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Sustainable Bio-methane generation from Petrochemical Wastewater using CSTR

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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 measured at hydraulic retention time (HRT) of 4 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, and pH was adjusted at 7 ± 0.5. Supreme COD removal competence was 98±0.5% (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-CODremoved d (r = 0.81), 0.60 L/g-CODremoved 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.

Index Terms—Anaerobic digestion, Petrochemical wastewater, CSTR, Methane

I. INTRODUCTION

Malaysia is facing two concurrent problems; discarding of wastes produced by manufacturers and requiring for novel sources of gasoline to meet the energy necessities. 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 principal method of an advanced technology for environmental safeguard [1]. To gather accumulative need for energy and gainful environmental safety, anaerobic digestion bioengineering has become a motivation for global attention. 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 optimum environmental impact as it provides waste stabilization with net energy generation and permits usage of effluent as fertilizer. Nevertheless, there are definite limitations of the application, such as lengthy start-up period and unstable process. . Currently, anaerobic digestion has scrupulous attraction for organic waste treatment due to the economic advantages of energy production. Anaerobic biodegradation is a superior option for PWW treatment because of the high organic and moisture contents. AD has latent of biogas production, which could use for cooking, heating, and electricity generation [2]. Since, PWW contains great quantity of organic matter; it is a valuable biomass source for AD [3],[4]. During AD, temperature and pH have somber effect on bacterial activity of the biomass [5][7]. The temperature should be in the range of 30–60˚C. 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. Methane-producing bacteria need a neutral to be light alkaline environment to produce maximum methane from food biomass. The feasibility of CSTR conception treating digest able wastewaters has adequately described at pilot and full scale. The CSTR is the most commonly used process, with more than 500 installations the world over. CSTRs was effectively applied to treat various wastewaters, 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 briefly stated in literature to date. The main objective of this study is to explore the feasibility of mesophilic anaerobic digestion of PWW using a CSTR reactor. The 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.

II. MATERIALS AND METHODS

A. Sample collection and characterization

A 100 L of PWW sample was collected in plastic containers at the point of discharge in 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 maintained at 6.5, using 5N NaOH solution. Alkalinity also maintained between 1400-1800 mg CaCO3/l by NaHCO3. Complementary nutrients like nitrogen (NH4Cl) and phosphorous (KH2PO4) employed to maintain a COD: N: P ratio of 250:5:1. Table 1 explains composition and characteristics of PWW. With a view to eliminate trash materials, the prepared sludge initially passed through a screen.

B. Seeding

Seeding of CSTR done using anaerobic decomposed sewage sludge collected from municipal sewage treatment plant situated in Kuantan. Collected sludge was initially sieve (<2 mm) to eliminate any fragments and bigger elements before feeding to the reactor. Reactor 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 supplemented to 50.0 mL sucrose and acetate in a 150-mL serum bottle (Minowa et. al, 1995). The generated biogas examined after 24 hours.

Table 1 Composition and Characteristics of PWW

Parameters	PWW
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	0.102-0.22
Volatile fatty acids	93-95
BOD	6.5-8.5

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

C. CSTR Construction and Operation.

A stainless steel laboratory scale CSTR (2160 cm3) with 2 L effective volume was used in this study as shown in Figure 1. Thermophilic condition adapted by gradual increase in temperature from 30 to 55˚C. The granular sludge bed volume was 795 cm3 (app. 37% portion of total reactor). The feed was introduced by peristaltic pump; with a flow rate of approximately 965 mL/d. NaHCO3 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 (CH4, CO2, and H2S) 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.

D. 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 measured by direct method of low, medium, and high range tests (N tube reagent set), using HACH DBR 200 TOC program in HACH apparatus. The yielding gas was determined every day, by a revocable device, which is having liquid displacement technology. Biogas configuration was determined by a Perkin Elmer gas chromatograph that have a thermal conductivity detector. A GC column packed with supelco 100/120 mesh employed to distinct CH4 and CO2. Helium employed as carrier gas maintaining flow rate 30 mL/ min. The columns sustained at 50˚C. Volatile fatty acids (VFAs) analyzed using that similar GC, having a flame ionization detector connected to a supelco capillary column. Helium employed as carrier gas maintaining flow rate 50 mL/ min. Injector and detector temperatures were 200 and 220˚C, individually. The kiln temperature fixed at 150˚C for 3 minutes and subsequently amplified to 175˚C. The recognition limit for VFA investigation was 5.0 mg/L.

