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Tertiary treatment of real abattoir wastewater using combined acoustic cavitation and ozonation

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A B S T R A C T

This work reports the influence of ultrasound alone and combined with ozone for the treatment of real abattoir wastewater. Three different frequencies were studied (44, 300 and 1000 kHz) at an applied power of 40 W. The injected ozone dose was fixed at 71 mg/L and the treatment time varied from 1 to 60 min. Using ultrasound alone, 300 kHz was the only frequency showing a reduction in chemical oxygen demand (COD, 18% reduction) and biological oxygen demand (BOD, 50% reduction), while no diminution in microbial content was measured for any of the frequencies studied. Combining ultrasound with ozone, on the contrary, led to a significant decrease in COD (44%) and BOD (78%) removal for the three frequencies under study. A complete inactivation of total coliforms (TC) was obtained, as well as a final value of 99 CFU/mL in total viable counts (TVC, 5 log reduction). That is, the ozonation-sonication combined system was the only treatment method (compared to sonication and ozonation alone) reaching direct discharge limits, as well as meeting drinking water standards for microbial disinfection (TC and TVC).

1. Introduction

Water shortage is increasing worldwide and becoming a concern not only for the environment, but also for the normal functioning of our society. To meet certain water discharge or reuse regulations, wastewater must be treated using a combination of physical, chemical and biological processes. Secondary treatments consist of biological methods that can be aerobic or anaerobic. Anaerobic systems are cheaper and easier to operate but less efficient at removing organic matter (BOD) [1–3]. The last step, the so-called tertiary treatment which includes microbial disinfection, is also used as a polishing step for organic matter and nutrient removal. Chemicals such as chlorine, chlorine dioxide, chloramines and hydrogen peroxide (H_2O_2) are currently used for tertiary treatment, as well as advanced oxidation processes [4,5].

Advanced oxidation processes (AOPs) are those processes that generate OH radicals ($OH^{\cdot}$) in sufficient quantity to improve water quality by removing organic and inorganic pollutants [4,6]. After fluorine (3.03 V), the $OH^{\cdot}$ (2.80 V) is the strongest known oxidant and capable of completely mineralising most organic matter [7]. Different methods fall within the name of AOPs, generating in situ $OH^{\cdot}$ and further reacting to produce other reactive agents such as H_2O_2 and super oxide (O_2^{-}). AOPs can be divided into ozone (O_3), photocatalytic, ultrasonic and Fenton processes, while the combination of multiple AOPs is commonly used for synergistic effects [4,7]. There has been an increasing interest in research and implementation in both municipal wastewater plants and industrial facilities for the application of AOPs, O_3 and ultrasound being two of the studied subjects [8–13].

During ozonation of wastewater, oxidation can occur through direct reaction involving molecular O_3 and via an indirect pathway through $OH^{\cdot}$. O_3 is unstable in water and selectively attacks organic compounds. $OH^{\cdot}$, on the contrary, react non-selectively with many water constituents [14–18]. By oxidation of the specific cell wall components and subsequent DNA damage by O_3 and $OH^{\cdot}$, O_3 kills bacteria and disinfects water [18,19]. O_3 can also increase the biodegradability of organic pollutants converting recalcitrant organic matter into more readily biodegradable compounds species [9,20,21].

Ultrasound is an acoustic (mechanical) wave whose frequency is above the upper audible limit of an average person, usually 20 kHz. Pre-existing bubble nuclei act as a source for cavitation. When the ultrasound pressure is above the threshold for cavitation, these bubble nuclei grow and coalesce, and once they reach a resonance size, the bubbles undergo violent inertial collapse [22–24]. During the inertial collapse, the bubble core can reach temperatures of 10,000 K and pressures of up to 1000 atm [22]. Due to the high temperatures reached upon bubble collapse, water vapour inside the bubble dissociates to form reactive radical agents such as $OH^{\cdot}$ (sonochemistry), as well as the emission of light (sonoluminescence) [22,23]. Along with chemical

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effects, mechanical effects can also occur via formation of localised microjets (with velocities of up to 120 m/s), formed when bubbles collapse asymmetrically near a surface. This can generate extreme shear forces that can contribute to water treatment by tearing apart micro-organisms and disinfecting water [24].

The type and combination of processes used in water treatment is governed by the quality of wastewater and regulatory limits [25]. Standards for direct discharge from urban wastewater treatment plants within the European Union (EU) are regulated by the 91/271/EEC Council Directive and dictates the maximum acceptable pollutant levels as follows: Chemical Oxygen Demand (COD), 125 mg O_2/L; Biological Oxygen Demand (BOD), 25 mg O_2/L; and Total Suspended Solids (TSS), 35 mg/L [26]. No regulation at EU level has been found on water reuse for agriculture irrigation, although the implementation of a common water reuse legislation is under discussion [27].

In regard to wastewater generation, current industrialised livestock agriculture generates more polluted (BOD) wastewaters in comparison to domestic sewage [1,28] and is being characterised by a high organic content and highly variable quality [29,30]. Additionally, the production of animal products is increasing yearly [31] leading to the increase in the generation of this type of wastewater [29,32–36]. Therefore, efficient and reliable wastewater treatment methods are needed to ensure the wastewater quality meets regulations before discharge.

