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Palm Oil Mill Effluent Treatment Process Evaluation and Fate of Priority Components in an Open and Closed Digestion System

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ABSTRACT

The evaluation for the degradability of chemical oxygen demand (COD) and biogas contents before and after closed tank reactor (CR) and open tank reactor (TP) were observed. COD reduction in the TP (maximum degradability rate of 60%) and CR (maximum degradability rate of 85%). The variation in CH_4, volatile fatty acid (VFA) and total suspended (TSS) contents in the effluent was more pronounced in the first six months and found stable afterward. The maximum organic loading rate (OLR) of 11.5 g-COD l/d attained corresponded to 85% overall COD removal. However, there is study to degradability of COD and quantify the actual CH_4 recover from the commercial scale wastewater treatment from TP and CR. The findings indicated that the CH_4 content was between 49% TP which was lower than the value of 57% reported in TP. The lower VFAs were found in the CR because of variation of palm oil mill effluent quality and quantity from palm oil mill industry.

Key words: Palm oil mill effluent, Aerobic and anaerobic treatment, COD, biogas, Methane.

INTRODUCTION

Palm oil mill effluent (POME) is a viscous brown liquid with fine suspended solids at pH between 4 and 5[1] and a highly polluting wastewater that directly and indirectly contaminates the environment[2]. The chemical properties of POME vary widely throughout the year because of mill operations and seasonal cropping[3]. Atmospheric methane concentrations incredibly increased by 30% in the last 25 years[4]. Net carbon emission from POME is approximately 1.4×10^6 tons per year[5]. Assuming a mean annual increase of 29% as experienced from 1990 to 2004[6], the estimated CH_4 gas emission may be 0.502×10^6 tons in the year 2020. Certified emission reduction (CER) can be obtained by using methane gas as a renewable energy[7].

At high organic loadings or at natural environment temperatures, the insoluble organic degradation of the effluent tends to accumulate within the granules or sludge density region of the ponds, leading to granule destabilization or inhibition of granule formation[8]. To date, 85% of POME treatment in Malaysia is based on an anaerobic and facultative ponding system, which is followed by another system consisting of an open-tank digester coupled with extended aeration. For every ton of treated POME, an average of 5.5 kg of CH_4 (or approximately 36% of biogas) is emitted from open digesting tanks[3]. Anaerobic digestion is the most suitable method for the treatment of effluents containing high concentration of organic carbon and thus producing biogas[9]. A typical biogas would comprise 60-70% methane, 30-40% carbon dioxide, 0-0.1% hydrogen sulphide, and 0-10% hydrogen[10]. Recently, both conventional single-phase and high-rate two-phase anaerobic digestion systems have been widely used, for the production of biogas-methane from various substrates, such as the organic fraction of the municipal solid waste, POME, food waste, waste-activated sludge, and sugar beet silage[11,12].

Periodic research has been performed to find amicable solutions for POME management[13-15]. The presence and activity of microorganisms in POME treatment are vital to the process. With regard to microbial degradation of POME effluent, biodegradation phenomenon is crucial. Therefore, the steady-state models are basically able to predict the parameters that have been considered in mass balance relations but are unable to estimate the other interrelated effluent quality parameters[16].

Biodegradation is a metabolism-independent consumption of organic to living cells, nonliving biomass, or microbial extracellular polymers[17,18]. Specific metabolic pathways resulting in bio-precipitation of organic molecules or their mechanisms of degradation have been provided elsewhere[19,20]. Moreover, surface exposure of organic-binding microbes improves organic-binding properties of microorganisms based on degradation and microbial metabolic activities[21]. Binding of organic molecules with microbes is known to reduce the COD and selected biogas (CH_4, CO_2, and VFAs)[22] Yacob *et al.*, 2006a S. Yacob, M.A. Hassan, Y. Shirai, M. Wakisaka and S. Subash, Baseline study of methane emission from anaerobic ponds of palm oil mill effluent treatment, Science of the Total Environment 366 (2006), pp. 187–196. Article | PDF (357 K) | View Record in Scopus | Cited By in Scopus (13). Consequently, the removal of COD and treatment of POME effluent with anaerobic and aerobic system also are affected, although many studies have shown that COD can be removed in POME treatment processes[23].

