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DESIGN AND PERFORMANCE OF PULSED ANAEROBIC DIGESTERS

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ABSTRACT

The development of a Pulse-Driven Loop Reactor (PDLR), a Pulsed Anaerobic Filter (PAF) and a Pulsed Anaerobic Baffled Reactor (PABR) is described. In a PDLR internal circulation is achieved by a specially designed pulse-nozzle together with a concentric draft tube. In a PAF and PABR an oscillation is superimposed onto the biosuspension by means of a pulsator unit. Pulsed digesters enhance mass transfer processes. Consequently they facilitate degassing and prevent a build-up of acid spots in sludge beds. Laboratory- and pilot-scale evaluation using highly polluted distillery slops (pear, cherry, raspberry) as industrial wastewater show a COD removal efficiency of 70 -80 % at loading rates of 10 - 5 kg/m^3*d. Contamination, both by sulfate (2 g/L) and copper (0.2 g/L), has a most adverse effect on anaerobic treatment of cherry-mashes, giving rise to a build-up of volatile fatty acids. Consequences for distillery plant operation are discussed.

KEYWORDS

Pulsed anaerobic digester; distillery slops; sulfate reduction; sulfide toxicity; inhibition of methanogens.

INTRODUCTION

Process technologies make widespread use of pulsation techniques for increasing mass transfer coefficients (Srinikethan et al., 1987). Plate-pulsed columns as well as liquid pulsed columns are used. In the field of aerobic wastewater treatment pulsing is adopted to achieve great turbulence and interfacial areas in a biosuspension of polluted water, air bubbles and bacteria. High shear forces prevent agglomeration of bacteria and enhance oxygen transfer due to an increase in k_La-values. This characterizes the reciprocating jet reactor (Brauer and Sucker, 1979). With lower energy input this reactor system has also been used for anaerobic wastewater treatment. Furthermore, a European patent (Edelmann, 1989) shows a dynamic anaerobic filter where material transfer from wastewater to immobilized biomass is increased by pulsatory relative movement.

Our study describes the development and performance of a Pulse-Driven Loop Reactor (PDLR), a Pulsed Anaerobic Filter (PAF) and a Pulsed Anaerobic Baffled Reactor (PABR) using distillery slops as a substrate. This work was initiated because severe degassing problems were encountered with organic carriers in an up-flow anaerobic filter. Consequently, two problems had to be solved: (a) enhance removal of gas bubbles from rough carrier surfaces and (b) avoid both the short-circuiting of influent wastewater and clogging.

MATERIALS AND METHODS

Surface modified hydrophilic polyurethane carriers (PUR) of Bayer AG, Leverkusen, (Germany) were used (Pascik and Henzler, 1988). Bulk density of air-dried support material was approximately 180 kg/m^3. Material with diameters of 4 to 8 mm (laboratory scale experiments) and an edge length of 10 mm (pilot plant operation) were used. Porosity was about 77% of the net volume. Other support materials tested were: Raschig rings (ϕ = 15 mm) of porous glass sponge with micro- and macropores produced by Schott Werke, Mainz, (Germany); pore size: 63 - 315 μm; porosity 60%, surface area 0.2 m^2/g; plastic rings made of surface treated, poly propylene ("hydrophilic" VSP 25 Füllkörper) produced by Vereinigte Füllkörper Fabriken, Ransbach (Germany); specific surface area: 185 m^2/m^3; void volume: 94%. Corrugated plastic blocks (Plasdek) with a specific area of 140 m^2/m^3 and a void volume of 95% were used in the PABR.

Chemical oxygen demand (COD, < mg O_2/L >), biochemical oxygen demand (BOD_5, < mg O_2/L >), total solids (TS, < mg/L >), total volatile solids (TVS, < mg/L >) as well as N,P,S,Cu were determined by standard methods (DEV, 1981). Ion chromatography on a HPIC AS1 column (Dionex) with 0.001 m octanesulfonic acid as eluent gave compositions with respect to individual volatile fatty acids. Gas flow rate was measured with a Ritter wet gas meter. Carbon dioxide was routinely checked by a Brigon CO_2 indicator. The main components of different slops used are summarized in Tab. 1.