To the best of the authors' knowledge, there are currently limited literature reports available on the potential of combined biological-AOPs on real abattoir wastewater. Few research articles were found on the treatment of abattoir wastewater via O_3 [34,37–40], while only two reports [37,39] used a combined biological-ozonation treatment. Alfonso-Muniozguren et al. [37] reported a reduction in COD by 93% (128 mg O_2/L) by an activated sludge-filtration-ozonation treatment, while Proesmans et al. [39] obtained a 66% reduction in COD (30 mg O_2/L) for the ozonation step. Although no published reports were found on the use of ultrasound alone for real abattoir wastewater treatment, a study by Abdurahman et al. [41] on the treatment of slaughterhouse wastewater using ultrasound assisted-membrane anaerobic system reported a 96.5% COD reduction. In addition, the destructive effect of ultrasound have shown to lower TSS in real wastewater [42]. Considering the above and the nature of the type of wastewater under study, this article looks into the further treatment of abattoir wastewater as polishing step using O_3 and ultrasound. This combined process could serve as an alternative treatment method with a potential for a higher efficiency and reliability.

2. Materials and methods

2.1. Abattoir wastewater

Abattoir wastewater samples were collected from an abattoir once per week over a six-month period and stored at 4 °C prior to use. Besides animal residues such as blood, fat and manure, the wastewater also contained onsite sewage, as well as traces of floor cleaning products. After an onsite pre-treatment via a grit removal system, followed by coagulation-flocculation and dissolved air flotation, the wastewater was collected to be treated using a lab scale activated sludge process (ASP). This onsite pre-treated and biologically treated effluent will be referred to as "treated wastewater". Physicochemical characteristics of the treated wastewater are shown in Table 1.

2.2. Experimental setup

The setup used to establish different treatment combinations such as activated sludge-ozonation, activated sludge-sonication and activated sludge-ozonation-sonication systems, is shown in Fig. 1.

2.2.1. Activated sludge reactor

Abattoir wastewater samples were fed at a rate of 2 L/day into an activated sludge reactor (10 L reactor) in a semi-batch mode and with a solid (sludge) retention time of 13 days and a hydraulic retention time of 24 h. The aeration (5 L/min) in the ASP was stopped for 30 min to allow the sludge to settle before removing the bio-treated effluent (from the top of the reactor), as well as the settled sludge. 400 mL of the effluent was used during the experimental study.

Table 1
Characteristics of treated wastewater. Sample variability from eight different samples shown as standard deviation.

Parameters (units)	Treated wastewater
COD (mg O_2/L)	242 ± 48
BOD (mg O_2/L)	53 ± 21
TSS (mg/L)	70 ± 23
TC (CFU/mL)	$4.1 \times 10^3 \pm 4.8 \times 10^3$
TVC (CFU/mL)	$4.1 \times 10^7 \pm 2.2 \times 10^7$
pH	7.7 ± 0.2

2.2.2. Ozonation

For the ozonation experiments, the treated wastewater was exposed to a fixed O_3 dose of 71 ± 17 mg/L (injected O_3 dose produced by an Okamizu Food Detoxifier V.2 at a rate of 2.3 L air/min), which was injected into the sample via an air stone diffuser placed at the bottom of a jacketed cylindrical glass vessel (15 cm height and 2.5 cm inner diameter). O_3 was injected from 1 to 60 min. The exhaust O_3 leaving the reaction vessel was measured with Aeroqual S-200 O_3 meter and trapped in two subsequent 1 L bottles of 0.1 M potassium iodide (KI) solution. The KI solution bottles were used to prevent human exposure to O_3, as well as to avoid O_3 to be released into the atmosphere.

2.2.3. Sonication

The same jacketed cylindrical glass vessel used for ozonation was used to run the sonication and the combined ozonation-sonication experiments. Three ultrasound transducers (Honda Electronics Co. LTD) with resonance frequencies of 44, 300 and 1000 kHz were used in this study. The selected transducer was fixed at the bottom of the glass vessel (Fig. 1) and driven at its resonance frequency by a power amplifier (T&C Power Conversion AG1006) coupled with an impedance matching unit. The same applied power of 40 W were used for all three frequencies and the calorimetric powers measured at this applied power were 17.1 W for 44 kHz, 34.4 W for 300 kHz, and 34.2 W for 1000 kHz.

During the combined ozonation-sonication experiments, O_3 was injected at the same dosage and rate as mentioned above. The temperature of the solution was kept at 16 ± 3 °C for all the experiments with a temperature control system (Julabo FL300) set at 10 °C and varying treatment time from 1 to 60 min. To avoid airborne contamination, all the experiments and subsequent sample analyses were run within a fume cabinet.

2.3. Analytical methods

Concentration of organic matter was measured as 5-day BOD (standard method [SM] 5210B) and as COD (SM 5220 D), as well as TSS (SM 2540 D). Additionally, TC (SM 9222B) and TVC (SM 9215C) were analysed before and after ozonation and sonication to evaluate the disinfection efficiency of the processes [43]. Temperature and pH (SM 4500H + B) were also monitored during the experiments. For $OH^{\cdot}$ production analysis, 400 mL of 0.1 M KI were sonicated and/or ozonated following a KI dosimetry method explained elsewhere [44,45]. Analyses for each of the measured parameters were repeated at least twice and the arithmetic mean of at least three samples is reported.

