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Anaerobic Biodegradation of High Strength Real Wastewater Stream Generated from Manufacturing of Solvent Black Dyes

Prablin Kaur*

Department of engineering, Maharaja Sayajirao University of Baroda, India

***Corresponding author:** Prablin Kaur (M.E. Environmental Engineering), Environmental Engineering Department, Faculty of Technology and Engineering, The Maharaja Sayajirao University, Baroda, India, Email: prabz.kaur.pk@gmail.com

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Abstract

The performance of up flow anaerobic sludge blanket (UASB) treating real wastewater generated from manufacturing of Solvent Black dyes (SB dyes) was investigated. Specifically, it was determined whether UASB could be used as treatment system at an existing dyestuffs production plant. Accordingly, UASB was developed with a reactor volume 25 L was being operated in different phases. Consistent chemical oxygen demand (COD) removal efficiency of around 90% was achieved at an organic loading rate (OLR) of 2 kg COD/ m^3 d at inlet COD of 20000 mg/L. Effect of varying OLR on COD removal efficiency and methane production was evaluated by feeding wastewater at COD of 10000 mg/L. The COD removal efficiency of >90% at OLR of 2 gradually decreased to~80% at OLR of 5 kg COD/ m^3 d. Methane production was 320-343 L/kg COD removed at OLR 2 kg COD/ m^3 d decreased to 147-200 L/kg COD removed at OLR of 5 kg COD/ m^3 d. Decolonization of wastewater led to generation of aromatic amines indicated by formation of a new peak at 286 nm in UV-Vis spectrum. Inlet pH of feed was in the range 6-6.3 which increased to 8.5-8.6 indicating degradation of acetate in the wastewater. Results of this study suggest that anaerobic treatment can be employed advantageously for SB dyes wastewater, resulting in excellent COD removal without any energy input and producing useful methane.

Keywords: Up flow anaerobic sludge blanket; Treatment of wastewater; Solvent black Dyes; Consistent chemical oxygen demand; Methane production

Abbreviations: UASB: Up Flow Anaerobic Sludge Blanket; SB Dyes: Solvent Black Dyes; COD: Consistent Chemical Oxygen Demand; OLR: Organic Loading Rate; DHS: Down-Flow Hanging Sponge; BOD: Biochemical oxygen Demand; TDS: Total Dissolved Solids; GLS: Gas-Liquid-Solid; DPA: Diphenyl Amine; MA: Metanillic Acid; VFA: Volatile Fatty Acid; ALK: Alkalinity

Introduction

Dyestuff sector is one of the cores chemical industries in India and also second highest export segment in chemical industry. Increased demand for Dye products, their production, and the use of synthetic dyes together contributed to dye wastewater, becoming one of the major sources of severe pollution now a days. Dyes are mostly introduced into the environment through industrial effluents. Dye leads to severe number of environmental & health hazards [1]. 10,000 different dyes and their pigments are used industrially and over 7 x 105 tons of synthetic dyes are annually produced worldwide [2]. Azo dyes are the largest group of dyes used in the textile industry. They have become a concern in wastewater treatment because their colour and potential toxicity to animals and human [3]. Treatment of dye effluents has been one of the major concerns to the environment. Various types of treatment can be used to treat dye wastewater.

Physical processes like adsorption [4,5], and membrane filtration [6]; Chemical processes like coagulation-Flocculation [7,8], Ozonation [9], Electrochemical process like Electro coagulation [10]. The treatment mentioned above lead to effective decolourization, but their application is restricted due to various reasons; Physical process leads to phase transfer of dyes from one phase to another without its destruction and also possess high maintenance cost. Chemical process is generally non selective due to high cost of chemicals and sludge production which is difficult to be disposed. Since, Biological treatment is less expensive, less energy consumption, and requiring lesser amount of chemicals, it can be efficiently used as an alternative to the above mentioned treatments [11]. In a study performed by [12], colour and COD removal efficiencies of 64±17 and 65±6 % were obtained, respectively in UASB that was used to treat reactive dyes wastewater in an up-flow anaerobic sludge blanket (UASB) coupled with down-flow hanging sponge (DHS) [13]. Obtained 94% colour removal and 69% COD removal in UASB that was used to treat 50 mg/L Methyl orange for 35 days [3]. Reported 99.8 and 61% colour and COD removal efficiencies, respectively, when using sequential anaerobic-aerobic system to treat Azo dye Reactive Black 5 dye.

Existing ETP of dyestuff industry was unable to treat SB dyes wastewater efficiently. As the SB dyes wastewater contains high concentration of acetates yielding high oxygen demand, which can be easily degraded by methanogens. Also, there is no so source of sulphate or is present in much less amount, so this gives a favorable situation for anaerobic bacteria. If the sulphate concentration is more it will lead to production of Hydrogen sulphide (H_2S) rather than methane. Hence, it gives favorable condition for anaerobic bacteria, where COD is high due to high amount of acetates and low concentration of sulphate. In the light of these facts, UASB was designed for the decolourization and anaerobic degradation of mother liquor generated from the manufacturing of SB46.

