# Anaerobic Pre-treatment of Pharmaceutical Wastewater using Packed Bed Reactor

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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. Consequently, in the present study, an anaerobic packed bed reactor was employed to treat highly polluted pharmaceutical wastewater. 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 chemical oxygen demand (COD) removal, volatile fatty acid (VFA), gas production, methane yield and pH. At an average reactor OLR of 1.58 kg COD.m$^{-3}$.d$^{-1}$ (HRT 5.6 d), the average soluble COD reduction was 73%. However, when the OLR was increased to 2.21 and 4.66 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 53% soluble COD removal (average) was observed at an OLR of 5.71 kg COD.m$^{-3}$.d$^{-1}$, signifying as OLR was increased; the increasing load of complex pharmaceutical wastewater may have affected the methanogens.**

***Index Terms***— **anaerobic digestion, anaerobic packed bed reactor, methanogens, pharmaceutical wastewater**

## I. 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 different [1]. 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 biodegradability [2].

Anaerobic digestion is the decomposition of organic and inorganic matter by micro-organisms in the absence of molecular oxygen. It has been used for over a century in the treatment of domestic and industrial wastewaters. The anaerobic digestion process (Fig. 1) involves the biological conversion, in a step-wise fashion, of organic material to various end products including methane ($CH_4$) and carbon dioxide ($CO_2$). The process offers several advantages and disadvantages over other treatment methods [3]:

Advantages:

1) Good removal efficiency, even at high loading rates and low temperatures.
2) The construction and operation of these reactors is relatively simple.
3) It can be easily applied on either a very large or a very small scale.
4) When high loading rates are accommodated, the area needed for the reactor is small.
5) Energy is produced during the process in the form of methane.
6) The sludge production is low, when compared to aerobic methods, due to the slow growth rates of anaerobic bacteria.
7) Especially in the case of sewage, an adequate and stable pH can be maintained without the addition of chemicals.

Disadvantages:

1) Pathogens are only partially removed. Nutrients removal is not complete and therefore a post treatment is required.
2) Due to the low growth rate of methanogenic organisms, the start-up takes longer as compared to aerobic processes, when no good inoculum is available.
3) Hydrogen sulphide is produced during the anaerobic process, especially when there are high concentrations of sulphate in the influent.
4) Post-treatment of the anaerobic effluent is generally required to reach the discharge standards for organic matter, nutrients and pathogens.

Anaerobic packed bed reactor were first proposed as a treatment process by Young and McCarty [4] and is similar to a trickling filter biomass is attached on inert support material in bio-film form. The material can be arranged in various confirmations, made out of different matter (plastics, granular activated carbon (GAC), sand reticulated foam

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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 [5, 6].

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 bio-film accumulation. These advantages assure a shorter start-up period due to greater amount of retained inoculum [7]. 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.

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

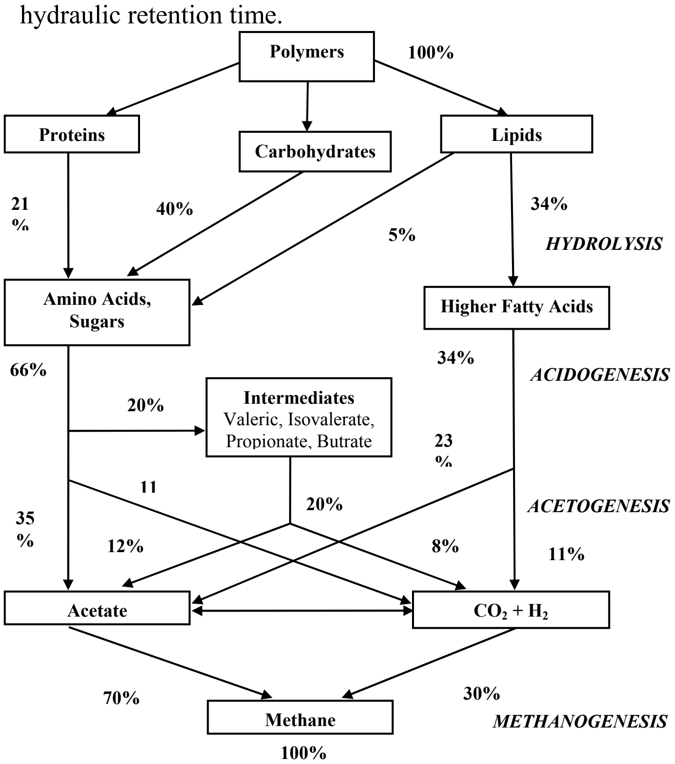


Figure 1. Reaction sequence for the anaerobic digestion of complex macromolecules with COD percentage [8]

