

Biological treatment of low-biodegradable composite chemical wastewater using upflow anaerobic sludge blanket (UASB) reactor: Process monitoring

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Upflow Anaerobic Sludge Blanket (UASB) reactor was investigated for the treatment of low biodegradable composite chemical wastewater, which was complex in nature and has low biodegradability (BOD/COD ratio ~0.32), with high concentrations of sulphate and total dissolved inorganic solids (TDIS). After inoculating with slaughterhouse wastewater treating anaerobic sludge, the reactor showed a rapid startup phase. The reactor was operated continuously for 60 days with an actual organic loading rate (OLR_{actual}) of 4.25 kg COD/ m³-d accounting for 37 h of detention time in continuous mode without recirculation at a mesophilic temperature of 29±2°C. At steady state conditions, the reactor resulted in 62% of COD removal efficiency accounting for substrate degradation rate (SDR_{actual}) of 2.6 kg COD/ m³-d. The experimental data demonstrated the applicability of UASB system for treating composite chemical wastewater with low biodegradable nature. Introduction of appropriate inoculum to the reactor during startup showed the effective biological treatment of composite wastewater, which is evident from the substrate and sulfate removal data and non-accumulation of VFA concentration in the reactor along with the generation of biogas.

Keywords: Upflow Anaerobic Sludge Blanket (UASB), Chemical wastewater, Low biodegradability, Composite, Organic loading rate (OLR), Substrate degradation rate

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Introduction

Wastewater from chemical based industries is generally complex due to presence of organic substances, inorganic salts and organic solvents¹, which result in high COD, low BOD, high salt concentration along with the presence of toxic and inhibitory substances. Presence of recalcitrant compounds and high concentrations of total dissolved inorganic solids (TDIS>2.5%) associated with low BOD/COD ratio (<0.35) of wastewater is generally considered as complex or non-biodegradable and has inhibitory effect on the biological process.

Anaerobic biological processes have received high attention in wastewater treatment, owing to high capacity to treat slowly degradable substrates at high concentrations, very low sludge production, low energy requirements and possibility for energy recovery through methane combustion²⁻⁴. Anaerobic processes, which can tolerate a wide variety of toxicants⁵, are effective in treating wastewaters

containing synthetic organics (organochlorine, phenolic compounds), which are refractory under aerobic conditions^{6,7} along with the renewable energy generation^{1,4,8,9}. Treatment of high strength wastewater is feasible with anaerobic treatment and provides a cost effective alternative to aerobic process with savings in energy, nutrient addition, reactor volume, rapid response to substrate additions after long periods without feeding and higher volumetric loadings^{1,2,4,9}. From economic perspective, anaerobic treatment can be considered when BOD exceeds 1000 mg/l¹⁰. Also, anaerobic sludge can be maintained for long time, thereby making the process attractive for seasonal industrial operations such as food processing industry.

One of the most notable developments in anaerobic treatment process technology was the upflow anaerobic sludge blanket reactor (UASB) in late 1970's by Lettinga group in Netherlands. UASB is widely accepted for treatment of a wide range of wastewater ranging from domestic sewage to industrial wastewater¹¹. It allows the use of high volumetric COD loadings compared to other anaerobic processes which results in high loading

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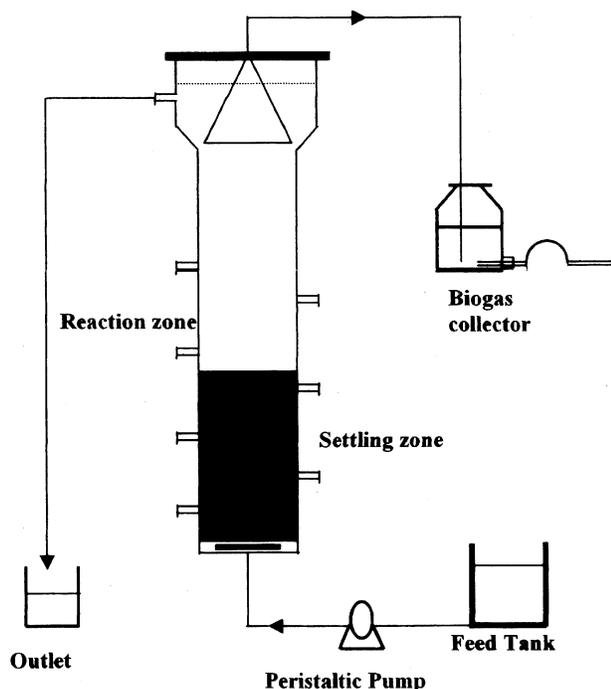