Material and Method

Solvent black dyes (SB dyes)

SB Dyes is a dye soluble in organic solvent. Molecular Weight and Molecular formula are shown in Table. 1 and Molecular structure of SB46 is shown in Figure1.

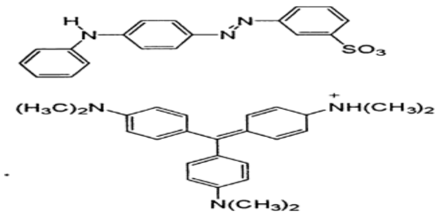

Figure1: Molecular structure of SB Dyes.

Molecular Formula	C43H44N6O3S
Molecular weight	726.93 g/mol

Table1: Characteristics of SB Dyes.
Source: (worlddyevariety.com/solvent-dyes/slvent-black-46.html, May 2015).

Source of solvent black dyes (SB dyes) effluent

The samples of mother liquor of solvent black dyes (SB dyes) was collected from dyestuffs industry located in GIDC Ankles war. The characteristics of the mother liquor of SB46 are shown in the Table 2.

Parameters	Values
pH	4-5
COD	19000-29500 mg/L
BOD	8000-10000 mg/L
Chloride	900-1100 mg/L
Conductivity	22000-25000 µ mho/cm
TDS	22000-24000 mg/L
Ammonical Nitrogen	20-25 mg/L
Sulphate	60-70 mg/L

Table 2: Characteristics of mother liquor of SB Dyes.

Analytics methods

The characteristics of mother liquor of SB dyes such as pH, COD, Biochemical oxygen Demand (BOD), Chloride, Conductivity, Ammoniac nitrogen, Total Dissolved Solids (TDS), Sulphate were determined according to the Standard Methods for Examination of water and wastewater (APHA 22^{nd} edition). Volatile Fatty Acid/Alkalinity (VFA/ALK) ratio was determined using Kapp's Method (Buchauer, 1997). Colour was determined using SHIMADZU UV-1800 spectrophotometer where UV-VIS spectrum of mother liquor of SB dyes shows 3 peaks: peak in visible region at 580 nm, indicates crystal violet and peak in UV region at 286 nm was due to unreached raw material used for metanil yellow and, 346 nm indicates metanil yellow.

The colour removal was calculated by change in absorbance of peak at 580 nm as for following formula:

% Colour removal = [(A0 – At)/A0]*100

Where, A0 represents absorbance at t = 0 min.

At represents absorbance at t = t min.

Experimental set up of UASB

UASB reactor was designed, and fabricated using polyacyrlic material with an influent distributor and six outlets with an effective volume of 25 L with L*W*H = 150*150*1150 (mm). Gas-Liquid-solid (GLS) separator was situated in the upper portion of the reactor to prevent the loss of sludge and for easy release of the biogas produced by UASB reactor. UASB was connected with the pumps and proper collection containers with proper leak proof pipelines. The reactor was inoculated with 10 L of sludge collected from septic tank. Total volatile solids of inoculum sludge were 44.24 g/L. As shown in Figure 2, two pumps were used: Pump 1 is the peristaltic pump for influent flow rate adjustments and pump 2 is the submersible pump for recycling the effluent internally to maintain up flow velocity 0.5-0.6 m/h inside the reactor. Flow rates in pump 1 were adjusted based on the desired flow rates. Influent was introduced from the bottom of the UASB reactor with the help of pump 1.The temperature during the study period was maintained to (27-35 ˚C). To maintain the temperature of the reactor in winters, UASB effluent was heated with the help of magnetic stirrer with heating coil. Collection and recirculation of heated effluent was carried out by maintaining up flow velocity in the range of 0.5-0.6 m/h. Biogas produced from the reactor was passed through the solution of KOH to dissolve the amount of CO2 with KOH. Hence, obtaining the amount of Methane, collected in rubber bladder. The amount of Methane in the bladder was measured using water displacement method.

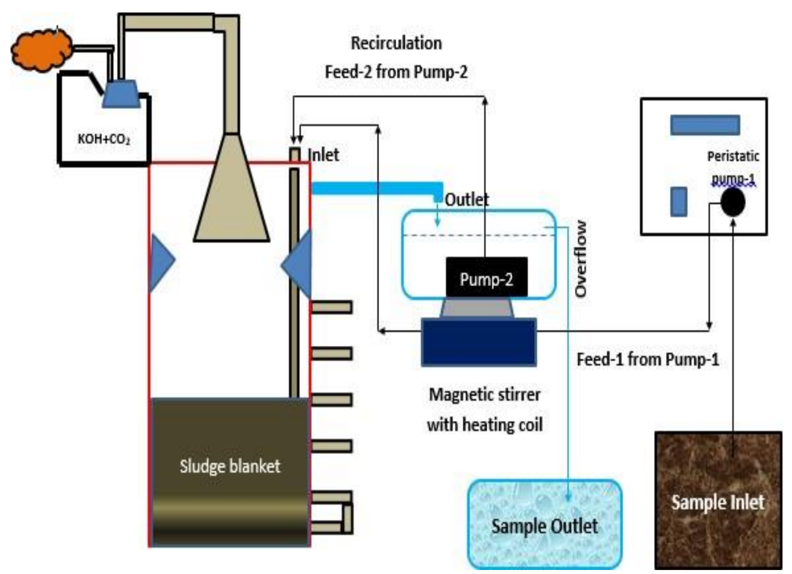

Figure2: Schematic Diagram of UASB Set up.

