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CONVENTIONAL AND NON-CONVENTIONAL ALTERNATIVES FOR VINASSE MANAGEMENT THROUGH PHYSICAL-CHEMICAL OR BIOLOGICAL TECHNOLOGIES: A REVIEW.

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1. INTRODUCTION

Today, waste management is of great importance since many wastes are produced in big scale and commonly generate several negative factors such as high levels of pollution. Vinasse is the residue obtained after distillation of fermented sugars, mainly in the ethanol industry. Vinasses are produced mostly from the fermentation of several raw materials like corn, wheat, rice, potatoes, sugar beets, sugarcane and sweet sorghum. Its composition vary considerably from one distillery to another depending on several factors such as the raw materials used, the different operation process, fermentation type and adopted distillation procedures (Krzywonos et al., 2009). Vinasse is the most important liquid effluent of the sugarcane industry where approximately 11 liters are produced per liter of ethanol.

Vinasse contains high loads of dissolved solids and recalcitrant organic matter (e.g., nitrogen-colored polymers of brown color, phenols, etc.), ash and low pH (3-5) (Janke et al., 2015). Biochemical and Chemical Oxygen Demand (BOD and COD, respectively) are indicators of the contamination potential which in vinasse ranges between 35,000-50,000 and 100,000-150,000 mg O₂ L⁻¹ respectively (Pant & Adholeya, 2007). Vinasse is commonly used as a culture medium in order to achieve the bioconversion from sugars or simple organic acids to high value added products. Furthermore, the organic load is reduced and therefore its toxicity.

Ethanol is the most widely used biofuel in the world. The global production of ethanol in 2016 was 98.6 billion liters being USA, Brazil and China the main producing countries (REN21, 2017). Furthermore, the global production of vinasse in 2016 was approximately from 1,084.6 to 1,281.8 billion liters. Figure 1 presents the average participation percentages in vinasse production of these countries. Source: ("Fuel ethanol production in major countries 2017").

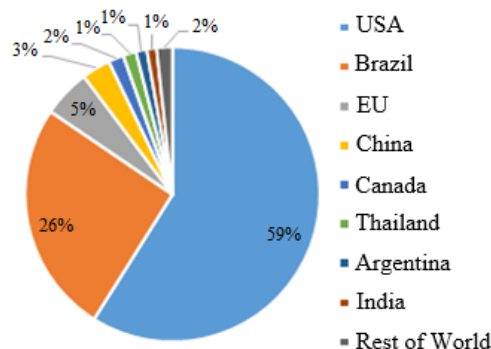



Figure 1. Vinasse production worldwide distribution.

The aim of this review is to show useful information about conventional and non-conventional technologies to vinasse management. This report was focused on a global situation since many vinasse producing countries have the same issues with the final disposal of

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this waste. Additionally, this work was performed facing vinasse management using physicochemical technologies and biological processes.

2. TECHNOLOGIES FOR VINASSE MANAGEMENT.

The environmental damage caused by discarding vinasse into the soil or body waters was an incentive to studies aiming to find alternative economic applications for this agroindustrial waste. Results from such studies indicate that, when properly used, vinasse could contribute to improvements in soil quality, agricultural productivity, clean energy generation and animal feedstock, among others.

2.1. PHYSICOCHEMICAL PROCESSES.

2.1.1 Conventional.

I) Fertigation.

Table I shows the main components in vinasse, namely organic matter, K, N, Ca, and Mg. K being the most relevant mineral element for the agricultural use of the waste. Therefore, vinasse utilization can contribute to enhance crops productivity with effects on the chemical-physical and biological soil qualities (Jiang et al., 2012).

Brito et al., (2007) studied the effect of vinasse applied at 0.350 and 700 m³ha⁻¹ on the leaching of mineral elements in three different soils. It was shown that cation concentrations in the leachate were less than in the vinasse, indicating a high cation retention of soils. Furthermore, soil microorganisms increase CO₂ emissions of resulting from the transformation of sugars and phenolic compounds present in vinasse irrigated soils.