During POME treatment, a large amount of sludge is produced (approximately 35% of the treated wastewater). The Malaysian government proposed and legalized standards for POME discharge into watercourses[24]. The results of a one-year evaluation on the POME degradation was using aerobic, anaerobic digestion of VFA, and removal of COD in terms of selected biogas (CH_4, H_2, and CO_2) by an OT and CR treatment system. The aim of the study were to compare COD, VFA, and biogas contents in the influent and effluent wastewater and to examine the COD and biogas contents in the effluent before and after digestion and compare the performance of our designed treatment system with LSHC POME treatment plant (LSHC-WTP).

MATERIALS AND METHODS

Description of the Gambang POME treatment plant

The main objective is to reduce the level of organic pollution and COD removal from POME before discharging it to the environment. Treatment processes were used are shown in Fig. 1

Sample collection

The raw POME samples were collected every month five sample from LHSC-Palm Oil Mill, situated in the state Pahang, Malaysia. The features and composition of the POME used are summarized in Table 1, which shows the average values of five replicate analyses for each parameter. In comparing the biogas contents in influent and effluent samples (collected from locations 1, 4, 5, and 6), their removal from the influent wastewater was assessed. Because accurate matching of influent and effluent samples was difficult because of large volumes of wastewater or treated sludge, 10 influent and effluent sample pairs were taken to obtain a composite grab sample. Five samples were collected once a month for one year. During each sampling day, three composite grab samples were collected from the influent stream using an automatic wastewater sampler, whereas sample collection from the effluent was done manually approximately 21 h later; this is an approximate time required for the influent stream to pass through all the wastewater treatment operation units between locations 1, 4, 5, and 6 was mentioned in Fig. 1. Grab samples of mixed sludge (location 4) and digested sludge (location 5) also were collected manually. Digested sludge biogas samples were collected 28 days (retention time of sludge in the anaerobic digester) after collecting the mixed sludge sample, which was the influent, into the TP and CR anaerobic digesters. During the period when these investigations were being conducted, the anaerobic digesters (TP and CR) were yet in operation (Fig. 1). To avoid deterioration or contamination of samples, sampling procedures and sample preservation were done according to the Standard Methods for the Examination of Water and Wastewater [25]. Characteristics of raw and pre-treated POME are provided in Table 1 and 2, respectively.

Analytical analysis

All the tests for the samples were analyzed according to the guidelines of the American Public Health Association[26] for the examination of water and wastewater. Biogas yield was measured with a wet gas meter (W-NK-O.SA, Shinagawa). Gas samples were obtained through an inverted funnel placed above baffles near the top of the reactor. Biogas composition was determined using a gas chromatograph (GC-8A, Shimadzu, Kyoto) with a thermal conductivity detector equipped with a steel column packed with WG-100 (GL Sciences, Tokyo) at 50°C. Volatile fatty acids (VFAs) were determined with a gas chromatography (W-NK-O.SA, Shinagawa) equipped with a 2 m × 4 mm glass column packed with Suplocopor (100-120 mesh) coated with 10% Fluorad FC 431. The temperatures of the column, the injection port, and the flame ionization detector were 130, 220, and 240°C, respectively. Effluent and biogas production rates were measured and analyzed weekly, whereas biomass concentration was analyzed biweekly for each loading rate.

