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Integrated ozonation and biomethanization treatments of vinasse derived from ethanol manufacturing

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ABSTRACT

Anaerobic digestion of vinasse derived from bioethanol manufacturing, in which total COD was found to be 68.56 ± 8.17 g/L, was studied in batch laboratory-scale reactors at mesophilic temperature (35 °C). The vinasse was subjected to a short ozonation pre-treatment (15 min) in which more than 50% reduction of phenols was observed, although the total organic carbon concentration remained approximately stable, indicating that the phenols were transformed into other simpler forms. The anaerobic biodegradability of raw and pre-treated vinasse was similar, reaching values close to 80% (COD). However, the methane yield coefficient and methane production rate enhanced by around 13.6% and 41.16%, respectively, when the ozonized vinasse was fed. These results indicate that the integration of chemical–biological treatments could be a viable option for the purification of this hazardous wastewater.

1. Introduction

Ethanol is an alcohol with wide applications as a solvent, scent, flavoring and medicine and has long been used as fuel for heating. Production of ethanol from agricultural materials for use mainly as an alternative fuel, solvent and for drinking has been attracting worldwide interest due to the increasing demand for energy resources and the variability of oil and natural gas prices [1].

In general, ethanol is produced in distilleries through mesophilic fermentation with *Saccharomyces cerevisiae* of agricultural products such as sugarcane, corn, wheat, sugar beet and cassava, among others. About 72% of the world's production in 2008 was from sugarcane and corn, which together account for 35.4 million cubic meters [2–4]. However, the industrial production of ethanol by fermentation results in the discharge of large quantities of high-strength liquid wastes generally called stillages, distillery slops or vinasses. The production of vinasses in a traditional alcohol factory is in the range of 9–14 L of wastewater per liter of ethanol obtained [5], although the production and the characteristics of the spent wash are highly variable depending on the raw material and the process itself [1,6]. These dark brown wastes are acidic (pH: 4–5) and have a high organic content (COD in the range of 50–100 g/L). The amounts of inorganic substances such as nitrogen, potassium, phosphates, calcium or sulfate are also very high [7,8]. Additionally, this waste contains a host of phenol compounds and melanoidins, which have antioxidant properties and render them toxic to many microorganisms such as those typically present in wastewater treatment processes. Apart from these compounds, caramel, a variety of sugar decomposition products, anthocyanins, tannins and different xenobiotic compounds are other recalcitrant compounds present in the waste [9,10].

The free disposal of this wastewater presents a serious challenge to natural ecosystems and can cause considerable environmental problems such as eutrophication or the reduction of sunlight penetration in natural water bodies [3]. Consequently, distillery industries have been forced to seek effective treatment technologies that are not only beneficial to the environment but also cost effective in order to fulfill the strict quality standards regarding environmental protection that are currently being developed [11]. Some researchers have reviewed several methods for the treatment, utilization and disposal of wastewaters from ethanol fermentation industries [1,3,5]. These methods include both chemical and biological treatments (aerobic or anaerobic classical methods, trickling filters, lagoons, evaporation/condensation with or without combustion, direct dispersion on soil as a fertilizer, etc.). Nevertheless, a common feature of all these methods is their relatively high cost and, in the case of certain methods, the simultaneous creation of other hazardous by-products or pollutants. Anaerobic digestion is an attractive waste treatment practice in which both pollution control and energy recovery can be achieved [12]. The advantages of anaerobic digestion include low levels of

