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Assessment of Biogas Production from Automotive Wastewater and Rice Straw Leachate in Continous Stirred Tank Reactor

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Abstract

This study investigated the efficiency of operating Automotive Wastewater and Rice Straw leachate for biogas production in anaerobic reactor. A Continuous Stirred Tank reactor (CSTR) was employed and controlled under mesophilic condition at temperature of 38°C with 4 liters working volume for approximately 55 days. Different parameters were analyzed which includes pH, organic loading rate, alkalinity ratio, COD removal and effect of Zinc and Copper which runs on automotive wastewater towards anaerobic digestion and biogas production. At initial stage of experiment, Mono Digestion (single substrates) of Automotive Waste Water (AWW) was conducted. The reactor was unstable which indicated by the decrease of biogas production, low pH below value of 6.0 and as well as low COD removal efficiency with value in range of 63.4%. The instability of the reactor seems to be linked to heavy metal inhibition contained in automotive wastewater which composed of inorganic material. However, co digestion of automotive wastewater with Synthetics Wastewater (SWW) enhances the performance of the reactor with highest methane production 0.140 L of CH_4 / day at day 42. The nutrient available in the Synthetic Wastewater could promote the synergistic effect in co digestion with Automotive Wastewater and hence performed better than mono digestion. This study reveals that co digestion AWW with rice straw leachate (RSL) perform better than in mono digestion of AWW with the highest COD removal rate at 73%. This findings implies co-digestion process can provide not only the necessary substrates and microorganisms but also the appropriate balance of nutrients to create favorable conditions for the methanogens to thrive. Effluent concentrations of Zinc and Copper were lower than influent concentrations indicating that Zinc and Copper has been removed in the reactor through sorption process of the heavy metal inside the anaerobic sludge.

Keyword: Anaerobic co- digestion, chemical oxygen demand, automotive wastewater, heavy metal

1.0 INTRODUCTION

Global energy demand is predicted to rise as countries industrialized and populations continue to grow. Presently, world is still very much dependence on non-renewable resources yield from fossil fuel as its main source energy. The relied on fossil fuels as main source of energy has result to increase the global climate change, environmental degradation and human health problems (Aragaw *et al*., 2013). Source of fossil fuel is getting limited and if it is no action to overcome this matter this valuable source will be diminished in future. In order to deal with the increasing demand for energy and at the same time will help to decreasing the negative impact to the world global warming, renewable energy would be the best option in the future (Haw *et al.*, 2006). Biogas can be seen as one of the sensible options towards renewable energy source, which can be used as a replacement to fossil fuels both in power and heat production, and also as gaseous vehicle fuel (Shin *et al*., 2010). Biogas can be captured and used as a potential energy resource and it is end product through the processes of Anaerobic Digestion (AD). Over the years and throughout the world, AD appears to be one of technology widely utilized for the treatment of organic waste and wastewater. Numerous studies has shown that this method can be used to treat various type of organic waste such as sewage sludge (Song, 2005), municipal solid waste (Hartmann and Ahring, 2005) and agricultural industries wastewater (Gavala, 1996). The main sources of wastewater in the automotive plants are vehicle painting process including associated pre-painting operations (Idrus, 2007).

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It may contain a variety of hazardous materials and toxic content such as heavy metals (like chromium, zinc, copper and nickel), organic micro pollutants (like polycyclic aromatic hydrocarbons), solvent, paints and other chemicals (El-Gohary et al., 1989; Ansari et al., 2013). Therefore, proper treatment of automotive wastewater (AWW) has drawn considerably attention before releasing into environment because of their association with various problems of the ground and water resources.

AD has obvious advantages over aerobic process such as it can produce and capture biogas production as a source of energy through the invention of anaerobic digester. Ward et al., (2008) described the sealed environment of the process reduce environmental pollution by preventing the exit of methane process into the atmosphere. One of the key for enhancing performance of anaerobic digestion of organic matter is co-digestion of multiple substrates. Co-digestion of combination of different waste stabilizes the feed to the bioreactor, thereby improving the Carbon to Nitrogen (C/N) ratio and decreasing the concentration of nitrogen (Hartman & Ahring, 2005). The main objectives of this study in the following chapters provides waste converted to energy through co-digestion of automotive wastewater with rice straw leachate using continuous stirred tank reactor (CSTR).