## II. Materials And Methods

### A. Anaerobic packed bed reactor

The anaerobic packed bed reactor (Fig. 2) is a PVC cylindrical reactor having a capacity of 22.5 L with plastic media packing. The influent wastewater entered through an internal down-comer tube in the head-plate that extended to within 20mm of the reactor base and allowed feed to flow up-ward 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 $^0$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%.

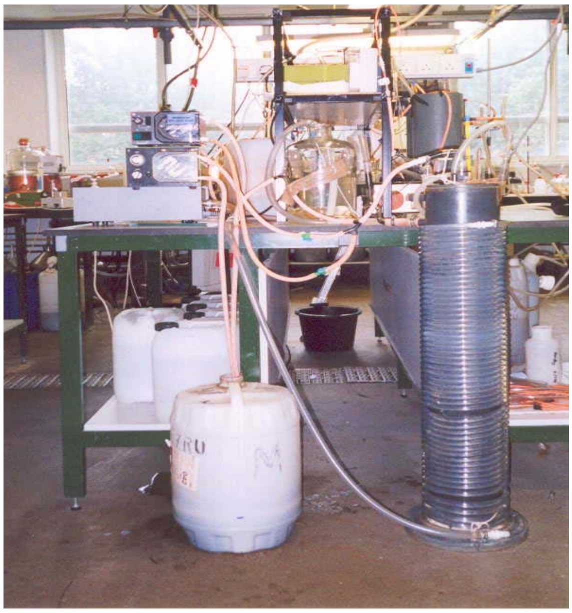

Figure 2. Anaerobic packed bed reactor set-up

### B. Pharmaceutical wastewater

The pharmaceutical 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. The trace elements deficiency of brewery wastewater was corrected by adding a trace elements solution [9], whereas the trace elements deficiency of pharmaceutical wastewater was corrected with a commercial micro-nutrient supplement, Nutromex TEA 310, supplied by OMEX Environmental Ltd., UK, with 0.01mL TEA supplement added for each 5000mg COD.

TABLE 1. Operating conditions of the packed bed reactor

| Day | Mean OLR (kg COD.m$^{-3}$.d$^{-1}$) | Mean HRT (d) |
|---|---|---|
| 1 - 5 | 0.50 | 5.6 |
| 6 - 9 | 0.75 | 5.6 |
| 10 – 66 | 1.58 | 5.6 |
| 67 – 80 | 2.21 | 4.1 |
| 81 – 89 | 3.11 | 4.1 |
| 90 – 99 | 4.66 | 2.6 |
| 100 – 109 | 5.71 | 2.0 |

### C. Reactor operation

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 [10]. The reactor was seeded with anaerobic digested sewage sludge from an anaerobic sludge digester at Hexham Municipal sewage treatment plant, Northumberland, UK. Once the reactor had reached steady state the feed to the reactor was supplemented incrementally with pharmaceutical wastewater. Stronach et al. [11] recommended a start-up strategy for pharmaceutical