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Nomenclature

Alk	alkalinity (mg $CaCO_3$/L)
BOD_5	biochemical oxygen demand at five days (g/L)
C_2	acetic acid
COD removed	removed chemical oxygen demand (g/L)
COD soluble	soluble chemical oxygen demand (g/L)
COD total	total chemical oxygen demand (g/L)
G	cumulative methane volume (mL)
Gm	cumulative methane volume at infinite time (mL)
G_T	experimental maximum methane volume (mL)
K_G'	apparent kinetic constant (h^{-1})
K_G	specific methane production kinetic constant (L/g VSS h)
MSS	mineral suspended solids (mg/L)
n.d.	not determined
r'	specific rate of methane production (mL CH_4/g VSS h)
$\bar{r}'$	mean specific methane production rate (mL CH_4/g VSS g COD d)
STP	standard temperature and pressure conditions (0 °C and 1 atm)
t	Time (h or d)
TOC	total organic carbon (mg/L)
TSS	total suspended solids (mg/L)
VA	volatile acidity (mg acetic/L)
VSS	volatile suspended solids (mg/L)
X	biomass concentration (mg VSS/L)
$Y_{CH4/COD\ added}$	methane yield coefficient (mL CH_4/g COD added)

biological sludge, low nutrient requirements, high efficiency and the production of methane which can be used as an energy source for on-site heating and electricity [13]. For these reasons, the anaerobic digestion of vinasse has been employed for this purpose in a number of studies using laboratory or pilot-scale digesters [1]. However, the presence of organic recalcitrant compounds such as phenols may cause low methane yield and process instability, thus preventing this technique from being widely applied [14]. As a result, many pre-treatment processes have been applied for the removal of recalcitrant compounds from industrial wastewater. These processes include photo-oxidation, chemical coagulation, sedimentation, filtration, disinfection or adsorption [15]. In these processes, the partial elimination of pollutants is achieved. It would thus be desirable to have a pre-treatment capable of converting recalcitrant compounds into simpler molecules of lower molecular weight readily used as substrates by anaerobic populations [16,17]. This has led to the development of new pre-treatment alternatives such as stronger oxidizing agents or what is known as advanced oxidation processes (AOPs). AOPs might be suitably employed to effectively oxidize these refractory organics as they involve the generation of non-selective and highly reactive hydroxyl radical (•OH), which is one of the most powerful oxidation agent with an oxidation potential of 2.33 V [18]. Among these processes, ozonation is particularly attractive for wastewater treatment because ozone, which consists of three atoms of oxygen, is soluble in water and can decompose quickly to form several free radicals including OH• (hydroxyl), HO_3•, HO_4• and O_2^- (superoxide). These free radicals are readily available to instantly react with any organic compounds present in water such as dyes, phenolic compounds, pesticides, organochlorides, and ammonium compounds [19,20]. Sangave et al. [21] recently demonstrated the suitability of the combined use of ozone and aerobic oxidation for the treatment of synthetic and real distillery wastewater. Nevertheless, few studies have been performed on the ozonation of this waste followed by an anaerobic digestion post-treatment [17,22–25]. Additionally, in most studies, synthetic solutions, highly diluted wastewater or long ozonation time were used [20]. For example, Peña et al. [24] evaluated the chemical oxidation of wastewater from molasses fermentation with ozone, after carrying out a conventional anaerobic–aerobic treatment. However, after the biological treatment the wastewater was still brown colored and had high organic load (4580 ± 100 mg COD/L). In contrast, Martín et al. [23], who estimated the selectivity of ozone in the removal of polyphenols from undiluted vinasse, used ozonation times up to 2 h. The main purpose of this study was to evaluate the performance, stability, biodegradability, methane yield coefficient and kinetics of methane production of the anaerobic digestion of vinasse derived from ethanol manufacturing after a light ozonation pre-treatment. The study was carried out at laboratory scale and can be considered of great interest to evaluate the viability of the integrated chemical–biological treatment at pilot and full scale.

2. Materials and methods

2.1. Experimental set-up

The experimental set-up used for the ozonation experiments is shown in Fig. 1. Ozonation pre-treatment was carried out in a 1 L Pyrex reactor in which a pure oxygen stream containing 34 g O_3/m^3 was conducted through a porous plate diffuser (500 L/h, 0 °C and 1 atm). The reactor was loaded with the wastewater to be treated and equipped with a magnetic stirrer system. The pH of vinasse was not modified as a previous study demonstrated that the ozonation of vinasse in acid media provides more selective elimination of phenolic compounds and a more readily biodegradable waste (i.e. an increased BOD_5/COD ratio) [22]. Ozone gas was produced using a GMF Ambiozón ozone generator. The outlet gas stream was measured and registered continuously by a H1 UV ozone analyzer and a data acquisition system. The residual gas stream was passed through potassium iodide solutions in order to eliminate the excess ozone. Each experiment was carried out for 2 h.

