

Performance of anaerobic thermophilic fluidized bed in the treatment of cutting-oil wastewater

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Abstract

This paper examines the effect of organic loading rate on the removal efficiency of COD and TOC anaerobic thermophilic fluidized bed reactor (AFBR) in the treatment of cutting-oil wastewater at different hydraulic retention time (HRT) conditions. The essays are development at laboratory scale using a porous support medium.

The AFBR reactor was subjected to a programme of steady-state operation over a range of hydraulic retention times, HRTs, in the range 12–2 h and organic loading rates, OLRs, between 11.9 and 51.3 kg COD/m³ d. The highest efficiency was 95.9% for an OLR of 13 kg COD/m³ d and HRT of 11 h. Over an operating period of 92 days, an OLR of 51.3 kg COD/m³ d was achieved with 67.1% COD removal efficiency (71.3% TOC) in the experimental AFBR reactor.

Although the level of biogas generation was not high, the anaerobic fluidized bed technology provided significant advantages over the conventional physico-chemical treatment applied in the factory. The effluent had a better quality (lower organic loading) and it was possible to reuse it in different applications in the factory (e.g., irrigation of gardens). The biological treatment did not lead to the generation of oily sludge, which is considered as hazardous waste by legislation. Furthermore, a continuous stream is produced and this reduced the impact of large flows discharged 4–5 times per week to the urban collector and MWWTP (municipal wastewater treatment plant).

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1. Introduction

The anaerobic treatment of industrial wastewater has become a viable technology in recent years due to the rapid development of high-rate reactors, such as the anaerobic filter and upflow anaerobic sludge blanket (UASB) (Fang et al., 1996; Lettinga, 1996; Dinsdale et al., 1997), both upflow and downflow stationary packed beds (Nebot et al., 1995; Perez et al., 1998, 2001; Romero et al., 2001),

and fluidized or expanded beds (García-Morales, 1997; Perez et al., 1997, 1998; Rodríguez-Cano, 2003). These developments are due to the fact that the methods combine a number of significant advantages – including low energy consumption, low excess sludge production, enclosure of odours and aerosols – over conventional aerobic methods with different activated sludge types for wastewater treatment (Ahring et al., 2002).

Interest in AFBR (anaerobic fluidized bed reactor) has grown as it combines the recovery of usable energy with good process efficiency and stability. Potential AFBR applications for the treatment of hazardous waste with inhibitory/recalcitrant compositions have also been reported (Seckler et al., 1996; Lin et al., 1998; Schreyer and Coughlin, 1999; Hansen et al., 1998; van Lier et al., 2001; Rodríguez-Cano, 2003).

Abbreviations: AFBR, anaerobic fluidized bed reactor; COD, chemical oxygen demand; COD_r, chemical oxygen demand removal; TOC, total organic carbon; TSS, total suspended solids; VSS, volatile suspended solids; HRT, hydraulic retention time; OLR_r, organic load rate removed; OLR₀, initial organic load rate.

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The treatment capacity of an anaerobic digestion system is primarily determined by the amount of active microbial biomass retained within the system, which in turn is influenced by wastewater composition, system configuration and operation of the anaerobic reactor. Unlike the conventional biofilm systems in which the growth support media are fixed in space either by gravity or by direct attachment to the reactor wall, the anaerobic fluidized bed system retains the growth support media in suspension by drag forces exerted by upflowing wastewater. Moreover, the distribution of biomass hold-up (in the form of a biofilm) is relatively uniform because of the completely mixed conditions maintained and the continuous biofilm sloughing process, which counterbalances the accumulation of biomass due to growth. Therefore, the anaerobic fluidized-bed system can be considered as a continuous-flow, completely mixed homogeneous microbial system (Tessele et al., 2002). The presence of growth support media in the reactor does not effect the interpretation of biomass hold-up in the anaerobic fluidized bed system. This is because the biomass hold-up can be directly measured in terms of attached volatile solids using the techniques developed by Shieh et al. (1985) and Mulcahy and Shieh (1987).

Cutting oils are emulsionable fluids that are widely used in metalworking processes (for lubrication and refrigeration during the machining of metallic pieces and, to a lesser extent, glass) (IHOBE, 1994). Cutting oils normally consist of oil, water and additives (fatty acids, surfactants, heavy metals, biocides, etc.) and generate toxic waste after prolonged use. Oily wastes derived from industrial processes are classified as Special Waste under current legislation. This means that there are restrictions on the movement, treatment and disposal of waste oil.

