Biotreatability studies of pharmaceutical wastewater using an anaerobic suspended film contact reactor

S. Venkata Mohan, R.S. Prakasham, B. Satyavathi, J. Annapurna and S.V. Ramakrishna
Biochemical and Environmental Engineering Group, Indian Institute of Chemical Technology, Hyderabad 500 007, India

Abstract The pharmaceutical industrial effluents, which include several organic solvents and other toxic chemicals, are generally treated by aerobic process, which is cost intensive in nature. The alternative anaerobic route to degrade the toxic effluents is attractive due to the lower cost of treatment and the generation of gas, which can supplement the energy requirements. There are few reports on the anaerobic treatment of the pharmaceutical effluents. In the present investigation, the effluents from a bulk drug industry, which utilizes several organic chemicals, have been taken to assess their applicability for anaerobic treatment. The organic loading rates were varied from 0.25 kg/m³/day to 2.5 kg/m³/day and the COD reduction was found to be in the range of 60 to 80%. Long term operation of an anaerobic suspended film contact reactor carried out with 1.25 kg/m³/day was found to be optimum. The biogas generated during the degradation process was monitored and the methane content was found to be 60–70%.

Introduction

Recent focus on renewable energy points towards anaerobic wastewater treatment technology for environmental protection and viable alternatives to combat the present day energy crisis. The anaerobic process is very much favorable for high strength wastewater, where aerobic oxidation of organic matter would result in higher energy consumption and production of huge quantities of sludge. Engineers worldwide focused their interest on advanced water treatment, particularly after the development of high rate anaerobic reactors. New anaerobic technology, with high rate reactors extends to benefit anaerobic treatment of low and medium strength effluents, substantially reducing the cost of treatment. The most important merits of anaerobic treatment are the ability to treat high strength wastes, low energy input, low sludge yield, low nutrient requirement, low operating cost, low space requirement and net benefit of energy generation in the form of biogas (Stafford and Wheatley, 1979; Pfeffer, 1979; Yu and Gu, 1996). Moreover, anaerobic treatment is found to be a feasible option for pretreatment of high strength waste for further treatment by aerobic means. Various anaerobic systems viz., anaerobic contact reactor, upflow anaerobic sludge blanket reactor, fluidized bed reactor, anaerobic filter, fixed film reactor, etc. (Collins and Gilliland, 1974; Gosh and Pohland, 1974; Stafford and Wheatley, 1979; Pfeffer, 1979; Khan et al., 1982; Sache et al., 1982; Ferranti et al., 1986; Berrueta and Lastrillon, 1992; Rebac et al., 1997; Benitez et al., 1999; Yu and Gu, 1996) are developed to treat the effluents of different mixtures. However, the reactors composed of fixed film and filters affect the operation by clogging and the reactors, such as upflow sludge blanket and fluidized bed, possesses operational problems with the mechanical moving parts in addition to the continuous monitoring. In contrast, the contact process is capable of dealing with the high strength waste without any moving parts and continuous monitoring.

Anaerobic technology is found to be more reliable for treating waste of distilleries, paper and pulp, tanneries, textile, food processing, and pharmaceutical industries ranging from high strength waste to low strength waste (Parthasarthy et al., 1967; Pfeffer, 1979;
The main objective of this investigation was to study the performance of an anaerobic suspended film contact reactor (ASCR) in degradation of high strength chemical wastes. This was studied at different organic loading rates by analyzing the various related parameters such as COD removal, alkalinity, pH and gas production. We showed that pharmaceutical wastes can be treated by this reactor up to 80% and the performance of the reactor depends upon the organic loading.

Materials and method

Reactor design

The basis for the anaerobic suspended film contact reactor (ASCR) design is to ensure effective contact with the anaerobic biomass in suspended form with the organic load to achieve high organic removal. To achieve this the inlet feed was introduced through the bottom of the reactor by which the settled sludge will be in continuous motion in the reactor. This enables the organic substrate to have good contact with the suspended film of the active biomass to ensure effective degradation. Also, the feed introduced in the bottom of the reactor will pass through the reactor from the bottom in a phased manner for the period of the hydraulic retention time.

