Effect of the water matrix and reactor configuration on *Enterococcus* sp. inactivation by UV-A activated PMS or H_2O_2

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A B S T R A C T

In this work, the influence of the matrix on the photolytic activation of peroxymonosulfate (PMS) and hydrogen peroxide (H_2O_2) has been studied for the inactivation of *Enterococcus* sp. Additionally, two different reactor configurations (batch reactor and tubular reactor) have been evaluated that achieve complete disinfection within 120 min when using a tubular reactor. Three water matrices (distilled water, saline solution and simulated wastewater) have been studied, and experiments have been carried out using radical scavengers to determine the main reactive species involved in each process. The hydroxyl radical ($^\bullet$OH) has been found to be the main responsible for the inactivation of bacteria in distilled water, while chlorinated species generated during treatments are responsible for disinfection in a saline matrix. The study of the influence of various inorganic ions (Br^-, F^-, PO_4^{3-}, NO_3^-, NO_2^-) on treatments revealed an increase in the efficacy of the PMS/UV-A system in the presence of Br^- due to the bromine generation. Furthermore, the effect of F^- has been studied for the first time, determining that the presence of this compound does not have a significant influence on the H_2O_2/UV-A system while inhibiting PMS/UV-A treatment. Overall, the results suggest that H_2O_2-based treatments would be less dependent on matrix composition than those involving PMS, and the presence of nitrites is a contraindication to the application of either process.

1. Introduction

Due to climate change and population growth, approximately two thirds of the population experience severe water shortages for at least one month a year and, by 2050, this number will continue to rise, so that 52% of the world's population will be at risk [1]. This has led researchers and governments to focus on finding alternative water sources to reduce water stress, allowing higher-quality water to be reserved for human consumption. Although one of the solutions that have attracted the most attention is the reuse of reclaimed wastewater, it is estimated that more than 80% of the wastewater (WW) generated on the planet is discharged into the natural environment without adequate prior treatment, according to the United Nations World Water Development Report (2018) [2]. This entails the introduction into the aqueous medium of many highly harmful contaminants (chemical, physical, and biological), which pose a risk not only for biodiversity but also for human health.

Several studies have demonstrated the presence of various contaminants in the effluent of conventional wastewater treatment plants (WWTP), revealing that some pollutants are recalcitrant to conventional treatments [3,4]. Pathogenic microorganisms, including bacteria, viruses, fungi, etc., are one of the most common pollutants present in wastewater [5–9]. Regulations generally determine which species of microorganisms should be used as indicator microorganisms. This is the case of *Escherichia coli*, a bacteria frequently used as an indicator of faecal contamination [10]. However, previous studies have shown that *Enterococcus* sp. might be more resistant to some disinfection treatments [11–13]. Therefore, this species may be more appropriate as an indicator in the study of advanced oxidation processes (AOPs), as they may not be correctly assessed by less resistant microbiological indicators.

Although chlorination and ozonation are the most well-established and commonly used disinfection techniques today [14], these techniques have some drawbacks. The most important is the formation of

disinfection by-products (DBPs) that can be a threat to human health [15], such as trihalomethanes (THMs), haloacetic acids (HAA), and bromate. DBPs are mainly formed by the reaction of the reagents used as a disinfectant with the organic matter present in the water. Therefore, if disinfection is to be implemented as a tertiary treatment in a wastewater treatment plant, the risk of formation of these compounds is very high, as the effluent to be treated may still contain a high concentration of organic matter [16]. This requires the development of new disinfection techniques that can be used in these cases to provide the quality necessary to ensure safe reuse.

In this context, AOPs have been demonstrated to be a great alternative to conventional treatments. AOPs consist of the generation of highly reactive free radicals capable of degrading organic molecules while inactivating microorganisms [17–20]. The hydroxyl radical (•OH), generated from hydrogen peroxide (H_2O_2), has been commonly used as an oxidizing agent in AOPs due to its high redox potential (1.8–2.7 V) [21,22]. However, sulfate radicals ($SO_4^{•−}$) also appear to be a great alternative, as they have a redox potential (2.5–3.1 V), equal to or greater than •OH [23]. $SO_4^{•−}$ can be generated through the activation of various oxidizing compounds, with peroxymonosulfate (PMS) one of the most widely used, together with sodium or potassium peroxydisulfate (PDS). PMS is commercially available as Oxone©, a triple potassium salt, highly unstable, facilitating its reaction with other compounds, and several studies have highlighted its disinfection efficacy over PDS [24,25]. Many different methods can be used to activate PMS and H_2O_2 for the generation of radicals, such as radiation, homogeneous and heterogeneous catalysis, heat, or ultrasound [26,27]. Within UV radiation, UV-C emission is one of the most widely used methods in AOPs. However, several authors have reported good efficacy in treatments that combine UV-A radiation with H_2O_2 [28,29] or PMS [11,30]. Although most of these studies combine radiation with other activation methods (such as iron for photo-Fenton processes), its efficacy is worth exploring as a single activation method.

