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ASSESSMENT OF OZONE AS A PRETREATMENT TO IMPROVE ANAEROBIC DIGESTION OF VINASSE

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Abstract - This paper presents an assessment of ozone oxidative effects on the biodegradability of sugar cane vinasse, aiming at increasing the methane yield by anaerobic digestion of this effluent. Furthermore, as a new approach, an economic balance of this process was made. Using a bench scale reactor, ozone was applied at 60, 120, 180, 240 $mgO_3.gCOD^{-1}$ doses in raw vinasse and at three initial pH values (4.8, 7 and 9). Applying 60 $mgO_3.gCOD^{-1}$, the biodegradability of vinasse was increased by 22.7% at the initial pH value of 4.8. The application of the two-way ANOVA test indicated a significant statistical interaction between the pH value and ozone. However, a preliminary energy assessment showed that the amount of electricity consumed in a full-scale ozonation plant would be almost 6 times higher than the energy recovered from the combustion of the additional methane produced (13.6%). These results indicate that ozonation of raw vinasse to increase the methane production in a subsequent anaerobic process is economically unfeasible.
Keywords: Ozonation of vinasse; Economic assessment; Anaerobic digestion; Vinasse biodegradability; Methane.

INTRODUCTION

It is widely known that, due to the high organic content of vinasse, its anaerobic processing to obtain methane is very interesting from an economical point of view. In this case, there is little or no power consumption, the sludge production is minimal and the nutrient demand is low. Energy from methane combustion could be an additional source of income for the distillery (Jiménez *et al*., 2003).

However, research indicates that the presence of certain recalcitrant and inhibitory substances in the vinasse severely hinders the anaerobic process. These substances are mainly phenolic compounds. In addition, heavy metals, melanoidins, glycerol, antibiotics and other organic xenobiotic pollutants are also present (Wilkie *et al*., 2000). According to several authors, these substances may decrease the efficiency of the anaerobic process in terms of its kinetics, COD removal and methane production (Pearson *et al*., 1980; Borja *et al*., 1993; Benitez *et al*. 1997; Jiménez *et al*., 2006; Chen *et al*., 2008). A way to overcome the toxic effect of some of these substances is to pretreat them with ozone (O_3), which can transform complex recalcitrant compounds into biodegradable molecules, improving the biodegradability ratio (BOD_5/COD) of the vinasse (Amat *et al*., 2003). As simpler molecules are more assimilable by anaerobic microorganisms than complex ones, ozonation of vinasse can lead to improvements in the anaerobic process in terms of greater stability and methane yield. Therefore, the objective of ozonation

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prior to a biological treatment should be the partial oxidation of refractory matter, not its complete mineralization, so that successful ozonation will result in an increase in the BOD_5/COD ratio.

Recent research has shown that vinasse ozonation resulted in an increase in its biodegradability, mainly by removing phenolic compounds (Martín Santos *et al*., 2003; Siles *et al*., 2010; Siles *et al*., 2011). Feeding anaerobic reactors with pre-oxidized vinasse resulted in a considerable increase in the kinetics of anaerobic digestion (15%) and methane yield (40%) (Benitez *et al*., 1997; Álvarez *et al*., 2005; Siles *et al*., 2011).

Nevertheless, vinasses may differ in characteristics and composition due to differences in the raw material used to produce ethanol (cassava, corn, beets, grapes, cherry, wine and sugar cane) and specific practices in industrial processing in the soil and climate of plantations (Wilkie *et al*., 2000). Consequently, it is difficult to extrapolate data from ozonation of one kind of vinasse to another one. In addition, the literature does not present an energy balance to justify the use of this oxidant.

Taking all this into account, the aim of this study was to evaluate the effects of ozone on the biodegradability of a vinasse from a Brazilian ethanol distillery processing sugar cane as a raw material. In addition, a preliminary energy balance completed this assessment.

MATERIAL AND METHODS

Vinasse

The vinasse used in this study consisted of samples collected from the effluent of the ethanol distillery plant of *Usina São Martinho* located in the municipality of *Pradópolis*, the state of São Paulo, Brazil. The plant processes approximately 8.500,000 tons of sugarcane per harvesting season. The effluent was fully analyzed upon receipt and stored at 4 ºC until use. Table 1 shows the effluent properties of interest to this work.