The experimental set-up for anaerobic digestion of vinasses and pretreated vinasses consisted of six 1 L Pyrex reactors with four connections to load feedstock, ventilate the biogas, inject inert gas (nitrogen) to maintain the anaerobic conditions and remove effluent [26]. The content of the reactors was magnetically stirred and temperature was maintained at 35 °C (mesophilic conditions) by means of a thermostatic jacket containing water at 37 °C. The volume of methane produced during the process was measured using 1 L Boyle-Mariotte reservoirs connected to each reactor. To remove the CO_2 produced during the process, tightly closed bubblers containing a NaOH solution (6N) were connected between the two elements. The methane volume displaced an equal measurable volume of water from the reservoir. The reactors were inoculated with methanogenically active granular biomass obtained from a full-scale anaerobic reactor used to treat brewery wastewater from the Heineken S.A. Factory (Jaen, Spain). The sludge contained 37.50 g VSS/L and 31.88 g MSS/L. The inoculum was selected on the basis of its high methanogenic activity [27], with values ranging from 0.87 to 0.99 g COD/g VSS day.

2.2. Vinasse

The wastewater used as a substrate in this study consisted of vinasse derived from the ethanol manufacturing process carried out by the firm Azucarera del Guadalfeo S.A. (Salobreña, Spain). This company produces ethanol by mesophilic fermentation of sugarcane juice with *Saccharomyces cerevisiae*. The characterization of

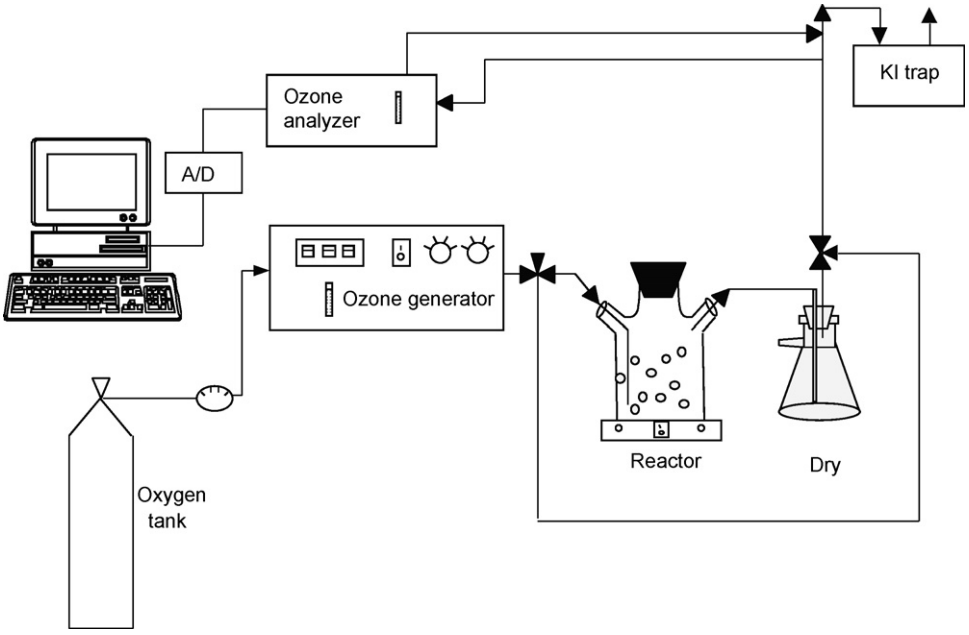

Fig. 1. Experimental ozonation system.

raw and pre-treated vinasse by ozonation (15 min) is shown in Table 1.

