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Cavitation–ozonation pretreatment boosts anaerobic biodegradability of mature landfill leachate

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ABSTRACT: Mature landfill leachate exhibits low biodegradability and high concentrations of recalcitrant organic matter, limiting the efficiency of conventional biological treatment. The effects of cavitation intensity and ozone load on chemical oxygen demand (COD) removal were evaluated, followed by anaerobic batch assays to assess biogas production and energy performance through the electrical energy per order (EEO) metric. The highest COD removal during pretreatment (26%) was obtained at an ozone load of 6.1 g h⁻¹, whereas the best overall performance was achieved with 4.6 g h⁻¹. Under this optimized condition, the integrated HC–O₃–anaerobic system attained an overall COD removal of 53.1%, compared with only 20% for untreated leachate, while cumulative biogas production increased by approximately 26%. The

optimum cavitation condition was observed at an inlet pressure of 5.5 bar (cavitation number $C_v = 0.16$). The integrated system also demonstrated favorable energy efficiency, with an EEO of $7.6 \text{ kWh m}^{-3} \text{ order}^{-1}$. These findings indicate that HC effectively enhances ozonation by increasing leachate biodegradability, making the combined pretreatment a technically viable and energy-efficient approach for treating mature landfill leachate.

Keywords: biogas production; Venturi tube; breakdown of resistant pollutants; biodegradability.

1. Introduction

Landfill leachate is a highly polluting liquid characterized by intense color and turbidity, generated by the interaction between rainwater infiltration and the biochemical degradation of solid waste deposited in sanitary landfills. Its composition consists of a complex mixture of organic and inorganic compounds [1, 2], which may also contain approximately 200 hazardous compounds [1]. For this reason, landfill leachate poses significant environmental risks, as it may contaminate groundwater and surface waters, contribute to atmospheric pollution through the emission of volatile compounds, and adversely affect aquatic ecosystems and human health [3]. Moreover, exhibits pronounced spatial and temporal variability, reflecting differences in waste composition, landfill age and climatic conditions. Therefore, landfill leachate treatment is considered one of the greatest challenges in environmental engineering due to its highly complex and variable chemical composition.

This complexity makes a single treatment method insufficient, often requiring combined systems for its effective remediation [4, 5]. Young leachate (landfill < 5 years) usually present acidic pH and high concentration of biodegradable organic matter (BOD/COD ratio > 0.3) [6]. For young leachate treatment, biological processes are recommended, amongst which anaerobic digestion stands out since it allows organic matter removal allied with biogas generation [4].

As the landfill ages, the organic matter undergoes a humification process. Mature leachate is dominated by high molecular weight humic and fulvic substances, which are resistant to biodegradation and confer a dark color and high turbidity to the wastewater [7, 8]. These complex molecules require physicochemical pretreatment technologies to enhance biodegradability and improve the performance of subsequent secondary biological treatment. Given that anaerobic digestion is the standard downstream process, effective pretreatment is crucial for increasing biogas production and sustaining long-term energy generation from landfill leachate.

Several pretreatment methods for mature landfill leachate have been investigated, including the physical ones: adsorption, air-stripping, membrane filtration, and sedimentation [9], and the chemical ones: coagulation-flocculation, chemical-electrochemical oxidation and precipitation [10]. Nonetheless, despite achieving satisfactory removal efficiencies, most of these approaches are associated with high operational costs and limited economic feasibility [4, 8].

A promising alternative for treating recalcitrant compounds is relying on the synergistic effects of mixing hydrodynamic cavitation (HC) with oxidative reagents like ozone, hydrogen peroxide, or Fenton's reagent. HC is a physical phenomenon involving the formation, growth, and subsequent collapse of microbubbles or cavities within a flowing liquid. This process occurs over short timescales and releases substantial amounts of energy upon bubble collapse [11]. Cavitation is induced when the local fluid pressure drops below the vapor pressure of the liquid, typically in constricted flow regions – as orifice plate, partially closed valve or a Venturi tube - and the subsequent collapse of bubble clouds downstream generates localized extreme conditions, with temperatures reaching approximately 10,000 K and pressures up to 1 GPa [8, 12].

By utilizing both radical-based oxidation and mechanical disruption, these hybrid procedures (HC + oxidants) greatly improve the breakdown of resistant pollutants, speeding up reaction kinetics and increasing treatment effectiveness while consuming less energy. Song et al. [13] showed that a HC-O₃ system can reduce operational costs by up to 75% compared to the use of HC alone.

Over recent decades, HC + oxidants have been extensively studied for degradation of pharmaceutical residues [14, 13], oxalic acid from mining waste [15], humic substances [16], textile dyes [17], surfactants [18], dairy cattle farming waste [19] and other bio-recalcitrant and toxic substances [12, 20]. The HC + O₃ approach was also studied for mature leachate treatment [21, 22], but these works focused mainly on evaluating COD removal and did not evaluate biogas production enhancement.

In this context, the combination of HC and ozonation can be an interesting alternative for landfill leachate pretreatment by modifying the structure of organic matter and increasing leachate biodegradability, thereby providing more favorable conditions for subsequent anaerobic degradation processes. Following this physicochemical stage, the pretreated effluent was subjected to secondary treatment using sequential batch anaerobic bioreactors. In addition to the assessment of biodegradability enhancement, we also examined the influence of the combined pretreatment on biogas generation during the anaerobic stage.

2. Materials and Methods

The experiments were designed in five stages. Stage 1 aimed to find the P1 value that would produce the maximum COD removal efficiency. In this step, O₃ load was kept constant (3.1 g h⁻¹). O₃ was injected into the reactor during the entire treatment time. Stage 2 consisted of measuring the COD removal efficiency at four distinct loads (1.6, 3.1, 4.6, and 6.1 g h⁻¹), with P1 held constant. In stage 3, the effluent generated from the HC system was subjected to anaerobic batch reactors. Two conditions were evaluated: with pretreatment (P) and with no pretreatment (NP). In the NP conditions, the leachate was not subjected to the HC system. The performance assessment of the anaerobic bioreactors focused on organic matter removal and biogas production. Stage 5 aimed to determine the optimal overall efficiency of the integrated system (O₃ + HC + anaerobic bioreactor) for organic matter removal and to evaluate its energy efficiency using the electrical energy per order (EEO) parameter.

2.1 Mature landfill leachate

Landfill leachate samples (>10 years of age) were collected from a private sanitary landfill located in Uberaba, Minas Gerais, Brazil. Sampling was performed during a single campaign, with leachate collected directly from the oldest landfill cell using a 200 L container. After collection, the leachate was stored under refrigerated conditions until used in experimental procedures.

2.2 Experimental setup and procedure for HC+O₃

The HC system consisted of a 3.0 L tank, copper coil heat exchanger, water pump for effluent recirculation between the tank and the heat exchanger, valves for flow control in the HC device, peripheral hydraulic pump with a power of 1.0 HP (KSB brand and P1000TNG model), register for system emptying and sample collection, Ozone (O₃) inlet and outlet from the tank and pressure gauge (Figure 1). Cavitation intensity was controlled by valve V1, which was adjusted to produce the pressure desired in P1. V2 controls the bypass line and is used to prevent cavitation in the registers when low pressure P1 is applied. The P1 (inlet pressure) and P2 (recovered pressure) pressures were measured in digital pressure gauges (PCT-400Ri, Full Gauge) of accuracy 0.1 bar and measuring range 0 to 34.4 bars.