Operation of UASB

The current study was carried out in different phases. PH of the feed was 4-5 which was adjusted around 6.5 using NaOH. Initially in phase 1, the study was carried out by directly using mother liquor of SB Dyes wastewater sample having COD=22000-29000 mg/L. This resulted in lowered efficiency of the reactor and methanogens stopped working. Therefore, phase 2 was carried out by diluting the wastewater sample using tap water, started with COD=1000 mg/L so as to acclimatize the microorganisms in the sludge and was done until reactor achieved steady state condition i.e. (93-95 % COD removal for minimum 2-3 HRT). The feed was supplemented incrementally to the reactor.

The feed COD was increased gradually from 1000 mg/L to 18000 mg/L simultaneously with increase in OLR from 0.1 to 3.37 kg COD/m^3 d. Afterwards, Phase 3, where OLR= 2 kg COD/m^3 d was kept constant with gradually increasing feed COD from 10000 to 20000 mg/L and Phase 4, where COD= 10000 mg/L was kept constant with gradually increasing OLR from 2 to 5 kg COD/m^3 d, were carried out. (Reason for considering COD=10000 mg/L only is because the mother liquor SB Dyes in industry when combines with washing water yields COD around= 10000 mg/L). Therefore, samples were diluted to obtain the feed COD=10000 mg/L. At the end of the study, combined wastewater i.e. mother liquor of SB dyes and washing water was treated in the UASB having COD around 10000 mg/L at OLR=4 kg COD/m3 d. COD: N: P ratio was maintained 100: 0.5: 0.1.

Results and Discussions

Initially in phase 2, acclimatization was carried out by diluting SB dyes wastewater to obtain a feed COD=1000 mg/L. When COD removal ≥ 90 % was achieved for 2-3 HRT, COD of the feed was increased gradually from 1000 mg/L to 13000 mg/L simultaneously with increase in OLR from 0.1 to 3.37 kg COD/ m^3 d, which resulted in % COD removal >90% , methane production was in the range of 312-346 L/kg COD removed and VFA/ALK ratio was consistent <0.1, when operated up to COD=13000 mg/L and OLR= 3.37 kg COD/ m^3 d. When the feed COD was further increased to 18000 mg/L at same OLR i.e. 3.37 kg COD/ m^3 d, performance of reactor suddenly lowered down and COD removal efficiency decreased to around 60% as shown in Figure 3, methane production also reduced to the range of 248-260 L/kg COD removed as shown in fig.5, and VFA/ALK ratio increased to >0.4. As shown in Figure 4 & 5.

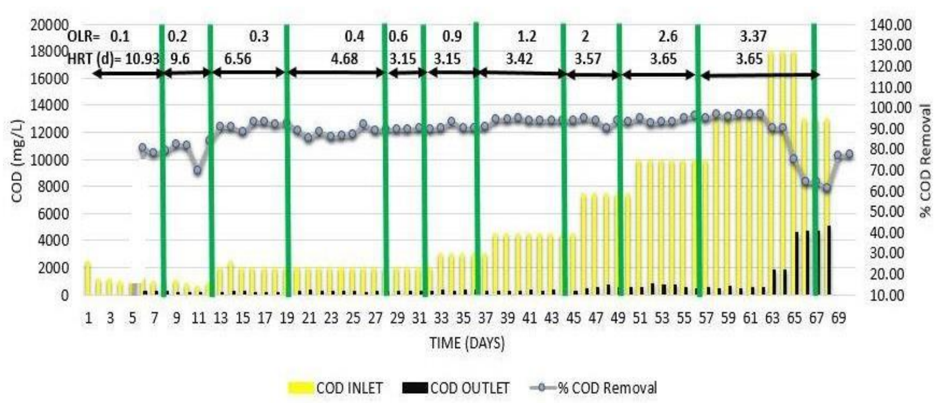

Figure 3: Inlet COD outlet COD and % COD removal from SB dyes waste water during Phase 2.