2.0 METHODOLOGY

2.1 Source of substrates and inoculum

The primary substrates used in this study is raw Automotive Wastewater collected from Perusahaan Otomobil Sdn Bhd (Proton), located at Hicom Industrial Estate, Shah Alam, Selangor. Samples were taken by grab sampling from incoming tank of the wastewater treatment plants.After sampling, the samples were stored in large capped container and transport to the laboratory and preserved at 4˚C as biological activity is significantly reduced and in order to preserve the property of the sample from aspect of physical, chemical and biological and as well as to ensure that the sample represent the actual condition at the study area. The inoculum used to inoculate the substrate during the experiment as well as an active source of microbes. For the present study, culture used as an inoculum was from wastewater treatment plant at Faculty of Engineering, University of Putra Malaysia. The first part of the work was carried out with sludge sieved to remove any non-biodegradables material. Source of inoculum used to inoculate the substrate during the experiment as well as an active source of microbes. For the present study, culture used as an inoculum was from wastewater treatment plant at Faculty of Engineering, University of Putra Malaysia. The first part of the work was carried out with sludge sieved to remove any non-biodegradables material.

2.1 Preparation of Synthetic Wastewater

Synthetic wastewater (SWW) will be utilized as a surrogate material as it allowed the use of a complex chemical feedstock of high biodegradability without the risk of exposure to pathogens present in real sewage. This synthetic wastewater content is essential for optimum anaerobic microbial growth.

2.2 Feed Composition of Samples used into CSTR

In this study, three series of experiments were used to investigate co-digestion of each substrate in single CSTR. CSTR were filled with 2L sludge as inoculum and 2L of substrates with various combinations. The CSTR were fed once per day for each trial as given in Table 2.1. After 24 hour of HRT, the digestate at the same amount of feeding were taken and was added back to keep the constant of 4L working volume of the reactor.

2.3 Type of Digester and Operation

Type of digester in a laboratory scale will be employ in this research is continuous stirred tank reactor (CSTR) with a total volume of 5 litres and 3 litres working volume and was built from graduated jacketed borosilicate glass reactor. The CSTR equipped with stainless steel top cover supported with feed tube and biogas tube along with cone bearing seal (anti-leak gas). The reactors had stirrer set using digital overhead stirrer motor provided with adjustable speed. The CSTR reactor were seeded with sludge (inoculum) and then acclimated to synthetic wastewater until steady state which is a condition of constant production of gas was achieved. Once the digester is ready, it was used for the anaerobic co-digestion. The digester will be running for the period of 42 days including acclimatization period and were controlled at mesophilic conditions with temperature of 35^{o}C by circulating hot water from water bath tank into the water jacketed of reactor. The CSTR were continuously mixed with mechanical agitator at 300rpm. The mixing was control by timer and the mixing process will ensure the homogeneity of the inoculum and the substrates. The reactor start-up is shown in Figure 1.

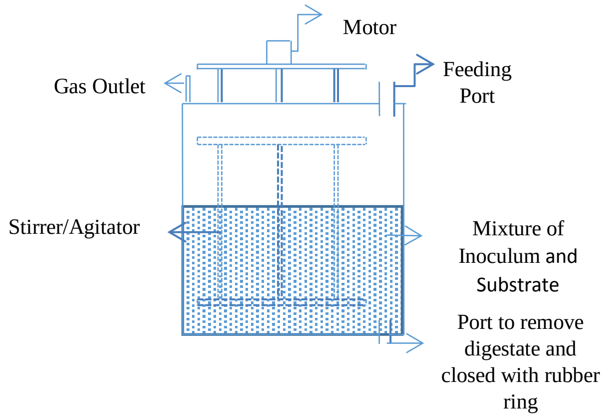


Figure 1: Schematic Diagram of Continuous Stirred Tank Reactor (CSTR).

2.4 Analytical Method

The digestate characteristic produce from CSTR were evaluated in laboratory such as COD, and pH right after the setup stage has been done. Meanwhile , total alkalinity ratio were recorded once in a week and heavy metal behaviour were monitored daily. Biogas volume samples are measured daily by using water displacement method whereas the percentage of methane by using gas chromatography. The percentage of biogas was captured by using Tedlar bag with 1.6 litres capacity. All analytical method were performed in accordance with Standard Methods for Water and Wastewater, 17th Edition (1998). Seven different phases of experiments were employed as shown in Table 1 below. The reactor was fed with OLR 0.12 g/L/d with feedstock concentration of 0.23 COD/L/d. The final OLR was chosen as the optimum working value based on the initial concentration of primary feedstock in this experiment which runs on AWW. Stability of the reactor system was monitored through the COD removal produced. The reactors become stable at the 0.12 g/L/d OLR and were kept under the operating conditions on day 13 till the end of experiments on day 42.

