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Investigating the feasibility and the limits of high rate anaerobic winery wastewater treatment using a hybrid-EGSB bio-reactor

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ABSTRACT

Biodegradability and activity tests of winery wastewater at 37 °C using inoculum from a paper mill suggested hydrolysis as the rate limiting step with hydrogen the predominant pathway to methane. Scaling-up to a Hybrid-EGSB showed that after 100 days acclimation at moderate temperatures (20 ± 2 °C) a 70 ± 2% COD removal is achievable, applying an OLR of up to 15.32 kgCOD m^{-3} day^{-1} and an SLR of 3.83 kgCOD $kgVSS^{-1}$ day^{-1}, respectively. Conventional operation and mesophilic temperature increase improved COD removal efficiency (≤96%) while sCOD concentration met the European COD effluent standards. COD:CH_4 conversion reached 0.31 ± 0.07 m^3 CH_4 $kgCOD_{removed}^{-1}$; COD:biogas estimated 0.45 ± 0.06 m^3 gas $kgCOD_{removed}^{-1}$, ~300% higher than the acclimation period. Operation remained stable at OLR < 39 kgCOD m^{-3} day^{-1}, which corresponds to an SLR of 4.8 kgCOD $kgVSS^{-1}$ day^{-1}. This limit results in an $Alk_{bicarb.}$:Alk_{tot} ~ 0.31 and a pH ~ 6.51, an irreversible status that demonstrates the limits of anaerobic treatment of winery wastewater with this reactor setup.

1. Introduction

Energy generation from fossil fuels has been the predominant path for industrialization for nearly 200 years (Rifkin, 2002) leading to intensive release of carbon dioxide and rendering the conventional wastewater treatment processes (mainly aerobic) unsustainable. As water is a human right and therefore a valuable resource, sustainable, carbon neutral industrial wastewater treatment increasingly plays a vital role in the water cycle and is essential for the preservation of life, and water supply.

The wine industry processes millions of tonnes of grapes each year, which subsequently leads to significant wastewater production (Nataraj et al., 2006; Coetzee et al., 2004). Through auxiliary processes (must production, filtration, cleaning of vats, machines, pipes, floors and bottles), organics-rich wastewater streams are generated, which typically exceed regulatory limits [E.C., UWWTD (91/271/EEC)] and require

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treatment prior to discharge to a water body. Vlyssides et al. (2005) demonstrated that wastewater from the winery industry of the Mediterranean region (Greece) originates mainly from the must production combined with wine filtration. These steps contribute to an overall winery wastewater stream with relatively high particulate COD streams resulting to BOD_5:COD of 0.49 (due to the presence of grape stems and skins combined with lees' particles). Until now, especially in the Southern European wine industry, winery wastewater treatment commonly involves the use of aerobic systems. The main disadvantage of the aerobic setups for winery wastewater treatment is the inefficiency to cope with the highly variant organic loads that correspond to the harvest (vintage) and non-harvest (non-vintage) seasons (Brito et al., 2007). Other disadvantages are relatively low OLR ($\leq$ 15.0 kgCOD m^{-3} day^{-1}, Basset et al., 2014; Petruccioli et al., 2002; Andreottola et al., 2002 etc.), higher sludge production and high energy use. Compared to conventional energy intensive aerobic systems anaerobic treatment provides numerous benefits (e.g. lower energy requirement, methane generation, lower biological sludge production) (Malina and Pohland, 1992; Pham et al., 2006; Cuff et al., 2014).

Many studies focused on the anaerobic treatment of winery wastewater treatment; however the majority could not exceed a certain OLR without greatly altering the reactor configuration or adding nutrients to optimize the process, achieving relatively poor COD removal efficiency or partially-treated effluent quality in terms of COD (Muller, 1998; Keyser et al., 2003; Andreottola et al., 1998; Garcia-Calderon et al., 1998; Moletta, 2005; Melamane et al., 2007; Chai et al., 2013). More promising results were achieved by Ganesh et al. (2010) and Yu et al. (2006) who achieved sufficient treatment using a fixed bed anaerobic reactor and an anaerobic filter, applying OLRs of 42 and 36.8 kgCOD m^{-3} day^{-1}, respectively. The increased likelihood of packed/filter material clogging after long-term operation in addition to the nature of the substrate (mainly sCOD from commercial wine and wastewater from a rice wine industry for the first and the second study respectively) limit the applicability of these studies.