2.3. Anaerobic digesters: experimental procedure

Three anaerobic reactors were simultaneously fed with raw vinasse, while the remaining reactors were fed with the pre-treated vinasse. All of the reactors were initially loaded with 10 g VSS of granular sludge as inoculum, and the anaerobic digestion of raw and pre-treated vinasse were studied. In all cases, the nutrient and trace element solutions described by Field et al. [27] and Fannin et al. [28] were added when the sludge was loaded. Both solutions are very important for activating bacterial growth and metabolism at the beginning of the process and for compensating the shortage of nutrients in the substrates.

In order to activate the biomass prior to the experiments, the reactors were first fed with a synthetic solution composed of glucose, sodium acetate and lactic acid (GAL solution) at concentrations of 50.0 g/L, 25.0 g/L and 20.8 mL/L, respectively. During this initial period, the organic load added to the reactors was gradually increased from 0.25 to 1.00 g COD over a 21-day period. After this previous stage, biomass acclimatization was carried out by increasing the added load with raw and pre-treated vinasse to 1 g COD/L over a 16-day period. During this acclimatization period, the volume of methane was measured as a function of time. Once this preliminary acclimatization step was finished, a series of batch experiments were carried out using both substrates. During each set of experiments, the organic load added to the reactors was gradually increased until reaching a final concentration of 3.0 g COD/L. In all cases, the volume of methane was measured as a function of time and samples were taken and analyzed before and after feeding. The duration of each experiment was equal to the time interval required for maximum gas production and COD removal, which was found to be in the range of 18–45 h. Each load was carried out at least in duplicate and the results expressed as means.

Table 1
Characterization of raw and pre-treated vinasse.

Parameter	Raw vinasse	Pre-treated vinasse (ozonation 15 min)
pH	3.75 ± 0.08	3.54 ± 0.10
COD_{total} (g/L)	68.56 ± 8.17	66.10 ± 8.17
$COD_{soluble}$ (g/L)	55.83 ± 2.12	54.02 ± 1.00
BOD_5 (g/L)	29.70 ± 0.10	33.35 ± 0.13
$TOC_{soluble}$ (g/L)	20.16 ± 0.05	19.76 ± 0.07
MS (g/L)	31.00 ± 1.17	n.d.
VS (g/L)	46.39 ± 0.79	n.d.
MSS (g/L)	5.30 ± 0.37	n.d.
VSS (g/L)	15.86 ± 0.65	n.d.
VA (g acetic acid/L)	1.50 ± 0.10	2.61 ± 0.60
Total phenols (g caffeic acid/L)	0.45 ± 0.01	0.27 ± 0.01

n.d.: not determined.

2.4. Chemical analyses

The following parameters were determined in the effluents of each load: pH, total chemical oxygen demand (COD total), soluble oxygen demand (COD soluble), biochemical oxygen demand (BOD_5), total suspended solids (TSS), mineral suspended solids (MSS), volatile suspended solids (VSS), volatile acidity (VA) and alkalinity (Alk). The BOD_5 tests were carried out using primary aerobic sludge obtained from a full-scale aerobic reactor used to treat urban wastewater from the La Golondrina water treatment facility (Cordoba, Spain). This inoculum was previously adapted to consume vinasse as substrate. All analyses were carried out in accordance with the Standard Methods [29]. Additionally, total organic carbon (TOC) was determined by using a Shimadzu Total Carbon Analyzer. The TOC analyzer was calibrated with a standard solution of potassium phthalate prior to the TOC analyses. The total phenol content was determined using the Folin-Ciocalteau method [30].

2.5. Software

Sigma-Plot software (version 11.0) was used to design graphs, perform the statistical analysis and fit the experimental data presented in this study.

