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Treatment of Petroleum Refinery Wastewater by using UASB Reactors

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Abstract**—**Petroleum refineries discharged large amount of wastewater -during the refining process- that contains hazardous constituents that is hard to degrade. Anaerobic treatment process is well known as an efficient method to degrade high strength wastewaters. Up-flow Anaerobic Sludge Blanker (UASB) is a common process used for various wastewater treatments. Two UASB reactors were set up and operated in parallel to evaluate the treatment efficiency of petroleum refinery wastewater. In this study four organic volumetric loading rates were applied (i.e. 0.58, 0.89, 1.21 and 2.34 kg/m^3·d), two loads to each reactor. Each load was applied for a period of 60 days for the reactor to acclimatize and reach steady state, and then the second load applied. The chemical oxygen demand (COD) removals were satisfactory with the removal efficiencies at the loadings applied were 78, 82, 83 and 81 % respectively.

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

I. Introduction

PETROLEUM refineries now more than ever are motivated by cheaper, cleaner and safer treatment processes and are choosing wastewater treatment methods that are simple, reliable, time effective and cost saving to ensure that they meet the regulatory discharge limit of effluent. Petroleum refineries wastewater contains high level of pollutants and are characterized by the presence of large quantities of oil products and chemicals [1] (e.g. BTEX and phenol). Biological treatment processes are economical and efficient methods and being used to treat the wastewater from oil industry [2].

Petroleum refinery wastewater treatment attracted researchers to provide reliable biological treatment process. Petroleum refinery wastewater and its major components such as phenols and BTEX has been studied to investigate the treatment efficiency by using aerobic, anaerobic and anoxic or a combinations of two or more biological conditions [3, 4, 5, 6].

Many toxic and recalcitrant organic compounds found in petroleum wastewater are degraded under anaerobic conditions, with the compound serving as a growth substrate [7]. The up-flow anaerobic sludge blanket (UASB) reactor is a proven process and its advantages are high organic loadings and relatively low detention time possible for anaerobic treatment, and the elimination of the cost of packing material.

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The UASB process has proven highly effective for the treatment of medium- and high-strength wastewaters within a wide range of hydraulic retention time (HRT) (3–48 h), and steady state conditions are generally able to predict the parameters that have been considered in mass balance relations [8].

UASB reactors have been successfully used to treat two types of wastewater, wastewater containing non-inhibitory substrates such as sucrose, and wastewater containing inhibitory substrates such as phenol which is one of the recalcitrant compounds that present in petroleum refinery wastewater [9].

II. Background

Synthetic wastewater containing phenol was treated under anaerobic thermophilic condition (55°C), the results showed that removal was 99 % at 40 h HRT for a wastewater containing 630 mg/L of phenol, corresponding to 1500 mg/L of chemical oxygen demand (COD) and a loading rate of 0.9 g COD/L·d. [4].

Four UASB reactors were operated successfully with petroleum refinery wastewater at low organic loading rate (0.05-0.1 kg COD/m^3·d). The organic loading rates were then gradually increased to about 2, 1.5, 0.5 and 1.5 kg COD/m^3·d for the reactors, at an influent COD of about 220 mg/L and hydraulic retention times of 2.5, 4.5, 8.5 and 4.5 hours respectively [10].

A UASB reactor operated with petroleum refinery wastewater at a high HRT (48 h) and influent COD (500 mg/L) at a constant organic loading rate (OLR) of 0.4 kg/m^3·d, COD removal was 81 %. The rate of biogas production increased when HRT increased; the biogas production rate was 559 mL/h at HRT of 40 h and an influent COD of 1000 mg/L [8].

In an experimental study investigating the influence of organic loading rate (OLR) on the efficiency of a UASB bioreactor treating a canning factory effluent, the chemical oxygen demand (COD) was increased stepwise from 2300 to 4000 mg/L. The hydraulic retention time was kept constant at 24 h and the OLR increased from 2.28 to 3.95 kg COD/m^3·d. The highest COD removal (92 %) was reported at OLR 2.5 kg COD/m^3·d [11].