Opportunities for cleaner production mainly involve the reduction in the use of toxic materials, the prevention of the formation of large volumes of wastewater, hazardous waste or air emissions containing toxic pollutants and, finally, improvements in energy conservation. The breakthroughs outlined above should enable this manufacturing sector to improve environmental management and benefit from economies gained by speeding up the adoption of emerging technologies that will reduce waste and costs in terms of environmental compliance and energy expenditure (Tilche and Orhon, 2002).

Conventional approaches to recovering oil from spent cutting fluids do not lend themselves to oil recovery. Cracking stable emulsions and separating oil and water phases results in an oily sludge and large volumes of strongly acidic water, both of which require further treatment before they can be safely disposed of. New technological alternatives have been developed and different treatment combinations have been investigated (Cosmen, 1996; Ortíz de Zárate and Abia Aguila, 1997; Abdel-Gawad and Abdel-Shafy, 2002). Biological treatment has been used to remove metal-working fluids (i.e., to trap oil and solids from cutting fluids). However, these systems are prone to fouling by the free oils. In addition, the oil concentrate still

needs to be disposed of and a large volume of water must be treated to separate a small (<5%) amount of oil. Generally, the oily wastes are too dilute to be incinerated.

The organic composition of the cutting-oil waste has led to numerous studies concerning the application of aerobic biological techniques to reduce the organic load in the cutting-oil waste. The applicability of anaerobic fluidized bed reactor has been demonstrated in the treatment of toxic and recalcitrant compounds, including cutting-oil waste (Schreyer and Coughlin, 1999). The anaerobic treatment of metal-cutting-oil fluid has been published by several authors (Kim et al., 1992; Sutton et al., 1994; Van der Gast et al., 2004). Nevertheless, the use of biological treatments requires further investigation.

The purpose of the study described here was to elucidate the treatment efficiency in a AFBR that decomposes cutting-oil wastewater. The experimental protocol was designed to examine the effect of organic loading rate on the efficiency of COD and TOC removal under different hydraulic retention times, HRT, conditions.

2. Methods

The study was conducted on a laboratory scale over a three-month period.

Description of anaerobic fluidized bed reactor (AFBR). The experimental system used in the lab-scale study consisted of a transparent Plexiglas column with a cross-section of 21.24 cm² and 135 cm in length. The bottom of the column was moulded into a conical shape in order to promote uniform fluidization of media and bioparticles (i.e., biofilm-coated media). Heated water was maintained at 55 °C and was pumped from a recirculation water bath through the constant temperature jacket surrounding the reactor.

The reactor was initially charged with 252.6 g of coated support medium (coated SIRAN), which had previously been colonized in semicontinuous anaerobic thermophilic fixed-bed reactor (Rodríguez-Cano, 2003). The support occupied an initial height of 35.5 cm in unexpanded mode. In expanded mode, the support occupied 400 mL (active volume).

The effluent from the AFBR was recycled through a variable speed centrifugal pump in order to provide upflow velocities for media and to maintain a bioparticle expansion level of 18–20%. Such upflow velocities also ensured that completely mixed conditions were maintained in the liquid phase (Rodríguez-Cano, 2003) and the active volume of the digester remained constant throughout the study. Recycle flow was drawn at a depth 7 cm below the free liquid surface in the enlarged section in order to avoid entrapment of gas accumulated in the headspace above. The recycle flow was then pumped into the bottom assembly. This stream was collected in a settler in order to separate the solid fraction from the liquid stream. The pumping rate was adjusted periodically to account for varying biomass to keep a constant fluidized bed level. Plugging

of the SIRAN bed was not observed at this level of expansion.

Feed was pumped directly from the refrigerator into the recycle lines. The reactor effluent passed through a sealed contact chamber connected to an inverted siphon to separate the gas from the liquid in the effluent.

Support media. Open-pore sintered glass beds (SIRAN) were used as the media for cell immobilization and retention. An essential advantage of sintered glass is the double-pore structure of the surface. The micropores in the range 1–10 μm provide the initially submerged microorganisms with a population area from which the entire carrier can be populated (Breitenbucher et al., 1990). The particles were sieved for uniformity and the resulting particles had an apparent diameter of approximately 1.5–2 mm. This material was chosen because of its uniformity and because it could be incinerated to measure dry organic matter concentrations. The main characteristics of SIRAN carriers are as follows: medium real density = 1832 g/L; bulk density = 570 g/L; pore volume = 50–60%; pore diameter = 60–300 μm , and high specific surface area (87000 m^2/m^3) suitable for use as a support medium in AFBR.

