

Article

Pretreatment of Landfill Leachate Using Hydrodynamic Cavitation at Basic pH Condition

Yina Qiao ^{1,*}, Chaoqi Wang ^{2,*}, Yu Jiang ¹, Xingqiao Feng ³, Kun Wang ⁴, Jian Xiong ⁵, Mengye Jia ¹ and Riya Jin ¹

¹ School of Environment and Safety Engineering, North University of China, Taiyuan 030051, China; gnfoysisatkom04@163.com (Y.J.); jmy96jmy@163.com (M.J.); jrya@nuc.edu.cn (R.J.)

² School of Human Settlements and Civil Engineering, Xi'an Jiaotong University, Xi'an 710049, China

³ Shanxi Provincial Institute of Forensic Science for Public Security, Jinzhong 030601, China; fxq1040@foxmail.com

⁴ Shanxi Diesel Engine Industry Co., Ltd., Datong 037036, China; 15536840621@163.com

⁵ Key Laboratory of Biodiversity and Environment on the Qinghai-Tibetan Plateau, (Tibet University & Wuhan University), Ministry of Education, School of Ecology and Environment, Tibet University, Lhasa 850000, China; jianxiong@utibet.edu.cn

* Correspondence: qiaoyina@nuc.edu.cn (Y.Q.); cqwangglx@stu.xjtu.edu.cn (C.W.)

Abstract: The leachate generated from a landfill can cause significant harm to the environment and human health, so it must be treated before being discharged. A biochemical method is effective to treat the landfill leachate, but it requires a physicochemical pretreatment to help reduce the organic load and improve the biodegradability of the landfill leachate. In this work, hydrodynamic cavitation was used to pretreat the landfill leachate due to it being cost-effective, without additional chemicals, and environmentally friendly. The pretreatment experiments were conducted under an inlet pressure of 0.4 MPa and a basic pH. The influence of operating parameters such as the orifice opening rate, the arrangement of orifices, and the reaction time on the chemical oxygen demand, ammonium nitrogen, and biochemical oxygen demand removal in landfill leachate was studied, and the energy efficiency was evaluated. The results showed that under the above conditions, the removal rate for the chemical oxygen demand of the orifice plate with an annular orifice arrangement was better than that of the orifice plate with a radiation orifice arrangement, and the orifice plate with an orifice opening rate of 0.0417 had the best effectiveness. The energy efficiency under these two optimization conditions was also the highest. When the optimal operation time was 60 min, the removal rate of the chemical oxygen demand was 22.63%. The biodegradability of the landfill leachate was significantly improved with BOD₅/COD increasing by 57.27%. The study provides a theoretical basis and data support for the application of hydrodynamic cavitation as a low-cost and efficient treatment method in the pretreatment of landfill leachate.

Keywords: landfill leachate; hydrodynamic cavitation; chemical oxygen demand; advanced oxidation processes; biodegradability



Citation: Qiao, Y.; Wang, C.; Jiang, Y.; Feng, X.; Wang, K.; Xiong, J.; Jia, M.; Jin, R. Pretreatment of Landfill Leachate Using Hydrodynamic Cavitation at Basic pH Condition. *Processes* **2023**, *11*, 3014. <https://doi.org/10.3390/pr11103014>

Academic Editor: Avelino Núñez-Delgado

Received: 14 September 2023

Revised: 12 October 2023

Accepted: 17 October 2023

Published: 19 October 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Landfill is one of the most widely employed methods for the disposal of municipal solid waste (MSW). However, landfill leachate (LL), which is extremely harmful to the environment and peoples' health, can easily cause secondary pollution and damage underground water sources. LL is a high-concentration organic wastewater with dark-brown and complex compositions. The quality and quantity of LL can vary from time to time. Complex components like humic substance, aromatic compounds, long-chain hydrocarbons, and halohydrocarbons are abundant in LL [1,2]. The values of the chemical oxygen demand (COD) and ammonia nitrogen (NH₃-N) are also fairly high (COD: 1863–13,100 mg/L, NH₃-N: 18.6–3210 mg/L) [3]. According to "Standard for Pollution Control on the Landfill Site of Municipal Solid Waste" (GB16889-2008) in China, the emission limits for LL are

100 mg/L for COD, 30 mg/L for biochemical oxygen demand (BOD₅), and 25 mg/L for NH₃-N [4]. Obviously, LL must be treated to meet the standards before being discharged.

Biological methods may be an effective and economical process for wastewater treatment [5–7]. Song et al. used an anaerobic moving-bed biofilm reactor with the help of rhamnolipids to improve the COD removal efficiency of LL from $86.0 \pm 2.9\%$ to $97.5 \pm 1.6\%$, and the removal efficiency of NO₃⁻-N was also slightly increased from $92.5 \pm 1.9\%$ to $95.6 \pm 1.0\%$ [8]. However, biological treatments are dependent on various factors like temperature, the composition of feed, oxygen level, and the toxicity [9]. In some young landfills, the biological method is effective for the treatment of LL. It becomes more and more difficult for biological methods to treat LL with the passage of time due to the decline of the BOD₅ and COD ratio (BOD₅/COD < 0.2), and refractory pollutants such as humic acids and fulvic acids accumulate gradually [10]. High concentrations of NH₃-N and toxic organics in LL could also hinder microbial treatment. Chin et al. studied the performance of the activated sludge system in the leachate treatment plant to remove pollutants of LL. The result showed that the activated sludge system was not satisfactory. The overall pollutant removal percentage did not reach 50% [11]. A biological treatment alone was not sufficient to treat LL due to the complex composition and varying concentration of pollutants in LL. Therefore, physical and chemical methods have received more attention.

During the treatment of LL, physical and chemical methods are often used for the pretreatment to improve the biodegradability of the leachate. In practical applications, physical and chemical methods are commonly combined for the pretreatment of LL. The physicochemical combination treatment is an efficient and more suitable method to treat LL because it considers the leachate age, season, climatic conditions, regulation criteria, and pollutant concentration.

The conventional physical and chemical treatment methods for LL, such as coagulation/flocculation [12], adsorption [13,14], membrane processes (microfiltration, nanofiltration, ultrafiltration, and reverse osmosis) [15,16], can only transfer pollutants from one medium to another and are unable to mineralize pollutants. In the pretreatment process, advanced oxidation processes (AOPs), including O₃ [17], Fenton, and Fenton-like processes [18,19], supercritical water oxidation (SCWO) [20], and electrochemical oxidation processes [21], etc., would modify the structures of pollutants, produce by-products which are biodegradable and less toxic, and enable subsequent biological treatments to be carried out more effectively.

