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Treatment of Tehran Refinery Effluents in UASB Reactors

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Abstract
This paper presents the results of an investigation into the treatment of Tehran Refinery effluents in UASB reactors. Four pilot-scale UASB reactors were built with similar dimensions, each with a volume of 45.78 l, and operated in parallel at 37 ºC. The sludge seed was prepared from the waste activated sludge of the wastewater treatment unit of the refinery. The organic loading rates were gradually increased from 0.05-0.1 kg COD/m^3.d to about 2, 1.5, 0.5 and 1.5 kg COD/m^3.d for reactors 1 to 4, respectively, at an influent COD of about 220 mg/l. This is in accordance with hydraulic retention times of 2.5, 4.5 and 8.5 hours for reactors 1 to 3 and 4.5 hours for reactor 4. Methanol was initially added to the reactors in order to increase the microbial activity of the sludge, except for the last one, in order to compare the effect of methanol on start-up. The addition of methanol was stopped after 37 days and the reactors were operated for another 30 days. At this stage, the influent COD was varied between 50-300 mg/l. The results show that the COD removal efficiencies of the reactors are around 30-50%. However, when the influent COD increases above 200 mg/l, the COD removal efficiencies increase up to 70%. It is found that methanol has no significant effect in shortening the start-up period in this case. Scanning Electron Microscopy (SEM) examination and image analysis of the granules of sludge were also performed in order to investigate the structure of granules and the size distribution. Analysis of the biogas shows more than 90% methane content. The results obtained in this research are promising for the anaerobic treatment of refinery wastewaters in UASB reactors.

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

Introduction
It is now proven that aliphatic and aromatic hydrocarbons, which are the main constituents of crude oil, are anaerobically biodegradable [1]. These products are found in the refinery wastewaters as a consequence of refining processes. The most attention on the anaerobic degradation of the petroleum constituents so far is related to bioremediation purposes where the soil and water are polluted by the leakage of tanks, underground pipes, spills at production wells, accidents during transport, and so on. Despite the promising results on the anaerobic degradation of the petroleum products, however, documentation of the anaerobic treatment of petroleum refinery wastewaters is very limited. In one of the few studies, Hovious, *et al*. found that an anaerobic lagoon was able to remove 53% of the COD from a petroleum refinery wastewater [2]. However, the treatment of

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undiluted wastewater of a used oil refinery in an anaerobic packed bed reactor was not satisfactory [3]. It was reported that acidogenesis bacteria were active while methanogenesis ones were not. But, with dilution of the wastewater to one third (TOC of 1270 mg/l) 52-67% TOC removal was achieved at an organic loading rate of 1.4 kgCOD/m^3.d and an HRT of 3.0 days.

In general, anaerobic treatments have been demonstrated to be feasible for pre-treatment of high-strength and dilute complex wastewaters [4,5]. The UASB reactor is one of the most popular anaerobic wastewater treatment systems. Since its innovation in 1980 by Lettinga, et al. [6], it has become increasingly useful for the treatment of various wastewaters from hot to cold and high-, to low-strength wastewaters. The core secret of the reactor is the presence of a dense granular sludge with a high specific activity inside the reactor. This allows for installation of more compact and economical wastewater treatment plants. Although the reactor was initially designed and applied for the treatment of medium- and high-strength industrial wastewaters, its application gradually expanded for the treatment of low-strength (less than 2000 mg COD/l) wastewaters, especially for treatment of domestic wastewaters [7-11]. Even though the treatment efficiency reported so far is not as high as for high-strength wastewaters, considering the low initial COD, it seems that such COD removal efficiencies may be enough for draining wastewater in the environment or for irrigation purposes.

So far, no results have been reported on the application or investigation of UASB systems for treatment of refinery effluents. Refinery wastewaters are usually in the group of low-strength, complex wastewaters. The increased application of UASB reactors shows that this systems offer a very practical treatment technology for a wide range from very high to very low strengths. Considering the advantages of the UASB reactor, Research Institute of Petroleum Industry (RIPI) of Iran initiated a project on the treatment of a petroleum refinery wastewater using this system. This paper presents the results of investigation into the feasibility of anaerobic treatment of Tehran refinery wastewater using UASB reactors.