Parameter	Vinasse			
	<i>da Silva et al., (2006)</i>	<i>Barros et al., (2010)</i>	<i>Brito et al., (2007)</i>	Average
COD (mg L ⁻¹)	—	48,860	26,771	37,815.5
BOD (mg L ⁻¹)	—	21,275	5,000	13,137.5
EC (dS m ⁻¹)	3.6	9.65	11.5	8.25
TDS (mg L ⁻¹)	—	19,000	11,352	15,176
pH	5.7	4.6	4.4	4.9
N (mg L ⁻¹)	560	—	—	560
P (mg L ⁻¹)	190	175	—	182.5
K (mg L ⁻¹)	960	1,392	1,123	1,158.33
Na (mg L ⁻¹)	—	110	113	111.5
Ca (mg L ⁻¹)	280	728	352	453.33
Mg (mg L ⁻¹)	130	29	16	58.33


Table I. Vinasse characterization. -Electrical Conductivity (EC), Total Dissolved Solids (TDS).

Although the scientific reports regarding the contaminating nature of the vinasses are not unanimous, the studies that reveal negative effects on the environment are in majority. However, several investigations highlight vinasses high valuation potential as this work shows. Different points of view indicate, on one hand, toxic effects on ground and surface waters and on the other hand, that rational use of this waste does not result in environmental risk.

II) Concentration by evaporation.

Vinasse *in natura* is a diluted solution and its application to soil is carried out in large quantities. The distribution of vinasse on the crops involves three different stages: i) the primary transport from industry to the storage tanks, ii) the secondary transport from the tanks to the fields and finally iii) the distribution on the crops (mainly of sugarcane). Each phase has logistic costs represented mainly on equipment, infrastructure, power and management techniques, making problematic its use in areas distant from the production places. However, vinasse can be concentrated by evaporation, resulting in a product with higher economic viability that can be transported to distant locations (Cortes-Rodríguez et al., 2018).

Larsson, E. & Tengberg, (2014) demonstrated that it is possible to evaporate vinasse up to a 72 % high dry solid content. This corresponds to removing 97 % of the water in the original vinasse. They mentioned that there is a critical region where particles start

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to form (20-35 % ds) which means that one of the most important factors in vinasse evaporation is the fouling. Most of the experiments showed that fouling had a negative effect on the heat transfer. However, fouling layers were also proven to be easily soluble in water.

III) Animal feed.

Products like vinasse are considered as non-conventional feedings, but are not universally used in animal feedstock. Hence, if they are properly used, they could be an important element in the sustainable animal feed production systems (Iranmehr et al., 2011). Vinasse may be used as an economical animal feed due to their low cost and the presence of organic compounds (acids, alcohols and sugars), minerals and nitrogen compounds (amino acids and peptides).

Vinasse showed an interesting amino acid profile compared with a FAO (Food and Agriculture Organization) pattern for monogastric species. It is important to emphasize that this waste has high values of essential amino acids (e.g., leucine, isoleucine, valine, tyrosine, histidine, phenylalanine, lysine, threonine), which reflects a high nutritional power for certain animals (Scull et al., 2012).

According to De Oliveira *et al.*, (2013), *in natura* liquid vinasse can be used to feed growing rabbits at 87.8 g per kilogram of diet. Vinasse also kept the intestinal flora in balance, preventing propagation of intestinal pathogens that could influence the total production negatively. Furthermore, this waste contains few fiber mainly represented by glucan and mannan, present in the yeast walls, also having a beneficial effect on protecting animal intestinal mucosa.

IV) Cation exchange resin

One of the most relevant problems when vinasse is used as animal feed is their high toxic potassium concentration of up to 17 g/L (Janke *et al.*, 2015; Hoarau *et al.*, 2018). Zhang *et al.*, (2012) studied potassium ions extraction from vinasses using a strong acid-cation exchange resin. The maximum extraction capacity of K⁺ was 56.79 mgL⁻¹ of resin. A 99.6% elution of the concentrated K⁺ from the resin was attained, concluding that this technology has a great potential for industrial production of potassium salt and the production of a vinasse which might be used as animal feed.


V) Combustion.

