

Pre-treatment of Antibiotic Wastewater Using an Anaerobic Reactor

Chelliapan S.¹ and Golar S.²

¹UTM Razak School of Engineering and Advanced Technology, Universiti Teknologi Malaysia (International Campus),
Jalan Semarak, 54100, Kuala Lumpur, MALAYSIA

²Environmental Engineering Group, School of Civil Engineering and Geosciences, University of Newcastle upon Tyne,
Newcastle upon Tyne NE1 7RU, UK

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Abstract

Effluents from manufacturing operations in the pharmaceutical industry, such as antibiotic formulation, usually contain recalcitrant compounds. An approach towards appropriate technology for the treatment of pharmaceutical wastewaters has become imperative due to strict water quality legislation for environmental protection. Typically, pharmaceutical wastewater is characterized by high chemical oxygen demand (COD) concentration and some pharmaceutical wastewaters can have COD as high as 80,000 mg.L⁻¹. Due to high organic content, anaerobic technology is a promising alternative for pharmaceutical wastewater treatment. Results from literature on the anaerobic treatment of antibiotic wastewaters demonstrate that anaerobic treatment is not commonly used as the means for treating pharmaceutical wastewaters containing antibiotics. Consequently, in the present study, an Up-Flow Anaerobic Packed Bed reactor was employed to treat pharmaceutical wastewater containing antibiotics. The effect of organic loading rate (OLR) was assessed by adjusting feed substrate concentration and hydraulic retention time (HRT). The reactor performance was characterized in terms of COD removal, volatile fatty acid (VFA), gas production, methane yield and pH. Results from the study showed a COD reduction of 60 – 70% at an OLR of 1.5 – 4.6 kg COD.m⁻³.d⁻¹, suggesting the biomass had acclimated to the antibiotics. However, when the OLR was increased the COD removal efficiency decreased gradually until only around 50% soluble COD removal was observed at an OLR of 5.6 kg COD.m⁻³.d⁻¹, indicating as OLR was increased, the increasing load of antibiotics may have affected the methanogens.

Keywords: Antibiotic wastewater, anaerobic reactor, methanogens.

Introduction

Industrial wastewater presents a potential hazard to natural water system. This wastewater contains organic matter, which is toxic to the various life forms of the system. Industrial wastewater has complex mixture of chemicals whose behaviour toward biological system can be different¹. Treatment of these wastes is therefore of paramount important. Wastewaters produced from pharmaceutical industries pose several problems for successful biological treatment. These wastewaters contain relatively high levels of suspended solids and soluble organics, many of which are recalcitrant. Furthermore, changes in production schedules lead to significant variability of the wastewater flow rate, its principal constituents and relative biodegradability². In the past, application of the anaerobic treatment process has been largely confined to the stabilization of sewage sludge. However, interest in the process has been expanding over recent years as a result of the increasing demand for energy and the growing problems of pollution control.

Anaerobic packed bed reactor were first proposed as a treatment process by Young and McCarty³ and is similar to a trickling filter biomass is attached on inert support material in biofilm form. The material can be arranged in various confirmations, made out of different matter (plastics, granular activated carbon (GAC), sand, reticulated foam, polymers, granite, quartz and stone) and can be packed in two configurations (loose or modular).

The reactors can be operated in up-flow or down-flow feed mode^{4,5}.

A fully packed up-flow anaerobic packed bed offers exceptional benefits by providing a quiescent inlet region for large dense biomass aggregates to develop, which are not prone to washout. Furthermore, the reactor also provides a surface, which facilitates biofilm accumulation. These advantages assure a shorter start-up period due to greater amount of retained inoculum⁶. A granule inoculum is preferable, but not necessary since ordinary municipal waste anaerobic sludge can be used if a start-up time is not imperative.

Therefore, the aim of present investigation was to determine the feasibility of using an up-flow anaerobic packed bed reactor system as a pre-treatment option for a pharmaceutical wastewater containing antibiotics by adjusting feed substrate concentration and hydraulic retention time (HRT).

Material and Methods

Up-flow anaerobic packed bed reactor: The reactor (figure 1) is a PVC cylindrical reactor having a capacity of 22.5 L with plastic media packing. The influent wastewater entered through an internal downcomer tube in the headplate that extended to within 20mm of the reactor base and allowed feed to flow upward through the sludge bed. The walls of the reactors were wrapped with a tubular PVC

water-jacket, 15mm internal diameter, to maintain the reactor temperature at 37°C. Peristaltic pumps (Watson Marlow 100 series) were used to control the influent feed rate. Gas production was monitored using an optical gas-bubble counter (Newcastle University) having a measurement range of 0 – 1.5 L.hr⁻¹ and precision within ±1%.