Table 1 Reactor operating conditions during experimental work

Time (days)	**Phase**	**Process**	**Feedstock**	**Feeding Ratio**	**OLR (g /L/day)**	**Concentration (g COD/L)**
1	1	Adaptation Period	Synthetic wastewater		0.25	0.50
5-11	2		Synthetic wastewater	100:0	0.40	0.80
12-17	3		Synthetic wastewater		0.12	0.23
18-29	4	Mono-Digestion	Automotive Wastewater	100:0	0.12	0.23
30-42	5	Co-Digestion	Automotive Wastewater + Synthetic wastewater	20:80	0.12	0.23
43-48	6	Single-Digestion	Synthetic wastewater	100:0	0.12	0.23
49-55	7	Co-Digestion	Rice straw leachate+ Synthetic wastewater	20:80	0.12	0.23

3.0 RESULTS AND DISCUSSIONS

The correlations experimental results and data analysis with respect to pH value, chemical oxygen demand (COD) removal, alkalinity, the effect of Copper (Cu) and Zinc (Zn) in anaerobic condition and biogas production from different processes of Automotive wastewater (AWW) and Synthetic wastewater (SWW) were presented and discussed.

3.1 Characteristics of Feedstock at Different Mixing Ratios

Table 2 depicts the characteristics of wastewater mixtures at different mixing ratios. The pH value ranged between 5.96 to 6.7. The initial pH for all mixtures of feedstock show the suitable pH prior to anaerobic digestion in CSTR process was operated. COD concentrations of wastewater indicate high organic content available in the feedstock.

Table 2 Characteristics of feedstock used in the experiment

Parameters	Unit	AWW	RSL	SWW	SWW+AWW	RSL+AWW
pH	-	5.96	6.7	6.4	6.10	6.50
COD	mg/L	230	800	256,000	121,600	48,000
Zinc	mg/L	2.4	-	0.52	0.95	0.78
Copper	mg/L	0.5	-	-	0.31	0.26

3.2 Effect of pH Value

Literally, pH in the system during the experiment ranged between pH 5.7 to 6.7**.** At the beginning stage of the adaptation process, the reactor was fed with synthetic wastewater which is started from Phase 1 to 3 for a period of two weeks. According to the Figure 2, pH distribution at the beginning of the process was around 6.3. Then the pH started to fluctuate from pH range 6.54 to 5.92 even though the OLR value is continuously constant from day 4 till day 11. The fluctuating in pH indicates that the reactor was in shock condition and worked under unstable condition value most probably due to accumulation of fatty acids caused by increased of OLR fed from 0.25 g/L/d to 0.4 g/L/d into the reactor as agreed by Hartmann et al., (1995). After that, the reactor were fed with lower OLR value of 0.12 g/L/d and the system recover itself with the pH value gradually rise at an average value of 6.22 in Phase 3. Thus, this indicates that the reactor has high buffer capacity and operated under stable condition.