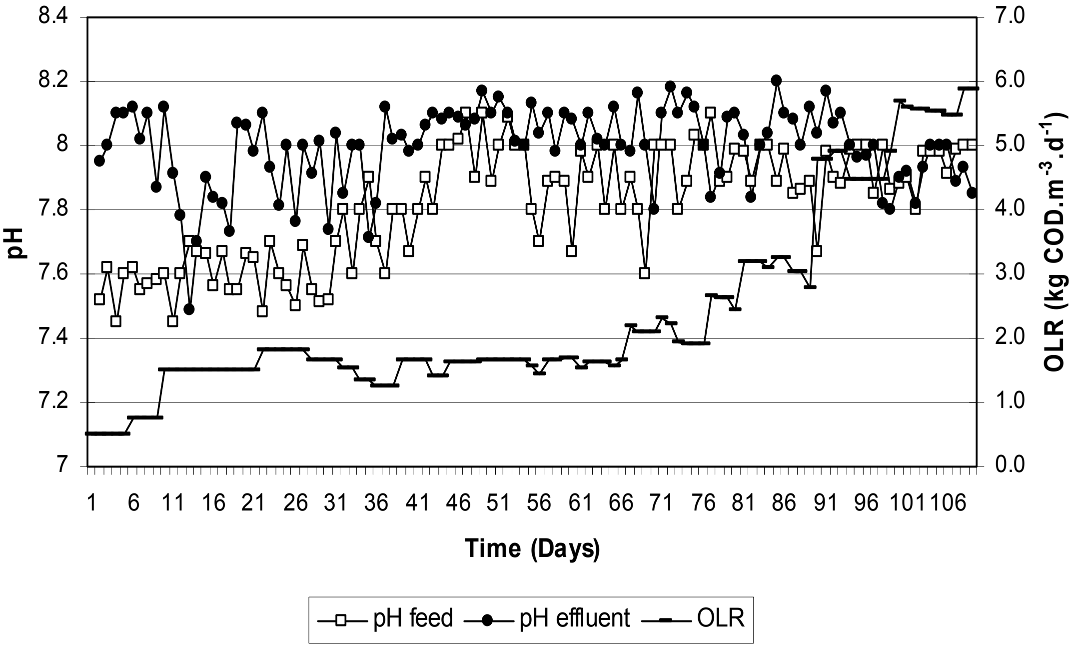


Figure 3. pH profile of the packed bed reactor treating pharmaceutical wastewater at different OLR

wastewater treatment involving gradual replacement of readily degradable substrates with industrial effluents. Table 1 shows the operating conditions of the study. 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 ($NH_3$-N), suspended solids (SS), volatile suspended solids (VSS), all according to Standard Methods [12]. Available $PO_4$-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). Reactor gas composition ($CO_2$ and $CH_4$) was determined by gas chromatography (Becker model 403 Gas Chromatograph with Unicam 4815 computing integrator).

Average values of the measured parameters quoted for each OLR were based on the mean of four data points taken after three HRT periods for each OLR, i.e. when reactor approached near steady-state.

## III. Results And Discussions

### A. *pH profile*

Microbial groups involved in anaerobic degradation have a specific pH region for optimal growth. The desired pH for anaerobic treatment is between 6.6. and 7.6 [13]. Values outside this range can be quite detrimental to the process, particularly to methanogenesis. Therefore, maintaining a suitable and stable pH within the digester should be a major priority for ensuring efficient methanogenic digestion. This is due to the fact that the hydrogen ion concentration has a critical influence on the microorganisms responsible for anaerobic digestion, the biochemistry of digestion, alkalinity buffering and several other chemical reactions affecting the solubility and availability of dissolved ions. The pH levels (Fig. 3) in the effluent of the anaerobic packed bed reactor were generally stable (pH 7.5 – 8.2) during the operational period when the OLR was increased from 0.50 – 5.71 kg $COD.m^{-3}.d^{-1}$. The high pH levels (more than 7.6) in the effluent were due to addition of sodium hydroxide to maintain the buffering capacity in the reactor. Without the addition of an alkaline solution, the pH of the reactor could not be maintained at desired level, especially at higher OLRs (4.66 – 5.71 kg $COD.m^{-3}.d^{-1}$). When an anaerobic process is overloaded an accumulation of VFAs often occurs, resulting in a decrease in the pH of the system if sufficient buffering capacity is not available. Generally, the alkalinity needed to maintain the pH is largely governed by the carbonate equilibrium [14].

