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ORIGINAL PAPER

Anaerobic treatment of Tequila vinasses in a CSTR-type digester

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Abstract Tequila industries in general produce great volumes of effluents with high pollutant loads, which are discharged (untreated or partially treated) into natural receivers, thus causing severe environmental problems. In this contribution, we propose an integrated system as a first step to comply with the Mexican ecological norms and stabilize the anaerobic treatment of Tequila vinasses with main design criteria: simple and easy operation, reduce operating time and associated costs (maintenance), integrated and compact design, minimal cost of set-up, start-up, monitoring and control. This system is composed of a fully instrumented and automated lab-scale CSTR-type digester, on-line measuring devices of key variables (pH, temperature, flow rates, etc.), which are used along with off-line readings of chemical oxygen demand (COD), biogas composition, alkalinity and volatile fatty acids to guarantee the operational stability of the anaerobic digestion process. The system performance was evaluated for 200 days and the experimental results show that even under the influence of load disturbances, it is possible to reduce the COD concentration to 85% in the start-up phase and up to 95% during the normal operation phase while producing a biogas with a methane composition greater than 65%. It is also shown that in order to maintain an efficient treatment, the buffering capacity (given by the alkalinity ratio, $\alpha =$ intermediate alkalinity/total alkalinity) must be closely monitored.

Keywords Wastewater treatment · Anaerobic digestion · CSTR reactor · Tequila industry

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Introduction

In the last four decades, the Tequila industry has seen a continuing growth due mainly to the increasing worldwide demand of Tequila, the traditional Mexican spirit, whose production reached 285 millions of liters of Tequila in 2007 (almost 100% more than that registered in 1995 when the *appellation d'origin controlé*, a.o.c., was granted to this alcoholic beverage). Such an increasing production has brought about the expansion of production lines as well as economical benefits and revenues to the well rooted and established Tequila industry but unfortunately, has multiplied the generation of solid and liquid effluents (6–7 kg of agave are needed and 7–10 l of Tequila vinasses are generated per liter of Tequila produced). These effluents contain high proportions of organic matter and are discharged, untreated or partially treated, into the ultimate discharge point (usually surrounding crop fields or water systems).

To meet much more stringent limitations on discharging into natural receivers and to respond to the increasing legislative pressure to reduce the impact such effluents have on the environment, the Tequila industry has adopted policies, practices and strategies to achieve sustainability that called for a balance between the economic and environmental domains. These included particular programs for the solid effluents (namely, agave leaves and bagasse) which did not render a solution to the solid wastes problems, such as pollution prevention, production of added value products (animal feedstuff, fiberboard, pulp and paper), and waste reduction (Idarraga et al. 1999; Iñiguez et al. 2001a, b). On the other hand, like all industrial and domestic wastewaters, Tequila vinasses must comply with certain pretreatment conditions prior to their release into soil or crop fields, urban sewers and water streams or reservoirs. These conditions include cooling of vinasses, partial separation of solids, filtration, neutralization and conventional treatments, such as dilution and recycling. However, the disposal in landfills has been a major source of foul odors, pests (flies and mosquitoes), loss of soil fertility, leaching and groundwater contamination, while the discharge of vinasses into the sewer has caused significant problems to local water authorities since the additional treatment has not met their own effluent quality limitations. These authorities are now insisting an on-site pretreatment of such streams before discharging into municipal sewage. Nevertheless, economical and financial aspects have hampered the implementation of appropriate treatment units in Tequila factories for the biodegradation of their vinasses.

