

**ANAEROBIC FLUIDIZED BED REACTOR WITH SEPIOLITE AS SUPPORT FOR
ANAEROBIC TREATMENT OF VINASSE**

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SUMMARY

An anaerobic fluidized bed reactor, using sepiolite as support, for the treatment of distillery wastewater was started-up using a stepped loading regime with addition of methanol. Six different steady states at hydraulic retention times between 0.5 and 2.48 days were studied achieving a COD removal efficiency of 70.5 to 88.6 %.

INTRODUCTION

The media used for biofilm attachment in anaerobic fluidized bed reactors has a significant effect on reactor performance. This media is fluidized by a high vertical velocity achieved by a high rate of recycle (Henze and Harremoës, 1983). This system has a great potential for the treatment of soluble organic wastewaters due to its ability to maintain a large concentration of biomass and excellent mixing characteristics for substrate-biomass contacting (Meunier and Williamson, 1981). To date, a variety of wastewaters have been successfully treated by the anaerobic fluidised bed process (Henze and Harremoës, 1983; Hickey and Owens, 1981).

A variety of materials have been used as support for the growth of attached microorganisms. Sand is the most widely used in fluidized bed reactors. However, media which have lower densities than sand require lower superficial velocities for fluidisation, and therefore, lower energy consumption. Other types of media include activate carbon (Chen *et al.*, 1985), pumice stone (Balaguer *et al.*, 1991), anthracite and granular activated carbon (Fox *et al.*, 1990).

A major objection to the use of anaerobic processes for industrial wastewater treatment is the long time required for start-up (Henze and Harremoës, 1983) due to the low growth rates of methanogens. One method of encouraging the growth of methanogenic bacteria is to supply a substrate that may be directly metabolised such as methanol (Bull *et al.*, 1983).

Start-up period can also be reduced with the adaption of the inoculum to the specific wastewater properties. It is preferable therefore to use a mix of several sources of active biomass instead of biomass from one source only (Weiland, 1990).

This paper presents the results of the start-up for an anaerobic fluidized bed reactor treating distillery wastewater and using sepiolite as support. Six different steady states at hydraulic retention times (HRT) between 2.48 and 0.5 days were also studied and compared.

MATERIALS AND METHODS

Wastewater Characteristics

The wastewater studied was the effluent of a wine distillery. Its main characteristics ranged as follows (in $\text{Kg}\cdot\text{m}^{-3}$): COD, 25-40; soluble COD, 13-16; pH, 4.5-5.2; ammonia nitrogen, 0.045-0.060; total and volatile solids, 20-25 and 13-15, respectively; total and volatile suspended solids, 9-11 and 0.8-1.4, respectively; acetic acid, 2.20-3.00; propionic acid, 0.11-0.15; n-butyric acid, 0.25-0.32; and i-valeric acid, 0.04-0.12.

Analytical methods

Total and soluble COD, alkalinity, total and volatile solids (TS, VS) and total and volatile suspended solids (TSS, VSS) were determined according to Standard Methods (APHA, 1981). Ammonia nitrogen and pH were measured with specific electrodes. Gas chromatography was used for biogas and VFA analysis.

Inoculum

The inoculum source was a mixture of anaerobic sludges proceeding from an UASB (Upflow Anaerobic Sludge Blanket) reactor treating potato-starch wastewater and from an anaerobic reactor treating pig slurry, and of anaerobically digested sewage sludge, yielding an initial volatile suspended solids concentration of $10.78 \text{ Kg VSS}\cdot\text{m}^{-3}$.

Anaerobic fluidized bed reactor

The experiments were performed with laboratory-scale upflow fluidized bed reactor with a total volume of 0.63 litres and a diameter of 3.2 cm. The reactor contained 200 ml of sepiolite as biological support material with an average diameter of 0.53 mm (calculated as described by Shieh *et al.*, 1981), and density of $1977.4 \text{ Kg}\cdot\text{m}^{-3}$. Sepiolite is a natural clay obtained from TOLSA S.A. (Madrid, Spain). Centrifugal pump was used to maintain 50% expansion within the reactor. Feed was pumped upward the bed continually. Effluent was collected in a settler to separate the solid fraction from the liquid stream. Gas production was measured by means of an electronic gas counter. Reactor temperature was maintained at 35°C with external heating water jackets.