Ozone Generation and Experimental Set-Up

An Eaglesat PXZ3507 generator (Brazil) produced the ozone for this experiment. This equipment consists of a PSA (Pressure Swing Adsorption) unit for oxygen enrichment and a corona discharge ozonator. The system was designed to have a maximum production capacity of 7 $gO_3.h^{-1}$ from the flow of oxygen produced by the oxygen generator (PXZ3507). However, according to the calibration tests (data not shown), as well as the environmental conditions in which the tests were performed, and mainly, by the ozone flow (1 Lpm), the actual production capacity used in this work was 0.65 $gO_3.h^{-1}$.

Oxidation System

In addition to the ozone generator, the oxidation system consisted of a reactor, the foam trap and the off-gas scrubber (Figure 1). The reactor used for applying the ozone to the vinasse was built using a PVC (polyvinyl chloride) pipe with the following dimensions: total height of 850 mm, of which 450 mm was the useful height. The internal diameter was 40 mm, giving a useful volume of 1 L. The experiments showed that there was great efficiency in the ozone transfer to the liquid column. This was known from the mass balance made between the amount of ozone applied to the system and that lost by the system (Table 2).

Analytical Methods

Calibration of the ozonator and the amount of ozone measurements lost from the system were measured by the titration method, using potassium iodide solution (KI) at 2%, which filled the gas scrubber.

Table 1: Chemical characteristics of vinasse used in this study and others.

Parameter	Vinasse (this study)	Martín *et al.* (2002)	Martín S.*et al.* (2003)	Acharya *et al.* (2008)	Siles *et al.* (2011)
pH	4.7	4.4	4.5	3-4.5	3.75
COD_{total} ($mg.L^{-1}$)	36.680	97.500*	108.200	140.000	68.560
BOD_5 ($mg.L^{-1}$)	15.500	42.228	41.000	50-60	29.700
Total Phenols ($mg.L^{-1}$)	< 0.5	477	660	650	450

* Soluble.

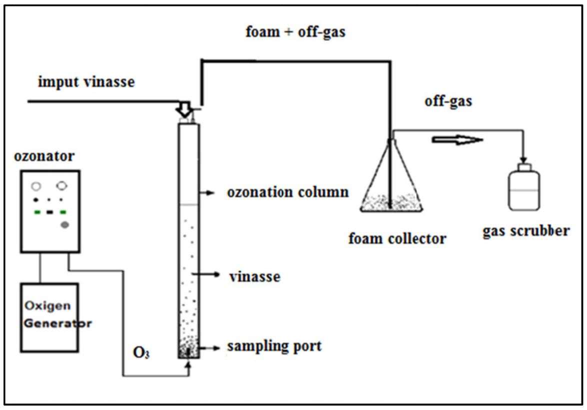

Figure 1: Advanced Oxidation System used in the experiments.

Table 2: Ozone percentage lost in each test run.

Ozone dose applied ($gO_3.L^{-1}$)	Ozone Lost (%)		
	pH 4.8	pH 7	pH 9
2	0	0	0
4	1	1	1
6	3	5	10
8	4	10	10

All samples were subjected to COD, BOD_5 and total phenol measurements, which were performed according to the Standard Methods 5220D, 5210B, and 5530D, respectively (APHA, 2005). The pH values were measured using a pH meter (Perp HecTmeter, Model 330, Thermo Orion, Waltham, MA, USA). The experimental errors were determined by calculating the sample standard deviation of the BOD_5 and COD measurements. The same methodology was used to calculate the errors in the BOD_5/COD ratios. These values were between 2% and 7.7% and are shown in Figure 2.

Experimental Design

A previous literature review showed that the best results were achieved when ozone was applied to vinasse with a natural pH value (about 4.5). However, as the characteristics of the vinasses differ greatly (Table 1), it was necessary to experimentally verify the best pH value for the oxidation of the vinasse used in this work. The effect of pH was considered by treating the vinasse at its natural pH (4.8) and at pH 7 and 9. The pH was adjusted using NaOH. The processed volume was 600 mL of raw vinasse.

The experiments followed a 4 (dose) ×3 (pH) factorial design. The ozone doses were calculated considering the reaction time (or contact time) in the reactor. It was assumed that the reaction ceases instantly when the ozone injection stops. Preliminary assays indicated that the remaining ozone in the vinasse reacts almost instantly in comparison to the total contact time in the reactor. The contact time was set at 2, 4, 6 and 8 hours, resulting in applied doses of 60, 120, 180 and 240 $mgO_3.g^{-1}{}_{COD}$. The mass and dose of ozone applied in the experiments with the respective contact times are shown in Table 3.

The statistical analysis was performed using Statistica® 12 software (StatSoft Inc.)

All experiments were performed at room temperature in an open and ventilated environment.

Table 3: Ozone dose and mass applied to vinasse with the respective contact times.