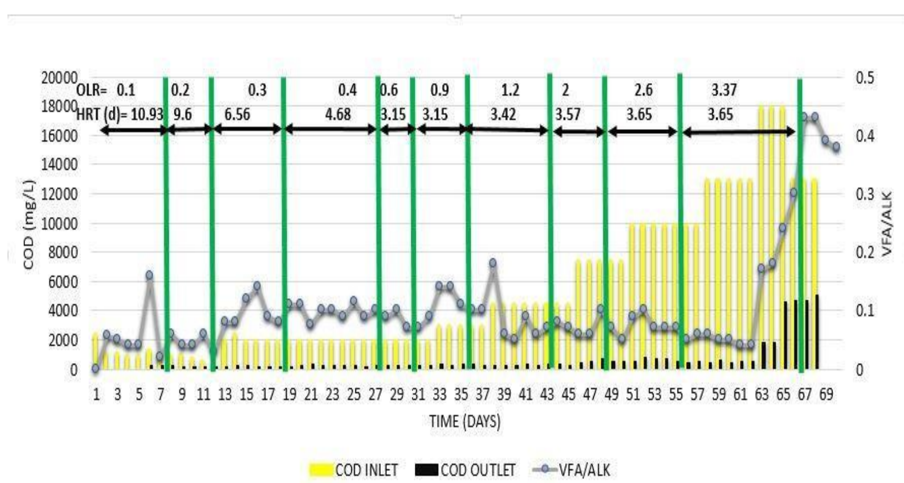

Figure 4: Inlet COD outlet COD and VFA/ALK ratio from SB dyes waste water during Phase 2.

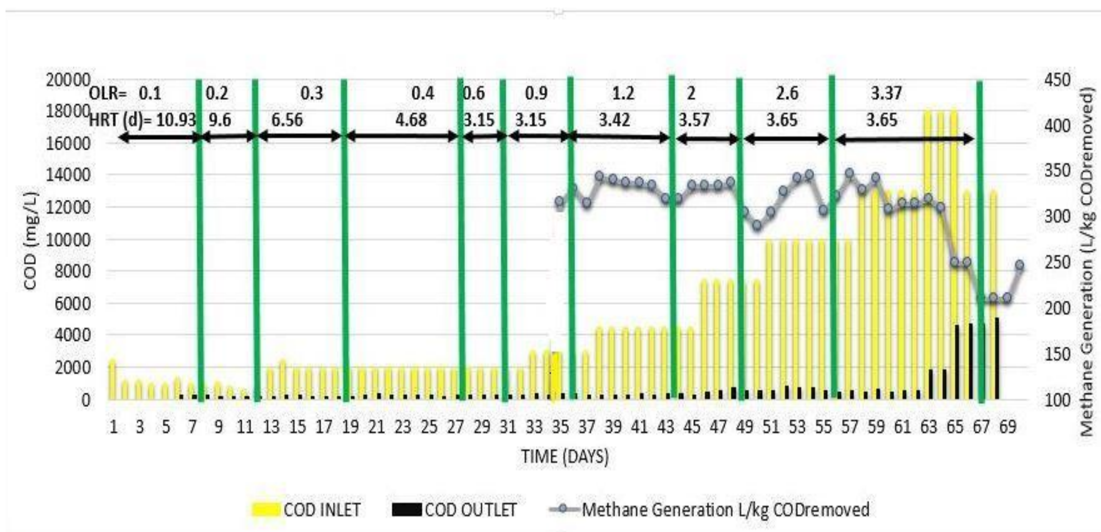

Figure 5: Inlet COD outlet COD and Methane Production from SB dyes waste water during Phase 2.

When COD removal efficiency was reduced, feed COD was again brought back to COD=13000 mg/L, but the system did not recovered as shown in Figure 3, infect COD removal decreased further. It shows that, biological activity of UASB was disturbed. Therefore, COD removal efficiency could not be recovered. Moreover, due to the sudden rise in feed COD and OLR, some loss of sludge also occurred. Hence, to overcome the above mentioned disturbance, new 2L of sludge of septic tank was appended. It seems that the above mentioned disturbance may be because of simultaneous increase in OLR as well as feed COD**.** Therefore, to determine the cause for sudden changes in the reactor, either it was feed COD or increase in OLR, phase 3 or phase 4 were carried out. After appending 2L of sludge, Phase 3 was carried out where feed COD was gradually increased from 10000 mg/L to 20000 mg/L simultaneously at constant OLR= 2 kg COD/ m^3 d so as to see the effect of feed COD. Consistent COD removal efficiency of >90% was observed as shown in Figure 6, VFA/ALK ratio observed was <0.1 as shown in Figure 7, and methane production was also consistent in the range of 320-343 L/kg COD removed as shown in Figure 8, indicating that at low OLR i.e. 2 kg COD/ m^3 d, even COD up to 20000 mg/L can be treated efficiently and COD removal observed was significant.

