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COMBINED TREATMENT OF VINASSE BY AN UPFLOW ANAEROBIC FILTER-REACTOR AND OZONATION PROCESS

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Abstract - The aim of the present study was to evaluate the efficacy of treating vinasse using anaerobic digestion (AD) followed by ozonation. The AD process was performed using a laboratory-scale upflow anaerobic filter reactor (UAFR) under continuous operation at 29 ± 1 °C. Stable conditions were reached at 10 kgCOD m^{-3} d^{-1} and a hydraulic retention time (HRT) of 5 days. Under these conditions, the efficiency of reduction of the chemical oxygen demand (COD) and the methane yield were 75.1% and 0.315 m^3CH_4 $kgCODr^{-1}$, respectively. The anaerobically digested effluent was further treated using ozone in a bubbling column. An experimental 2^3 array [$C(0_3)_g$= 70; 100 mgO_3 L^{-1}; pH= 7.5; 10; tc = 1 and 3 h] was used. The best conditions for effluent ozonation were 100 mgO_3 L^{-1}, pH 7.5 and 3 hours of contact with ozone. The average efficiencies for COD, color and turbidity reduction were 82.4, 93.8 and 99.3%, respectively.
Keywords: Anaerobic digestion; Combined treatment; Methane; Ozonation; Upflow anaerobic filter reactor; Vinasse.

INTRODUCTION

Vinasse is a by-product of the ethanol-distillation process. Its final disposal is a serious problem because vinasse is a high-strength liquid residue that has negative effects on the environment. The vinasse generation rate has been reported to range from 8 to 20 L per L of ethanol produced, and its chemical oxygen demand (COD) and biochemical oxygen demand (BOD) levels have been reported to range from 50 to 150 kgCOD m^{-3} and from 20 to 80 kgBOD m^{-3}, respectively (España *et al*., 2011; Mohana *et al*., 2009). Vinasse is characterized by a low pH (<5) and a dark-brown color, which can be attributed to the presence of phenolic compounds and melanoidins.

Melanoidins are polymers that occur in both low- and high-molecular-weight forms (ranging from 5,000 to 40,000 Da). These compounds are the products of

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a non-enzymatic reaction involving sugars and amino acids, known as the Maillard reaction (Martins and van Boekel, 2005). The empirical formula of melanoidins is $C_{17\text{-}18}H_{26\text{-}27}O_{10}N$ (Satyawali and Balakrishnan, 2007).

Alternative methods for the final disposal of vinasse are fertilization/irrigation due to its high levels of organic matter and nutrients, for biomethanation and direct discharging into bodies of water. The fertilization/irrigation technique is currently questioned due to the negative impacts of its long-term application on the soil and groundwater. Environmental impact studies have been conducted on the effects of using raw or digested vinasse for irrigation on the properties of soil and groundwater (Lyra *et al*., 2003; Jain *et al*., 2005; Biswas *et al*., 2009; Hati *et al*., 2007; Fuess and Garcia, 2014). The main effects of vinasse treatment on the characteristics of soil were improving its physical structure, carbon content, aggregate stability, cationic exchange capacity (CIC) and microbial activity (Biswas *et al*., 2009, Hati *et al*., 2007). However, some ion-leaching and salinization problems were detected.

In contrast, the reported effects of vinasse on groundwater varied considerably due to differences in the monitoring processes employed and which soil characteristics were evaluated, seasonal variations and differences in how the vinasse was discharged. The main problems that have been identified were the increment of electrical conductivity (EC), total dissolved solids (TDS) and ion concentrations (Lyra *et al*., 2003; Jain *et al*., 2005; Hati *et al*., 2007). Vinasse discharge into bodies of water affected the aquatic biota due to the diminishment of the level of dissolved oxygen in the water that occurred as the organic matter degraded. Severe disorders of the respiratory systems of fishes also developed, inducing lethal intoxication (Kumar *et al*., 1995; Ramakritman *et al*., 2005).

Anaerobic or aerobic biological processes or a combination of both have been widely used for vinasse treatment (Rajagopal *et al*., 2010) because their application resulted in the reduction of organic matter (in terms of both COD and BOD) at high efficiency. Moreover, in the case of utilizing a biological anaerobic process for vinasse treatment, the additional benefits include the recovery of energy and the production of a biofertilizer (Moraes *et al*., 2014). Nevertheless, utilizing these processes has been insufficient to completely solve the problem of the organic-load content, coloration level and recalcitrant-compound content of vinasse effluents exceeding the limits of environmental regulations.