RESULTS AND DISCUSSION

Start-up period

Start-up of the anaerobic fluidized bed reactor was accomplished over a 2-month period using a procedure involving stepped increases in organic load and substrate replacement by methanol. An initial organic load of $0.47 \text{ Kg COD}\cdot\text{m}^{-3}\cdot\text{d}^{-1}$ was applied by diluting the wastewater to an initial concentration of $1.93 \text{ Kg COD}\cdot\text{m}^{-3}$, methanol being 30% of this COD. Organic load was gradually increased up to $5.16 \text{ Kg COD}\cdot\text{m}^{-3}\cdot\text{d}^{-1}$, keeping constant the percentage of methanol. Afterwards, this percentage was progressively decreased: 20% at days 45-50, 10% at days 50-55, 5% at days 55-61 and 3% at days 61-63. After day 63 the methanol content was reduced to zero. HRT remained constant at 2.48 days during this period.

Figure 1 shows the organic load, COD removal, ammonia nitrogen concentration and total and volatile solids concentration. COD removal rates increased rapidly and remained around 90% independently of the organic load increases.

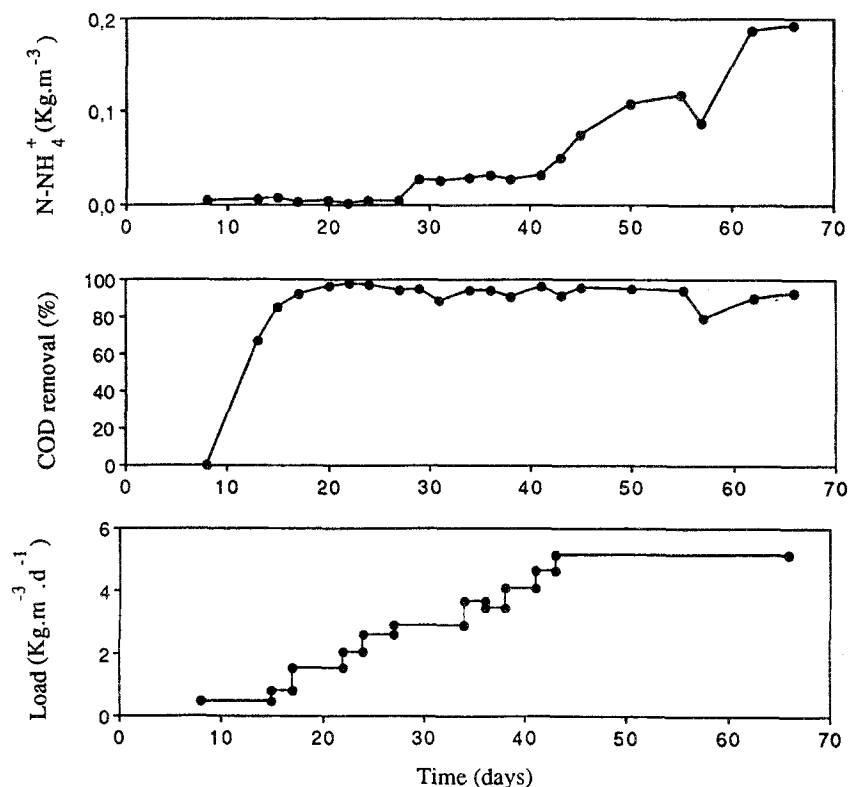


Figure 1.- Scheme of the fluidized bed experimental installation

The ammonia nitrogen concentration was low during the early start-up period but after day 45 this concentration began to increase. This was related to the decrease of the percentage of methanol in the influent. That was expected because methanol enhances the growth of methanogenic bacteria. When the percentage of methanol decrease in the influent, the growth of methanogenic bacteria also decrease and the ammonia nitrogen consumption is lower. So, the ammonia nitrogen concentration in the effluent was increased when the percentage of methanol in the influent was progressively decreased.