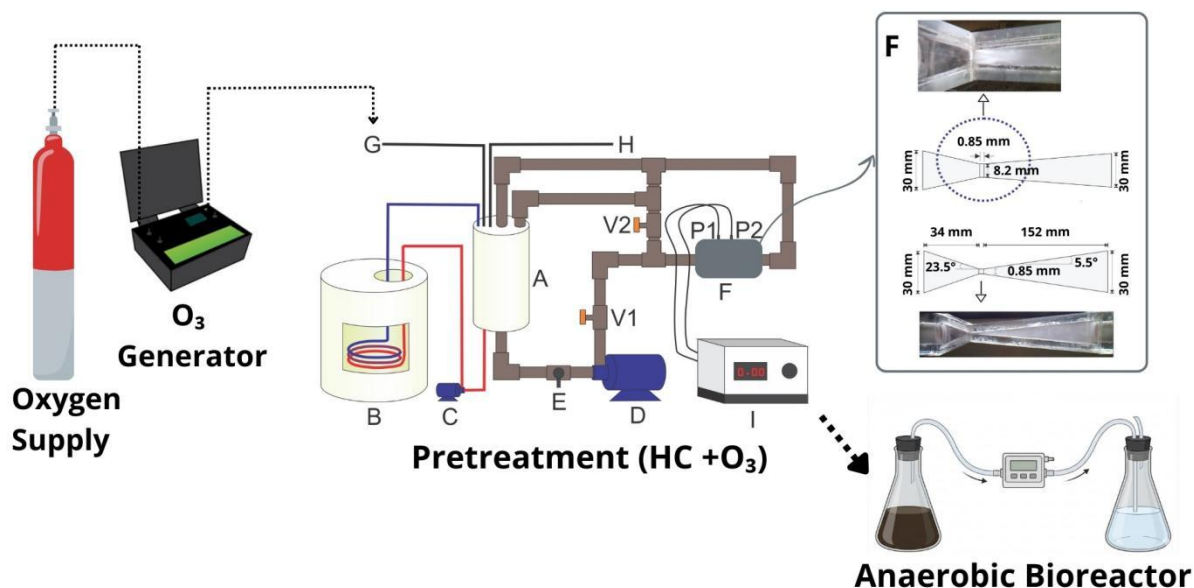


Figure 1 - Schematic representation of the experimental apparatus: A tank; B heat exchanger; C heat exchanger water pump; D peripheral hydraulic pump; E register for taking samples; F Venturi; G O₃ inlet; H output of residual O₃; and I pressure gauge.

Ozone gas was generated from oxygen gas using an ozone O₃ generator (myOZONE M10, Brazil). O₃ was injected directly into the hydrodynamic cavitation loop (G, Figure 1), ensuring intimate contact between the oxidant, the circulating leachate, and the cavitation-induced microbubbles. This integrated configuration was designed to exploit the synergistic effects between HC and ozonation, including improved mass transfer, increased formation of reactive radical species, and enhanced oxidation efficiency. To prevent excessive temperature increases associated with continuous recirculation and pump operation, thermal control was achieved using a cooling system composed of a copper-coil heat exchanger coupled with a submersible pump, which maintained the system within the desired temperature range (35 ± 3 °C). HC device performance was assessed at four different cavitation intensities, which were represented by their respective cavitation numbers (Equation 1). Table 1 shows the flow characteristics within the herein used cavitation device.

$$Cv = \frac{(P_2 - P_v)}{0.5 \rho v_0^2} \quad (\text{Eq. 1})$$

Where: Cv is the cavitation number, P_v is the vapor pressure of the liquid (Pa), ρ is the liquid density (kg m⁻³), and v₀ is the flow velocity at the Venturi throat (m s⁻¹).

Table 1 – Flow characteristics of the HC device. P1 and P2 correspond to the inlet and outlet pressures, respectively; Cv is the cavitation number calculated from the orifice geometry and flow conditions. Data were obtained under steady-state flow for each tested inlet pressure.

Pressure P1 (bar)	Pressure P2 (bar)	Flow rate (L s ⁻¹)	Velocity (m s ⁻¹)	Cv
1.0	0.061	0.10	14.35	0.92
2.5	0.064	0.17	24.39	0.32
4.0	0.065	0.20	28.69	0.23
5.5	0.067	0.24	34.43	0.16

For each pretreatment experiment (made in triplicate), the HC reactor tank was fed with 3.0 L of effluent. The treatment time was 30 minutes and samples were collected at the beginning and end of this period.

2.3. Biochemical biogas potential assays

Anaerobic digestion experiments were carried out in 250 mL sealed Erlenmeyer flasks adapted to operate as anaerobic batch reactors. Each reactor was equipped with a silicone stopper and a stainless-steel outlet connected to silicone tubing for biogas collection. The reactors were placed in a temperature-controlled shaker incubator (Tecnal TE-4200) and operated under mesophilic conditions at 35 °C.

The batch time cycle (TC) was fixed at 24 h and defined as the period immediately following reactor feeding. After the reaction phase, a sedimentation and decantation step of 20 min was applied prior to the withdrawal of the treated effluent. To enhance contact between biomass and substrate, intermittent agitation was applied at 130 rpm for 5 min every hour, resulting in a total agitation period of 6 h per operational cycle.

The food-to-microorganism (F/M) ratio was maintained at 0.06 mg COD mg⁻¹ VSS. To ensure adequate buffering capacity and pH stability throughout reactor operation, sodium bicarbonate (NaHCO₃) was added at a dosage of 1 g per g of COD in each experimental cycle [23]. Stage 4 consisted of analyzing the biogas production on P and NP conditions. All experiments were conducted in triplicate.

Anaerobic sludge used as inoculum was obtained from upflow anaerobic sludge blanket (UASB) reactors operating at the Francisco Velludo Wastewater Treatment Plant, located in Uberaba, Minas Gerais, Brazil. Prior to its application in the anaerobic digestion assays, the sludge was subjected to an acclimation procedure to promote microbial adaptation to the landfill leachate and to minimize potential inhibitory effects. During acclimation, the substrate

composition was progressively shifted from a synthetic sucrose solution to raw landfill leachate, thereby reducing microbial stress and preventing process inhibition. The acclimation strategy consisted of an initial stage with 100% sugar solution, followed by successive stages with increasing proportions of leachate (25%, 50%, and 75%), and a final stage in which 100% leachate was applied for 28 days.

As a byproduct of the anaerobic digestion process, biogas was generated during reactor operation and systematically monitored throughout the experimental runs. Biogas production was measured at regular intervals of 30 min during the first 6 h of reactor operation, corresponding to the main active digestion phase, and again after 24 h to account for cumulative gas generation. Gas volume quantification was performed using 250 mL Mariotte bottles, which allowed reliable and continuous measurement of the produced gas volume [24]. The biogas collection and measurement system consisted of a tube that conveyed the biogas generated in the anaerobic reactor to the upper portion of the Mariotte bottle, above the water surface. The gas pressure accumulated inside the bottle displaced an equivalent volume of liquid through a second outlet tube into a graduated cylinder. This displacement-based principle enabled direct, accurate, and reproducible determination of the biogas volume produced during each operational cycle.