Fig. 1—Schematic representation of the UASB reactor

rates with relatively low detention times and elimination the cost of packing material. They are quite successful in separation between hydraulic retention time (HRT) and sludge retention time (SRT) thereby giving way to slow growing microorganisms to settle even at high volumetric loading rates¹². UASB reactors have also been applied to treat toxic compounds such as nitro aromatics and polychlorophenol^{13,14}. This communication elucidates the application feasibility of UASB reactor configuration for treating low biodegradable composite chemical wastewater.

Materials and Methods

Wastewater characteristics

Wastewater was a composite chemical effluent collected from various chemical based industries such as pharmaceutical, bulk drug, dye and dye intermediates, pesticides, etc. The characteristics of wastewater were as follows: suspended solids (SS), 1000; TDIS, 14500; total alkalinity, 2000; chlorides, 3240; sulphates, 1360; COD, 6600; BOD, 2140 mg/l and pH, 2.0.

Reactor Configuration and Operation

The laboratory scale UASB reactor was fabricated using perplex acrylic material (total vol 14.2 l, working vol 12.4 l) with a provision of inlet and outlet arrangement. The reactor has following designed

parameters: internal diam, 9.0 cm; total height, 1.34 m; sludge height, 0.3 m; VSS of sludge, 46400 mg/l; total reactor vol, 12.36 l; working vol, 12.0; gas holder vol, 0.36; sludge vol, 4.6 l; liquid vol in reactor, 7.75 l; influent feed, 5 l/d; upflow velocity, 0.2 m/h; detention time (actual), 37 h; detention time (overall), 58 h; OLR_{actual} , 4.25 kg COD/ m³-d and OLR_{total} 2.67 kg COD/ m³-d. UASB reactor consisted of reaction zone and settling zone (Fig. 1). For uniform distribution of wastewater throughout the reactor, feed was injected through nozzle distribution system arranged at the bottom of reactor downward. The flow from nozzle discharges downwards through the bottom of the reactor to facilitate uniform upflow of liquid without disturbing the bed comprising of a uniform pore size (1 mm diam) by means of a peristaltic pump (Watson Marlow 101). Outlet from the reactor was collected from the gas-liquid-solid separator (GLSS). The biogas produced was measured by water displacement method.

Reactor was inoculated with anaerobic sludge acquired from full scale UASB treating slaughterhouse wastewater. Sludge was inoculated immediately after transporting from the site. Reactor was operated in continuous mode at a constant mesophilic temperature of $29 \pm 2^\circ\text{C}$. It was fed with chemical wastewater (pH 7.0 ± 0.2) at a feeding rate of 5 l/d without recirculation.

Analytical Procedures

The performance of UASB reactor was assessed by monitoring COD removal efficiency. In addition, pH, ORP, VFA, alkalinity, sulphate and biogas production were also monitored during the reactor operation. The analytical procedures for monitoring the above parameters were adapted from the procedures outlined in Standard Methods¹⁵.

Results and Discussion

In UASB reactor, influent wastewater is distributed from the bottom of reactor and travels in upflow mode throughout the blanket. Under proper hydraulic conditions, anaerobic sludge will develop as high-density granules and forms sludge blanket with a high concentration of biomass. After successful startup (24 d), reactor was operated continuously for another 61 days at OLR_{actual} excluding biomass/sludge blanket volume and taking only the liquid volume (4.25 kg COD/cum-d) of the reactor into consideration. However, OLR calculated on the basis of total liquid volume of the reactor was 2.67 kg COD/cum-d.