Contact time (h)	2	4	6	8
Ozone dose (g $O_3.L^{-1}$)	2	4	6	8
Mass of ozone (gO_3)	1.3	2.6	3.9	5.2

Preliminary Economic Assessment

A preliminary economic assessment was performed based on data representing an average Brazilian ethanol distillery, according to data from Coopcana (Regional Cooperative of Agricultural Producers of Cane). The efficiency of anaerobic reactors of the UASB class, as well as the calculation of the electrical energy that could be obtained from the combustion of methane was estimated according to equations presented by van Haandel (2005). The calculation of the amount of additional methane (generated by the ozonation) was performed based on data published by Siles *et al*. (2011). In order for the energy balance results to reflect industrial reality, we used energy requirement data (($kWh.kgO_3^{-1}$) provided by manufacturers from ozonators on an industrial scale (Qingdao Guolin Industry Co., Ltd. - Guolin).The economic feasibility is expressed in terms of an energy balance.

RESULTS AND DISCUSSION

In general, the chemical characteristics of vinasse vary greatly, as shown by Wilkie *et al.* (1999). According to the values found in the literature, in terms of the parameters analyzed (COD, BOD_5 and total phenols) the vinasse used in this study was very different from the vinasses used by other authors (Martín Santos *et al*., 2002; Martín Santos *et al*., 2003, Siles *et al*., 2011). Table 1 shows the chemical characteristics of the vinasse used in this research and in other studies.

Effects of Ozone on the Biodegradability

The effect of ozone on the biodegradability of vinasse was assessed by comparing the changes in BOD_5/COD (Figure 2).

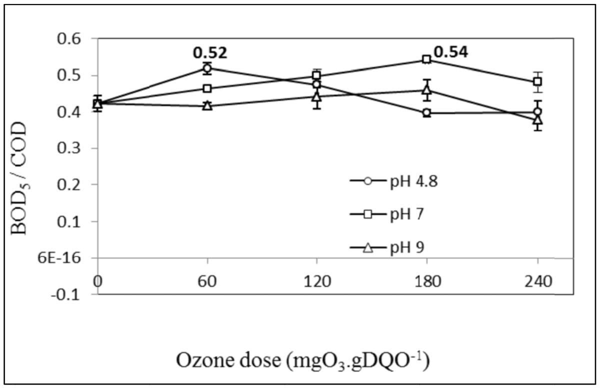

Figure 2: Effect of different ozone doses on the biodegradability of vinasse - BOD_5/COD ratio.

Considering the experimental errors of the DBO_5 and DQO measurements and, consequently, the errors in the changes of the BOD_5/COD relations, it can be observed that this changed slightly. Most of the values are quite close. Therefore, the analysis that follows has more validity in terms of comparing the results with similar studies in the literature, as well as for the discussion concerning the effects of ozone on vinasse. The same experimental errors can also be observed in Martín Santos *et al.* (2003 and 2005) and Siles *et al.* (2011). Despite this, using the values that are more distant from the experimental error (Figure 2), an analysis can be made of the effect of ozone on the vinasse. Initially, it can be observed that the application of the first dose of ozone caused an increase in the biodegradability of the vinasse at the natural pH and at pH 7 (22.7% and 9.6%, respectively), while this did not cause a change in this ratio at pH 9. These results are in agreement with Siles *et al*. (2011), who obtained an increase of 25% in the BOD_5/COD ratio. However, the amount of ozone used by those authors was approximately 120 $mgO_3.g^{-1}{}_{COD}$, i.e., twice the amount of ozone used here. Results from the current work indicate that, for pH 4.8, the application of higher ozone doses (or treatment times) did not provide a further increase in biodegradability. At this pH, the BOD_5/COD ratio decreased for higher doses, reaching 5% depletion in relation to the initial value when the dose increased to 180 $mgO_3.g^{-1}{}_{COD}$. In contrast, Martín Santos *et al.* (2003 and 2005) and Siles *et al*. (2011) observed a significant rise in BOD_5/COD as the ozone dose increased. Although these researchers also used vinasse from sugar cane, these differences may be related to the characteristics of the vinasse, higher COD and BOD_5 and phenols, as shown in Table 1. There are further differences in the reactor design that can also influence the transfer of ozone gas. Table 4 summarizes the most significant results obtained in this work.

Table 4: Percentage change in the biodegradability of vinasse (BOD_5/COD ratio).

