and acidogenesis and methanogenesis. Therefore, the process of mass transfer and adequate seeding microorganisms will be important in anaerobic bioreactor (Vavilin et al., 2002).

This research aims to analyze the effect of temperature-pH on the liquid phase mass transfer coefficient; $k_L$, and solute diffusion coefficient, $D_L$ in leachate treatment in anaerobic bioreactor.

**MATERIALS AND METHODS**

The leachate used came from Sambutan Landfill, Samarinda, East Kalimantan, Indonesia. Bioreactor anaerobic tools used were equipped with a heater, leachate recirculation pump, leachate recirculation flowmeter, manometer, inlet of leachate feeding, biogas thermometer, pressure gauge, leachate thermometer, sampling ports, inlet valve of leachate recirculation, outlet valve of leachate recirculation and leachate effluent valve. This is pilot-scale experiment research with a semi-batch system.
This research used an anaerobic bioreactor with the volume of 160 L. After characterizing and analyzing leachate quality, then leakage and calibration test of anaerobic bioreactor system was performed. Seeding and acclimatization stage were respectively executed for 10 days, while the leachate treatment was performed for 21 days. Seeding, acclimatization and leachate treatment were performed in a bioreactor anaerobic at temperature 35°C; pH ambient, temperature 45°C; pH ambient, temperature 35°C; pH 7.2 and temperature 45°C; pH 8.0. Microorganisms used came from cow rumen fluid as inoculums and leachate with a ratio of 1:3 and then it was filtered to take the extract. Analytical and parameters test of COD and VFA were performed every two days. Leachate treatment process was stopped if the reduction percentage of COD (COD removal) had reached 60-80%.

RESULTS AND DISCUSSION

Results

Anaerobic treatment was at a temperature of 35°C, then ambient pH was treated; constant leachate temperature was at 35°C, biogas temperature was at 34-35°C, pH tended to fall in the range of 7.9-7.3. In addition, BOD had decreased from 3,850.32-693.50 mg/L, COD had decreased from 6,520-1,327.45 mg/L. Meanwhile, the VFA concentration was up and down, on day 21st, it was 166.5 mg/L, then it rose to the highest concentration at 25th day, which was 1,698.97 mg/L, and then it was up and down until the 41st day to 331.85 mg/L.

Anaerobic treatment was at a temperature of 45°C, then ambient pH was treated; constant leachate temperature was at 45°C, biogas temperature was at 42-44°C, pH tended to fall in the range of 7.3-7.9. In addition, BOD had decreased from 4,104.18-902.88 mg/L, COD had decreased from 7,445.11-1,563.45 mg/L. Meanwhile, the VFA concentration was up and down, on 21st day, it was 166.5 mg/L, and then it rose to the highest concentration at 27th day, which was 1,232.1 mg/L, and then it was up and down until the 41st day to 80.78 mg/L.

Anaerobic treatment was at a temperature of 35°C, then ambient pH of 7.2 was treated; constant leachate temperature was at 35°C, biogas temperature was at 34-34.9°C, pH was constant at 7.2. In addition, BOD had decreased from 3,925.50-689.50 mg/L, COD had decreased from 6,155.9-1,124.5 mg/L. Meanwhile, the VFA concentration was up and down, on the 21st day, it was 234.8 mg/L, then it rose to the highest concentration at 27th day, which was 1,678.5 mg/L, and then it was up and down until the 41st day to 338.5 mg/L.

Meanwhile, Anaerobic treatment was at a temperature of 45°C, then pH of 8.0 was treated; constant leachate temperature was at 45°C, biogas temperature was at 42-44.5°C, pH was constant at 8.0. In addition, BOD had decreased from 3904.20-702.68 mg/L, COD had decreased from 6,531.1-1,306.35 mg/L. Meanwhile, the VFA concentration was up and down, on the 21st day, it was 266.5 mg/L, then it rose to the highest concentration at 29th day, which was 1,566.5 mg/L, and then it was up and down until the 41st day to 168.7 mg/L.

Mass Transfer Rate of rDL and Solute Diffusion Rate of rDL

The average of mass transfer rate per day, rDL, and the solute diffusion rate per day, rDL, on temperature variation, are presented in Figure 1 and Figure 2. At a temperature of 35°C; ambient pH, it was found that the lowest average of mass transfer per day was 0.04069 mg/L, while the highest was on the 31st day, which was 0.26068 mg/L per day. The solute diffusion rate initially fell and then rose, with a range between 2.16678.105-8.18626.105 cm²/s. At a temperature of 45°C; ambient pH, it was found that the lowest average mass transfer rate per day was 0.00584 mg/L, while the highest was on the 23rd, which was 0.24842 mg/L, per day. The solute diffusion rate initially fell and then rose, with a range between 2.80848.105-1.5488.104 cm²/s.