Although these advanced oxidation technologies are effective in treating leachate, they also have some drawbacks. Firstly, it is difficult and costly to modify these advanced oxidation technologies based on the original treatment process of the leachate. Secondly, the treatment conditions required by these advanced oxidation technologies are relatively strict, such as the need to adjust the treated liquid for acidity in most cases by a Fenton reaction. SCWO requires high-temperature and high-pressure reaction vessels and consumes a large amount of electrical energy. Furthermore, these advanced oxidation technologies require the addition of additional chemical agents such as oxidants, which may inhibit microbial activity and hinder further biological treatment. The purpose of the pretreatment is to mitigate the inhibition of biological processes and reduce the organic load. At the same time, the addition of chemicals must be restricted during the pretreatment process. Therefore, these advanced oxidation technologies are not applicable in the pretreatment of leachates. One needs to find a method with a low cost, low energy consumption, and no chemical reagent addition. Hydrodynamic cavitation (HC) technology precisely meets this requirement.

HC is a special technology which can speed up the oxidation process without the use of any additional additives. It can be considered that HC is a physical phenomenon which is caused by the formation, development, and collapse of microbubbles [22]. The HC generator is used to limit the flow of water to create local pressure changes. When the local pressure of the liquid is reduced below the saturated vapor pressure, the gas core containing permanent gas prompts HC. As the liquid continues to flow, HC bubbles will

collapse due to the pressure recovery in the system [23]. HC microbubbles' collapse can generate instantaneous high temperatures (4000~6000 K) and high pressures ($1 \times 10^7 \sim 7 \times 10^7$ Pa) [24]. The release of powerful energy breaks water molecules (H_2O) into hydroxyl radical ($\bullet OH$) along with several other processes such as thermal decomposition, microjets, shockwaves, and shear forces [25,26]. H_2O molecules are cracked in the HC condition of high temperature and pressure according to the following reactions:



The produced $\bullet OH$ can act on organic matters. Meanwhile, HC leads to SCWO which can oxidize organic matters in water since the instantaneous reaction conditions of the HC process reaches the supercritical state of water [23,27–29]. It can be seen that HC can degrade organic pollutants solely by relying on the kinetic energy and pressure of water without additives or external energy. In addition, it is easy to operate and environmentally friendly. Therefore, HC has enormous application potential. It can be used to treat LL.

At present, many studies have shown that HC is effective for the degradation of organic pollutants, such as pesticide [30], dyes [31,32], phenolic compound [33,34], and polycyclic aromatic hydrocarbon (PAH) [35]. Some studies that combined HC and AOPs (such as O_3 and persulfate) to treat actual wastewater achieved good results, like effluents from the production of bitumen [36], but the introduction of too many chemicals can also have a negative impact on water.

As a result, HC was chosen in this work as the physicochemical pretreatment method before a biological process because the physical and chemical effects of HC microbubbles' collapse can avoid the introduction of chemicals. The orifice plate was used as an HC generator in this study. Under the basic pH conditions of the effluent, the influence of operating parameters such as β , the arrangement of orifices, and the reaction time on COD, NH_3-N , and BOD_5/COD in LL was studied, and the energy efficiency was evaluated. The effectiveness and capability of HC were evaluated by exploring the removal effect of HC.

This study aims to improve the biodegradability of the leachate through a low-power and low-cost HC pretreatment to meet the economical and environment-friendly requirements.

2. Materials and Methods

2.1. Materials

LL samples with a foetor and a dark brown color were collected with polyethylene buckets (100 L) from a municipal sanitary landfill. The samples were stored at 4 °C to maintain the effluent characteristics unaltered. The raw liquid sample of LL is shown in Figure 1. Table 1 indicates the main characteristics of the LL.

Table 1. The characteristics of LL samples.

Parameter	Value
COD (mg/L)	4844.2
BOD_5 (mg/L)	535
BOD_5/COD	0.11
pH	7.18
NH_3-N (mg/L)	2178.82
Turbidity (NTU)	10,688.9
Total suspended solids (mg/L)	57
UV_{254}	1.72

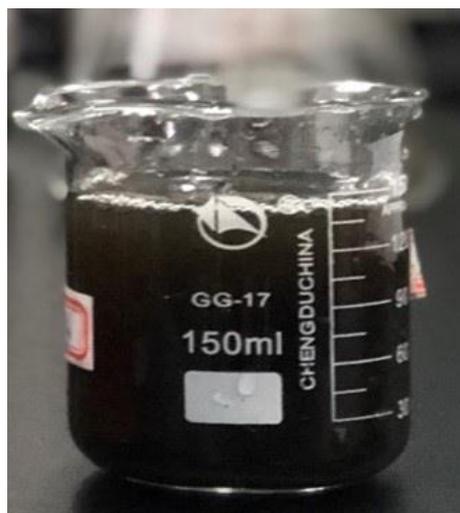


Figure 1. Raw liquid sample of LL.

2.2. Experiment Setup

In this work, the schematic diagram of the HC equipment is shown in Figure 2, and the physical picture of the HC device is shown in Figure 3. The components and functions of the device are listed in Table 2. The functions of the HC device are listed in Table S1 of the Supplementary Materials. The equipment was composed of a tank (150 L), a booster pump (rated power, 2.2 kW; rated flow, 2 m³/h; head, 81 m), and regulating valves (V1, V2, and V3), pressure gauges, and a flowmeter. Perforated plates were used as the HC generator, which were made of stainless steel and fitted in the main line. The tank was designed with a condensing tube to adjust the temperature of the liquid. Pressure gauges were set to measure the inlet pressure (p_1) and fully recovered pressure (p_2) downstream (p_1 and p_2 are absolute pressures). The flowmeter was installed on the main line to measure the flow rate. The temperature was measured by a thermocouple.

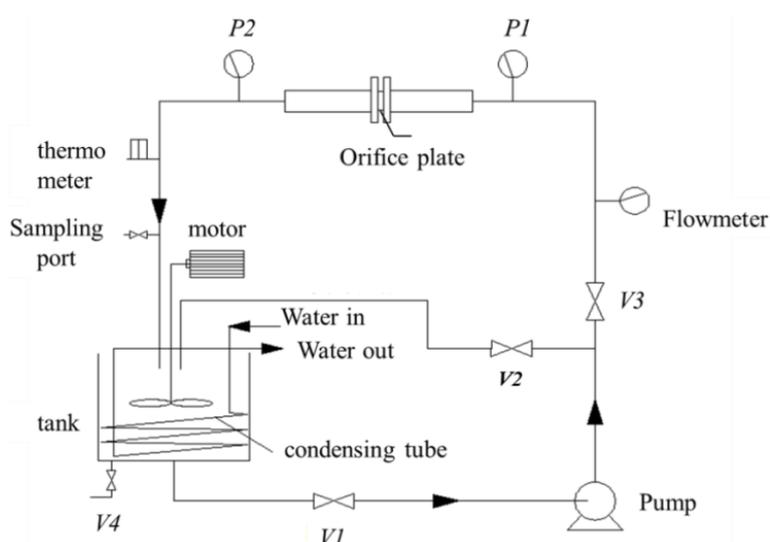


Figure 2. Schematic diagram of the HC experimental device. Arrows indicate the direction of water flow.