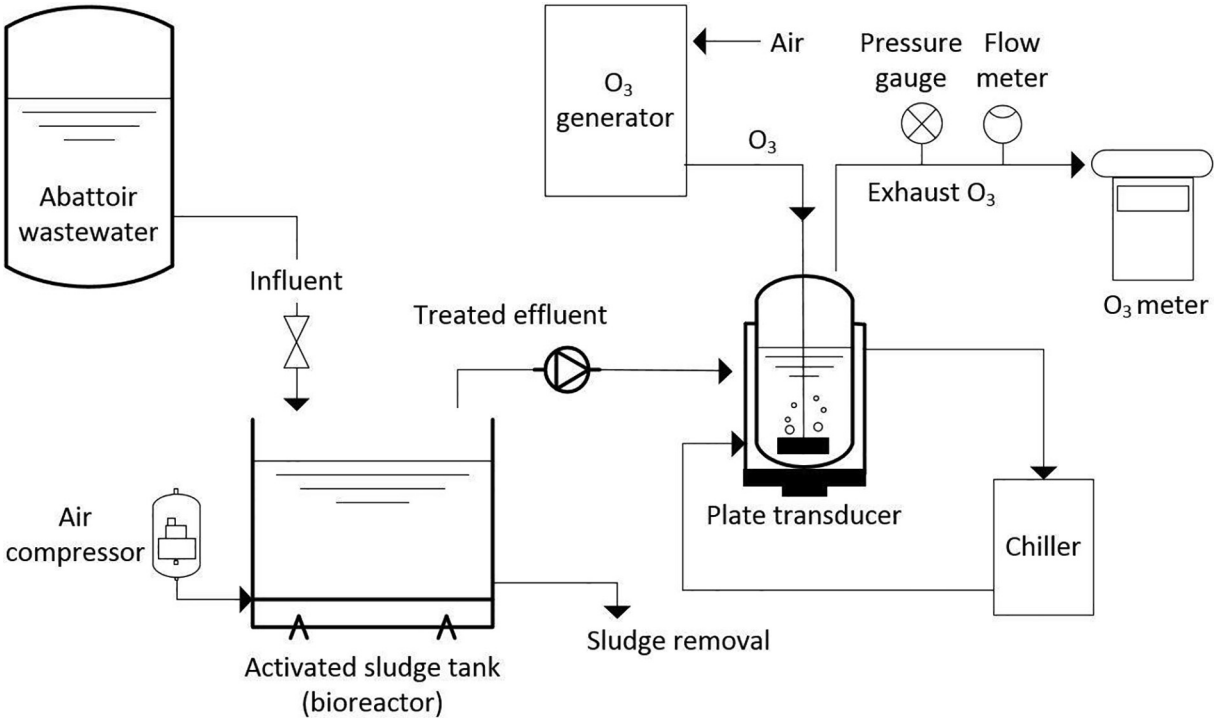

Fig. 1. A schematic diagram of the experimental setup: activated sludge-ozonation system (ultrasonic plate transducer off), activated sludge-sonication system (ozonation off) and activated sludge-ozonation-sonication system (ozonation and ultrasonic plate transducer on).

3. Results and discussion

3.1. OH radical yield

The rate of $OH^{\cdot}$ production is important for understanding the effect of sonication, ozonation and combined ozonation-sonication treatment has on the degradation of organic matter. The common method of evaluating the amount of $OH^{\cdot}$ yield is via KI dosimetry, where the concentration of I_3^- can be assumed to be proportional to the concentration of $OH^{\cdot}$ (the production of $OH^{\cdot}$ is believed to be the dominant reaction, although other oxidising agents could be measured, being the production of oxidants hindered by the presence of air) [46]. Fig. 2 shows that sonication at 300 kHz gave the highest $OH^{\cdot}$ yield compared to 1000 kHz and 44 kHz. This optimum frequency for sonochemical yield has been previously reported [47–50] and attributed to the balance between increase in population of cavitation bubbles and decrease in cavitation collapse intensity with increasing frequency [22,23]. However, the $OH^{\cdot}$ yield under sonication alone is considerably lower compared to ozonation alone and for the combined ozonation-sonication, similar $OH^{\cdot}$ production rate as ozonation only were obtained. It is interesting to note that a linear $OH^{\cdot}$ production is obtained for the sonication and ozonation systems, but for combined ozonation-sonication, the production rate slightly reduces as the treatment time increases (time > 30 min).

