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Treatment of Effluents in Refinery using UASB Reactors

[1]Arun kumar Jena, [2]Anusaya Nanda,[3]Smita Mohanty
[1]*Asst Prof. Deaprtment of Basic Science, Raajdhani Engineering college, Bhubaneswar, Odisha*
[2]*Asst Prof. Deaprtment of Basic Science, Aryan Institute of Engineering and Technology, Bhubaneswar ,Odisha*
[3]*Asst Prof. Deaprtment of Basic Science, NISS Institute of Engineering and Technology, Bhubaneswar ,Odisha*

Abstract
This study presents the treatment of refinery effluents using Upflow Anaerobic Sludge Blanket (UASB) reactors. Four pilot-scale UASB reactors, each with a volume of 45.78 liters and identical dimensions, were operated simultaneously at 37 ºC. The seed sludge was sourced from the waste activated sludge of the refinery's wastewater treatment unit. Organic loading rates were gradually increased from 0.05–0.1 kg COD/m³·d to approximately 2, 1.5, 0.5, and 1.5 kg COD/m³·d for reactors 1 through 4, respectively, with an influent COD concentration of about 220 mg/L. These loading rates corresponded to hydraulic retention times of 2.5, 4.5, and 8.5 hours for reactors 1 to 3, and 4.5 hours for reactor 4. To enhance microbial activity during start-up, methanol was initially added to all reactors except the fourth, allowing comparison of its effect. Methanol addition ceased after 37 days, and the reactors were operated for an additional 30 days with influent COD ranging from 50 to 300 mg/L. The results demonstrated COD removal efficiencies between 30% and 50%, increasing up to 70% when influent COD exceeded 200 mg/L. Methanol was found to have no significant impact on reducing the start-up period. Additionally, Scanning Electron Microscopy (SEM) and image analysis were conducted on the sludge granules to study their structure and size distribution. Biogas analysis revealed methane content exceeding 90%. These findings suggest promising potential for anaerobic treatment of refinery wastewater using UASB reactors.

Keywords: *UASB reactors, petroleum refinery, anaerobic treatment, granulation*

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I. Introduction

It has now been established that aliphatic and aromatic hydrocarbons, which constitute the primary components of crude oil, can be biodegraded under anaerobic conditions [1]. These compounds are present in refinery wastewaters as a result of refining operations. Most research on the anaerobic degradation of petroleum hydrocarbons has focused on bioremediation, particularly addressing contamination in soil and water caused by leaks from storage tanks, underground pipelines, spills at production wells, transportation accidents, and similar incidents. Although anaerobic degradation of petroleum products shows great potential, there is still limited information available on the anaerobic treatment of petroleum refinery wastewaters. In one of the few investigations conducted, Hovious et al. reported that an anaerobic lagoon could achieve a 53% removal of chemical oxygen demand (COD) from petroleum refinery wastewater [2]. The anaerobic treatment of undiluted wastewater from a used oil refinery in a packed bed reactor, however, yielded unsatisfactory results [3]. It was observed that acidogenic bacteria were active, but methanogenic bacteria were not. When the wastewater was diluted to one-third strength (with a TOC of 1270 mg/L), a TOC removal of 52–67% was achieved at an organic loading rate of 1.4 kg COD/m³·d and a hydraulic retention time (HRT) of 3.0 days.

Overall, anaerobic treatment has proven feasible for the pretreatment of both high-strength and dilute complex wastewaters [4,5]. Among anaerobic systems, the Upflow Anaerobic Sludge Blanket (UASB) reactor is one of the most widely used. Since its development by Lettinga et al. in 1980 [6], it has been increasingly applied for treating a broad range of wastewaters, from hot to cold and from high to low strength. The key feature of the UASB reactor is its dense granular sludge with high specific microbial activity, enabling the design of more compact and cost-effective treatment plants. Although originally designed for medium- to high-strength industrial wastewaters, its use has expanded to include low-strength wastewaters (less than 2000 mg COD/L), particularly for domestic wastewater treatment [7–11]. While treatment efficiencies for low-strength wastewaters are generally lower than for high-strength ones, these efficiencies are often sufficient for safe discharge into the environment or for irrigation, considering the relatively low initial COD levels.

