Temperature and organic loading rate influence on biomethanation of Petrochemical wastewater using CSTR

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ARTICLE INFO	ABSTRACT

The effect of gradual increase in organic loading rate (OLR) and temperature on biomethanation from petrochemical wastewater treatment was investigated using CSTR. The digester performance was measured at hydraulic retention time (HRT) of 4d to 2d, and start up procedure of the reactor was monitored for 60 days via chemical oxygen demand (COD) removal, biogas and methane production. By enhancing the temperature from 30 to 55 ˚C thermophilic condition was attained while pH was adjusted at 7 ± 0.5 during the experiment. Supreme COD removal competence was $98\pm0.5\%$ (r = 0.84) at an OLR of 7.5 g-COD/Ld and 4d HRT. Biogas and methane yield were logged to an extreme of 0.80 L/g-$COD_{removed}$ d (r = 0.81), 0.60 L/g-$COD_{removed}$ d (r = 0.83), and mean methane content of biogas was 65.49%. The full acclimatization was established at 55 ˚C with high COD removal efficiency and biogas production. An OLR of 7.5 g-COD/L.d and HRT of 4 days were apposite for petrochemical wastewater treatment.

1. Introduction

Malaysia is facing two concurrent problems -1) the discarding of wastes produced by manufacturing and 2) the requirement for novel sources of gasoline to meet up the energy necessities of society. Anaerobic co-digestion, a sustainable green technology, extensively applied to various waste treatments, especially animal manure. The anaerobic digestion system among all methods has been renowned as the principal method of an advanced technology for environmental safeguard (Latif et. al, 2011). To meet up accumulative need for energy and gainful environmental safety, anaerobic digestion bioengineering has become the motivation of global attention (Hanssan et. al, 2001). In comparison to other treatment methods, the key benefits of anaerobic digestion are minor sludge generation, less costly, elevated energy proficiency and process easiness. Besides, it proposes an optimistic environmental impact as it provides waste stabilization with net energy generation and permits usage of effluent as fertilizer. Nevertheless, there are definite limitations of its application, like as lengthy start-up period and process instability (Nazri et. al, 2008). Currently, anaerobic digestion has scrupulous attraction for organic waste treatment due to the economic advantages of energy production (Yu et. al, 2002; Edgar et. al, 2006; Boha et. al, 2000). Due to high organic and moisture contents, anaerobic biodegradation is a superior option for PWW treatment. AD has latent of biogas production that can be used for cooking, heating, and electricity generation. Since, PWW contains great quantity of organic matter (Rao

et. al, 2004; Han et. al, 2005); it is a valuable biomass source for AD. During AD, temperature and pH have somber effect on bacterial activity of the biomass (Mchugh et. al, 2004). The temperature should be in the range of 30–60˚C (Berand et. al, 2007). Hence, it is a principle process for tropical climate due to high fluctuation in daily temperature. Optimum pH (values) ranges between 6.8 and 7.2 for most microbial growth, but pH below 4.0 or above 9.5 does not give satisfactory results (Gerardi et. al, 2003). Methane-producing bacteria need a neutral to lightly alkaline environment to produce maximum methane from food biomass. The feasibility of CSTR conception treating digest-able wastewaters has been adequately described at pilot and full scale (Malina et. al, 1992). The CSTR is the most commonly used process, with more than 500 installations the world over (Tchobanoglous et. al, 2003). CSTRs have been effectively applied to treat various wastewater, such as, fruit wastewater, cassava pulp, molasses alcohol slops, domestic and municipal wastewater, palm oil mill effluents, etc. Nevertheless, the application of CSTRs treating PWW has shortly been stated in literature to date. The main objective of this study is to explore the feasibility of mesophilic anaerobic digestion of PWW by using a CSTR reactor. The co objective of this study is to examine the performance of CSTR reactor on PWW at various organic loading rates and temperatures for waste reduction and biogas production.

2. Methodology

2.1 Sample collection and characterization

A100 L of PWW sample was collected in plastic containers at the point of discharge in to the main stream and from the receiving stream. Then, transported to the laboratory and preserved at 4˚C for further study were physicochemical analysis and treatment. Effluent pH was maintained at 6.5, using 5N NaOH solution. Alkalinity was maintained between 1400-1800 mg $CaCO_3$/l by $NaHCO_3$. Complementary nutrients like nitrogen (NH_4Cl) and phosphorous (KH_2PO_4) were employed to maintain a COD: N: P ratio of 250:5:1. Table1 explains composition and characteristics of PWW. With a view to eliminate trash materials,

the prepared sludge was initially passed through a screen.

2.2 Seeding

Seeding of CSTR was done using anaerobically decomposed sewage sludge collected from municipal sewage treatment plant situated in Kuantan. Collected sludge was initially sieved (<2 mm) to eliminate any fragments and bigger elements before feeding to the reactor. Reactor was fed 50% sludge having suspended solids 3.09 g-TSS/L and 2.09 g volatile suspended solids (VSS) per liter. In order to measure the bacteriological performance of seed sludge, 5 mL of sludge was supplemented to 50.0 mL sucrose and acetate in a 150-mL serum bottle (Minowa et. al, 1995). The generated biogas was examined after 24 h.