Low calorific fuels such as molasses and vinasses have calorific values that are too low to be burnt with conventional burners (10.45 and 7.47 MJkg⁻¹ respectively). However, it is possible to burn such fuels in a SSB-LCL (SAACKE Swirl Burner for Low Calorific Liquids) firing system and to feed the resulting exhaust gases to a boiler or a combustor. The system consists of a SAACKE swirl burner with a special burner throat. The SSB is a well-proven gun-type burner for industrial and power station plants. This burner was developed for the combustion of natural gas and fuel oil and operates according to the 'mixing at the burner mouth' principle. This burner results in particularly low CO and NO_x emissions. It is meanwhile also used in many applications for low calorific gases with even below 3.0 MJm⁻³ LHV (Lower Heating Value) (Schopf & Erbino, 2010).

VI) Gasification.

Gasification is a widely explored technology for its potential in providing higher efficiency cycles. Patel & Nikhil, (2000) studied gasification of concentrated vinasse using a spray-type air-blown laboratory reactor at a temperature range of 677–727 °C. Gasification experiments were conducted in an inclined plate reactor with rectangular cross section (80 mm x 160 mm) and 3000 mm long. A support flame was found necessary in the injection zone in addition to the regenerative heat transfer. Effluent with 60% solids was injected as film on the reactor bed. The typical gas fractions obtained during gasification condition (air ratio = 0.3) were around 10.8% of CO₂, 11.0% of CO, 7.4% of H₂, 1.75% of CH₄, 0.3% of H₂S and about 2.0% of saturated moisture. The carbon conversion obtained was in the range of 95.5%.

Dirbeba *et al.*, (2016) studied the gasification of vinasse at temperatures between 600 and 800 °C using a simultaneous differential scanning calorimetry and thermogravimetric analyzer (DSC-TGA). They first pyrolyzed the vinasse in a single particle reactor to obtain vinasse chars and to determine the yield of pyrolysis. Vinasse ash content on a dry fuel basis was 34.1 wt% based on the ashing test. The ash content obtained from the TGA experiments at 600 °C was about 37.5 wt% on original dry vinasse basis. Potassium, calcium, chloride, and sulfur are the major inorganic components present in vinasse ash. The pyrolysis char yield was 52.5 wt% dry vinasse after 20s at 800 °C.

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2.1.2. Non-conventional.

I) Membranes.

Membrane technology has achieved over the last years a great commercial and strategic importance. The increasing interest in this technology is mainly associated to its relative simplicity, ease of use, low energy consumption and application in the separation of liquid and gas mixtures (van de Water & Maschmeyer, 2004, Hoarau *et al.*, 2018).

Sugarcane vinasse can be concentrated through membranes. This waste management process is a promising approach for improving its use. Moreover, concentrating vinasse may increase fertilization quality and may both reduce transport costs and broaden the application range. This approach may represent an alternative method to evaporation (Amaral *et al.*, 2016). Thus, the permeate stream arising from the membrane module could be recycled, whereas the retentate stream could be used in fertigation. .

In a study performed by Queiroga *et al.*, (2018), asymmetric tubular membranes were successfully prepared by the co-use of the slip casting and dip-coating techniques. On one hand, it was observed that a slip-cast support showed an expressive capacity in separating the solid particles present in vinasse from water. On the other hand, the deposition of a boehmite coating on this sample led to a further increase in membrane performance. Reductions as high as 31, 98 and 89% for COD, turbidity and color, respectively, were detected when vinasse was permeated through such asymmetric membrane.

II) Electrochemical process.

Among the different treatment technologies, biological processes are commonly the preferred option based on the economy of the treatment. However, when recalcitrant compounds are involved, biological processes may not be totally effective since the inhibitory effects associated with the presence of such recalcitrant organic compounds may cause low yields and process instabilities (Ioannou *et al.*, 2015).

An interesting alternative for vinasse treatment is the use of electrochemical processes to achieve a partial oxidation of the organic compounds before the biological step. The electrochemical oxidation process is expected to decrease the toxicity of some organic materials and allow subsequent degradation of the substrate by an anaerobic consortium (Tröster *et al.*, 2002). Electrochemical oxidation is an attractive technology due to its capability to treat (under moderate conditions, ambient temperature and pressure) toxic and/or complex organic contaminants present in industrial or domestic wastewaters (Flores *et al.*, 2017).