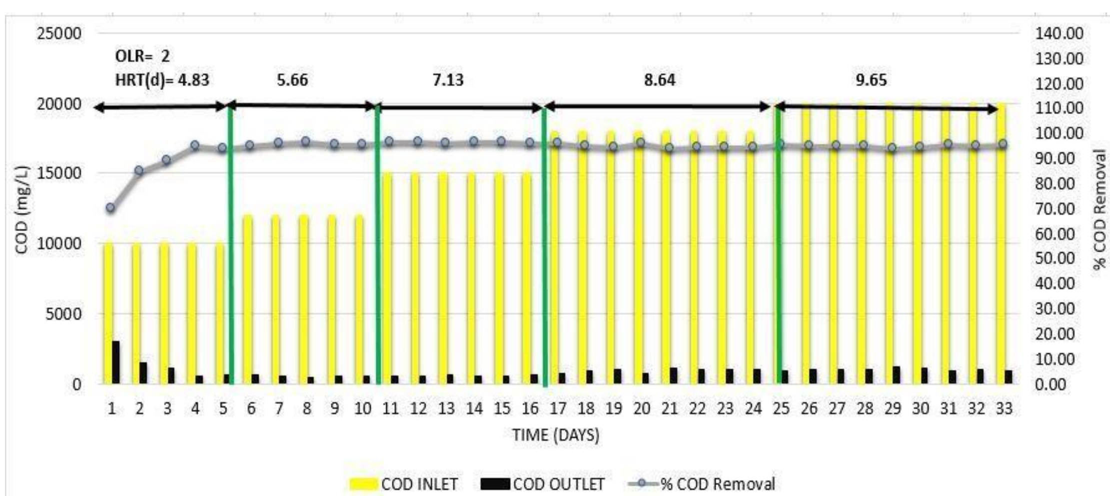

Figure 6: Inlet COD, Outlet COD, and % COD Removal from SB dyes waste water during Phase 3.

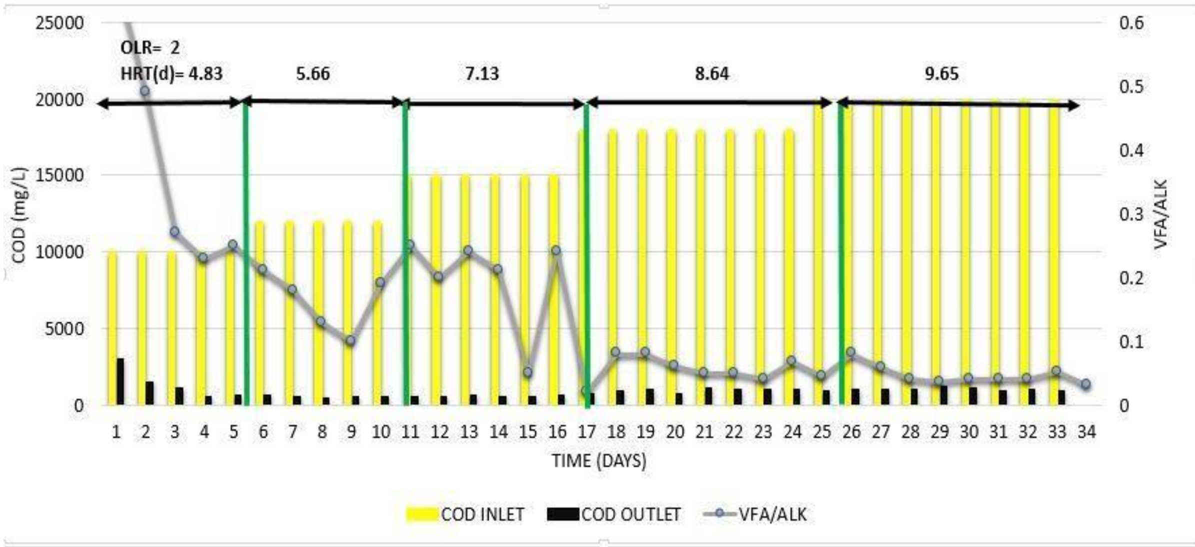

Figure7: Inlet COD, Outlet COD, and VFA/ALK ratio from SB dyes waste water during Phase 3.