Among the anaerobic technologies applied to vinasse treatment, those based on the use of an anaerobic filter reactor (AFR) have been widely investigated (Bories and Ranyal, 1988; Rivera *et al*., 2002; Acharya *et al*., 2008). AFR systems have been shown to be able to accommodate drastically high organic shock loads (Kumar, 2008), making them appropriate for vinasse treatment. However, as noted above, an anaerobic treatment may not be entirely effective in vinasse processing; thus, it has been suggested that a combination of biological and physical-chemical treatments might guarantee the appropriate final disposal of vinasse. Numerous investigations of vinasse post-treatment methods have been conducted, including those of adsorption treatments (Figaro *et al*., 2009; Satyawali and Balakrishnan 2007) and coagulation-flocculation, electrocoagulation, ozonation and ultrasonic treatments (Zayas *et al*., 2007; Inanc *et al*., 1999; Peña *et al*., 2003; Sangave *et al*., 2007). The disadvantages of these post-treatments include their operational difficulties, the high doses of required reagents, the high energetic costs, the unsatisfactory coagulant-recovery rates and the production of polluted sludge.

Moreover, most of the recalcitrant compounds in vinasse are oxidizable using advanced-oxidation processes (AOPs) (Beltrán *et al*., 1997). These processes are found to be highly effective in oxidizing organic matter and inactivating the microorganisms present in the residual material. Ozonation is a viable alternative for the pre-treatment or treatment of high-strength wastewater, including that containing recalcitrant compounds (Subha and Muthukumar, 2012). Ozonation has been used to pretreat vinasse to partially oxidize both the biodegradable and non-biodegradable compounds present and to reduce the level of phenolic compounds. Ozonation was found to enhance the biodegradability of vinasse (Siles *et al*., 2011). Other authors conducted a kinetic study of wine vinasse using ozonation and reported that the COD reduction rate reached 16.6% and 25.2% after 9 h of batch operation and 16 h of continuous operation, respectively (Benítez *et al*., 2003).

A review of the literature indicated that ozonation has not been reported as a post-treatment strategy for digested vinasse to date. Furthermore, most of the relevant studies of ozonation utilized a combination of anaerobic/aerobic treatments with high ozone dosification (Peña *et al*., 2003) or intermediate treatments between the anaerobic and the aerobic process (Inanc *et al*., 1999; Sangave *et al*., 2007).

Therefore, the aim of the present study was to evaluate the efficacy of utilizing a novel combined

process with anaerobic-digestion and ozonation as the final step of raw vinasse treatment.

MATERIALS AND METHODS

Substrate and Inoculum

Raw vinasse was collected from a sugar factory in Cuba. These materials were stored frozen at -20 ºC until used. The inoculum used to initiate the anaerobic process was collected from a mesophilic septic tank operated under environmental conditions. The inoculum was acclimated to anoxic conditions at 30 °C and to vinasse prior to use.

Anaerobic Filter Reactor Set-Up

An upflow anaerobic filter reactor was used for the anaerobic treatment of the raw vinasse. The reactor, constructed of plastic (PVC), was 58 cm high, with an internal diameter of 9.5 cm. The effective volume was 3.4 L, and the packed effective volume was 3.23 L, as shown in Figure 1. Randomly dispersed cylindrical corrugated hollow PVC particles with a specific area of 205 m^2 m^{-3} were used as the supporting material for the adhesion of microbes.

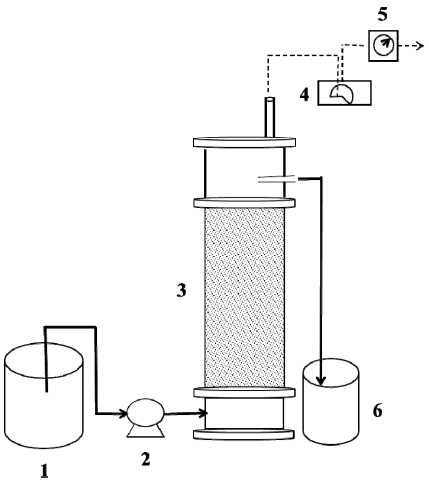

Figure 1: Schematic diagram of the UAFR utilized in this study. 1: Feeding vessel; 2: Peristaltic pump; 3: Upflow anaerobic filter reactor; 4: Gas flowmeter submerged in a solution of 15% w/v NaOH; 5: Analog counter; 6: Vessel containing the digested effluent.

Starting-Up the Upflow Anaerobic Filter-Reactor Process

The filter was inoculated using 1.5 L of the previously adapted sludge, after which the UAFR was operated for the next 180 days. During the first 45 days, the reactor was operated at a low organic-loading rate (OLR), ranging from 1 to 2.5 kgCOD m^{-3} d^{-1}, with recirculation, to promote biofilm formation on the packed bed. When the levels of methane production and COD reduction had stabilized, the OLR was gradually increased from 5 to 10 and finally to 15 kgCOD m^{-3} d^{-1}, which corresponded to hydraulic retention times (HRTs) of 10, 5 and 3 days, respectively. The pH value of the raw vinasse-containing effluent was adjusted before feeding it into the reactor using a solution of 25% v/v $NaHCO_3$. The rate of gas flow was measured online, with the line having been previously submerged in a solution of 15% w/v NaOH to count only the amount of methane produced. The reactor was continuously fed using a Watson Marlow 313 peristaltic pump. The temperature was maintained at 29 ± 1 °C.