The orifice plates were used as an HC generator with a plate thickness of 5 mm, and an outside diameter of 45 mm. In order to explore the influence of different orifice plates on the pretreatment effect of LL, in this study, six orifice plates with different orifice opening rates and arrangements of orifices were used for experiments. The structures and parameters of different orifice plates are showed in Figure 4 and Table 3.

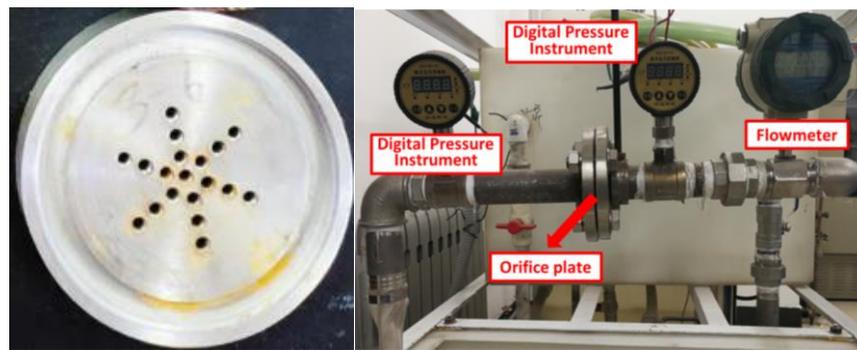


Figure 3. Physical picture of the HC device.

Table 2. The components of the HC device.

Device Composition	Model and Manufacturer
Booster pump	Model: CDLF-100 (Shanghai Yuquan Pump Co., Ltd., Wenzhou, China)
Water tank	Made of PVC material, dimensions: 500 mm × 500 mm × 600 mm, thickness: 5 mm, capacity: 150 L
Condensing tube	Made with stainless steel pipe
Valve	Stainless steel, DN40 ball valve
Pipeline	The main pipeline is made of stainless steel. The side piping is made of PVC, and the pipe diameter is DN40
Flowmeter	Model: LWSY-25, measuring range: 1–10 m ³ h ⁻¹ (Dongtai Dongxing Instrument Factory, Donxing, China)
Pressure gauge	Model: BD-801 K, range: 0–1.0 MPa (Shanghai Kaixun Technology Co., Ltd., Shanghai, China)

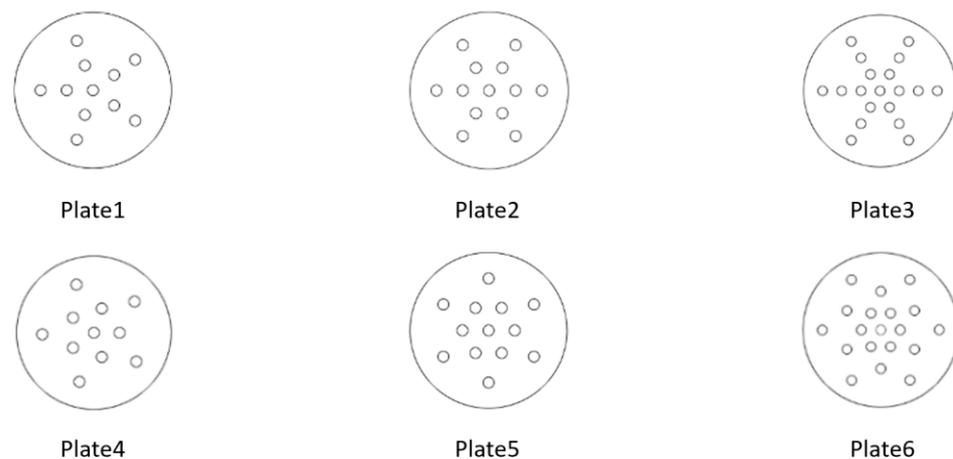


Figure 4. The arrangement of orifices of different orifice plates.

Table 3. The parameter of the orifice plates.

Orifice Plate Number	The Diameter of the Hole, d/mm	Number of Holes, N	Area Occupied by the Holes, mm ²	Orifice Opening Rate, β	Arrangement of Orifices
1	2.5	11	4.9086	0.0671	Radiation distribution
2	2	13	3.1415	0.0508	Radiation distribution
3	1.5	19	1.7671	0.0417	Radiation distribution
4	2.5	11	4.9086	0.0671	Annular distribution
5	2	13	3.1415	0.0508	Annular distribution
6	1.5	19	1.7671	0.0417	Annular distribution

The orifice opening rate (β) is the ratio of the total flow area of the holes on the orifice plate to the cross-sectional area of the upstream pipeline. It is a relative value and is calculated by the formula:

$$\beta = N \left(\frac{d}{D} \right)^2 \quad (5)$$

where d is the circular hole diameter, in mm, D is the pipe diameter of the pipeline up-steam of the orifice plate, which was 32 mm, and N is the number of holes on the orifice plate.

2.3. Analytical Method

All the parameters were measured according to the methodology described in the “Standard for Pollution Control on the Landfill Site of Municipal Solid Waste” (GB 16889-2008.CN). The COD was determined by the potassium dichromate method. The COD was calculated according to the method described in the Supplementary Information. NH₃-N was measured by the Nessler’s reagent colorimetry using an UV–visible light spectrophotometer (model Lambda 650, PerkinElmer Co., Ltd., Waltham, MA, USA). BOD₅ was determined by a BOD analyzer (model ET99724, Lovibond Co., Ltd., Amesbury, UK). The pH value was determined by using an electronic pH meter (ZD-2, Shanghai INESA Scientific Instrument Co., Ltd., Shanghai, China).

2.4. Experimental Method

After the required HC generator was installed, 50 L of LL was added into the water tank, and then the stirrer was opened to make it homogeneous. All the experiments were carried out under with pH = 7.18, the water temperature was 35 °C, and p_1 was 0.5 M Pa. According to our previous experiments, all orifice plates used in this work had the best HC effect under that pressure and temperature for our HC experimental device [37]. The cavitation number (σ) of all orifice plates was 0.24. σ was calculated by Formula (6) [38]:

$$\sigma = \frac{p_2 - p_v}{\frac{1}{2}\rho U^2} = \frac{p_2 - p_v}{p_1 - p_2} \quad (6)$$

where p_v is the vapor pressure of the test water, U is the flow velocity at the orifice throat, and ρ is the density of the test water.

When the pressure was stable, the COD was sampled every 10 min for testing, and NH₃-N was tested only after one experiment.

The energy efficiency was evaluated in terms of the COD reduction supplied per energy unit, which can be calculated by Formula (7):

$$\eta = \frac{\Delta m}{E} \quad (7)$$

where η is the energy efficiency in mg COD/J, Δm is the COD reduction in mg, and E is the energy input into the system in J.