The laboratory scale anaerobic suspended film contact reactor was designed to have total volume of 10 L with a working volume of 8 L. The reactor was made of Borosil glass with a provision for inlet and outlet arrangements and operated at a constant mesophilic temperature of 35±2°C. The reactor was covered with a black polythene sheet to maintain effective anaerobic conditions in the reactor. The feed was pumped by means of a peristaltic pump (Watson and Marlow 101/UR). The flow rate of one litre per day was maintained throughout the study to give a hydraulic reaction time (HRT) of 8 days. The wastewater was introduced at the bottom of the reactor and the outlet was collected from the top of the reactor through the overflow from the liquid gas separator. The gas produced was measured using a wet gas meter.

Analytical methods

During the reactor operation, the characteristics of the inlet and outlet were measured daily for COD, pH, alkalinity and sulphates. In addition to this, gas production volume and its composition was also measured. The gas composition was analyzed using Gas Chromatography (Necon). All the solutions used were made with glass distilled water. All the chemicals used were of analytical reagent grade. Colorimetric analysis was performed by a Spectrophotometer (CECIL 202 (2000 series)).

Characteristics of the wastewater

The pharmaceutical wastewater from a large bulk drug-manufacturing unit is used as feed for the anaerobic reactor. The characteristics of the wastewater used are depicted in Table 1. The wastewater contains large numbers of aromatic and aliphatic organic chemicals in addition to inorganic chemicals. The BOD/COD ratio of the wastewater is in the range of 0.4 to 0.6m, which is amenable to anaerobic treatment.

Results and discussion

Startup of the reactor

To start up the reactor, two litres of active anaerobic seed sludge from an active anaerobic unit was inoculated for acclimatization with 6 L of synthetic feed (COD 1600 mg/L) (Glucose – 30 g/L; \(\text{NH}_4\text{Cl} - 7.5 \, \text{g/L}\); \(\text{KH}_2\text{PO}_4 - 2.5 \, \text{g/L}\); \(\text{K}_2\text{HPO}_4 - 1.0 \, \text{g/L}\); \(\text{NaHCO}_3 - \))
5.5 g/L and Yeast extract – 0.2 g/L) into the reactor to promote the formation of biomass. After 15 days, one litre of synthetic feed per day was added to the reactor in a fed-batch mode process for a period of 10 days. After 25 days, the reactor was introduced to the pharmaceutical wastewater with an organic loading rate of 2 g of COD per day in a continuous mode operation with a hydraulic retention time of 8 days. The reactor was operated at a pH range of 7.2 ± 0.5 and alkalinity = 700 ± 300 mg/l (to reduce sulphate inhibition). The nutrient was supplemented by addition of nitrogen and phosphorus source to the reactor mixer on the basis of organic loading (BOD:N:P = 100:2.5:0.5) for optimum growth of microbial population. The hydraulic retention time of 8 days was fixed to retard the CO₂ toxicity, to control the alkalinity and to achieve optimum methane production and moreover to cut off any possible draining of active biomass (Pfeffer, 1979).

Table 1 Characteristics of the pharmaceutical wastewater

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.65–7.40</td>
</tr>
<tr>
<td>Total alkalinity</td>
<td>1800–2100</td>
</tr>
<tr>
<td>TDS</td>
<td>15500–16700</td>
</tr>
<tr>
<td>VS</td>
<td>6400–6600</td>
</tr>
<tr>
<td>SS</td>
<td>9150–9240</td>
</tr>
<tr>
<td>COD</td>
<td>23700–24500</td>
</tr>
<tr>
<td>BOD₅</td>
<td>11500–12100</td>
</tr>
<tr>
<td>Chlorides</td>
<td>3900–4100</td>
</tr>
<tr>
<td>Sulphates</td>
<td>400–650</td>
</tr>
<tr>
<td>Phosphates</td>
<td>&lt; 98</td>
</tr>
</tbody>
</table>

Reactor operation

The reactor after acclimatization for a period of 25 days, was first operated with an organic loading rate of 2 g of COD per day until steady state condition was achieved. Subsequently the reactor was operated with organic loading rates of 4, 10 and 20 g COD/day for a period of 30 days each. The results obtained from the study were presented in a graphical form and subsequently discussed. Operation of the reactor at different organic loading rates relating COD removal with respect to time are depicted in Figure 1.