Feed. The wastewaters were supplied by Delphi Automotive Systems S.A., which is located in Puerto Real (Cadiz) and is involved in the machining of metallic pieces for the automotive sector. In this installation, different types of oily waste are generated and the natures of these mainly depend on the working system and the type of machine used in each process. The factory also has a conventional depurative treatment plant (physico-chemical) for the effluent generated in the manufacturing processes.

The feeds used in this study were cutting-oil wastewaters that arise from different production streams from the factory. The wastewaters were not treated in any conventional way prior to the study.

The main characteristics of the wastewaters are shown in Table 1. As can be observed, all feeds have a neutral or alkaline pH. The different physico-chemical characteristics of the wastewaters can also be seen; namely soluble COD, TOC, TSS, VSS and acidity concentrations. COD values and TOC concentrations were 1049–4000 $\text{g O}_2/\text{m}^3$ and 123–211.5 ppm C, respectively. The organic fraction was from 59% to 87% SS. Total acidity concentrations were between 13.32 and 2.30 $\text{g AcH}/\text{m}^3$.

Feed F6 was diluted to give a value of 2000 $\text{kg O}_2/\text{m}^3$. All feeds used in this experimental work were collected,

transported and maintained frozen and were subsequently maintained at 4 °C to minimize microbial growth in the feed stream.

Performance and reactor operation. The experimental protocol was designed to examine the effect of organic loading rate on the efficiency of COD and TOC removal of AFBR in the treatment of cutting-oil wastewater at different HRT conditions.

Experiments were performed with the expanded bed height in the reactor controlled at 18–20% expansion, yielding a working reactor volume of 0.4 L at a recirculation rate of 30 L/h. Under all conditions tested, the liquid phase in the reactor was completely mixed (tracer studies corroborate this situation) (Rodríguez-Cano, 2003).

The empty HRT bed was defined in terms of the expanded bed volume occupied by bioparticles (active volume: 400 mL). The main characteristics of the different stages of the operation are shown in Table 2.

The AFBR was subjected to a programme of steady-state operation over a range of HRT between 12 and 2 h. The volumetric COD loadings were between 11.9 and 51.3 $\text{kg COD}/\text{m}^3 \text{ d}$.

Initially, the reactor was fed with cutting-oil wastewater at strength of 1049 kg/m^3 to give an organic loading rate of 4.5 $\text{kg COD}/\text{m}^3 \text{ d}$ with an HRT of 12 h. After this adaptation period, the organic loading rate was increased until it reached 11.1, with the HRT maintained at the same level (12 h). The COD of the feed increased to 2800 kg/m^3 .

The HRT was gradually decreased and remained constant during each stage until reaching the steady-state conditions. The attainment of the steady state was verified

Table 2
Characteristics of the different stages of operation with AFBR

Stage	HRT (h)	OLR ₀ (kg COD/m ³ d)	Feed used
S0	12	4.46	F1
S1	12	11.91	F2
S2	11	12.96	F2
S3	10	14.29	F2
S4	8	12.10	F3
S5	6	16.15–19.55	F3–F4
S6	5	20.41	F5
S7	4	25.64	F6
S8	3	33.90	F6
S9	2	51.28	F6

Table 1
Main characteristics of the feeds used

Feed	pH	Soluble (COD kg O ₂ /m ³)	TOC (ppm C)	TSS (kg/m ³)	VSS (kg/m ³)	Organic fraction (% SS)	Total acidity (g HAc/m ³)
F1	6.95	1.049	150.6	0.227	0.198	87.2	13.32
F2	7.27	2.800	147.5	1.325	1.111	84.9	7.38
F3	7.23	1.936	152.7	0.493	0.293	59.45	3.65
F4	7.07	2.346	157.1	0.337	0.210	62.4	4.65
F5	7.41	2.041	123.2	0.880	0.575	65.3	2.61
F6	8.30	4.001	211.5	2.735	1.880	68.7	2.30

after an initial period (three times the HRT) by checking whether the constant effluent characteristic values (COD removal and methane generation) were the mean of the last measurements in each stage (Rodríguez-Cano, 2003).

Sampling and analysis. Parameters measured in the influent and effluent were as follows: soluble chemical oxygen demand (COD), total organic carbon (TOC), total suspended solids (TSS), volatile suspended solids (VSS), pH, alkalinity, metallic cations and heavy metals. Gas production and gas composition (methane and carbon dioxide percentages) were also periodically determined.

Feed and effluent samples were taken daily for the analysis of filtered COD, TOC and both TSS and VSS. Metallic cation and heavy metal analyses were carried out at the beginning and at the end of each stage of the test. All analytical determinations were performed according to Standard Methods (APHA-AWWA-WPFC, 1989).