At the temperature of 35°C; pH 7.2, it was found the lowest average of mass transfer rate per day was 0.01552 mg/L, while the highest was on the 31st day, which was 0.16000 mg/L per day. The solute diffusion rate initially fell and then rose, with a range between 2.30263.105-6.62193.105 cm²/s. Meanwhile, at a temperature of 45°C; pH 8.0, it was found that the lowest average of mass transfer rate per day was 0.03415 mg/L, while the highest was on the 23rd day, which was 0.19148 mg/L, per day. The solute diffusion rate initially fell and then rose, with a range between 2.50138.105-9.96698.105 cm²/s.

Discussion

By the presence of concentration gradient, there would be movement of mass transfer from the high concentration areas to low concentration areas. This movement was utilized to build intensive contact between solute and microorganisms, therefore, it enabled more frequently mass transfer to occur (Geankoplis, 2003; Welty et al., 2007). The occurrence of Mass transfer in the liquid phase was due to the difference of solute substrate concentration (organic and inorganic) inside. Movement among the solute, solvent and microorganisms occurred continuously. Then, as a result of its collisions, the solute, solvent and microorganism moved in irregular and randomly.
During the process of anaerobic treatment, substrates were biodegraded simultaneously by one phase to another phase, where complex organic substrates were biodegraded into intermediate product (VFA) and then converted into biogas (CH₄ and CO₂) (van Lier et al., 2008). The more the dissolved substrate mass biodegraded, the lower the substrate mass dissolved, therefore, the dissolved substrate concentration dissolved in leachate would be also decreased.

**Mass Transfer Rate, rkL.**

The average mass transfer per day was the amount of solute biodegradable substrate every day. COD reduction was accompanied by the increase in the mass transfer rate, average rkL per day. There was increase of rkL average per day because at that time, the activities of microorganisms and the amount of dissolved substrate was still high. Intensive contact between substrate and microorganisms occurred in areas of the highest average of mass transfer per day, which occurred between 29th-30th day. However, on the 31st day, the average of mass transfer per day began to fall. As solute substrate reduced, the average of rkL per day also reduced. As shown in Figure 1.

![Figure 1](image1.png)

*Figure 1. a. rkL on Temperature-pH variation. b. rkL vs COD on Temperature-pH variation*

Based on this research, it is found that if COD decreases, mass transfer will be higher. It is important to note before and after the highest average of rkL per day at all operating conditions of leachate treatment in anaerobic bioreactor. Before the highest average of rkL per day, organic substrate solute is still high. While, after the highest average of rkL per day, the concentration of solute organic substrate decreases.

Figure 1 also shows that the condition before the peak and highest rkL were in the 21st to 27th day and 29th to 30th day, and basically, it can be considered as stage of exponential and stationary of microorganism growth. The highest microorganism activity was in both conditions. Therefore, the average rkL per day indirectly implies that the rate of solute substrate mass biodegradation occurs in the leachate. Actually, this condition must be preserved because it is the average optimum condition at all operating conditions of leachate treatment that is performed. Because the thrust of the liquid phase mass transfer, then the highest concentration gradient is at these both stages.

After this condition, which is after the 31st day, the decrease of average COD at all processing operations is > 64.5%. So the mass transfer occurring after the 31st day is the "insufficient" mass transfer. Because substrate concentrations have been greatly reduced, the thrust of mass transfer is small.

**Diffusion Rate, rDL.**

In the early stages of anaerobic treatment, the average solute diffusion rate; rDL is seen to decrease. As the time goes by, rDL continues to increase. As seen in Figure 2. Similarly with rkL. It is important to note before and after the highest average of rDL per day at all operating conditions of leachate treatment in anaerobic bioreactor. Before the lowest average of rDL per day, organic substrate concentration is still high. While, after the lowest average of rDL per day, the concentration of solute organic substrate has decreased. The lowest rDL was on 27th-29th day, wherein the decrease of average COD substrate concentration on all processing operations is > 56.8%.