Ozonation time (h)	pH	Ozone Dose (mgO_3.gCOD^{-1})	Increase in BOD_5/COD (%)
2	4.8	60	22.7
6	7	180	27.8
6	9	180	8

Organic and inorganic compound oxidation by ozonation can occur by direct reaction due to molecular ozone, prevailing in acidic media, or by indirect reaction due to the hydroxyl radical, prevailing in alkaline media, although both mechanisms occur simultaneously in actual treatment systems (von Gurten, 2003; Lage Filho, 2010). According to Martín Santos *et al*. (2003), the optimum pH operating conditions vary with the particular type of waste. However, these authors noted that, for the purpose of selective oxidation of phenolic compounds and thereby an increase in the biodegradability (BOD_5/COD), ozonation at acidic pH would be more appropriate, where the principal reaction mechanism must be with molecular ozone.

Álvarez *et al.* (2005) and Siles *et al*. (2011) linked phenolics removal to ozonation – 75% and 39%, respectively –with positive effects on the anaerobic biodegradability of vinasse. The results presented in this study showed that applying ozone at natural pH would be more suitable to increase the biodegradability of vinasse at a lower cost, as there was the highest increase (22.7% more) with the least dose of ozone (60 mgO_3.gCOD^{-1}). It can be observed that, even though an increase of 27.9% of the BOD5/COD was reached at pH 7, the dose applied was three times higher (180 mgO_3.gCOD^{-1}). Moreover, in this case there would also be the cost of NaOH to increase the pH of the vinasse before ozonation.

However, it should be noted that phenol was not detected in the vinasse used in this study (Table 1).Therefore, the increase in biodegradability observed here may be related to the removal, or partial oxidation, of compounds other than phenols. According to Speece (1983), there is a common misconception that anaerobic microorganisms are vulnerable to the toxicity of chemicals in wastewater.

Data were analyzed via factorial two-way ANOVA (Table 5). It can be observed that the effect of the interaction between the pH and ozone was significant in the biodegradability increase of vinasse (p-value 0.01712). Using the same statistical analysis for the absolute values of BOD_5 and COD, it was found that this interaction improved due to the effect caused on the BOD_5 (p-value = 0.003407) since the effects on COD were not significant (p-value = 0.149749) (data not shown). Therefore, when the BOD_5/COD ratio increased, it was due more to a result of increasing the BOD_5 values rather than decreasing the COD values (which remained almost unchanged). As a direct consequence of this fact, the BOD_5/COD ratio increased.

Table 5: ANOVA analysis of the interaction between pH and ozone on the biodegradability of vinasse.

Effect	SS	df	MS	F	P-value	F critic
pH	0.0129	2	0.0064	7.399	0.0059	3.682
Ozone	0.0134	4	0.0033	3.836	0.024	3.055
interaction	0.0245	8	0.0030	3.522	0.017*	2.640
waste	0.0130	15	0.0009			
Total	0.0638	29				

*$p<0.05$
SS: total sum of squares; df: degrees of freedom; MS: mean square

As the results from this work and from other researchers show, the increase in vinasse biodegradability and methane production is not very high. Thus, the economic feasibility of ozonation becomes an important issue that is seldom considered in vinasse oxidation studies.

Preliminary Economic Assessment

Using the results from this work and from the literature, a preliminary energy balance evaluation was prepared as a surrogate for an economic feasibility study. The evaluation is presented for a model Brazilian distillery to better represent the order of magnitude of ozone and energy consumption. This model is based on data from Coopcana (Cooperativa Agrícola Regional de Produtores de Cana), which indicate that an average size Brazilian distillery produces around 800 m^3 of alcohol daily. Taking into account the production of 12 litres of vinasse per litre of ethanol, the model distillery flow rate (Q) of vinasse to be ozonised would be 9.600 $m^3.d^{-1}$ with a COD concentration of 40 $gO_2.L^{-1}$(concentration and flow rate held constant for calculations).

According to the results presented here, it was necessary to apply 60 $mgO_3.gCOD^{-1}$to increase the biodegradability of vinasse by 22.7%. Therefore, this plant would require 23.040 $kgO_3.d^{-1}$.

Data from industrial ozonator manufacturers indicate that the electrical energy required to produce one kilogram of ozone from air is 14 $kWh.kgO_3^{-1}$ or 7 to 8 $kWh.kgO_3^{-1}$ using pure oxygen (Qingdao Guolin Industry Co., Ltd. – Guolin).

Therefore, it would be required to have 322.560 kWh to pre-treat the vinasse of the model distillery. For comparison purposes, the reader should be aware that this amount of ozone is more than enough for a very large bleach plant in a cellulose pulp mill, perhaps the industrial operation with the highest consumption of ozone (Germer *et al*., 2011).