Gas produced in the process was collected in a gas meter filled with acidified saturated salt solution. A gas sampling valve was installed at the top of the collector to allow direct gas sampling with a syringe. The volume of gas produced in the reactor was directly measured in terms of the volume of salt solution displaced from the gas collector. Gas composition (methane and carbon dioxide) analysis was carried out by gas chromatographic separation with a stainless steel column packed with Carbosive SII (diameter of 1/8" and 2 m length) in conjunction with a thermal conductivity detector. The injected sample volume was 1 mL and the operating conditions were as follows: 7 min at 55 °C; ramped at 27 °C/min to 150 °C; detector temperature: 255 °C; injector temperature: 100 °C. The carrier gas was helium and the flow rate used was 30 mL/min. A standard gas (from Carburros Metálicos, S.A.; composition: 4.65% H₂; 5.33% N₂; 69.92% CH₄ and 20.10% CO₂) was used to calibrate the system.

3. Results and discussion

In the adaptation period (S0), the COD and TOC removal efficiencies at the end of the period were very high, with values greater than 90% and 70%, respectively. The TSS and VSS tended to stabilize at 0.2 and 0.1 kg/m³, respectively (maintaining an organic fraction of 50%). Effluent volatile fatty acids were detected in the ppm range and the pH remained constant at values near to neutral.

Performance and operation parameters during stages S1–S9 of the essay are shown in Fig. 1. Organic loading and removal rate, OLR₀ and OLR_r, organic removal efficiency (as a percentage of initial COD and TOC), VSS and TSS versus time are presented.

The changes in OLR_r at different OLR₀ applied are represented in Fig. 2. During the initial period of operation, including HRTs between 12 and 10 h, both parameters had almost identical values. This indicates that, under these conditions, the experimental reactor provides good COD reduction. Subsequently, for HRT values below 3 h (stage S8 and S9), the differences between the OLR₀ and OLR_r

values were higher due to the gradual decrease in the COD removal efficiency with the decrease in HRT.

The relationship between COD removal efficiency and the HRT in the reactor is shown in Fig. 3. Initially, removal efficiencies were quite high at an applied OLR value of 12 kg/m³ d. Under these conditions, the reduction in the COD by the microbial consortium was approximately 94% of the total pollution load (i.e., 20–30% more effective than conventional treatment).

COD soluble removals were observed to decrease from 93.3% to 67% at HRTs when HRTs decreased from 12 to 2 h and the respective organic loads were 11.91 and 51.28 kg COD/m³ d. Clearly, the efficiency of the substrate removal process is a function of the HRT and is concomitant with the organic loading rate: the COD removal efficiency decreased as the HRT (increased load) decreased and was comparatively ineffective at HRT < 2 h (loading rates >51.28 kg COD/m³ d).

The last value obtained for the organic removal efficiency (at HRT = 2 h) shows a significant decrease in COD removal efficiency to a level below 70%, and this is due to the very high organic loading rate applied (51.3 kg COD/m³ d). Physico-chemical treatment in the factory can reach levels of 85–90% COD_r. Therefore, at OLR > 100.00 kg COD/m³ d, the efficiency was very low and was not of interest in terms of industrial applications because conventional physico-chemical treatment can achieve better results.

The changes in TOC and COD at different applied OLR are represented in Fig. 4. The percentages of COD removal are influenced by the nature of the cutting-oil wastewater used. Hence, COD_r decrease with increasing OLR₀. However, the obtained TOC removals are quite variables in the range of 54–76% independent of the OLR applied to the system. Also, the TOC removal percentages are lower than the COD removals. This is due to the fact that the COD analysis includes the determination of several compounds, such as metallic cations, inorganic compounds etc., that are chemically oxidisable but are not included in the TOC determinations. Also, some of these compounds can be absorbed in biofilms (Hwu et al., 1997).

The application of the conventional treatment in the factory can achieve 23–32% TOC removal, which is lower than the results obtained for the biological treatment under all conditions investigated.

An important variable for effluent quality is the VSS concentration from the reactor. The effect of OLR₀ on TSS and VSS is shown in Fig. 5. As can be seen, the evolution of TSS and VSS shows two trends. During the first stage (from HRT 12 to 5 h), a detachment of immobilized biomass was produced and the values of effluent solids increased from 0.12 to 0.25 kg VSS/m³. After this stage, the effluent TSS and VSS are low due to the nature of the feed employed. In any case, the effluent suspended solids tend to increase on increasing the OLR applied, a situation that has been observed by several authors in similar AFBR (García-Morales, 1997; Romero et al., 2001).