2.4 Analytical Methods and data analysis

The landfill leachate was characterized by determining pH, biochemical oxygen demand (BOD), COD, and ammoniacal nitrogen [25]. Sludge characterization was conducted by determining the ratio of volatile suspended solids (VSS) to total solids (TS), which provides an estimate of the active biomass fraction. These measurements were performed both prior to the acclimation phase and at the end of experimental runs, allowing the assessment of potential changes in biomass activity resulting from exposure to the landfill leachate and tested operational conditions.

3. Results and Discussion

3.1 Landfill leachate characterization

The landfill leachate sample presented a low BOD/COD ratio (Table 2), and the COD was lower than those typically reported in literature [2]. Such characteristics are typical of

stabilized and aged leachates and are often linked to the presence of humic and fulvic substances that are resistant to biological degradation. In addition, the near-neutral pH values indicate that the acidogenic phase of waste degradation had already occurred, with volatile fatty acids subsequently consumed during the methanogenic stage [26].

The ammoniacal nitrogen concentration observed in the leachate falls within a range that does not negatively affect anaerobic digestion processes [27]. This suggests that, despite the presence of nitrogenous compounds, anaerobic biological treatment remains feasible under controlled operational conditions. Conversely, the relatively low total alkalinity reveals a limited intrinsic buffering capacity, which could compromise pH stability during anaerobic treatment. This characteristic therefore justified the supplementation of sodium bicarbonate to ensure adequate buffering and stable conditions throughout the anaerobic digestion process [23].

Table 2 – Physicochemical characterization of the mature landfill leachate used in this study. Values are expressed as mean $\pm$ standard deviation.

Parameter	Value
COD (mg L ⁻¹)	1070 $\pm$ 30.59
BOD (mg L ⁻¹)	240 $\pm$ 4.80
Ammoniacal nitrogen (mg L ⁻¹)	490 $\pm$ 5.01
Total alkalinity (mg L ⁻¹)	250 $\pm$ 2.30
pH	6.99 $\pm$ 0.07
BOD/COD	0.22

3.2 Effect of inlet pressure on mature landfill leachate treatment

The maximum COD removal (20%) was obtained at $P_1 = 5.5$ bar, corresponding to $C_v = 0.16$, whereas the minimum removal (9%) occurred at $P_1 = 1.0$ bar, corresponding to $C_v = 0.92$ (Figure 2). The difference in COD removal between these two operating conditions can be attributed to the fact that higher inlet pressures promote more intense cavitation, increasing cavity formation, turbulence, liquid microcirculation, and the generation of reactive species [28, 29]. However, several studies have shown that pollutant degradation by hydrodynamic cavitation is maximized within an optimal cavitation regime rather than at the lowest possible cavitation number [18, 20, 30]. This limitation is commonly associated with the transition from

isolated bubble collapse to cloud cavitation or supercavitation regimes, in which vapor cavities interact, coalesce, and form larger cavitation clouds, damping individual bubble collapse and reducing the effective formation of hydroxyl radicals [31, 32].

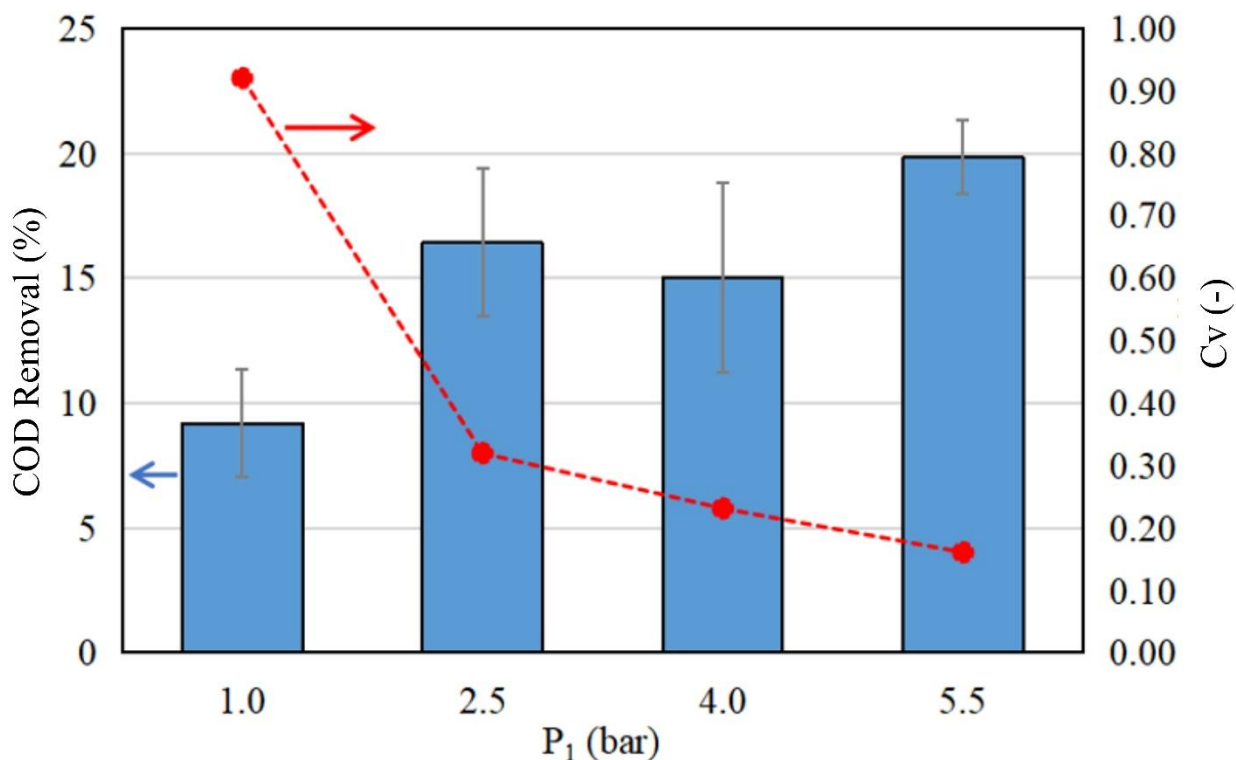


Figure 2 - Effect of inlet pressure (P_1) and corresponding cavitation number (C_v) on COD removal efficiency during HC- O_3 pretreatment. Experiments were conducted for 30 min using 3.0 L of mature landfill leachate, with continuous ozone injection at a fixed O_3 load of 3.1 g h^{-1} . The outlet pressure (P_2) was maintained at approximately 0.065 bar. All assays were performed triplicate; error bars indicate standard deviation.