![Figure 2](image2.png)

*Figure 2. rDL on Temperature-pH variation*

Solutes diffusion rate, rDL will decrease if the pressure increase. However, in the “limit” of particular biogas pressure, rDL increases, hence it can be considered that there is optimal limit for pressure. As seen in Figure 3.
Liquid phase mass transfer is affected by the substrate concentration (Cubas et al., 2007), the liquid phase mass transfer coefficient; $k_L$, and the solute and solvent diffusion coefficient; $D_v$ on leachate treatment in anaerobic bioreactors. Hence, the substrate concentration (COD) will affect the VFA, the liquid phase mass transfer; $r_{DL}$, and solutes diffusion; $r_{D_L}$, which are shown in Figure 4 and Figure 5.

On the treatment of temperature variation, even though it is seen that if temperature $T$ is higher, then $k_L$ will increase while $D_v$ will decrease, then the condition is up and down, $k_L$ is on $T \leq 35^\circ C$, pH 7.2; $T > 35^\circ C > T \leq 45^\circ C$, pH 8.0 > $T > 45^\circ C$. Meanwhile, $D_v$ is on $T > 45^\circ C > T \leq 45^\circ C$, pH 8.0 > $T > 35^\circ C > T \leq 35^\circ C$, pH 7.2, as described in Figure 6.

In general, it can be said that, the more the affecting variables, the bigger the factor of "obstacle" on the process of anaerobic treatment. Liquid-phase mass transfer coefficient, $k_L$, is a function of the solutes physical chemical properties (pH, COD and VFA), internal characteristics and operating conditions of the bioreactor (geometry bioreactor, recirculation flow rate, temperature, pressure) (Zaiat et al., 2000; Geankoplis, 2003; Kraakman et al., 2011). Several studies of mass transfer and the comparison of this research are shown in Table 2.
CONCLUSIONS

Based on the research results and discussion, the conclusion that can be drawn are as follows; Liquid phase mass transfer coefficient; \( k_L \), on the T 35°C, T 45°C, T 55°C; pH 7.2; and T 45°C, pH 8.0 respectively are 0.085 cm/s, 0.053 cm/s, 0.087 cm/s and 0.067 cm/s. Diffusion coefficient \( D_{li} \) on T 35°C, T 45°C, T 55°C, pH 7.2 and T 45°C, pH 8.0 respectively are 1.10 10 cm/s, 5.10 10 cm/s, 2.10 10 cm/s and 2.10 10 cm/s. The higher the temperature and pH, the higher the \( k_L \), but the lower the \( D_{li} \) will be. \( k_L \) is on T 35°C, pH 7.2 > T 35°C > T 45°C, pH 8.0 > T 45°C, while \( D_{li} \) is on T 45°C > T 45°C, pH 8.0 > T 35°C > T 35°C, pH 7.2. Based on this research, that there is dependency on mass of solutes organic substrate (COD) in the leachate, at all operating conditions of leachate treatment in anaerobic bioreactor. Hence, the organic substrate concentration (COD) will affect the VFA, the liquid phase mass transfer and diffusion of solute organic. Consequently, the higher the temperature-pH, the higher the liquid-phase mass transfer, but lower diffusion coefficients is.

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NOMENCLATURE

**Symbols**

- \( D_{li} \): solute and solvent liquid phase diffusion, cm²/s
- \( k_L \): liquid phase mass transfer coefficient; cm/s
- \( M_B \): molecular weight of solvent, 18 g/gmol
- \( N_L \): liquid phase mass transfer fluxes, mg/cm².d
- \( r_{ol} \): solute diffusion rate, cm²/s
- \( r_{bl} \): mass transfer rate, mg/L.d
- \( S_l \): substrate concentration on bulk liquid, mg COD/L
- \( S_s \): substrate concentration on solid-liquid interface, mg COD/L
- \( T \): temperature, K
- \( V_A \): solute molar volume on normal boiling point, cm³/gmol
- \( V_R \): Reactor volume, L
- \( \Psi_B \): association parameter of solvent, water = 2.6
- \( \mu_L \): viscosity solution, cP

**Abbreviations**

- ASBR: Anaerobic Sequencing Batch Reactor
- COD: Chemical Oxygen Demand
- HAIB: Horizontal-Flow Anaerobic Immobilized Biomass
- HRT: Hydraulic Retention Time
- SASBR: Stirred Anaerobic Sequencing Batch Reactor
- UASB: Upflow Anaerobic Sludge Bed Reactors
- VFA: Volatile Fatty Acids

REFERENCES


DEUBLEIN, D., & STEINHAUSER, A., 2008, Biogas from waste and renewable resources. Weinheim, Willey-VCH Verlag GmbH & Co. KGaA.