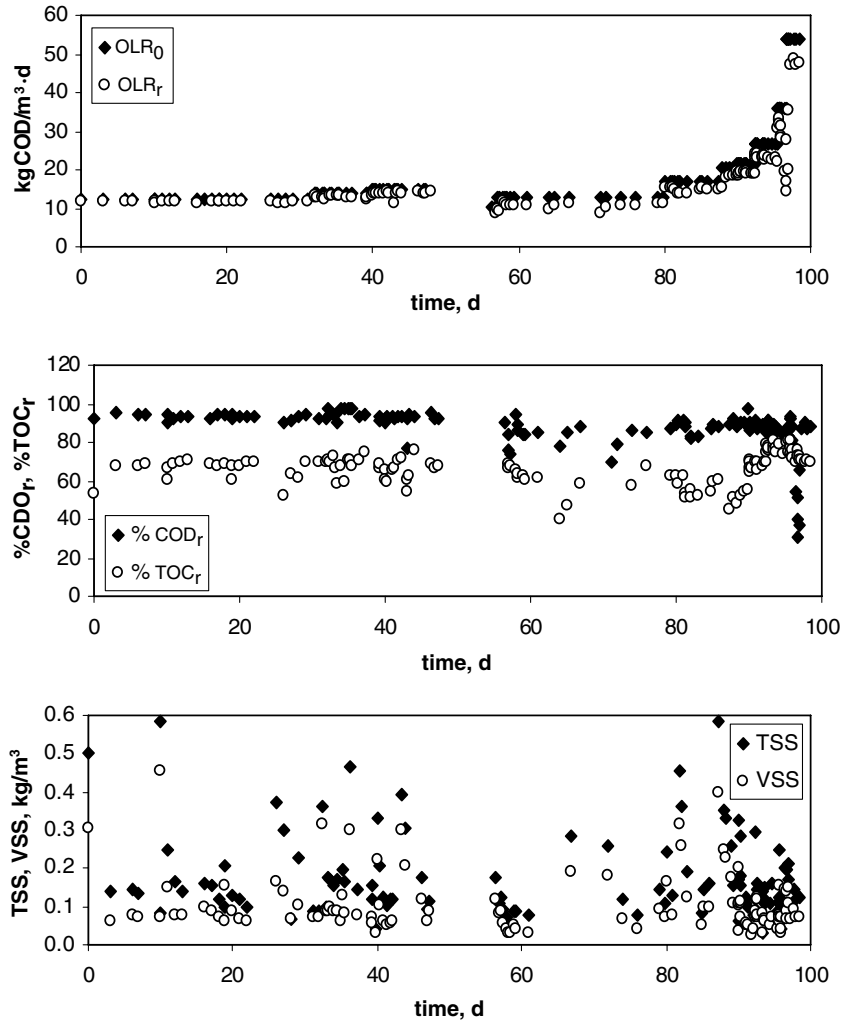


Fig. 1. Evolution of the parameters of the anaerobic process with time: (a) organic loading and removing rate, OLR_0 and OLR_r , as $\text{kg COD/m}^3 \text{ d}$; (b) organic removal efficiency (as percentage of initial COD and initial TOC); (c) VSS and TSS, as kg/m^3 .

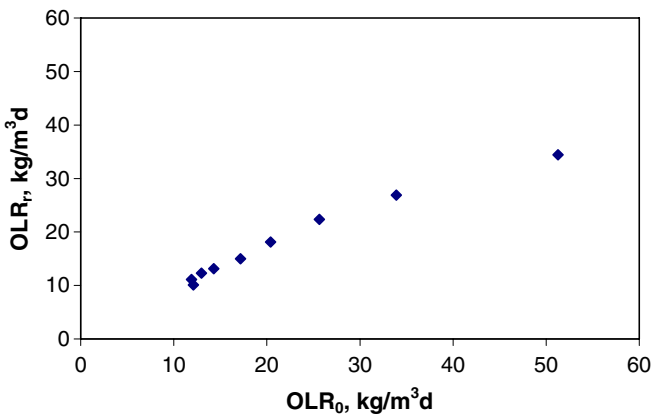


Fig. 2. Organic loading rate applied versus organic loading rate removal (as $\text{kg COD/m}^3 \text{ d}$).