Martínez *et al.*, (2017), propose a study to evaluate the electrochemical oxidation of vinasses using dimensionally stable anodes (DSA, Ti/SnO₂-Sb) and boron-doped diamond anodes (BDD). The maximum reduction of organic compounds and color was achieved with the use of BDD electrode after 10 h of operation at a current density of 6.6 mAcm⁻². The efficiency obtained was about 90% with a specific energy consumption (SEC) of 17 kWhkg⁻¹COD removed. The DSA were capable of removing 6–47% of the organic material and reached 60% decolorization but with a lower current efficiency and much higher SEC values.

III) Ozone oxidation

The effectiveness of this technology in converting recalcitrant compounds into less toxic and more biodegradable ones is based on the direct effects produced by the oxidative activity of ozone and on the indirect effect of products of the reaction such as OH[•]-radicals (Sangave *et al.*, 2007; Hoarau *et al.*, 2018). This technology was implemented before using aerobic digestion in distiller effluents and enhanced 25 times achieving a maximum rate of 45.6% COD reduction; compared to 1.8% COD reduction for the control (Sangave *et al.*, 2007). Ozone was also used for pretreatment of anaerobic digestion of vinasse, resulting in a reduction of phenols without effect on the total organic carbon content and enhanced methane yield coefficient by 13.6% (Siles *et al.*, 2011).


2.2. BIOLOGICAL PROCESSES.

2.2.1. Conventional.

I) Vermi-composting.

Composting is considered as a technique in which aerobic mesophilic and thermophilic microorganisms consume organic matter as a substrate under controlled conditions. This biological process produces a stabilized, mature, deodorized and hygienic material free of pathogens and plant seeds, and rich in humic substances that can be used as soil conditioner (Lim *et al.*, 2015).

If earthworms are applied in this method, it can be called as an integrated composting-vermi-composting process. Earthworms can transform the organic fraction of solid wastes to a nutrient rich fertilizer under aerobic conditions. *Eisenia fetida* is an earthworms species which under suitable pH, temperature, and moisture, has the potential to convert organic waste into products with a high nutritious value that can be used as biofertilizer (Prado *et al.*, 2013).

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For example, co-composting followed by vermi-composting of the mixtures of vinasse, cow manure and chopped bagasse was performed for 60 days using earthworms of *Eisenia fetida* species by Alavi et al., (2017). The results showed that the trend of changes in C/N was decreasing. The pH of the final fertilizer was in alkaline range (8.1–8.4). Total potassium decreased during the process ranging from 0.062 to 0.15%, while the total phosphorus increased from 0.06 to 0.10%. The germination index (GI) for all samples was 100%, while the cellular respiration maturity index was $< 2 \text{ mg C-CO}_2 \text{ g}^{-1} \text{ organic carbon day}^{-1}$, confirming a very stable compost.

II) Biogas production.

The anaerobic digestion of vinasse can be regarded as a favorable strategy, since the digestate could still be used to partially substitute the mineral fertilizers on the sugarcane crops and the produced biogas could be improved to biomethane and sold as a new energy product by the sugarcane plants (Janke et al., 2014).

In order to obtain an appropriate anaerobic digestion process a balance among the main nutrients: carbon, nitrogen, phosphorus and sulfur is necessary. If a substrate has a too high C/N ratio, or in other words, has a lack of nitrogen, it may negatively influence on the functioning microbial community (Janke et al., 2014). According to a study performed by Janke et al., (2015), the lowest methane yield for vinasse after 35 days was $246 \pm 15 \text{ NmL} \cdot \text{gCOD}^{-1}$, and the maximum yield was $302 \pm 06 \text{ NmL} \cdot \text{gCOD}^{-1}$.

España-Gamboa et al., (2012) modified a laboratory-scale upflow anaerobic sludge blanket (UASB) reactor to obtain methane by treating vinasse. The report showed that the COD removal efficiency was 69% at an optimum organic loading rate (OLR) of $17.05 \text{ kg COD} \cdot \text{m}^{-3} \cdot \text{day}^{-1}$, achieving a methane yield of $0.263 \text{ m}^3 \cdot \text{kg}^{-1} \text{COD}$ and an 84% biogas methane content.