Ozonation Experimental Set Up

The ozonation trials were conducted on the laboratory scale using a bubbling column with a 1-L capacity and 4-cm diameter, as shown in Figure 2. A porous borosilicate diffusor was placed in the lower part, inputs and outputs of the column to discharge the residual effluent. A sampling valve was located midway in the liquid column. A foam-collection system was connected to the gas outlet in the upper portion of the column, proximal to the site of the residual ozone-destruction system.

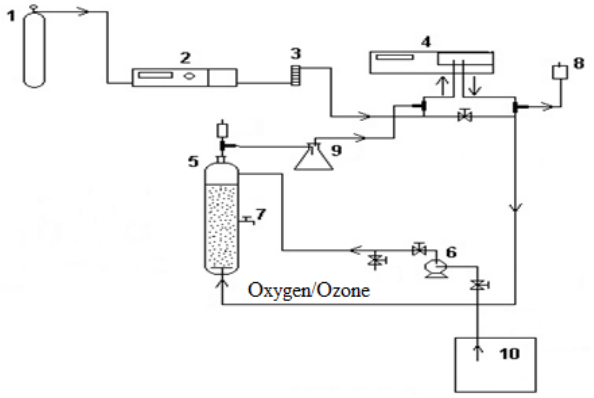

Figure 2: Schematic diagram of the ozonation apparatus utilized in this study: 1: Oxygen bottle; 2: Ozone generator; 3: Gas flowmeter; 4: Spectrophotometer; 5: Bubbling column; 6: Peristaltic pump; 7: Sampling valve; 8: Ozone-destruction system; 9: Foam-collection trap; 10: Vessel of the anaerobically digested effluent.

Ozonation Trials

The ozonation trials were conducted in triplicates according to the best operational conditions obtained

during the anaerobic process for further processing of 600 mL of anaerobically digested raw vinasse effluents. Ozonation was performed in semi-bacth operation because the liquid was only charged initially but the gas was continuosly fed at a gas-flow rate of 15 L h^{-1}. The experimental conditions were designed according to a 2^3 array, as shown in Table 1. The pH value was adjusted to 10 using a solution of 0.1 M NaOH. The ozone doses applied and consumed and the transference efficiency (TE) were calculated according to Equations (1), (2) and (3), respectively.

$$\text{Applied dose of } O_3(mgO_3L^{-1}) = \frac{c(O_3)g_{(in)} * Q_g)}{V_L} * t_c \quad (1)$$

$$\text{Consumed dose of } O_3(mgO_3L^{-1}) = \frac{(c(O_3)g_{(in)} - c(O_3)g_{(out)}) * Q_g}{V_L} * t_c \quad (2)$$

$$T.E.(\%) = \frac{\text{Consumed dose}}{\text{Applied dose}} * 100 \quad (3)$$

where $c(O_3)_{g\ (in)}$ and $c(O_3)_{\ g\ (out)}$ are the gaseous ozone concentrations at the input and output sites of the column, respectively, in [$mgO_3\ L^{-1}$], Q_g is the gas flow rate [L h^{-1}], V_L is the volume of the digested effluent to be treated [L] and t_c is the contact time of ozone with the digested effluent [h].

Table 1: Experimental design applied to the ozonation process.

Factor	Range of levels	
$C(O_3)_g$ ($mgO_3\ L^{-1}$)	70	100
tc (h)	1	3
pH	7.5	10

Analytical Methods

The levels of total COD (COD_t), soluble COD (COD_s), BOD_5, coloration, conductivity, turbidity, solids, total Kjeldahl nitrogen (TKN), P_{total}, Ca^{2+}, Mg^{2+} and K^+, as well as the pH value in the feeds and effluents were determined according to standard methods (APHA, 2005). The K^+ concentration was determined by flame photometry using a Corning 410 instrument. The COD, color and P_{total} levels were determined using a Pharmacia LKB-Ultrospec III spectrophotometer, as well as the inlet and outlet gas concentrations at 256 nm with a gas flow cell with 1 mm optical path. The concentrations of Ca^{2+} and Mg^{2+} were determined through titration using EDTA.

The volatile fatty acid (VFA)/total alkalinity ratio was determined according to the method of Lossie and Pütz (2008). The online methane flow rate was measured using a calibrated gas-flow meter with an analog output, and the methane value was standardized at 0 °C and 1 atm. The composition of the biogas was determined using a Biogas CDM gas analyzer.