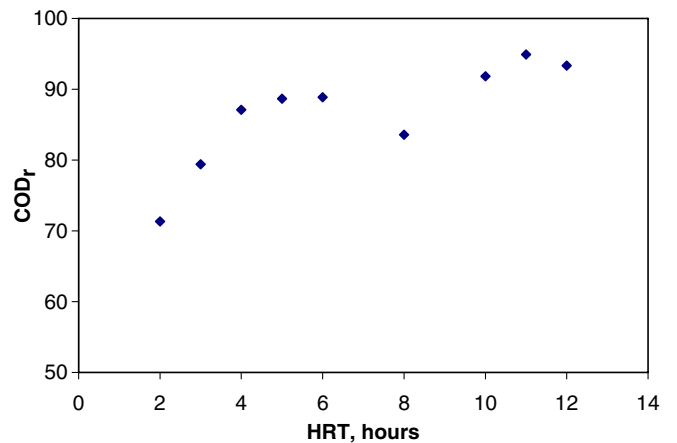


Fig. 3. Effect of HRT (h) on the organic removal efficiency ($\% \text{COD}$ removal).

In biofilm systems, the amount of suspended biomass is negligible with respect to the attached biomass. This aspect allows low HRT levels to be maintained with respect to the suspended systems and this causes the washing of the sus-

pended biomass (the fluidized bed retains the growth support media in suspension by drag forces exerted by upflowing wastewater). Therefore, the levels of suspended

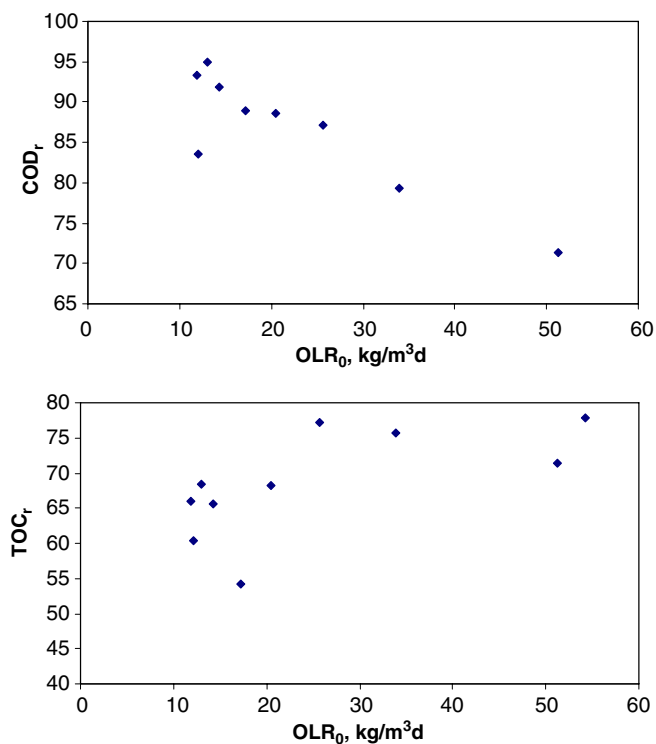


Fig. 4. Effect of OLR_0 ($\text{kg}/\text{m}^3\text{d}$) on the organic removal efficiency (% COD and % TOC removal).

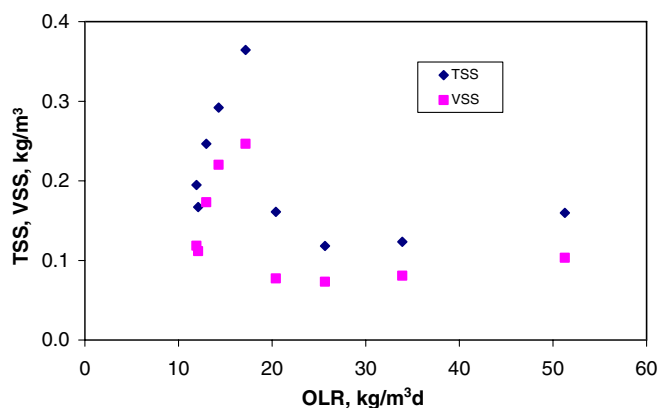


Fig. 5. Effects of OLR applied ($\text{kg}/\text{m}^3\text{d}$) on the effluent total and volatile suspension solids (TSS and VSS, as kg/m^3).

solids in the effluent arising from the detachment of biomass are higher at the beginning of each stage, when changes are taking place in the applied OLR. In the assay described here, the detachment is due to the fact that SIRAN beads had been previously colonized in a fixed bed reactor and, consequently, the initial biofilm thickness was very high. The required increase in the superficial velocity through a bed medium to maintain a fluidized state (and the consequently large drag forces exerted by upflowing wastewater) causes an elevated level of biomass detachment, which is noted in the initial evolution of VSS in the effluent. Subsequently, the effluent VSS concentration increases only slightly for large increases in the hydraulic

loading rate (period between S1 and S5). The AFBR effluent contained an average of 0.08 and 0.10 $\text{kg TSS}/\text{m}^3$ at HRT of 5 and 2 h, respectively. Biomass immobilization is one of the major advantages of the AFBR system over a suspended microbial system in that it allows the system to operate under higher loading speeds (both hydraulic and organic).