To date, there have been no published reports on the use or investigation of UASB reactors for treating refinery effluents. Refinery wastewaters are typically low-strength and complex in composition. Given the growing use of UASB reactors, this system offers a practical solution for treating a wide spectrum of wastewater

strengths. Recognizing these advantages, the Research Institute of Petroleum Industry (RIPI) in Iran launched a project to evaluate the treatment of petroleum refinery wastewater using UASB reactors. This paper presents the findings from an investigation into the feasibility of anaerobic treatment ofrefinery wastewater with UASB reactors.

Wastewater Characterstics

Prior to initiating the UASB pilot experiments, samples were collected from various streams within the treatment unit of the Refinery to assess pollution levels. Table 1 summarizes the characteristics of these wastewater streams, including BOD_5 , COD, ammonium nitrogen, phosphate (as phosphorus), hydrogen sulfide (H_2 S), and oil content. All analyses were conducted in accordance with the Standard Methods for the Examination of Water and Wastewater [13].

Given the significant role of metals in biological treatment processes [14], the concentration of metallic elements in the DAF (Dissolved Air Flotation) effluent was also measured. To obtain a representative sample, a composite was prepared

Table I. Metal composition of DAF effluent of refienery

Metals	**Concentration (mg/l)**
Ca	105
Mg	77.1
Pb	Trace < 0.18
Fe	0.21
Ni	Trace < 0.04
Zn	0.09
Mn	Trace < 0.025

over a 15-hour period by collecting 200 mL of wastewater every hour. The sample was then analyzed using atomic absorption spectroscopy. The results are shown in

As indicated in Table 1, the refinery wastewater exhibited relatively low COD levels. Correspondingly, the measured concentrations of metals were also low, which is favorable for anaerobic treatment. Consequently, no additional metallic compounds were introduced into the influent during the course of the experiments.

Sample	**BOD_5**	**COD**	**+ $N\text{-}NH_4$**	**$P\text{-}PO_4^{-3}$**	**H_2S**	**Oil**
Effluent of the API separator	111	415	15	0.55	2	55.5
Influent of the equalizer	209	735	36	Trace	n.a.	n.a.
Effluent of the equalizer	97	225	23	.95	3	17

Table . Wastewater characteristics of refinery treatment unit streams (units: mg/l)

material in this sludge could be good nuclei for the granulation. The waste activated sludge was collected in 20-liter containers and kept in a warm environment for approximately two weeks. During this period, the sludge volume in each container was reduced to about one-third of its original level. A scum layer formed on the surface, caused by gas bubbles that buoyed the sludge upward. As time passed, the sludge became increasingly concentrated, and continuous gas bubble formation was observed at the surface—an indication of active anaerobic microbial activity. Notably, by this stage, the unexpected formation of sludge granules was observed.

Sludge Preparation

Due to the lack of available anaerobic granular sludge, waste activated sludge from the Refinery's treatment plant was used to prepare the inoculum for the experiments.

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Reactor Properties	**Reactor No.**			
	1	2	3	4
Designed upflow velocity, m/h	0.7	0.55	0.35	0.65
Applied mean upflow velocities, m/h	0.5	0.45	0.25	0.45
Applied mean detention time, h	2.5	5.0	8.5	4.0
Organic loading rates, kg COD/m^3.d	1.9	1.52	0.5	1.45
Sludge loading rate, kg COD/ kg VSS.d	0.6	0.51	0.2	0.2

There was some uncertainty as to whether true granules had formed or if they were merely large, fragile flocs resulting from biomass aggregation under static conditions. To assess the quality and strength of the sludge at this stage, a series of tests were conducted.