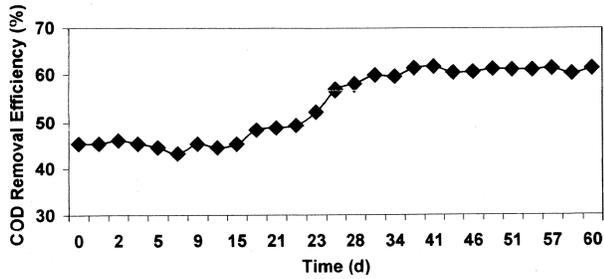


Fig. 2—Variation of COD removal efficiency during UASB operation

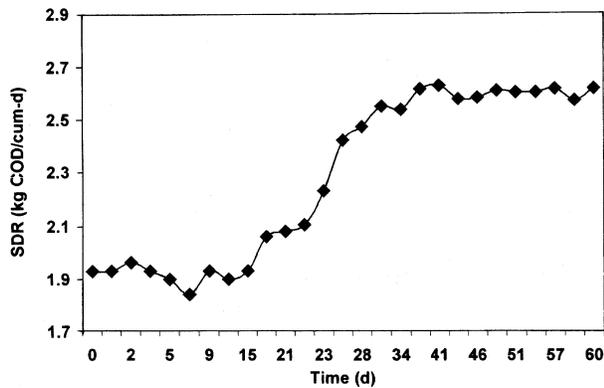


Fig. 3—Substrate degradation rate (SDR) during UASB operation

Reactor Performance

COD removal efficiency (43-62%) varied initially till 34th day, but remained almost constant (Fig. 2). Reactor performance was also assessed by evaluating the substrate degradation rate (SDR), which varied between 1.8 and 2.6 kg COD/m³-d of SDR_{actual} (Fig. 3). Immediately after startup, system showed 40 percent COD removal efficiency, which may be attributed to the efficiency of the inoculated anaerobic sludge. Reactor took 34 days after inoculation to reach stabilized steady state performance. Rapid startup in this case may be attributed to the ability of inoculum and the operating conditions adopted. Startup of anaerobic reactors can be satisfactorily achieved in a very short time if adequate inoculum is available¹⁶. During this phase of operation, COD removal efficiency of the reactor increased (43-62%) accounting for SDR_{actual} of 1.84 kg COD/ m³-d and 2.6 kg COD/ m³-d. Subsequently, there was a marked increase in COD reduction and it approached a maximum (62%) and remained more or less constant thereafter. It was evident from data that the reactor took relatively less time for achieving stable performance and after achieving steady state the performance remained more or less stable.

