Anaerobic Treatment of Petroleum Refinery Wastewater

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Abstract**—**Anaerobic treatment has many advantages over other biological method particularly when used to treat complex wastewater such as petroleum refinery wastewater. In this study two Up-flow Anaerobic Sludge Blanket (UASB) reactors were operated in parallel to treat six volumetric organic loads (0.58, 1.21, 0.89, 2.34, 1.47 and 4.14 kg COD/m^3·d) to evaluate the chemical oxygen demand (COD) removal efficiency. The reactors were continuously adapting to the changing of operation condition with increase in the removal efficiency or slight decrease until the last load which was more than two times the load, at which the reactor stressed and the removal efficiency decreased to 75% with effluent concentration of 1746 mg COD/L. Other parameters were also monitored such as pH, alkalinity, volatile fatty acid and gas production rate. The UASB reactor was suitable to treat petroleum refinery wastewater and the highest COD removal rate was 83% at 1215 kg/m^3·d with COD concentration about 356 mg/L in the effluent.

Keywords**—**Petroleum refinery wastewater, anaerobic digestion, UASB, organic volumetric loading rate

I. INTRODUCTION

MANY industries use anaerobic biological processes for the treatment of their wastewater; motivated by the fact that they are cheaper, cleaner and safer methods. The advantages of anaerobic digestion include energy recovery from methane gas produced as well as cost saving, low sludge and process simplicity. During refining process of crude oil, petroleum refineries produce large amounts of wastewater that needs to be treated prior to discharge to water bodies. The quality of this wastewater depends on the refining process configuration but is generally characterized by the presence of oil products and chemicals [1].

The handling and treatment of refinery wastewater streams vary from one facility to another depending on the specific characteristics of wastewater generated, as well as the type of crude oil, composition of condensate and pretreatment processes applied [2]. While conventional refinery wastewater treatment technology is mainly focused on the removal of oil, organics, and suspended solids prior to discharge; end-of-pipe treatment became a necessity for many refineries because of stringent discharge requirements for the effluent [3]. Biological treatment modifications are economically feasible because most of the toxic and recalcitrant organic compounds can be easily biodegraded under anaerobic conditions, with the compound serving as a growth substrate [4].

Various studies have been reported in literature on the treatment and disposal or reuse of wastewater effluent from petroleum refineries facilities [5]. Many researchers have shown biological treatment of petroleum refinery -or some its compounds- wastewater to be effective and efficient methods [6-10].

The up-flow anaerobic sludge blanket (UASB) reactor is a high rate system that can retain biomass with high treatment capacity in low site area requirement and hence commonly used for treatment of various industrial wastewater [11]. It advantages include high organic loadings, low detention time and elimination of the cost of packing material, in addition to the potential for net energy production [12] makes it favorable and proven process. UASB reactors have been successfully used to treat petroleum refinery wastewater [13] of medium- and high-strength within a wide range of hydraulic retention time (HRT) [14], temperature [8] and organic loading rate [15, 16]. A study was successfully conducted to determine the biodegradability of a local petroleum refinery wastewater in a mixture with mineral nutrients and sludge in a single batch run for 28 days [17]. The treatability of this wastewater was further investigated using anaerobic sequencing batch reactor (ASBR) [18, 19]. A high strength (7.3 kg COD/m^3) batch from this petroleum refinery wastewater was pretreated in UASB as part of a train of biological reactor; the chemical oxygen demand (COD) removal was found to be 80% [20]. UASB reactors were also used to evaluate the treatment efficiency of this petroleum refinery wastewater under four organic volumetric loading rates. The COD removals efficiencies were 78, 82, 83 and 81 % as the load increased [21]. The present study follows from the previous investigation by monitoring more parameters and applying additional organic volumetric loading rates of petroleum refinery wastewater in two up-flow anaerobic sludge blanket (UASB) reactors.

II. MATERIALS AND METHODS

A. Feed

Wastewater samples for the study were collected from a local petroleum refinery's balancing tank that receives raw wastewater from the petroleum refinery. The wastewater was stored in a cold room (4°C) before used. The petroleum refinery wastewater characteristics are shown in Table 1 [21].

