

Transforming Alcoholic Vinasse: Improving Biodegradability and Reducing Toxicity through Hydrodynamic Cavitation – A Review

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Abstracts: This review examined the viability of hydrodynamic cavitation as a pretreatment method to improve biodegradability and reduce toxicity in alcoholic vinasse. The growing interest in environmental impacts and the demand for sustainable solutions in the alcohol production industry have driven the search for efficient methods to treat vinasse, a complex and polluting by-product. The basic principles of hydrodynamic cavitation and its application in contaminant removal are explored in detail. Through a critical review of existing research, the efficiency of removal of organic load and recalcitrant contaminants, the influence of geometric parameters, the operational parameters of the process, and the challenges of applying hydrodynamic cavitation as pretreatment of alcoholic vinasse are analyzed. Despite its limitations, its potential as a solution to address pollution problems in alcohol production stands out. Ultimately, this review aims not only to collect and analyze the available information but also to encourage future research in this direction. Therefore, this review article is presented as an essential resource that guides future researchers and practitioners towards more sustainable and effective solutions, significantly contributing to environmental improvements in the industry.

Keywords: Alcoholic Vinasse Pretreatment, Distillery Spent Wash, Distillery Wastewater, Cavitation Reactor for Pretreatment of Vinasse, Distillery Spent Wash by Cavitation.

1. INTRODUCTION

The production of alcohol from sugarcane molasses is one of the main industrial activities in Latin America, which has a significant influence on the global economy [1,2]. The appearance of the COVID-19 pandemic in early 2020 led to an increase in ethyl alcohol production, primarily for applications such as sterilization, sanitation, and disinfectant formulation [1,3–5]. However, this surge in production also resulted in the generation of significant volumes of wastewater, commonly known as vinasse [5,6] or spent wash from distilleries [7]. Approximately 10 to 15 liters of vinasse are produced for each liter of alcohol produced [8–10]. For example, a local distillery with a daily alcohol production of approximately 13,200 liters could generate up to 198,000 liters of vinasse [11].

Vinasses exhibit notable attributes that contribute to their environmental impact, among which their high chemical oxygen demand (COD) and high biochemical oxygen demand (BOD₅) stand out as two important parameters indicating the presence of an organic load [3]. This organic load leads to a series of adverse consequences, including a decrease in dissolved oxygen in surface waters, a change in pH, the deterioration of aquatic fauna and flora, and the emission of unpleasant odors [12]. Additionally, vinasses contain other components such as phenols, sulfates, ammoniacal nitrogen, melanoidins, and salts. Polyphenols manifest themselves primarily as phenolic acids, flavonoids, and tannins. These compounds inhibit microbial activity in the context of anaerobic

digestion [13]. On the other hand, the high ammoniacal nitrogen content leads to instability and a reduction in biogas-methane production yield [14]. The presence of elevated levels of sulfates, a result of the use of sulfuric acid for pH regulation during the alcohol production process, results in reduced efficiency of anaerobic digestion [9]. The dark color of vinasses is attributed to the presence of melanoidins, products generated during non-enzymatic reactions between amino acids and carbohydrates [15]. These compounds, with their antioxidant nature and resistant to biodegradation, present an additional challenge [16]; When they are discharged into aquifer sources, they obstruct the passage of light, thus catalyzing the eutrophication of aquatic vegetation. The flow of vinasse pollutants and their impacts on the environment are shown in Figure 1.

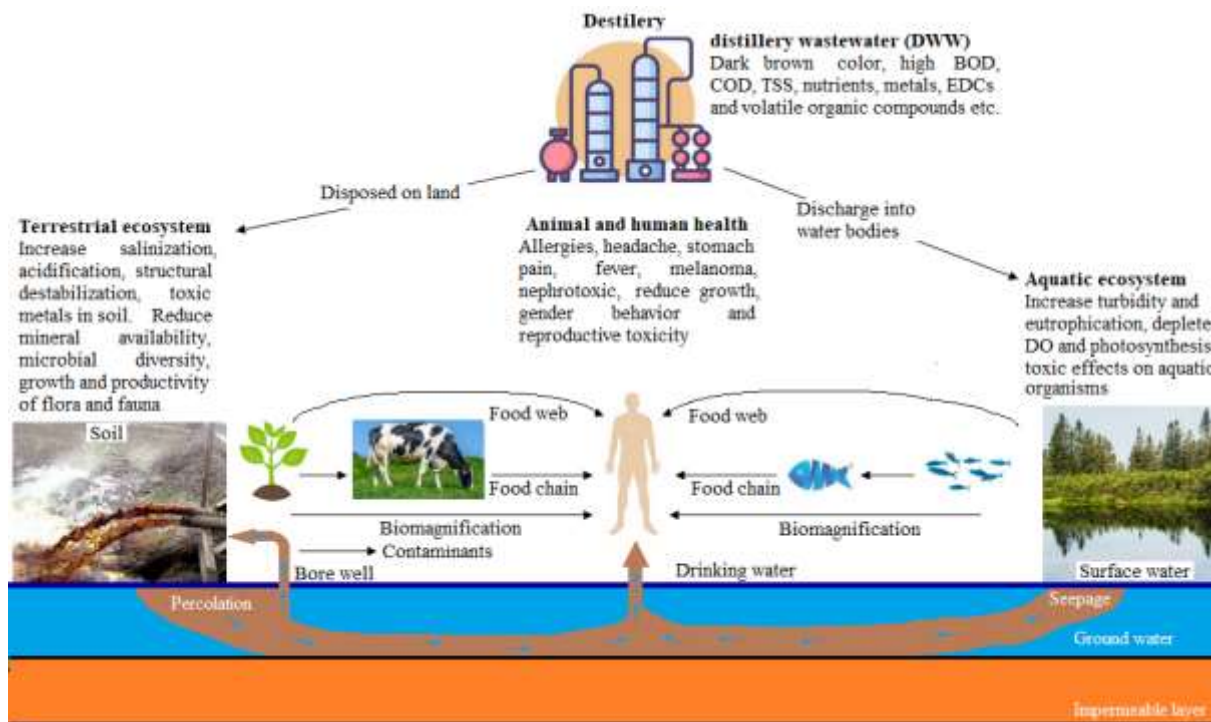


Figure 1. Flow of vinasse pollutants and their impact on the environment, adapted from [17]

To improve biodegradability and reduce toxicity in alcoholic vinasse, it is essential to implement pretreatment before its discharge into bodies of water or disposal in the ground. These pretreatment methods aim to address contaminants present in vinasse that may be resistant to degradation and impede biological activity [18]. These recalcitrant pollutants present significant challenges in terms of their effective removal from effluent. Various investigations and applications of pretreatments have been conducted to address this problem, including submerged nanofiltration [16], coagulation-flocculation coupled with advanced oxidation processes [19], the integration of ultrafiltration and nanofiltration without precoagulation [20], fermentation-controlled anaerobic digestion [21], ozonation-assisted anaerobic digestion [22], coagulation-flocculation using porous $\alpha\text{-Fe}_2\text{O}_3$ particles [23], one- and two-stage anaerobic digestion [8], as well as the advanced oxidation process of Fenton [3].