Despite the many advantages of AOPs, several studies have revealed that one of the drawbacks of these processes is that their effectiveness is highly affected by the composition of the aqueous matrix [31,32]. The presence of components such as organic matter or carbonates has been widely investigated [31], since they may act as inhibitors of treatments, since they are scavengers of free radical species [33]. However, some water constituents have been reported to promote parallel reactions that could accelerate degradation processes [34]. Consequently, individual matrix components can affect water treatment processes depending on the nature of the target pollutant, the dissolved compounds, or the chemicals involved in the treatment process [31,34,35].

The main objective of this work is to study the influence of the water matrix on the photolytic activation of H_2O_2 and PMS applied to the inactivation of *Enterococcus* sp. in water streams. In addition, two different reactor configurations have been compared to determine which is the most efficient in terms of radiation distribution. The influence of the matrix has been evaluated by comparing three aqueous matrices with different compositions (distilled water, saline solution, and simulated wastewater). The influence of five inorganic anions ($Br^−$, $F^−$, $PO_4^{3−}$, $NO_3^−$, $NO_2^−$) whose effects on AOPs have been less explored so far has been studied in this work. Finally, experiments have been carried out using scavengers to identify the main radicals involved in the inactivation of bacteria in the proposed scenarios.

2. Materials and methods

2.1. Aqueous matrix

Three aqueous matrices with different levels of complexity have been used throughout the study, the simplest matrix being distilled water (DW). A saline solution (SS) with a sodium chloride concentration (NaCl, Scharlau) concentration of 0.9% has also been used and, finally, to test the viability of treatment in a more complex matrix, some

experiments were carried out using simulated wastewater (SWW). The composition of SWW was: meat peptone (Scharlau; 160 mg/L), meat extract (Scharlau; 110 mg/L), urea (Scharlau; $CO(NH_2)_2$; 30 mg/L), NaCl (Scharlau; 7 mg/L), $CaCl_2•2H_2O$ (Scharlau; 4 mg/L), $MgSO_4•7H_2O$ (Scharlau; 2 mg/L), K_2HPO_4 (Scharlau; 28 mg/L) and deionized water [36].

2.2. Chemical and reagents

In addition to the reagents used in the preparation of aqueous matrix and the preparation and analysis of *Enterococcus* sp. (see Section 2.3), other reagents have been used throughout the experiments. Treatments were carried out using different doses (0.01–1.5 mM) of potassium peroxymonosulfate ($2•KHSO_5•KHSO_4•K_2SO_4$, PMS, Oxone® Sigma-Aldrich) and hydrogen peroxide (H_2O_2, 30% in water, Chem-Lab). Furthermore, furfuryl alcohol (FFA, $C_5H_6O_2$, Aldrich) tert-butyl alcohol (TBA, $C_4H_{10}O$, Scharlau), and methanol (MeOH, CH_3OH, Chem-Lab) have been used as radical scavengers in a molar ratio of 20:1 (scavenger: oxidant). Tests have been carried out to ensure that these concentrations are not harmful to *Enterococcus* sp.

Other reagents used during this work were sodium nitrite ($NaNO_2$, Scharlau), sodium nitrate ($NaNO_3$, Scharlau), sodium fluoride (NaF, Scharlau), sodium bromide (NaBr, Scharlau), tri-sodium phosphate (Na_3PO_4, Scharlau), iron sulfate (II) heptahydrate ($FeSO_4•7H_2O$, Sharlau), iron(III) sulfate ($Fe_2(SO_4)_3•12H_2O$, Chem-Lab), 1,10-phenanthroline ($C_{12}H_8N_2$, Aldrich), sodium acetate trihydrate ($CH_3COONa•3H_2O$, Chem-Lab), oxalic acid dihydrate ($C_2H_2O_4•2H_2O$, Chem-Lab) and sulfuric acid (H_2SO_4, JT Baker).