This study aims at the design and evaluation of an integrated system for the anaerobic treatment of Tequila vinasses, a highly polluted wastewater with a temperature around 90°C, $pH < 4$ and chemical oxygen demand (COD) concentrations ranging from 30 to 80 g l^{-1}. This system combines the well-known properties of the anaerobic digestion (reduced waste biomass disposal costs, high organic loading rates, production of energy, elimination of off-gas pollution, etc.) with the proper on-line and off-line monitoring of key variables (pH, temperature, volatile fatty acids (VFA) and alkalinity) to improve the treatment process and achieve better COD removal and biogas production. The system also takes into account the application of advanced control schemes to compensate for pH drops by regulating the buffering capacity and thus, avoiding the process breakdown. We will show that it is possible to comply with the Mexican ecological norms (reduce the COD content), meet an appropriate alkalinity ratio and prevent acidification, biomass washout and, in general, the loss of operational stability with main design criteria: simple and easy operation, reduce operating time and associated costs (maintenance), integrated and compact design, minimal cost of set-up, start-up, monitoring and control. All these factors make this treatment option an economically and environmentally sustainable solution for Tequila factories.

Materials and methods

Vinasses and anaerobic sludge acclimatization

Tequila vinasses were collected from a cooling reservoir in a Tequila factory located at La Laja-Jalisco, Mexico. Anaerobic granular sludge was harvested from a full-scale up-flow anaerobic sludge blanket (UASB) reactor used in the treatment of malting effluents in a local brewery located at Guadalajara-Jalisco, Mexico. This sludge was acclimated in a 40 l batch reactor to treat Tequila vinasses under fed-batch conditions at room temperature during 5 months by using diluted vinasses (70% H_2O–30% vinasses) as substrate and whose COD concentration was around 10 g l^{-1}. The acclimatization step consisted of feeding diluted vinasses every 14 days, whose pH was previously adjusted to 7.4 by adding a NaOH solution. pH, COD, VFA and alkalinities were daily determined. Also, total suspended solids (TSS), volatile suspended solids (VSS) and biogas composition were determined just before the beginning of each cycle. The biogas was collected in Tedlar gas sampling bags for its subsequent analysis. The acclimatization period ended once the COD removal was greater than 70%, the alkalinity factor α was close to 0.3 ($\alpha = IA/TA$, see Analytical measurements section) and the methane content in the biogas greater than 50%.

Reactor instrumentation and operating conditions

The schematic layout of the vinasses treatment set-up is shown in Fig. 1. In this work, the anaerobic digestion (AD) process was carried out in a CSTR-type digester, which was made of polyvinyl chloride (PVC) with an effective volume of 5 l. The first part of the process consists of a 6 l dilution tank, where known volumes of fresh water and vinasses can be mixed in different proportions allowing the manipulation of the influent COD concentration. In this point, the vinasses pH is regulated around 6.5–7.0 by adding a NaOH solution through an off–on control scheme computed by the control device. A remotely controllable peristaltic pump is connected to the dilution tank to ensure the desired influent flow rate. The feeding flow is entered from the bottom and comes out from the top of the reactor (up-flow), where it is collected by overflow in a receiving vessel. Fresh substrate is mixed with the recycled liquid just before entering to the reactor by using a recycle ratio greater than six, in order to ensure homogeneous mixing conditions, because it has been demonstrated that the perfectly mixed assumption holds under these conditions (Buffière et al. 1998). The digester was fully instrumented and automated, allowing the on-line monitoring of pH, temperature, pressure and the biogas and wastewater flow rates. A *National Instruments* cRIO9004® device equipped with analogical and digital cards was used in the acquisition, treatment and storage of the data. This device also included the appropriate ports and capabilities that allow us the remote monitoring and control of the process from an internet connection. The programming of this device was carried out by using the LabVIEW® 8.2 software. The start-up of the digester was implemented as follows: the reactor was inoculated using 2 l of acclimated anaerobic sludge with 43.4 and 28.9 g l^{-1} of TSS and VSS, respectively. An anaerobic atmosphere was induced by feeding nitrogen to the reactor. The hydraulic retention time (HRT) was fixed at around 14 days with an organic loading rate (OLR) close to 1 gCOD l^{-1} day^{-1}. The digester pH was regulated around 7.4 by adding a NaOH solution through an off–on control scheme computed by the cRIO9004® device. The digester was operated under mesophilic conditions, where the reactor temperature was regulated at 35 ± 1°C by using an immersion circulator and water as heat transfer liquid which was conducted through the reactor jacket. The start-up phase was ended once the following conditions were reached: a continuous COD removal (≥80%), an alkalinity factor $\alpha < 0.3$ and a constant production and composition of biogas ($CH_4 \geq 60\%$). To test the experimental set-up high load rate capability and tolerance to process shock loadings, several load disturbances were introduced to the digester during the normal operating phase by increasing the COD inlet composition from 10 to 33 gCOD l^{-1}, while the HRT was decreased from 14 to 5 days in order to increase the OLR from 0.7 to 6 gCOD l^{-1} day^{-1}.