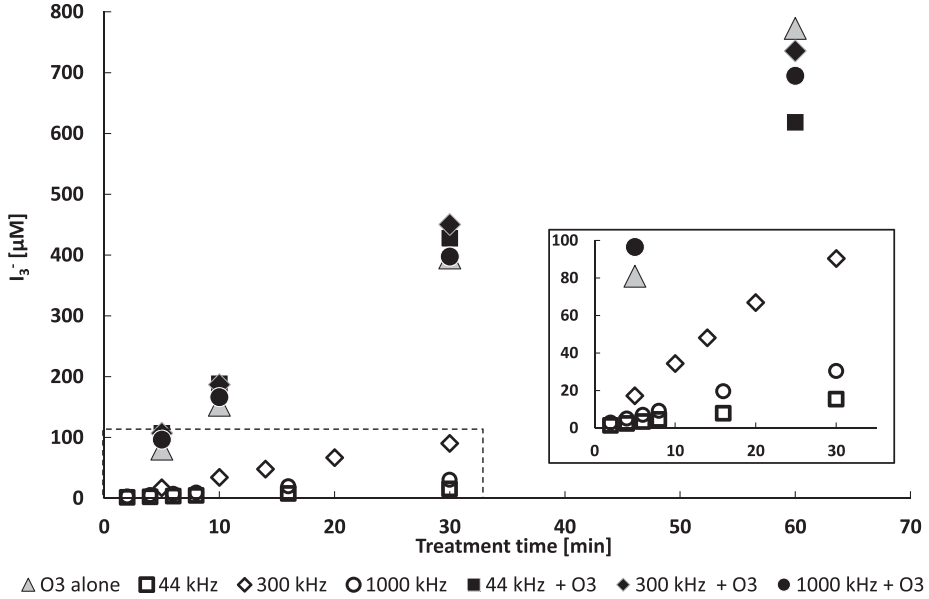

Fig. 2. I_3^- concentration as a function of time for ozonation (71 mg /L), sonication (44, 300 and 1000 kHz at 40 W) and ozonation-sonication treatments (71 mg /L and 44, 300, 1000 kHz at 40 W). The insert shows the zoomed in plot of I_3^- concentration as a function of time for sonication the ultrasound only systems. Sample volume 400 mL and 0.1 M KI.

3.2. Effect of ozonation

For O_3 alone experiments, a substantial reduction in organic matter was observed. COD and BOD were reduced down to 133 ± 20 and 17 ± 4 mg O_2/L, respectively (33% COD and 74% BOD removal), whereas TSS decreased from 60 ± 11 mg/L to 20 ± 5 mg/L. At the same time, a complete inactivation of total coliforms (TC) was obtained after 30 min ozonation, while 537 ± 151 CFU/mL of total viable counts (TVC) were measured after 60 min ozonation (4 log reduction)..

During ozonation in liquid media, oxidation can occur through direct reaction involving molecular O_3 (low O_3 decomposition rate at pH < 7, leading to direct O_3 oxidation pathway when pH < 4) and via an indirect pathway through $OH^{\cdot}$ formed during O_3 decomposition (high O_3 decomposition rate at pH > 7, with radical pathway dominated degradation when pH > 10) [51,52]. That is, at pH between 4 and 8, both $OH^{\cdot}$ and molecular O_3 would take part in the oxidation process of compounds when O_3 is applied. At pH values above 8, the $OH^{\cdot}$ would be the main oxidising agent, while at pH values of 4 or below, molecular O_3 would be the agents leading compound removal [53]. During the present study, a slight increase in pH of 0.2 (initial pH 7.7) was measured after 60 min of treatment with no apparent change in the behaviour of the system. This is consistent with reported findings [53], showing that an increase in pH from 6.7 to 7.9 (wastewater from a wastewater treatment plant) does not affect significantly $OH^{\cdot}$ generation. This strongly suggests that both $OH^{\cdot}$ and molecular O_3 would play a role in organic matter removal. These results are in agreement with those reported by Alfonso-Muniozguren et al. [37], although the slightly higher absolute values can be attributed to the higher organic load and TSS in the abattoir wastewater used in the present study.

3.3. Effect of sonication

Shown in Fig. 3 are COD and BOD values during 60 min sonication time for the three frequencies (44, 300 and 1000 kHz) under study. Only the experiments at 300 kHz showed a notable decrease in organic matter concentration with an 18% reduction in COD to 228 ± 13 mg O_2/L in 60 min and a 50% reduction in BOD to 13 ± 1 mg O_2/L after 10 min. Further treatment up to 60 min showed no change in the BOD value. The biodegradable carbon (measured by BOD) was probably easier to oxidise within the first minutes of ozonation and further increasing ozonation up to 60 min did not reduce BOD further, as the BOD value was already low. The difference in the final COD and BOD values for the three frequencies could be explained by the $OH^{\cdot}$ production rate. It is well known that $OH^{\cdot}$ production rate peaks at around 300 kHz [54], producing more $OH^{\cdot}$ compared to 44 and 1000 kHz for a given applied power. As observed in Fig. 2, after 60 min of sonication and 40 W applied power, the concentration of $OH^{\cdot}$ with 300 kHz was three times higher than that of 1000 kHz and six times higher than with 44 kHz. The increase in $OH^{\cdot}$ concentration induces more chemical effects and therefore, leads to a better degradation efficiency [55]. Similarly, Petrier and Francony [47] reported that higher phenol decomposition rate is achieved with 200 kHz compared to frequencies of 20, 500 and 800 kHz. The highest formation of H_2O_2 (comparable to $OH^{\cdot}$ production) is also observed with 200 kHz, indicating a link between $OH^{\cdot}$ formation and phenol degradation. Others have also reported similar optimum frequencies between 200 and 550 kHz for phenol degradation [47–50]. Berlan et al. [49] obtained a complete removal of phenol with 541 kHz (30 W calorimetric power) after 100 min (100 mg/L initial concentration), while Lesko et al. [50] achieved a 10% TOC reduction after 400 min sonication at 358 kHz and 100 W applied power. The latter was substantially improved in combination with O_3. It is important to highligh that the aforementioned experiments were carried out with synthetic waters (simple water mixtures), whereas the present study showed results for complex water matrixes (real wastewaters).