Table 1: Composition and Characteristics of PWW

Parameters	CPW
pH	6.5-8.5
BOD	8-32
COD	15-60
TOC	6-9
Total solids	0.02-0.30
Acetic acid	46.60
Phenol	0.36
Total Nitrogen	0.05-0.212
Total Phosphate	0.102-0.227
Volatile fatty acids	93-95

*Except pH and Acetic acid, all parameters in gL^{-1}

2.3 CSTR Construction and Operation

A stainless steel laboratory-scale CSTR (2160 cm^3) with 2 L effective volume was used in this study (Figure 1). Thermophilic condition was adapted by gradual increase in the temperature from 30 to 55˚C. The granular sludge bed volume was 795 cm^3 (app. 37% portion of total reactor). The feed was introduced by peristaltic pump; with a flow rate of approximately 965 mL/d. $NaHCO_3$ was fed from separate dosing tank to control the acidity. The CSTR was uninterruptedly fed with diluted PWW for 72 days. The CSTR was monitored daily for flow rate, TOC, COD, SS, VSS, volatile fatty acids

(VFAs), biogas (CH_4, CO_2, and H_2S) and methane yield, while temperature and pH were monitored quarterly a day. The diluted PWW was uninterruptedly fed into CSTR with gradual increase in organic loading rate from 2.0 to 7.5 g-COD/Ld.

2.4 Analytical Methods

The COD was measured by direct digestion method, using HACH apparatus LR (3–150 COD), HR (20–1500 mg/L COD), and HR plus (20–15,000 mg/L COD and above). Total organic carbon was measured by direct method of low, medium, and high range tests (N tube reagent set), using HACH DBR 200 TOC program in HACH apparatus. Day-to-day gas yield was determined, by a revocable device, having liquid displacement technology. Biogas configuration was determined by a Perkin Elmer gas chromatograph having a thermal conductivity detector. A GC column packed with supelco 100/120 mesh was employed to distinct CH_4 and CO_2. Helium was employed as carrier gas maintaining flow rate 30 mL/ min. The columns sustained at 50˚C. Volatile fatty acids (VFAs) were analyzed using that similar GC, having a flame ionization detector connected to a supelco capillary column. Helium was employed as carrier gas maintaining flow rate 50 mL/ min. Injector and detector temperatures were 200 and 220˚C, individually. The kiln temperature was fixed at 150˚C for 3 min and subsequently amplified to 175˚C. The recognition limit for VFA investigation was 5.0 mg/L.

2.5 Statistical Analysis

Data analysis was performed with Microsoft EXCEL 2010. Regression coefficient (R^2) was calculated to analyze the effect of OLR on COD removal efficiency, biogas, and methane.

3. Result and discussion

3.1 Chemical Oxygen Demand

The COD elimination capability with gradual increase in OLR is explained in Figure 1, and influent COD concentration in Table 1. During the first week of experiment, COD concentration was 4 g/L. The lower organic loading rates were, in fact, due to lower COD concentrations at early stages in PWW treatment (Figure 1). Stepwise increase in COD concentration was done in terms of increasing the OLR and reducing the HRT. COD removal efficiency was low in the first week (40–55%), but it recovered during second week (add value) although OLR was enhanced from 2.0 to 5.0 g-COD/L_d. During fourth and fifth week, sudden drop in COD reduction was observed where COD removal efficiency decreased to 62% (R^2 = 0.92). As OLR was further enhanced, COD removal efficiency reached to 98% (R^2 = 0.95) at an OLR of 7.50 g-COD/L_d. Choorit and Wisarnwan (2007) reported 71.10% and 70.32% COD reduction at mesophilic (37˚C) and thermophilic (55˚C) temperatures respectively, treating palm oil mill effluent in continuous stirrer tank. Rittmann and McCarty (2001) investigated that optimum development of microorganisms occurred in a restricted temperature limit and once this limit surpassed, development lowered down quickly. The overall COD removal efficiency of the reactor was found 75%.

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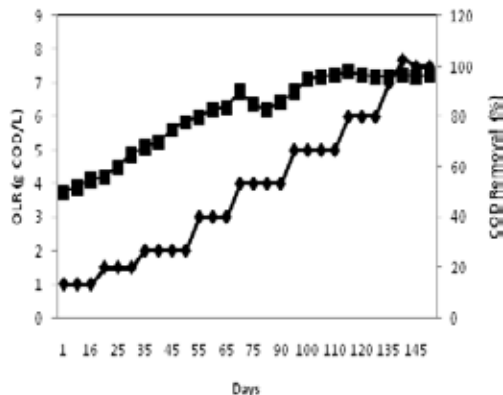

Figure 1: COD removal efficiency in terms of OLR influence, where ♦ OLR (g COD/L), ■ COD removal %

3.2 Effect of Organic Loading Rate

Organic loading rate affects several parameters such as COD, biogas, methane, and volatile fatty acids. Stepwise increase in OLR from 1.5.0 to 7.50 g-COD/Ld showed a satisfactory COD removal efficiency with a strong correlation ($r = 0.78$) which shows that by increasing the organic loading rate, COD removal percentage will be higher as shown in Figure 1. Results indicate that increased organic loading rates produce more biogas and methane (Figure 1). When the organic loading was low, the pH was enhanced steadily up to day 21.

