Biological Treatment of Metoprolol Contaminated Wastewater using Upflow Anaerobic Sludge Blanket (UASB) Reactor

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Abstract: ***Upflow Anaerobic Sludge Blanket (UASB) reactors have been widely used for treatment [3]of industrial wastewater. In this study, performance of a lab-scale up-flow anaerobic sludge blanket (UASB) reactor, treating a chemical synthesis-based pharmaceutical wastewater, was evaluated under different operating conditions. Tubular section is a 240 cm long column with 14 cm internal diameter (ID) and a volume of 9.2 liters. The length of the gas-liquid-solid separator is 80 cm and volume is 20.4 litres The GLSS section is further separated into two parts; bottom half is tapered with a slope angle of 60° and top half is a 20 cm long column with an internal diameter of 22 cm. The COD concentrations used in the present investigation 9900mg/L. At steady state conditions, the reactor resulted in 65% of COD and 70.2% of Metoprolol removal efficiency accounting for Substrate Degradation Rate (SDR) of 2.72 kg COD/ m^3.d During this study, which lasted for 60 days actual organic loading rate (OLR $_{actual}$) of 4.25 kg COD/ m -d, the temperature of the wastewater entering the reactor ranged from 30 to 35^0C, Oxidation Reduction potential was between no heat exchanger was used.***

Keywords: Metoprolol, UASB, ASP, Biological treatment, Pharmaceuticals, waste water

1. Introduction

The importance of the pharmaceutical industry has constantly increased over the last 50 years, reflecting the increasing demand for pharmaceuticals. Ultimately, these drugs are either excreted by human, or simply disposed of, and end up into the environment [1]. Hence, the accumulation into the environment of pharmaceuticals is now recognized as a serious problem [2]. Many regions, in India, have reported the presence of low concentration of pharmaceuticals in their sewage, surface and ground water [3]. Pharmaceutical pollution of water in India rushed to international attention, when a Swedish research team revealed that pharmaceutical levels in water downstream of a wastewater treatment plant in Patancheru, Andhra Pradesh, India were 150 times the highest levels in the US. Environmental and human harms of such pollution are extensive, leading to disease, destitution, disenfranchisement, and, in some cases, protest. Meanwhile, regulatory institutions deny claims and shirk their responsibility to enforce regulations. Metoprolol is a beta-blocker and while hydrochlorothiazide is a potent thiazide diuretic that enhances natriuresis, leading to reduction in plasma volume and cardiac output. Therefore, it is used widely alone or in combination with other antihypertensive drugs for the treatment of cardiovascular disorders, viz, hypertension, angina, and congestive cardiac failure [4-7]. Chemically, metoprolol succinate is 2-propanol, 1-[4-(2- methoxyethyl) phenoxy]-3-[(1-methylethyl) amino]-, (±)-, butanedioate.

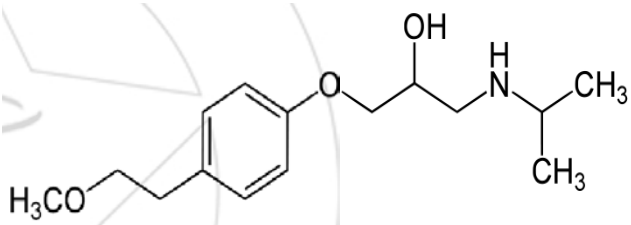

Figure 1: Structure of Metoprolol

Table 1: Optimized conditions for analysis of Metoprolol

Parameter	Optimized condition
Chromatograph	RP-HPLC
Column	Inertsil C18, 5m , 150 mm x 4.6 mm
Mobile phase*	methanol-water (50:50 v/v) containing 0.1% TFA (v/v)
Flow rate	1.0ml/min
Detection	248nm
Injection volume	5µl
Temperature	20^0C
Reaction time-Nimesulide	5.38 min

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 combustion [8]. 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 [9] along with the renewable energy generation [10]. 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 [11]. 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 wastewater [12]. It allows the use of high volumetric COD loadings compared to other anaerobic processes which results in high loading rates with relatively low detention times and elimination the cost of packing material.