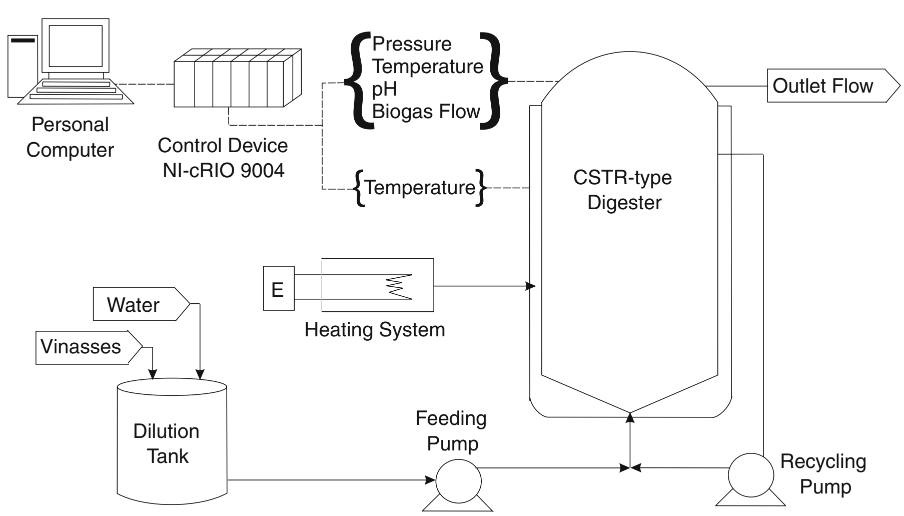

Fig. 1 Process diagram of the CSTR-type digester used in the treatment of Tequila vinasses

Table 1 Features and composition of the Tequila vinasses used in this work

Parameter	Value (g l^{-1})	Parameter	Value (mg l^{-1})
pH, 25°C	3.35	Heavy metals	
Temperature (°C)	50.4	Cadmium	<0.010
Biochemical oxygen demand (BOD)	13–24	Copper	0.364
Chemical oxygen demand (COD)	28–50	Chromium	<0.033
Sediment solids (ml l^{-1})	333	Nickel	<0.033
Total suspended solids (TSS)	12	Zinc	0.399
Volatile suspended solids (VSS)	9.8	Lead	<0.065
Total volatile fatty acids (acetic acid)	2.5–3.4	Mercury	0.0088
Total nitrogen	0.243	Biological parameters	
Total phosphorus	0.021	Total coliforms	>3 MPN by 100 ml
Fats and oils	0.018–0.031	Helminth eggs	>1 eggs l^{-1}

MPN most probably number

Analytical measurements

The features and composition of Tequila vinasses were evaluated according to the Mexican ecological norm NOM-ECOL-001-1996, whose results are shown in Table 1. Notice that the COD/N/P ratio is completely unbalanced, which makes attractive the anaerobic treatment of Tequila vinasses because of its capability to deal with wastewaters with unbalanced COD/N/P ratio (Moletta 2005).

In addition to the on-line readings previously described, TSS and VSS were measured off-line according to Standard methods (APHA-AWWA-WEF 2005). The COD was also determined off-line by the closed reflux colorimetric method by using the HACH digester DBR200 and spectrophotometer DR2800. Partial (PA), total (TA) and intermediate (IA) alkalinities as well as bicarbonates (B) were measured according to Ripley et al. (1986). VFA was measured by using a HPLC Watters 600 using a 2410-IR detector. Finally, the biogas composition was determined with a GC Perkin-Elmer AutoSystem XL using a TCD detector.