RESULTS AND DISCUSSION

COD removal in TP and CR

Fig. 2 presents the average COD removal efficiencies in %. The values were calculated based on the 12-month COD contents in the influent and effluent in TP and CR. The variations in COD concentration and removal in CR was greater than those in the TP (Fig. 2). In the latter case, variations in the concentration of COD in primary treatment lead were sharper than those in the secondary treatment. The maximum degradability rate of COD 59.9% was faster and COD removal was found to be 85.5% by CR, whereas that in the TP was only 70%, which was varying and higher than those of primary treatment where COD removal is approximately 53% Table 3. These trends were observed throughout the study period of 12 months, indicating that these COD originated from the same respective sources. COD degradability depends on the CH4 emission rate in both TP and CR. An average of 0.109 g of CH_4 was produced from a 1 g of COD (Fig. 2). During the operation an average COD of POME was 45000 ± 2189 mg/l while the CR treated POME was 2435±1176 mg/l[18].

The COD removal occurs in both primary treatment (where a portion of organics is adsorbed on to the particles) and secondary biological treatment (where COD is removed by anaerobic digestion of volatile fatty acids)[8]. Biological treatment systems are chiefly designed for the removal of organic carbon by activated sludge microorganisms. Therefore, removal of organics by these systems may be regarded as a side benefit, minimizing the amount of carbon emission and sludge disposal and producing biogas and methane[9,20].

As shown in Fig. 2, the COD concentration in both tanks was almost the same until September, but open tank showed a comparatively low COD concentration in October and November 2011, perhaps because there was more rainfall during these months in which COD concentration was reduced because of rain water dilution in the open tank. On the other hand, the closed tank was obviously not affected by rainfall because of closed anaerobic environment. [27] studied pollution control technologies for the treatment of POME and reported similar observations.

The variation in the contents of CH_4 (Fig. 3) and CO_2 (Fig. 4) in the effluent was more pronounced. The variation in the content of CH_4 was the most pronounced, whereas that of VFA and CO_2 varied in the first six months and later remained stable, with few exceptions. These observed stable contents of CH_4, CO_2, and biogas in the effluent corresponded well with their respective stable contents in the influent stream.

VFA conversion and biogas production are affected by the treatment system itself. For example, when removal efficiencies are calculated, only the COD/VFA contents in the influent stream are considered in comparison with that in the effluent. However, from the conceptual model shown (Fig. 1), the biological treatment system is potentially overloaded with VFA contained in the returned streams, namely, recycled activated sludge and returned wastewater. The treatment and degradation of VFA in the treatment systems seem to be influenced by the following mechanisms: (1) acetogenesis, conversion of butyrate to acetate and hydrogen; (2) methanogenesis, cleavage of acetate to CH_4 and CO_2; and (3) reduction of CO_2 to CH_4 [28,29]. The effects of VFA contents were in the return streams (Fig. 5) on the wastewater influent and effluent COD/VFA contents (consequently, on their removal efficiencies). In addition, it is not known which organic and inorganic components of the sludge are anaerobically degraded and how such degradation processes affect the contents of CH_4 and COD in the sludge.

Volatile fatty acid concentration

Fig. 5 shows the VFA concentrations in TP and CR during a one-year period. From August to July, the VFA concentration in both tanks was increased slightly, although the CR had higher VFA concentration because of anoxic treatment conditions. However VFA reduction from 790 to 230 mgl^{-1}; this reduction could not increase the biogas production because dilution of normal water during biodegradation of organic matter lowers the reaction rate during the treatment process.

The VFA concentrations in the CR were relatively high (400-1240 mgl^{-1}) because the treatment process is totally anaerobic. The high concentration of VFA in the closed tank is due to the faster reaction rate in the absence of oxygen. Moreover, the conversion of acidogenesis into acetogenesis requires less time compared with that during partial anaerobic conditions

