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Anaerobic Biotechnology for Pharmaceutical Wastewater Treatment

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ABSTRACT

The wastewater generated from the pharmaceutical industry contain high organic load and the treatment are primarily carried out using two major types of biological methods; aerobic and anaerobic. However, due to high strength, it is infeasible to treat some pharmaceutical wastewater using aerobic biological processes. As an alternative, an anaerobic process is preferred to remove high strength organic matter. Anaerobic wastewater treatment is considered as the most cost effective solution for organically polluted industrial waste streams. In particular the development of the high rate systems, in which hydraulic retention times (HRT) are uncoupled from solids retention times (SRT), has led to a worldwide acceptance of anaerobic wastewater treatment. In this paper, a brief literature on anaerobic digestion, anaerobic reactor technology and existing anaerobic treatment of pharmaceutical wastewater are presented. A case study of a laboratory investigation into the treatment of pharmaceutical wastewater containing antibiotics in an Up-Flow Anaerobic Stage Reactor (UASR) was also given. Specifically, it was determined whether a UASR could be used as a pre-treatment system at an existing pharmaceutical production plant. Results from this study showed a chemical oxygen demand (COD) reduction of 70 – 75% was achieved in the UASR.

Keywords: anaerobic digestion; anaerobic reactor; pharmaceutical wastewater; antibiotics

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INTRODUCTION

Anaerobic Digestion

Anaerobic digestion is the decomposition of organic and inorganic matter by microorganisms 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 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 [1]:

Advantages

- Good removal efficiency, even at high loading rates and low temperatures.
- Construction and operation of reactor is relatively simple.
- Easily applied on large or small scale.
- Area needed for reactor is small at high loading rates.
- Energy is produced during the process in the form of methane.
- Sludge production is low compared to aerobic processes due to slow growth rates of anaerobic bacteria.