TABLE 1 Characteristics Of Slops Used

Type of slops	pH	TS [%]	TVS [% TS]	COD [g/l]	Cu^{++} [mg/l]	SO_4^{--} [mg/l]
Morello Cherry #	3.5-4.0	4.9-6.5	76-93	65-95	30-48	30-38
Cherry/Raspberry*	2.7-2.9	3.7-4.9	75-85	50-70	150-200	1800-2150
Raspberry*	2.9-3.8	4.5-5.1	85-90	65-75	3-12	28-45
Pear*	3.4-3.8	1.7-2.0	81-87	45-50	5-35	145-170

* After decantation, # lactic acid for stabilization

A continuously stirred vessel reactor (CST) with an active volume of 12.5 l and pH-control was used to study hydrolysis of slops in bench-scale experiments. About 10 % of the reactor`s volume was filled with PUR carriers for biomass retention. Freshly distilled slop was added quasi-continuously at room temperature. Reactor temperature was kept at 32 ± 1°C. A magnetic stirrer (U= 220 rpm) was used for mixing. Hydraulic residence time of the liquid phase was 2.5 days. At the distillery plant all wastewater streams passed a sieve with 4 mm holes. Next they were decanted to decrease suspended solids. pH was brought to about 6.5 by addition of $Ca(OH)_2$.

In laboratory-scale studies the acidification reactor was filled with waste solution and brought to 32 ± 1°C. Innoculation was carried out with sludge from the anaerobic stage of the municipal sewage treatment plant. Degradation of slop in PDLR and PAF was initiated by 20% of active sludge (v/v) and biomass fixed on PUR-carriers (originating from biomethanation of acetic acid). Adaption period was two months increasing the percentage of slops continuously. Prior to initial start up the PABR was partially filled with diluted slops derived from pears (pH 6.5). Next each compartment was seeded with effluent from a municipal sewage sludge digester, giving rise to an active biomass of approximately 1 kg TVS per m^3. The initial loading rate of pear-slops was 0.4 kg COD per m^3 per day. Later on PDLR was inoculated with sludge from PABR in pilot-scale investigations.

DESIGN OF REACTORS

A scheme of the experimental set up is given in Fig. 1. The staged anaerobic process is composed of a pulse-driven loop reactor (PDLR) in series with a pulsed anaerobic filter (PAF) followed by a tube clarifier (SED). In laboratory scale investigations PDLR consists of a slender cylindrical vessel of 150 mm in diameter and 1400 mm in height. It has a draft tube of 60 mm in diameter and a length of 800 mm fixed centrally to the axle with a distance of 100 mm from the base. The main reactor volume is limited by two sieves at a distance of 10 mm and 1000 mm from the base. The sieves were made from thin aluminium plates with holes of about 1.5 mm in diameter, 9 holes per cm^2.

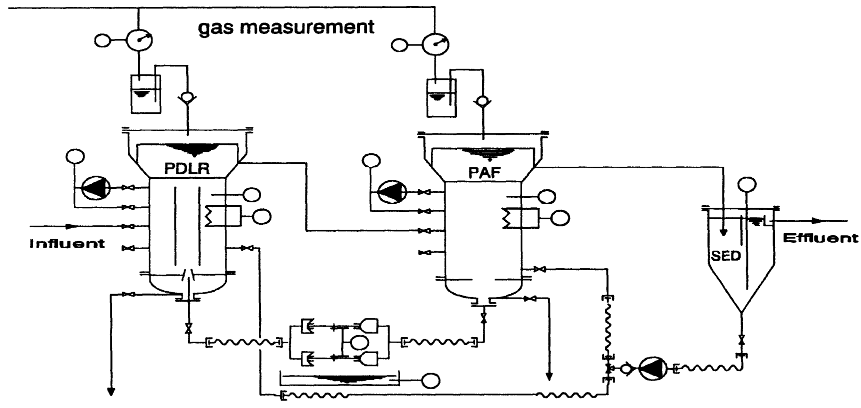


Fig. 1. Experimental arrangement of PDLR, PAF and SED. Pilot-scale reactors have a volume of 0.6 m^3 each.