When the VFA concentrations in the two tanks were compared, the organic decomposition under full anaerobic conditions was observed to be stronger than that under partial anaerobic condition (Fig. 5). Furthermore, by comparing the biogas production at the same time, the closed anaerobic tank produced more gas than the open tank, although VFA concentration in the closed tank was relatively higher than that in the open tank. Fatty acid accumulation inhibits biogas production as reported in earlier studies; however, up to a certain level of VFA accumulation (2,000-3,000 mgl^{-1}), biogas production is not disturbed [30]. Because of this, the biogas production rate in both tanks was almost low, but it was continued because of the low concentration of VFA in the organic matter[31] found low biogas yield and organic matter removal because of the accumulation of inhibiting substances, such as volatile fatty acids[32] reported that COD removal was greater than VFA removal at the same pH and initial concentrations[20]. Furthermore, VFA removal efficiency is affected not only by VFA species and concentration but also by other conditions, such as operating parameters and physical, chemical, and biological factors[33]. For example, it is known that VFA removal by activated sludge is dependent on dissolved organic matter [34] and pH[35,36], whereby

Table 1: Physio-chemical characteristics (POME)

Parameter*	Raw POME
pH	4.5
Biological oxygen demand (BOD)	31.5
Chemical oxygen demand (COD)	65.0
Alkalinity	2993
Total solid (TS)	39.0
Suspended solid (SS)	18.9
Total phosphorus (TP)	950
Total organic carbon (TOC)	25000
Total nitrogen (TN)	945
Total kjeldal nitrogen (TKN)	0.77
Volatile fatty acid (VFA)	1900
Oil &Grease	3.97
SO_4	5

* All parameters are in g L^{-1} except pH
[a] as TSS
[b] as total nitrogen

Table 2: Composition and characteristics of the pre-treated POME

Parameters	Concentration
pH	4.2
COD	43.4 g/l
BOD_5	9.8 g/l
TSS	15.3 g/l
VSS	10.5 g/l
TVFA	2.54 g/l
TKN	536 mg/l
P	98 mg/l
Fe	290 mg/l
Ca	310 mg/l
Mg	235 mg/l
Na	7 mg/l
K	720 mg/l

the removal efficiency increases with increasing pH until fatty acids precipitate as hydroxides. Moreover, biological wastewater treatment is normally conducted at pH 7–9. A major limitation of the anaerobic digestion of fruit and vegetable wastes in single-stage system is the rapid production of volatile fatty acids attributed to pH decrease during acidification that stressed and inhibited the activity of methanogenic bacteria [29]. The relationship between influent COD contents and their removal efficiencies (Fig. 2) is consistent with the findings of other researchers[22,37], who observed that COD and VFA removal efficiencies were directly proportional to influent concentrations.

Comparison of TP and CR treatment

The waste sludge from primary and secondary treatment processes is stabilized by anaerobic digestion, which involves microbial decomposition of organic and inorganic matter. In the treatment plant investigated, the mixed sludge was introduced in the TP at intervals, retained in the digester for 38 days, and then intermittently disposed of as digested sludge. COD in the sludge is present as organic compound, precipitates in the sludge flocks, complexes of soluble organics and biopolymers, and degraded soluble organics in the microbial cells [38]Brown and Lester, 1979. M.J.

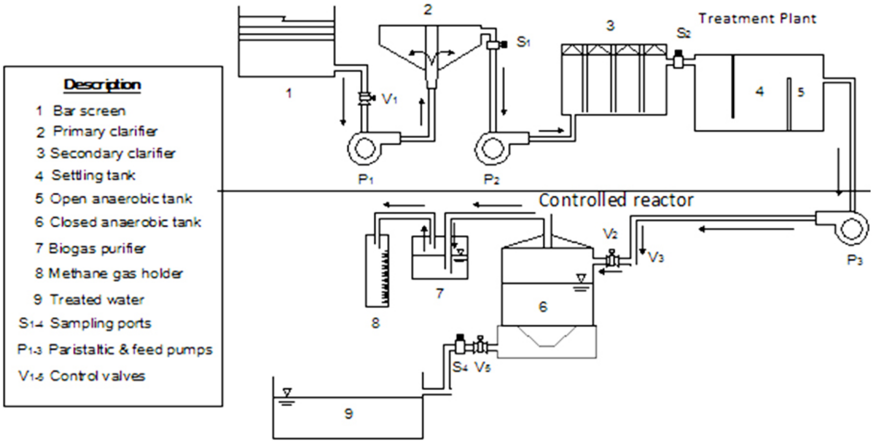

Fig. 1. Experimental setup of biological treatment systems of palm oil mill effluent (POME)