### B. *COD removal*

Fig. 4 shows temporal changes in the total COD removal of the packed bed reactor treating antibiotic wastewater. Initial fluctuations were attributed to technical problems with the peristaltic feed pump. At a reactor OLR of 1.58 kg $COD.m^{-3}.d^{-1}$ (HRT 5.6 d), the average soluble COD reduction was around 73%. However, when the OLR was increased to 2.21 and 4.66 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 53% soluble COD removal was observed at an OLR of 5.71 kg $COD.m^{-3}.d^{-1}$, signifying as OLR was increased; the increasing load of complex pharmaceutical wastewater affected the methanogens. Pharmaceutical wastewaters containing a high proportion of spent fermentation broths

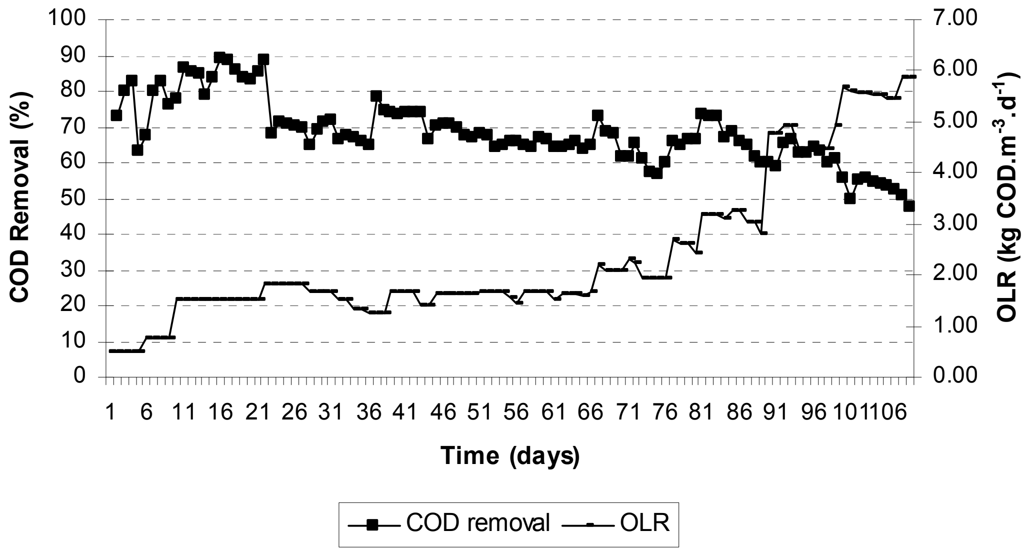


Figure 4. COD reduction (%) of the packed bed reactor treating pharmaceutical wastewater at different OLR

have been shown to require long HRT for efficient treatment [15], 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 Martinez [16] 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%. They also found that an increase in the OLR resulted in the accumulation of hydrogen sulphide (sulphate in the feed was 3200 mg.L$^{-1}$) which affected the efficiency of the reactor. Nandy and Kaul [17] have demonstrated that substrate removal efficiency increases with increase in HRT in anaerobic treatment of herbal-based pharmaceutical wastewater using fixed-bed reactor. Consequently, the drop in treatment efficiency at higher OLR in the packed bed reactor system could be due to reduced HRT (from 5.6 to 2 d).

### *C. Volatile Fatty Acid (VFA) Profile*

It is well documented that high VFA concentrations in the anaerobic processes cause the inhibition of methanogenesis. Under conditions of overloading and in the presence of inhibitors, methanogenic activity cannot remove hydrogen and volatile organic acids as quickly as they are produced. The result is the accumulation of acids and the depression of pH to levels that also inhibit the hydrolysis or acidogenesis phase. It has also been shown that even when process pH is optimal, the accumulation of VFAs may contribute to a reduced rate of hydrolysis of the solid organic substrate. Organic acids such acetic, propionic, butyric and isobutyric are central to evaluating the performance of anaerobic digestion. The total VFA concentration of the packed bed reactor is shown in Fig. 5 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 1.58 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 4.66 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 5.71 kg COD.m$^{-3}$.d$^{-1}$ with an average value of 1,200 mg.L$^{-1}$. At high OLRs and low HRTs, the relatively complex pharmaceutical wastewater caused pre-acidification resulting in accumulation of COD (as VFA), which did not subsequently convert to methane, resulting in an accumulation of VFA. In another word, short contact times between the substrate and biomass could have been favour the activity of acidogens, leading to a low conversion of substrate to methane by the biomass flocs, and substantial amounts of VFAs being washed through the reactor into the effluent. According to previous studies, higher organic loadings and shorter HRTs generally provide the optimum conditions for acid-forming bacteria and greatly affected VFA production [18, 19].