However, most of these pretreatments involve significant costs, raising concerns about their feasibility in practice. An example of this is the use of ozone to treat vinasse, a type of pretreatment that manages to improve biodegradability, reduce toxicity, and increase biogas production. However, this pretreatment is limited by the fact that the necessary electrical consumption is six times greater than the energy produced in the process [24]. Similarly, when vinasse is treated through by anaerobic digestion with the purpose of producing biogas-methane, it is observed that despite this process, recalcitrant components, such as color, still persist in the resulting vinasse, thus generating the need for a post treatment [5]. As a result, the removal efficiency of contaminants is closely related to the operating conditions of treatment and the specific physicochemical characteristics of vinasse, which inevitably increases operating costs [25]. For this reason, there is a demand for treatment alternatives that are low-

cost and respectful of the environment, as is the case with hydrodynamic cavitation. In this context, the exploration of this technique is considered a feasible alternative to face the treatment challenges related to vinasse handling.

Hydrodynamic cavitation is emerging as a promising technology for process intensification [26–28]. This technique, characterized by its high energy efficiency, cost-effective operation, and ability to catalyze chemical reactions, displays remarkable possibilities for expand its application [28] and remove harmful and toxic contaminants present in liquid wastes [26]. Hydrodynamic cavitation is based on the nucleation, growth, and violent collapse of microbubbles in small time intervals with the subsequent release of energy in a limited region. Furthermore, hydrodynamic cavitation materializes by generating of pressure gradients in devices such as orifice plates, Venturi meters, and vortices [29,30]. Under extreme cavitation conditions, water molecules break down into a variety of substances with high oxidation potential, such as $\cdot\text{OH}$, $\cdot\text{OOH}$, H_2O_2 . These reactive species have the ability to interact with organic compounds present in wastewater, thereby initiating significant reactions [31].

Hydrodynamic cavitation also stands out for its affordability in terms of equipment acquisition, its ease of scaling, its absence of the use of chemical inputs, and its ability to be effectively integrated with other processes [32]. With these characteristics, hydrodynamic cavitation emerges as a highly useful technology in the set of technologies available to address wastewater treatment challenges from the environmental and alcohol distillery. In this context of research and scientific applications, hydrodynamic cavitation has established itself as an effective pretreatment method, with important applications in various aspects related to wastewater treatment and environmental processes. This approach has demonstrated efficient results in phenol removal using a Venturi tube [33]. In addition, its application has been confirmed in the disinfection of water, where its implementation through the use of orifice plates demonstrated high efficiency [34]. Likewise, this method has demonstrated its efficiency in cyanide removal [30]. The potential of hydrodynamic cavitation has been extended to the removal of ammoniacal nitrogen [35]. Similarly, its efficacy was demonstrated in the elimination of bisphenol [32] and in the improvement of the physicochemical properties of sugarcane juice by hydrodynamic cavitation with orifice plates [36]. In addition, this technology with orifice plate devices has been used to reduce the hardness of the rejected water from reverse osmosis [37].

Although the presence in the literature on the application of hydrodynamic cavitation in the pretreatment of vinasse is limited, several studies have been carried out that have used the basic principles of hydrodynamic cavitation in various applications. For example, it has been used in the treatment of wastewater from distilleries, using a Venturi tube [38], in the treatment of pisco production vinasse with hydrodynamic cavitation and combined with ultrasound and heterogeneous photocatalysis [39]. Similarly, utility has been found to improve the efficiency of anaerobic digestion using wheat straw as a substrate [40]. In addition, optimization of distillery wastewater pretreatment has been explored using vortex cavitation [41].

This review aims to highlight the essential aspects related to hydrodynamic cavitation as a pretreatment to improve the biodegradability and reduce the toxicity of alcoholic vinasse, including the geometric parameters of cavitation devices, such as their shape, size and number of holes, and process operating conditions, such as inlet pressure, flow rate, and cavitation number, based on the evaluation of the current literature. Finally, the review highlights the emerging challenges in research within the field of hydrodynamic cavitation as a pretreatment of alcoholic vinasse.

2. CHARACTERISTICS OF ALCOHOLIC VINASSE

Vinasse is a liquid by-product of the fermentation and distillation process of alcoholic beverages. It has a characteristic dark brown color, emits a strong odor, and its pH is in the moderately acidic range. In terms of biochemical oxygen demand, vinasse has values ranging between 70 g/L and 80 g/L. Furthermore, its composition includes approximately 93% water, 2% inorganic compounds (such as potassium, calcium, sulfates, chlorides, nitrogen, phosphorus, among others) and 5% recalcitrant compounds [42]. This liquid waste is known for its ability to cause significant contamination of both the soil and the water [43].

In response to this problem, various treatment methods have been developed to reduce the biodegradability and toxicity of vinasse. These methods include both physicochemical and biological treatments [43]. Physicochemical treatments include processes that combine physical and chemical aspects with the aim of reducing the chemical demand for soluble oxygen and eliminating suspended materials. These treatments include coagulation, flocculation, cavitation, advanced oxidation processes, ozonation, catalysis, as well as membrane technologies, among others. In particular, during the last decades, advanced oxidation processes (AOPs) have been proven to be effective in the removal of color and the degradation of contaminants present in wastewater. AOPs generate highly potent oxidants, such as hydroxyl radicals, which are derived from sources such as ozone (O_3), hydrogen peroxide (H_2O_2), photocatalysis, the Fenton process, and combined ultraviolet radiation [2]. On the other hand, biological treatments imply the use of microorganisms with the purpose of degrading the organic load present in vinasse, generating products such as biogas and additional by-products. Among the most widely used biological treatments, anaerobic digestion stands out, because it allows high levels of organic load elimination. However, it is important to note that even after anaerobic digestion, digested vinasse can still contain some recalcitrant contaminants that are not biodegradable [18].

In this context, it is crucial to focus on the characteristics of the contaminants found in alcoholic vinasse. It is important to recognize that the nature and quantity of these contaminants can vary significantly depending on the raw materials used and various factors inherent to the alcohol production process [43].

2.1 Organic Matter

Biodegradability, a crucial aspect in this context, refers to the predisposition of the effluent to undergo biological treatment and is intrinsically related to the chemical oxygen demand (COD) and biochemical oxygen demand. COD is defined as the amount of oxygen required to oxidize the organic matter present in the residual effluent. On the other hand, BOD represents the amount of oxygen necessary for microorganisms to keep organic matter stable at 20 °C for a period of 5 days [44]. Both parameters, COD and BOD, are the main indicators of the organic load in the effluent [3]. In general, vinasse has a significant polluting load, with levels of BOD ranging between 45,000 mg/L and 60,000 mg/L, and COD values varying between 80,000 mg/L and 120,000 mg/L [45]. This organic load present in vinasse due to organic contaminants has a significant impact on the aquatic environment. This results in a decrease in dissolved oxygen in surface waters, a decrease in pH, the death of aquatic life and plants, and the emanation of unpleasant odors [12]. Therefore, the high levels of BOD and COD in vinasse represent a threat to the ecosystem and make it difficult to completely eliminate them in soil or water resources. Knowledge of biodegradability and organic load in alcoholic vinasse is essential to understand the impact of resistant contaminants on these effluents.

2.2 Polyphenols

The presence of phenolic compounds in vinasse represents an environmental challenge. These compounds are found as phenolic acids, flavonoids, and tannins. In previous studies, various polyphenols have been identified in distillery wastewater, including benzoic acid and its derivatives such as gallic acid, as well as cinnamic acid and its derivatives such as coumaric acid, caffeic acid, chlorogenic acid, and ferulic acid [46]. This diversity and the presence of polyphenols in distillery wastewater not only negatively impact microbial activity, inhibiting it [13], but also make it difficult to treat using conventional biological processes, such as activated sludge, due to its biotoxicity and recalcitrant nature [47]. The concentration of polyphenols present in vinasse reaches levels of 0.2 g/L to 0.8 g/L [48].