With the aid of a specially designed pulse-nozzle as seen in Fig. 2 (Etzold and Stadlbauer, 1990) a stable circulation system is established. A moving piston made of a material with water-like density is integrated into the nozzle at the bottom of the reactor. On the down-stroke, the piston allows a large portion of the liquid to stream in through the nozzle into the pulsator. Therefore a large part of the biosuspension sucked in comes from the outer ringlike area of the reactor, where the direction of circulation is downward. On the up-stroke this area is closed by the lifted piston and forces the liquid through the small opening at the tip of the nozzle. The current-areas of the nozzle are fit for the passage of 9 mm ball-diameters. With the pushing stroke, biosuspension and suitable carrier material situated in the environment of the bottom of the reactor are sucked into the nozzle stream and lifted upward through the draft tube. This transport of material causes a gradual regrouping of packed beds. Consequently the surface area of the carriers is frequently renewed and degassing is promoted.

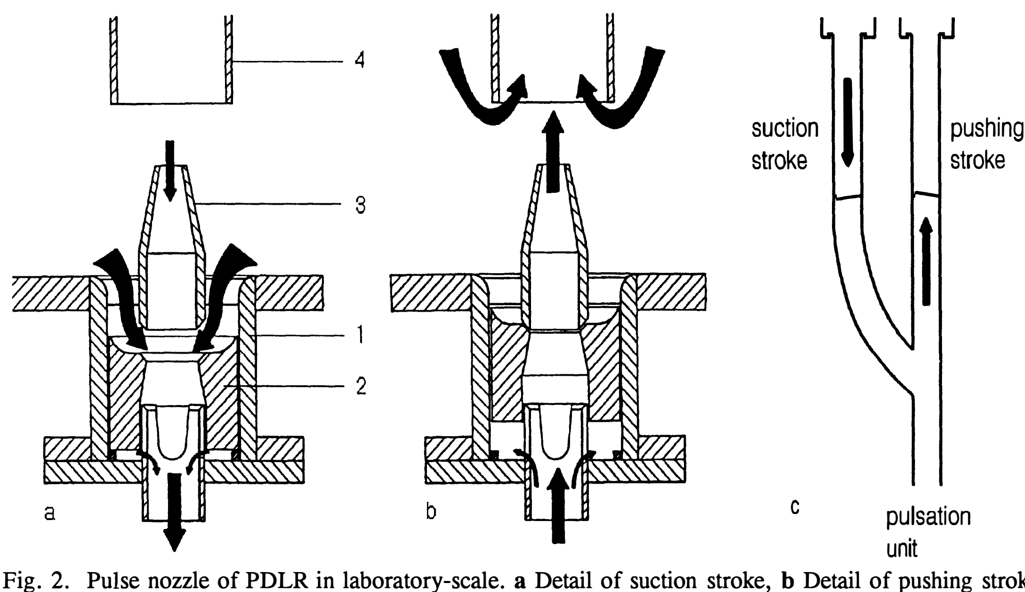


Fig. 2. Pulse nozzle of PDLR in laboratory-scale. **a** Detail of suction stroke, **b** Detail of pushing stroke: *1 Pulsation nozzle (Complete unit), 2 Alternating piston, 3 Nozzle, 4 Draft-tube* , **c** Pilot-scale: Detail of pushing and suction stroke.

Pulsators used were mechanically coupled membrane pumps directly connected to a motor with eccentric sheave.

The following diameter ratios may be advantageous:
Reactor/draft-tube/nozzle-outlet = 12 /4/1. The height to diameter ratio should range between 10 to 20, referring to the achieved reactor volume. To minimize energy input pulsation at intervals is recommended. In general, pulsation cycles should be optimized with respect to sufficient degassing, prevention of clogging and limited hydraulic stress to bacteria. Standstill / running time of 5 min to 1 min seems to be a reasonable compromise. Using granular polyurethane (PUR) carriers the following observation and operation modes were made by increasing height-ratios (h_r) of carrier-bed (h) to active reactor-height (H):

$0 < h_r < 0.3$: circulating fluidized bed with all support material in motion during pulsation mode.