The biodegradability of a local petroleum refinery wastewater was studied previously [12]. The wastewater was ultimately biodegradable in a mixture with mineral nutrients and sludge in a single batch run for 28 days. Anaerobic sequencing batch reactor (ASBR) was successfully used to treat petroleum refinery wastewater [13, 14].

In this study, four organic volumetric loading rates of petroleum refinery wastewater were treated in two up-flow anaerobic sludge blanket (UASB) reactors to evaluate the COD removal efficiency.

III. Materials And Methods

A. Feed

The wastewater samples for the study were collected from a local petroleum refinery's balancing tank that received the refinery raw wastewater. The wastewater was stored in a cold room (4°C) before used. Petroleum refinery wastewater characterization results are shown in Table 1.

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

Parameter measurements namely pH, alkalinity, mixed liquor suspended solid (MLSS), mixed liquor volatile suspended solids (MLVSS) biological oxygen demand (BOD), were mostly performed in triplicates, and were conducted in accordance with Standard Methods [15]. Chemical oxygen demand (COD) volatile fatty acids (VFA), ammonia nitrogen, nitrate nitrogen, phosphorus, were determined by colorimetric method using a DR 2000 spectrophotometer (Hach Co.)

C. Experimental procedure

Two laboratory-scale up-flow anaerobic sludge blanket (UASB) bioreactors were operated in parallel at room temperature (25-29°C). Reactor volume, diameter and height were 2.36 L, 94 mm and 430 mm, respectively. It was operated with an internal effluent recycle ratio of 1:1 to well distribute the influent and provide better mixing. The influent was pumped continuously to the system by a peristaltic pump, while the effluent exits the bioreactor through water-sealed tube to prevent any atmospheric air from entering the system. The gas was collected by water displacement method. Figure 1 shows the schematic diagram of the UASB experimental set-up.The seed biomass was obtained from a local palm oil mill effluent treatment plant and petroleum refinery site. The flowrate to the reactors was set at 1.4 L/d while the hydraulic retention time (HRT) was maintained at 40 h.

The steady state performance was studied under four organic volumetric loading rates (L_{org}) which were gradually applied over approximately 120 days, two loads for each reactor.

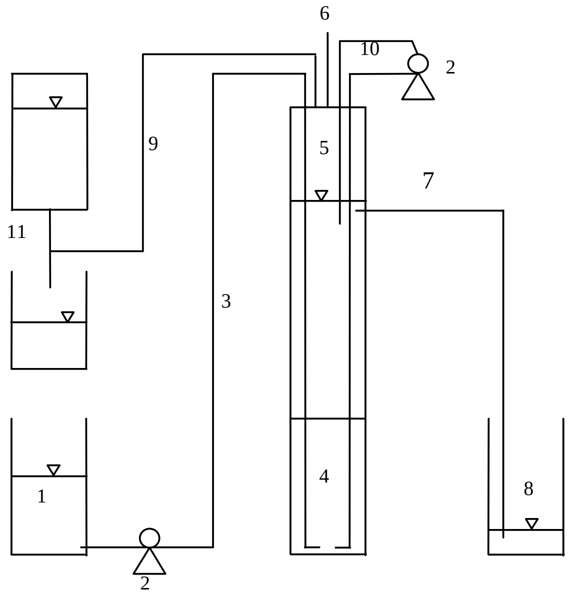

Fig. 1 Schematic diagram of the UASB experimental set-up. 1. Influent tank, 2. Pump, 3. Influent, 4. Sludge zone, 5. Gas zone, 6. Sampling point, 7. Effluent, 8. Effluent tank, 9. Gas line, 10. Recycle, 11. Gas collection.

IV. Results And Discussion

A. Alkalinity and pH

The two reactors were monitored for over approximately 120 days. Alkalinity was elevated for the influent to maintain buffer for the bioreactors from turning sour, while pH for the bioreactors' influent and effluent were left without adjustment as shown in Figure 2.

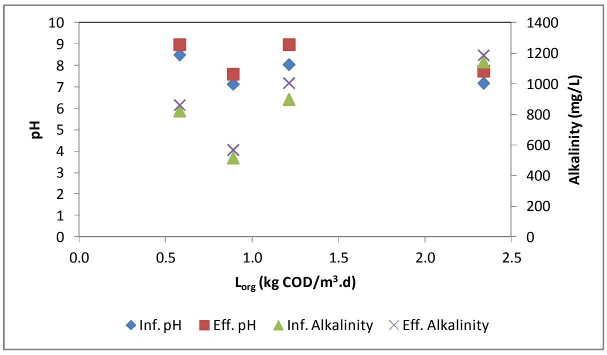

Fig. 2 pH and Alkalinity measurements vs. four volumetric organic loading rates applied.