In the present study, the optimum cavitation number of 0.16 falls within a low- C_v range commonly associated with developed cavitation and intense bubble collapse. Although cavitation number cannot be directly generalized across different reactor configurations, previous studies provide useful support for this range. Saharan et al. [33] used a Venturi device for the degradation of Reactive Red 120 and evaluated C_v values from 0.09 to 0.45, reporting the highest degradation efficiency at $C_v = 0.15$. Saharan et al. [33] also indicated that efficient degradation of organic pollutants is generally favored under intense, but not excessive, cavitation conditions, with optimum conditions depending on reactor geometry, pressure recovery, and operating parameters. In contrast, Musmarra et al. [14] reported efficient

ibuprofen degradation at a higher Cv value of 0.32 within an evaluated range of 0.26–0.56, suggesting that the optimal cavitation regime may shift according to the target compound and cavitation system. Therefore, the optimum Cv observed in the present study should not be interpreted as a universal value, but rather as a reactor-specific condition that is consistent with literature reports showing maximum degradation under cavitation, often within or near the low-Cv interval of approximately 0.15–0.40. Nevertheless, as emphasized by Šarc et al. [34], the cavitation number should not be interpreted as a universal comparison parameter without considering the specific hydraulic configuration of each system.

3.3 Effect of O₃ load on mature landfill leachate treatment

A progressive increase in COD removal efficiency was observed as the O₃ load increased from 1.6 to 6.1 g h⁻¹, with the highest removal, approximately 26%, obtained at 6.1 g h⁻¹ (Figure 3). This behavior indicates that, within the investigated operational range, the increase in ozone availability enhanced the oxidation of recalcitrant organic matter present in the mature landfill leachate. The improved performance may be attributed to the synergistic interaction between ozonation and HC, since cavitation promotes gas–liquid dispersion, improves ozone transfer to the aqueous phase, and facilitates ozone decomposition into highly reactive oxygen species capable of oxidizing resistant organic structures.

The oxidative role of ozone in the degradation of refractory organic matter is further supported by Mateus et al. [35] and Mateus et al. [16] which evaluated the ozonation of melanoidin and humic substances, respectively. In the study with humic substances, the authors reported that non-catalytic ozonation achieved 38.3% total organic carbon (TOC) removal after 60 min, indicating that ozone can oxidize complex humic structures and convert part of the recalcitrant organic matter into more oxidized intermediates. This evidence is relevant to the present study because mature landfill leachate contains humic-like substances that are resistant to biological degradation. Therefore, the increase in COD removal observed with higher O₃ loads can be associated with the direct and indirect oxidative action of ozone on these refractory organic fractions.

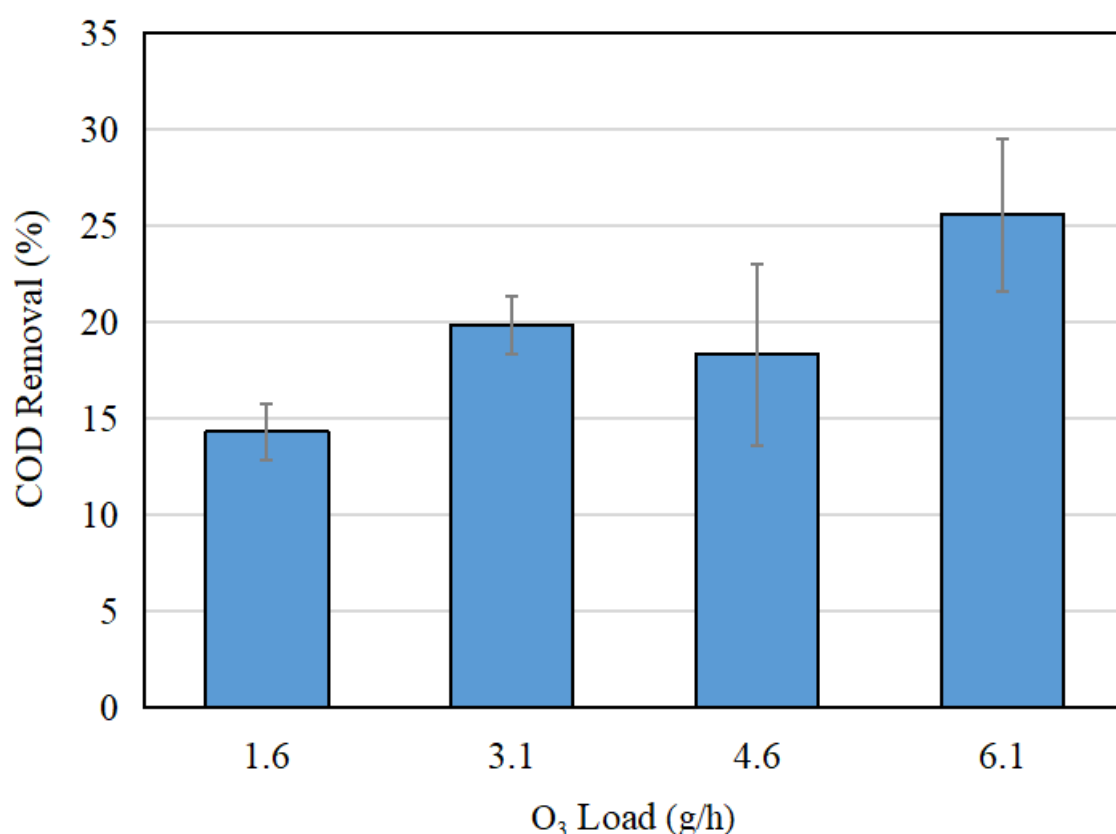


Figure 3 - Effect of ozone load (ranging from 1.5 to 7.6 g h⁻¹) on COD removal efficiency during HC–O₃ pretreatment. Experiments were performed for 30 min using 3.0 L of mature landfill leachate, with inlet pressure fixed at the optimized value of P₁ = 5.5 bar (C_v = 0.16). All assays were performed in triplicate; error bars indicate standard deviation.

The behavior observed in the present study is consistent with the findings reported by Pereira et al. [18], who evaluated a hybrid system combining HC, and ozone for the degradation of surfactants and TOC in a real industrial effluent from tattoo ink production. HC alone promoted only partial degradation, whereas the association with ozone substantially increased removal, reaching 34% of TOC degradation at an O₃ load of 3.1 g h⁻¹ [18]. The authors attributed this improvement to the synergistic interaction between cavitation and ozonation, mainly due to enhanced ozone mass transfer and the accelerated formation of reactive species during bubble collapse [18]. These results support the interpretation that, in complex real effluents, the combined HC + O₃ process is more effective than the isolated processes, although complete mineralization may remain limited by the presence of refractory organic compounds.

Similar evidence was also reported by Brito et al. [17], who investigated the degradation of the triazo dye Direct Blue 71 using HC and ozonation, both as isolated and combined advanced oxidation processes. The authors observed that the combined HC + O₃ system rapidly

removed the dye from influent and anaerobic effluent samples, achieving color removal efficiencies above 98% and promoting substantial reduction of UV-absorbing intermediate compounds within the first 20 min of treatment. They further demonstrated that ozone load and contact time significantly influenced organic carbon removal, confirming that the performance of the hybrid process depends on an adequate balance between oxidant availability and cavitation intensity [17]. Therefore, the results of that study reinforce the trends observed here, particularly the existence of an optimal O_3 load and the role of HC in intensifying ozonation through improved dispersion, mass transfer, and radical generation.

3.4 Effect of HC and O_3 pretreatment on COD removal from leachate in the anaerobic bioreactor

After pretreatment by HC combined with ozonation, the effluent was subjected to an anaerobic post-treatment. An aliquot of the pretreated leachate, corresponding to each applied O_3 load, was fed to the reactors for anaerobic batch tests. Figure 4 presents the COD removal efficiencies obtained under different operating conditions, comparing the raw leachate (NP) and the integrated cavitation–ozonation process at increasing ozone loads.