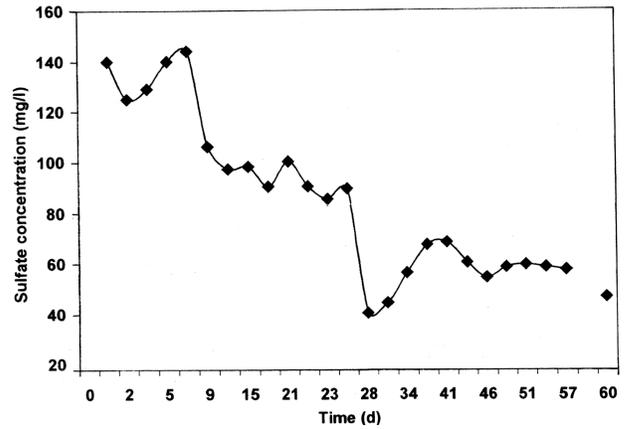


Fig. 4a—Variation of sulphate removal efficiency (%) during UASB operation

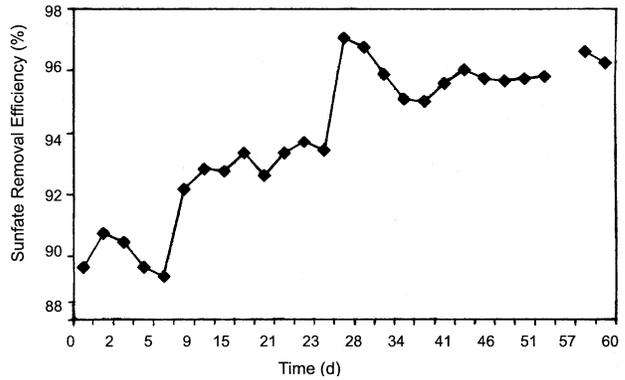


Fig. 4b—Variation of sulphate concentration during UASB operation

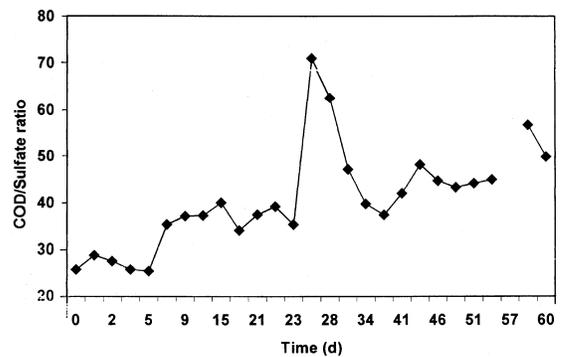


Fig. 4c—Variation of COD/Sulphate ratio during UASB operation

Influent sulfate concentration (Fig. 4a) was 1,350 mg/l while the outlet sulfate concentration varied (55-140 mg/l) accounting for 89-95 percent sulfate reduction (Fig. 4b) to sulfide, which was found to have gradually improved and stabilized after 41 days of the reactor operation. Treatment of sulfate-rich wastewater was possible by anaerobic process applying adequate measures allowing integration of

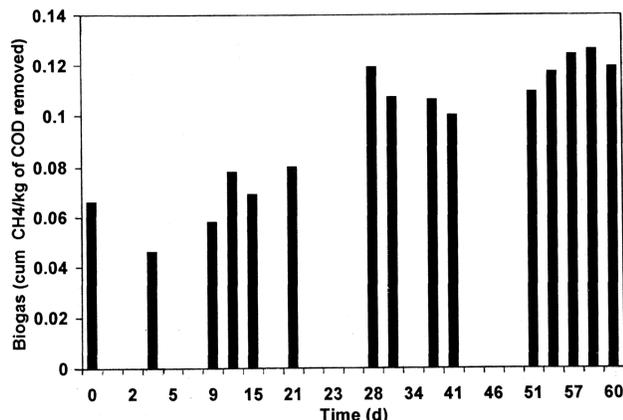


Fig. 5—Variation in biogas production during UASB operation

sulfate reduction with methanogenesis^{4,17}. Sulfate reducing bacteria (SRB) carry out the dissimilatory reduction of sulfur as their primary or even obligate metabolic reaction by using low molecular weight compounds as electron donors^{4,17,18}. SRB are obligate anaerobes, which include a heterogeneous assemblage of microorganisms and their role is analogous to that of methanogenic bacteria (MB) that form CH₄ and CO₂ as final anaerobic end products^{2,4,19,20,21}. The growth of SRB was dependent on the carbon and sulfate concentration, whereas the growth of MB was solely dependent on the concentration of carbon (acetate)²². At low sulfate concentration, growth of SRB would be sulfate limited and enables MB to out compete SRB. Although thermodynamic and kinetic considerations favor sulfate reduction over methanogenesis, it was often observed that MB were able to effectively out compete SRB for acetate^{23,24}. COD/SO₄⁻² ratio (Fig. 4c), an important controlling parameter for the electron flow in anaerobic fermentation, varied in feed in the lower range (4.6 - 4.8) while the outlet COD/SO₄⁻² ratio varied in higher range (25-49). It was reported that at high COD/SO₄⁻² ratios (>6), MB predominated while at lower COD/SO₄⁻² ratios (<1.5), SRB were more competitive²⁵. COD/SO₄⁻² ratio of the outlet was initially 25 up to 38 days of the reactor operation and gone up to 49 percent by the end of the experiment. The increase in COD/SO₄⁻² ratio favored the anaerobic fermentation by the effective performance of the reactor (COD removal) along with the increase in biogas yield, which was observed up to the termination of the experiments. It was evident from the data that sulfate reduction in the reactor was significantly high (89-95%) with the existing COD/SO₄⁻² ratio of the wastewater and demonstrated significant variation after the anaerobic treatment.

Biogas production (Fig. 5) was initially less but increased gradually (0.04 – 0.126 m³ of CH₄/kg of COD removed) but remained uniform at the end. Due to complexity of wastewater, biogas yield was comparatively less (0.2 - 0.3 m³ of CH₄/kg of COD removed). The biogas production also showed concomitant increase with COD reduction and SDR_{actual}.