A reduction in pH value has been observed when temperature was shifted from 37 to 50˚C. This shows that pH affects the COD removal, VFA concentrations, and biogas production due to sudden temperature change. Ivan and Herbert (1998) investigated that the temperature shock causes biomass failure, dropping of the pH, and agglomeration of VFA. Nonetheless, reactor stability was recovered within 7 days through

pH adjustment by supplementation of alkaline solution.

Thus, appropriate organic loading rate design is necessary for better reactor performance and process stability. In this study, the OLR was enhanced gradually by dropping HRT from 4 to 2 days (Table 2). Movaedyan et. al, (2007) maintained OLR up to 1.5 kg-COD/m^3 d for 1 week and then enhanced up to 10 kg-COD/m^3 d for 40 days. Nevertheless, biogas and methane production was low at lower organic loading rates. Michaud et. al, (2002) and Rincon et. al, (2006) investigated that lesser OLR caused minor COD removal and

Table 2: CSTR operational design

Runs	Time frame/ run (d)	Organic loading rate (g COD/L.d)	HRT (d)	COD$_{in}$ (g/L)
1	7	1	4	4
2	11	1.5	4	6
3	9	2	3.5	7
4	7	3	3	9
5	15	5	2	10
6	13	6	2	12
7	11	7	2	14
8	7	7.5	2	15

biogas yield. The high OLR perhaps created channeling via sludge bed, reverting indigent substrate–biomass contact and minimum digestion of inward COD. These deliver supplementary provision to previous conventions that in plug-flow states, inward influent stays in CSTR, for single retention time, permitting extreme time for adaptation. Moreover, excessive substrate feeding results due to the lack of distribution that may inhibit bacterial activity (Sallis et. al, 2003). Kalyuzhnyi et. al, (1998) operated with UASBR for chip processing industry wastewater treatment. For lab scale experimental setup with OLR of approximately 14 kg-COD/m^3 d degradation was more than 75% and 63% for centrifuged and total COD of substrate. Grover et. al, (1999) used anaerobic baffled reactor, for the treatment of pulp and paper liquors at 35˚C and showed a highest COD degradation approximately 60% at an OLR of 5 kg-COD/m^3 d and 2 days HRT.

3.3 Biogas and Methane Production

Figure 2 ellustrates the change in biogas and methane production along with organic loading rate. At an OLR of 2.0 g-COD/L_d, biogas and methane production were 0.50 L/g-COD$_{removed}$_d and 0.29 L/g-COD$_{removed}$_d, respectively. The biogas production progressively enhanced thru increasing OLR and mean biogas yield was 0.45 and 0.80 L/g- COD$_{removed}$_d at OLR of 3 and 7.5 g-COD/ L_d, respectively. The methane generation was between 0.25 and 0.60 L/g COD$_{removed}$_d at an OLR of 1.5–7.50 g-COD/L_d, respectively. A strong correlation (r = 0.82) was observed with varing organic loading rate and biogas production during PWW anaerobic treatment in CSTR. Results indicate that high organic loading rates result in more biogas production but the reduction in biogas is caused due to the sudden change in temperature and VFA accumulation in the reactor.
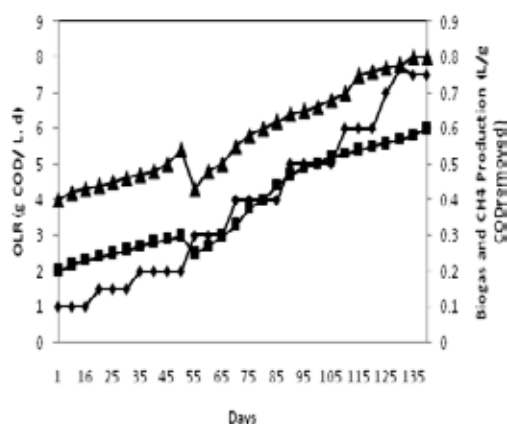

Figure 2: Biogas and CH$_4$ production in terms of OLR influence, where ♦ OLR (g COD/L), ■ CH$_4$ production (L/g COD$_{removal}$),▲ Biogas production (L/g COD$_{removed}$).

4. Conclusion

A CSTR reactor is efficient for COD removal and high methane production. A lab scale reactor was constructed to study the mesophilic to thermophilic anaerobic treatment of food waste. VFA accumulation was low, and methane production was comparatively high due to controlled temperature and pH. However, a sudden change in temperature had adverse effect on biogas production and system stability. The high COD loadings in the initial state at 37°C offer a satisfactory substrate source for succeeding acidogenesis and methanogenesis steps. Thus, at 55°C temperature and OLR of 7.5 g- COD/L_d with 4 d HRT support a highest biogas generation of 0.6 L/g-COD$_{removed}$_d.

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