It is evident from the figure that COD removal ranging from 30 to 82% was registered for different loading rates. An organic loading rate of 2 g COD/day resulted in 66% of COD removal with a COD utilization rate of 1.34 g of COD/day and 4 g of COD/day yielded 55%

Figure 1 Performance of the Anaerobic Suspended Film Contact Reactor at different organic loading rates
of COD removal with a COD utilization rate of 2.24 g of COD. While 10 g COD/day yielded highest percentage of COD removal (83%) with COD utilization rate of 8.2 g of COD/day and subsequent increase to 20 g of COD/day yielded only 33% of COD removal with a COD utilization rate of 6.4 g of COD/day. From the above data, it can be confirmed that increase in organic loading rate from 2 to 10 g of COD/day increased the COD removal rate and the subsequent increase from 10 to 20 g of COD/day decreased the COD utilization rate from 80% to 30%. Therefore the present anaerobic reactor designed can take the organic loading rate of 10 g of COD/day (optimum loading rate), and subsequent increase with suppress the activity. The low COD removal rate at low organic loading rate may be attributed to the imbalance between the availability of organic matter and the load of microorganisms. In case of higher organic load (10g of COD/day) there may exist a balance (equilibrium) between the availability of organic load and mass of microorganisms, resulting in higher utilization of the organic load. At an organic loading rate of 20 g of COD/day, the reduction in COD removal may be due to the micro-toxic effect of the high organic load on the microorganisms.

The amount of COD removed (g of COD/day) was related to the organic loading rate (Figure 2). This trend of the plot visualized a gradual increase in the organic utilization rate up to 10 g of COD/day and subsequently the removal rate has dropped. From the above discussion, COD removal rate is dependent on the organic loading rate and the steady state condition is governed by the operation time which subsequently is directly proportional to the loading rate.

Since maximum COD removal was observed at 10 g COD/day loading the reactor was further operated for a period of 100 days. The COD removal rate at this organic loading rate is presented in Figure 3. From the figure, it is indicated that COD removal rate was stabilized after a period of 50 days at 83–84% of COD removal and remained more or less constant thereafter.

During the operation of the reactor, the pH and alkalinity of the effluent were analysed. The pH value of the effluent was between 8.2 to 6.8 which is well within the optimum pH range for methanogenesis. The same was the case for all the organic loading rates. Occasional peak pH values (above 7.5) were registered. Upon long term operation, the alkalinity was stabilized at 1500 mg/L after an initial variation of 500 mg/L to 1500 mg/L at all the organic loading rates, which is in the optimum range for anaerobic operation. The alkalinity values for organic loading rate of 10 g COD/day are presented in Figure 4.
Biogas production

The production of biogas in the anaerobic organic degradation makes this process a feasible alternative to aerobic treatment methodology. The biogas produced was daily monitored for each organic loading and the average value is presented in the graph (Figure 5). After a satisfactory start, the reactor was operated until a steady state performance was reached as indicated by a constant gas production rate (± 5%) and effluent COD concentration (± 8%). The amount of COD converted to methane ranged from 69% to 71%, with an average of 70%, as the organic loading rate was increased from 2 to 10 g of COD/day (COD utilization rate of 1.34 to 8.2 g of COD/day). A substantial decrease in the gas production was observed as the organic loading rate was increased from 10 to 20 g of COD/day (COD utilization rate from 8.2 to 6.4 g COD/day). The specific methane production rate ranged from 0.29 to 0.33 m$^3$ CH$_4$/kg COD removed, which was comparable to data reported in the literature (Yu and Gu, 1996), such as 0.25 to 0.36 m$^3$ CH$_4$/kg COD removed. The gas chromatography analysis showed it was composed of 70% methane, 26% CO$_2$ and 4% N$_2$. Since CO$_2$ is highly soluble in water relative to methane, low HRT greatly affects biogas composition. Assuming saturation concentration of CO$_2$ is achievable, the effluent streams acts as a CO$_2$ removal mechanism (Farhantel et al., 1997), which lowers the relative CO$_2$ content in the biogas. The presently adopted HRT of 8 days seems to be the optimum to retard the CO$_2$ toxicity for the present system with relatively uniform CO$_2$ content (36–38%) at all organic loading rates throughout the study. Based on the above data, the potential usable energy is found to be 9–12 kJ/kg of COD by this reactor, an important consideration, especially in light of energy supplied to the treatment facility.
References