$0.3 < h_r < 0.7$: hybrid operation with stationary and suspended parts. A portion of the carriers formed a slowly down-moving stationary bed, which was carried off from the reactor bottom with the draft-tube by means of pulsation. After leaving the draft-tube, the support material sinks down giving rise to a refill of stationary bed from above. This frequent circulation of all carriers prevents the bed from blocking.
$h_r > 0.7$: increasing current-resistance will bring forth a quasi-stationary bed with slow internal regrouping of carriers. This method of operation characterizes the behaviour of a Pulsed Anaerobic Filter (PAF). In this case the concentric draft tube may also be omitted. Furthermore, the use of a variety of support materials different in density, size and chemical nature is possible.

A multistep cascade of pulsed anaerobic filters gives rise to a baffled design. A diagram of the Pulsed Anaerobic Baffled Reactor used in pilot-scale investigations may be seen in Fig. 3. The biosuspension is trapped between vertical baffles in a number of compartments. In hybrid operation microorganisms are present in the form of granular biomass in sludge beds as well as the colonized blocks of Plasdek support material. Again, mechanical agitation by pulsation promotes mixing of substrate and bacteria. The pilot-scale reactor has an active volume of 3.2 m^3.

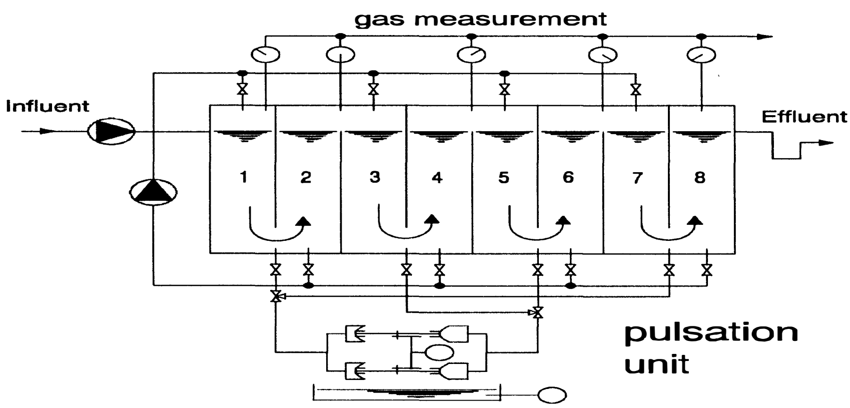


Fig. 3. Pulsed Anaerobic Baffled Reactor (PABR) with 8 compartments

RESULTS AND DISCUSSION

Acidification of Distillery Slops.

The relative extent of hydrolysis was evaluated by the amount of VFA produced (T= 32 °C; t = 2.5 d; $B_{R,CSB[raspberry]} = 28$ kg/m^3*d; $B_{R,CSB[cherry]} = 12$ kg/m^3*d).

Distillery slops have highly different susceptibilities to spontaneous as well as controlled hydrolysis. Results of acidification of raspberry slops in the above mentioned CST are shown in Fig. 4.

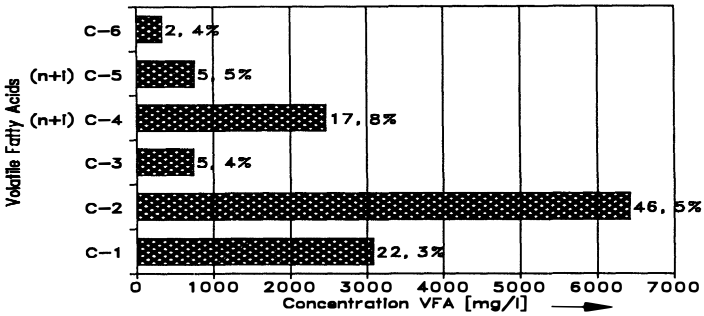


Fig. 4. Distribution pattern of VFA produced in hydrolysis of raspberry slops at pH 6.5

Hydrolysis is accompanied by a minor COD reduction in the range of 1-3%. VFA show a dependence of the reaction velocities on the type of carbon chain for conversion by anaerobic bacteria. This is reflected by a height-dependent decrease of VFA in upflow operation of PAF. The following sequence was found: C1 > C4 > C2 > C3. Consequently, preferable pH regions for hydrolysis are characterized by low propionic acid concentrations. This pH dependent C-3 fingerprint has to be established for each substrate. A typical example is shown in Fig. 5 for cherry slops.