2.3 Melanoidins

Melanoidins, substances known to be highly recalcitrant, because they are difficult to biodegrade and can exhibit toxic characteristics [49], also represent an environmental challenge. The concentration of melanoidins in this type of wastewater is high, reaching approximately 20 g/L, while the concentration of polyphenols is lower [46]. Both melanoidins and polyphenols are mainly responsible for the persistent color in wastewater resulting from the distillery process. Regarding the nature of melanoidins, these substances are highly complex and heterogeneous,

containing heterocyclic nitrogen. They are formed as high molecular weight biopolymers through a series of chemical reactions, including the condensation of amino acids and reducing sugars, followed by the rearrangement and isomerization of intermediates of low molecular weight from products of the Maillard reaction [50].

The formation of melanoidins occurs through the Maillard reaction, between sugars and amino acids during the sugar manufacturing process. Its characterization represents a continuous challenge in scientific research [51]. The presence of melanoidins in wastewater generates significant environmental impacts, such as reducing sunlight penetration, which, in turn, decreases the concentration of dissolved oxygen and slows photosynthesis when released into freshwater. Therefore, effective removal of melanoidins is crucial in the treatment of distillery effluents [52]. However, this process is complicated by the presence of other complex phenolic compounds, such as polyphenols that also exhibit antioxidant properties and are notoriously resistant to biodegradation [53].

2.4 Ammoniacal Nitrogen

The presence of ammoniacal nitrogen is a critical factor that must be considered when treating vinasse. Ammoniacal nitrogen, measured in the form of ammonium ions (NH_4^+), represents a form of nitrogenous organic matter and is a toxic pollutant that can have detrimental effects both directly on human health and on the balance of aquatic ecosystems. Water quality standards generally require ammonia nitrogen levels to be below 30 mg/L to 50 mg/L [54], although these limits may vary based on geographic location and specific regulations. Certain industries, such as dyes and pigments, fertilizers, nitrogenous chemicals, and specialty chemicals, generate wastewater with significantly elevated levels of ammoniacal nitrogen, which can range from 1,500 mg/L to 3,000 mg/L [35].

These situations require specific wastewater treatment solutions adapted to these ammoniacal nitrogen loads. Removal of ammoniacal nitrogen from effluent is a significant challenge in many wastewater treatment plants, including those that handle vinasse. This compound is conventionally removed through a variety of methods, which can be biological, such as nitrification and denitrification, involve physical or chemical processes, or even a combination of these methods [35].

3 HYDRODYNAMIC CAVITATION: BASIC PRINCIPLES

Hydrodynamic cavitation, as one of the advanced oxidation processes, is emerging as a promising technology for wastewater treatment. This technique has distinctive advantages, including its versatility in various applications, its simplified operation, and the absence of the generation of secondary pollutants [55]. Hydrodynamic cavitation, a long-known phenomenon, is becoming more relevant due to its integration in various technical and chemical processes, such as extraction of lipids from wet microalgae [56], pretreatment of distillery effluents, and its influence on biogas production [41], purification of effluents contaminated with pesticides [57] and water disinfection [34].

Hydrodynamic cavitation is caused by the formation, growth, and violent collapse of micro- and nanobubbles generated by devices such as orifice plates and Venturi tubes [58]. The process begins with the formation of cavities in the liquid, composed of vapor and dissolved gases. Downstream of this region, an area of biphasic flow is generated, also known as a hydrodynamic cavitation cavity. If the characteristic time frame of the vaporization process is significantly less than that of the liquid flow, cavitation occurs under conditions close to thermodynamic equilibrium. The hydrodynamic cavitation system can be conceptualized from a series of relationships that describe the thermodynamic equilibrium of a homogeneous fluid composed of two phases: a liquid, its vapor, and a dissolved inert gas, supposed to behave ideally [56].

Furthermore, cavitation can be explained through the velocity-pressure relationship of the fluid, according to the Bernoulli equation. As the fluid flows through the constriction, the pressure drops below the liquid-vapor saturation point corresponding to the flow temperature. This results in the formation of steam cavities that collapse in the downstream region, generating highly destructive shock waves that cause enormous pressures, vigorous turbulence, and high stresses [59]. The collapse is energetic enough to release large amounts of energy in a short period of time [60]. The violent implosion of these cavities causes the release of notable amounts of energy, giving rise to areas of high temperature (can reach between 1,000 K - 15,000 K) and high pressures (from 500 bars to

5,000 bars), accompanied by intense turbulence and liquid currents of circulation. This environment favors the generation of hydroxyl radicals [61]. These synergistic processes act together to degrade recalcitrant pollutants or decompose organic matter present in different types of effluents [58]. The resulting phenomenon of high pressure and temperature induces the formation of a variety of radicals, including highly oxidizing hydroxyl radicals [61].

With respect to the characteristic effects of hydrodynamic cavitation, it is important to take into account the possible decrease in efficiency due to long treatment times. To improve efficiency, the volume of the cavitation chamber could be increased or several cavitation devices could be connected in series or parallel [62]. Hydrodynamic cavitation is carried out in a reactor or holding tank through various cavitation devices, such as plates with one or more holes, Venturi tubes with converging and diverging sections that induce pressure drops in the fluid, and rotational hydrodynamic cavitation reactors with various configurations and devices based on vortex diodes of various designs. The inclusion of ultrasound devices is also considered a valid alternative [63].

The most widely reported hydrodynamic cavitation devices, particularly in wastewater treatment applications, are usually those with linear flow. These include Venturi tubes and orifice plates, characterized by different throat geometries or multiple orifices, respectively [34,41,68]. These devices, due to their versatility and effectiveness in generating cavitation, have received significant attention in research and development to efficiently address the challenges associated with removing recalcitrant contaminants in different types of effluents.

3.1 Mechanism of Removal of Contaminants

Hydrodynamic cavitation is capable of generating high-temperature zones, referred to as hot spots. This property leads to the thermal decomposition of any molecules trapped in the cavities or near the interface between the cavity and the liquid, resulting in the formation of smaller molecules and highly reactive free radicals. When wastewater is subjected to cavitation, water molecules dissociate into hydroxyl radicals ($\bullet\text{OH}$) under extreme temperature and pressure conditions. These hydroxyl radicals, known for their strong oxidative power, can oxidize any organic molecule present in the wastewater solution, ultimately facilitating the mineralization of these compounds. Two main mechanisms contribute to the degradation of organic contaminants through the cavitation process [64].

First, thermal decomposition or pyrolysis of volatile contaminant molecules trapped within the collapsing cavity occurs. Second, a reaction occurs between the $\bullet\text{OH}$ radicals and the contaminants present. These mechanisms can occur both at the core of the cavity and at its interface with the surrounding medium, which can be a bulk liquid. In certain cases, mechanical effects also play a significant role in degrading these contaminants. The high-intensity shock waves generated during the collapse of the cavity can break molecular bonds, especially in complex compounds with high molecular weights. The intermediate products resulting from this decomposition become more susceptible to attack by $\bullet\text{OH}$ radicals and are also more amenable to biological oxidation. As a result, it is feasible to increase the rate of mineralization or oxidation of these compounds using hydrodynamic cavitation as a pretreatment method [65]. Consequently, the most significant degradation of contaminants is attributed to the considerable number of passes through the cavitation device. This process ensures that the liquid is more frequently exposed to cavitational conditions. Operating pressure in hydrodynamic cavitation is generated by the pronounced variation in the acceleration and deceleration of the fluid within a closed conduit [64].