Thus far numerous anaerobic high-rate reactor setups (MBBR (Chai et al., 2013), UAF (Rajagopal et al., 2009; Rajagopal et al., 2010 etc.), UASB with or without an AF unit (Muller, 1998 and Andreottola et al., 1998, respectively), SBR (Ruiz et al., 2002), DFBR (Garcia-Calderon et al., 1998) etc.) have been studied for the treatment of winery wastewaters. Another well-established anaerobic reactor is the Expanded Granular Sludge Bed (EGSB); however, its application technology for winery wastewater treatment is minimal. The advantages of this reactor configuration e.g. ease in accommodation of the hydraulic variable loads in addition to its small footprint renders this setup ideal for the winery industry that has variable loads and requires low capital/maintenance treatment costs. Hence, the aim of this study is to examine the feasibility of high-rate anaerobic treatment of actual winery wastewater. Batch assays were performed initially to investigate the biodegradability-activity and the kinetics of the inoculum (granular sludge from paper industry) to the substrate, followed by scale-up in a continuous and innovative EGSB setup. Further goals were to identify and improve the treatment process and estimate the corresponding COD removal efficiency at both ambient (acclimation) and mesophilic temperatures (37 °C), and finally to demonstrate that this reactor setup is able to treat at a high rate so it could be adopted by environmental and chemical engineers for the treatment of winery wastewater, especially for applications at small/medium sized wineries. Currently these industries rely on either energy intensive aerobic processes or require large land areas for treatment in lagoons or wetlands (Bustamante et al., 2005).

2. Materials and methods

2.1. *Activity and biodegradability in batch assays*

The activity tests were conducted in 2 L plastic containers (AEMA, ES) which contained both inoculum and substrate according to VDI 4630. The produced gas accumulated in a connected graded 300 mL plastic chamber, submerged in water with a valve and a release port to withdraw the excess volume of gas. The design guaranteed pressure stability within the system.

Six duplicate batch reactors (Table 1) were set up to investigate the potential hydrolytic and methanogenic/treatment capacity of the granular sludge on winery wastewater at mesophilic conditions (37 °C). The sludge prior to inoculation was stored at 20 ± 2 °C for three months to reduce endogenous respiration rate to near zero. Controls were performed both with substrate only and inoculum only. Additionally, batches with 2-Bromoethanesulfonic acid (B.E.S.) inhibitor allowed the accumulation of intermediates (Bowen et al., 2014) and subsequently contributed to dissolved COD (sCOD) accumulation that led to the determination of the winery effluent hydrolysis rate.

Substrate was raw winery wastewater collected from the Aldea Nueva Winery wastewater treatment plant (La Rioja, ES) immediately after the screening process. The substrate was diluted with water to reach the desired concentration. The average COD of the substrate after dilution was 1256 ± 42 mg L^{-1} with a sCOD:COD of 0.88 ± 0.00. The VSS:TSS ratio of the substrate was 0.82 ± 0.06 with the VSS:COD equal to 0.02 ± 0.01.

The batch reactors were filled with substrate and granular sludge from the paper mill industry (SAICA, Zaragoza, ES): total liquid volume of 1 L, allowing a liquid:gas ratio of 1:1, and incubated at 37 °C.

The operational solids concentration was 1040 and 735 mg TSS L^{-1} and VSS L^{-1} respectively, which corresponded to a mass of 0.13 g VSS in each batch reactor. This led to a high F:M ratio (~10 kgCOD $kgVSS^{-1}$); the rationale behind this

Table 1 – Substrate concentration and theoretical methane potential from each setup.

Substrate	Theoretical concentration (mM)	Concentration (COD mg L^{-1})	Theoretical methane potential (mmol)
Acetate	20.0	1310 ± 84	18.4
Formate	80.0	1327 ± 64	18.7
Inoculum, WW	N/A	1256 ± 42	17.7
Inoculum, WW with B.E.S.	10.0	1250 ± 53	00
Unamended controls	N/A	0.0	0.0
Only WW controls	N/A	1280 ± 5	18.1