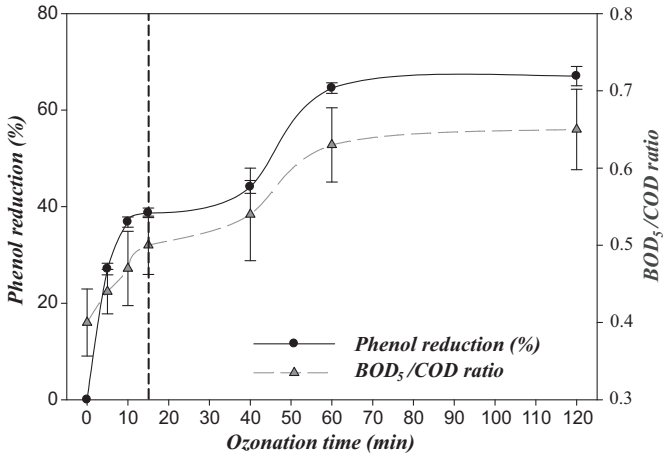

Fig. 2. Variation of the phenol reduction percentage and BOD_5/COD ratio with ozonation time.

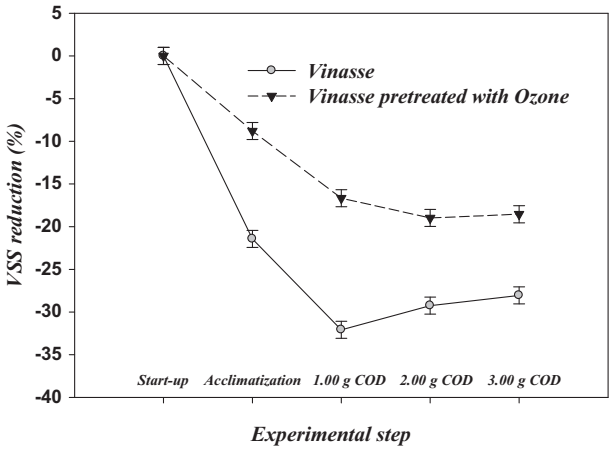

Fig. 3. Variation of the VSS reduction percentage across the different steps of the anaerobic digestion process of raw and pre-treated vinasse: start-up, acclimatization and loads of 1.00, 2.00 and 3.00 g COD.

3. Results and discussion

3.1. Ozonation pre-treatment

Fig. 2 shows the effect of ozone on the reduction percentage of phenol compounds after two hours of ozonation time. As can be seen, the percentage of phenol reduction increased markedly, reaching a mean value of 39% after 15 min of pre-treatment. Subsequently, this variable was observed to enhance by as much as 65% after 60 min of ozonation. These results indicate that the vinasse contained two groups of phenols with different resistance to the oxidation [22]. A similar behavior was observed for the variation in the BOD_5/COD ratio; a variable that indicates the aerobically biodegradable organic fraction contained in the wastewater. During the first 15 min, this ratio was observed to increase from 0.40 to 0.50. After 60 min, the ratio reached a mean value of 0.65. Consequently, the phenol removal had a positive influence on the aerobic biodegradability of the vinasse, although it has shown practically no influence over COD concentration (Table 1). Although the BOD_5/COD ratio was higher for the highest ozonation times, a major drawback of ozonation processes is their high operation costs due to the need for expensive equipment to generate ozone from O_2 and the cost of oxygen and electricity. To reduce the costs involved in using ozone, the efficiency of the ozonation process should be maximized and combined with other treatment technologies [20]. To achieve this aim, the ozonation time was fixed at 15 min, allowing around 39% of the phenol content to be removed and the BOD_5/COD ratio to be increased by 25%. This ozonation time is in line with the experiments carried out by Peña et al. [24], who obtained values for color removal of over 80% after 20 min of ozonation of biologically pre-treated wastewater from molasses fermentation. Moreover, the BOD_5/COD ratio of 0.50 is between the limits of 0.1 and 1.0 established as the biodegradable zone where organic matter can be decomposed by microbes under natural and man-made treatment conditions [31].

On the other hand, some chemical variables such as pH, COD and TOC remained approximately constant during the pre-treatment (Table 1), while the enhancement of volatile acidity (from 1.500 to 2.610 mg acetic acid/L) indicates the transformation of complex compounds into short chain acids such as acetic or oxalic acid that are much more biodegradable than the previous ones [32].