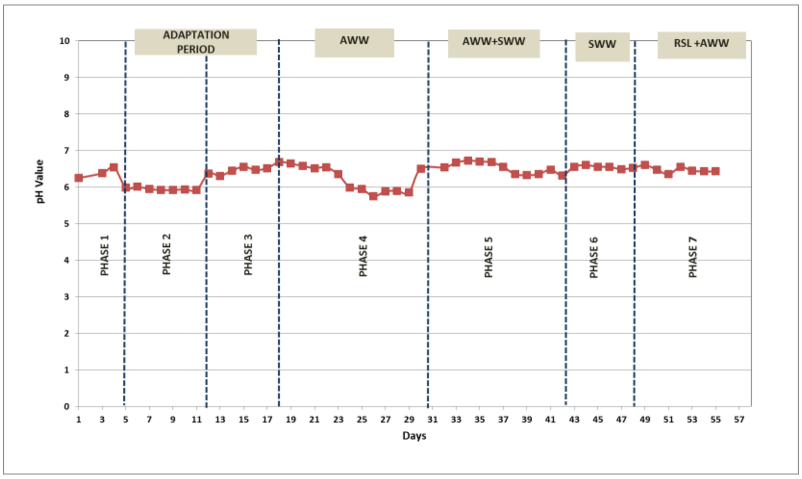


Figure 2 Behavior of pH in the reactor digesting different feedstock

However, after the addition of AWW in the reactor on day 18 onwards until day 29, pH started to be fluctuated and rapidly decreased and finally dropped to 5.85 during the digestion (absolute minimum 6). The dropped of pH indicating that the system operating at unstable conditions (Strik, 2005). In the next following occasions during the co digestion period of SWW and AWW namely Phase 5, the pH value was observed to be fluctuated at the beginning process before it was started to drop again and stable to be less or almost less than 6.32 with an average pH of 6.50. The results showed that the pH stability of the reactor was improved comparing to digestion of AWW alone. In the next phase, SWW was reintroduced as feeding material into the reactor. The results showed that the stability of the reactor increased with pH value in the range of 6.5. Over the next cycle, the experiment was continued with system fed with RSL and AWW. During the phase, the results observed to be fluctuated within the range of 6.3-6.6 with an average pH working value of 6.47. The curves of pH in single digestion and co digestion had similar trends. The pH increased observed when the different feedstock was change into the reactor by day 18, 30, 42 and 49. The average pH value was 6.3 which were below the recommended pH range which was not suitable for anaerobic digestion.

The dropped of pH in the anaerobic systems may lead to imbalance of the system, as anaerobic digestion system is limited to a relatively narrow pH interval from 6.8-7.4 (Rajendran and Balasubramaniam, 2011). If pH value below or above this range, it will caused to imbalance to the reactor performance. The optimal pH for methanogenisis bacteria ranges from 6.5 to 7.8 while hydrolysis and acidogenesis occurs efficiently at pH within pH 5.5 and 6.5 respectively (Khalid et al 2011).

3.3 Chemical Oxygen Demand (COD) Removal

Figure 3 shows the COD removal during the CSTR operation. At the beginning stage of the experiments, COD removals in the reactor showed to be fluctuated indicating that the microbes present in the sludge were still adapted to the given feedstock. However, when lower OLR had been used to the system, average COD removal around 91.6% were observed. Hence, the decreasing of OLR from 0.4 g COD/L to 0.12 g COD/L had resulted to higher percentage of COD removal which is showed that the decreasing of OLR would enhance the performance of microbes to consume the organic matter in the given feedstock. In phase 4, COD removal efficiency decreased from 96% to 65.20 % as the new feeding material from SWW to AWW was introduced into the reactor. The mono digestion of AWW is composed of inorganic materials which include heavy metal thus caused slow ability to biodegrade and take longer time to break down before being converted to methane. This may describe with the trend of COD removal during this phase was fluctuated from day 18 to day 29 with average removal during the digestion was 64%.

In Phase 5, feeding material in reactor has changed to co-digestion of SWW and AWW. At the beginning of the co-digestion the COD removal decreased and fluctuated in the range of 65% to 70%. However, the COD removals become stable and increased gradually for the rest of the day indicating that the microbes have been adapted to the given feedstock. The highest COD removal being recorded was on day 42 with value of 88% and the reactor achieved steady state at 86.6% of COD removal. Hence, the co-digestion of SWW and AWW could improve the ability of COD removal in the reactor. In other hand, co-digestion process can provide not only the necessary microorganisms but also the appropriate balance of nutrients to create favorable conditions for the methanogens to thrive (Gadde *et al*, 2009). These results suggested that co digestion of this feedstock were possible.

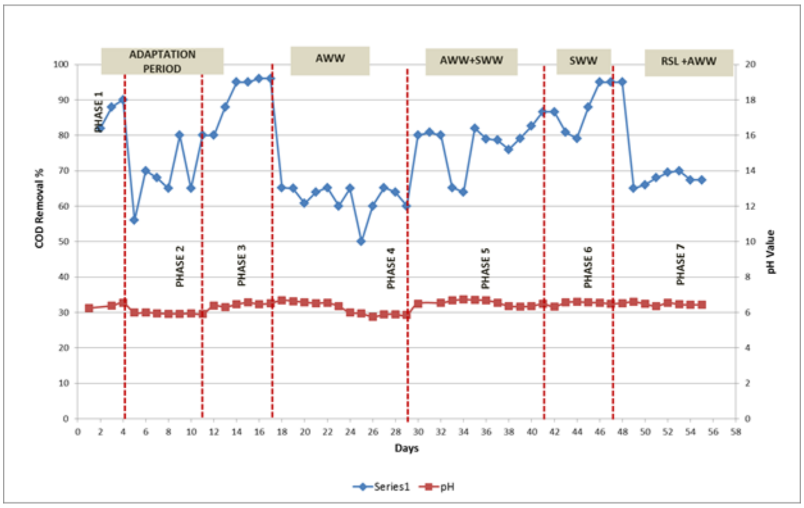


Figure 3 Behavior of COD Removal in reactor digesting different feedstock.