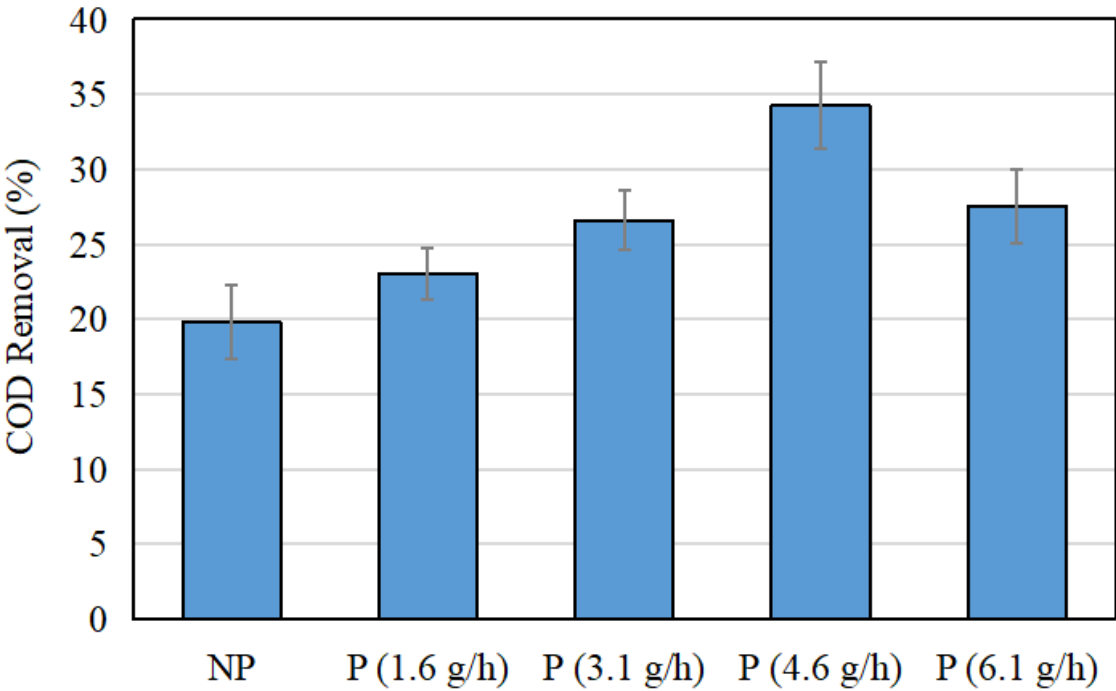


Figure 4 - Overall COD removal efficiency in the integrated HC– O_3 –anaerobic system: comparison between untreated leachate (NP, no pretreatment) and leachate subjected to HC– O_3 pretreatment (P) at four different ozone loads (1.5, 3.1, 4.6, and 6.1 g h⁻¹). The anaerobic

bioreactor was operated with a TC of 24 h, and COD removal was measured after reaching steady-state conditions. NP samples were not submitted to the HC system. Values represent mean $\pm$ standard deviation.

The raw leachate exhibits the lowest COD removal efficiency, close to 20%, and is therefore used as a reference for the untreated system (Figure 4). The COD removal efficiency increased in all tested O_3 loads. The highest COD removal efficiency (34–35%) was achieved at an ozone dose of 4.6 g h^{-1} (Figure 4), suggesting that this condition provides the most favorable balance between cavitation intensity and ozone availability. At the highest ozone load evaluated (6.1 g h^{-1}), COD removal decreased in comparison with the optimum condition, indicating that the improvement promoted by ozone addition was not linear. This behavior can be explained by changes in gas–liquid hydrodynamics and oxidant utilization when excessive gas is introduced into the cavitation loop. Although the coupling between HC and ozonation is generally reported to enhance ozone mass transfer, ozone self-decomposition, and hydroxyl radical generation [36, 13], these benefits depend on maintaining adequate bubble dispersion and effective cavity collapse. At excessive ozone/oxygen flow rates, gas accumulation may increase gas holdup, disturb the formation and collapse of cavitation bubbles, and reduce the local intensity of cavitation events. In addition, very high oxidant availability can favor non-productive reactions, including radical recombination or scavenging, decreasing the fraction of reactive species effectively used for organic matter oxidation [36, 13]. Therefore, the reduction observed at 6.1 g h^{-1} reinforces the existence of an optimal ozone load, at which ozone availability, mass transfer, and cavitation intensity are balanced to maximize the synergistic performance of the HC– O_3 pretreatment.

The beneficial effect of cavitation-based pretreatment on subsequent biological processes was also demonstrated by Gogate et al. [37]. The authors evaluated real municipal and industrial wastewaters and showed that cavitation, either alone or combined with oxidants such as H_2O_2 , O_3 , or Fenton reagents, improved biological oxidation performance [37]. For municipal wastewater, the application of ultrasonic cavitation pretreatment increased the biodegradability index from 0.33 to 0.60 and reduced the biological treatment time from 60 to 36 h. For real industrial wastewater, hydrodynamic cavitation combined with Fenton oxidation led to higher overall COD removal than biological oxidation of the untreated effluent [37]. These findings support the interpretation that cavitation-based pretreatment promotes partial oxidation and structural modification of complex organic matter, increasing its availability for

microbial degradation and thereby improving both biological oxidation and wastewater biodegradability.

Recent studies emphasize that mature landfill leachate usually requires physicochemical or advanced oxidation steps before biological treatment, since ozone can attack aromatic, unsaturated, and humic-like structures, reduce molecular complexity, and improve the suitability of the effluent for subsequent biodegradation [4, 2]. More recently, Becerra-Moreno et al. [5] demonstrated that magnetite-catalyzed ozonation enhanced landfill leachate biodegradability and enabled more efficient coupling with a UASB reactor. These studies support the interpretation that the HC-O₃ pretreatment applied in the present work increased the biological treatability of mature leachate by partially oxidizing recalcitrant compounds and generating lower-molecular-weight intermediates more accessible to anaerobic microorganisms.

Considering the sequential contribution of the HC-O₃ pretreatment and the anaerobic bioreactor, the overall COD removal efficiency was determined from the removals presented in Figures 3 and 4. Although the highest COD removal during the pretreatment stage was obtained at 6.1 g O₃ h⁻¹ (Figure 3), the best performance of the anaerobic bioreactor occurred when the leachate was pretreated with 4.6 g O₃ h⁻¹ (Figure 4). Under this condition, the integrated HC-O₃-bioreactor system achieved an overall COD removal of 53.1%, representing the most favorable balance between chemical oxidation and subsequent biological degradation. This result indicates that maximum oxidation in the pretreatment stage does not necessarily lead to the highest overall treatment efficiency, since excessive ozone input may reduce the biodegradability of the intermediate compounds or impair the synergistic effect between cavitation and anaerobic digestion. Therefore, the ozone load of 4.6 g h⁻¹ was considered the optimal condition for the integrated system proposed in this study, combining sufficient oxidation of recalcitrant organic matter with improved accessibility of the remaining substrate to anaerobic microorganisms.