On the other hand, and as seen in Fig. 4, TSS values decreased progressively as sonication time increased. After 60 min of treatment, an average TSS removal of 25% was achieved, independently of the applied frequency. Although the lowest TSS value (45 ± 9 mg/L) was obtained with 300 kHz, it had a lower initial TSS value of wastewater. The lack of frequency effect on the TSS suggests that although mechanical effects are higher at lower frequencies (44 kHz), cavitation intensities at higher frequencies (300 and 1000 kHz) are strong enough to fragment suspended solids into soluble particles. That is, even though stronger cavitation is produced with low frequencies, the higher number of cavitation events produced with high frequencies [23] could lead to similar TSS reduction.

The disinfection performance of ultrasound plate transducers is shown in Fig. 5. After 60 min of sonication at the three frequencies studied, < 1 log reduction in TC and insignificant removal in TVC was measured. The high amount of suspended solids and the complex matrix of the treated wastewater would be responsible for the poor

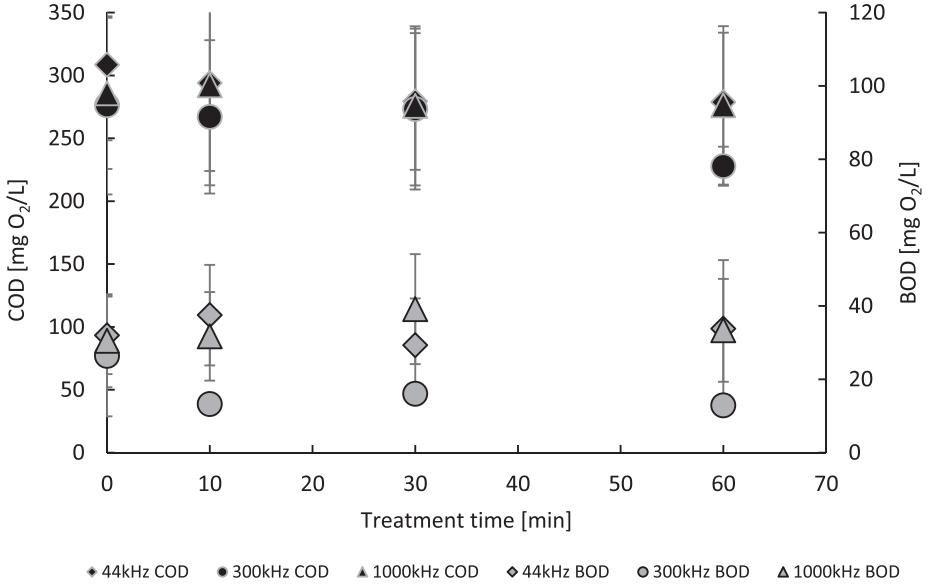

Fig. 3. COD and BOD values as a function of sonication time for three different frequencies (44, 300 and 1000 kHz) at 40 W applied power. Error bars expressed as standard deviation.

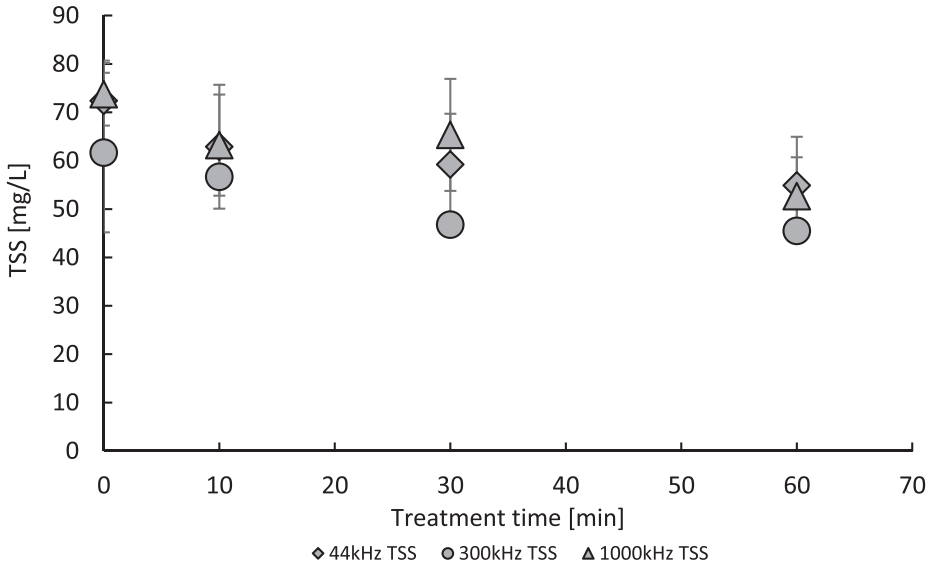

Fig. 4. TSS values as a function of sonication time for three different frequencies (44, 300 and 1000 kHz) at 40 W applied power. Error bars expressed as standard deviation.

disinfection performance of ultrasound. Similarly, Gómez-López et al. [56] used a 20 kHz horn to achieve 1 log reduction on *E.coli* applying 56 W (400 mL sample) for 60 min to a synthetic wastewater. However, increasing power to 448 W showed a 5 log reduction on *E.coli* after 30 min of treatment. A 5 log reduction was also obtained by Hua and Thompson [57] using a 205 kHz multi-frequency reactor at an approximate total power of 128 W (3 times the power used in the present study) and a sample volume of 300 mL. These experiments, nonetheless, were carried out in oxygenated solutions and as stated by the authors, the type and amount of the dissolved gas can influence the formation of free radicals and thus, lead to a better performance.