In Phase 6, it was observed that COD removal efficiency was rise gradually with average COD removal of 87.4% with the highest of COD removal at value 95% after SWW was reintroduced as feeding material. However in phase of co digestion between RSL and AWW (phase 7), COD removal decreased gradually and fluctuated with average removal of 67.6%. This result may have been due to different organic content and biodegradability between RSL and AWW. The co-digestate mixture consists of rice straw leachate which is a lignocellulosic biomass that consists of high lignin content which is not easily degraded under anaerobic digestion (Sahito, 2013). In addition, according to study conducted by Mussoline (2013), rice straw contain lingo-carbohydrate complexes creates strong barrier and the cell of the plant is rejected to microbial attack which could disturbed the degradation process. Furthermore, most of the crop residue is contains high carbon but lack in nitrogen content which is an essential part of supplement for the cell growth of the microbial (Hartmann and Ahring, 2005). Hence, imbalance nutrients of C: N may contribute low protein formation and thus low energy which could resulted to slow down the microorganism multifunction and as well as structural material metabolism of the microbes (Zupanic and Grilc, 2012). Moreover, AWW itself contained inorganic material which is also less biodegradability.

From the result observed, lower substrate degradation efficiency indicated with the lower COD removal percentage has been recorded at mono digestion of AWW (Phase 4) and co digestion of RSL with AWW (Phase 7). These COD removal results during that phase show that the CSTR operating under unstable conditions (Ramsamy et al., 2012). This unstable reactor has been observed due to imbalance of nutrients in the feedstock mainly C: N ratio in RSL and AWW and inorganic material especially heavy metal which runs on AWW. However, these results also suggested that co digestion of SWW and AWW as a feedstock were possible and yield better COD removal efficiency.

3.4 Alkalinity Ratio (IA/PA)

Alkalinity ratio was investigated and the distribution of alkalinity values obtained for reactor is shown in Figure 4. Volatile acids/Alkalinity ratio (IA/PA) could provide information on the stability of the reactors. For a good performing anaerobic digestion process the values should be below 0.3 while values 0.3-0.5 show deficiencies in the operating system (Andreoli, 2007). In phase 4, which runs on single digestion of AWW, it seems buffering capacity for this type of sample recorded higher than 0.8, indicate the reactor was unstable and vulnerable to any change in environment. If the ratio reaches values higher than 0.8, the reactor has become acidic condition which may result to anaerobic digestion failure (Andreoli, 2007). Besides, the pH values during this phase also recorded reduced to values lower than 6.0

However during phase 5, when reactor was feeding with new feedstock the reactor performance become stable with alkalinity ratios between 0.2-0.5. Pereira et al. (2009) stated that it is possible to gain stability in the digestion system with values differ from 0.3, due to differentiation in the composition of each effluent. This indicates that the reactors have sufficient buffering capacity for the anaerobic digestion process and less deficiencies in the digestion process. In comparison from the results obtained, the reactors have a good performance and stability in phase 5.

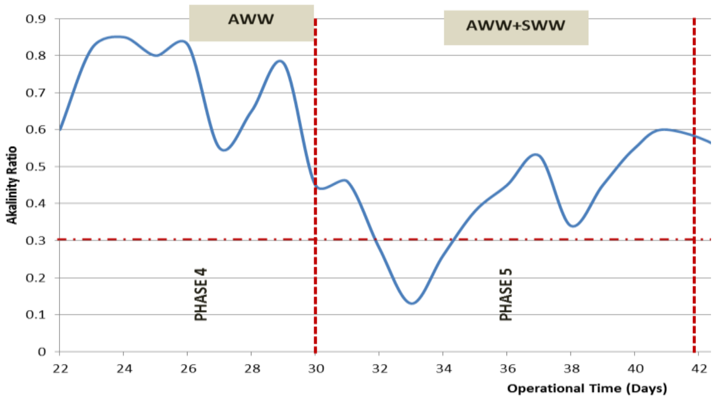


Figure 4 Behavior of alkalinity ratio in reactor digesting different feedstock.