3.2 Hydrodynamic Cavitation Unit

A conventional cavitation setup typically encompasses a several key components, including a pump, holding tank, flow meters, control valves, pressure gauges, and cavitation devices. With respect to pump selection, various types and powers are used in different contexts. For example, in the cavitation of sugarcane juice, a single stage centrifugal pump of 1.5 kW at 2900 RPM was used [36]. In research related to the extraction of lipids from wet microalgae, a 2.1 kW, 60 Hz, and 200 V - 240 V centrifugal pump was used, with a flow rate of 4.5 m³/h - 6 m³/h [56]. Similarly, in the context of ammoniacal removal nitrogen, a 3 kW multistage centrifugal pump was used at 2,900 RPM, with a flow rate of 1.2 m³/h [35]. Removal of melanoidins in alcohol distillery wastewater involved the series arrangement of two pumps, a 1 HP peripheral pump followed by a 3 HP centrifugal pump. Similarly, to

address phenol removal in wastewater, a 5 kW positive displacement pump was used [33]. Figure 2 illustrates the schematic of a hydrodynamic cavitation unit with an orifice plate.

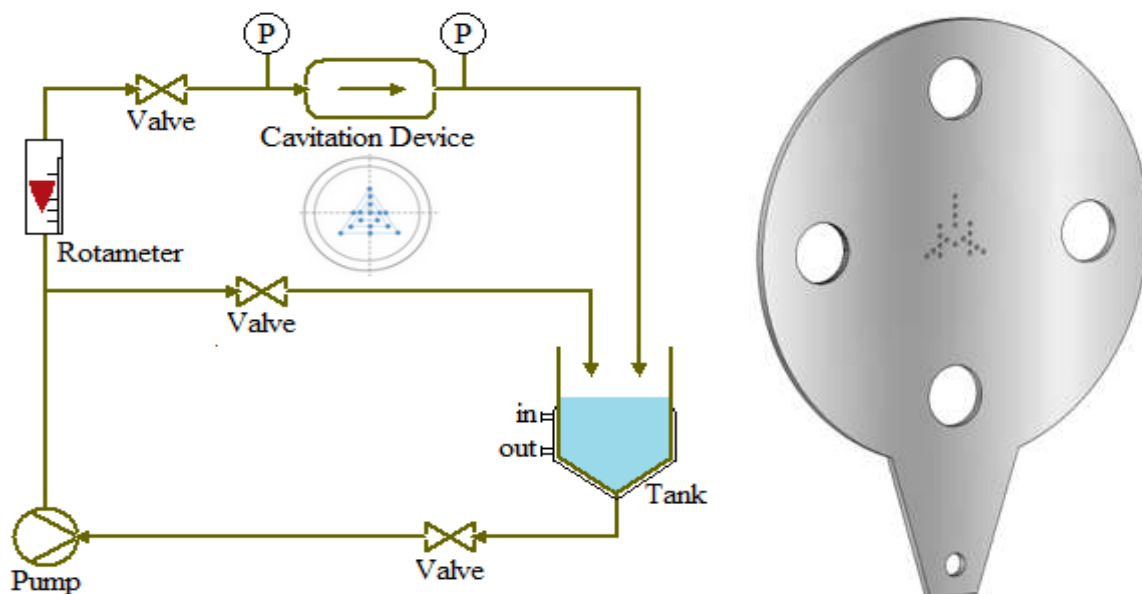


Figure 2. Hydrodynamic cavitation unit flow diagram with orifice plate

In terms of widely used cavitation devices, the Venturi tube, the vortex diode, and the orifice plate stand out [66,67]. The Venturi tube consists of a converging section, a throat, and a diverging section; however, it has a cost disadvantage compared to the orifice plate design. On the contrary, the orifice plate is distinguished by its simplicity and ease of design, allowing for change in various geometric parameters, such as the number of holes, their size, their shape, and their arrangement [67]. This advantage makes the use of these devices an essential tool in the design of effective hydrodynamic cavitation systems for the removal of contaminants in alcoholic vinasse and other industrial environments.

3.3 Design Parameters

3.3.1. A Geometrical Parameters

The two most studied cavitation devices are the Venturi tube and the orifice plate [34,68]. The Venturi tube is distinguished by its ability to promote the growth of cavitation bubbles and prolong their useful life, thanks to its smooth convergent and divergent sections [69]. In comparison, for the same throat opening area and inlet pressure, the liquid flow velocity in the Venturi tube exceeds that of the orifice plate. However, unlike a multi-orifice plate, the Venturi tube has limitations in terms of flow capacity due to its unique throat structure [69,70]. This limitation restricts its applicability in practical settings. Furthermore, due to specialized manufacturing processes and specific materials, the production cost of Venturi tube is relatively high, which represents challenges for large-scale wastewater treatment implementation.

Instead, the use of multiple orifice plates has received significant attention from researchers due to their cost-effectiveness and high processing capacity [70]. This alternative raises the possibility that orifice plates, as highly efficient throttling devices, could effectively replace Venturi tubes in large-scale wastewater treatment, particularly in distillery wastewater treatment. By increasing the number of holes in the orifice plates and applying an appropriate inlet pressure, a processing effect equivalent to the simultaneous operation of dozens of Venturi tubes is possible

[55]. For a clearer visualization of these differences, a comparative scheme between a Venturi tube and an orifice plate is presented in Figure 3. Additionally, Table 1 provides detailed geometric parameters of the Venturi tube, while Figure 4 illustrates various multi-orifice plate configurations, demonstrating the versatility and adaptability of this technology.