A 20 kHz ultrasonic horn was also employed to treat two different sample volumes (50 and 100 mL) of abattoir wastewater for 30 s at two different applied powers (210 W for 30% amplitude and 350 W for 50% amplitude). The results are shown in the supplementary information: no significant difference was observed in COD, BOD and TSS (Figure S 1 and Figure S 2), or in TC (Figure S *3* and Figure S *4*) and TVC (Figure S *5* and Figure S *6*) before and after the treatment.

3.4. Combined ozonation-sonication

The combined ozonation-sonication experiments (Fig. 6) performed slightly better for COD removal (44% reduction after 60 min treatment with a final value of 114 ± 15 mg O_2/L) compared to the results achieved with O_3 alone. It is important to highlight that frequency variation does not play a role in COD removal for the combined system. The slight increase in performance of the combined system could be explained by the dual benefit of ultrasound at increasing O_3 mass transfer into the aqueous solution (i.e. increasing molecular O_3 concentration in the water matrix), as well as the direct degradation of organic compounds through mechanical effects. The improvement would not be caused by direct $OH^{\cdot}$ attack, as the results obtained show no difference in $OH^{\cdot}$ production rates between O_3 alone and ozonation-sonication systems (Fig. 2). As with O_3 alone experiments, an insignificant increase in pH of 0.2 was observed.

The small difference in efficiency between the combined system and O_3 alone could be related to the high O_3 dose used. Considering the

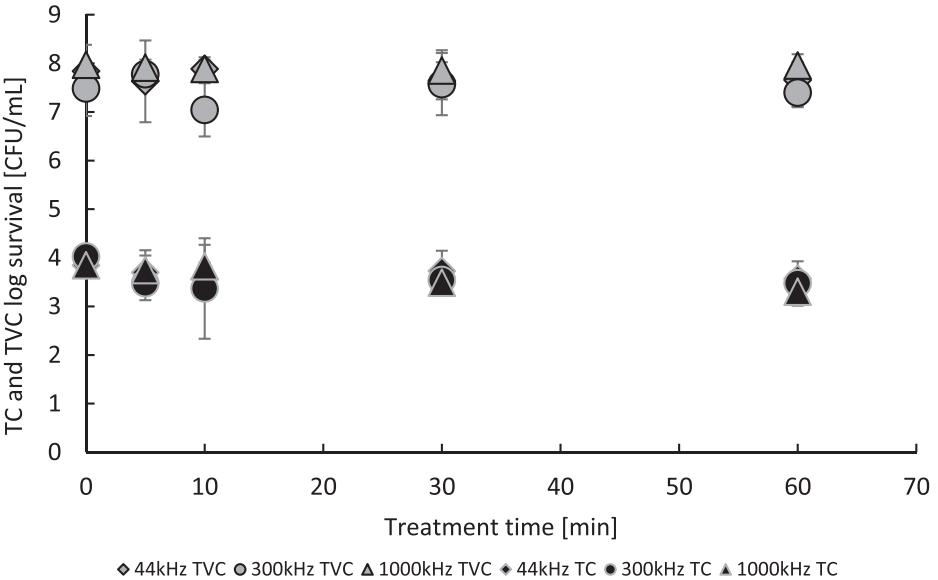

Fig. 5. TC and TVC log survival values as a function of sonication time for three different frequencies (44, 300 and 1000 kHz) at 40 W applied power. Error bars expressed as standard deviation.

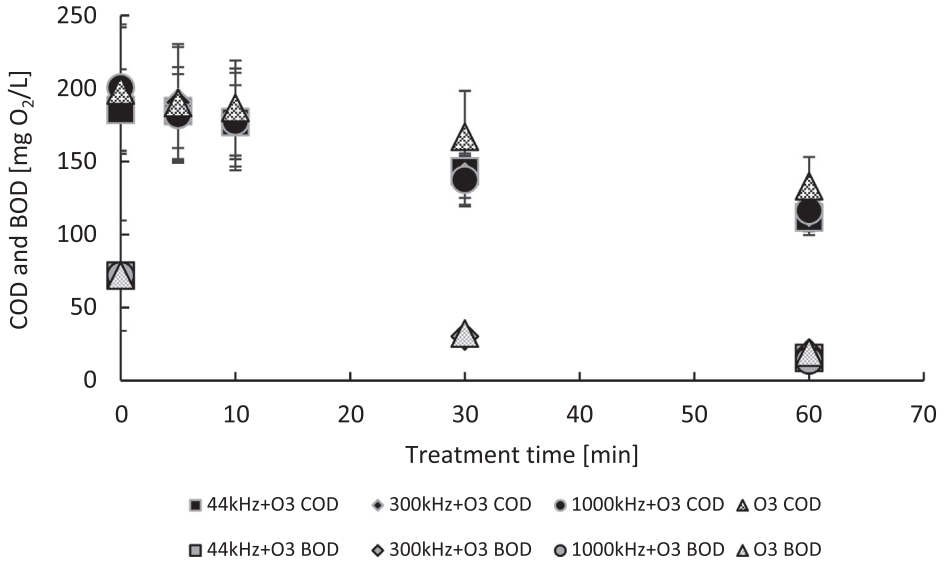

Fig. 6. COD and BOD values as a function of ozonation (O_3) alone (71 mg /L) and O_3 + sonication time (44, 300 and 1000 kHz) at 40 W applied power. Error bars expressed as standard deviation.