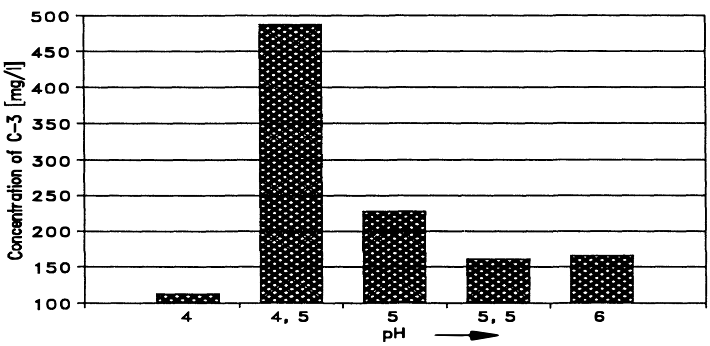


Fig. 5. Propionic acid formed during hydrolysis of cherry slops depending on pH

It is important to note that prolonged storage (weeks to months) of slops at room temperature should be avoided. Chemical changes including uncontrolled hydrolysis may have a highly unfavourable influence on further anaerobic degradation, especially if propionic acid accumulates (Fig. 6).

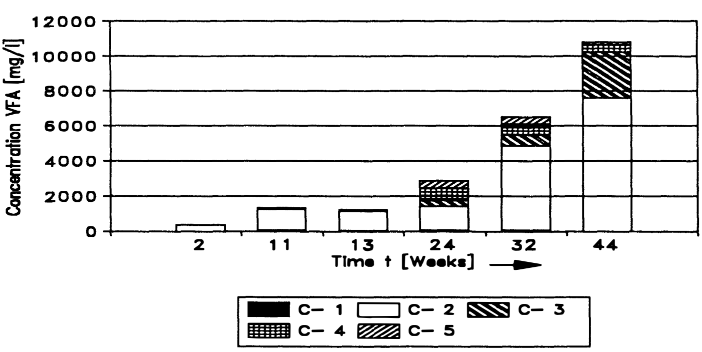


Fig. 6. Spontaneous hydrolysis of cherry slops in storage tank at pH 2.9

Performance of Laboratory-Scale Reactors (PDLR, PAF).

Fig. 7 details the COD concentration patterns of wastewater consisting of morello cherry slops. A staged arrangement of PDLR, PAF and tube clarifier was used. Concentration C_0 (kg COD/m^3) of inflowing substrate and effluent concentrations C (kg COD/m^3) of PDLR, PAF and tube clarifier (SED) are shown. Data obtained during adaption period mentioned above are omitted. Stones from influent cherry slops were screened out. However, no decantation of suspended solids was performed. The amount of PUR carriers in the PDLR was 10% of the active volume and 75% in the case of PAF.

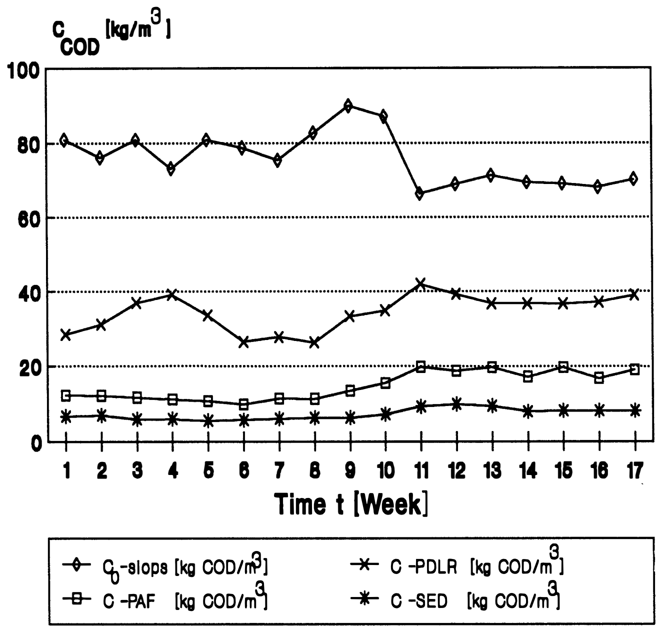


Fig. 7. Degradation pattern of morello cherry slops in the laboratory-scale investigations