The reason for this process behaviour could be related to the organic overloading due to the increase in the detachment of biomass adhered onto the media support particles. This observation is in agreement with the findings reported by Garcia-Morales (1997) from a study of wine vinasses (4.1–9.1 $\text{kg COD}/\text{m}^3$) in AFBR.

The fluidized bed technology attains higher SS concentrations than the corresponding physico-chemical treatment in the factory at all stages of operation. Even so, the concentrations are very low in relation to the SS content of the cutting-oil waste.

The pH remained within the range 7.5–7.8 throughout the process, thus demonstrating the stability of this system. Only in the last stage is it necessary to add a small amount of 0.5 N NaOH as the alkalinity drops. Hence, the buffer capacity of the system means that the pH remains almost neutral. Biodegradation processes were favoured at pH range from 6 to 7.5 (Desh Deepak et al., 1994).

The acidity registered in the effluent is related to the nature of the cutting-oil waste. Nevertheless, the measured values are not very high, again indicating the stability of the process. Desh Deepak et al. (1994) confirmed that, under stable conditions, the volatile fatty acid concentration in the reactor remains constant. In the study described here, there is a low dispersion of the data, which also indicates the stability of the process.

The alkalinity of the effluent decreased on increasing OLR (or decreasing HRT). However, the system has a high buffer capacity and the acidity/alkalinity ratio remained below 0.1 during the assay (Desh Deepak et al., 1994).

Metallic compounds analyzed in cutting-oil wastes and in samples of effluents are shown in Tables 3 and 4.

Table 3
Metallic compound concentrations in the feeds

Compound	F1	F2	F3	F4	F5	F6
Na (mg/L)	172.3	209.1	153.2	219.7	274.2	455.1
K (mg/L)	27.1	32.4	10.5	13.5	21.3	33.2
Ca (mg/L)	45.7	35.1	68.4	8.57	231.0	167.0
Mg (mg/L)	9.71	7.98	11.2	4.46	14.20	24.50
B (mg/L)	0.95	0.95	0.95	0.82	1.29	2.14
Cu ($\mu\text{g}/\text{L}$)	<20.0	<25.0	<20	<20.0	<25.0	<20.0
Zn ($\mu\text{g}/\text{L}$)	83.2	146.0	341	128.0	137	391.0
Cr ($\mu\text{g}/\text{L}$)	8.6	42.1	33.2	862.0	42.2	21.7
Ni ($\mu\text{g}/\text{L}$)	405.1	415.2	239.4	538.1	679.2	855.2
Pb ($\mu\text{g}/\text{L}$)	<20	<25.0	<20.0	<20.0	<25.0	<20.0
Cd ($\mu\text{g}/\text{L}$)	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Ag ($\mu\text{g}/\text{L}$)	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Fe ($\mu\text{g}/\text{L}$)	158.0	295.0	295.0	158.0	21.3	3303
Mn ($\mu\text{g}/\text{L}$)	252.0	162.0	58.7	10.4	153.0	750.0

Table 4
Metallic compound concentrations in effluents

Compound	S1	S2	S3	S4	S5	S6	S7	S8	S9
Na (mg/L)	144.0	238.0	236.0	205.0	267.0	363.0	266.0	214.0	218.0
K (mg/L)	33.9	58.7	53.2	23.5	20.4	34.3	31.2	21.5	18.5
Ca (mg/L)	44.8	32.2	35.8	61.2	29.5	137.0	73.9	79.0	71.2
Mg (mg/L)	10.4	11.2	12.6	13.3	7.5	13.6	17.0	18.3	18.3
B (mg/L)	1.0	0.9	0.9	1.1	1.0	1.3	1.1	0.9	1.0
Cu ($\mu\text{g/L}$)	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0
Zn ($\mu\text{g/L}$)	46.1	5.9	4.1	12.3	12.9	4.6	6.6	<1.0	4.5
Cr ($\mu\text{g/L}$)	14.4	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0
Ni ($\mu\text{g/L}$)	184.0	66.0	111.0	63.0	271.0	136.0	93.0	155.0	194.3
Pb ($\mu\text{g/L}$)	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0	<25.0
Cd ($\mu\text{g/L}$)	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Ag ($\mu\text{g/L}$)	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0
Fe ($\mu\text{g/L}$)	311.9	92.7	71.52	76.2	72.3	64.6	98.1	43.8	57.2
Mn ($\mu\text{g/L}$)	53.4	37.2	60.8	67.6	23.1	73.5	54.6	53.5	79.5