TABLE I
CHARACTERISTICS OF PETROLEUM REFINERY WASTEWATER

Parameter	Unit	Amount
COD	mg/L	7896
BOD$_5$	mg/L	3378
pH	-	8.48
VFA	mg/L	198
Ammonia-N	mg/L	13.5
Nitrate-N	mg/L	2.23
TKN	mg/L	40.6
Total P	mg/L	10.2
Total alkalinity	mg/L	990

B. Analytical methods

pH, alkalinity, mixed liquor suspended solid (MLSS), mixed liquor volatile suspended solids (MLVSS), biochemical

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oxygen demand (BOD) were determined in accordance with Standard Methods [22]. Chemical oxygen demand (COD), volatile fatty acids (VFA), ammonia nitrogen, nitrate nitrogen, phosphorus, were determined by colorimetric method using a HACH DR 2000 spectrophotometer.

C. Experimental procedure

Two laboratory-scale up-flow anaerobic sludge blanket (UASB) bioreactors were operated in parallel at room temperature (25-29°C). The volume, diameter and height of each bioreactor were, 2.36 L, 94 mm and 430 mm, respectively. Both bioreactors were operated with an internal effluent recycle ratio of 1:1 to distribute the influent and provide better mixing. The influent was pumped continuously to the bioreactors by peristaltic pumps, while the effluent exits the bioreactors through water-seal to prevent any atmospheric air from entering the bioreactors. The biogas that produced during the anaerobic digestion was collected by water displacement method. Figure 1 shows the schematic diagram of the UASB experimental set-up [21]. Seed biomass was obtained from a local palm oil mill effluent (POME) treatment plant and the petroleum refinery site and mixed together. Flowrate to the reactors was set at 1.4 L/d with hydraulic retention time (HRT) maintained at 40 h. Steady state performance was studied under six organic volumetric loading rates (L_{org}) which were gradually applied over more than 170 days, with each reactor receiving three organic loads as described in Table II.

TABLE II
OPERATION CONDITION

Load	Reactor	Unit	CODin	MLVSS
1	A	mg/L	982	7808
2	A	mg/L	1504	12049
3	B	mg/L	2048	10677
4	A	mg/L	2476	12419
5	B	mg/L	3944	11377
6	B	mg/L	6972	11831

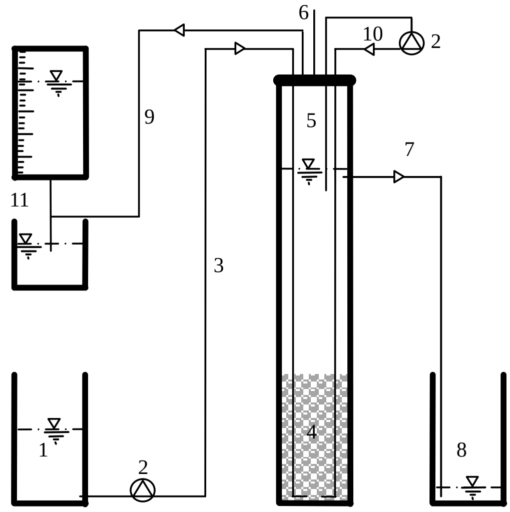

Fig. 1 Schematic diagram of the UASB experimental set-up. 1. Influent tank, 2. Pump, 3. Influent, 4. Sludge zone, 5. Gas zone, 6. Sampling point, 7. Effluent, 8. Effluent tank, 9. Gas line, 10. Recycle, 11. Gas collection

III. RESULTS AND DISCUSSION

A. pH and Alkalinity

Influent pH throughout the experimental period was found to be on average slightly above neutral and increased more in the effluent without any pH adjustment made to the influent or inside the reactor. To maintain buffering capacity for the reactors and prevent them from turning sour, alkalinity was added in the form of sodium bicarbonate to the influent of the bioreactors, and it could be observed that effluent alkalinity was slightly higher than the influent as shown in Figure 2 with respect to the organic load.

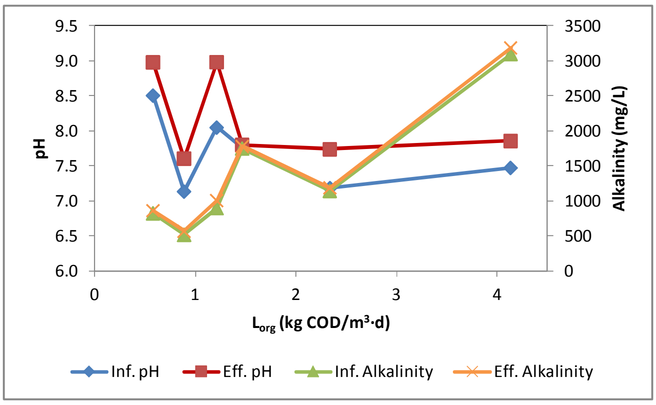

Fig. 2 pH and alkalinity vs. volumetric organic loading rates applied.