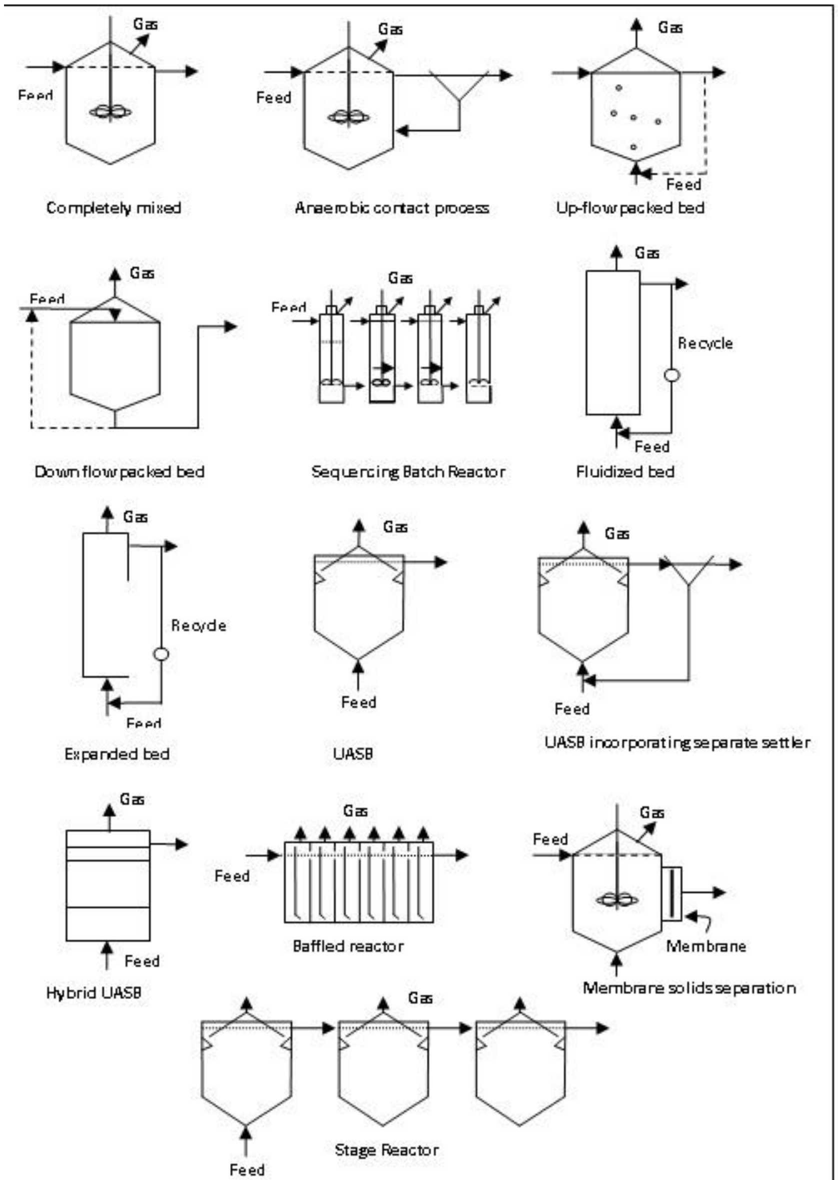
Disadvantages

- Reactor start-up takes longer compared to aerobic processes.
- Production of hydrogen sulphide during anaerobic process, when high concentrations of sulphate in the influent.
- Post-treatment is required to reach discharge standards for organic matter, nutrients and pathogens.

Anaerobic Reactor Technology

In the past, application of the anaerobic treatment process has been largely confined to the stabilization of sewage sludge, mainly due to the lack of fundamental knowledge of the process and its limitations. 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. Several processes have been developed in order that anaerobic fermentation of wastes may be carried out more efficiently. These processes can be classified either as suspended growth processes or attached growth processes (also known as fixed-film processes) depending on whether the biomass is in suspension or attached to some inert media. Suspended growth processes that have been developed for the anaerobic treatment of wastes include conventional (completely mixed) anaerobic digesters, the anaerobic contact process, the up-flow anaerobic sludge blanket (UASB) reactor and the membrane anaerobic reactor systems. The attached growth processes that have been developed for the same purpose includes the anaerobic filter (anaerobic packed-bed reactor), the anaerobic rotating biological contactor (ARBC) and the anaerobic expanded and fluidized bed reactors. An illustration of the anaerobic reactor configurations is given in Figure 1.

Figure 1. Anaerobic reactor configurations



Existing Anaerobic Treatment of Pharmaceutical Wastewater

Effluent from pharmaceutical wastewater normally treated using flocculation, flotation, coagulation, filtration, settling, ion exchange, carbon adsorption, detoxification of active ingredients by oxidation (using ozone wet air oxidation ultraviolet systems or peroxide solutions), and biological treatment (using trickling filters, anaerobic, activated sludge, and rotating biological contactors). In the following paragraphs, the use of anaerobic technology for pharmaceutical wastewater is discussed.

There are few reports on the treatment of industrial pharmaceutical wastewater under anaerobic conditions. Table 1 shows treatment of various pharmaceutical wastewater using anaerobic processes. Fox and Venkatasubbiah [3] have demonstrated the use of anaerobic baffled reactor (ABR) in the treatment of high sulphate containing pharmaceutical wastewater (Isopropyl Acetate fermentation). These workers found that by inserting a sulphide oxidation unit, the COD removal efficiency could be increased up to 50% at HRT 1 d.

Table 1

Anaerobic Reactor	Type of Pharmaceutical Wastewater	COD Rem. (%)	References
ABR	Antibiotic formulation (Ampicillin, Aureomycin)	77 - 90	[12]
UASB	Antibiotic formulation (Penicillin)	90	[11]
SBR	Phenols and O-Nitroaniline	95 - 97	[10]
UAF	Chemical synthesis	65	[9]
Fluidized bed	Cephalexin drug, anti-osmotic drug	88.5	[7, 8]
Fixed-film fixed-bed	Herbal-based	76 – 98	[6]
Suspended film contact	Bulk drug (aromatic, aliphatic)	60 – 80	[5]
Sequencing batch	Swine manure slurry containing antibiotics	80	[4]
ABR	Isopropyl Acetate	50	[3]

Massé et al. [4] have explored the effect of antibiotics on psychrophilic anaerobic digestion of swine manure slurry in sequencing batch reactors (SBRs). In their research, six antibiotics, Tylosin, Lyncomycin, Tetracycline, Sulphamethazine, Penicillin and Carbadox, were individually added to a pig diet. It was concluded that only Penicillin and Tetracycline had an inhibitory effect on methane production.