short residence time of the ozonated bubbles within the reactor (1 s approximately), it is unlikely that ultrasound would cause a significant increase in the performance of the system. In addition, the degassing of the system by ultrasound [58] could have also reduced, to some extent, the dissolved O_3 in the water matrix thus reducing the degradation efficiency in the combined configuration. However, since O_3, was continuously injected during the experiment, the degassing effect of ultrasound in the combined system would be minor. Boczkaj et al. [59] used a similar O_3 dose (9.41 g/h vs 9.8 g/h of our system, equivalent to injecting 71 mg /L_{air} at 2.3 L_{air}/min) coupled with hydrodynamic cavitation (2 mm diameter throat Venturi tube at 6–10 bar inlet pressure and a flowrate of 470–590 L/h) to treat 5 L of real wastewater from bitumen production for 6 h. In that case, the initial COD concentration ranged between 8000 and 12000 mg O_2/L (compared to 249 mg O_2/L here). Consequently, this combination of O_3 and hydrodynamic cavitation led to a substantial improvement in performance after 60 min of treatment (30% COD removal with the combined system compared to approximately 8% reduction for O_3 and hydrodynamic cavitation alone). The reported improved performance under the combined system could be attributed to the much higher COD which would result in a faster consumption of O_3 and $OH^{\cdot}$. Therefore, the application of ultrasound would increase O_3 mass transfer into the aqueous phase, replacing the consumed O_3 and leading to a higher COD removal percentage. On the contrary, Ibanez et al. [60] reported no additional COD reduction when combining O_3 (7–12 mg O_3/L) and ultrasound for urban wastewater treatment. In that case, no significant difference was found on the reduction of different contaminants between O_3 alone and O_3-ultrasound combined. The reported COD concentrations (26–50 mg O_2/L) were substantially lower than those given by Boczkaj et al. [59] and the present study. When it comes to the use of O_3-ultrasound systems to treat wastewaters, it appears that the role ultrasound plays in performance efficiency is inversely related to the O_3 dose used. It is also important to take into account the initial concentration of organic carbon (the initial COD value seems to be crucial in the performance improvement of the combined system compared to individual systems) and sonication power. Thus, Weavers et al. [61] and Barbier and Petrier [62] obtained a significant increase in carbon removal adding ultrasound to low O_3 injection dosages (0.01 g/h and 7–8 mg/L, respectively) compared to O_3 alone. Whereas Tezcanli-Guyer and Ince [63] and Destaillats et al. [64] showed only a slightly better mineralisation performance with ozonation-sonication compared to ozonation alone when using a substantially higher O_3 dose of 40 mg/L and 15 mg/L, respectively.

BOD is reduced progressively as the treatment time increases with no significant difference between the two systems (O_3 alone and ozonation-sonication). Final BOD values of 14 ± 5 mg O_2/L were measured after 60 min of treatment for both systems, leading to a reduction in BOD of 74% independent of the frequency (Fig. 6). Similar values were obtained after applying 300 kHz alone (13 ± 1 mg O_2/L) with a final BOD reduction of 50%.

As observed with BOD, TSS values did not show any difference between the combined system (independent of the frequency used) compared to O_3 alone, achieving 18 ± 6 mg/L after 60 min (Fig. 7). This value represents a 78% reduction, substantially higher than that obtained with ultrasound alone (25%). The organic fraction of suspended solids is composed of natural organic compounds which are prone to hydrolysis and oxidation due to ozonation. O_3 reacts with the organic fraction of suspended solids to convert it into dissolved organic matter, and further mineralisation occurs at higher O_3 dose. Additionally, O_3 can also remove suspended solids by flotation.

As opposed to the disinfection efficiency of ultrasound alone, both the combined system with 44, 300 and 1000 kHz, as well as O_3 alone were able to achieve a complete inactivation of TC after 30 min (Fig. 8). The high O_3 dose applied would be responsible for the observed TC inactivation as shown by [37]. Regarding TVC removal, Fig. 8 shows a slight improvement for the combined system compared to O_3 alone.

It is important to emphasise that even though the ozonation-sonication process did not show any synergism, it was the only treatment method that reduced the COD, BOD and TSS levels down to direct discharge limits. Additionally, drinking water standards were met (99 ± 23 CFU/mL) with ozonation-sonication experiments, while O_3 alone (537 ± 151 CFU/mL) was insufficient to reach the minimum value of 100 CFU/mL (Table 2) set by the Council Directive 98/83/EC on the quality of water intended for human consumption [65].

4. Conclusions

Ultrasound alone was not efficient in reducing organic carbon and inactivating microorganisms when treating real wastewater with high organic load and microbial population such as that coming from an abattoir. In the application of combined O_3-ultrasound systems, the role ultrasound plays in the performance efficiency is dependent on the initial concentration of organic carbon and inversely related to the O_3 dose. In this study the combining ultrasound with O_3 led to a significant