3.5 Heavy Metal Inhibition

The heavy metal concentrations of Zinc and Copper in influent and effluent were analyzed. Average concentration of heavy metal in effluent (mg/L) is given in the Table 3. It was observed that influent of sample from single digestion of AWW showed concentrations of 2.4 mg/L of Zn and 0.5 mg/L of Cu. Yue et al., (2013) reported that heavy metal in its soluble form above 1.0 and 0.5 mg/L concentrations for Zn and Cu respectively would lead to anaerobic system failure. The concentrations of the influents have reached inhibitory of anaerobic digestion as agreed by Zupancic and Grilc (2012).

Meanwhile initial Zn concentrations and Cu present in the Figure 5 and Figure 6 below for both co- digestions of different phases were found to be decreased than single digestion due to dilute waste or feeding substrate. The experimental result of Zn present in influent for co digestion of AWW with SWW and RSL with AWW was 0.95 mg/L and 0.78 mg/L respectively. Initial Cu concentration in the influent during co digestion of AWW with SWW was 0.31 mg/L and 0.26 mg/L for co digestion between RSL and AWW. The result showed that the toxicant of heavy metal for Zn and Cu after co digestion is below heavy metal toxic threshold for anaerobic system.

Table 3 Average Concentration of Heavy Metal (Cu and Zn) in effluent (mg/L)

Heavy Metal	AWW		AWW+SWW		RSL+AWW	
	Influent	Average of Effluent	Influent	Average of Effluent	Influent	Average of Effluent
Zn (mg/L)	2.4	1.94	0.95	0.91	0.78	0.62
Cu (mg/L)	0.5	0.21	0.31	0.01	0.26	0.12

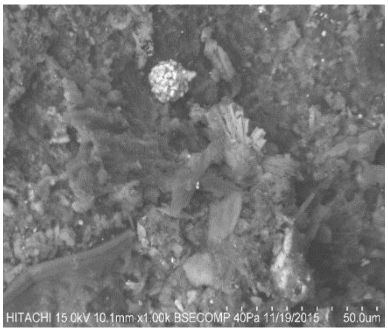
Figure 5 Average Removal Efficiency of Zinc in reactor

Heavy metals are not degradable and could lead to anaerobic system failure which may occur at several concentrations of heavy metal. According to Cantrell and Co Workes (2008), high concentrations of soluble metal have come to completely stop the production of biogas in anaerobic system. From the Table 3, the results recorded during this experiment, average concentrations of Zn and Cu in the effluent was lower than in influent concentrations indicating that Zn and Cu has been removed in the digester. The reason of this might be of sorption process of the heavy metal inside the anaerobic sludge (Sarioglu, 2009). Precipitation of salts as carbonates and sulphides is one of the main factors governing to accumulation of heavy metals in the sludge. The accumulation of heavy metals in the sludge could promote synergistic effects during the reactor operation but however at excess concentrations the toxicity may occur in the reactor and could possible to reactor failure. In addition to that, microbes consume heavy metals to maintain ionic equilibrium in cell, thus allow metal speciation process. During heavy metal speciation, three processes occurred involving of the heavy metal-microbe interaction, heavy metal-liquid phase interaction and salts interaction with carbonates and sulphides (Idrus et al., 2007).

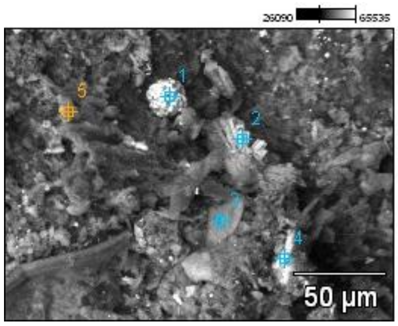
Figure 6 Average Removal Efficiency of Copper in reactor

3.5.1 Accumulation of Heavy Metal inside sludge after 55 days experiment

The scanning electron microscope (SEM) images below in Figure 7 were analyzed before and after experiments. The SEM shows accumulation of heavy metal on the sludge cross section. Figure 8 showed the result of EDX associated with the SEM. The EDX analysis showed the agglomerates contained of Zinc and Cu with others accumulation type of heavy metals presents in the sludge.