B. Volatile fatty acid

Volatile fatty acid (VFA) was monitored inside the two reactors to ensure the VFA/alkalinity ratio within the range of 0.05-0.15 by adjusting the reactors alkalinity. The VFA average concentration and the VFA/alkalinity ratio was plotted against the four applied volumetric organic loading rates as shown in Figure 3. The ratio was successfully maintained for three loads out of four. In the first load the reactor VFA concentration were low for that the alkalinity were kept low but not to the critical level and as a result the ratio were lower than the recommended level. As the L_{org} applied to the reactors was increased, the VFA inside the reactors was also increased showing that the process was stable at different VFA concentrations.

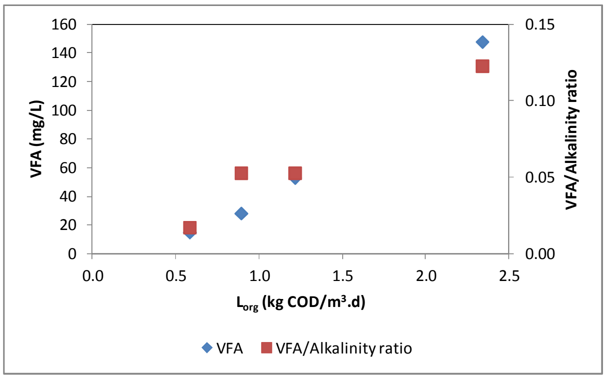

Fig. 3 VFA and VFA/Alkalinity ratio measurements vs. four volumetric organic loading rates applied.

C. Chemical oxygen demand

The average influent and effluent total COD results are shown in Figure 4. From the start up to day 60 represent the first L_{org} 0.58 and 1.21 $kg/m^3 \cdot d$ applied to reactors A and B, respectively. The removal efficiency was 78% and 83% respectively. From day 60 represent L_{org} 0.89 and 2.34 $kg/m^3 \cdot d$ applied to reactors A and B, respectively. The removal efficiency was 82% and 81% respectively.

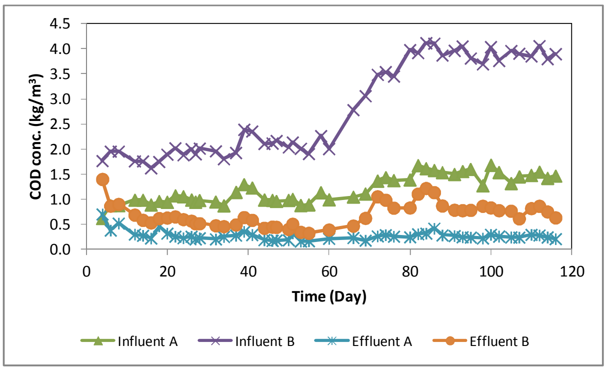

Fig. 4 COD concentration vs. time for two loads to reactor A and two loads for reactor B.

COD removal efficiency versus organic volumetric loading rates (L_{org}) applied to the reactors were plotted and shown in Figure 5. It can be observed that when the L_{org} was increased, the COD removal efficiency increased to a maximum value, after which the COD removal efficiency dropped with further increase in L_{org}.

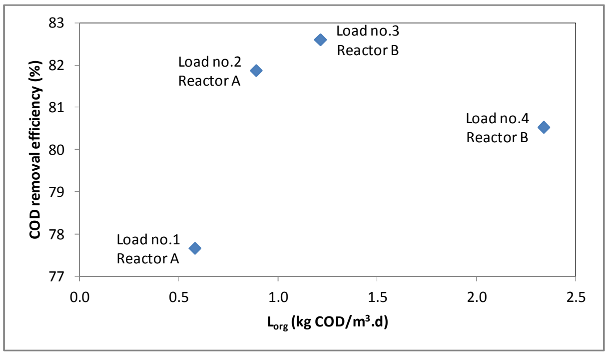

Fig. 5 COD removal efficiency percentage vs. volumetric organic loading rate applied.