Materials and Methods

The Treatment Unit of Tehran Refinery

Tehran Refinery was built in 1973 in two parallel platforms called North and South Refineries. The oily wastewater streams of both refineries enter a common wastewater treatment plant after oil separation in API separators. The treatment plant consists of an equalizer unit, a Dissolved Air Flotation (DAF) system and an aeration pond, to which a part of the settled sludge from the clarifier also is returned [12].

Characteristics of the Wastewater

Before starting the UASB pilot experiments, some samples were taken from the different streams of the treatment unit of Tehran Refinery in order to determine the pollution levels. Table 1 presents the wastewater characteristics of some of the streams in terms of BOD_5, COD, ammonium nitrogen, phosphorus as phosphate, H_2S and oil content. All the experiments were carried out according to the Standard Methods for the Examination of Water and Wastewater [13]. Also, due to the importance of metals in biological treatment [14], the metallic elements of the DAF effluent wastewater were measured. For this purpose, a composite sample was taken in a 15-hour period by collecting 200 cc samples hourly, that was analysed using an atomic absorption instrument. Table 2 presents the results of such measurements. Considering the low COD concentration of the refinery wastewater as Table 1 indicates, the low amounts of metals would be suitable for its anaerobic treatment. Therefore, no metallic compounds were added to the influent wastewater during the experiments.

Table 1. Wastewater characteristics of Tehran refinery treatment unit streams (units: mg/l)

Sample	BOD_5	COD	$N\text{-}NH_4^+$	$P\text{-}PO_4^{-3}$	H_2S	Oil
Effluent of the API separator	110	416	16	0.5	3	56.5
Influent of the equalizer	210	736	37	Trace	n.a.	n.a.
Effluent of the equalizer	96	224	23	0.9	2	18

Table 2. Metal composition of DAF effluent of Tehran refinery

Metals	Concentration (mg/l)
Ca	106
Mg	77
Pb	Trace < 0.19
Fe	0.2
Ni	Trace < 0.04
Zn	0.08
Mn	Trace < 0.03
Co	Trace < 0.08
Cr	Trace < 0.04
Cu	Trace < 0.03

Experimental System

In order to shorten the duration of the experiments, four UASB reactors were used. Each reactor was made of Plexiglas with a diameter of 18 cm, a height of 180 cm and a total volume of 45.78 l. On top of each reactor was a gas-liquid-solid separator with an internal diameter of 15 cm and a height of 25 cm. Figure 1 shows the schematic diagram of the reactor. The wastewater is first heated to 37 °C and then entered to the reactors via four dosing pumps. Further information on the experimental setup consisting of four UASB reactors in parallel could be found in [15].

Sludge Preparation

Due to unavailability of anaerobic granular sludge, the waste activated sludge of the treatment plant of Tehran Refinery was used to prepare the required sludge for the experiments. The likely presence of inert material in this sludge could be good nuclei for the granulation. The waste activated sludge was collected in 20-litre containers and left in a warm condition for about two weeks. After this time, the sludge volume in all containers was almost reduced to a third. A layer of scum was formed on the surface of all containers. The formation of the scum was due to lightening of the sludge by gas bubbles. The sludge gradually became more and more condensed and the gas bubbles were observed evolving from the surface. This was the sign of an active anaerobic sludge. By this time, sludge granules had surprisingly been observed.