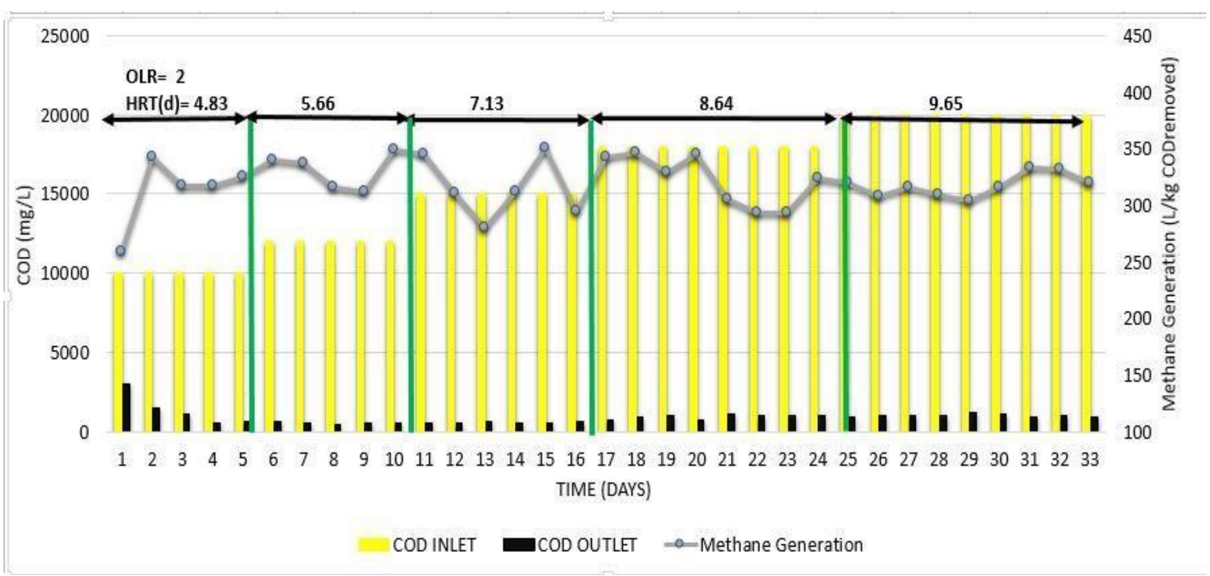

Figure 8: Inlet COD, Outlet COD, and Methane Production from SB dyes waste water during Phase 3.

Next, to determine the effect of increase in OLR, phase 4 was carried out, where OLR was gradually increased from 2 kg COD/ m^3 d to 5 kg COD/ m3 d at constant feed COD= 10000 mg/L. Whenever the OLR was increased,% COD removal slight decreased to around 80% in initial stage of each OLR, but afterwards steady results >90% were obtained, methane production was in the range of 280-325 L/kg COD removed VFA/ALK ratio was also <0.15. This has been observed when operated up to OLR=3.6 kg COD/ m^3 d. Further increase in OLR to 4- 5 kg COD/ m3 d, COD removal efficiency gradually reduced from 90% to around 80% as shown in Figure 9, Methane production gradually starts decreased to the range of 147-200 L/kg COD removed as shown in Figure 10 , and VFA/ALK ratio increased to >0.2 as shown in Figure 11.

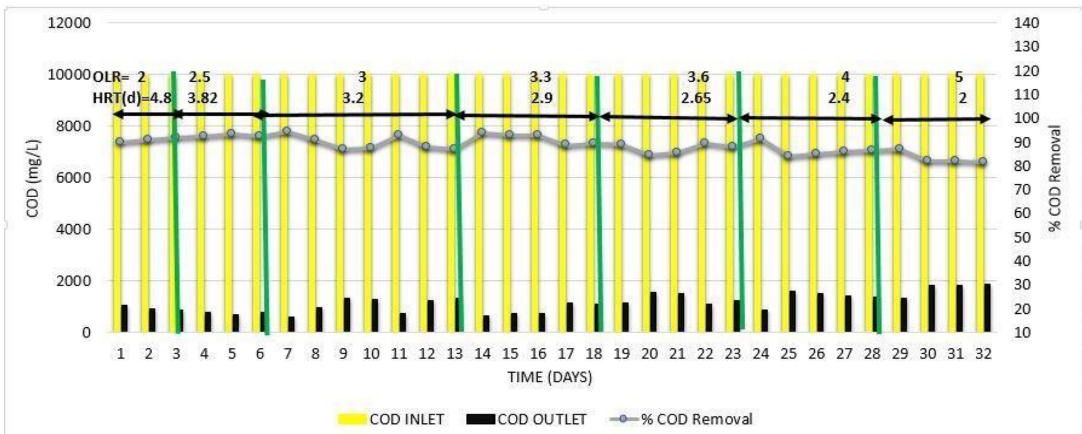

Figure 9: Inlet COD, Outlet COD, and % COD Removal from SB dyes waste water during Phase 4.

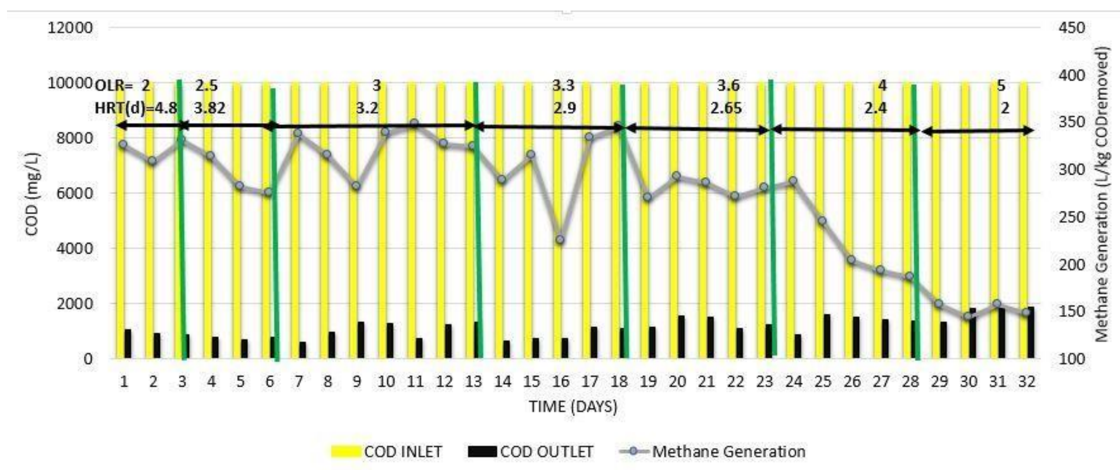

Figure10: Inlet COD, Outlet COD, and Methane Production from SB dyes waste water during Phase 4.