Results

Start-up phase

During the start-up phase, one of the main objectives was to achieve the efficient adaptation of the anaerobic sludge to continuous operation. As a result, an experimental operating procedure was devised to start with a low OLR and a high HRT in order to stress as less as possible the microbial population during the adaption period. As seen in Fig. 2, these conditions effectively allowed the good interaction between the microbiological system and the continuous conditions even at the start-up. This phenomenon can be interpreted as a direct result of the sludge adaptation for the assimilation of the different nutrients contained in Tequila vinasses. Notice that this step allowed the reduction of the start-up time in contrast to that presented by similar processes treating vinasses from other wine distillery industries which is normally higher than 2 months (Beltrán et al. 1999).

It can also be seen in Fig. 2 that the COD removal yield increased from 30 to 85% in 50 days with a constant OLR, while the alkalinity factor α decreased from 0.45 to 0.2. In contrast, the biogas production was rather poor at this stage, which can be explained by the low OLR. However, more important than the numerical value, it was the fact that the biogas production showed a persistent increasing behavior until stabilization around 1 l day^{-1}, with a methane composition greater than 60%. Furthermore, the average VFA concentration was 0.7 g l^{-1}, which was mainly composed by acetate. Another VFA normally found in AD process is the propionic acid; however, its presence in high concentrations (propionate/acetate ratio $\geq$ 1) is usually related with operational instability in AD processes (Marchaim and Krause 1993). Then, the fact that only negligible