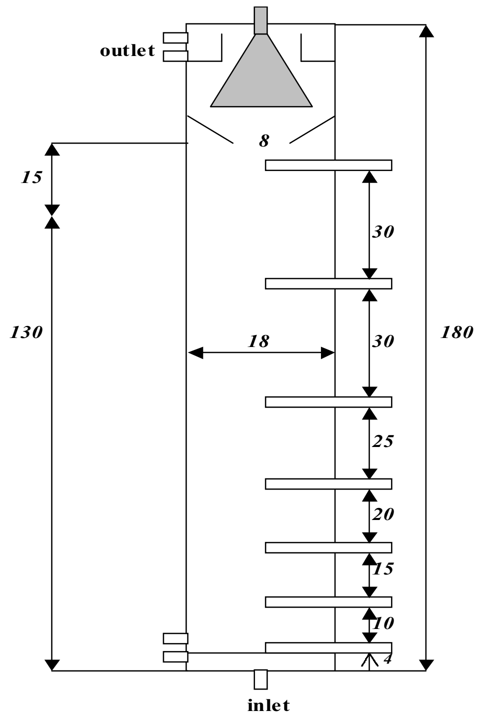

Figure 1. Schematic diagram of the UASB reactors used for the experiments (units: cm)

There was a doubt whether real granules are formed or they are simply large fragile flocs built by the biomass adherence under the static conditions. Some tests were performed in order to investigate the quality of the sludge, mostly the strength of the granules, at this stage. For this purpose, the tap water pressure was exerted on the sludge in a long glass column to see whether the sludge would break easily or not. But, even under high flow rate of water for about 6 hours duration, no breakage of granules was obvious and only the wash out of light granule had occurred. The MLSS and MLVSS of the sludge was 18.2 g/l and 14.1 g/l, respectively, and the ash content about 22.3%. The reactors were filled with this sludge to a height of 120 cm, equal to almost two thirds of the total reactor volume, and the reactors were then started up.

Start-up of UASB Reactors

Stage 1

In the first attempt, the effluent of the API separator was introduced to the reactors 1 to 4. The upflow velocities in reactors 1 to 4 were considered to be 1, 0.75, 0.5 and 0.25 m/h, respectively. This is equivalent to hydraulic retention times of 1.8, 2.5, 3.6 and 6.9 hours and organic loading rates of about 6, 4.2, 2.9 and 1.6 kg COD/m^3.d for reactors 1 to 4, respectively, for an influent COD of about 450 mg/l. The wastewater upflow velocities were set at a low value of 0.1 m/h to be gradually increased up to the determined velocities for each reactor. But, because this stream contained about 50-100 mg/l of oil and the sludge was not adapted to the high oily wastewater, the efficiency of the reactors started to decrease in spite of low flow rate of influents and finally approached zero. This stage lasted 23 days.

Stage 2

In the next attempt, the influent of the reactors were changed to the effluent of the DAF system with much less oil content. In order to increase the activity of the sludge, methanol was added to the influent of the reactors because it was reported that methanol reduces the start-up period by increasing the activity of the sludge [16]. Methanol was added to the influent such that the overall COD did not exceed 400 mg/l, which was almost the maximum value in equalizer effluent. But, the fourth reactor was started up without adding methanol in order to study the effect of methanol in the start-up of UASB reactors. The hydraulic retention times of wastewaters were chosen to be 2.5, 4.5 and 8.5 hours for reactors 1 to 3, and 4.5 hours for reactor 4. The organic loading rates were gradually increased from 0.05-0.1 kg COD/m^3.d to about 1.92, 1.62 and 0.48 kg COD/m^3.d for reactors 1 to 3, respectively, and 1.44 kg COD/m^3.d for the last one, at a COD level of about 220 mg/l. The hydraulic conditions of the reactors at this stage are indicated in Table 3.

Table 3. Hydraulic conditions of reactors in the final stage of start-up.

Reactor properties	Reactor No.			
	1	2	3	4
Designed upflow velocity, m/h	0.75	0.5	0.25	0.5
Applied mean upflow velocities, m/h	0.6	0.44	0.21	0.4
Applied mean detention time, h	2.6	4.0	8.4	4.5
Organic loading rates, kg COD/m^3.d	1.92	1.62	0.48	1.44
Sludge loading rate, kg COD/ kg VSS.d	0.58	0.41	0.19	0.21

Table 4. Sludge Characteristics in the UASB reactors.