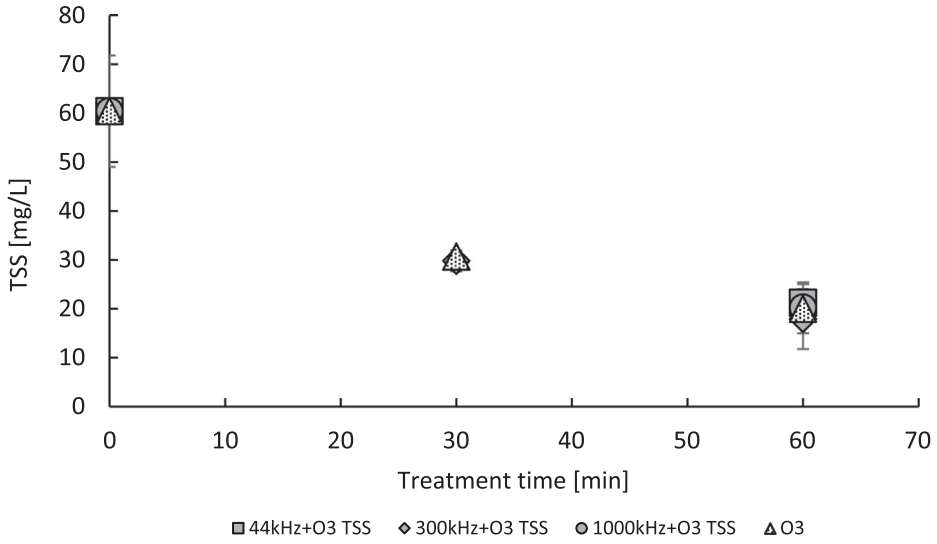

Fig. 7. TSS values as a function of ozonation (O_3) alone (71 mg /L) and O_3 + sonication time (44, 300 and 1000 kHz) at 40 W applied power. Error bars expressed as standard deviation.

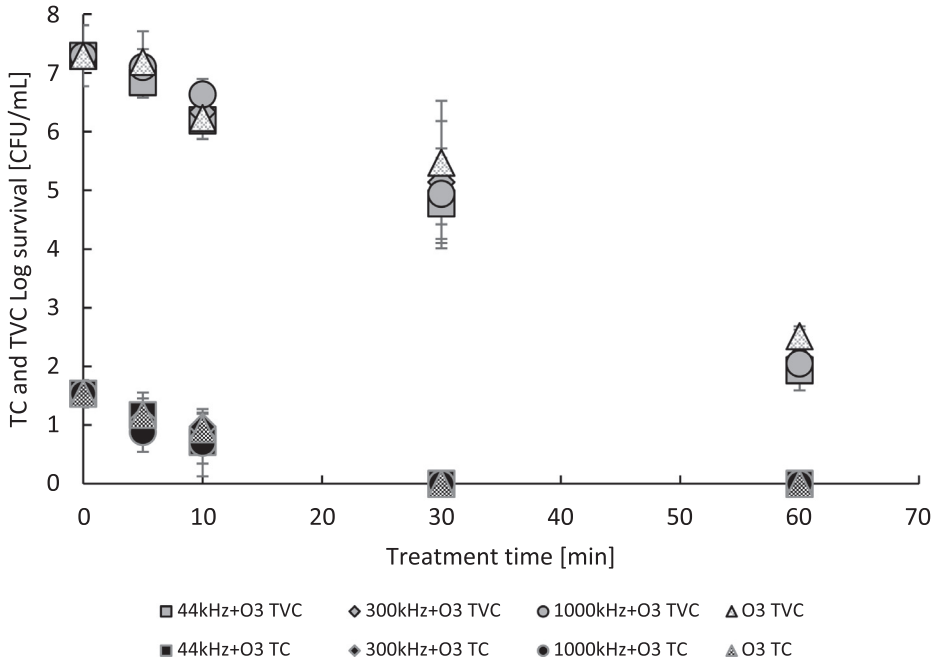

Fig. 8. TC and TVC log survival values as a function of ozonation (O_3) alone (71 mg /L) and O_3 + sonication (44, 300 and 1000 kHz) at 40 W applied power. Error bars expressed as standard deviation.

Table 2
COD, BOD, TSS, TC and TVC values before and after the combined ozonation-sonication process, as well as direct discharge limits (COD, BOD and TSS) and drinking water standards (TC and TVC).

	COD (mg O_2/L)	BOD (mg O_2/L)	TSS (mg/L)	TC (CFU/mL)	TVC (CFU/mL)
Initial value	198 ± 34	65 ± 3	60 ± 11	4.1 ± 21	$2.0 \times 10^7 \pm 2.2 \times 10^7$
Final value O_3	133 ± 20	17 ± 4	20 ± 5	0	537 ± 151
Reduction O_3	33%	74%	67%	100%	4 log
Final value ultrasound + O_3	**114 ± 15**	**14 ± 5**	**18 ± 6**	**0**	**99 ± 23**
Reduction ultrasound + O_3	44%	78%	70%	100%	5 log
Direct discharge limits [26]	**125**	**25**	**35**	–	–
Drinking water standards [65]	–	–	–	**0**	**100**

increase in COD and BOD removal (down to 114 and 14 mg O_2/L, respectively), as well as achieving complete inactivation of TC and a 5 log reduction in TVC. Furthermore, a substantial performance improvement was seen in TSS removal using ozonation-sonication from 25% (sonication alone) to 70% (ozonation-sonication), obtaining 18 mg/L with the coupled system. Thus, the combined system was the

only treatment method in our study (compared to sonication and ozonation alone) able to reach direct discharge limits for COD, BOD and TSS, as well as meeting drinking water standards for microbial disinfection.

Declaration of competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ultsonch.2020.104986.

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