2.3. Bacterial preparation and analysis

Wild strains of *Enterococcus* sp., previously isolated from real wastewater and stored in cryovials in a freezer, were used in this study to contaminate the water samples. To activate frozen bacteria, the content of a cryovial (0.5 mL) was inoculated in 50 mL of Luria Bertani broth (Scharlau; Spain) and incubated for 24 h (37 °C). After this time, the broth was divided into two 50 mL Falcon tubes (25 mL of broth in each one) and centrifuged for 15 mins at 4200 rpm to ensure complete separation of bacteria from the feeding broth. Once the supernatant was discarded, the pellets were resuspended in the same volume of saline solution (NaCl 0.9%) and stored in the fridge for later use.

To evaluate the effectiveness of the treatments, the culture and enumeration of the bacteria were carried out mainly using the drop plate method [38] through a 10-fold serial dilution in sterile saline solution (NaCl 0.9%). However, the spread plate method (*Standard Method 9215C*) [39] was also used to increase the detection limit (DL) when needed. The samples were plated on Slanetz & Bartley agar (Scharlau; Spain) and the colonies formed were counted after 48 h of incubation at 37 °C. The number of colonies was expressed as Colony-Forming Units per mL (CFU/mL) and the detection limit was 10 CFU/mL and 100 CFU/ mL when using the spread plate method or the drop plate method, respectively. Analyses were performed in triplicate and the standard deviation of the results was calculated.

2.4. Experimental setup

In this study, two different reactor configurations have been assessed. The optimizations of PMS and H_2O_2 were carried out in a 500 mL batch reactor agitated with a magnetic stirrer. Two black-light lamps (Philips TL 6 W; 365 nm) were placed over the reactor at a distance such that the radiation on the water surface was 8.5 W·m^{-2}. Since the position of the lamps in this configuration is not fixed, the irradiance was checked before each experiment using an HD 2102.1 portable luxmeter (Delta OHM) to ensure that the radiation intensity at the surface was constant in all experiments. The rest of the experiments were carried out in a tubular reactor, with continuous recirculation and a total volume of

1 L. The illumination of this reactor was provided by a black-light lamp located on the axis and, according to the illuminated volume (0.252 L, 25.2% of the total water sample) and the flow rate (1.2 L min^{-1}), the UV-A contact time was 12.6 s. For more detail, photographs of both reactors have been included in the supplementary material (Fig. S1). For all experiments, the water sample was inoculated with *Enterococcus* sp. so that the initial concentration of cultivable bacteria was 8·10^5–1·10^6 CFU/mL, and the necessary concentrations of reagents were added. The experiments lasted 120 min and were carried out at natural pH ($\approx$ 6). The temperature of the water varied between 26 °C and 30 °C due to the slight heating caused by the recirculating pump. However, no impact of this variability was observed during the experiments.

To determine incident radiation reaching water during treatments, ferrioxalate actinometry experiments were carried out using DW, both in batch and tubular reactors, following the procedure described elsewhere [37]. In addition, free chlorine generation was monitored using a multiparameter photometer (Hanna HI83399) together with the HI93701-F reagent kit of the same brand.

In order to compare inactivation under various conditions, pseudo first-order rate constants (k [min^{-1}]) were estimated by linear regression fitting. A synergistic factor was calculated to evaluate the synergistic effect [40] following Eq. (1):

$$S = \frac{k_{(oxidant+UV-A)}}{k_{oxidant} + k_{UV-A}} \tag{1}$$

3. Results

3.1. Photolytic activation of PMS and H$_2$O$_2$

The inactivation of *Enterococcus* sp. was studied over time for different concentrations of PMS and H$_2$O$_2$ in a batch reactor with the incidence of UV-A radiation, and the results were plotted in Fig. 1. For optimization, DW samples were used as the aqueous matrix. UV-A radiation alone was not able to inactivate the microorganisms present in the medium, but once PMS was added, the elimination of *Enterococcus* sp. began to increase (Fig. 1A). Inactivation was practically negligible for a PMS dose of 0.01 mM, obtaining a disinfection rate of 0.33 log after 120 min of irradiation. However, by increasing the concentration of oxidants to 0.05 mM and 0.1 mM, the disinfection rate increased to 1.2 log and 4.3 log for the same time. Higher doses of oxidant led to complete inactivation of the bacteria in less than 15 min, considering that when the detection limit had been reached. Non-activated PMS has been stated to have some disinfection capacity [41], so dark experiments were carried out. No significant inactivation was observed for the doses assessed (data not shown).