Antibiotic wastewater and reactor operation: The wastewater was supplied by a pharmaceutical production company and had the following characteristics; soluble COD, 11,000 ± 1000 mg.L⁻¹; Total Kjeldahl Nitrogen (TKN), 464 ± 80 mg.L⁻¹; and pH, 5.2 – 6.8. Initially, the start-up of reactor was established with a brewery wastewater feed due to its ease of degradation, high COD values and well-established use in continuous anaerobic reactors. Once the reactor had reached steady state the feed to the reactor was supplemented incrementally with antibiotic wastewater. Table 1 shows the operating conditions of the study.

Table- 1
Operating conditions of the up-flow anaerobic packed bed reactor

| Day | Mean OLR (kg COD.m ⁻³ .d ⁻¹) | Mean HRT (d) |
|-----------|---|--------------|
| 1 - 5 | 0.5 | 5.6 |
| 6 - 9 | 0.75 | 5.6 |
| 10 – 66 | 1.50 | 5.6 |
| 67 – 80 | 2.20 | 4.1 |
| 81 – 89 | 2.95 | 4.1 |
| 90 – 99 | 4.6 | 2.6 |
| 100 – 103 | 5.6 | 2.0 |
| 104 - 109 | 5.6 | 2.0 |

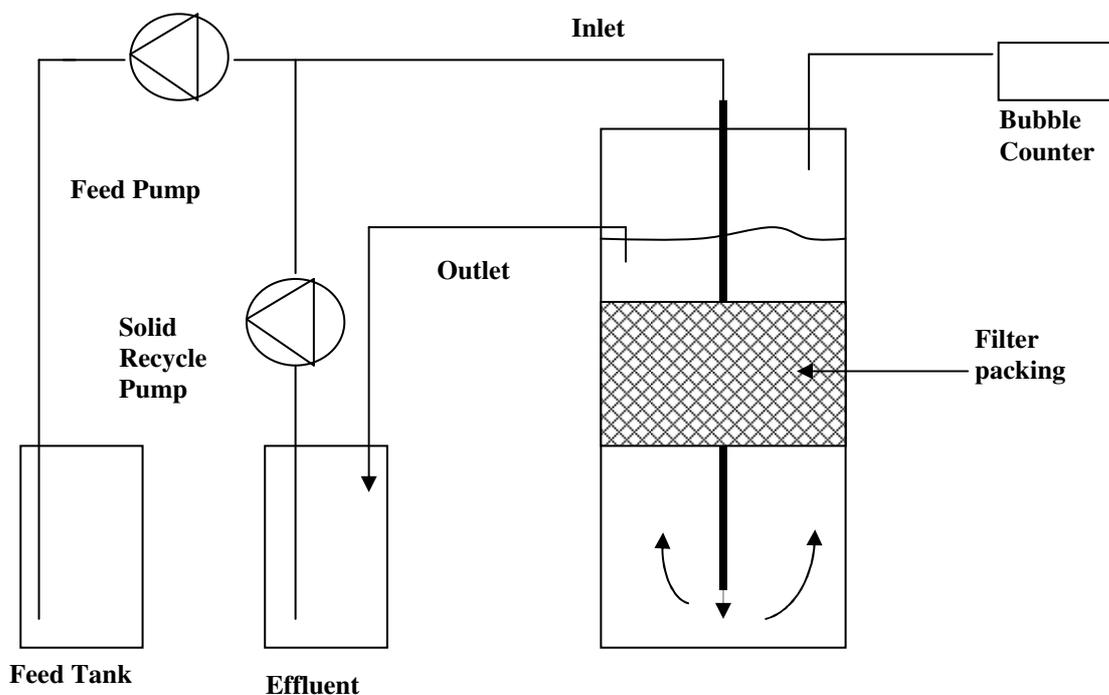


Figure- 1
Up-flow anaerobic packed bed reactor set-up

Chemical analysis: Supernatant liquor and gas samples were taken for chemical analysis. In addition, gas production rate was also determined. Sample analysis included chemical oxygen demand (COD), pH, alkalinity, total Kjeldahl nitrogen (TKN), ammonium nitrogen (NH₃-N), suspended solids (SS), volatile suspended solids (VSS), all according to Standard Methods⁷. Available PO₄-P was determined by ion-chromatography (Dionex, DX-100 Ion Chromatograph), volatile fatty acids (VFA) by gas-liquid chromatography (Unicam 610 Series Gas Chromatograph with auto-injector and PU 4811 computing integrator).