The set-up has a total COD reduction efficiency of 80 to 90 percent based on unfiltered samples. Hydraulic retention time was 5-8 days. The extent of degradation of this highly complex substrate demonstrates the compatibility of low hydrodynamic stress caused by pulsation forces with the metabolic interactions of biomethanation. Fig. 8 shows loading rates as well as concentration of VFA of fermenters. At a pH level of 6.4 to 6.8 both hydrolysis and methane production take place in the PDLR. Concentrations of VFA range between 6 - 11 g/L. In contrast, the PAF shows lower levels of VFA concentrations in the range of 0.2 - 2 g/L at a pH pattern of 7.2 - 7.6.
It should be noticed that no dilution of feed by pre-purified reactor effluent occurred. Obviously, critical spots of acids or pH values are avoided due to the complete mixing behaviour of a pulse-driven loop reactor and the back and forth movement of the biosuspension as well as slow carrier regrouping in the PAF by pulsation.

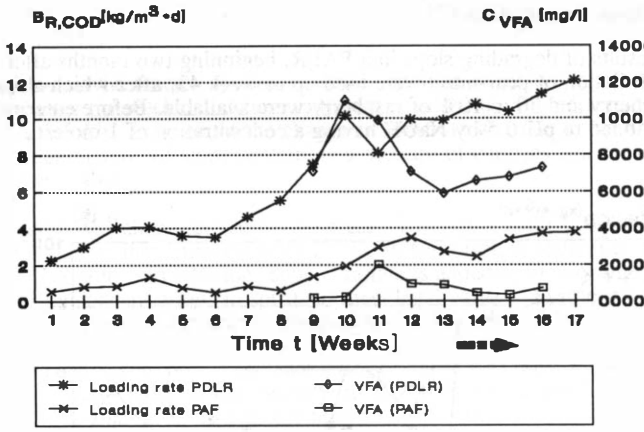
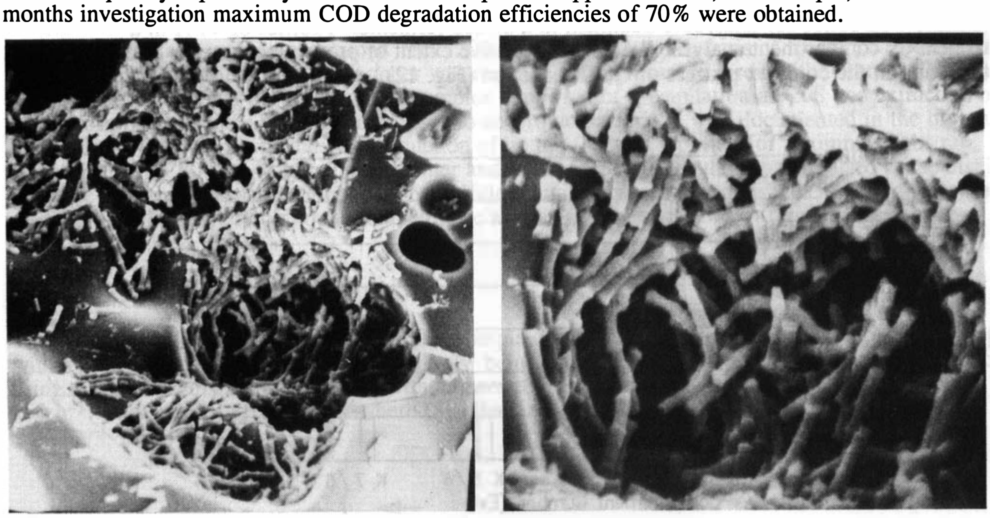


Fig. 8. Synopsis of loading rate and VFA in the laboratory-scale arrangement of PDLR and PAF using morello cherry slops as substrate