The same procedure was carried out for hydrogen peroxide (Fig. 1B), but none of the concentrations applied had a significant effect on the bacteria population. However, according to other authors, a dose of H$_2$O$_2$ of 1.5 mM (51 mg·L^{-1}), when Fenton-like methods are used, is sufficient for microorganism inactivation [42,43]. This could indicate that UV-A radiation is not capable of activating the oxidant to generate radicals that attack the bacteria present in the water under the experimental conditions tested. Since the treatment is carried out in distilled water, there are no particles in the medium that scatter light or organic matter that absorbs it, so the reason that the radiation does not have the desired effect could be that incident radiation is not sufficient to activate H$_2$O$_2$.

A concentration of 1.5 mM H$_2$O$_2$ and a concentration of 0.05 mM PMS were chosen, and the same treatments were carried out in a tubular reactor to check whether a different reactor and light distribution could improve the inactivation of *Enterococcus* sp. In this new arrangement, the lamp was placed on the central axis of the reactor, surrounded by the fluid, so a better light distribution is expected than in previous experiments in which the lamp was placed over the reactor. As expected, greater bacteria inactivation was achieved in the tubular reactor, with
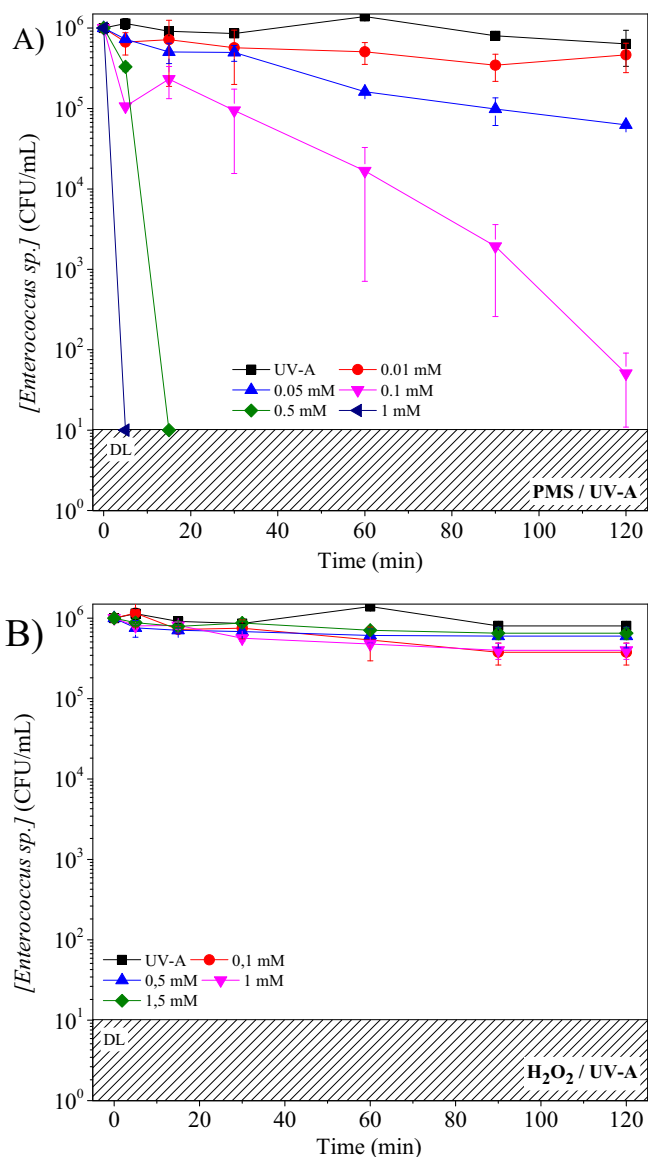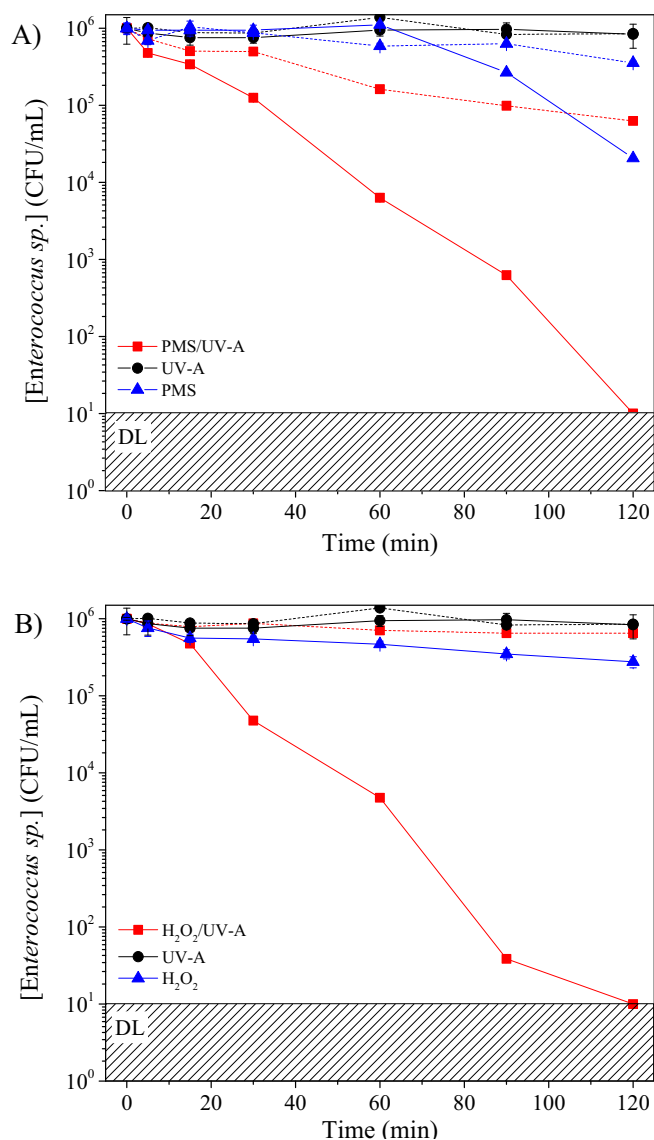