E. Statistical Analysis

Data analysis performed with Microsoft EXCEL 2010. Regression coefficient (R2) calculated to analyze the effect of OLR on COD removal efficiency, biogas, and methane.

III. RESULT AND DISCUSSION

A. Sample collection and characterization

The COD elimination capability with gradual increase in OLR explains as in Figure 1, and influent of 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 as shown in Figure 1. Stepwise increased in COD concentration done by increasing the OLR and reducing the HRT. COD removal efficiency was low in the first week (40–55%), but it recovered during the second week (add value) although OLR was enhanced from 2.0 to 5.0 g-COD/L_d. During the 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. [8] 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. [9] Investigated that optimum development of microorganisms occurred in a restricted temperature limit and once this limit surpassed, development lowered down quickly [9]. The overall COD removal efficiency of the reactor found 75%.

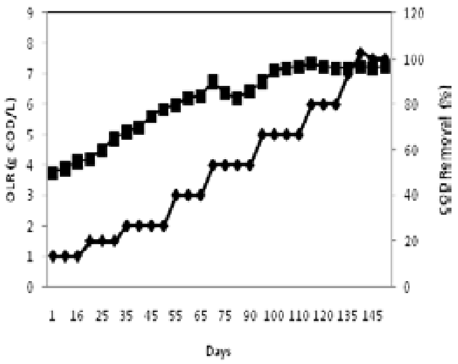

Fig. 1.COD removal efficiency in terms of OLR influence, where ♦ OLR (g COD/L), ■ COD removal %.

B. 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 shows a satisfactory COD removal efficiency with a strong correlation (r = 0.78) 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 enhanced steadily up to day 21.

A reduction in pH value has observed when temperature shifted from 37 to 50˚C. This showed that pH affects the COD removal, VFA concentrations, and biogas production due to sudden temperature change.[10] investigated that the temperature shock causes biomass failure, dropping of the pH, and agglomeration of VFA.

Nonetheless, reactor stability recovered within 7 days through pH adjustment by supplementating 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). [11] 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. [12], [13] Investigated that lesser OLR caused minor COD removal and

Table 2 CSTR Operational Design

Runs	Time frame/ run (d)	Organic loading rate (gCOD/L.d)	HRT (d)	CODin (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, [14] excessive substrate feeding results due to the lack of distribution that may inhibit bacterial activity. 15] Operated with UASBR for chip processing industry wastewater treatment. In the 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) [16] 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.

C. Biogas and methane production

Figure 2 illustrates the changes 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-CODremoved_d and 0.29 L/g-CODremoved_d, respectively. The biogas production progressively enhanced thru increasing OLR and mean biogas yield was 0.45 and 0.80 L/g- CODremoved_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 CODremoved_d at an OLR of 1.5–7.50 g-COD/L_d, respectively. A strong correlation (r = 0.82) was observed with varies organic loading rate and biogas production during PWW anaerobic treatment in CSTR. Results indicate that high organic loading rates contribute more biogas production but the reduction in biogas is caused due to the sudden changes in temperature and VFA accumulation in the reactor.

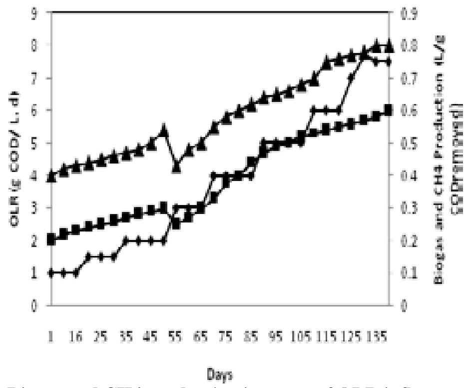

Fig. 2. Biogas and CH4 production in terms of OLR influence, where ♦ OLR (g COD/L), ■ CH4 production (L/g CODremoval),▲Biogas production (L/g CODremoved).

IV. CONCLUSION

A CSTR reactor is efficient for COD removal and high methane production. A lab scale reactor constructed to the study of 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 the highest biogas generation of 0.6 L/g-CODremoved_d.

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