All experiments repeated three times and all results were averaged. After one experiment, the pretreated LL would be discharged, and the water tank should be fully cleaned for repeating the experiment.

3. Results

3.1. The Influence of β and Arrangement of Orifices on the LL Treatment

In this part, orifice plates 1–6 were selected to pretreat LL for 60 min under a basic pH condition of effluent, and the results are shown in Figure 5a,b. As can be seen from Figure 5a, all orifice plates could reduce the COD in various degrees after the 60 min pretreatment. As β increased, the removal rates of COD of the orifice plates with an annular orifice arrangement were 22.63%, 6.48%, and 14.60%, those of the orifice plates with a radiation orifice arrangement were 15.33%, 7.27%, and 8.76%, respectively. For orifice plates with the same β , except for $\beta = 0.0508$, the removal of the COD of the orifice plates with an annular orifice arrangement was better than that of the orifice plates with a radiation orifice arrangement.

From Figure 5b, although the NH₃-N content decreased to different extents when different orifice plates were used to pretreat LL, the final removal efficiency of NH₃-N was small, with a maximum removal rate of only 7.13%.

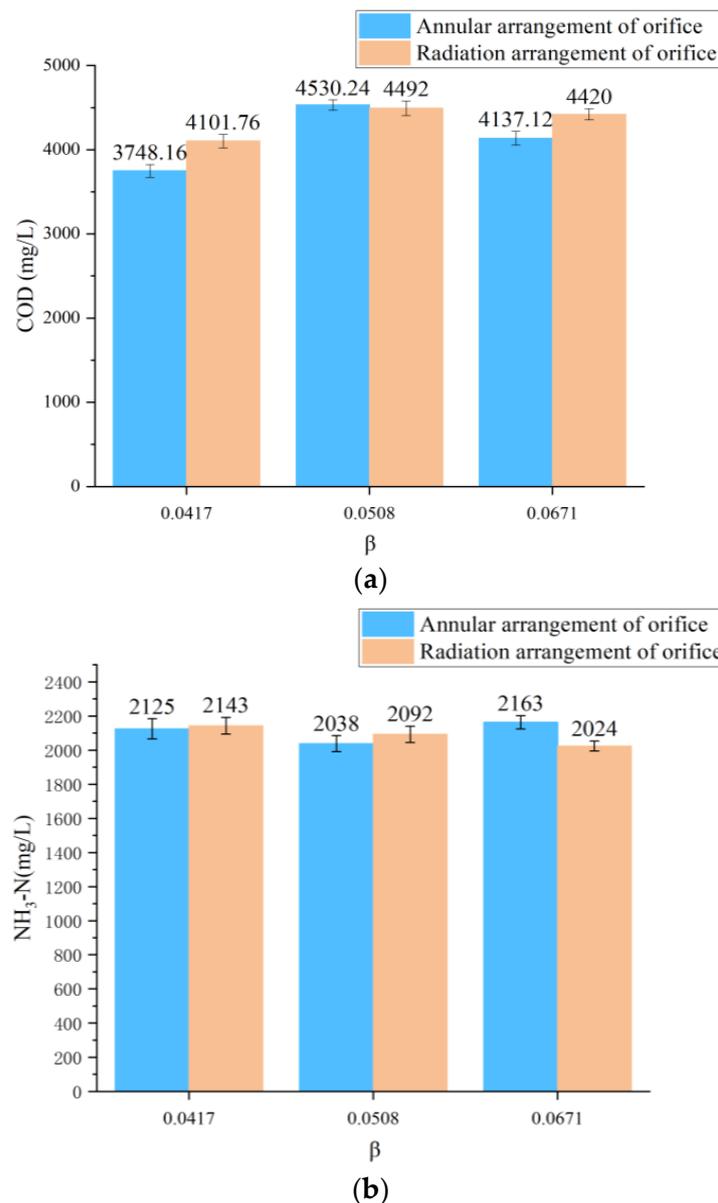


Figure 5. The effect of β and arrangement of orifices on the removal of (a) COD and (b) NH₃-N. The reaction time was 60 min, and pH = 7.18.

3.2. The Influence of Reaction Time on the LL Treatment

In order to investigate the effect of the reaction time on the pretreatment of LL, the experiments were carried out by using plate 4 ($\beta = 0.0671$), plate 5 ($\beta = 0.0508$), and plate 6 ($\beta = 0.0417$) with an annular orifice arrangement. Figure 6a showed the change in COD with time, and Figure 6b showed the change in NH₃-N with time.

From Figure 6a, when $\beta = 0.0417$, the COD continued to decrease with the increase in reaction time and dropped to 3748.16 mg/L at 60 min. When $\beta = 0.0508$, the COD decreased rapidly to 3960.32 mg/L within the first 20 min, but it increased significantly from 20 min to 40 min. After 40 min, COD stabilized at 4530.24 mg/L. When $\beta = 0.0671$, the COD increased slightly above the initial value at the beginning of the reaction, then decreased slowly, and also decreased steadily to 4134.12 mg/L at 60 min. The phenomenon of rising COD is similar to that in Martin Petkovšek's study [39].

From Figure 6b, the concentration of NH₃-N changed slightly with time. When $\beta = 0.0417$, the removal rate of NH₃-N was higher, reaching 14.6%. When $\beta = 0.0508$ and $\beta = 0.0671$, the removal rate of NH₃-N did not exceed 10%.