3.5 Biogas production

The cumulative biogas production and the specific biogas production rate attained at the anaerobic batch assays are shown in Figure 5. It can be observed that the HC-O₃ pretreatment increased biogas generation by nearly 26%, since the maximum production was 24.7 mL under the P condition (4.6 g h⁻¹), whereas the minimum production was 19.7 mL under the NP condition. The same trend was observed for the production rate, which showed the lowest value (0.68) under the NP condition (Figure 5).

400 This positive effect is consistent with the findings reported by Brito et al. [17], who
401 evaluated hydrodynamic cavitation and ozonation for the treatment of textile wastewater
402 containing the triazo dye Direct Blue 71. In that study, HC used as a pretreatment improved
403 wastewater biodegradability and enhanced the subsequent anaerobic stage, doubling the
404 maximum methane production from 2.96 to 6.81 N mL-CH₄ compared with the untreated
405 condition. The authors also observed faster dye reduction during the initial anaerobic period,
406 with 74.7% removal after 16 h for pretreated wastewater compared with 57.2% for the untreated
407 wastewater, indicating that cavitation reduced molecular complexity and decreased the
408 inhibitory effect of recalcitrant compounds on anaerobic microorganisms.

409 Recent studies have also confirmed the positive effect of HC pretreatment on methane-
410 rich biogas production during anaerobic digestion. Dębowski et al. [19] evaluated HC as a
411 pretreatment for waste from dairy cattle farming and reported increased organic matter
412 solubilization, with COD and TOC solubilization degrees close to 49% and 52%, respectively;
413 under laboratory conditions, the best pretreatment resulted in 367 biogas g⁻¹ COD, while large-
414 scale tests produced 327 biogas kg⁻¹ COD. Similarly, Zieliński et al. [38] applied HC to aerobic
415 granular sludge and observed 37% COD solubilization, 42% TOC solubilization, and a methane
416 production efficiency of 496 CH₄ g⁻¹ VS, corresponding to a 19.6% increase compared with
417 raw biomass. More recently, Nayak and Ranade [39] showed that HC pretreatment of primary
418 digestate increased biochemical methane potential by 100–200%, improved the
419 biodegradability index by almost threefold, and reduced the lag phase of methane production.
420 Together, these studies support the interpretation that cavitation improves anaerobic
421 performance by increasing soluble organic matter, accelerating substrate availability, and
422 enhancing the conversion of complex organic matrices into methane and biogas.

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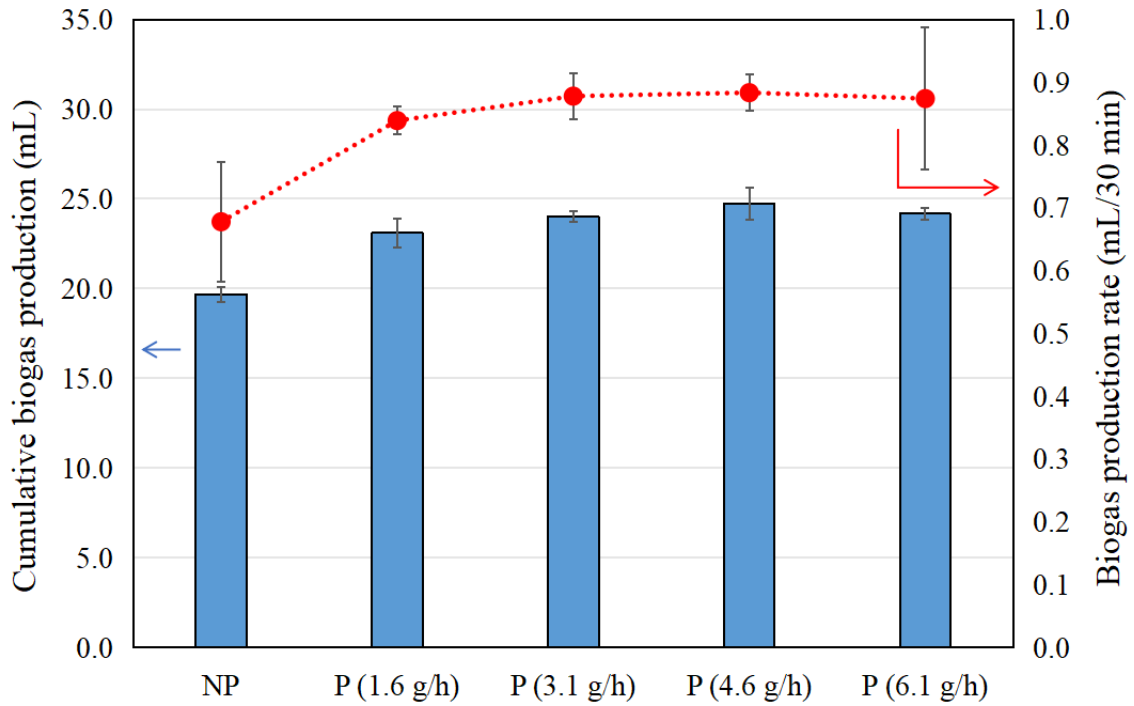


Figure 5 - Cumulative biogas production (mL) and specific biogas production rate (mL/30 min) in the anaerobic batch assays, without HC–O₃ pretreatment and with pretreatment under different O₃ loads. Error bars indicate standard deviation.

3.6 Energy efficiency presented by the integrated system (HC–O₃)

The energy efficiency presented by the integrated system (HC + O₃) was estimated through the parameter EEO (Eq. 2) [12]. This parameter quantifies the electrical energy (kWh) per order for the estimation of the process feasibility. The higher the EEO, the lower the pollutant removal efficiency in terms of electric power consumption.

$$EEO = \frac{P \times t \times 1000}{V \times 60 \log(C_i/C_f)} \quad (\text{Eq. 2})$$

Where: P is the power required by the system (kW); V is the pollutant volume to be treated (m³); t is treatment time (h); and 1000 is the conversion factor.

Using a total power input of 0.9 kW (0.15 kW of an O₃ generator + 0.75 kW of a pump), t = 0.5 h, V = 3.0 L, and C_i/C_f = 1.88 (corresponding to 53.1% DOC removal), the EEO was estimated at 7.6 kWh m⁻³order⁻¹. This value indicates a highly energy-efficient performance, especially when compared with other hybrid cavitation–ozonation systems. As shown in Table 3, the EEO obtained in the present study was lower than values reported for other hybrid cavitation-based AOPs, including the HC–O₃ system applied by Brito et al. [17] to textile

wastewater, the HC–O₃–persulfate system evaluated by Choi et al. [15] for oxalic acid decomposition and by Alves et al. [40] for sucrose treatment. This comparison suggests that the integrated HC–O₃ pretreatment evaluated here presented favorable energy performance, particularly considering that the process was applied to a complex mature landfill leachate and was followed by anaerobic biological treatment.

Table 3 - Comparison of EEO (in kWh m⁻³ order⁻¹) reported in the literature for different HC + oxidants systems applied to recalcitrante wastewater matrices. Lower EEO values indicate higher energy efficiency.