Stage 1

In the initial trial, the effluent from the API separator was fed into reactors 1 through 4. The upflow velocities were set at 1, 0.75, 0.5, and 0.25 m/h for reactors 1 to 4, respectively, corresponding to hydraulic retention times (HRTs) of 1.8, 2.5, 3.6, and 6.9 hours. The organic loading rates were approximately 6, 4.2, 2.9, and 1.6 kg COD/m³·d for reactors 1 to 4, respectively, based on an influent COD concentration of around 450 mg/L. Initially, the wastewater upflow velocities were kept low at 0.1 m/h and gradually increased to the target values for each reactor. However, since this wastewater contained relatively high oil concentrations (50–100 mg/L) and the sludge had not yet adapted to such oily conditions, the reactors' performance began to decline despite the low influent flow rates, eventually dropping close to zero. This phase lasted for 23 days.

Stage 2

In the subsequent phase, the influent to the reactors was switched to the effluent from the DAF system, which had significantly lower oil content. To enhance sludge activity and accelerate start-up, methanol was added to the influent—based on reports that methanol can shorten the start-up period by stimulating microbial activity [16]. Methanol was dosed so that the total COD did not exceed 400 mg/L, roughly the maximum COD level in the equalizer effluent. The fourth reactor was operated without methanol to serve as a control for assessing methanol's impact on start-up.

The hydraulic retention times were set at 2.5, 4.5, and 8.5 hours for reactors 1 through 3, and 4.5 hours for reactor 4. Organic loading rates were gradually increased from 0.05–0.1 kg COD/m³·d to approximately 1.92, 1.62, and 0.48 kg COD/m³·d for reactors 1 to 3, respectively, and 1.44 kg COD/m³·d for reactor 4, all at an influent COD of about 220 mg/L. The hydraulic conditions during this stage are detailed in Table 3.

Stage 3

After 37 days, methanol addition to the influent of reactors 1, 2, and 3 was discontinued, and the reactors were fed with the equalizer effluent instead of the DAF effluent. The reactors were then operated under these conditions for an additional 30 days before the experiments concluded. The MLSS, MLVSS, and sludge height in each reactor at the end of the study are summarized in Table 4.

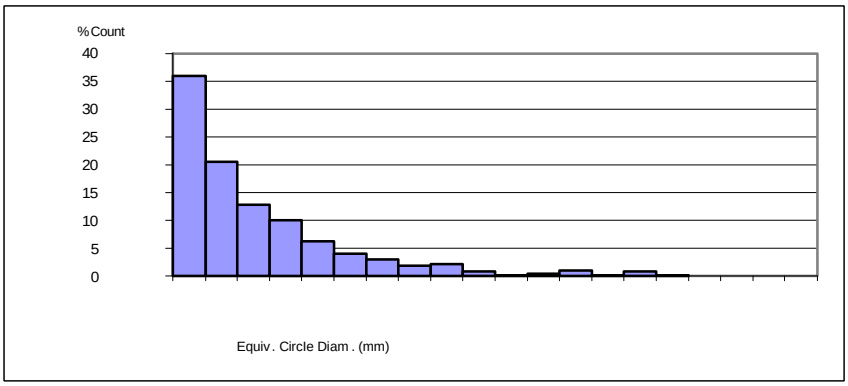
Measurements

To evaluate the performance of the reactors, the COD, N and P of the influents and effluents were measured daily. All these experiments were done according to Standard Methods for the Examination of Water and Wastewater [13].

To evaluate the anaerobic sludge in terms of the settling velocity and the structure and size of granules, some experiments were performed. The settling velocity of sludge was examined by measuring the falling time of particles in a long glass tube visually. Scanning Electron Microscope (SEM) (Cam- bridge Stereoscan, Model 360) equipped with an Energy Dispersive X-ray (EDX) device was used for observation of structure of granules. For this purpose, the granules were washed with 0.1 M phosphate buffer (pH=7.2) and then fixed in 2% glutaraldehyde in buffer over night. The granules then were dehydrated with graded ethanol series (10, 25, 50, 75, 90 and 100 %) and then freeze-dried [17]. Dried granules were mounted on studs with colloidal carbon and finally sputter-coated with gold and examined under SEM. From EDX analysis the structural elements of

granules were determined. However, for more accurate determination of elements involved in the granules structure, Wavelength Dispersive X- ray (WDX) Spectroscopy was also per- formed.