### *D. Biogas composition*

The effect of organic loading rate on biogas composition can be used as a direct indicator of the vitality of the anaerobic digester. Biogas composition was monitored in the anaerobic packed bed reactor throughout the operation, mainly for the assessment of methanogenic activity. Fig. 6 illustrates the methane productivity and showed that the reactor had relatively higher levels of methane composition (around 80 – 90%) during the period of low OLR (0.5 – 3.11 kg COD.m$^{-3}$.d$^{-1}$), but this was reduced to 65% when the OLR was increased to 5.71 kg COD.m$^{-3}$.d$^{-1}$. Considering the changes in VFA concentration, that occurred with these step increases in OLR it is likely that a large part of the methanogenic population was affected by physico-chemical conditions created by the acidogens at the higher levels of OLR.

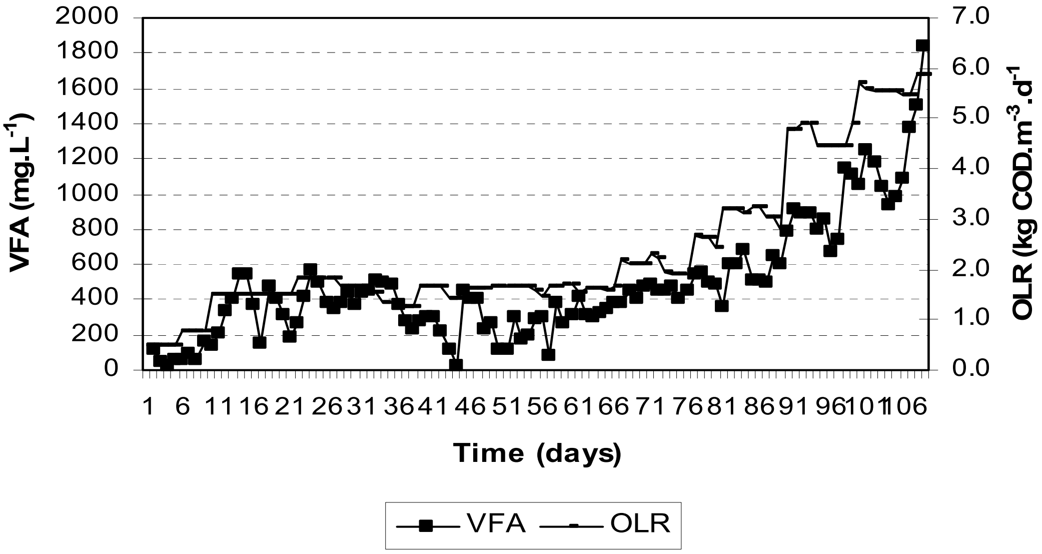


Figure 5. Total VFA profile in the packed bed reactor treating pharmaceutical wastewater at different OLR

Figure 6. Proportion of CH4 (%) and CO2 (%) in the biogas in the anaerobic packed bed reactor treating pharmaceutical wastewater

## IV. Conclusions

In conclusion, this study has demonstrated that the anaerobic packed bed reactor can be used effectively as an option for pre-treatment of pharmaceutical wastewaters. Using a packed bed reactor, the pharmaceutical wastewater could be pre-treated, with an acclimated biomass, providing sufficiently high degradation of COD that the treated effluent could be discharged to the sewer for further treatment. Changes in the HRT affected the operation of the reactor by increasing acidogenic activity at the increased OLR which generally resulted in reduced methanogenic activity; increased COD and VFA in the effluent of the reactor. Efficient degradation may be dependent on the composition of the pharmaceutical wastewater which was variable from batch to batch and may have upset the degradation process. The treatment efficiency of the reactor was affected at high OLRs probably due the complexity of the pharmaceutical wastewater. 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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