An accumulation of volatile fatty acids indicates an instabilization of the reactor. During the start-up only traces of acetic acid was obtained.

Steady state performance

Six different HRT (between 2.48 and 0.5 days) were studied during the experimental period. A concentration of 18 Kg.m⁻³ was maintained in all steady states studied.

Attainment of the steady state was verified after an initial period of 3 times the HRT by checking the constant values of the characteristics of the effluent measured during an additional week. The steady state adopted values of the characteristics were the mean of the last measurements.

The steady state operating characteristics of the anaerobic fluidized bed reactor are given in Table 1.

Table 1.- Performance of laboratory fluidized bed reactor

HRT (d)	2.00	1.50	1.00	0.74	0.50
Load (Kg COD.m ⁻³ .d ⁻¹)	9.00	12.00	18.00	24.32	36.00
COD _{removal} (%)	72.22	83.00	78.16	88.56	70.55
COD _{sol,removal} (%)	89.32	N.D.	93.37	93.00	80.00
CH ₄ (%)	N.D.	69.50	N.D.	80.20	65.24
CO ₂ (%)	N.D.	29.15	N.D.	19.62	33.39
H ₂ S (%)	N.D.	1.35	N.D.	0.18	1.36
Biogas production (m ³ .m ⁻³ .d ⁻¹)	2.61	4.97	6.07	9.65	10.70
pH	8.9	8.1	8.3	8.1	7.6
AI/AP	0.16	N.D.	0.30	0.21	0.36

N.D.: Not done

Removal efficiencies were quite high. COD removal ranged from 70.55 to 88.56 and COD soluble removal were observed to vary from 80 to 93.37%. COD_{sol} removal is always higher than COD removal because of the high influent volatile suspended solids values. These solids are difficult to eliminate in a fluidized bed process.

The ratio of intermediate to partial alkalinity (AI/AP), recommended as an indicator of digester stability (Riplay *et al.*, 1986), was used to follow-up the stability of the reactor. If this ratio is kept below 0.4 the process is stable (Balaguer *et al.*, 1989). In all steady states AI/AP ratio remained below 0.4.

At HRT of 0.74 days, a COD removal of 88.56% was obtained at organic load of 24.32 Kg.m⁻³.d⁻¹, but at HRT of 0.5 days, COD removal decreased to 70.55%.

Other wine distillery waste studies have been reported using other anaerobic processes such as the anaerobic filter (Bories *et al.*, 1982) and the UASB reactor (Craveiro *et al.*, 1986) with 92% and 83% COD removal at organic loads of 14 and 13.2 Kg.m⁻³.d⁻¹ and HRT of 1.6 and 2.4 days, respectively.

Methane production averaged 0.35, 0.36 and 0.28 l CH₄.g⁻¹ COD removal at HRT of 1.5, 0.74 and 0.5 days, respectively. This is 89.7%, 92.3% and 71.8% respectively of the theoretical value of 0.39 l CH₄.g⁻¹ COD removal predicted by stoichiometry at 35°C.

The wastewater studied in this work was treated without any nutrient addition or any neutralization of the pH of the incoming waste.

CONCLUSIONS

The start-up procedure, by using a stepped loading regime with addition of methanol as initial co-substrate, took a period of 66 days. During this period, COD removal remained around 90% while organic load increased from 1.15 to 5.16 Kg.m⁻³.d⁻¹.

At HRT of 0.74 days, a COD removal of 88.56% was obtained at organic load of 24.32 Kg.m⁻³.d⁻¹ with a gas production of 9.65 m³.m⁻³.d⁻¹.

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