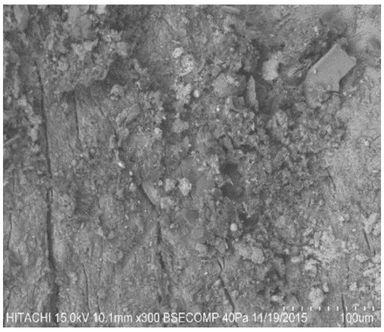


(i) Cross-section of the sludge before operation

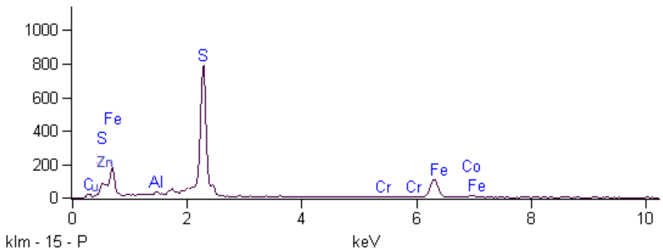


(ii) Cross-section of the sludge with heavy metals accumulation after operation.

Figure 7: Scanning Electron microscope (SEM) of sludge after 55 days of experiments



(i) *EDX point shoot images*



(ii) *EDX analysis show the presence of Zn and Cu inside the sludge*

Figure 8 Energy Dispersed Extra (EDX) analysis after 55 days of operation

3.6 Biogas Production

The biogas production was symbolized based on volume production (mL) as given in Figure 9. Basically the biogas comprise of 60% of methane (CH_4) and 40% of carbon dioxide (CO_2) in the anaerobic digestion, but however, the methane content varies with type of feedstock used because each substrates has different composition (Siripong and Dulyakasem, 2012). The effectiveness of the anaerobic digestion can be determined from pH value, % COD removal and gas production. Gas production can be useful indicator in observing reactor suffering from toxicants.

During the first occasions for single anaerobic digestion of AWW sample, the gas production decreased over the time. Gas production can be useful indicator in observing reactor suffering from toxicants. Considering to the previous study from Zayed (2000), it was assumed that the presence of heavy metal concentrations in AWW during mono digestion might have cause inhibition in the reactor performance. Accumulation of heavy metals may indicate by reduced level in gas production and biogas methane content (Yue et al., 2013). Low pH value observed in the phase also believed to yield for low optimal performance of methanogens in gas generation. In relation to the situation, COD removal were erratic with average removal during the digestion was 63.4% and gas production yield at day 29 was only 5ml and there was no methane achieved. These results showed that anaerobic digestion with AWW has proved difficult and the reactor was operating under unstable condition. The gas composition produced during this phase was compose of N_2 (74.04%), O_2 (24.60) and CO_2 (1.36%). The high percentage of nitrogen in the reactor indicates that denitrification was the main biological process yield in the system during this phases (Bernet et al., 2000). Denitrification is a process in which nitrate is reduced to nitrogen gas by facultative *anaerobic* bacterium (Akkunna et al., 1992).

In the phase of co digestion of SWW and AWW, pH value was quite stable within the range of 6.3-6.7 with the rates of COD removal 78.7%. The COD removal rate was better than single digestion. The result of biogas production increased from the beginning of co digestion until day 35 when it started declined steadily with some fluctuations before reach steady state. The methane production recorded as 24.51% for day 42. Table 4 illustrated the theoretical and actual CH_4 yield during this experiment based on COD removed. In correspondence to the COD removal rate of 86.67% the volume of methane produced during the co digestion of SWW and AWW were 0.07 L of CH_4 / day.