Table 3: Results obtained during primary treatment of POME

Time (m)	VFA (g/l)	TOC (g/l)	Biogas (l)	TSS (g/l)	VSS (g/l)	COD (mg/l)	COD degradability rate %
Aug 10	4.2	0.04	0.092	5.2	4.0	19704	54.6
Sep 10	2.2	0.05	0.049	5.9	4.1	21787	49.8
Oct. 10	3.0	0.03	0.059	5.6	3.9	19053	56.1
Nov. 10	2.5	0.04	0.071	5.5	3.8	24493	58.9
Dec. 10	2.6	0.02	0.035	6.7	5.2	24955	42.5
Jan. 11	3.6	0.02	0.025	5.9	4.3	21222	51.1
Feb. 11	4.5	0.04	0.047	5.6	4.0	17403	59.9
Mar. 11	3.1	0.05	0.036	6.0	5.0	18488	57.4
Apr. 11	4.8	0.05	0.031	5.8	4.4	20181	53.5
May 11	3.0	0.06	0.037	6.1	4.5	19182	55.8
June 11	3.5	0.05	0.063	6.2	4.1	19703	54.6
Jul 11	4.4	0.06	0.078	6.5	4.2	21396	50.7

Brown and J.N. Lester, Metal removal in activated sludge: the role of bacterial extracellular polymers. Water Research **13** (1979), pp. 817–837. Abstract I PDF (2013 K) I View Record in Scopus I Cited By in Scopus (120). Fig. 2 and 5 show the results of COD and VFA of organic contents in both undigested and digested sludge. Both streams were characterized by highly fluctuating COD, VFA, and organic contents. Moreover, TP and CR digestion caused a decrease in TSS content in Fig. 6 that mean COD and VFA reduction on dry weight basis. The reduction in TSS contents in the effluent from 3615 to 1026 mgl^{-1} by TP and from 3617 to 438 mgl^{-1} by CR. After treatment of POME by CR the reduction of TSS approximately 65% means this technique reduce the burden of sludge in our environment. (Fig. 6) and organic matters are degraded into end products including CH_4, CO_2, N_2, H_2S, and some trace gases[39].

Because the determination of CH_4 contents was based on COD reduction, the reduction of such organic and inorganic matters probably caused the observed increase in CH_4 contents in the CR is more than TP, where as the degradation of COD in TP 58% and 85% in CR.[40] indicated that the digestibility of organic components in the POME was in the following order: VFA<CH_4<CO_2<H_2. Furthermore, the volatilization/solubilization of organics to the atmosphere from activated sludge systems also is known[41]. Such organic losses, although probably not a major factor, could have contributed to the inconsistency and variation in CH_4 and CO_2 content increases in the digested sludge. [8] investigated the treatment of POME using aerobic oxidation based on an activated sludge process. A possible reason for the increased removal of organic matter as well as oil and grease in the anaerobically digested sample was the presence of partially degraded organic and oil

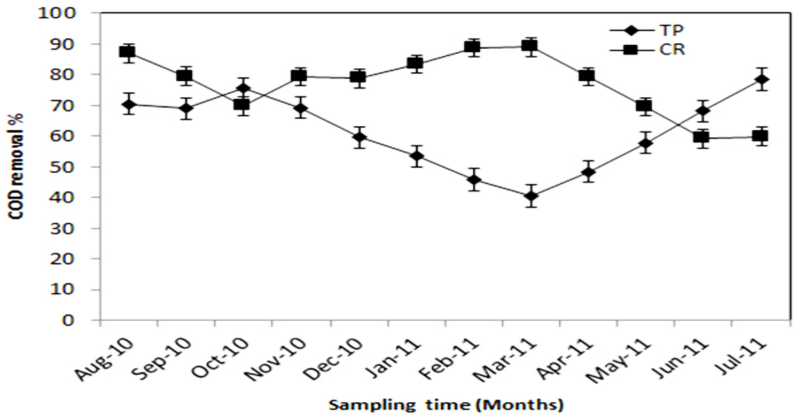

Fig. 2: COD removal % in TP and CR.