B. Volatile fatty acid

Figure 3 illustrates the average data for volatile fatty acid (VFA) concentration at steady state condition and the VFA/alkalinity ratio for the reactors versus the six volumetric organic loads applied to the two reactors. The VFA concentration for the first five loads was found to be less than 150 mg/L indicating high methanogenic activity [12] that could keep the concentration low even when the load was constantly increased. But when the load was further increased to much higher than initial as represent by the sixth load, the VFA suddenly increased to higher concentration. The VFA/alkalinity ratio was targeted to be less than 0.4 which was necessary for the anaerobic reactor to be able to balance all potential fluctuations without major change in pH [23]. The ratio was successfully maintained by adjusting the reactors alkalinity for all loads applied. When the first load was applied to the reactor, the VFA concentration was low, for that the alkalinity was also kept low. As the L_{org} applied to the reactors was increased, the steady state average VFA also increased and alkalinity was elevated to maintain the ratio. Overall, the VFA/alkalinity ratio was found to be always much lower than the failure limit (0.3-0.4) value [12].

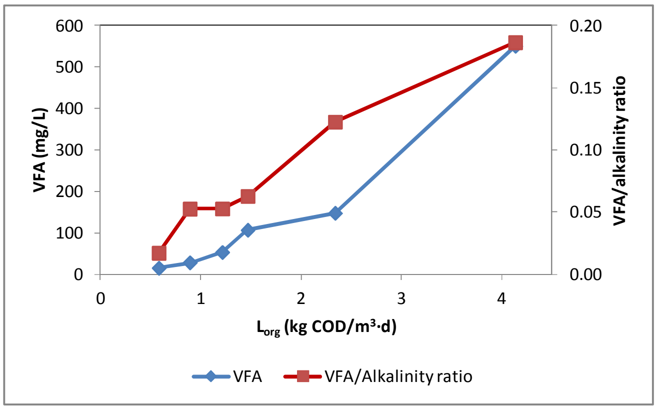

Fig. 3 VFA and VFA/alkalinity ratio vs. volumetric organic loading rates applied

C. Chemical oxygen demand

COD was the key parameter to monitor the performance of the reactors, summary for concentration applied to the reactors and after treatment concentration are shown in Table 3. Figure 4 illustrates the average influent and effluent total COD results throughout the study period. Day 1 to day 60 represent the first L_{org} 0.58 and 1.21 kg/m^3·d applied to reactors A and B, respectively. The removal efficiency was found to be, 78% and 83% respectively. From day 60 to day 120, when the L_{org} applied to reactors A and B, was 0.89 and 2.34 kg/m^3·d, the COD removal efficiency was found to be 82% and 81%, respectively. From day 120 to the end of study, L_{org} of 1.47 and 4.14 kg/m^3·d were applied to reactors A and B, respectively. The COD removal efficiency was found to be 80% and 75%, respectively.

TABLE III
REACTORS PERFORMANCE

Load	Reactor	Unit	CODin	CODout	MLVSS
1	A	mg/L	982	219	7808
2	A	mg/L	1504	273	12049
3	B	mg/L	2048	356	10677
4	A	mg/L	2476	494	12419
5	B	mg/L	3944	768	11377
6	B	mg/L	6972	1746	11831

From the data obtained, the reactors gave efficient COD removal, which was always above 75% for the entire duration of the study. The highest percentage COD removal was 83% and was achieved by Reactor B at 1.21 kg/m^3·d and influent COD concentration of 2048 mg/L, whilst the lowest effluent COD concentration was 219 and was achieved by Reactor A at 0.58 kg/m^3·d and influent COD concentration of 982 mg/L.

The performance of the reactors at organic loading rate (OLR) of 1.21 kg/m^3·d, hydraulic retention time (HRT) of 40 h and influent COD of 2048 mg/L and 83% COD removal was found to be better than that recently reported in literature [14] with 81% COD removal at organic loading rate (OLR) of 0.4 kg/m^3·d and hydraulic retention time (HRT) of 48 h and influent COD of 1000 mg/L.