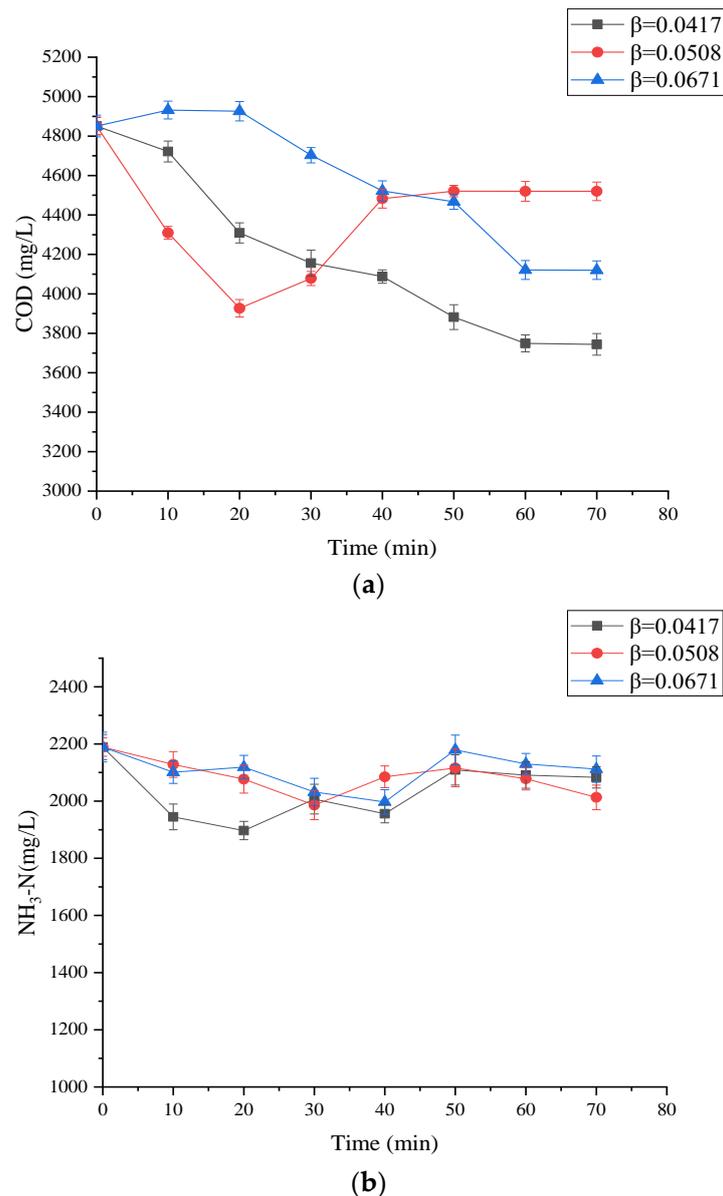


Figure 6. The changes of (a) COD and (b) NH₃-N with reaction time. Orifice plates with an annular arrangement were equipped, and the pH value was 7.18.

3.3. Changes in the Biodegradability of LL

The biodegradability indexes of LL pretreated by HC are listed in Table 4. After LL was pretreated by orifice plate 6, we found that the value of BOD₅/COD increased. The value of BOD₅ increased from 535 mg/L to 648 mg/L. The value of BOD₅/COD increased from 0.110 to 0.173, with a significant growth of 57.27%. By contrast, the removal rate of COD was low, at only 22.63%.

Table 4. The results of a 60 min pretreatment by using orifice plate 6 ($\beta = 0.0417$, annular orifice arrangement) under the basic pH.

Process	COD	BOD ₅	BOD ₅ /COD	NH ₃ -N
Before HC treatment (mg/L)	4844.20	535	0.110	2178.82
After HC treatment (mg/L)	3748.16	648	0.173	2129.10
Changes	22.63% reduction	21.12% increase	57.27% increase	2.28% increase

3.4. Energy Efficiency Evaluation

In this work, the volume of LL was 50 L, and the efficiency of the centrifugal pump with a power of 2.2 kW was 84%. The power and flow of the pump could not be changed, so the power dissipation per unit volume was constant (36.96 W/L). At a 60 min pretreatment with an inlet pressure of 501,325 Pa and the original pH (7.18) of the effluent, the COD reduction is showed in Table 5. The energy efficiency was calculated by Formula (7), and orifice 6 had the best effect on COD removal (22.63%) and the highest energy efficiency (8.24×10^{-3} mg COD/J).

Table 5. The energy efficiency for different orifice plates with a 60 min pretreatment.

Orifice Plate Number	COD Reduction (mg/L)	COD Removal Rate (%)	Energy Efficiency $\times 10^{-3}$ mg COD/J
1	424.20	8.76	3.19
2	352.20	7.27	2.65
3	742.44	15.33	5.58
4	707.08	14.60	5.31
5	313.96	6.48	2.49
6	1096.04	22.63	8.24

4. Discussion

For the effect of the arrangement of orifices on COD removal, according to hydrokinetics, when a fluid flows through the pipe, whether a laminar or turbulent fluid, the flow velocity distribution of the fluid section has a maximum at the center of the pipe, and the flow velocity decreases gradually from the center of the pipe towards the walls of the pipe. Since the holes of the annular orifice arrangement were more evenly distributed in the center of the plate, the resistance of the fluid passing through was greatly reduced and a higher energy efficiency under the same p_1 was obtained, which enhanced the HC [27]. Therefore, the orifice plates with an annular orifice arrangement had a better effect of removing the COD. Compared with the orifice plates with an annular orifice arrangement, the orifice plates with a radiation orifice arrangement increased the resistance when the fluid passed through, reduced the efficiency of the energy conversion, and reduced the HC intensity, which was not conducive to the removal of the COD [40].

For the plates with the same arrangement of orifices, the removal of the COD of the orifice plate with $\beta = 0.0417$ had a better effect than that of the orifice plate with $\beta = 0.0508$ and $\beta = 0.0671$. This is because the turbulent kinetic energy generated by a fluid flowing through orifice plates with different β 's was different. An appropriate β would increase the turbulent region and zonal flows downstream of the orifice plate to some extent, thus HC would be enhanced. However, under the same p_1 , as β increased continuously, numerous HC microbubbles coalesced and combined with each other and formed a cavity cloud. The cavity cloud cushioned the collapse of HC microbubbles and decreased the intensity of HC [41].

Some studies used HC to treat LL and found that $\text{NH}_3\text{-N}$ in LL was blown off due to the high-speed-flow fluid, resulting in a reduction in $\text{NH}_3\text{-N}$ content [42]. This study was carried out under a basic pH (7.18) condition of effluent, so $\text{NH}_3\text{-N}$ in LL existed as NH_4^+ ion, which could not be blown off from the LL. Therefore, the $\text{NH}_3\text{-N}$ content was almost constant. The small reduction in $\text{NH}_3\text{-N}$ could be attributed to the fact that a little NH_4^+ was oxidized to $\text{NO}_2^+\text{-N}$ and $\text{NO}_3^+\text{-N}$.

Considering the above-mentioned, it can be concluded that our HC device was almost ineffective at removing $\text{NH}_3\text{-N}$ at the basic pH of the effluent. For COD removal, the orifice plates with an annular orifice arrangement were better than those with a radiation orifice arrangement, and the plate with $\beta = 0.0417$ was the best for COD removal (22.63%).

The macromolecular organic substances in LL were decomposed into lower-molecular-weight organic matters, and the organic ring compounds were cleaved into chain compounds because of the high mechanical shear force, pyrolysis, and free radical action [43]. According to the principle of COD detection, most organic compounds can be oxidized by

acid potassium dichromate. When Ag_2SO_4 is added as a catalyst, straight-chain aliphatic compounds can be oxidized entirely, while aromatic organic compounds are harder to oxidize, and pyridine can also be degraded during this step. Volatile straight-chain aliphatic compounds (benzene and other organic compounds) can exist in the vapor phase and not directly contact with the oxidant liquid, so the oxidation effect is weakened [44]. Therefore, the rise of COD can be explained as follows: LL contains a variety of complex organic compounds, especially humus and aromatic substances with benzene ring. After the HC process, these complex organic compounds were oxidized into chain-hydrocarbon secondary molecules, which were easier to oxidize by potassium dichromate, increasing in this way the level of COD. The decline in COD was due to the following: On the one hand, compounds which are more easily oxidized were oxidized firstly after just a few passes through the HC zone, which led to a reduction in the COD of the effluent [45]. On the other hand, with the prolonging of the HC pretreatment time, these secondary organics were further mineralized, leading to the decline in COD. In the process, we preliminarily speculated that the decomposition of refractory organic substances and mineralization of readily oxidizable compounds occurred simultaneously. When the degree of mineralization was higher than that of the decomposition, the COD decreased, and vice versa. However, the specific substances which caused the increase in COD still need to be further tested. Plate 6 ($\beta = 0.0417$, annular orifice arrangement) reduced the COD continuously, which proved that plate 6 was the best for the pretreatment.