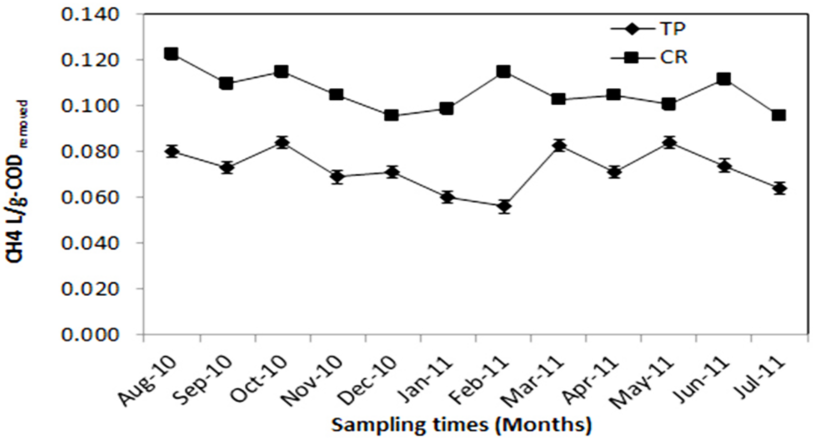

Fig. 3: CH_4 gas content in TP and CR conditions.

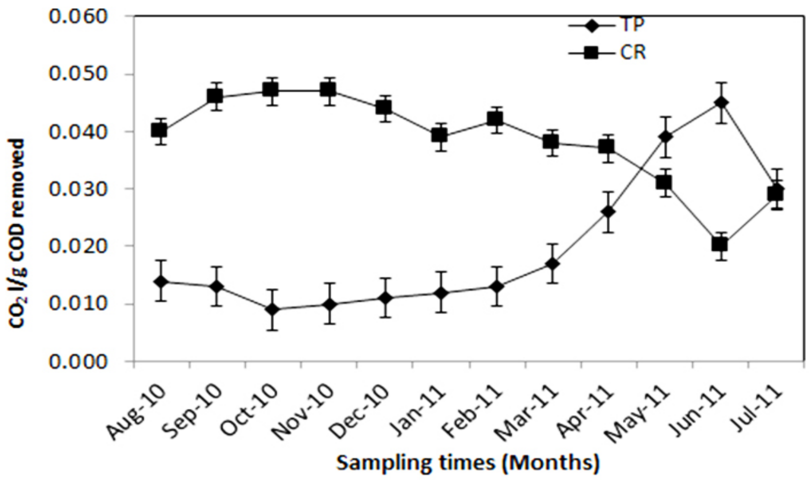

Fig. 4: CO_2 gas reduction mean capture in TP and CR conditions.