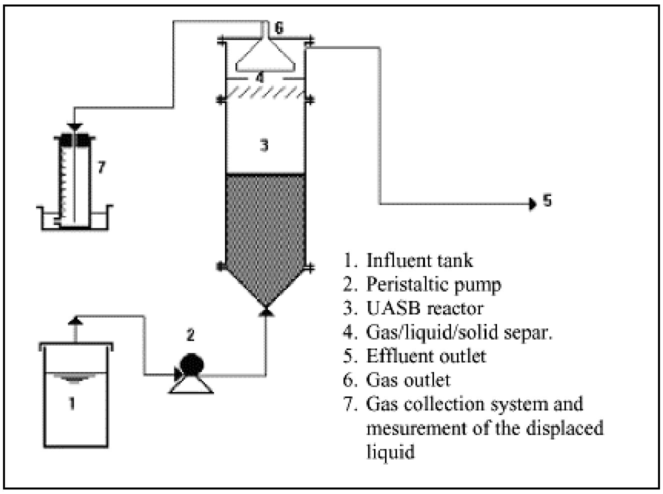

Figure 2: Schematic representation of the UASB reactor

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 rates [13]. UASB reactors have also been applied to treat toxic compounds such as nitro aromatics and polychloropheno [14]. This communication elucidates the application feasibility of UASB reactor configuration for chemical contaminated wastewater.

2. Materials and Methods

Wastewater characteristics

Wastewater was a composite chemical effluent collected from chemical based industry located near bollaram village, Hyderabad. The characteristics of wastewater were as follows: suspended solids (SS), 1500; TDIS, 21750; total alkalinity, 3000; chlorides, 4860; sulphates, 2040; COD, 9900; BOD, 3210mg/l, pH, 2.6 and metoprolol 174 mg/L

Reactor Configuration and Operation

Radily available bench scale UASB reactor was used in this study. This setup consisted of a pair of UASB reactors, influent tank, peristaltic pump, effluent collection tank and gas trapping system. Schematic diagram of the reactor set-up is shown in Figure 2.

The UASB reactor is made of acrylic glass, and is consisted of a tubular section at the bottom and an extended was made for gas- liquid-solid separator (GLSS) at the top. Tubular section is a 240 cm long column with 14 cm internal diameter (ID) and a volume of 9.2 liters. The length of the gas-liquid-solid separator is 80 cm and volume is 20.4 litres The GLSS section is further separated into two parts; bottom half is tapered with a slope angle of 60° and top half is a 20 cm long column with an internal diameter of 22 cm. An inverted cover is also attached with the top lid of GLSS in order to enhance coagulation of suspended/colloidal particles, increase the collection of biogas and to control the washout of particles [15].

UASB reactor consists of reaction zone and settling zone. 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 [16]. Outlet from the reactor was collected from the gas-liquid-solid separator (GLSS).

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±2oC. 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 Metoprolol removal efficiency. In addition, pH, ORP, VFA, production were also monitored during the reactor operation. The analytical procedures for monitoring the above parameters were adapted from the procedures outlined in Standard Methods [17].

Analytical Method for Detection of Metoprolol

Analyses were done at a column temperature of 24 ± 2 °C under isocratic conditions. The mobile phase consisted of a volumetric mixture of aqueous 50mM disodium hydrogen phosphate (pH adjusted to 5.0 with orthophosphoric acid): methanol: acetonitrile (in the ratio of 525:225:250). The flow rate was 1.0 ml/min and volume of injection was 20 µl. UV detection was made at 222 nm [18].