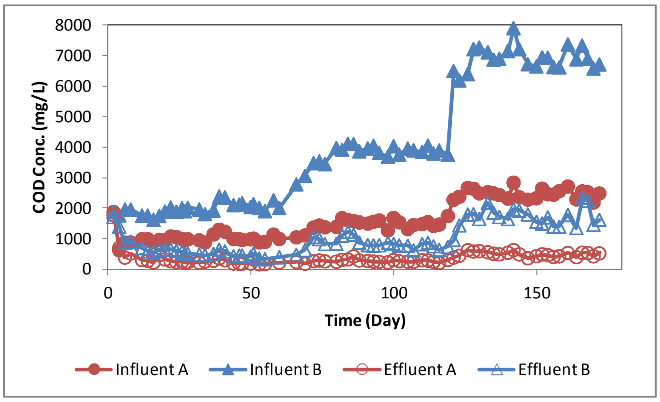

Fig. 4 COD concentration vs. time for three loads to reactor A and three loads for reactor B

As can be seen from Figure 5 the COD removal rate and efficiency versus organic volumetric loading rates (L_{org}) applied to the reactors shows the linearity of the removal rate. COD removal efficiency initially increased with increasing L_{org} and reached the highest removal efficiency of approximately 83% at L_{org} 1.21 kg/m^3·d. However, it started to decrease afterwards until it reached 75% when L_{org} was increased to 4.14 kg/m^3·d.

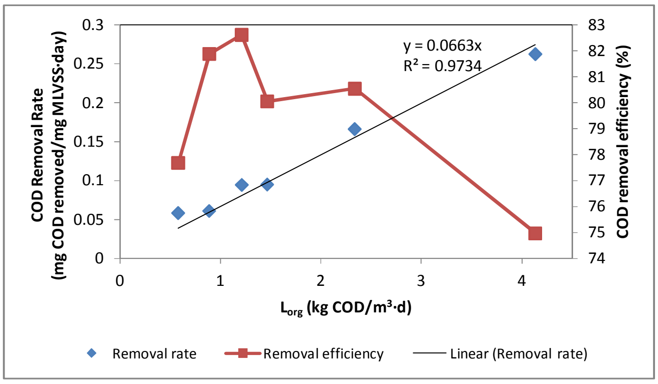

Fig. 5 COD removal rate and efficiency percentage vs. volumetric organic loading rate applied

D. Gas production rate

The gas production rate plotted versus the COD removal rate for the six volumetric organic loading rates applied to the two reactors as Figure 6 shows. The data linearity has correlation coefficient (R^2) of 0.92, indicating that the gas production increased as the loading increased without reaching the maximum limit.

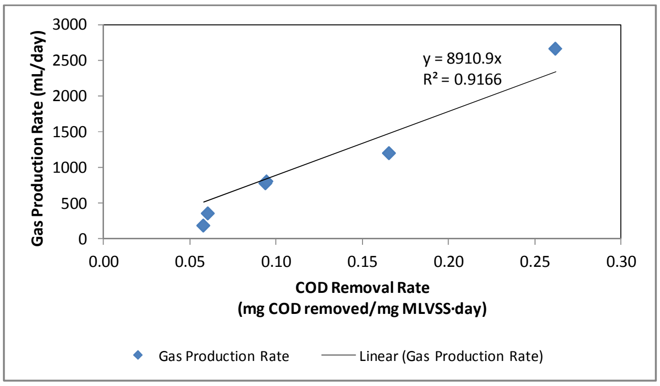

Fig. 6 Gas production rate vs. COD removal rate

IV. CONCLUSION

Petroleum refinery wastewater was treated efficiently with six different loads using two UASB reactors with satisfactory COD removal ranging from 83% as highest to 75% as lowest throughout the experiment.

The reactors coped with the increase in the volumetric organic loads up to two times the load, stressed at higher organic load resulting in increase VFA and decrease in the COD removal efficiency.

Anaerobic treatment of petroleum refinery wastewater at room temperature was proven successfully even with high influent concentration of about 7000 mg COD/L. The increase in the load did not affect much the performance even when the load increased two times.

This treatment could be considered as a pretreatment as effluent concentration remains high indicating the need for further treatment.

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