D. Specific substrate removal rate constant

The Specific substrate removal rate constant, *k*, is determined from the slope of the COD removed per MLVSS concentration per day versus effluent COD concentration from four steady-state conditions. The corresponding biomass concentration to the four L_{org} applied were 7.8, 12, 10.7, and 11.4 kg vss/m^3, respectively. Specific substrate removal rate versus reactor steady state effluent COD concentration is shown in Figure 6; the correlation coefficient R^2 for the linear line for the four variables was found to be 0.9581.

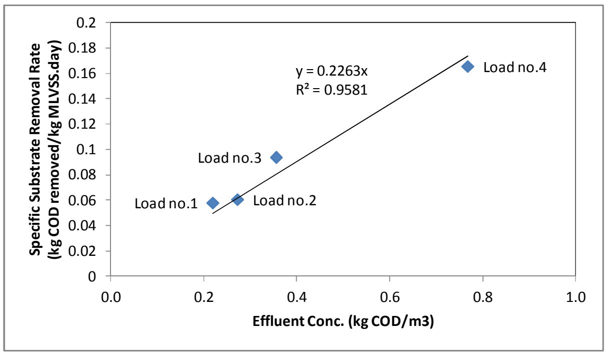

Fig. 6 Specific COD removal rate vs. effluent COD concentration for four loads applied

The substrate removal rate constant *k* ($d^{-1} \cdot m^3/kg$) was obtained from the linear line slope in Figure 6 and found to be 0.23 $d^{-1} \cdot m^3/kg$; from which the first order kinetic constant *K* was in the range of 1.8 to 2.8 day^{-1}. Reference [16] reported wide range for *K* values (0.016-23) using UASB with different operation conditions (temperature, feed, biomass concentration).

E. Actual measured and predicted COD concentration

Assuming first-order kinetics applied and represented by the following equation:

$$dS/dt = K.S_e \quad (1)$$

where:

K = First order kinetic constant
S_e = Effluent substrate concentration

$$q = K.S_e/X_v = (S_o - S_e)/X_v.t_h \quad (2)$$

where:

q = Specific substrate removal rate
X_v = MLVSS
S_o = Influent substrate concentration
t_h = HRT

$$k = K/X_v \quad (3)$$

where:

k = Substrate removal rate constant from the slope

by substitute (3) into (2)

$$q = (S_o - S_e)/X_v.t_h = k.S_e \quad (4)$$

$$k = (S_o - S_e)/X_v.t_h.S_e \quad (5)$$

to verify the result

$$S_e = S_o/k.X_v.t_h+1 \quad (6)$$

Actual measured effluent COD concentration and the predicted concentrations using (6) are plotted in Figure 7. The predicted results are slightly lower than the measured values at the beginning of loads showing slow respond acclimatization to load change.

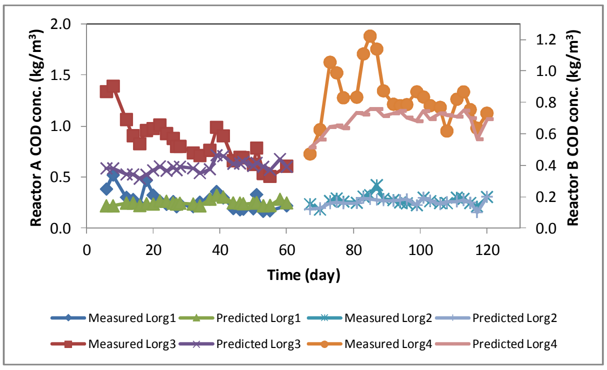

Fig. 7 Measured and predicted COD concentration vs. time for two loads to reactor A (1 and 2) and two loads for reactor B (3 and 4).

V. Conclusion

Both UASB reactors showed satisfactory COD removal (77-83%) throughout the experimental period for the four organic volumetric loads applied. The highest efficiency was found to be 83% when the organic volumetric loading rate of 1.21 $kg/m^3 \cdot d$ was applied.