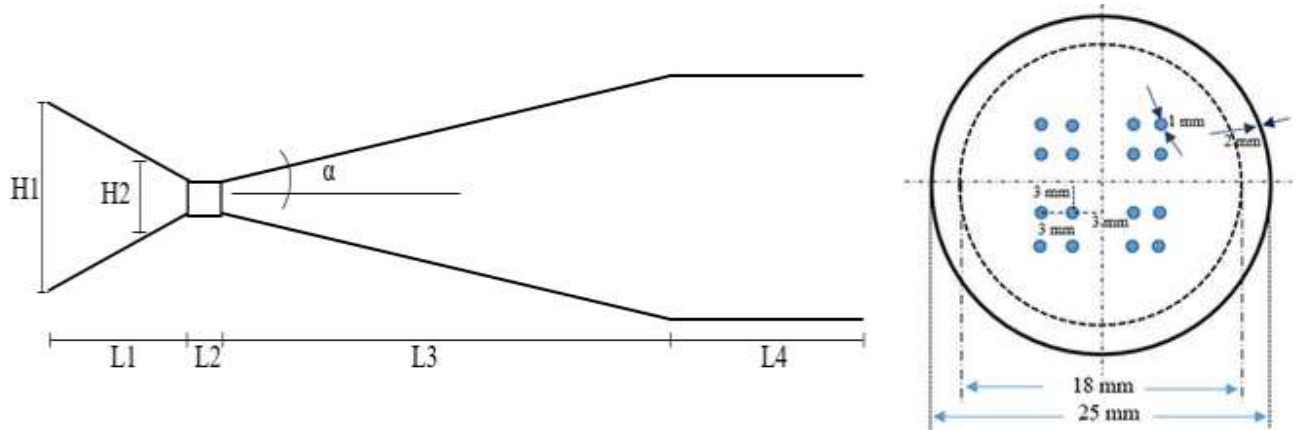


Figure 3. Venturi and orifice plates devices with its geometric specifications

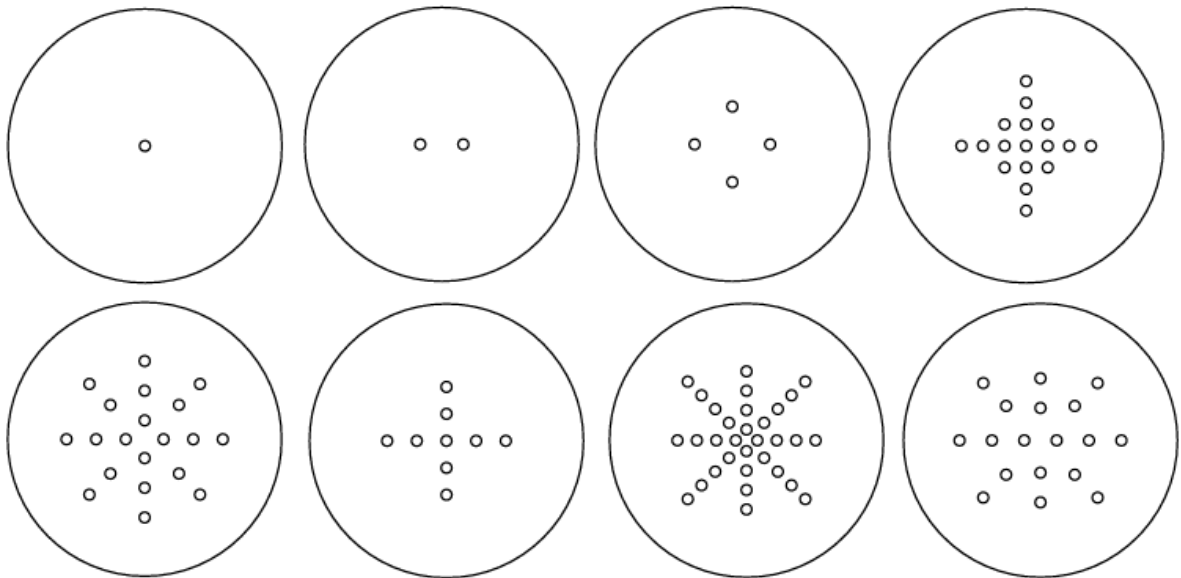


Figure 4. Different combinations of multiple orifice plates, adapted from (36,56)

Table 1. Geometric parameters of Venturi tube (mm)

Divergent angle α	Height		Length				Reference [71]
	H1	H2	L1	L2	L3	L4	
4	25.4	2.0	31.4	2.0	181.6	0.0	
8	25.4	2.0	31.4	2.0	83.3	98.3	
11	25.4	2.0	31.4	2.0	60.2	121.4	
14	25.4	2.0	31.4	2.0	50.9	130.7	
90	25.4	2.0	31.4	2.0	0.0	181.6	

When focusing on the influence of cavitation variables, it is crucial to consider geometry as a highly relevant factor. Various studies have shown that the geometry of the devices used has a significant impact on the size, appearance, and dynamics of cavitation, which can vary significantly [36,72,73]. For example, when the divergence

angle in the geometry of these devices is varied, noticeable variations in cavitation behavior are observed. In situations where the angle of divergence is 4° , the cavity remains intact without the formation of cavitation clouds. However, as this angle increases, the cavitation clouds periodically detach from the cavitation pocket, and this phenomenon is even more pronounced in geometries with sharp transitions. Furthermore, it has been observed that the length of the cavitated cavity increases with increasing divergence angle, and significant differences become evident between the geometries of the round and tapered sections [72].

This evidence highlights the critical importance of geometry in the study of hydrodynamic cavitation. Now, focusing specifically on the Venturi tube, it should be noted that its geometric parameters have a substantial impact on both the local pressure and the observed cavitation. The pressure varies along the length of the tube, being the highest at the inlet and decreasing at the throat as the flow velocity increases. The pressure then returns to atmospheric levels at the outlet of the Venturi tube. The throat pressure is particularly relevant because bubble nucleation is expected when this pressure reaches vapor pressure. Furthermore, the inlet pressure characterizes the energy losses and ultimately the energy consumption associated with the Venturi tube. However, increasing the diameter ratio of the outlet throat has a noticeable effect on increasing the pressure difference, which, in turn, leads to a higher intensity of cavitation at a given flow rate. On the contrary, increasing the length of the tube throat does not significantly influence the pressure losses through the tube, but it does result in an increase in the size of the cavitated bubbles [68]. In summary, the geometry of the Venturi tube emerges as a highly relevant factor in the formation of cavitation bubbles, with the relationship between the diameter of the exit throat and the length of the tube throat playing key roles in influencing the intensity of the bubbles, cavitation and bubble size, respectively [68,72].

After exploring the aspects of the geometric parameters of the Venturi tubes, it is essential to consider the geometric parameters of the orifice plates in the context of hydrodynamic cavitation. These parameters play a fundamental role in both the cavitation process and the effective removal of contaminants in wastewater treatment systems. A key aspect is the number of holes in the orifice plates and their arrangement. For example, it has been observed that using orifice plates with a hole diameter of 1.5 mm and 17 holes, resulting in a cavitation number of 1.54 led to a removal efficiency of 60% for chemical oxygen demand (COD) and a 98% degradation of chlorpyrifos in a reaction time of 2 h. In contrast, the use of an orifice plate with a single hole and a diameter of 2 mm, resulting in a cavitation number of 0.53, achieved a 40% COD removal efficiency and a 96% chlorpyrifos removal in the same time frame during the treatment of pesticide effluents [57].

Next, we analyzed how the distance between the orifice plate and the cavitation tube significantly influences the contaminant removal efficiency, particularly the chlorophyll and total organic carbon (TOC) content. As this distance is reduced, a low pressure region is created behind the orifice plate with a longer retention time, allowing for more efficient degradation of contaminants [74]. This consideration becomes crucial in maximizing the efficiency of hydrodynamic cavitation in the removal of contaminants. Furthermore, it has been observed that increasing the number of holes in the orifice plates can have a positive impact on the removal of color and the microbial load of the treated fluid.

Furthermore, experiments were realized using orifice plates with different hole configurations, in order to evaluate their impact on the physical properties and microbial load of sugarcane juice. For example, plates with 1 hole of 2 mm, 9 holes of 1 mm, and 17 holes of 1 mm were utilized during a processing period of 40 min, in a range of inlet pressures of 2.5 bars to 3.5 bars. The results demonstrated a significant variation in the color removal of sugarcane juice, with values ranging from 2.4 to 27.33, indicating a substantial improvement in the quality of the final product. Furthermore, a notable reduction in microbial load was observed, measured in colony formation units (CFU) per ml, with a maximum microbial inactivation of $3.2 \log_{10}$ CFU/ml, compared to untreated cane juice, which had $5.53 \log_{10}$ CFU/ml. In contrast, the pH of the juice treated with cavitation did not show significant variations with changes in the inlet pressure or the number of holes in the orifice plates [36]. It is essential to note, however, that while these results are promising, specific outcomes may vary depending on the operating conditions and the particular parameters employed in hydrodynamic cavitation.