3. Results and Discussion

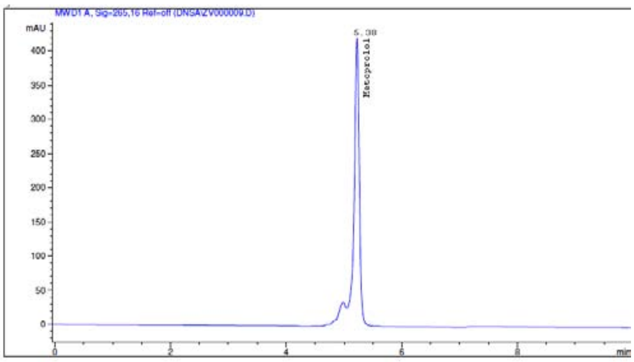

Figure 3: Chromatogram showing pure Metoprolol in HPLC

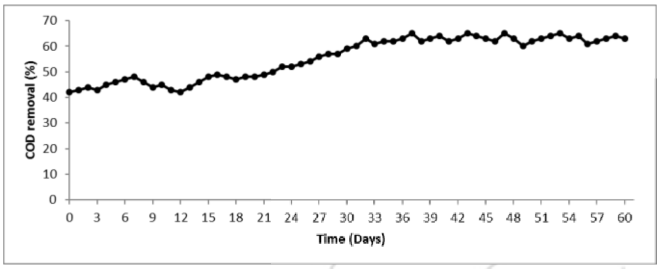

Figure 5: COD Removal Efficiency during UASB Operation

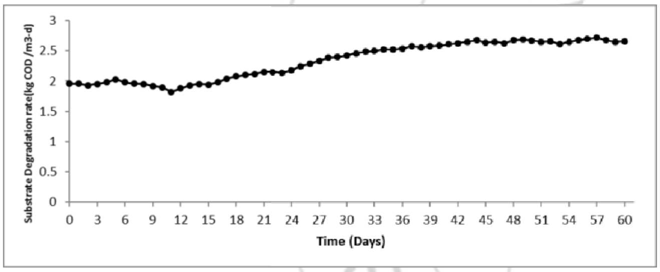

Figure 6: Substrate degradation rate (SDR) during UASB operation

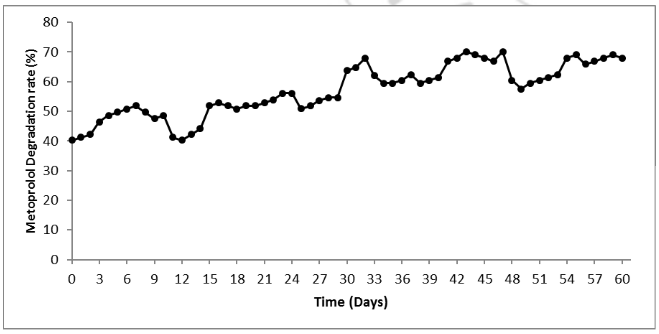

Figure 7: Variation of Metoprolol concentration during UASB operation

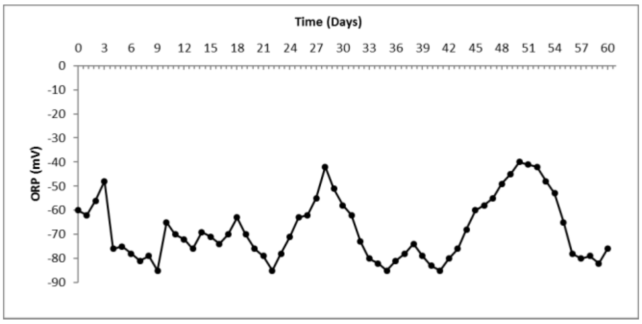

Figure 8: ORP variation during UASB operation

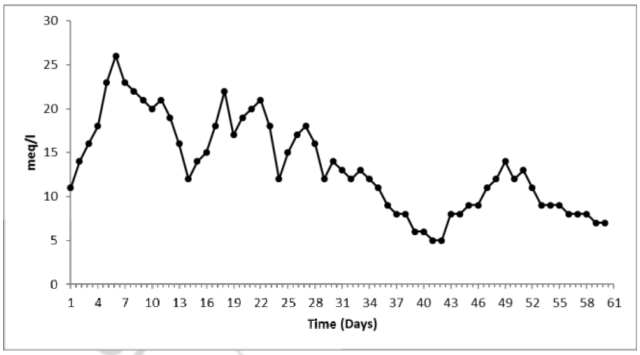

Figure 9: VFA Variation during Treatment Process

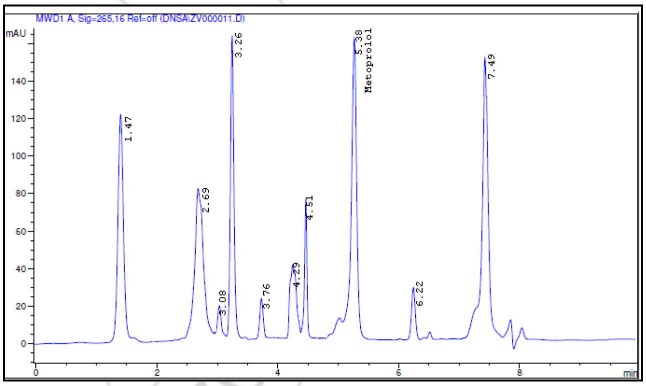

Figure 10: Metoprolol concentration in industrial waste water before treatment

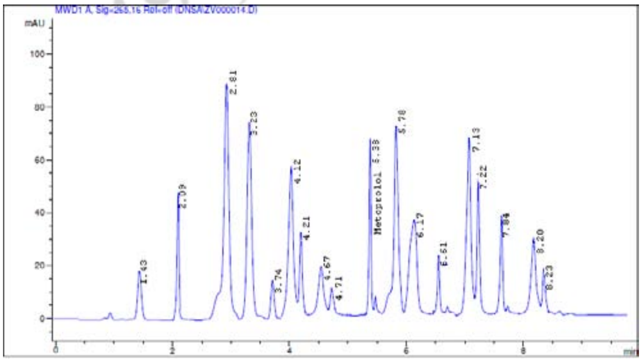

Figure 11: Metoprolol concentration in industrial waste water after treatment

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 (30 days), reactor was operated continuously for another 60 days at OLR_{actual} excluding biomass/sludge blanket volume and taking only the liquid volume (4.25 kg) of the reactor into consideration. However, OLR calculated on the basis of total liquid volume of the reactor was 2.67 kg COD/m^3-d.

4. Reactor Performance

COD removal efficiency (43-62%) varied initially till 34th day, but remained almost constant (Figure 5). Reactor performance was also assessed by evaluating the substrate degradation rate (SDR), which varied between 1.8 and 2.6 kg COD/m^3-d of SDR_{actual} (Figure 6). Immediately after startup, system showed 42 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 available. During this phase of operation, COD removal efficiency of the reactor increased (42-65%) accounting for SDR_{actual} of 1.82 kg COD/ m^3-d and 2.76 kg COD/ m^3 -d. Subsequently, there was a marked increase in COD reduction and it approached a maximum (65%) 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.