Statistical Analysis

A multifactorial analysis of variance (ANOVA) was used to analyze the experimental results and evaluate the significance of the effects of the ozone concentration, pH and tc. The COD, color and turbidity were the response variables. A multiple-range LSD Fischer test was applied using a 95% confidence level. The statistical analyses were conducted using Statgraphics Centurion XV software.

RESULTS AND DISCUSSION

Characterization of the Substrate and Inoculum

The inoculum used for the anaerobic-digestion process had a pH value of 7.8 and a total suspended solid (TSS) content, volatile suspended solid (VSS) content and VSS/TSS ratio of 107.3, 58.2 and 0.54 g L^{-1}, respectively. As shown in Table 2, the raw vinasse used as a substrate had a high level of COD and a BOD_5/COD ratio of 0.48, indicating that this material was moderately biodegradable and was suitable for biological treatment (Ahn *et al*., 1999).

The levels of macro- and micronutrients in the raw vinasse were favorable for microorganism growth, methanogenesis and degradation of organic matter, with a COD:N:P ratio of 100:1.3:0.38. This value was consistent with that observed by McCarty (1964), who reported a COD:N:P ratio of 100:0.75:0.25. The presence of the inorganic salts Ca^{2+}, Mg^{2+} and K^+ in the raw vinasse guaranteed good microbial growth. The concentrations of Ca^{2+} and Mg^{2+} in this effluent were lower than the levels that reportedly inhibit anaerobic digestion, and the concentration of K^+ in this effluent was only slightly inhibitory (Chen *et al*., 2008).

Table 2: Characteristics of the raw vinasse and the effluents with different OLRs that were digested in the UAFR.

Parameter	Raw vinasse	Digested effluents with different OLRs (kgCOD $m^{-3}d^{-1}$)		
		5	10	15
pH	4.67 ± 0.31	7.4 ± 0.21	7.5 ± 0.12	7.45 ± 0.22
COD (g L^{-1})	50 ± 1.65	8.72 ± 1.17	12.45 ± 1.03	22.12 ± 0.47
BOD_5 (g L^{-1})	24 ± 0.12	1.3 ± 0.12	4.2 ± 0.28	9.89 ± 0.28
Conductivity (mS cm^{-1})	12.2 ± 0.61	14.44 ± 0.25	16.7 ± 0.42	17.5 ± 0.11
TKN (g L^{-1})	0.65 ± 0.1	0.67 ± 0.05	0.7 ± 0.08	0.74 ± 0.1
P_{total} (g L^{-1})	0.019 ± 0.002	0.02 ± 0.01	0.07 ± 0.002	0.09 ± 0.01
Ca^{2+} (g L^{-1})	1.6 ± 0.25	0.4 ± 0.11	0.88 ± 0.08	1 ± 0.05
Mg^{2+} (g L^{-1})	0.98 ± 0.22	0.55 ± 0.12	0.61 ± 0.15	0.67 ± 0.05
K^{+} (g L^{-1})	4.5 ± 0.11	3.1 ± 0.14	3.8 ± 0.1	4.3 ± 0.11
TS (g L^{-1})	46.9 ± 1.24	22.6 ± 3.8	22.26 ± 2.64	28.28 ± 3.21
TFS (g L^{-1})	12.5 ± 1.06	16 ± 2.4	15.9 ± 1.24	16.6 ± 2.14
TVS (g L^{-1})	34.4 ± 0.18	6.5 ± 0.24	6.3 ± 2.27	6.3 ± 1.58
Color (UPt-Co)	7 329 ± 52.3	6 670 ± 43.7	7 113 ± 28.5	7 293 ± 17.6
Turbidity (UNT)	20 843 ± 286	17 843 ± 325	19 280 ± 186.5	20 268 ± 316

Experimental Anaerobic Treatments at Different OLRs

The main response variables evaluated during the anaerobic process are shown in Table 3.

Table 3: Response variables evaluated during anaerobic processes conducted at different OLRs.

Response variable	OLR (kgCOD m^{-3} d^{-1})		
	5	10	15
η(%)	82.6 ± 2.25	75.1 ± 1.88	55.8 ± 0.93
$COD_{Red.}$(g d^{-1})	12.34 ± 0.86	23.84 ± 1.63	31.93 ± 1.82
YCH_4 (m^3CH_4 kg $CODr^{-1}$)	0.314 ± 0.019	0.315 ± 0.014	0.316 ± 0.021

As expected, the efficiency of the anaerobic process in terms of COD reduction decreased with an increase in the OLR of the effluent. The low percentage of COD reduction (55.8%) when 15 kgCOD m^{-3} d^{-1} was applied indicated that the UAFR should not be operated at OLRs higher than 10 kgCOD m^{-3} d^{-1} if higher COD reduction efficiencies are desired. Rivera *et al*. (2002) reported lower efficiencies of COD reduction when an UAFR was operated at OLRs of less than 7.32 kgCOD m^{-3} d^{-1}. The efficiency of COD reduction reached in this study at 10 kgCOD $m^{-3}d^{-1}$ (75.1%) was similar to that obtained by Bories and Ranyal (1988), which was between 71% and 73.8% COD reduction at an OLR of 11.45 kgCOD $m^{-3}d^{-1}$ with an HRT of 2.4 days. Cabrera and Díaz (2013) reported a COD-reduction efficiency of approximately 70%. In contrast, Acharya *et al*. (2008) reported a COD-reduction efficiency of 64% with an OLR of 23.25 kgCOD m^{-3} d^{-1} and an HRT of 8 days using a coconut fiber-packed bed.