Concerning the calculations, data published by Siles et al. (2011) were used. Vinasse anaerobic digestion previously treated with ozone would yield 13.6% more methane than vinasse digestion that was not previously treated with ozone. This increase in production is due to the conversion of non-biodegradable matter into a biodegradable one, and can be expressed as an increase in the organic matter conversion efficiency of the reactor. Assuming for the calculation that 70% of the total organic load (384.000 kg $COD.day^{-1}$) would be removed, 268.800 kg of methane would be produced in one day. As a result, considering that stoichiometrically 400 kg of COD removed from a reactor yields 100 kg of methane, an extra 9.140 kg of CH_4 (M_{CH_4}) could be produced by processing the ozonated vinasse. Thus, one kilogram of ozone added to the vinasse would produce only 0.4 kg of additional methane.

The electrical energy (E_{el}) produced using a given mass of methane (M_{CH_4}) can be calculated considering its calorific power (H_c) and the overall efficiency of chemical energy conversion of methane into electrical energy using an electrical generator coupled to an internal combustion engine (η_{conv}). Based on manufacturer's data, this electrical efficiency was assumed to be 44% (Caterpillar, 2014). The calorific power of methane is equal to 50.4 MJ per $kgCH_4$ (van Haandel, 2005). Equation (1) is used to evaluate the energy produced:

$$E_{el} = 0.2778 \times H_c \times M_{CH_4} \eta_{conv} \quad [\text{kWh}] \tag{1}$$

where 0.2778 is the conversion factor from MJ to kWh.

Therefore, with ozonization, it can be concluded that an extra 56.440 kWh of electricity would be obtained per day. This represents 2.450 $kWh.kgO_3^{-1}$. Nevertheless, every day, the plant would also be spending 322.560 kWh to generate the needed 23.040 kg of ozone. Therefore, it is clear that pre-ozonation of raw vinasse aimed at increasing electrical power generation by using the additional methane is still unfeasible from an economical point of view. Approximately 5.7 times more energy would be necessary for ozone production than the energy that can be recovered by burning the additional methane.

To complete the energy balance, an evaluation of the lowest possible energy expenditure to produce ozone was compared with the energy gain from ozonation.

The lowest theoretical energy required to produce ozone is the standard enthalpy of ozone formation, represented in Equation (2) (Atkins, 2002).

$$3O_{2(g)} \rightarrow 2O_{3(g)} \quad \Delta_{fH} = +284.6\,\text{kJ} \qquad (2)$$

The enthalpy of ozone formation from its elemental species $\Delta_f H^o (O_3)$ is +142.3 kJ.mol.$^{-1}$ (Atkins, 2002), and results in a minimum theoretical power consumption of 0.825 kWh.kgO_3^{-1}. In this case, 2.450 kWh generated from each kilogram of O_3 injected into the vinasse would pay this cost, resulting in a positive final balance of 1.625 kWh. Although progress has been observed with respect to ozonator efficiencies, there is still a long way to go to reach values that will make vinasse pre-ozonation an economically feasible process (where the specific objective is to increase the methane yield in its anaerobic digestion). Simply to balance the required energy with the energy produced by the additional methane combustion, it would be necessary to increase the overall efficiency of an ozonator using air as an oxygen source from its current value of 6% to 34%.

CONCLUSIONS

By adjusting operational parameters, ozonation can be used to increase the biodegradability of raw vinasse.

The increase in the BOD_5/COD ratio of vinasse was not associated with reduced phenol content in this study, as phenol was not found in the raw vinasse.

Economically, the application of ozone to raw vinasse at its natural acidic pH (4.8) is more appropriate for increasing the biodegradability of vinasse, as alkali substances (such as NaOH) would not be needed to adjust the pH to 7 or 9.

In order to make a profit from the ozonation of vinasse, ozonators would be required to spend less than 1.645 kWh.kgO_3^{-1}, instead of the current 14 kWh.kgO_3^{-1}.

Using these results, it can be concluded that, while it may be of scientific interest to study the mechanisms of biodegradability improvement and increase of methane production by ozonation of vinasse, the practical applicability of this process is still not justified.

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NOMENCLATURE

BOD_5	Biochemical oxygen demand (mgO_2.L^{-1})
H_c	calorific power of methane (50.4 MJ per kgCH_4)
COD	Chemical oxygen demand (mgO_2.L^{-1})
$\Delta_f H^o(O_3)$	standard enthalpy of ozone formation
E_{el}	equivalent amount of electrical energy
η_{conv}	overall efficiency (of the motor-generator) to convert methane chemical energy into electricity.

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