Reference	Matrix/target compound		Process	Main response	EEO (kWh m ⁻³ order ⁻¹)
This study	Mature landfill leachate		HC–O ₃ followed by anaerobic bioreactor	53.1% DOC removal	7.6
[17]	Textile wastewater containing Blue 71	Direct	HC–O ₃	56% TOC removal under optimized condition	19.0
[15]	Oxalic acid from rare-earth extraction processes		HC–O ₃ –persulfate	Oxalic acid decomposition	58.7
[40]	Sucrose solution		HC combined with H ₂ O ₂	90% COD removal	33.7

4. Conclusions

This study demonstrated that hydrodynamic cavitation combined with ozonation is an effective pretreatment strategy for improving the anaerobic treatment of mature landfill leachate. The hybrid process partially oxidized refractory organic matter, increased leachate biodegradability, and enhanced the subsequent performance of the anaerobic reactor. The performance of pretreatment was strongly influenced by the operating conditions. Although the highest COD removal during the oxidation stage (26%) was achieved at an ozone load of 6.1 g h⁻¹, the best overall performance of the integrated process was obtained at 4.6 g h⁻¹, indicating that excessive oxidation does not necessarily maximize biodegradability. Under these optimum conditions, the HC–O₃–anaerobic system achieved an overall COD removal of 53.1%, representing an improvement of approximately 165% compared with the anaerobic treatment

of untreated leachate. In addition, pretreatment increased cumulative biogas production by approximately 26%, demonstrating its positive effect on anaerobic biodegradation.

The integrated process also showed favorable energy performance, with an EEO of 7.6 kWh m⁻³ order⁻¹, lower than values reported for several hybrid advanced oxidation processes. Overall, the results demonstrate that hydrodynamic cavitation effectively intensifies ozonation by improving mass transfer and oxidation efficiency, making the HC–O₃–anaerobic system a promising, scalable, and energy-efficient alternative for the treatment of mature landfill leachate.

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Author contribution Silva, J. V. A.: laboratory analyses, formal analysis, writing-original draft. Rocha, V. C.: conceptualization, supervision and laboratory analyses. Chaves, H. H.: reviewing and editing. Teixeira, G. A.: reviewing and editing. Costa, R., B.: reviewing and editing. Luz, M. L.: reviewing, editing and visualization. Santos, C. E. D.: conceptualization, writing-original draft, reviewing and editing. Goncalves, J. C. S. I: conceptualization, funding, supervision, reviewing and editing.

Declarations

Ethics approval and consent to participate All authors have read, understood, and have complied as applicable with the statement on “Ethical responsibilities of Authors” as found in the Instructions for Authors.

Competing interests The authors declare no competing interests.

References

1. Luo H, Zeng Y, Cheng Y, He D, Pan X (2020) Recent advances in municipal landfill leachate: A review focusing on its characteristics, treatment, and toxicity assessment. *Sci Total Environ* 703:135468 <https://doi.org/10.1016/j.scitotenv.2019.135468>
2. Wang J, Qiao Z (2024) A comprehensive review of landfill leachate treatment technologies. *Front Environ Sci* 12:1439128 <https://doi.org/10.3389/fenvs.2024.1439128>

3. Budi S, Suliasih BA, Othman MS, Heng LY, Surif S (2016) Toxicity identification evaluation of landfill leachate using fish, prawn and seed plant. *Waste Manag* 55:231–237 <https://doi.org/10.1016/j.wasman.2015.09.022>
4. Kamal A, Makhatova A, Yergali B, Baidullayeva A, Satayeva A, Kim J, Inglezakis VJ, Pouloupoulos SG, Arkhangelsky E (2022) Biological treatment, advanced oxidation and membrane separation for landfill leachate treatment: a review. *Sustainability* 14:14427 <https://doi.org/10.3390/su142114427>
5. Becerra-Moreno D, Zuorro A, Machuca-Martínez F, Ramírez-Rios LF, García-Martínez JB, Barajas-Solano AF (2025) Coupling advanced oxidation and anaerobic treatment for landfill leachate: magnetite-catalyzed ozone and UASB reactor efficiency. *Inorganics* 13:218 <https://doi.org/10.3390/inorganics13070218>
6. Liu J, Gu Z, Wang X, Li Q (2022) The molecular differences of young and mature landfill leachates: Molecular composition, chemical property, and structural characteristic. *Chemosphere* 287:132215 <https://doi.org/10.1016/j.chemosphere.2021.132215>
7. Kang KH, Shin HS, Park H (2002) Characterization of humic substances present in landfill leachates with different landfill ages and its implications. *Water Res* 36:4023–4032 [https://doi.org/10.1016/S0043-1354\(02\)00114-8](https://doi.org/10.1016/S0043-1354(02)00114-8)
8. Montusiewicz A, Bis M, Pasieczna-Patkowska S, Majerek D (2018) Mature landfill leachate utilization using a cost-effective hybrid method. *Waste Manag* 76:652–662 <https://doi.org/10.1016/j.wasman.2018.03.012>
9. Bohdziewicz J, Bodzek M, Górská J (2001) Application of pressure-driven membrane techniques to biological treatment of landfill leachate. *Process Biochem* 36:641–646 [https://doi.org/10.1016/S0032-9592\(00\)00259-4](https://doi.org/10.1016/S0032-9592(00)00259-4)
10. Ahn DH, Chung YC, Chang WS (2002) Use of coagulant and zeolite to enhance the biological treatment efficiency of high ammonia leachate. *J Environ Sci Health A* 37:163–173 <https://doi.org/10.1081/ESE-120002580>
11. Gogate PR (2011) Hydrodynamic cavitation for food and water processing. *Food Bioprocess Technol* 4:996–1011 <https://doi.org/10.1007/s11947-010-0418-1>
12. Wang B, Liu Y, Zhang H, Shi W, Xiong M, Gao C, Cui M (2022) Hydrodynamic cavitation and its application in water treatment combined with ozonation: a review. *J Ind Eng Chem* 114:33–51 <https://doi.org/10.1016/j.jiec.2022.07.031>
13. Song Y, Guan S, Wang Y, Zhang C, Liu J, Zhang L (2025) The application of hydrodynamic cavitation technology and the synergistic effect of hybrid advanced