The decline in $\text{NH}_3\text{-N}$ with time could be attributed to air stripping and oxidation, and its rise could be attributed to the fact that the amino groups attached to the organic matters were oxidized to ammonium salts, which existed in the effluent as ammonium ions [46].

The BOD_5/COD of LL showed the sensitivity of organic pollutants degraded by microorganisms through biochemical reactions. The larger the value, the better the effects of biodegradation methods on the effluent treatment [36,45]. Although the removal rate of COD was low (only 22.63%), HC destroyed and detoxified the organics, and improved the biodegradability of the LL.

The efficiency of the degradation of organic pollutants present in the LL by HC was investigated in terms of changes in BOD_5 and BOD_5/COD . In Table 4, the results showed that many effects of the HC process could destroy the molecular structures of organic matters and convert non-biodegradable organic pollutants into different forms that are more biodegradable, including shockwaves, shear forces, thermal decomposition, and $\bullet\text{OH}$ radicals. In addition to obtaining a more favorable biodegradability, this pretreatment resulted in the partial reduction in total contaminant load. The schematic diagram of the HC pretreatment principle for LL is shown in Figure 7.

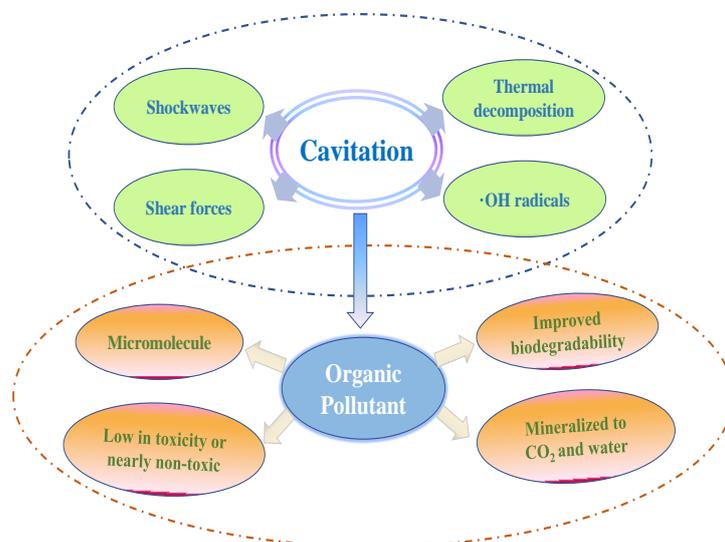


Figure 7. Schematic diagram of HC-pretreated LL.

5. Conclusions

The leachate generated from landfill can cause significant harm to water bodies, the atmosphere, and human health, and must be effectively treated before being discharged. A biochemical method is an effective method for treating LL, but the composition of LL changes under various factors such as time and temperature, which poses a huge challenge to the microbial activity in biochemical treatment and seriously affects the treatment efficiency of LL. Therefore, it is necessary to improve the biodegradability of LL through a pretreatment in order to improve the treatment effect of biochemical methods. Physicochemical methods are commonly used for the LL pretreatment, which requires additives.

In this work, HC was selected as the physicochemical method due to its low cost, low energy consumption, and the lack of need for chemical additives. It was introduced into the pretreatment of LL by orifice plates as the generators. The impact of the HC pretreatment was discussed and evaluated on the removal of pollutants in LL under different conditions in this work. Based on the results obtained, the following conclusions were drawn.

Under the conditions that the inlet pressure was 0.4 MPa and the original pH of effluent was 7.18, the orifice plate with an annular orifice arrangement was better than that with a radiation orifice arrangement for LL, and when $\beta = 0.0417$, the optimal COD removal was 22.63%. Meanwhile, the biodegradability of LL was significantly improved with BOD₅/COD increasing by 57.27%. As a result, HC could significantly improve the LL quality and decompose refractory organic compounds and non-biodegradable organic compounds in LL without adding any chemicals.

With regard to energy efficiency, the application of orifice plate 6 appeared to be more profitable due to a significantly higher energy efficiency of 8.24×10^{-3} mg COD/J. However, the HC device was almost ineffective at removing NH₃-N at the basic pH of the effluent. After a further removal of NH₃-N, the treated LL may be used as an additional organic carbon resource for the biological treatment of other wastewater, which could not only save resources but also reduce the cost of water treatment.

This work has preliminarily demonstrated that HC is an effective pretreatment technology for the removal of organic pollutants in LL. It can significantly improve the biodegradability of LL, which is beneficial after a biochemical treatment. Moreover, HC requires no additional chemicals and is cost-effective, easily implementable in industrial settings, and environmentally friendly. The study provided an application basis for the efficient treatment of landfill leachate.

Although HC can effectively remove organic pollutants due to its special oxidation effect, the detailed process of the reaction of pollutants in LL in an HC system needs to be further examined. In future work, it also needs to be combined with other physicochemical technologies to improve the removal rates of inorganic pollutants such as NH₃-N and nitrates.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/pr11103014/s1>. Text S1: The calculation of COD value; Table S1: The components and functions of the HC device.

Author Contributions: Project administration, Y.Q.; writing—original draft preparation, K.W.; analysis, C.W.; writing—review and editing, Y.J. and X.F.; funding, J.X.; methodology, M.J. and R.J. All authors have read and agreed to the published version of the manuscript.

Funding: This work was funded by Tibet University Central Financial Support Special Funds for Local Colleges and Universities, 2023 & 2024, from Finance Department of Tibet; the Science and Technology Project of Tibet Autonomous Region Supported by the Central Government, grant number XZ202202YD0027C, from Science and Technology Department of Tibet; the Shanxi Province Graduate Student Innovation Project, grant number 2022Y589, from Shanxi Provincial Education Department.