The Na^+ , K^+ and Mg^{2+} concentrations increased during the process but the amounts detected are not sufficient to inhibit the microbial community. The Calcium and Boron concentrations remain constant after the biological treatment. The Zn^{2+} , Ni^{2+} and Fe concentrations decrease during the treatment. Hence, Zn^{2+} can be used in the anaerobic metabolism and by adsorption into biofilm. Ni is used as a nutritional requirement by *Archaea methanogenics*. Likewise, Fe is also used by the microorganisms.

Tyagi (1990) reported the heavy metal and metallic cationic concentrations that are inhibitory or toxic for the anaerobic microorganisms as well as the metallic cationic concentrations that stimulate the concentration of the anaerobic microorganisms.

Biofilm can adsorb toxic compounds in different ways. Heavy metal adsorption is caused by polymeric extracellular substances (PES). Furthermore, cationic compounds (such as Zn, Cu, Cr) are adsorbed more readily than anionic or non-ionic compounds.

The volumetric rate of biogas formation was very difficult to assess in this study due to the small amounts generated. Evaluation of the gas composition (methane and carbon dioxide) by gas chromatography also proved to be very arduous.

Previous investigations indicate that the nature of the feed influences the activity of the methanogenic microorganisms and, therefore, the generation of biogas (Rodríguez-Cano, 2003; Perez et al., 2006). A survey of the literature in this field shows that several recalcitrant wastewaters can be anaerobically digested and generate only small amounts of biogas (Hansen et al., 1998). However, the volume of biogas can be increased by the addition of a co-substrate (van Lier et al., 2001; Rodríguez-Cano, 2003; Perez et al., 2006) and by allowing sufficient time for the adaptation of the biomass (Zeeman et al., 1985).

The analysis of biogas sampling indicates that the methane concentrations fluctuate in the range 10–15% and at times even reach 20%. H_2 is detected only at the beginning of the start-up of each stage and is found in very low con-

centrations. The CO_2 level generated is very low and this gas is used for the formation of a $\text{CO}_3^{2-}/\text{CO}_3\text{H}^-$ buffer.

The stimulation of anaerobic biomass by the addition of a co-substrate (e.g., amino acids or cofactors) is an important avenue for future investigation.

Although the generation of biogas is not high, the AFBR provides good chemical reduction and eliminates the generation of oily sludge.

The microbiology and biochemistry of the anaerobic digestion are not completely understood and the situation is even less clear for recalcitrant and toxic compounds. However, there is evidence that anaerobic digestion is a suitable treatment for wastewater containing fatty oil and fatty acids (Lettinga, 1996). Schink (2002) proposed several strategies to improve the applicability of anaerobic digestion by means of the addition of a similar compound that causes an increase in the microbial activity.

Another advantage of AFBR is that it reduces matter transfer limitations and favours the digestion process.

Other cutting-oil waste studies have been published and these concern other anaerobic processes such as the anaerobic filter (Van der Gast et al., 2004), which removed 85% of total pollution.

4. Conclusions

Laboratory results confirm that AFBR provides a good reduction in COD when operating at low HRT and high organic loading rates. The greatest efficiency in terms of substrate removal was 95% for an OLR of 13 kg COD/ m^3 d and a HRT of 5 h.

Experimentally, it was confirmed that AFBR can achieve >70% COD reduction at a COD loading of 51 kg COD/ m^3 d (HRT: 2 h) in the treatment of cutting-oil waste under steady-state conditions. Under such conditions the effluent obtained can be discharged to municipal collectors.

The nature of the feed influences the methanogenic activity and, therefore, the low biogas generation rate.

The results of this study confirm that the AFBR provides a highly effective method for the biodegradation of cutting-oil wastewater under thermophilic conditions.

The application of AFBR provides significant advantages in relation to the conventional physico-chemical treatment applied in the factory under investigation. The effluent has a better quality (lower organic loading) and it is possible to reuse it in different applications within the factory (e.g., irrigation of gardens). The biological treatment does not lead to oily sludge generation (considered as dangerous waste in current legislation). Finally, a continuous stream is produced and this minimizes the impact of large flows discharged 4–5 times per week to the urban collector and MWTP (municipal wastewater treatment plant).

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