Figure 3 presents the methane-yield behavior at the three different OLRs tested. The average methane yield was 0.315 m^3CH_4 $kgCODr^{-1}$. This value is consistent with that obtained by Rivera *et al*. (2002), who reported yields ranging from 0.280 to 0.380 m^3CH_4 $kgCODr^{-1}$ at OLRs ranging from 0.2 to 10.52 kgCOD m^{-3} d^{-1} and temperatures ranging from 20 to 25 ºC. Conversely, Cabrera and Díaz (2013) obtained a yield of 0.270 m^3CH_4 $kgCODr^{-1}$ at an OLR of 16 kgCOD m^{-3} d^{-1} and an HRT of 2 days.

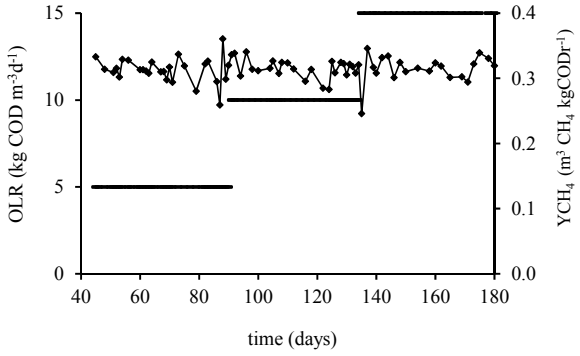

Figure 3: Methane-yield behavior at different OLRs.

The biogas productivity rates at the three OLRs were also determined and were found to reach average values of 1.72, 3.35 and 4.49 m^3_{biogas} m^{-3}_{reac} d^{-1} at OLRs of 5, 10 and 15 kgCOD $m^{-3}d^{-1}$, respectively. A direct relationship between the increase in the biogas productivity level and the OLR was found. The results were consistent with those obtained by Bories and Ranyal (1988), who reported a biogas productivity level of 4.5 m^3_{biogas} m^{-3}_{reac} d^{-1} at an OLR of 9.2 kgCOD $m^{-3}d^{-1}$ and an HRT of 4.9 days using a similar packed bed. The difference in the results might be

attributed to differences in the set-up of the feeding reactor inlet (upflow or downflow).

In contrast, in a relevant study, Acharya *et al.* (2008) obtained a biogas productivity rate of 7.25 m^3_{biogas} m^{-3}_{reac} d^{-1} at an OLR of 23.25 kgCOD m^{-3} d^{-1} and a HRT of 8 days. This result might have been due to the nature of the packed bed (coconut fiber) enhancing the formation and adhesion of the biomass-based biofilm. The biogas was composed of 66.5% CH_4, 25.3% CO_2 and 0.2% O_2, on average.

Table 4 shows the average values of the control variables. The pH value of the effluent under each operational condition was between 7.4 and 7.5, which was the best alternative for the anaerobic-treatment process (Kumar, 2008). According to Lossie and Pütz (2008), the VFA/total alkalinity ratio of digested effluents under stable operating conditions should be between 0.2 and 0.3. In the case of the UAFR, when OLRs of 5 and 15 kgCOD $m^{-3}d^{-1}$ were applied, this ratio reached values of 0.05 and 0.75, respectively, both of which were not inside the recommended values, indicating the presence of insufficient biomass at 5 kgCOD m^{-3} d^{-1} and excess biomass at 15 kgCOD m^{-3} d^{-1}. Nevertheless, the pH value remained constant under the latter condition. The VFAs that accumulated under this condition were neutralized due to the high total alkalinity level caused by CO_2 generation (Kumar, 2008).

Table 4: Behavior of the control variables at different OLRs.

Control variable	OLR (kgCOD m^{-3} d^{-1})		
	5	10	15
Effluent pH	7.4 ± 0.21	7.5 ± 0.12	7.45 ± 0.22
VFA (gHAc L^{-1})	1 ± 0.85	5.1 ± 0.65	5.88 ± 0.92
Total Alk. ($gCaCO_3$ L^{-1})	18.51 ± 1.49	21.61 ± 2.35	7.8 ± 1.52
VFA/Total Alk.	0.05	0.24	0.75

Characterization of the Digested Effluents

The effluents that had been digested at the three OLRs studied were characterized. The results are shown in Table 2. During the operation of the UAFR, the TKN and P_{total} of the digested effluents were slightly higher than those of the raw vinasse, indicating no microbial requirements for these compounds and their possible generation through the degradation of the organic materials.