Finally, it is important to emphasize that the increase in the number of holes in the orifice plates also significantly influenced the removal of the hardness of the water. Orifice plates with multiple holes demonstrated higher cavitation formation efficiency compared to single hole plates, resulting in a maximum hardness removal efficiency of 66.76% [37]. These findings emphasize the significance of the geometry of the orifice plate in hydrodynamic cavitation performance and its capacity to influence the quality of treated effluents.

3.3.2. B Parameters α and β

The parameter α represents the relationship between the total perimeter and the total flow area, while the parameter β is defined as the relationship between the throat area and the cross-sectional area of the pipe. To achieve optimal efficiency in the treatment of cavitation, it is important that α exceed the value of 2 [67]. The values of α and β are calculated with equations 1 and 2 [36]:

$$\alpha = \frac{n * \pi * d_h}{n * \pi * \left(\frac{d_h}{2}\right)^2} = \frac{4}{d_h} \quad (1)$$

$$\beta = n * \left(\frac{d_h}{d_p}\right)^2 \quad (2)$$

Where, n = total number of the holes on the orifice, d_h = orifice hole diameter (mm), d_p = pipe diameter (mm).

3.3.3. C Flow Velocity and Flow Area

The velocity of the cavitation device and flow area are calculated with equations 3 and 4 [67]:

$$v = \frac{Q}{A} \quad (3)$$

$$A = \frac{\pi * d_h^2}{4} \quad (4)$$

Where Q = Volumetric flow rate (m^3/s), A = Flow area (m^2), v = velocity (m/s).

3.3.4. D Number of Passes

It is the number of passes the fluid makes through the cavitation device [66].

The number of passes is calculated using equation 5 [67]:

$$\text{Passes} = \frac{\text{treatment time (min)} * \text{Volumetric flow rate (L/min)}}{\text{Total volumen (L)}} \quad (5)$$

3.3.5. E Operating Conditions

Operating conditions play a significant role in the effectiveness of hydrodynamic cavitation in removing the organic load and contaminants present in distillery wastewater. Therefore, at this point, the main operating conditions are described.

3.3.6. Inlet Pressure

The inlet pressure of the cavitation device is of great importance. Cavitation requires a significant pressure drop in the system for induction and maintenance. This pressure drop not only affects removal efficiency but also influences operating costs. To illustrate this point, in the case of an orifice plate with a concentration of 100 ppm ammoniacal nitrogen in the vinasse, a pressure drop of 2 bars manages to remove 36.7% ammoniacal nitrogen in 2 h of operation, while a pressure drop of 5 bars only achieves a removal of 29.2% under the same cavitation conditions. Furthermore, increasing pressure drop to a certain point has been found to lead to optimal removal, but beyond that, removal efficiency decreases at high pressure drops [35].

A similar phenomenon has been observed in the treatment of pesticide effluents, where an increase in the inlet pressure from 2 bars to 5 bars, using two orifice plates (one with 17 holes of 1.5 mm and the other with 1 hole of 2 mm) over a 2-h interval had a significant effect on the efficiency of contaminant removal. However, after reaching 5 bars, the removal efficiency started to decrease due to the phenomenon of supercavitation. In this phenomenon, the bubbles generated in the cavitation reactor do not implode but instead form a vapor cloud on the line [57]. Additionally, a similar trend was observed in the removal of the chemical oxygen demand (COD) from vinasse. The initial COD was 34,000 mg/L, and after cavitation at 5 bars for 100 min, it decreased to 23,442 mg/L. On the contrary, at a pressure of 13 bars during the same period, COD reached 22,325 mg/L [38].

It is important to note that there exists an optimal pressure point that maximizes cavitation efficiency [38,75]. Beyond this point, further increases in pressure may not yield significant improvements in removal and could, conversely, raise operating costs, potentially leading to feasibility problems in large-scale operations [38]. On the other hand, if the pressure is too low, cavitation might not be sufficiently potent to effectively remove contaminants. Research has demonstrated that the optimal pressure varies depending on the composition of the vinasse and the specific characteristics of the hydrodynamic cavitation [35,38,75].

3.3.7. Cavitation Number

The cavitation number is a dimensionless number that quantifies the intensity of cavitation, that is, the lower its value, the more intense the formation and collapse of bubbles [34]. That is, it is used to describe the cavitation conditions in a device. Furthermore, the cavitation number has a significant influence on the cavitation efficiency and is related to the pressure downstream of the cavitation device. The cavitation number is described by equation 6: [72].

$$C_v = \frac{P_2 - P_v}{\frac{1}{2} * \rho * v^2} \quad (6)$$

Where P_2 : = pressure at the exit of the cavitation device, P_v = vapor pressure, ρ = density of the fluid, v = velocity in the throat of the device.

Cavitation effects are generally observed when the cavitation number value falls below unity. In this case, the equality between the pressure and velocity heads is altered by the difference in the head being used in the generation of cavities [75]. The formation of cavities occurs when the cavitation number is less than or equal to unity [66]. A cavitation number greater than unity indicates a greater tendency for cavitation formation, and therefore a greater cavitation intensity. However, it is important to note that cavitation number is not a determinant parameter of cavitation conditions, but is interrelated with other factors such as fluid temperature, fluid quality, and device geometry, which can also influence formation and cavitation dynamics [72].

3.3.8. Fluid Temperature

Fluid temperature has a significant influence on cavity cavitation. Initially, the cavitation cavity expands, and then its length is reduced to a smaller size than it was initially when the fluid temperature is increased. This phenomenon is known as thermal lag of cavitation. As the temperature increases, the density of the vapor also increases. Meanwhile, the transfer of heat from the liquid to the vapor causes a decrease in the temperature of the liquid and, consequently, a local reduction in the evaporation pressure, initiating the formation of the next cavitation bubble at a lower pressure. and smaller [68].

It has been observed that the final temperature and the increase in temperature increase in sugarcane juice varied according to the inlet pressure, the processing time, and the geometry of the orifice. For example, by increasing the pressure from 2.5 bars to 3.5 bars over 40 min, the final temperature and the temperature increase in sugarcane juice were 40 ± 1 °C and 11 ± 1 °C, respectively, when a plate with a single hole was used. Furthermore, the temperature of the treated juice reached its maximum value of 50 ± 1 °C at a pressure of 3.5 bars during a processing time of 40 min using a plate with 17 holes of 1 mm diameter [36]. It is important to note that an increase in temperature during the hydrodynamic cavitation process can have beneficial effects, such as inactivation of microorganisms and improvement of product quality. However, it is essential to optimize the operating parameters to minimize the negative effects and maximize the beneficial effects of hydrodynamic cavitation.

3.3.9. Fluid Velocity

Flow velocity is another key parameter in the hydrodynamic cavitation process and also has a significant impact on the removal of contaminants present in vinasse and other fluids treated by cavitation. Inlet pressure in the system directly affects fluid velocity and flow rate through the cavitation devices. For example, in the case of the Venturi tube, an increase in inlet pressure translates into an increase in the velocity of the effluent in the Venturi throat. This, in turn, results in a higher flow through the Venturi [75].