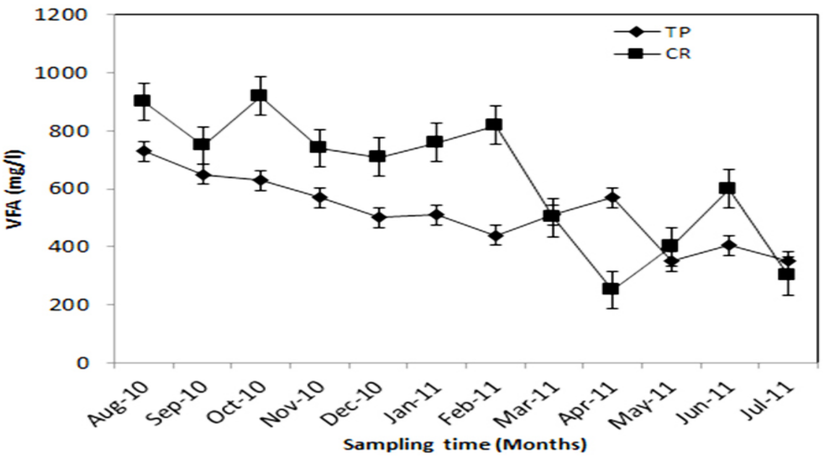

Fig. 5: A-VFA concentration B- VFA reduction in TP and CR conditions.

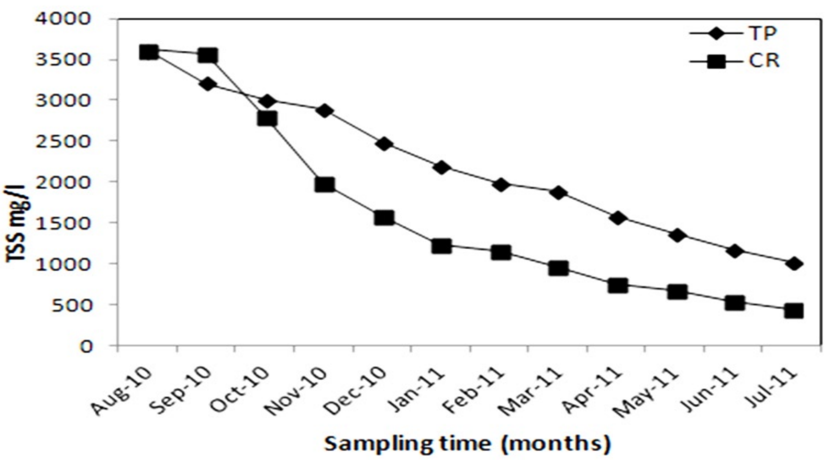

Fig.6: TSS concentration in TP and CR conditions.

molecules, making them more amenable to aerobic digestion.

Fig. 3 show the average CH_4 contents in undigested sludge. The increase in the content of VSS, which was the highest in the undigested sludge, was seemingly the lowest. Also, the content of CH_4, which was the lowest in the undigested sludge, increased more (approximately 97%) than that of the other parameters. As per survey a total amount of POME was discharge 235640 t in 2005 and COD was 45000 ± 2189 mgl^{-1}. After the treatment of POME by TP sludge was 506±254 and CR 354±127 gl^{-1} in l^{-1} of POME. This is best techniques to evaluate the treatment of by TP and CTE to CH_4 production g^{-1} of COD and sludge management. In principle, the results of this study indicate that LHSC meets the compliance limits (COD, VFA, CH_4 and TSS) for treated wastewater in accordance with the decree issued by the Malaysian Ministry of Environmental Protection about the characteristics of wastewater for disposal to water or land.

CONCLUSIONS

For the wastewater treatment system investigated, when the contents of COD and VFA are equal to 19.9 and 1240 mgl^{-1}, respectively, their reduction is insignificant. Thus, the COD removal is directly proportional to the influent concentrations. The reduction of COD contents was in the following increasing order: CH_4 <VFA <CO_2, which directly corresponded to their COD initial influent wastewater contents. A relation was also established between TP and CR for VFA reduction rates where 110 mg/l in CR, where as in TP 570 ml^{-1} in November month was observed. The investigated CR system meets the compliance limits for treated wastewater. While for every g of COD of POME discharged, an average of 0.106 l of CH_4 will be produced from the CR compared to TP 0.072 l of CH_4. The results presented herein indicate that a long term observation is crucial to determine the CH_4 POME (t^{-1} d) CH_4 (t^{-1} d). Relationship between CH_4 from VFA reduction 86% showing high rate degradability rate of POME through our system. However, after treatment of POME by CR the reduction of TSS approximately 65% means this technique reduces the burden of sludge in our environment.

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