At a maximum loading rate of 11 kg COD per m^3 per day PUR carriers in the PAF were substituted by porous glass. It was known that this support medium is very suitable for the colonization of biomass (Aivasidis, 1986). However, in hybrid reactors pores at the surface of sintered glass tend to be closed by sludge growth. Thus the internal volume of this material is no longer accessible for degradation of substrates. Among others, agitation by means of pulsation proved to be an effective tool for removal of sludge covering the surface of porous glass, giving rise to COD removal rates as high as 85 percent. Surface of porous glass and microbial attachment may be seen in Fig. 9. Most unfortunately randomly packed sintered glass didn`t sufficiently resist the mechanical stress caused by carrier regrouping during pulsation cycles. Within a period of 3 months about 70% of glass volume was reduced resulting in the accumulation of (highly active) glass-powder at the bottom of the reactor. For this reason, porous glass was subsequently replaced by mechanical stable plastic support material, for example, VSP 25. In a 3 months investigation maximum COD degradation efficiencies of 70% were obtained.



a b

Fig. 9. Porous glass colonized by anaerobic bacteria. Magnification a: 2400 fold, **b**: 6000 fold

Performance of Pilot-Scale Reactor (PABR)

Figure 11 shows the results of degrading slops in a PABR, beginning two months after initial start-up. Slops derived from distillation of pear-mash were used up to week 43, after which slops containing a mixture of 70 - 90% cherry and 30 to 10% of raspberry were available. Before entering the reactor wastewater was conditioned to pH 6.5 by NaOH having a concentration of 1 mole/L.

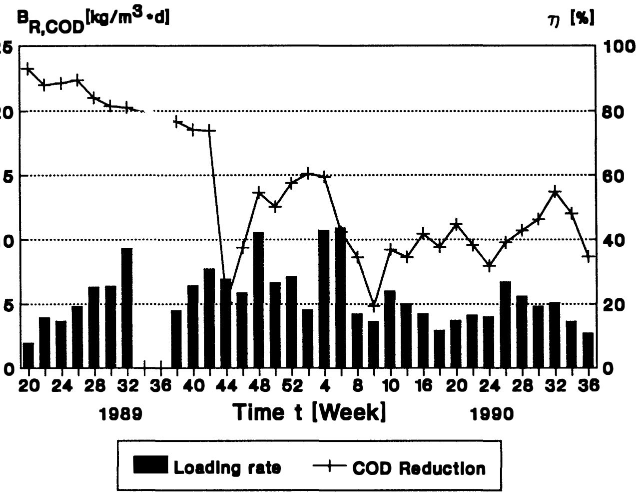


Fig. 10. Degradation characteristics of different slops in PABR.
Pear: Week 20 - 43 (1989); Cherry - raspberry: Week 44 (1989) - 36 (1990)

Correlation of loading rate and COD removal efficiency for pear-mash describes the degradation pattern of a substrate well suited for anaerobic treatment in a pulsed fermenter. Profiles of VFA in a compartment by compartment analysis illustrate the relative extent of predominant stages of acidification or methanation in the complex process of COD reduction (Fig. 12).

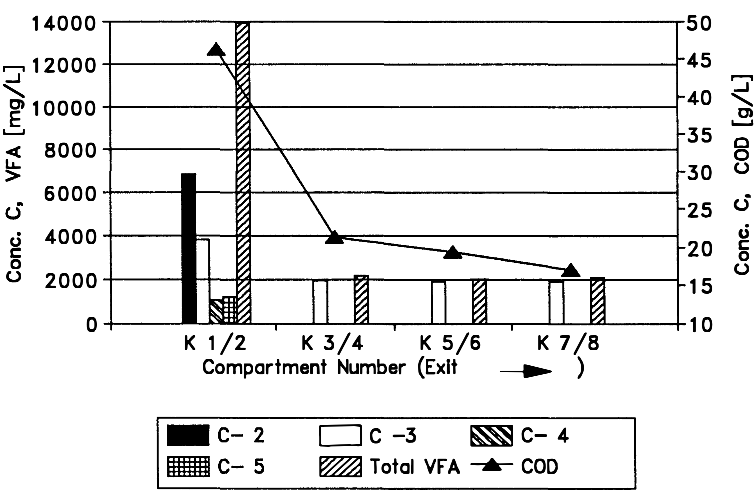


Fig. 11. Concentration of VFA and COD in PABR, Week 30, 1989

Hydraulic shock loads are traced by a gradual forward-moving front of acidification or rollback in recovering. This is paralleled by a shift in the CH_4/CO_2 ratio of individual compartments.