Results and discussion

COD Removal: Figure 2 shows temporal changes in the total COD removal of the up-flow anaerobic packed bed reactor treating antibiotic wastewater. Initial fluctuations were attributed to technical problems with the peristaltic feed pump. At a reactor OLR of 1.50 kg COD.m⁻³.d⁻¹ (HRT 5.6 d), the soluble COD reduction was around 80 - 90%. However, when the OLR was increased to 2.20 and 4.6 kg COD.m⁻³.d⁻¹ the COD removal efficiency decreased gradually until 60 - 70% soluble COD removal was observed. Further increase of the OLR resulted in only

around 50% soluble COD removal was observed at an OLR of 5.6 kg COD.m⁻³.d⁻¹, signifying as OLR was increased; the increasing load of antibiotics affected the methanogens. Antibiotic wastewaters containing a high proportion of spent fermentation broths have been shown to require long HRT for efficient treatment⁸, presumably on account of their complex organic carbon content, and this is probably limits the packed bed reactor performance at lower HRT (2 d). The above results are consistent with observations made by Martinez⁹ in an Up-Flow Anaerobic Sludge Bed (UASB) treating pharmaceutical wastewater containing Penicillin G antibiotics, who found that the COD removal efficiency was 90% at an OLR of 1.5 kg COD.m⁻³.d⁻¹ and HRT 11 d. However, when the OLR was increased to 2.09 kg COD.m⁻³.d⁻¹ by reducing the HRT to 7 d, the COD removal efficiency dropped dramatically to 70%. Nandy and Kaul¹⁰ have demonstrated that substrate removal efficiency increases with increase in HRT in

anaerobic treatment of herbal-based pharmaceutical wastewater using fixed-bed reactor.

Volatile Fatty Acid (VFA) Profile: The total VFA concentration of the up-flow anaerobic packed bed reactor is shown in Figure 3 and indicates a low concentration of total VFA (average 350 mg.L⁻¹) was present in the reactor effluent when operated at OLR in the range 0.50 to 1.50 kg COD.m⁻³.d⁻¹ (table 1). However, the VFA concentration increased to 1000 mg.L⁻¹ when the reactor OLR was increased to 4.6 kg COD.m⁻³.d⁻¹. Further increases in reactor OLR, by reducing the HRT, resulted in higher VFA concentrations being produced in the effluent. The highest of these were found when OLR was 5.6 kg COD.m⁻³.d⁻¹ with an average value of 1,200 mg.L⁻¹. According to previous studies, higher organic loadings and shorter HRTs generally provide the optimum conditions for acid-forming bacteria and greatly affected VFA production^{11,12}.

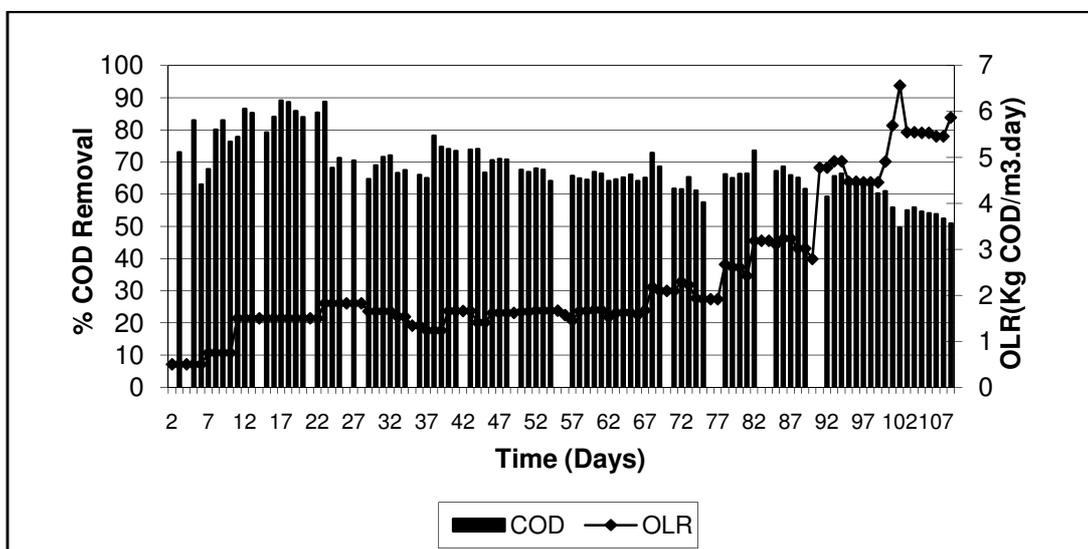


Figure-2

COD reduction (%) of the up-flow anaerobic packed bed reactor treating pharmaceutical wastewater at different OLR