Acknowledgement

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References

[1] TV Otokunefor, C. Obiukwu, "Impact of refinery effluent on the physicochemical properties of a water body in the Niger delta". Applied ecology and environmental research 3(1): 61-72. ISSN 1589 1623. 2005.

[2] CJ.G. Jou, and G.C Huang, (2003), A pilot study for oil refinery wastewater treatment using a fixed film bioreactor. Adv. Environ. Res., 7: 463-469.

[3] S. T. Sami Sarfaraz, "Anoxic Treatment of Phenolic Wastewater in Sequencing Batch Reactor". Water Research 38, 965–971. 2004.

[4] H.H.P. Fang, D.W. Liang, T. Zhang, Y. Liu, "Anaerobic treatment of phenol in wastewater under thermophilic condition", Water Research, Volume 40, Issue 3, Pages 427-434, ISSN 0043-1354. DOI: 10.1016/j.watres.2005.11.025. February 2006.

[5] E.T. Yoong, A. P. Biodegradation of High Strength Phenolic Wastewater Using SBR. Wat.Sci.Tec. - Iwa , Vol 43 No 3 Pp 299–306. 2001.

[6] G. Ma, A. N. "Creating Anoxic and Microaerobic Conditions in Sequencing Batch Reactors Treating Volatile BTX Compounds". Water Science and Technology - Iwa, Vol 43 No 3 Pp 275–282. 2001.

[7] L. Metcalf, H. Eddy, "Wastewater Engineering, Treatment, Disposal and Reuse", fourth ed., McGraw Hill, New York, 2003, Pp 637.

[8] S.O. Rastegar, S.M. Mousavi, S.A. Shojaosadati, S. Sheibani, "Optimization of petroleum refinery effluent treatment in a UASB reactor using response surface methodology", Journal of Hazardous Materials, Volume 197, Pages 26-32, ISSN 0304-3894, 10.1016/j.jhazmat.2011.09.052. 15 December 2011.

[9] H.H. Chou, J.S. Huang, "Comparative granule characteristics and biokinetics of sucrose-fed and phenol-fed UASB reactors", Chemosphere, Volume 59, Issue 1, Pages 107-116, ISSN 0045-6535, 10.1016/j.chemosphere.2004.09.097. March 2005.

[10] F. Ghavipanjeh, J. Shayagen, "Treatment of Tehran refinery Effluents in UASB Reactors", Iranian Journal of Chemical Engineering, Vol. 1, No.2 summer & autumn 2004, IACHE. 2004.

[11] W Trnovec. and T.J. Britz, "Influence of organic loading rate and hydraulic retention time on the efficiency of a UASB bioreactor treating a canning factory effluent", ISSN 0378-4738, Water SA, Vol. 24 No. 2 Pp1147-1152. April 1998.

[12] H.A. Gasim, S.R.M. Kutty, M.H. Isa, "Biodegradability of Petroleum Refinery Wastewater in Batch Reactor", Proceeding of International Conference on Sustainable Building and Infrastructure (ICSBI 2010), Kuala Lumpur Malaysia. 2010.

[13] S.R.M. Kutty, H.A. Gasim, P.F. Khamaruddin, A. Malakahmad, "Biological Treatability Study for Refinery Wastewater using Bench Scale Sequencing Batch Reactor Systems", WIT Transactions on Ecology and the Environment, Water Resources Management VI, Vol 145, 2011 WIT Press, ISSN 1743-3541(online), pp 691-699. 2011.

[14] H.A. Gasim, S.R.M. Kutty, M.H. Isa, "Petroleum Refinery Effluent Biodegradation in Sequencing Batch Reactor", International Journal of Applied Science and Technology, Vol. 1 No. 6;, Pages 179-183, ISSN 2221-1004. November 2011.

[15] L. S. Clesceri, A. D. Eaton, A. E. Greenberg, M. A. H. Franson, "Standard methods for the examination of water and wastewater". American Public Health Association, American Water Works Association, & Water Environment Federation. Washington, DC: American Public Health Association. 1996.

[16] V. Diamantis, and A. Aivasidis, "Kinetic Analysis and Simulation of UASB Anaerobic Treatment of a Synthetic Fruit Wastewater", Global NEST Journal, Vol 12, No 2, pp 175-180, 2010.