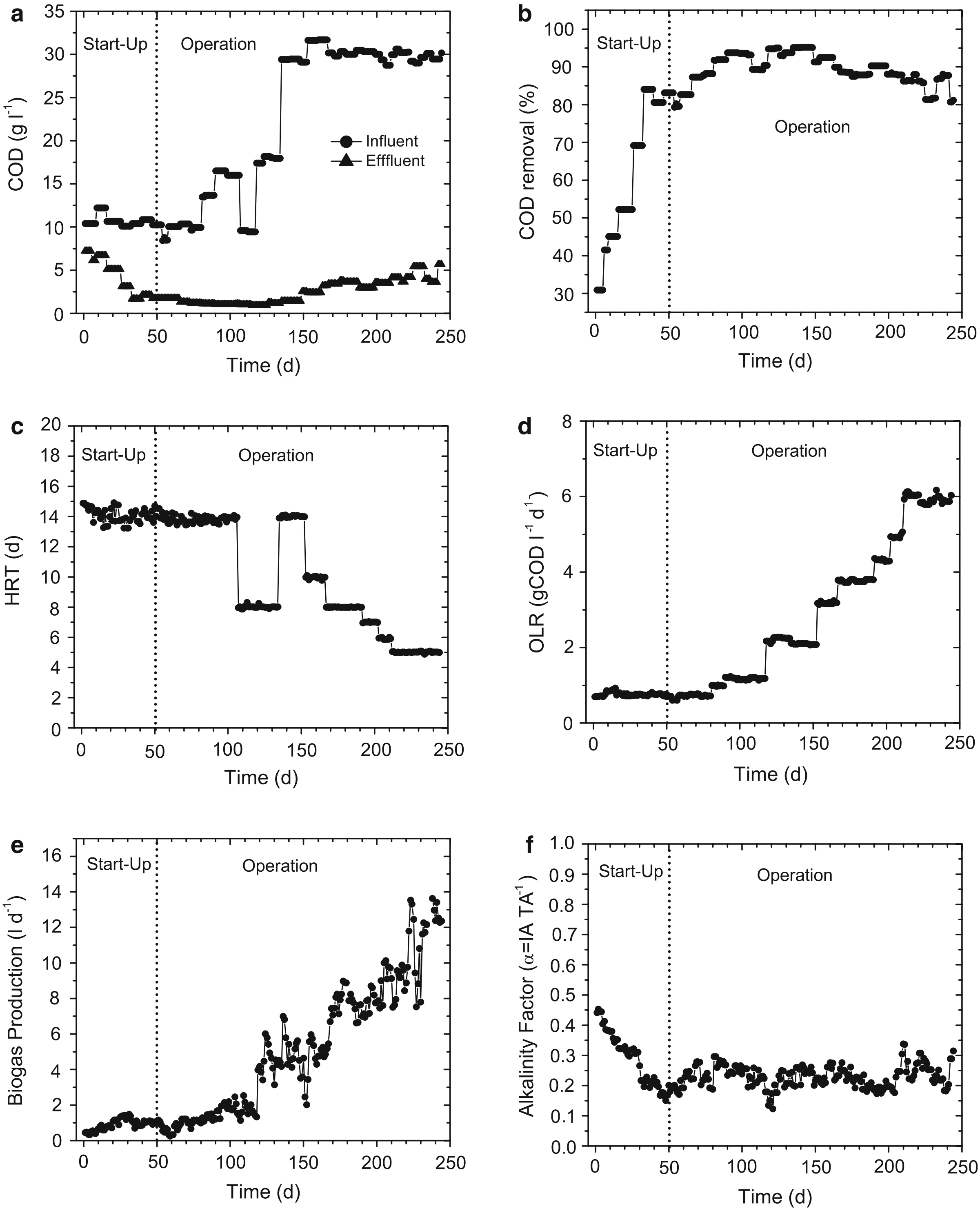

Fig. 2 Experimental results obtained during the start-up and operation phases of the CSTR-type digester used in the treatment of Tequila vinasses

concentrations of propionic acid were found, confirms that the digester was operated under stable operating conditions in the start-up phase, which allowed us to proceed testing the performance of the integrated system during the normal operating phase.

Normal operating phase

Once the start-up phase ended, the AD process was operated during 200 days, whose results are depicted in Fig. 2. In order to evaluate the performance of the process under the influence of load disturbances, the influent COD and the HRT were varied to increase the OLR from 1 to 6 g l^{-1} day^{-1} which corresponds to the OLR when only raw vinasses were feed to the digester. Results show that the COD removal yield was not drastically affected by the induced load disturbances, which was nearly 90% (except for a period of 20 days, when it reached 95%). Moreover, notice that the alkalinity factor α kept around 0.25 in the face of the load disturbances, preventing the accumulation of VFA and as a consequence, guaranteeing the operational stability of the process (Ripley et al. 1986). On the other hand, Fig. 2e shows that the biogas production increases proportionally with the OLR, reaching a maximal production of 14 l day^{-1} with a methane composition greater than 65%. These results are in agreement with typical values reported for the anaerobic treatment of winery and distillery wastewaters (Moletta 2005); however, its extension to Tequila vinasses has had very limited success as the few Tequila factories operate their anaerobic treatment processes under relatively moderate conditions (i.e., high HRT and diluted vinasses) in contrast to the ones reported in this study.

The results presented in this work are encouraging to scale-up biological treatment of vinasses in Tequila factories of all sizes and liquid waste flowrates which range from 2 to 600 m^3 day^{-1} (Linerio and Guzmán 2004). Furthermore, it reveals experimental data for a large set of operating conditions and for long continuous time periods which can be used as startup point for future researches.

Conclusions

An integrated system for the anaerobic treatment of Tequila vinasses was presented. It was shown that it is possible to maintain a 90–95% COD removal and a production of 537 l of biogas per kg of COD removed with more than 60% of methane content in the resulting biogas. Results also indicated that the acclimated anaerobic sludge was able to tolerate changes in the OLR from 1 to 6 g COD l^{-1} day^{-1}, even under an unbalanced COD/N/P ratio.

Furthermore, the process operational stability was guaranteed by maintaining and controlling the alkalinity factor α below 0.3. These results together with the proper operation make this system an economically and environmentally sustainable solution especially for medium and small size Tequila factories. Additional experimental runs are currently underway to optimize the COD removal yield by reducing the HRT and by using other bioreactor configurations (such as fixed or fluidized bed). These results will be reported in the near future.

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