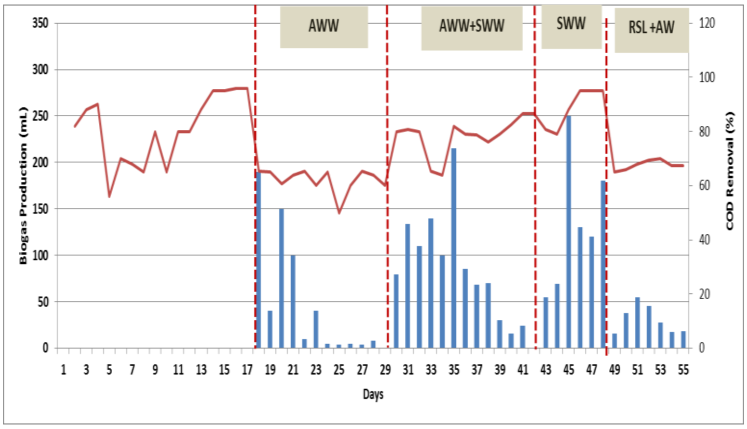


Figure 9: Biogas produced in the reactor digesting different feedstock

For the next phase of single digestion of SWW, there was an increase observed in gas production. Similar to the gas production, the % of COD removal was also high (95%). In relation with pH, it could be said that pH being fluctuated during the period. These findings are similar to Zhang (2010) who investigated that that biogas production increased with an increase in COD removal. The methane content achieved was 28.97% as for day 48. Hence the COD removal rate of 95%, the volume of methane produced during SWW was 0.08 L of CH_4 / day. The final phase during this experiment was co digestion between Rice Straw Leachate and Automotive Wastewater. The pH range in stable condition but the biogas production yield decreased. The highest COD removal rate was 73% but however the methane percentage composition was only 0.5%. It was apparent that the system was unbalanced inhibiting the activity of methane bacteria. The low levels of methane yield could be related to the quality of the feedstock as RSL material contained fibre and lignin and tended to accumulate with other non-biodegradable material which runs on AWW.

Table 4 : Theoretical and actual methane production in reactor

Time (Day)	**Feedstock**	**COD_{added} (g)**	**$COD_{removed}$ (g)**	**Theoretical CH_4 (L of CH_4 / day) *a**	**CH_4 produced from COD (L of CH_4 / day) *a Removed**	**Deviation CH_4 (L of CH_4 / day) *a**
29	Automotive Wastewater	0.460	0.280	0.161	0.098	0.063
42	Synthetic Wastewater + Automotive Wastewater	0.460	0.400	0.161	0.140	0.021
49	Synthetic Wastewater	0.460	0.440	0.161	0.154	0.007
55	Rice Straw Leachate + Automotive Wastewater	0.460	0.310	0.161	0.109	0.052

[*a] Theoretical methane production by assuming 1g COD = 0.35 L of CH_4

[*b] Calculated from the difference between theoretical and actual obtained per gram of COD removed

According to Siripong and Dulyakasem (2012), the combination of feedstock with low and high C/N ratio is preferable to obtain the optimum gas production. In addition, crops residuals as a feedstock have a high of C/N ratio may contribute lower methane production. Thus from this experiment, feedstock with high of C/N ratio which lack of nitrogen content and high inorganic material may results to poor biogas production. Therefore, once again this shows that the rice straw leachate with high lignin content can actually inhibit the biogas production in the reactor (Kadam *et al*, 2000). Besides, the lack of nitrogen in rice straw leachate will limit the methanogenesis process thus causes the reduction in biogas volume.

The results for missing methane as given in 4 showed that the highest missing methane was observed during process mono digestion of AWW and followed with co digestion RSL with AWW with value 0.063 L of CH_4 / day and 0.052 L of CH_4 / day respectively . Based on study from Idrus et al., (2007), this result may indicate that when heavy metal accumulation present in the reactor, the amount of the energy available from COD conversion is not being converted into methane production.

4.0 CONCLUSION

The results of AWW digestion demonstrate that the process was operating with low biodegradation rate. The process was indicated by the decrease of biogas production, low pH below 6.0 and low COD removal efficiency. Final pH observed was drop to 5.85 during the digestion which may inhibit methanogens particularly. COD removal were erratic with average removal was 63.4% and there was no methane achieved. A poor results of anaerobic single digestion of this sample seems to be linked to heavy metal inhibition due to the presence of Zn and Cu in AWW. The reactor achieved stability in Mono Digestion of SWW sample with highest COD removal at 95%. Co-digestion of AWW with SWW proved to improve the performance of the reactor. The nutrient content available in the SWW could promote the synergistic effect in co digestion with AWW and hence performed better than mono digestion of AWW. During this phase, the reactors have sufficient buffering capacity as showed in alkalinity ratio value of less than 0.3. The COD removal rate was higher and better than mono digestion of AWW with highest removal achieved at steady state was 86.6%. Biogas production recorded to be increased from the beginning of co digestion on day 30 until reach steady state on day 42. Co digestion of AWW and RSL as substrates has improved biogas production to 0.109 L of CH_4 / day which 12% more than mono digestion. SEM and EDX analysis confirmed accumulation of metals which includes Zinc and Cu in sludge after prolonged exposure to AWW.

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