Small variations in the color of the effluents compared with that of the raw vinasse were detected despite some color alteration having occurred after the neutralization process was performed. The turbidity values decreased for each applied OLR, but the conductivity value increased with the increase in the OLR due to the addition of dissolved salts to the UAFR to adjust the pH of the effluents. The BOD_5/COD ratios of the effluents were 0.15, 0.34 and 0.45 at OLRs of 5, 10 and 15 kgCOD m^{-3} d^{-1}, respectively, indicating the presence of residual organic matter and the low efficiency level of the anaerobic process when the OLR was increased. Based on the observed anaerobic behavior, an OLR of 10 kgCOD m^{-3} d^{-1} and an HRT of 5 days were selected as the best operational conditions for the UAFR-based digestion of vinasse, the product of which would be further treated using an ozonation process.

Effect of the Ozonation Process on the Reduction of COD, Color and Turbidity from the Digested Effluent

The effluent obtained using the selected operational conditions for the UAFR was processed by ozonation. The aim of this post-treatment was to attain further reductions of the COD, color and turbidity. Figure 4 (a and b) presents the average results of ozonation at pH values of 7.5 and 10 and gas-ozone concentrations of 70 and 100 mgO_3 L^{-1} for a contact time of 3 h.

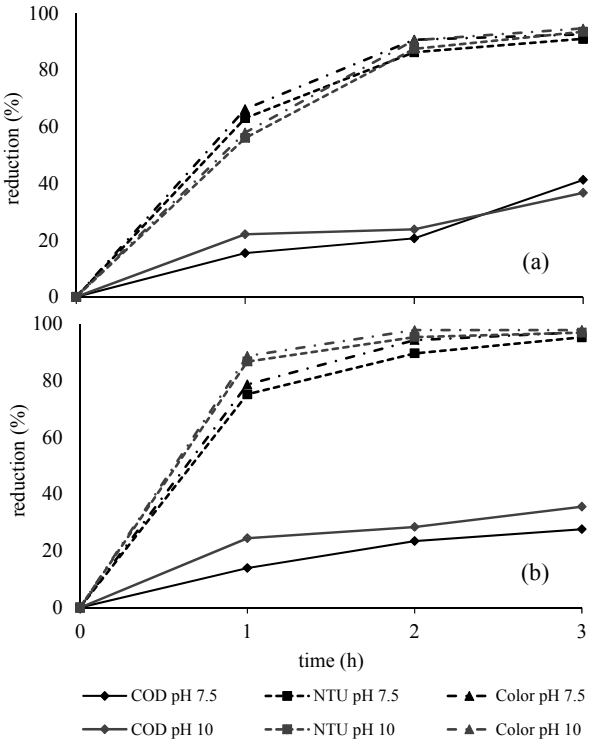

Figure 4: Effects of ozonation at $c(O_3)g$=70 mgO_3 L^{-1} and pH=7.5 or pH=10 (a) and $c(O_3)_g$= 100 mgO_3 L^{-1} and pH=7.5 or pH=10 (b).

Reduction of the Chemical Oxygen Demand (COD)

Using an ozone concentration of 70 $mgO_3\ L^{-1}$, the level of COD reduction of the digested effluent was slightly higher at pH 7.5 than at pH 10 after 3 hours of contact. However, when the ozone concentration was 100 $mgO_3\ L^{-1}$, the level of COD reduction was slightly higher (8%) at pH 10 compared to the results obtained at pH 7.5. The latter result might be due to the organic compounds being mineralized at the basic pH, which would have strongly inhibited the reaction between hydroxyl radicals and organic materials. Therefore, increased pH values did not favor high-level COD reduction (Peña *et al*., 2003). In the present study, the total alkalinity values were high (21.61 g L^{-1}), and the COD level was reduced by 30% and 40% after 3 h of contact.

These results were superior to those obtained by Peña *et al.* (2003), who reported achieving 15% and 25% COD reduction when vinasse was treated using a combined anaerobic/aerobic process at a rate of 1.6 to 11.5 g $O_3\ h^{-1}$.

Reduction of the Turbidity and Color Levels

The high levels of reduction of compounds that contributed to turbidity and color exhibited a similar behavior at both of the tested pH values of 7.5 and 10 at the lower ozone concentration evaluated. The color level was reduced by more than 90% due to the double-bonded chains of the phenolic and sugar-containing compounds, as well as those in the melanoidins (color contributors), being strongly and rapidly oxidized by ozone at a low level of ozone consumption (Rodriguez *et al*., 2008; Peña *et al*., 2003). When the ozone concentration was 100 $mgO_3\ L^{-1}$, the best color reduction levels were obtained at pH 10, with 87% of the color removed during the first hour of ozonation.