III) Recycling in fermentation.

Vinasse can replace certain percentages of the molasses since this waste still has fermentable sugars and many nutrients in its composition. Therefore, it can be used again as substrate in another fermentation with *Saccharomyces cerevisiae*. According to Fadel et al., (2014), ethanol yields can vary depending of the volume proportion used in the vinasse recirculation as shown in Table II.

Vinasse (% v/v)	Ethanol Yield (%)	Residual Sugars (%)	Fermentation Efficiency (%)
0	11.0	1.8	100.0
20	11.1	1.9	100.9
40	10.7	2.2	97.3
60	10.2	2.5	92.7
80	9.3	3.8	84.6
100	8.5	4.9	77.3

Table II. Effect of recycling varying vinasse amounts on the alcoholic fermentation.

Thus, there is no effect on ethanol yield or fermentation efficiency up to 30% v/v of vinasse recirculation. There was a slight change in the efficiency when 40% v/v vinasse was used instead of water and a relative decrease is observed in the ethanol yield and fermentation efficiency when vinasse was introduced above 50% v/v instead of water in the fermentation medium.


IV) Yeast production.

The bioconversion of agricultural and industrial wastes into microbial protein has been receiving increasing attention from the 1970s. The reduction of organic loads and at the same time the production of a valuable commodity is the greatest advantage of such a processes (Saura et al., 2003). Among the yeast species that can be used for such purposes, *Candida utilis* is particularly attractive taking into account its high protein content, good amino acid profile and the possibility of growth from different substrates. Through this technology, the organic load of vinasse was reduced by 75 or 60% when the process was carried out in batch or in continuous regimes, respectively. Cell concentration reaches values around 8 gL^{-1} .

2.2.2. Non-conventional.

I) Biohythane production.

Biohythane is a mixture of biohydrogen and biomethane. Most of the studies performed in this area report a two-stage biohythane generation technique where the first stage consists principally of a hydrogen fermentation followed by a methane fermentation

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reaction in a specific bioreactor. Lab-scale bioreactors have been developed and evaluated with different kinds of substrates in order to produce biohythane (Farghaly & Tawfik, 2017).

Different microorganisms have been used for biohythane production. Costa et al., (2015) reported biohythane production from *Sargassum sp.*; Jariyaboon et al., (2015) used *Thermoanaerobacterium sp.*, *Clostridium sp.*, *Methanosarcina mazei* and *Methanothermobacter defluvi* to synthesize biohythane.

Pinto et al., (2018), submitted a study about the co-digestion of three abundant coffee residues (green coffee powder, parchment and defatted cake) and sugarcane vinasse under thermophilic anaerobic conditions. The initial conditions were acidogenic regimes (pH 5.0–6.5) followed by methanogenic conditions (pH 6.5–8.0). The bioreactor produced a hydrogen-rich biohythane for the first 15 days with a maximum yield on day four (31.45% hydrogen). For the co-digestion of the defatted cake and vinasse, the only gas of interest produced was biohydrogen 32% v/v between the 9th and 32nd day.

II) Dark fermentation.

The use of microbial consortia and industrial wastes for biohydrogen production by dark fermentation is seen as a crucial strategy in an effort to overcome the economic and technical disadvantages of this potential technology. Sydney et al., (2018), carried out a fermentation in a vinasse-based medium supplemented with pure or complex carbon sources. Authors demonstrated that consortia LPBAH1 and LPBAH2 were predominantly composed by *Oxalobacteraceae* and *Lactobacillaceae*, while LPBAH3 was rich in sporulating *Lactobacillaceae* (> 96%). The highest biohydrogen yield was achieved with LPBAH1 (> 50 % *Oxalobacteraceae*) in a vinasse medium supplemented with sugarcane juice ($1.59 \pm 0.21 \text{ mol H}_2 \text{ mol}^{-1} \text{ glucose}$). The lower H_2 yields were achieved with LPBAH3, which otherwise produced the highest amount of butyric acid (up to 10 gL^{-1}).