These results agree with Bernoulli's equation, which establishes a direct relationship between the inlet pressure and fluid velocity in a conduit. On the other hand, when studying the removal of pesticide effluents, the number of cavitation decreased from 5.76 to 0.35 as the flow velocity increased from 5.74 m/s to 25 m/s due to the increase in pressure input from 2 bars to 8 bars [57]. Consequently, the flow rate must be considered in conjunction with other operating parameters, such as the inlet pressure and the device geometry. The interaction between these parameters can have a highly complex impact on cavitation efficiency and contaminant removal.

3.3.10. Processing of Reaction Time

Another parameter that significantly influences the efficiency of contaminant removal is the processing or reaction time.

One study realized a comparison of the efficiency of COD removal in a sucrose solution using the Venturi tube and an orifice plate with a single hole of 3 mm diameter. The Venturi tube was found to achieve an efficiency of 90% in COD removal after 3 min of treatment, while the orifice plate required 9 min to achieve the same efficiency. Furthermore, they observed that in both devices, COD removal efficiency increased in proportion to time and inlet pressure [57].

Another study analyzed the treatment of biomethanated distillation wastewater using a cavitation reactor with a Venturi tube. They observed that at an inlet pressure of 5 bars for 150 min, the removal of COD decreased from 34,391 mg/L to 23,302 mg/L. In parallel, the biochemical oxygen demand (BOD) increased from 4,853 mg/L to 5,500 mg/L and biodegradability (BOD/COD) also increased from 0.14 to 0.24. When treatment was performed for 50 min, the COD decreased to 23,723 mg/L, the BOD increased to 5,120 mg/L, and the biodegradability index increased to 0.22 [38]. It is important to note that the removal efficiency of COD and BOD and the improvement of biodegradability was influenced by the processing time.

Regarding, the removal of ammoniacal nitrogen present in wastewater was analyzed with a vortex diode and an orifice plate. For this, experiments were carried out under conditions of a pressure drop of 2 bars with an initial concentration of 100 mg/L of ammoniacal nitrogen. The removal of ammoniacal nitrogen was 45% with the use of the vortex diode and 40% with the use of the orifice plate. It is inferred that the vortex diode was more important in removing ammoniacal nitrogen during the first hour of treatment [35]. In conclusion, a longer processing time in the cavitation unit usually leads to greater efficiency in contaminant removal, because hydrodynamic cavitation involves the repetitive formation and collapse of bubbles, which allows for greater interaction between the bubbles, cavitation and contaminants present in the fluid.

3.4 Hydrodynamic Cavitation Applied to Vinasse Pretreatment

The scientific literature on the treatment of alcoholic vinasse by hydrodynamic cavitation is analyzed and discussed to improve biodegradability and reduce toxicity.

Padoley et al. [38] conducted studies on the use of hydrodynamic cavitation as a pretreatment of distillery wastewater containing biomethane. The main objective was to improve the biodegradability and reduce the toxicity of this wastewater. The configuration of the hydrodynamic cavitation unit included a Venturi tube installed in the main line, a 15 L holding tank, a 1.1 kW positive displacement pump, control valves, flanges to accommodate the cavitation device, and a main line along with a bypass line. They evaluated the inlet pressure to 5 bars and 13 bars, dilution at 0%, 10%, and 25%, and with reaction times of 50, 100, and 150 min. Observations showed a significant improvement in biodegradability, with a 47.5% reduction in COD, a 60% reduction in color, and a biodegradability index of 0.32. At the same time, at 5 bars, a dilution of 25% and a reaction time of 150 min, the COD was reduced by 32.4%, the TOC by 31.43%, the vinasse color by 48%, and the biodegradation index was 0.25. The results showed improved biodegradability at 13 bars and reduced toxicity at an inlet pressure of 5 bars. In conclusion, the treatment of biomethanated distillery wastewater with hydrodynamic cavitation represents an effective and energetic efficient alternative to improve biodegradability and reduce toxicity.

Poblete et al. [39] realized a study on the treatment of vinasse generated in pisco production, using a combination of ultrasonic cavitation and heterogeneous photocatalysis. The purpose of the research was to evaluate various treatment methods, including ultrasound (US), heterogeneous photocatalysis (HP), the combination of both (US+HP), heterogeneous photocatalysis with titanium dioxide (HP) and ultraviolet light (UV), and a combination of heterogeneous photocatalysis with titanium dioxide, ultraviolet light, and ultrasound (HP+UV+US), for the removal of organic matter, color, and phenols present in vinasse. Evaluations were carried out at different time intervals: 15, 30, 45 and 60 min. Organic matter was measured according to COD, color was measured by absorbance at 420 nm and phenols were quantified using the Folin-Ciocalteu technique.

The results revealed that after a 60 min treatment, the concentration of polyphenols was 68%, 62%, 36%, 16%, and 8% for the HP+US, HP, US+UV, US and UV treatments, respectively. Regarding color removal within the same period of time, the percentages were 48.8%, 40.3%, 35.2%, 11.3% and 14.7% for the same treatments in the same order. In terms of COD removal, percentages of 70%, 59%, 23.6%, 8.7% and 13% were obtained for the HP+US, HP, US+UV, US and UV treatments, respectively. The results of this study indicate that ultrasonic cavitation alone can be effective in removing organic load, but the combination of ultrasound and heterogeneous photocatalysis significantly improves its effectiveness, especially when combined with other treatments. Furthermore, ultrasonic cavitation can improve catalyst transport and catalytic reactions, thereby enhancing overall treatment effectiveness. These results indicate the combination of ultrasonic cavitation and heterogeneous photocatalysis is a promising option for the treatment of vinasse, offering an effective and efficient approach to reducing organic matter, color, and phenols in this industrial waste.

Nagarajana and Ranade [41] realized a study on the application of hydrodynamic cavitation as a pretreatment method to improve biogas production from distillery wastewater, specifically vinasse. The main objective of their research was to investigate the use of a vortex-based cavitation device to improve vinasse treatment and, as a result, increase biogas generation with a net energy gain. The cavitation device used had a nominal capacity of 1.2

m³/h, an initial feed temperature in the holding tank of 18 °C and a net pumping energy of 25.5 Wh. The two key operating parameters for the hydrodynamic cavitation device were the pressure drop and the number of passes through the device.

The results of the study showed that the application of hydrodynamic cavitation had a significant impact on the production of biogas from distillery effluents. A 20% increase in biogas production will be observed, accompanied by a notable improvement in the biodegradability of the vinasse. The COD of the vinasse was reduced from 157 g/L to 127 g/L, while the BOD decreased from 74 g/L to 20 g/L after pre-treatment with hydrodynamic cavitation at an inlet pressure of 3.9 bars. In summary, the results indicate that the application of hydrodynamic cavitation as pre-treatment can have a significantly positive impact on the production of biogas from distillery effluents, while improving the biodegradability of vinasse.

Soeira et al. (71) realized a study to investigate the impact of the divergent angle in hydrodynamic cavitation devices on melanoidins degradation, and evaluated the use of an oxidant in combination with the hydrodynamic cavitation reactor to improve the degradation efficiency. The main objective of the study was to determine the optimal conditions for achieving the most effective degradation of melanoidins. The experiment was carried out in a closed circuit that included a 6 L holding tank, a series pumping system, with a 1 HP peripheral pump, followed by a 3 HP centrifugal pump, flow control valves, pressure gauges, a cavitation chamber, and tubes with polyvinyl chloride fittings.