The distribution size of granules was evaluated using an Image Analyser (LEICA, Quantiment, Model 570). The sludge samples after dilution with water were transferred into perti dishes of 15cm diameters. The image analysis could determine the total number, equivalent diameter and number and also the surface area of granules. The biogas samples, taken in an air-lock syringe, were analysed on a Shimadzu GC model 4CPT with a TDC equipped with 1/8 inch (d) stainless steel column packed with molecular sieve. The oven temperature was 50 ºC while the detector was at 120 ºC.



II. Results and Discussion

Figure 2 shows the COD removal efficiency of each reactor versus time in days during the second and third stages of the start-up. As already mentioned, the first stage was ineffective. But clearly, when methanol is added in the second stage of start-up, the COD removal efficiencies are increased considerably. This is because of rising the influent COD and the fact that methanol is easily biodegradable. However, due to the presence of variations in the addition of methanol added to the reactors, the resultant efficiencies also fluctuate and are sometimes more than 90 percent at a high dose of methanol.

After stopping the addition of methanol to the reactors (the third stage, shown by a vertical dashed line in Figure 2), the efficiencies slightly decrease. However, due to increasing influent COD as a result of changing the influent wastewater from the DAF effluent to the equalizer effluent, the efficiencies increase again and reach 30-50%, similar to that of previous stage. Further- more, whenever the influent COD is increased, the efficiencies also increase. The results show that when the influent COD is decreased below 60 mg/l, the efficiencies severely decrease and even tend to zero.

The average COD removal efficiencies of both reactors 1 and 2 are about 38% and that of reactor 3 is about 30%. The reason for the lower efficiency of reactor 3 in comparison with reactors 1 and 2 can be the low organic loading rate in this reactor, as indicated in Table 3. The results also show that the effluent COD of the reactors are always less than 100 mg/l and the same as the effluent COD of the DAF system in the wastewater treatment unit of the Refinery. The results of reactor 4 in comparison with the others show that the addition of methanol has no major effect on the COD removal efficiency.

The composition of the produced biogas, as analysed by gas chromatography, shows an average CH_4/CO_2 ratio of 23.2 and the amount of hydrogen gas is trace. In other words, more than 90 percent of the produced gas is methane and the rest is carbon dioxide with traces of H_2S and H_2O. This reinforces the results of other researchers that although at lower COD values the biogas production decreases, the methane content is always above 80% [18]. Also, because of the higher amount of CH_4 compared to CO_2, it can be concluded that the conditions for the growth of H_2-utilising and CO_2-utilising bacteria are provided. In other words, the biochemical reaction pathways are such that the produced CO_2 is consumed by bacteria, as a result of low incoming COD.Figure 3 shows the granule and the sliced section of the granule under SEM. Clearly, colonies of bacteria can be observed from the figure. No bacteria identification was made at this stage, as further research was needed. The EDX analysis of the surface of the granule and the bacteria revealed the presence of Ca, Mg, Si, and P on the surface of the granule and Ca, Mg, K, Si and S on the surface of the bacteria. However, in order to determine the elements of the granules more accurately, a WDX analyser was used and Fe, Ca, K, S, P, Si, O, N and C were detected. From the image analysis of the sludge granules, the mean and median diameter of the granules based on the equivalent circle diameter were found to be 0.4 and 0.25 mm, respectively. The results show that about 70% of the granules have diameters of less that 0.6 mm and only 10% are larger than 1.2 mm in diameter. Figure 4 shows the size distribution of the granules.

III. Conclusions

This study explored the treatment of effluent from the Refinery using four UASB (Upflow Anaerobic Sludge Blanket) reactors, marking a novel application of UASB technology for refinery wastewater. The findings demonstrate promising potential for the anaerobic treatment of such wastewater using UASB systems. Although the treatment efficiencies under the experimental conditions were not particularly high, the final effluent COD levels were comparable to those achieved by the DAF (Dissolved Air Flotation) system, using the same influent stream. This suggests that UASB reactors could serve effectively as a pre-treatment step.