- oxidation processes: a review. *Water Sci Technol* 92:301–325
<https://doi.org/10.2166/wst.2025.102>
14. Musmarra D, Prisciandaro M, Capocelli M, Karatza D, Iovino P, Canzano S, Lancia A (2016) Degradation of ibuprofen by hydrodynamic cavitation: Reaction pathways and effect of operational parameters. *Ultrason Sonochem* 29:76–83
<https://doi.org/10.1016/j.ultsonch.2015.09.002>
15. Choi J, Cui M, Lee Y, Ma J, Kim J, Son Y, Khim J (2019) Hybrid reactor based on hydrodynamic cavitation, ozonation, and persulfate oxidation for oxalic acid decomposition during rare-earth extraction processes. *Ultrason Sonochem* 52:326–335
<https://doi.org/10.1016/j.ultsonch.2018.12.004>
16. Mateus MV, Silva LRS, Gelamo RV, Rocha VC, Campos A, Santos CED, Poletto C, Moreto JA, Gonçalves JCSI, Luz MS (2026) Catalytic ozonation of humic substances with multi-layer graphene. *Braz J Chem Eng* <https://doi.org/10.1007/s43153-026-00667-3>
17. Brito R, Carneiro RB, Gonçalves JCSI, Gavazza S, Damianovic MHRZ (2025) Advanced oxidation via hydrodynamic cavitation and ozonation for enhanced decolorization and biodegradability of triazo dyes in textile wastewater. *ACS Omega* 10:62067–62077
<https://doi.org/10.1021/acsomega.5c09276>
18. Pereira JCR, Mateus MV, Malpass GRP, Ferreira DC, Luz MS, Gonçalves JCSI (2023) Hybrid technology combining hydrodynamic cavitation and oxidative processes to degrade surfactants from a real effluent. *Braz J Chem Eng* 40:723–732
<https://doi.org/10.1007/s43153-022-00285-9>
19. Dębowski M, Kazimierowicz J, Nowicka A, Dudek M, Zieliński M (2024) The use of hydrodynamic cavitation to improve the anaerobic digestion of waste from dairy cattle farming - from laboratory tests to large-scale agricultural biogas plants. *Energies* 17:1409
<https://doi.org/10.3390/en17061409>
20. Yeneneh AM, Al Balushi K, Jafary T, Al Marshudi AS (2024) Hydrodynamic cavitation and advanced oxidation for enhanced degradation of persistent organic pollutants: a review. *Sustainability* 16:4601 <https://doi.org/10.3390/su16114601>
21. Gutierrez-Mosquera LF, Arias-Giraldo S, Zuluaga-Meza A (2022) Landfill leachate treatment using hydrodynamic cavitation: exploratory evaluation. *Heliyon* 8:e09019
<https://doi.org/10.1016/j.heliyon.2022.e09019>
22. Qiao Y, Wang C, Jiang Y, Feng X, Wang K, Xiong J, Jia M, Jin R (2023) Pretreatment of landfill leachate using hydrodynamic cavitation at basic pH condition. *Processes* 11:3014
<https://doi.org/10.3390/pr11103014>

23. Kiyuna LSM, Fuess LT, Zaiat M (2017) Unraveling the influence of the COD/sulfate ratio on organic matter removal and methane production from the biodigestion of sugarcane vinasse. *Bioresour Technol* 232:103–112
<https://doi.org/10.1016/j.biortech.2017.02.022>
24. Walker M, Zhang Y, Heaven S, Banks C (2009) Potential errors in the quantitative evaluation of biogas production in anaerobic digestion processes. *Bioresour Technol* 100: 6339–6346 <https://doi.org/10.1016/j.biortech.2009.07.018>
25. American Public Health Association, American Water Works Association, Water Environment Federation (2017) Standard methods for the examination of water and wastewater, 23rd edn. APHA, Washington DC
26. Costa AM, Alfaia RGSM, Campos JC (2019) Landfill leachate treatment in Brazil - An overview. *J Environ Manage* 232:110–116 <https://doi.org/10.1016/j.jenvman.2018.11.006>
27. Mutegoa E, Hilonga A, Njau KN (2020) Approaches to the mitigation of ammonia inhibition during anaerobic digestion: a review. *Water Pract Technol* 15:551–570
<https://doi.org/10.2166/wpt.2020.047>
28. Soeira TVR, Luz MS, Osiro L, Gonçalves JCSI (2023) The divergent angle of cavitation devices influences melanoidin degradation. A new look through experimental and computational analysis. *J Water Process Eng* 53:103684
<https://doi.org/10.1016/j.jwpe.2023.103684>
29. Cunha PCR, Ulmann G, Vieira LGM, Damasceno JJR, Gonçalves, JCSI (2024) Study of the degradation of sodium dodecyl sulfate surfactant from hydrodynamic cavitation coupled to oxygen injection generated by a low-cost electrolytic cell using solar energy. *J Water Process Eng* 64:105562 <https://doi.org/10.1016/j.jwpe.2024.105562>
30. Pagan FS, Mateus MV, Soeira TVR, da Luz MS, Ferreira DC, Moruzzi R, Simões ALA, Gonçalves JCdSI (2026) Integrating coagulation and flotation via hydrodynamic cavitation: the key role of venturi divergent angle for humic substance removal. *Clean Technol* 8:27 <https://doi.org/10.3390/cleantechnol8020027>
31. Onishi T, Li K, Ji H, Peng G (2024) Shedding of cavitation clouds in an orifice nozzle. *Fluids* 9:156 <https://doi.org/10.3390/fluids9070156>
32. Shahsavari M, Eakins D, Vagovič P, Soyama H, Koliyadu JCP, Sato T, Graceffa R, Mazzolari A, Birnšteinová Š, Moško D, Szeles P, Uličný J, Yashiro W, Meents A (2026) Experimental investigation of cavitation dynamics at mesoscale and microscale in swirled and non-swirled venturi tubes. *Phys Fluids* 38:033335 <https://doi.org/10.1063/5.0310693>

33. Saharan VK, Rizwani MA, Malani AA, Pandit AB (2013) Effect of geometry of hydrodynamically cavitating device on degradation of orange-G. *Ultrason Sonochem* 20:345–353 <https://doi.org/10.1016/j.ultsonch.2012.08.011>
34. Šarc A, Stepišnik-Perdih T, Petkovšek M, Dular M (2017) The issue of cavitation number value in studies of water treatment by hydrodynamic cavitation. *Ultrason Sonochem* 34:51–59 <https://doi.org/10.1016/j.ultsonch.2016.05.020>
35. Mateus MV, Luz MS, Gelamo RV, Lemos DA, Poletto C, Gonçalves JCSI (2022) Study of the catalytic activity of multilayer graphene (MLG), molybdenum oxide (MoO_3), and manganese ferrite (MnFe_2O_4) on the melanoidin removal by ozonation process. *Braz J Chem Eng* 39:55–66 <https://doi.org/10.1007/s43153-021-00198-z>
36. Yang T, Zhang L, Liu F, Cheng C, Li G (2024) Hydrodynamic cavitation–impinging stream for enhancing ozone mass transfer and oxidation for wastewater treatment. *J Water Process Eng* 58:104799 <https://doi.org/10.1016/j.jwpe.2024.104799>
37. Gogate PR, Thanekar PD, Oke AP (2020) Strategies to improve biological oxidation of real wastewater using cavitation-based pre-treatment approaches. *Ultrason Sonochem* 64:105016 <https://doi.org/10.1016/j.ultsonch.2020.105016>
38. Zieliński M, Dębowski M, Kazimierowicz J, Nowicka A, Dudek M (2024) Application of hydrodynamic cavitation in the disintegration of aerobic granular sludge-evaluation of pretreatment time on biomass properties, anaerobic digestion efficiency and energy balance. *Energies* 17:335 <https://doi.org/10.3390/en17020335>
39. Nayak JK, Ranade VV (2025) Hydrodynamic cavitation-based pretreatment of primary digestate: feasibility and role in overall enhancement of valorization. *ACS Omega* 10:36276–36284 <https://doi.org/10.1021/acsomega.5c04230>
40. Alves PHL, Silva PSL, Ferreira DC, Gonçalves JCSI (2019) COD removal from sucrose solution using hydrodynamic cavitation and hydrogen peroxide: a comparison between Venturi device and orifice plate. *Braz J Water Resour* 24:e12 <https://doi.org/10.1590/2318-0331.241920180147>