Reactor properties	Reactor No.			
	1	2	3	4
Initial sludge height, cm	110	120	128	120
Final sludge height, cm	45	47	35	90
MLSS, g/l	18.3	16.3	22.5	17.6
MLVSS, g/l	14.2	12.4	17.1	13.3
Ash, %	22.5	23.9	23.7	24.4

Stage 3

Finally, the flow of methanol to the influent of the reactors (1, 2 and 3) was stopped after 37 days and the effluent of the equalizer was fed to the system, instead of the DAF effluent. Then, the reactors were operated for another 30 days before the experiments were ended. The MLSS, MLVSS and height of sludge inside each reactor at the end of experiments are reported 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) (Cambridge 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 performed.

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.

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. Furthermore, 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 40% 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 Tehran 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.

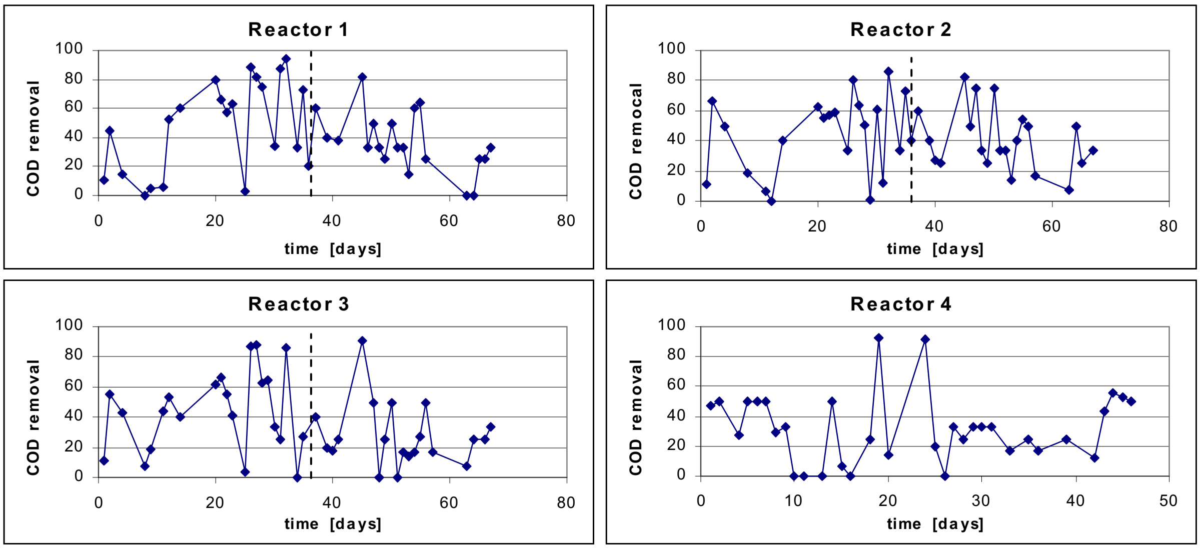

Figure 2. COD Removal efficiency of each reactor (%) *VS.* time in days. The dashed vertical line indicates the 37^{th} day, on which the addition of methanol was stopped.