Data Availability Statement: The additional data can be found in Supplementary Materials.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Wu, C.; Chen, W.; Gu, Z.; Li, Q. A review of the characteristics of Fenton and ozonation systems in landfill leachate treatment. *Sci. Total Environ.* **2020**, *762*, 143131. [[CrossRef](#)]
2. Teng, C.; Zhou, K.; Peng, C.; Chen, W. Characterization and treatment of landfill leachate: A review. *Water Res.* **2021**, *203*, 117525. [[CrossRef](#)] [[PubMed](#)]
3. Tripathy, B.K.; Kumar, M. Suitability of Microwave and Microwave-coupled Systems for Landfill Leachate Treatment: An Overview. *J. Environ. Chem. Eng.* **2017**, *5*, 6165–6178. [[CrossRef](#)]
4. GB 16889-2008; Standard for Pollution Control on the Landfill Site of Municipal Solid Waste. General Office of the Ministry of Ecology and Environment, National Standard of the People's Republic of China: Beijing, China, 2008.
5. Mojiri, A.; Zhou, J.L.; Ratnaweera, H.; Ohashi, A.; Ozaki, N.; Kindaichi, T.; Asakura, H. Treatment of landfill leachate with different techniques: An overview. *Water Reuse* **2020**, *11*, 66–96. [[CrossRef](#)]
6. Lu, W.; Lei, S.; Chen, N.; Feng, C. Research on two-step advanced treatment of old landfill leachate by sequential electrochemical peroxidation-electro-Fenton process. *Chem. Eng. J.* **2022**, *451*, 138746. [[CrossRef](#)]
7. Belouhova, M.; Yotinov, I.; Schneider, I.; Dinova, N.; Todorova, Y.; Lyubomirova, V.; Mihaylova, V.; Daskalova, E.; Lincheva, S.; Topalova, Y. Purposely Development of the Adaptive Potential of Activated Sludge from Municipal Wastewater Treatment Plant Focused on the Treatment of Landfill Leachate. *Processes* **2022**, *10*, 460. [[CrossRef](#)]
8. Zhang, F.; Peng, Y.; Liu, Z.; Liu, Y.; Zhao, L. Development of a novel partial nitrification, fermentation-based double denitrification bioprocess (PN-F-Double/DN) to simultaneous treatment of mature landfill leachate and waste activated sludge. *Water Res.* **2021**, *203*, 117540. [[CrossRef](#)]
9. Hube, S.; Eskafi, M.; Hrafnkelsdóttir, K.F.; Bjarnadóttir, B.; Bjarnadóttir, M.Á.; Axelsdóttir, S.; Wu, B. Direct membrane filtration for wastewater treatment and resource recovery: A review. *Sci. Total Environ.* **2020**, *710*, 136375. [[CrossRef](#)]
10. Brennan, R.B.; Clifford, E.; Devroedt, C.; Morrison, L.; Healy, M.G. Treatment of landfill leachate in municipal wastewater treatment plants and impacts on effluent ammonium concentrations. *J. Environ. Manag.* **2017**, *188*, 64–72. [[CrossRef](#)]
11. Chin, P.M.; Naim, A.N.; Suja, F.; Ahmad Usul, M.F. Impact of Effluent from the Leachate Treatment Plant of Taman Beringin Solid Waste Transfer Station on the Quality of Jinjang River. *Processes* **2020**, *8*, 1553. [[CrossRef](#)]
12. Hu, Y.; Gu, Z.; He, J.; Li, Q. Novel strategy for controlling colloidal instability during the flocculation pretreatment of landfill leachate. *Chemosphere* **2022**, *287*, 132051. [[CrossRef](#)] [[PubMed](#)]
13. Kim, M.; Mo, K.; Kim, M.; Cui, F. Development of a Novel Hydrodynamic Sequencing Batch Reactor for Landfill Leachate Treatment by Shortcut Biological Nitrogen Removal. *Processes* **2023**, *11*, 1868. [[CrossRef](#)]
14. Shadi, A.M.H.; Kamaruddin, M.A.; Niza, N.M.; Omar, F.M.; Hossain, M.S. Facile isotherms of iron oxide nanoparticles for the effectively removing organic and inorganic pollutants from landfill leachate: Isotherms, kinetics, and thermodynamics modelling. *J. Environ. Chem. Eng.* **2022**, *10*, 107753. [[CrossRef](#)]
15. Chen, W.; Gu, Z.; Ran, G.; Li, Q. Application of membrane separation technology in the treatment of leachate in China: A review. *Waste Manag.* **2021**, *121*, 127–140. [[CrossRef](#)]
16. Kamal, A.; Makhatova, A.; Yergali, B.; Baidullayeva, A.; Satayeva, A.; Kim, J.; Inglezakis, V.J.; Pouloupoulos, S.G.; Arkhangelsky, E. Biological Treatment, Advanced oxidation and membrane separation for landfill leachate treatment: A review. *Sustainability* **2022**, *14*, 14427. [[CrossRef](#)]
17. Ren, T.; Zhang, X.; Chen, S.; Huang, X.; Zhang, X. Hydrogen peroxide and peroxydisulfate intensifying Fe-doped NiC–Al₂O₃–framework-based catalytic ozonation for advanced treatment of landfill leachate: Performance and mechanisms. *Sci. Total Environ.* **2022**, *843*, 156904. [[CrossRef](#)]
18. Roudi, A.M.; Salem, S.; Abedini, M.; Maslahati, A.; Imran, M. Response surface methodology (RSM)-based prediction and optimization of the Fenton process in landfill leachate decolorization. *Processes* **2021**, *9*, 2284. [[CrossRef](#)]
19. Hussain, S.; Aneggi, E.; Comuzzi, C. Abatement of the ecotoxicological risk of landfill leachate by heterogeneous Fenton-like oxidation. *Environ. Sci. Pollut. Res.* **2023**, *30*, 21025–21032. [[CrossRef](#)] [[PubMed](#)]
20. Parthenidis, P.; Evgenidou, E.; Lambropoulou, D. Wet and supercritical oxidation for landfill leachate treatment: A short review. *J. Environ. Chem. Eng.* **2022**, *10*, 107837. [[CrossRef](#)]
21. Jegadeesan, C.; Somanathan, A.; Jeyakumar, R.B. Sanitary landfill leachate treatment by aerated electrochemical Fenton process. *J. Environ. Manag.* **2023**, *337*, 117698. [[CrossRef](#)] [[PubMed](#)]
22. Montusiewicz, A.; Bis, M.; Pasieczna-Patkowska, S.; Majerek, D. Mature landfill leachate utilization using a cost-effective hybrid method. *Waste Manag.* **2018**, *76*, 652–662. [[CrossRef](#)] [[PubMed](#)]
23. Kong, W.-D. Study on the Degradation of Phenol by Hydrodynamic Cavitation and Chlorine Dioxide. Master's Thesis, North University of China, Taiyuan, China, 2017.
24. Wang, B.; Su, H.; Zhang, B. Hydrodynamic cavitation as a promising route for wastewater treatment: A review. *Chem. Eng. J.* **2021**, *412*, 128685. [[CrossRef](#)]
25. Bis, M.; Montusiewicz, A.; Ozonek, J.; Pasieczna-Patkowska, S. Application of hydrodynamic cavitation to improve the biodegradability of mature landfill leachate. *Ultrason. Sonochem.* **2015**, *26*, 378–387. [[CrossRef](#)]
26. Bagal, M.V.; Gogate, P.R. Wastewater treatment using hybrid treatment schemes based on cavitation and Fenton chemistry: A review. *Ultrason. Sonochem.* **2014**, *21*, 1–14. [[CrossRef](#)]