During the study, several parameters were varied, including the divergent angle of the Venturi tube (4°, 8°, 11°, 14° and 90°), the pH (2.5, 3.3, 4.2, 5.4, 6.5 and 7.4), the inlet pressure (150, 300, 440, 600, 760 kPa) and the H₂O₂ concentration (0.9, 2.8, 4.7 and 6.6 g/L) for a treatment period of 30 min. The results highlighted that hydrodynamic cavitation achieved the highest degradation efficiency of melanoidins (14.32%) when a divergent angle of 11° was used at an inlet pressure of 600 kPa. Furthermore, a significant increase in degradation efficiency was observed when combined with hydrodynamic cavitation with H₂O₂, reaching a degradation of 60.84% when dosing 2.8 g/L of H₂O₂ with a pH of 2.5. In summary, this study conclusively demonstrates the influence of the divergent angle of the Venturi tube and the use of H₂O₂ to improve the degradation efficiency of melanoidins.

According to the studies analyzed, hydrodynamic cavitation was demonstrated to be an effective technique for improving biodegradability and reducing the toxicity of vinasse. These studies have demonstrated that the application of hydrodynamic cavitation as a pretreatment can reduce both the COD and TOC of the vinasse while reducing its coloration and improving its biodegradability index. However, the effectiveness of this technique can depend on various factors, such as inlet pressure, the pressure drop, and the number of passes through the cavitation device. Furthermore, the results may be influenced by the specific geometric parameters of the hydrodynamic cavitation device used. Therefore, it is essential to carry out detailed studies to evaluate the efficiency of hydrodynamic cavitation in various applications and conditions, considering the varied effects generated by the geometric and operational parameters. These investigations have the potential to contribute significantly to the optimization of the efficiency of the technique as a pretreatment, which, in turn, would improve the biodegradability and reduce the toxicity of vinasse from the alcohol industry.

4. CHALLENGES

A detailed understanding of nature chemical of alcoholic vinasse is required, which includes the precise identification of the specific compounds that contribute to its toxicity and biodegradability. Therefore, one of the challenges is to investigate in depth this chemical and biological complexity of vinasse, to effectively address its transformation. In this line of research, the use of advanced analytical techniques, such as high-performance chromatography or dosimetry [76,77], is crucial to identify and quantify hydroxyl radicals (•OH) and the key components present in vinasse. This approach consists in studying the influence of hydrodynamic cavitation on the compounds contained in the vinasse at the molecular and chemical levels, as well as the formation of hydroxyl radicals under the influence of both geometric and the operational parameters of the process. As part of these

studies, it is important to examine the chemical reactions that occur, the formation of degradation products, and the effects of these changes impact the biodegradability and toxicity of the vinasse.

On the other hand, another major challenge is the optimization of the cavitation parameters to achieve an effective transformation of the vinasse. These parameters include inlet pressure, flow rate, processing or reaction time, and cavitation device geometry. Optimization requires these parameters to achieve significant improvements in both biodegradability and reduction of vinasse toxicity. Therefore, it is necessary to emphasize the research and development of more efficient and stable cavitation equipment, designed specifically for implementation in the industry. This approach could include the creation of custom cavitation devices, designed exclusively for the treatment of vinasse. Likewise, strategies such as placing cavitation devices in series [62,78], in parallel [79], or in the bypass line [80] should be considered. The integration of modeling and computational simulation in the study of hydrodynamic cavitation processes in vinasse treatment systems also becomes a common need. This tool will allow the results to be evaluated and predicted more accurately under various operating conditions, which in turn, will allow a more effective optimization of the parameters involved in the transformation of alcoholic vinasse.

However, the transformation of alcoholic vinasse is not only about reducing toxicity but also about avoiding the formation of toxic byproducts or the persistence of residual toxicity, a challenge of utmost importance. This becomes even more relevant if one considers the possible use of industrial vinasse in agricultural applications or its release into the environment. Therefore, comprehensive environmental toxicity studies are necessary to identify and quantify any toxic residues present in the treated vinasse. For this purpose, it is necessary to incorporate specific biological assays and make use of advanced analytical techniques to accurately evaluate the safety of industrial vinasse. Therefore, it becomes essential to ensure that degradation products do not represent an environmental risk. Furthermore, current environmental and safety regulations must be rigorously followed, making compliance with local and international standards a priority. This includes adequate management of by-products and comprehensive responsibility in the management of waste generated during the process.

Regarding the energetic efficiency of hydrodynamic cavitation, it is a significant challenge because the generation of cavitation often requires a considerable amount of energy. However, this aspect is important to the economic viability and environmental sustainability of the process. Therefore, it becomes essential to investigate methods that improve energy efficiency, such as optimizing cavitation generation and the implementation of energy recovery systems. It is important to emphasize that improving energy efficiency must go hand in hand with evaluating operational and maintenance costs. Hydrodynamic cavitation may require upfront investments in equipment and energy costs, but can offer long-term advantages in terms of waste removal and toxicity reduction. To properly evaluate the implementation of hydrodynamic cavitation at an industrial level, it is suggested to perform a cost-benefit analysis and economic feasibility studies. These investigations will be essential to determine the profitability and economic sustainability of this technology, which would help make informed decisions about its application in the industry.

Addressing these challenges takes a significant step towards more sustainable management of the by-products of alcohol production. By improving the energy efficiency of hydrodynamic cavitation, optimizing the parameters of vinasse treatment and conducting a cost-benefit analysis, we can significantly contribute to environmental protection and improve quality of life. This research not only contributes to emphasizing the efficiency of hydrodynamic cavitation to reduce toxicity and eliminate toxic by-products from alcoholic vinasse, but it also promotes the economic sustainability of the alcohol industry as we move towards a more environmentally friendly future.

CONCLUSIONS

In this Review, the application of hydrodynamic cavitation as a pretreatment of alcoholic vinasse to improve biodegradability and reduce toxicity has been discussed. This liquid byproduct of the alcohol industry presents notable challenges due to its high organic load and the presence of contaminants such as polyphenols, melanoidins, and ammoniacal nitrogen, compounds widely recognized for their toxicity and resistance to

degradation. The application of hydrodynamic cavitation leads to a substantial improvement in the biodegradability of the effluent, which has positive implications for its subsequent biological treatment, such as anaerobic digestion to improve the performance of biogas production. These results contribute significantly to a comprehensive understanding of the application of this technology in the treatment of alcoholic vinasse and similar situations of wastewater treatment.

Furthermore, the efficiency of hydrodynamic cavitation as a pretreatment of alcoholic vinasse is influenced by the geometric parameters of the cavitation devices and the operational parameters of the process. On the other hand, their implementation requires an initial investment in equipment and erosion control of cavitation devices. Additionally, more investment in research and development is required to further refine the geometric parameters and operating conditions of the process. Finally, this review highlights the importance of hydrodynamic cavitation research and development in close collaboration with the scientific community and industry. This collaboration is essential to achieve effective distillery waste management and move toward a more sustainable and environmentally friendly distillery industry. The continuous search for innovative and sustainable solutions in the treatment of vinasse continues to be essential in our commitment to a future that is more respectful of the environment and improving quality of life.

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Conflicts Of Interest

The authors declare no conflict of interest.

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