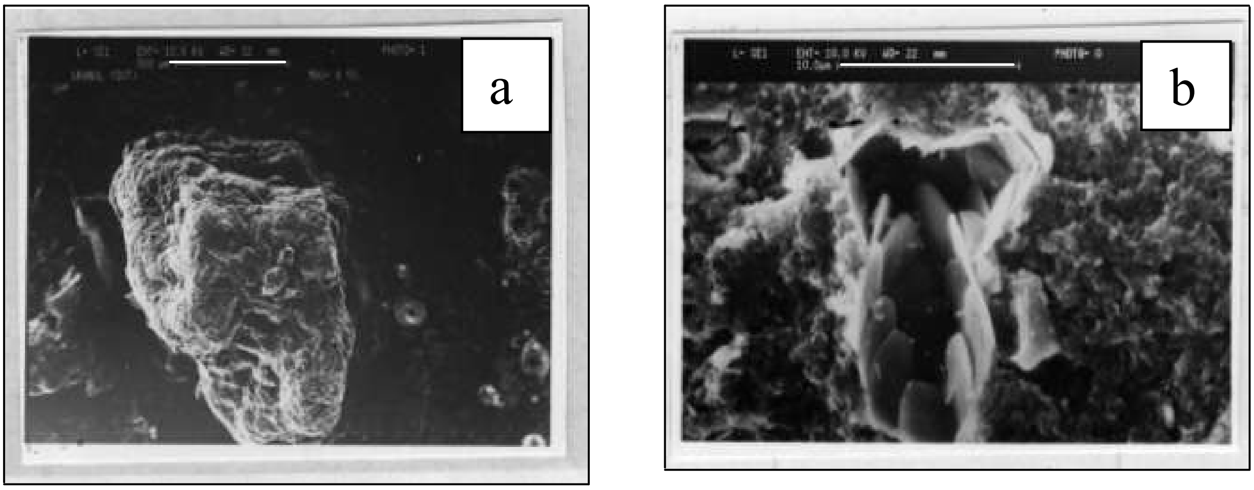

Figure 3. (a) Granule of the sludge under SEM, bar =500 μm; (b) section of the granule under SEM, bar =10 μm

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.

Conclusions

In this study, the treatment of Tehran Refinery effluent using four UASB reactors was investigated. This is novel in terms of application of UASB systems for refinery wastewaters. The results are promising for the anaerobic degradability of such waste-waters in UASB reactors. Although the treatment efficiencies at the applied experi-mental conditions are not so high, the resultant effluent COD is the same as the effluent of the DAF system (their influents are the same stream). This suggests the application of UASB reactor as a pre-treatment system here. Since the efficiencies of the reactors do not differ considerably, it can be concluded that a long retention time has no improving effect on the efficiencies of the reactors. Therefore, in order to decrease the required volume of the reactor, it is advantageous to design the reactor for the maximum upflow velocity that the sludge can tolerate. It was also found that methanol has no major effect on the rapid start-up of the UASB reactors, but the reactors that were started up with methanol had better efficiencies in lower influent COD (<80 mg/l) in comparison with reactor 4 -the one without methanol. The analysis of the biogas showed that the amount of methane in the produced biogas was considerably high-more than 90 percent. It may be concluded that due to lack of substrate availability, CO_2 is also consumed by microorganisms for growth. The presence of oval-shaped and some rod-shaped microorganisms with less accumula-tion were derived from SEM observations.

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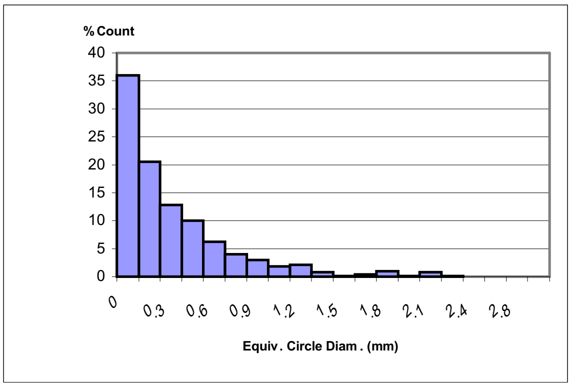

Figure 4. Size distribution of granules of the sludge sample taken from reactor 1.

Notation

API = American Petroleum Institute
DAF = Dissolved Air Flotation
EDX = Energy Dispersive X-Ray
HRT = Hydraulic Retention Time
RIPI = Research Institute of Petroleum Industry
SEM = Scanning Electron Microscopy
TSS = Total Suspended Solids
UASB = Upflow Anaerobic Sludge Blanket
VSS = Volatile Suspended Solids
WDX = Wavelength Dispersive X-Ray

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