In week 32 a breakdown of the reactor system occurred due to an excessive input of NaOH and air as control devices failed over the weekend. After readjustment of pH by diluted acidic slops the digester recovered remarkably quickly. In week 44 the change in substrate was due to plant operation. During the following 10 months degradation of slops containing a mixture of cherries and raspberries was investigated as mentioned above.

This wastewater situation was characterized by the presence of 150 - 200 mg Cu/L and 1850 to 2150 mg SO_4/L. The reason for this is that approximately 2.5 kg sulfuric acid is added per m^3 of cherry-mash for stabilization prior to distillation. In addition, copper sulfate is added to bind cyanide in an effort to minimize ethylcarbamate concentrations in spirits to meet legal values. Furthermore, rectification of spirits is done in the presence of other copper compounds, giving rise to increasing Cu contamination.

The effect of this new wastewater stream on reactor performance was most remarkable. During that period, COD conversion rates reduced significantly to 40 -60 % even at loading rates as low as 4 kg COD per m^3 per day. The inhibition of methane production is reflected in a build-up of fatty acids as shown in the VFA profile of effluents.

We discuss two main reasons for this failure:

(a) The erratic performance is predominantly linked to an input of sulfur in the range of 700 to 800 mg S/L with COD/S ratios of 50 - 70. Consistent with this interpretation cherry slops without this excessive amount of sulfate (and copper) are well degradable as can be seen from laboratory scale experiments. Effluent sulfate concentrations were in the range of 550 - 850 mgSO_4/L, indicating a sulfate conversion rate of 60 -70 percent.

Literature indicates that H_2S produced from ingesting sulfate is toxic to various anaerobic bacteria, first manifested at about 50 mg S/L (Nielson and Iversen, 1988). Recent investigations (Parkin et al., 1990) have shown that the picture is complicated by the interaction of sulfate reducers and methanogens, where cyclic patterns of inhibition were obtained. Sulfide produced inhibits sulfate reducing bacteria along with at least partial inhibition of methanogens. Depending on the organic loading rate and COD/S ratio irreversible failure was reported to be at approximately 62 mg S/L for acetate as substrate and 60 mg S/L for a propionate system. In the presence of a highly complex substrate such as cherry slops various steps of the anaerobic breakdown of organic compounds are presumably affected by sulfide toxicity.

(b) In addition influent slops contained 150 - 200 mg/L of copper. Analysis of filtered samples from the effluent showed that about 90% of copper was removed during passage through the reactor. Obviously, soluble levels of copper are the result of complex equilibria of precipitation as CuS and extraction by a variety of organic agents. Toxicity of copper to anaerobic bacteria is well documented in the literature. Inhibition of COD removal and gas production of up to 60% was reported for a complex substrate contaminated by 500 mg/L of copper (Steiner and Müller, 1988). For the substrate used at the distillery plant the relative importance of copper and sulfide inhibition was not established. Instead an attempt was made to exclude copper compounds and sulfuric acid as additives to slops in future plant operation.

PDLR and PAF

The pilot-scale effectiveness of a PDLR as a completely mixed reactor for acidification in a staged process with a PAF as methanation reactor is currently being investigated. Aerobic post treatment is performed using a newly developed loop reactor with an aerated gas-liquid-system showing K_La values over 250 h^{-1}. This is to be reported elsewhere (Stadlbauer et. al., 1991).

CONCLUSION

1. Pulsed digesters faciliate degassing from carriers, avoid clogging and channelling and allow a variety of packed bed to fluidized bed operations with levels of hydrodynamic stress compatible to anaerobic microbial communities.

2. Porous glass has been shown to possess excellent surface characteristics for microbial colonization. To improve mechanical stability under pulsed conditions randomly packed systems should be substituted by stackable porous glass blocks.

3. Anaerobic digestion proved not to be successfully applicable to industrial wastewater based on cherry slops contaminated by both sulfate (2 g/L) and copper (0.2 g/L).

4. As a consequence, installation of a technical plant will be paralleled by both substitution of sulfuric acid by lactic acid in fruit-mash conditioning and an electrochemical elimination of Cu from freshly distilled slops.

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