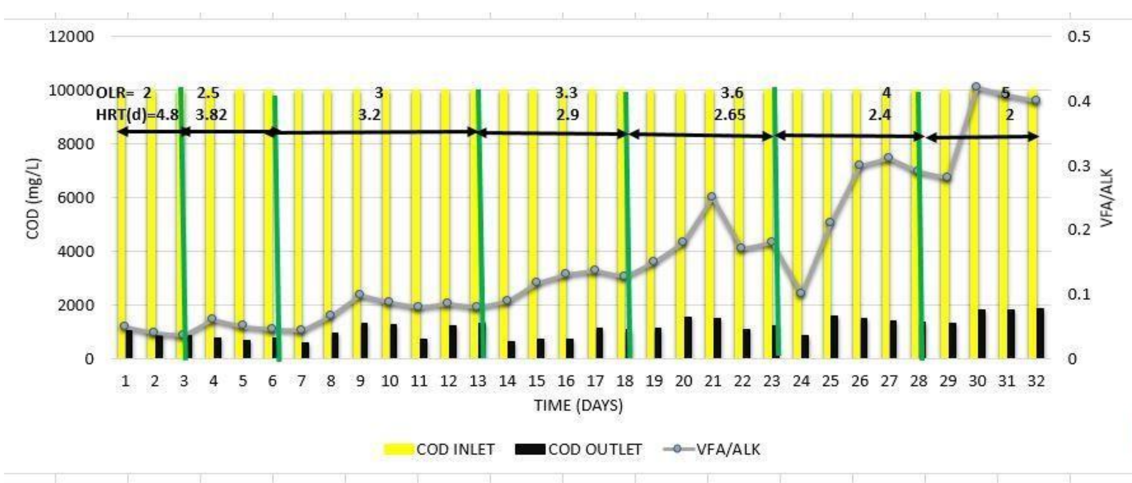

Figure 11: Inlet COD, Outlet COD, and VFA/ALK ratio from SB dyes waste water during Phase 4.

Chelliapan S, et al. [14], studied that when pharmaceutical wastewater containing microcline antibiotics was treated in UASB, having COD around 7.5 g/L at OLR 1.86 kg COD/ m^3 d, COD reduction was around 70-75%. When OLR was increased to 2.41 kg COD/ m^3 d, COD removal efficiency decreased gradually to 45 %. Despite poor performance at high OLR, COD removal efficiency was recovered to previous levels when OLR was reduced to 1.86 kg COD/ m^3 d and also pharmaceutical wastewater has low concentration of total VFA concentration (avg. 300 mg/L) was present in effluent when operated at OLR in the range of 0.43-1.5 kg COD/ m3 d. Further increase in OLR at 3.37 kg COD/ m3 d resulted in higher VFA concentration in the range of 3300 mg/L, indicating the reduction in acetate degradation. Studied that when UASB was fed with coffee wastewater having COD concentration 1-6 g/L at OLR 1.89 kg COD/ m3 d, COD removal efficiency of 77% was attained. When OLR of reactor was increased rapidly reaching value of 2.36 kg COD/ m3 d resulting in dropped COD removal efficiency to 25%, which forced to a reactor shutdown for 7 days.

After then, reactor was resumed with low OLR 1.78 kg COD/ m3 d for same COD, resulted in average COD removal efficiency of 63%, indicating that when operated at optimum OLR for COD, results observed are significant [15]. Stated that volumetric biogas production increased with increasing OLR but afterwards began to decrease due to deterioration of COD removal efficiency during treatment of distiller's grains wastewater in UASB. Torkian A, et al. [16], studied that UASB treating slaughterhouse effluent produced up to 300 L/kg COD removed at OLR 27 kg COD/ m^3 d. Methane production rate seemed to decline below 200 L at high OLR up to 39.5 3.37 kg COD/ m^3 [17], studied that methane production with COD loading rate and was maximum of 3.8 L/L.d at OLR 16 kg COD/ m3 d for treatment of sugar industry wastewater in UASB reactor. When OLR was increased from 16 to 24 kg COD/ m3 d, Methane production decreased from 3.8 L/L.d to 2.6 L/L.d. This sudden decrease in methane production was due to VFA accumulation as acetate which inhibited biomass resulting in lower COD removal and ratio of VFA/ALK varied between 0.19-0.33 during treatment of sugar industry wastewater in UASB at OLR up to 16 kg COD/ m3 d. When OLR was further increased to 24 kg COD/ m3 d, VFA/ALK ratio reached value of 0.7 indicating system instability. This can be attributed to insufficient alkalinity generation in reactor. SB dyes is an dye made up of crystal violet which is not an azo dye and Metanil Yellow (C18H14N3SO3Na) as shown in Figure 12 is an azo dye compound having N=N bonds is mainly responsible for colorization in SB dyes waste water.