Venkata Mohan et al. [5] have demonstrated the use of anaerobic suspended film contact reactor (ASFCR) in the treatment of pharmaceutical wastewater from large bulk drug manufacturing unit (aromatic and aliphatic organic chemicals). The organic loading rates were varied from 0.25 to 2.5 kg $COD.m^{-3}.d^{-1}$ and the COD reduction was in the range of 60 to 80% with methane content of around 60 - 70%.

Nandy and Kaul [6] demonstrated anaerobic pre-treatment of herbal-based pharmaceutical wastewater (e.g. herbs, fruits, flowers, roots, seeds, etc) using fixed-film reactor

(FFR) and showed 76 – 98% COD removal at OLR of 10 kg $COD.m^{-3}.d^{-1}$. However, when the OLR was increased to 48 kg $COD.m^{-3}.d^{-1}$, the COD removal efficiency dropped to 46 – 50%. These researchers also found that the reactor did not show destabilization under hydraulic and organic shock loadings.

Saravanane et al. [7] has demonstrated that a fluidized bed reactor (FBR) under anaerobic conditions could be used to treat anti-osmotic drug based pharmaceutical effluent (Acetic acid and Ammonia). It was reported that COD reduction attained a maximum value of 88.5% using bioaugmentation through periodic addition of acclimated cells every 2 days with 30 - 73.2 g of cells (1 to 2.5 $g.L^{-1}$ of reactor volume) from an off-line enriched reactor. Furthermore, they also adventured into studying on bioaugmentation and treatment of Cephalexin drug based pharmaceutical effluent in an up-flow anaerobic fluidized bed (UAFB) system [8]. The results of the study showed that bioaugmentation improved removal efficiency and reactor stability.

Ince et al. [9] carried out a study on the performance of an up-flow anaerobic filter (UAF) treating a chemical synthesis-based pharmaceutical wastewater (Bacampicilline and Sultamicilline Tosylate) and showed 65% COD removal with methane yield being low at 0.20 m^3 $CH_4.kg\ COD_r^{-1}$.

The performance of a sequencing batch biofilter (SBB) integrating anaerobic-aerobic conditions in one tank to treat a pharmaceutical wastewater (Phenols and O-Nitroaniline) was studied by Buitron et al. [10]. The results showed that at HRT 8 – 24 h and OLR of 4.6 – 5.7 kg $COD.m^{-3}.d^{-1}$, a COD removal of 95 – 97% was achieved in the combined system.

Anaerobic treatment of pharmaceutical wastewater (Penicillin) containing sulphate (3200 $mg.L^{-1}$) was carried out by Rodríguez-Martinez et al. [11] in an UASB and showed 85 - 90% COD and a sulphate removal of more than 90% were achieved at an OLR of 1.5 kg $COD.m^{-3}.d^{-1}$ and HRT of 8.3 d. However, the performance of the reactor was affected (COD removal dropped to 70%) when the loading rate was increased to 2.09 kg $COD.m^{-3}.d^{-1}$ by reducing the HRT to 7 d. The authors suggested that the accumulation of sulphides could be responsible for the reduced performance.