III) Soil bioremediation.


The use of biomass to clean up polluted soils is an effective approach because of the critical role the microorganisms play in biodegradation of organic pollutants and removal/stabilization of heavy metals (Polti et al., 2014).

Aparicio et al., (2017), used *actinobacteria* biomass to clean up contaminated soils as an attractive biotechnology approach. The authors report the ability of four *actinobacteria*, *Streptomyces sp.* M7, MC1, A5, and *Amycolatopsis tucumanensis*, to generate biomass from sugarcane vinasse. Optimal vinasse concentration to obtain the required biomass (more than 0.4 gL^{-1}) was 20% for all strains, even if grown as a mixed culture. In all cases, the decrease in pesticide presented in studied soils was about 50% after 14 days of incubation. However, chromium removal was statistically different depending on the preparation methodology of the inoculum. While the combined *actinobacteria* biomass recovered from their respective single cultures removed about 85% of the chromium and the mixed culture biomass removed more than 95%.

2.3. ADVANTAGES AND DISADVANTAGES

Table III summarizes the most important advantages and disadvantages of using the aforementioned technologies. The characteristics most relevant in waste management can be grouped in five factors. Technologies that meet the greatest amount of these criteria indicate a greater degree of effectiveness as an alternative for vinasse management (Gebreyessus et al., 2019).

Technology	High processing capacity	Low implementation costs	Low processing costs	High reduction of recalcitrant and toxic compounds	Generation of value-added products	Reference
Fertigation	X	X	X			Prado et al., 2013
Concentration by evaporation	X	X				Larsson, E. & Tengberg, 2014
Animal feed	X	X	X			De Oliveira et al., 2013
Cation exchange resin			X	X	X	Zhang et al., 2012
Combustion	X	X				Schopf & Erbino, 2010
Gasification	X	X			X	Dirbeba et al., (2016)
Membranes			X	X		Queiroga et al., 2018
Electrochemical processes		X	X	X		Flores et al., 2017

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Ozone oxidation		X		X		Siles <i>et al.</i> , 2011
Vermi-composting		X	X		X	Alavi <i>et al.</i> , 2017
Biogas production	X	X	X		X	España-Gamboa <i>et al.</i> , 2012
Recycling in fermentation		X	X			Fadel <i>et al.</i> , 2014
Yeast production		X	X		X	Saura <i>et al.</i> , 2003
Biohythane production				X	X	Pinto <i>et al.</i> , 2018
Dark fermentation				X	X	Sydney <i>et al.</i> , 2018
Soil bioremediation	X	X	X			Aparicio <i>et al.</i> , 2017

Table III. Advantages and disadvantages of using the aforementioned technologies. X means applied.


3. CONCLUSIONS

Agroindustrial wastes from distilleries have been the target by the scientific community and environmentalists. Among the produced wastes, sugarcane vinasse has received special attention, facing the endless possibilities for its reuse and disposal. Nowadays, the fertigation, or the use of untreated sugarcane vinasse as fertilizer in the sugarcane crops, is one of the most applied technology for sugarcane vinasse reuse and disposal. However, the low pH, electric conductivity and chemical elements present in sugarcane vinasse may cause changes in the chemical and physical-chemical properties of soils, rivers, and lakes.


There are still other conventional technological alternatives for sugarcane vinasse destination, like concentration by evaporation, combustion, livestock feed production, gasification, vermi-composting, yeast production, biogas production and recycling in fermentation. Based on the foregoing, many efforts have been directed to allocate, properly, the large volume of this waste. Hence, new studies and green non-conventional methods have been developed aiming at recycling and disposing sugarcane vinasse. Most of the non-conventional technologies were emerging for improving the environmental and economics sustainability. Some of them are membrane and electrochemical processes from a physical-chemical point of view and biohythane production, dark fermentation and bioremediation as biological alternatives. Those technologies are not completely developed but the studies about this processes are increasing exponentially since these emerging new technologies despite reducing contamination burdens, allow the formation of added value products or the generation of clean energy alternatives.

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