Process Monitoring

In the reactor, variation was observed in pH (7.38-8.28) and ORP (-42.8 to -85.8 mV), which were ideal for anaerobic biological treatment (Fig. 6). Regular shift in pH indicated survival of the acid producing and acid utilizing anaerobic microbial community. Compared to feed pH (7.0±0.2), outlet pH was found to be slightly alkaline (7.6-8.3). ORP provides information on the electrochemical equilibrium (the reducing or the oxidizing powers of such environment) of a particular aqueous environment²⁶. Presence of carbonaceous organic matter as VFA in highly reducing environments showed ORP values between -600 to -400 mV whereas, presence of H₂S and SO₄⁻² are observed at higher ORP values (-300 to -100 mV). While highly oxidized forms of nitrogen was in the other extreme of the scale at positive ORP (+400 mV). ORP after anaerobic treatment showed negative values. The maximum ORP (-85m mV) reveals that presence of sulphate was not encountered due to its reduction and reasonably good concentration of VFA (23 meq/l). ORP visualized a mirror like image to corresponding pH.

pH and VFA are integral expressions of the acid-base conditions of any anaerobic treatment process as well as intrinsic index of the balance between two of the most important microbial groups (ACB and MB)^{4,27}. VFA concentration in anaerobic system acts as good electron donors for SRB^{28,29}. VFA has shown an initial increase in the outlet (Fig. 7) and gradually decreased indicating the conversion of VFA (from 22 to 8 meq/l) signifying the effectiveness of AB activity. It was recommended that desirable operating range of VFA is 0-8.3 meq/l³⁰. Compared to influent pH (6.8-7.2), outlet pH was found to be higher (7.2-8.3). Interestingly, considerable reduction in outlet VFA concentration was observed, indicating the effective functioning of MB (Fig. 7). After steady state conditions, outlet VFA approached near 8 meq/l. Concomitant decrease in VFA concentration in the reactor system facilitated effective degradation of the