3.2. Stability of the anaerobic digestion process

The stability of the process was evaluated based on the evolution of the pH, alkalinity, volatile acidity, volatile acidity/alkalinity ratio (VA/Alk) and VSS concentration during the anaerobic digestion of raw and pre-treated vinasse by ozonation (15 min). Table 2 shows the mean value and standard deviation of the pH and volatile acidity/alkalinity ratio in the effluents of the reactors for the different loads added. The pH was always lower for raw vinasse than for pre-treated vinasse, although this variable remained within the optimal range for methanogenic bacteria in all cases [12,28]. On the other hand, the volatile acidity/alkalinity ratio values were always found to be lower than 0.30–0.40 (equiv. C_2/equiv. $CaCO_3$), thus indicating that the process operated favorably without risk of acidification [33]. Nevertheless, it should be noted that the variation of the VA/Alk ratio was slightly higher for the untreated vinasses than for the pre-treated vinasses. These results indicated worse maintenance conditions in the anaerobic process when raw vinasse was fed. Moreover, Fig. 3 shows the variation of the VSS reduction percentage across the experiment (start-up, acclimatization and loads of 1.00, 2.00 and 3.00 g COD/L) when both substrates were fed. As can be observed, this variable decreased in both cases, especially during the start-up and acclimatization steps. At the end of the experiments (3.00 g COD/L), the VSS reduction percentage was 28.05% for the raw vinasse and 18.54% for the ozonized vinasse. Given that the adaptation step of the inoculum was appropriate, the marked VSS reduction observed when the raw wastewater was fed could be attributed to the accumulation of phenols in the reactors [34].

Table 2
pH and VA (equiv. C_2)/Alk (equiv. $CaCO_3$) ratio for the different loads studied with raw vinasse and vinasse pre-treated by ozonation (15 min).

	Raw vinasse		Pre-treated vinasse	
Load (g COD)	pH	VA/Alk (equiv. C_2/equiv. $CaCO_3$)	pH	VA/Alk (equiv. C_2/equiv. $CaCO_3$)
1.00	7.54 ± 0.11	0.21 ± 0.02	7.72 ± 0.05	0.21 ± 0.01
2.00	7.40 ± 0.09	0.27 ± 0.01	7.60 ± 0.03	0.23 ± 0.01
3.00	7.02 ± 0.17	0.29 ± 0.02	7.40 ± 0.07	0.24 ± 0.01

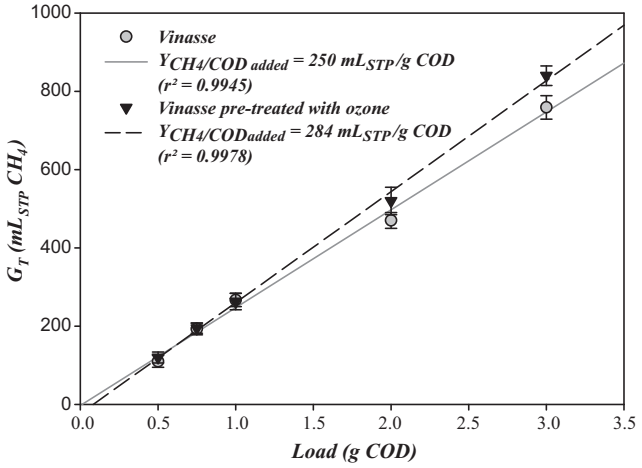

Fig. 4. Variation of the experimental maximum methane volume produced (G_T) (at 1 atm, 0 °C) with the COD added to obtain the methane yield coefficient for raw and pre-treated vinasse.