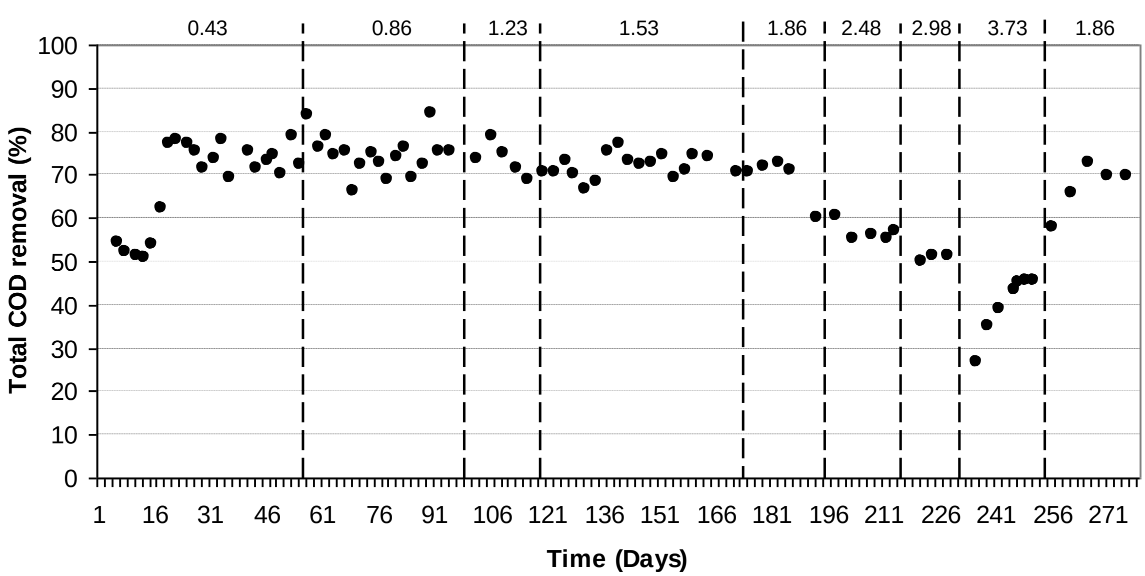
Anaerobic-aerobic treatment of pharmaceutical containing antibiotics (Ampicillin and Aureomycin) was investigated by Zhou et al. [12] in an anaerobic baffled reactor (ABR) followed by a biofilm airlift suspension reactor (BASR). The combined system resulted in total COD removal of 97.8% when ABR and BASR were operated at HRT 2.5 d and 12.5 h, respectively. The Ampicillin and Aureomycin removal efficiencies were 42.1% and 31.3% in the ABR, respectively but did not show substantial removal (less than 10%) in BASR for both antibiotics.

Treatment of Pharmaceutical Wastewater – A Laboratory Study

An Up-Flow Anaerobic Stage Reactor (UASR) was employed to treat pharmaceutical wastewater containing antibiotic. The UASR was developed with an active reactor volume of 11 L being divided into four 2.75 L stages. Each stage of the reactor was an up-flow sludge blanket reactor and had a 3-phase separator baffle to retain biomass. The reactor was fed with real pharmaceutical wastewater and operated with step-wise increases in the reactor organic loading rate (OLR) from 0.43 to 3.73 kg COD. $m^{-3}.d^{-1}$, and then reduced to 1.86 kg COD. $m^{-3}.d^{-1}$, over 279 days. The operational set-up, flow diagram and the reactor design are presented in Chelliapan et al. [13]. The antibiotic wastewater was originated from a fermentation process and had the following characteristics; soluble COD, 7000 ± 800 $mg.L^{-1}$; soluble BOD_5, 3500 ± 500 $mg.L^{-1}$; Total Kjeldahl Nitrogen (TKN), 364 ± 50 $mg.L^{-1}$; and pH, 5.2 – 6.8.

At a reactor OLR of 1.86 kg $COD.m^{-3}.d^{-1}$ (HRT 4 d), the soluble COD reduction was around 70 - 75% (Figure 2). However, when the OLR was increased to 2.48 kg $COD.m^{-3}.d^{-1}$ the COD removal efficiency decreased gradually until only around 45% soluble COD removal (average removal when reactor approached steady-state) was observed at an OLR of 3.73 kg $COD.m^{-3}.d^{-1}$. Pharmaceutical wastewaters containing a high proportion of spent fermentation broths have been shown to require long HRT for efficient treatment [14], presumably on account of their complex organic carbon content, and this is probably limits the UASR performance at HRT below 4 d. Nevertheless, COD reduction improved when the reactor OLR was reduced to 1.86 kg COD/m^3 day, demonstrating that the system was capable of recovering from the overloading.

Figure 2. Total COD reduction (%) of the UASR treating pharmaceutical wastewater



CONCLUSIONS

Anaerobic biotechnology is a promising alternative for pharmaceutical wastewater treatment. Results from literature on the anaerobic treatment of pharmaceutical wastewaters clearly demonstrate that anaerobic treatment is not commonly used as the means for treating pharmaceutical wastewaters. The case study showed that UASR could be used to treat pharmaceutical wastewater containing antibiotics and a COD reduction of 70 - 75% suggesting the biomass had acclimated to the antibiotics. Whilst the COD degradation is affected by the complexity and variability of the pharmaceutical wastewater, long HRT in the UASR can lessen these effects.

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