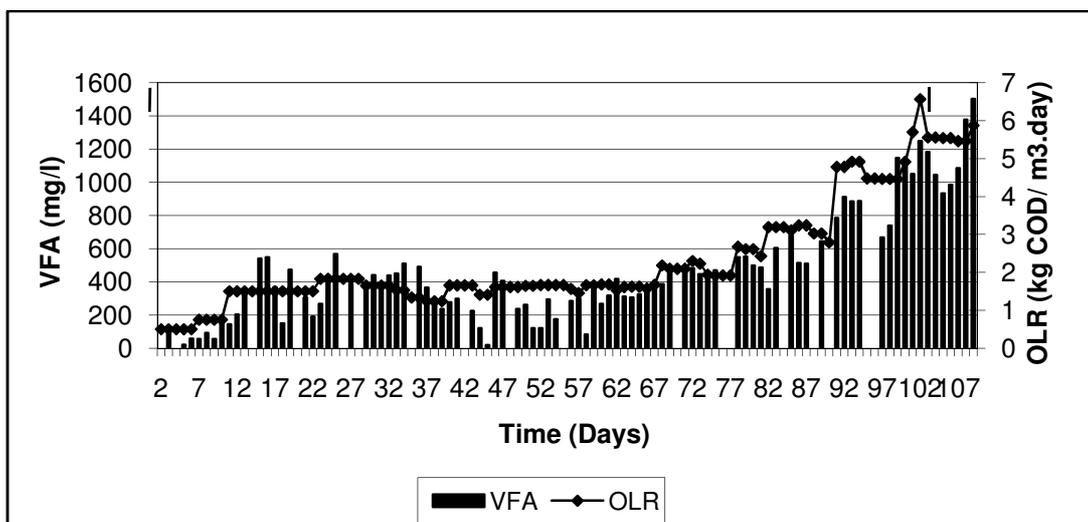


Figure- 3

Total VFA profile in the up-flow anaerobic packed bed reactor treating pharmaceutical wastewater at different OLR

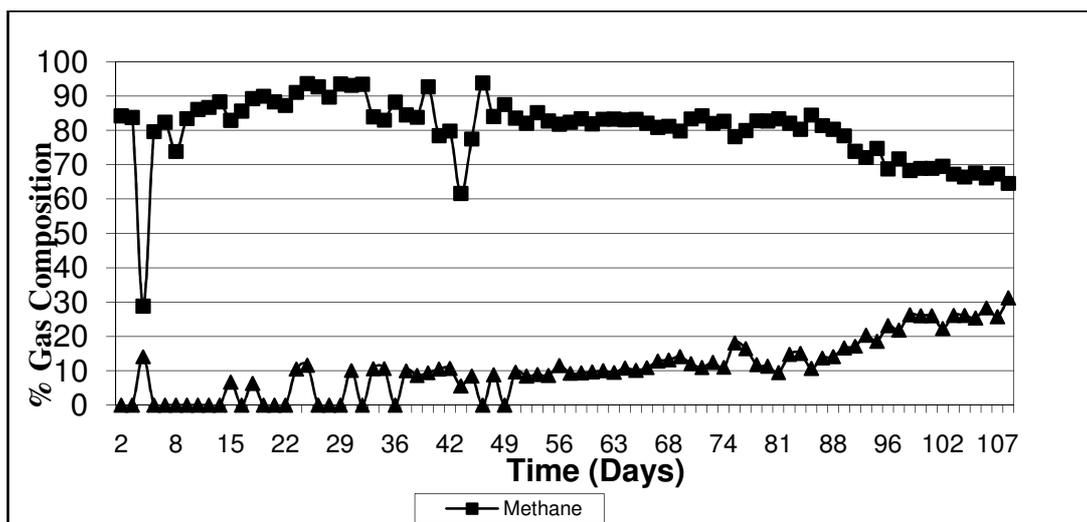


Figure -4
Proportion of CH₄ (%) and CO₂ (%) in the biogas in the up-flow anaerobic packed bed reactor treating pharmaceutical wastewater

Biogas Composition: Biogas production (data not presented) was monitored in the anaerobic reactor throughout the operation of the reactor, mainly for the assessment of methanogenic activity. Figure 4 illustrates the methane productivity and showed that the reactor had relatively higher levels of methane production (around 80 – 90%) during the period of low OLR (0.5 – 2.95 kg COD.m⁻³.d⁻¹), but this was reduced to 65% when the OLR was increased to 5.6 kg COD.m⁻³.d⁻¹. Considering the changes in pH (data not presented), and VFA concentration, that occurred with these step increases in OLR it is likely that a large part of the methanogenic population was adversely affected by physico-chemical conditions created by the acidogens at the higher levels of OLR.

Conclusion

In conclusion, this study has demonstrated that the up-flow anaerobic packed bed reactor can be used effectively as an option for pre-treatment of antibiotic wastewaters that contain antibiotics. Whilst COD degradation efficiency might be affected by the complexity and variability of the real pharmaceutical wastewater, long HRT in the packed bed reactor can lessen these effects.

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