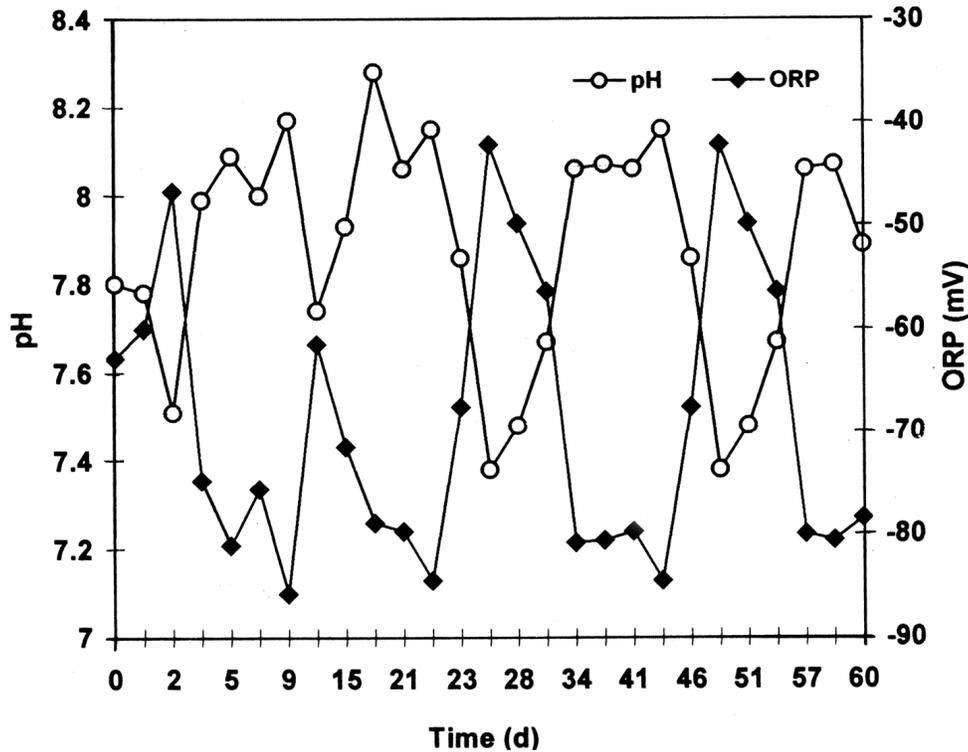


Fig. 6—pH and ORP variation during UASB operation

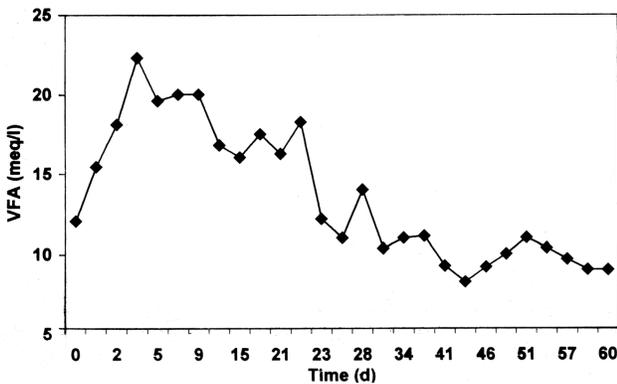


Fig. 7—VFA variation during UASB operation

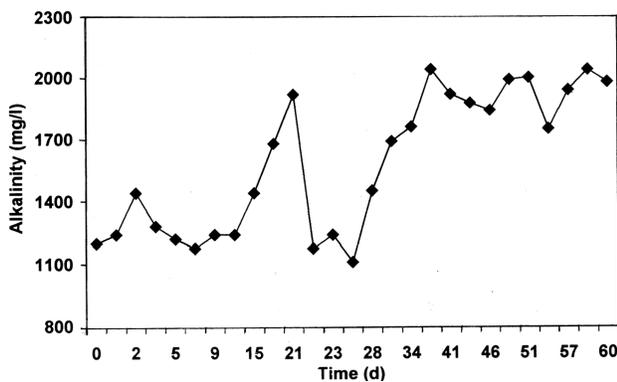


Fig. 8—Alkalinity variation during UASB operation

substrate. VFA accumulation results in unbalanced microbial consortia, which is detrimental in the anaerobic process operation, leading to the total system failure^{4,31,32}. This was prevented in the system by utilization of accumulated VFA, which was substantiated by the decreasing trend in the VFA values in the outlet.

Alkalinity in the reactor was monitored to understand the condition of buffering activity of reactor. While inlet concentration of alkalinity ranged from a minimum of 2440 mg/l, the outlet alkalinity was varying from 1110 to 2040 mg/l through out the study (Fig. 8). Initially, alkalinity remained low (1250 ± 150 mg/l) for the first 15 days but later started building up and by the time the reactor stabilized (34th day), it reached 1900 mg/l and varied within a range of ± 100 . This helped in attaining better balance among the acid producers and acid utilizers resulting in higher COD and sulphate reduction, low VFA accumulation and higher biogas production.

Inhibition of the anaerobic biochemical reactions due to the overload on the system, especially with complex wastewater often could be evidenced through a sudden increase in the VFA concentration^{2,4}. In the present study, VFA/alkalinity ratio varied (0.6-1.0). VFA produced by the AB

during fermentation of complex organics tend to reduce the system pH, this effect was counteracted by subsequent degradation of the acids by MB and reformation of bicarbonate buffer (alkalinity) during the methane fermentation. pH and VFA were integral expressions of the acid-base conditions of anaerobic process, as well as intrinsic index of the balance between microbial groups in the anaerobic system^{33,34}. However, if an imbalance of the process occurred, by rapid change of the environmental conditions, AB out beats MB resulting in VFA accumulation in the system. If balanced digestion was not restored, the buffer capacity (alkalinity) exceeds leading to a drop in system pH. Methane production was hindered completely due to the acidic conditions, but VFA formation was hindered only slightly³⁵.

Conclusions

The study demonstrated the applicability of UASB system for treating low biodegradable composite chemical wastewater. The reactor showed rapidity in achieving the startup along with steady state conditions, which may be attributed to the effectiveness of the inoculated anaerobic sludge and the operating conditions used. Effective sulphate removal (up to 95%) was observed in the studied system operation.

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