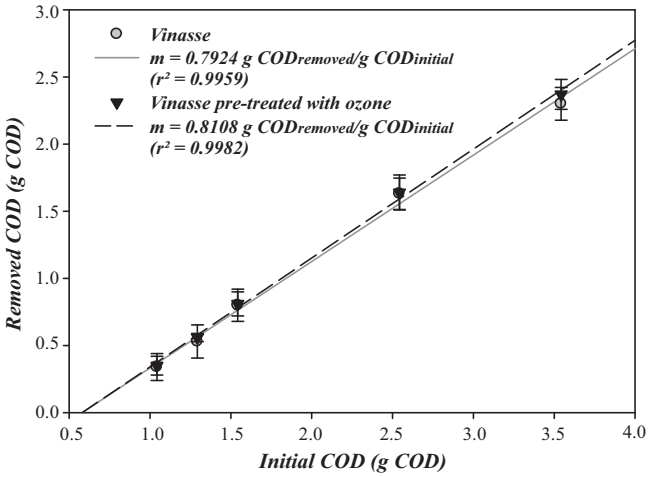

Fig. 5. Plot of the amount of substrate removed against the initial substrate for all the experiments with raw and pre-treated vinasse to obtain the biodegradability percentage.

3.3. Methane yield coefficient and biodegradability

Methane yield coefficient was determined from the experimental total methane volume produced (G_T) and the added COD, which were known in all loads. As shown in Fig. 4, by fitting the value pairs (G_T, COD added) to a straight line, the methane yield coefficient matches with the slope of the regression line. The methane yield coefficient was found to be 250 mL CH_4/g COD added (at 1 atm, 0 °C) for raw vinasse and 284 mL CH_4/g COD added (at 1 atm, 0 °C) when pre-treated vinasse was fed. According to Wheatley [12] and considering the biomass growth and cell maintenance null, 350 mL of methane are theoretically produced (at 1 atm, 0 °C) per gram of COD removed. In experimental terms, these results indicate that most of the COD removed is employed for methane production, which is a useful product due to its caloric power (Lower Caloric Power: 35,793 kJ/m^3, equivalent to 9.96 kWh/m^3) and that the microbial metabolism is chiefly oriented towards generating gas. Similar results were found by Jiménez et al. [5], who obtained a methane yield coefficient of 305 mL methane at STP conditions per g of COD removed in molasses previously fermented with *P. decumbens*. Moreover, the biodegradability of the raw and pre-treated vinasse was calculated by plotting the amount of substrate removed against the initial substrate concentration for each experiment. These data are shown in Fig. 5 where the slope of the straight line denotes the percentage biodegradability of raw and pre-treated vinasse, which were found to be around 79% and 81%, respectively. In all the cases, the reactors contained soluble and non-biodegradable COD before adding the vinasse, reaching a mean value of 0.580 g COD. These results are in agreement with those obtained by Vijayaraghavan and Ramanujam [35], who obtained a 73–98% COD removal by feeding distillery effluents (19,000 mg COD/L) in an anaerobic contact filter working at 4 days of hydraulic time. Moreover, Acharya et al. [8] studied the anaerobic treatment of distillery spent wash in an upflow anaerobic fixed film bioreactor using coconut coir as supporting material. A 64% COD reduction with a biogas production of 7.2 m^3/m^3 d were obtained working at 8 d hydraulic retention time and an organic loading rate of 23.25 kg COD/m^3 d.

These results indicate that although biodegradability remained stable with and without pre-treatment in the organic loading range studied, the methane yield coefficient was 13.6% higher when pre-treated vinasse was fed. This indicates that some compounds contained in the substrate were transformed into more amenable forms of the anaerobic microorganisms for methane production. In contrast, the removed COD was not as oriented towards methane production when the raw vinasse was fed since the energy requirements for microbial growth were greater in this case.

3.4. Kinetics of methane production

Kinetic studies are helpful for reproducing the empirical behavior of the process and understanding the inhibitory mechanisms of biodegradation, while saving time and money [36]. In order to characterize each set of experiments kinetically, and thus facilitate comparisons, the methane production first-order kinetic model described by Borja et al. [37] was used to fit the experimental data obtained for the volume of accumulated methane as a function of time for all the loads with raw and pre-treated vinasse. According to this model, the volume of methane accumulated (G) (mL, at 1 atm, 0 °C) at a given time t (h) fits the following equation:

$$G = Gm[1 - \exp(-K'_G t)] \quad (1)$$

where Gm is the maximum methane volume accumulated at an infinite digestion time, G is zero at $t = 0$, and the rate of gas production becomes zero at t equal to infinite. K_G' is an apparent kinetic constant for methane production (h^{-1}) that includes biomass concentration:

$$K'_G = K_G X \quad (2)$$

where K_G is the specific methane production kinetic constant (L/g VSS h) and X is the biomass concentration (g VSS/L), which remained relatively constant throughout the experiments.