The reduction in the turbidity level showed a similar behavior at 70 $mgO_3\ L^{-1}$ and pH values of 7.5 or 10. When the ozone concentration was 100 $mgO_3\ L^{-1}$, the level of turbidity reduction was slightly greater, reaching approximately 90% between the first and second hours of ozonation at pH 10.

Peña *et al.* (2003) reported a color reduction rate of between 80% and 90% achieved during the first 30 min of ozonation at a rate of 3.7 g $O_3\ h^{-1}$. In the present study, between 60 and 80% of the color was removed when ozone was applied at rates of 1.05 and 1.5 g h^{-1} during the first hour of contact. The differences might be attributed to the high COD of the digested effluent (12.45 $g_{COD}\ L^{-1}$) and the lower rate of ozonation applied in this study. Therefore, investigating the ozonation of effluents biologically treated in an anaerobic system with a higher COD-reduction efficiency is recommended to reduce the applied ozone dose and contact time.

Ozonation Efficiency

The transfer efficiency (TE) of the ozone dose applied and that consumed was evaluated. These doses were related to the ozone concentrations at the input and output of the ozonation reactor operating at a particular gas-flow rate, with a particular volume of residue to be treated and a particular contact time. Figure 5 (a and b) presents the increase in the ozone concentration at the output over time with respect to the ozone concentration at the input. The rate of ozone consumption was high during the first hour of ozonation due to the reaction of ozone with the easily oxidized organic compounds, which were the most prominent contributors to color and turbidity. The transfer efficiency during this period reached high values (87-98%) at both ozone concentrations and pH values. After this period, the TE decreased to an average of 52% due to the presence of a high salt content. These salts were not easily degraded or oxidized in the ozone reactor during the tested contact period.

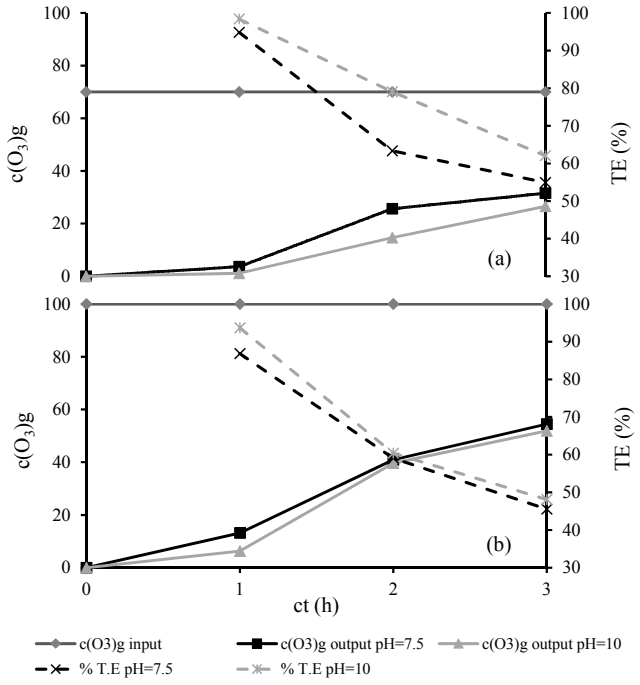

Figure 5: Ozone transfer efficiency at $c(O_3)_g$ = 70 $mgO_3\ L^{-1}$ and pH = 7.5 or pH = 10 (a) and at $c(O_3)_g$ = 100 $mgO_3\ L^{-1}$ and pH = 7.5 or pH = 10 (b).

Best Conditions for Ozone Treatment

Based on the results of the statistical analysis, the contact time had a significantly positive effect on COD reduction as well as on color and turbidity reduction. Additionally, the ozone concentration had a positive effect on color and turbidity reduction. Table 5 summarizes the results of the multiple-range tests. X denotes the variables that had a significant effect on the reduction of various factors. As shown, the ozone concentration ($c(O_3)_g$) had a significant effect on color and turbidity reduction, which was due to the larger amount of oxidant being available to react with the organic compounds in the vinasse effluents. Therefore, ozonation should be conducted at 100 $mgO_3\ L^{-1}$.

Table 5: Summary of the results of the multiple-range tests.

Variable	% COD red	% Color red	% Turbidity red
$C(O_3)_g$ ($mgO_3\ L^{-1}$)	-	X	X
pH	-	-	-
tc. (1-3) h	X	X	X

Because the pH value did not significantly affect the reduction rates, it was preferable to conduct ozonation at the pH value of the anaerobically processed effluent (pH 7.5). This criterion is in agreement with the recommendation of Peña *et al*. (2003). A longer contact time was also recommended to increase the rate of nutrient degradation and the amount of salts that could be recovered for use in future processes.