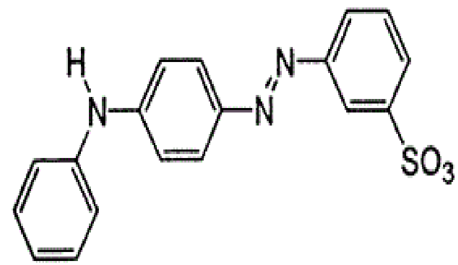

Figure 12: Molecular structure of metanil yellow.

SB dyes wastewater had a peak in visible region at 580 nm which was due to crystal violet & peak in UV region at 286 nm was due to unreacted raw materials used for production of metanil yellow and 346 nm was due to metanil yellow. SB dyes wastewater was treated in UASB, the degradation proceded, disappearance of absorbance peak at 346 nm, reflected signal of almost complete decolorization & breakdown of azo bond cleavages of Metanil yellow in SB dyes and 580 nm which seems to be because of anaerobic degradation of crystal violet as shown in Figure 13. Intermediates used for metanil yellow were examined and its UV-VIS spectra. It seems new peak appeared in outlet at absorbance of 286 nm reflecting signal of formation of intermediates of metanil Yellow i.e. pure diphenyl amine (DPA) & Metanillic acid (MA) which can be confirmed by Figure 14. This can be said because of occurrence of the peak of mixture of intermediates i.e. DPA+MA on the absorbance value close to the absorbance value of the peak in the outlet. That is why it seems that metanil yellow part is reduced by breakdown of cleavage of azo bond forming aromatic amines at 286 nm in the outlet [18].

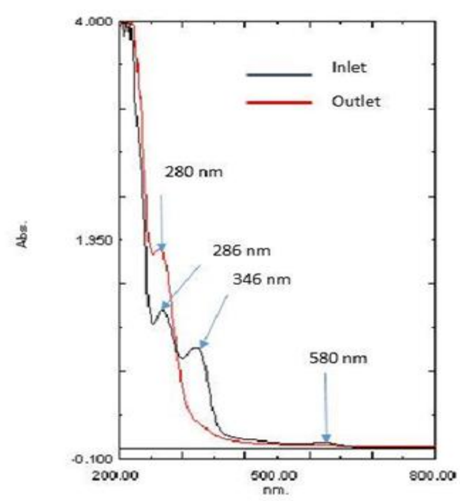

Figure 13: UV-VIS spectrum of SB dyes waste water.

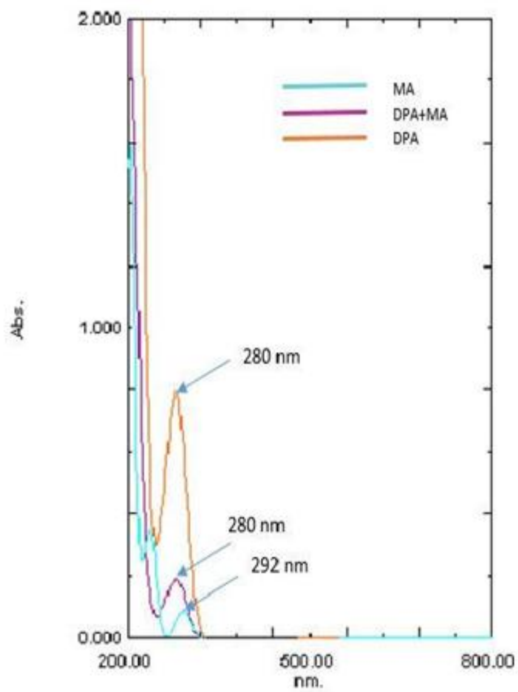

Figure 14: UV-VIS spectrum of intermediates before and after treatment of methanol yellow.

Conclusion

It was concluded that the steady state condition of the reactor can be obtained by balancing both, OLR as well as feed COD. Decolourization of SB dyes wastewater did not correlate with COD concentration, % COD, OLR or methane production. It seems that the color removal of SB46 wastewater may be attributed to the fermentative bacteria. Inlet pH of feed was 4-5 which was adjusted ~6.5 using NaOH, which increased to 8.5-8.6 due to degradation of acetate in the wastewater in the outlet throughout all the phases, indicating outlet pH to be independent of OLR for SB dyes wastewater. Therefore, results of this study suggest that anaerobic treatment can be employed advantageously for SB dyes wastewater, resulting in excellent COD removal without any energy input and producing useful methane.

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