The different loads were compared by defining the specific methane production rate r' (mL CH_4/g VSS d) based on eq (1) as the volume of methane generated per gram of volatile suspended solid and per day for each set of experiments:

$$r' = \frac{1}{X}\frac{d\mathrm{CH_4}}{dt} = G_m K_G \exp(-K_G X t) \quad (3)$$

From Eq. (3), the mean value of the specific methane production rate, $\bar{r}'$, was calculated as follows:

$$\bar{r}' = \frac{\int_0^1 r' dt}{\int_0^1 dt} = \frac{Gm}{tX}[1 - \exp(-K_G X t)] \quad (4)$$

Fig. 6 shows the evolution of the specific methane production rate ($\bar{r}'$) obtained with raw and pre-treated vinasse according to the load added. The linear fitting of ($\bar{r}'$, load) pair values allowed the slope of the line to be obtained, which reached values of 31.73 mL

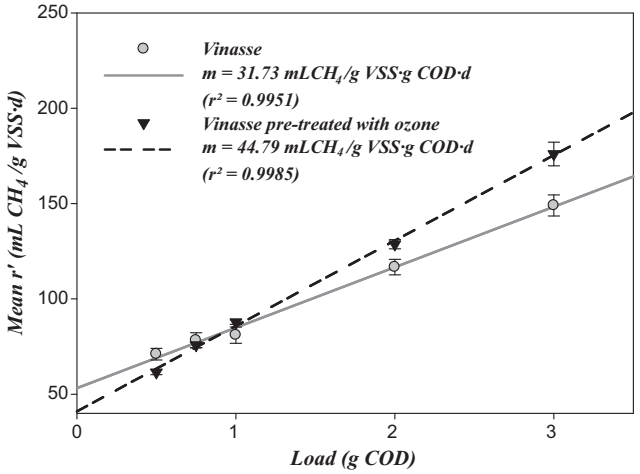

Fig. 6. Variation of the mean specific methane production rate with the initial substrate added with raw and pre-treated vinasse.

CH_4/(g VSS g COD d) without pre-treatment and 44.79 mL CH_4/(g VSS g COD d) for ozonized vinasse, in spite of COD removal being around 80% in both cases. Although the specific methane production rate–load ratio was constant in both cases, it was higher with the pre-treated vinasse for the highest loads. Low substrate loads with raw vinasse produced slightly higher $\tilde{r}'$ than pre-treated vinasse due to the phenol accumulation in the reactors was still low and the ozonation, being a non selective treatment, eliminated some of the more biodegradable organic compounds which could have been available for the anaerobic bacteria. This variable reached a similar value (37.20 mL CH_4/g VSS g COD d) when anaerobic co-digestion of glycerol and wastewater derived from biodiesel manufacturing was studied [26]. The proportionality between the pair values ($\tilde{r}'$, load) indicates that the kinetics of methane production remained constant in the organic loading rate studied and that the pre-treatment enhanced the methane production rate, which is an interesting aspect from an economic point of view.

4. Conclusions

The integration of ozonation and anaerobic digestion treatment of vinasse could be a good alternative for treating this wastewater. Following the ozonation pre-treatment, the vinasse showed a high level of anaerobic biodegradability (around 80%) and stability, permitting a larger quantity of methane to be obtained (284 mL CH_4/g COD added, at 1 atm and 0 °C) in comparison to the untreated vinasse. The methane production kinetic increased until reaching a mean value of 44.79 mL CH_4/(g VSS g COD d) in the range of the organic loading studied. Consequently, the ozonation pre-treatment would allow the anaerobic reactor volume to be reduced, while lowering costs and enhancing the production of methane.

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