The statistical modeling equations that described the reduction in the COD, color and turbidity were as follows:

$$COD = 10.76 + 8.10 * tc$$

$$(R^2 = 87.5\%)$$

$$Color = -26.60 + 1.03 * CO_{3\,(g)} + 37.95 * tc - 0.31 * CO_{3(g)} * tc$$

$$(R^2 = 84.3\%)$$

$$Turbidity = -28.04 + 1.01 * CO_{3(g)} + 37.12 * tc - 0.30 * CO_{3(g)} * tc$$

$$(R^2 = 85.2\%)$$

Results for the Combination of Anaerobic Digestion and Ozonation Process

The digested effluent was subjected to the ozonation process using the best operational conditions obtained via the anaerobic digestion process. This effluent was treated under the conditions of $c(O_3)_g$ = 100 $mgO_3\ L^{-1}$, tc = 3 h and pH = 7.5. The results obtained are shown in Table 6. The ozonation treatment increased the biodegradability (BOD_5/COD) of the effluent from 0.34 to 0.53. This increase might be due to the organic matter having been solubilized to a degree that was previously unattained. Regarding the COD reduction, the efficiencies are close to 30%, similar to the efficiency reported by Rodriguez *et al.* (2008). These authors noted that less than 50% of the COD had been removed after the ozonation process was completed due to the presence of ozone-resistant compounds in the residual material, as well as the presence of carbonates and bicarbonates that cause the decomposition of hydroxyl radicals.

Table 6: Characteristics of the anaerobically digested effluent before and after ozonation treatment.

Parameter	Anaerobically digested effluent	Effluent after ozonation	% Reduction or increase
pH	7.5 ± 0.12	8 ± 0.1	-
COD ($g\ L^{-1}$)	12.45 ± 1.03	8.82 ± 1.21	-29.1
BOD_5 ($g\ L^{-1}$)	4.2 ± 0.12	4.67 ± 0.15	11.1
Conductivity ($mS\ cm^{-1}$)	16.7 ± 0.42	15 ± 0.34	-10.2
Ca^{2+} ($g\ L^{-1}$)	0.88 ± 0.08	0.86 ± 0.1	-2.3
Mg^{2+} ($g\ L^{-1}$)	0.61 ± 0.15	0.3 ± 0.16	-50.8
K^{+} ($g\ L^{-1}$)	3.8 ± 0.1	3.8 ± 0.11	0
Color (UPt-Co)	7 113 ± 28.5	451.16 ± 14.8	-93.7
Turbidity (UNT)	19 280 ± 186.5	149.13 ± 4.55	-99.2

The concentrations of compounds such as potassium salts were unaffected by the ozonation process; these elements are highly valuable for conducting future recovery processes and for agricultural use. The magnesium and calcium concentrations were decreased by the ozonation process, which increased the pH of the treated material slightly due to the reduction of Ca^{2+} and Mg^{2+} to Ca and Mg respectively. It might be due to a precipitation process of carbonates if the constant for the product of solubilization was exceeded during the ozonation procedure.

The ozonation treatment was effective in reducing the color and turbidity levels, attaining values of 451.16 UPt-Co and 149.13 UNT with reduction percentages of 93.7 and 99.2, respectively.

The results of this study confirmed the efficacy of utilizing a combined process with anaerobic-digestion and ozonation as the final step of raw vinasse treatment. The combination of UAFR treatment and ozonation of raw vinasse was appropriate for attaining reductions of 82.4, 81.4, 93.8 and 99.3% in the COD, BOD_5, color and turbidity levels, respectively. The use of this combination might improve the final disposal of treated vinasse and the quality of soils, groundwater and bodies of waters.

CONCLUSIONS

This study showed that it was feasible to treat raw vinasse biologically using an UAFR at 10 kgCOD $m^{-3}d^{-1}$ and a HRT of 5 days. Under these conditions, the methane yield was 0.315 m^3CH_4 $kgCODr^{-1}$, with 75.1% COD reduction and 82.6% BOD_5 reduction achieved. The digested effluent was post-treated by ozonation using the best conditions of 100 mgO_3 L^{-1} for the ozone concentration and a contact period of 3 h. This ozonation process resulted in a 29.1, 93.7 and 99.2% reduction in the COD, color and turbidity of the effluent, respectively, indicating that this procedure was appropriate for the final disposal of digested vinasse effluents. This study demonstrated that the pH value did not significantly affect the reduction of the COD, color or turbidity, which recommends conducting the ozonation procedure at the same pH as that of the digested effluent. The results of this study proved that the combination of UAFR treatment and ozonation of raw vinasse was appropriate for attaining reductions of COD, BOD_5, color and turbidity levels for a better final disposal of vinasse in different receptors.

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