Influent Metoprolol concentration (Figure 7) was 34 mg/l while the outlet Metoprolol concentration varied (13.6 - 23.8 mg/l) accounting for 40-70 percent. UASB reactor was found to have gradually improved and stabilized after 41 days of the reactor operation.

5. Process Monitoring

In the reactor, variation was observed in ORP (-40. to -85. mV), which were ideal for anaerobic biological treatment (Figure 8). ORP provides information on the electrochemical equilibrium (the reducing or the oxidizing powers of such environment) of a particular aqueous environment [19]. 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 (26 meq/l).

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) [20]. VFA concentration in anaerobic system acts as good electron donors for SRB [21]. VFA has shown an initial increase in the outlet (Figure 9) and gradually decreased indicating the conversion of VFA (from 26 to 5 meq/l) signifying the effectiveness of microbial activity. It was recommended that desirable operating range of VFA is 0-8.3 meq/l [22].

Considerable reduction in outlet VFA concentration was observed, indicating the effective functioning of methanogenic bacteria. After steady state conditions, outlet VFA approached near 7 meq/l. Concomitant decrease in VFA concentration in the reactor system facilitated effective degradation of the substrate. VFA accumulation results in unbalanced microbial consortia, which is detrimental in the anaerobic process operation, leading to the total system failure [23, 24]. 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.

6. Conclusion

The study demonstrated the applicability of UASB system for treating Metorolol contaminated wastewater. Metoprolol removal rate up to 69% was observed in the system operation. 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.

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