Since there were no significant differences in performance among the reactors, it can be inferred that extended retention time does not enhance treatment efficiency. Therefore, to minimize reactor volume, it is preferable to design for the highest upflow velocity that the sludge can withstand. Additionally, the use of methanol during reactor start-up did not notably accelerate the process, but reactors started with methanol exhibited better performance at lower influent COD levels (<80 mg/L), compared to reactor 4, which was started without methanol.

Biogas analysis revealed a high methane content—over 90%—suggesting that in conditions of limited substrate availability, microorganisms may also consume CO_2 for growth. SEM observations identified primarily oval-shaped and some rod-shaped microorganisms, with relatively low accumulation.

References

[1]. Holliger C. and Zehnder A. JB (1996) Anaerobic biodegradation of hydrocarbons. Current Opinion in Biotechnology, 7, 326 - 330.

[2]. Hovious J. C., Fisher J. A. and Conway R. A (1972) Anaerobic treatment of synthetic organic wastes. U.S. EPA Report, project No. 12020 DIS.

[3]. Parkers W. and Farquhar G. J. (1989) Treatment of a petrochemical wastewater in an anaerobic packed bed reactor. Wat. Poll. Res. J. Canada, 24(2), 195-205.

[4]. El-Gohary F. A. and Nasr F. A. (1999) Cost - effective pre-treatment of wastewater. Wat. Sci. Tech. 39(5), 97-103.

[5]. Lettinga G. and Vinken J. N. (1980) Feasibility of the Upflow Anaerobic Sludge Blanket (UASB) process for the treatment of low- strength wastes. Proc. 35th Industrial Waste Conference, Purdue University, 625 - 634.

[6]. Lettinga G., Van Velsen A. F., Hobma S. W., Zeeuw de W. and Klapwijk A. (1980) Use of the upflow sludge blanket (USB) reactor concept for biological wastewater

[7]. treatment, especially for anaerobic treatment. Biotechnol. Bioeng. 22, 699-734.

[8]. Sperling M. von, Freire V. H. and Chernicharo C. A. de L. (2001) Performance evaluation of a UASB - activated sludge system treating municipal wastewater, Wat. Sci. Tech. 43(11), 323−328.

[9]. Kalter T. J. J., Mass J. A. W. and Zwaag R. R. (1999) Transfer and acceptance of UASB technology for domestic wastewater: two case studies. Wat. Sci. Tech. 39(5), 219-225.

[10]. Driessen W. and Yspeert P. (1999) Anaerobic treatment of low, medium and high strength of effluents in the agro - industry, Wat. Sci. Tech. 40(8), 221-228.

[11]. Kato M. T., Field J. M. and Lettinga G. (1996) The anaerobic treatment of low strength wastewaters in UASB and EGSB reactors, Wat. Sci. Tech. 36(6-7), 375-382.

[12]. Grin P., Roersma R. and Lettinga G. (1985) Anaerobic treatment of raw domestic sewage in UASB reactor at temperatures from 9-20 ºC. Proc. of the seminar/workshop: anaero - bic treatment of sewage, 109-124.

[13]. Ghavipanjeh, F. and Shayegan, J. (2000) Treatment of refinery effluents using UASB reactors. Conference on Innovations in conventional and advanced water treatment processes, Amsterdam, The Netherlands, Sep. 26-29, 2000.

[14]. APHA, AWWA & WPCF (1992) Standard Methods for the Examination of Water and Wastewater, 18th ed. American Public Health Association, Washington, D.C.

[15]. Qasim S. R. (1999) Wastewater Treatment Plants: Planning, Design and Operation. 2nd ed. Technomic Pubishing Company, Inc., U.S.A.

[16]. Ghavipanjeh, F. and Shayegan, J. (2004) Feasibility of refinery effluents treatment in UASB reactors. 10th Anaerobic Digestion Conference, 29 Aug. −2 Sep. 2004, Montreal, Canada.

[17]. Cayless S. M., Margues D. M. L. and Lester J. N. A. (1990) Study of the effect of methanol in the start-up of UASB reactors. Biological Wastes, 31, 123-135.

[18]. Fang H. H. P. and Chui H. K. (1994) Comparison of start-up performance of four anaerobic reactors for the treatment of high - strength wastewater. Resources, Conserva - tion and