27. Gagol, M.; Przyjazny, A.; Boczkaj, G. Wastewater treatment by means of advanced oxidation processes based on cavitation: A Review. *Chem. Eng. J.* **2018**, *338*, 599–627. [[CrossRef](#)]
28. Deng, Y.; Chen, N.; Hu, W.; Wang, H.; Kuang, P.; Chen, F.; Feng, C. Treatment of old landfill leachate by persulfate enhanced electro-coagulation system: Improving organic matters removal and precipitates settling performance. *Chem. Eng. J.* **2021**, *424*, 130262. [[CrossRef](#)]
29. Shi, S.-T. Study on Methyl Orange Degradation by Hydrodynamic Cavitation with Chlorine Dioxide. Master's Thesis, North University of China, Taiyuan, China, 2016.
30. Sunita, R.-J.; Badve, M.P.; Pinjari, D.V.; Saini, D.D.R.; Sonawane, S.H.; Pandit, A.B. Treatment of the pesticide industry effluent using hydrodynamic cavitation and its combination with process intensifying additives (H₂O₂ and ozone). *Chem. Eng. J.* **2016**, *259*, 326–335.
31. Cai, M.-Q.; Su, J.; Zhu, Y.-Z.; Wei, X.-Q.; Jin, M.-C.; Zhang, H.-J.; Dong, C.-Y.; Wei, Z.-S. Decolorization of azo dyes orange g using hydrodynamic cavitation coupled with heterogeneous Fenton process. *Ultrason. Sonochem.* **2016**, *28*, 302–310. [[CrossRef](#)]
32. Gore, M.M.; Saharan, V.K.; Pinjari, D.V.; Chavan, P.V.; Pandit, A.B. Degradation of reactive orange 4 dye using hydrodynamic cavitation based hybrid techniques. *Ultrason. Sonochem.* **2014**, *21*, 1075–1082. [[CrossRef](#)]
33. Pradhan, A.A.; Gogate, P.R. Removal of p-nitrophenol using hydrodynamic cavitation and Fenton chemistry at pilot scale operation. *Chem. Eng. J.* **2010**, *156*, 77–82. [[CrossRef](#)]
34. Barik, A.J.; Gogate, P.R. Degradation of 4-chloro 2-aminophenol using a novel combined process based on hydrodynamic cavitation, UV photolysis and ozone. *Ultrason. Sonochem.* **2015**, *30*, 70–78. [[CrossRef](#)]
35. Wang, C.-Q.; Jin, R.-Y.; He, Z.-D.; Qiao, Y.-N.; Wang, Y.; Wang, K.; Lu, Y.-R.; Wang, X.-J.; Liu, D.-D. A new water treatment technology for degradation of B[a]A by hydrodynamic cavitation and chlorine dioxide oxidation. *Ultrason. Sonochem.* **2020**, *61*, 104834. [[CrossRef](#)] [[PubMed](#)]
36. Fedorov, K.; Dinesh, K.; Sun, X.; Soltani, R.D.C.; Wang, Z.; Sonawane, S.; Boczkaj, G. Synergistic effects of hybrid advanced oxidation processes (AOPs) based on hydrodynamic cavitation phenomenon—A review. *Chem. Eng. J.* **2022**, *432*, 134191. [[CrossRef](#)]
37. Yang, S.-J. The Study on the Mechanism of Breaking Methyl Orange and Benzo[a]pyrene by ClO₂ Enhanced with Hydrodynamic Cavitation. Ph.D. Thesis, North University of China, Taiyuan, China, 2018.
38. Soyama, H.; Hoshino, J. Enhancing the aggressive intensity of hydrodynamic cavitation through a venturi tube by increasing the pressure in the region where the bubbles collapse. *AIP Adv.* **2016**, *6*, 045113. [[CrossRef](#)]
39. Petkovšek, M.; Mlakar, M.; Levstek, M.; Strazar, M.; Širok, B.; Dular, M. A novel rotation generator of hydrodynamic cavitation for waste-activated sludge disintegration. *Ultrason. Sonochem.* **2015**, *26*, 408–414. [[CrossRef](#)]
40. Kovačič, A.; Škufca, D.; Zupanc, M.; Gostiša, J.; Bizjan, B.; Krištofelc, N.; Dolenc, M.S.; Heath, E. The removal of bisphenols and other contaminants of emerging concern by hydrodynamic cavitation: From lab-scale to pilot-scale. *Sci. Total Environ.* **2020**, *743*, 140724. [[CrossRef](#)]
41. Wang, K.; Jin, R.; Qiao, Y.; He, Z.; Wang, X.; Wang, C.; Lu, Y. 2,4,6-Triamino-1,3,5-Trinitrobenzene explosive wastewater treatment by hydrodynamic cavitation combined with chlorine dioxide. *Propellants Explos. Pyrotech.* **2019**, *45*, 1243–1249. [[CrossRef](#)]
42. Li, H.; Li, H.; Huang, X.; Han, Q.; Yuan, Y.; Qi, B. Numerical and experimental study on the internal flow of the venturi injector. *Processes* **2020**, *8*, 64. [[CrossRef](#)]
43. Scandelai, A.P.J.; Rigobello, E.S.; Oliveira, B.L.C.D.; Tavares, C.R.G. Identification of organic compounds in landfill leachate treated by advanced oxidation processes. *Environ. Sci. Technol.* **2017**, *27*, 1–51. [[CrossRef](#)]
44. Banch, T.J.H.; Hanafiah, M.M.; Alkarkhi, A.F.M.; Amr, S.S.A.; Nizam, N.U.M. Evaluation of different treatment processes for landfill leachate using low-cost agro-industrial materials. *Processes* **2020**, *8*, 111. [[CrossRef](#)]
45. Boczkaj, G.; Gagol, M.; Klein, M.; Przyjazny, A. Effective method of treatment of effluents from production of bitumens under basic pH conditions using hydrodynamic cavitation aided by external oxidants. *Ultrason. Sonochem.* **2018**, *40*, 969–979. [[CrossRef](#)] [[PubMed](#)]
46. Tejera, J.; Gascó, A.; Hermosilla, D.; Alonso-Gomez, V.; Negro, C.; Blanco, Á. UVA-LED technology's treatment efficiency and cost in a competitive trial applied to the photo-Fenton treatment of landfill leachate. *Processes* **2021**, *9*, 1026. [[CrossRef](#)]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.