Fig. 1. Photoactivation of PMS (A) and H$_2$O$_2$ (B) for inactivation of *Enterococcus* sp. in a batch reactor. Experimental conditions: pH = natural; Matrix = distilled water; Irradiation = UV-A.

consequent higher disinfection rates. Fig. 2B shows how, when using the new configuration, *Enterococcus* sp. inactivation reaches the detection limit after 120 min of H$_2$O$_2$/UV-A treatment, while elimination was almost non-existent in the batch reactor. Similarly, the effectiveness of the PMS/UV-A treatment improved, increasing the disinfection rate from 1.2 log to complete inactivation after 120 min (Fig. 2A).
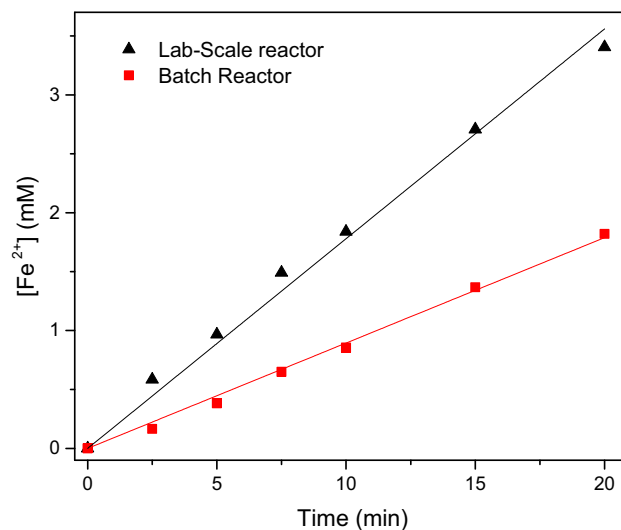
As in the batch configuration, the effect of UV-A radiation alone on the bacterial population was studied, concluding that the amount of radiation emitted by the lamps is not sufficient to inactivate *Enterococcus* sp. An increase in the disinfectant power of the non-activated reagents was observed. The disinfection rate achieved by PMS and H$_2$O$_2$ was 1.68 and 0.55 log, respectively. This may be due to a higher decomposition of the compounds as a consequence of the more aggressive agitation generated by the passage of the liquid through the feed pump. The synergy factor (S) of the combination of reagents and ultraviolet-visible (UV-A) radiation was calculated, for which it was first necessary to calculate the pseudo-first-order kinetic constant. Table S1 (Supplementary material) shows the inactivation rate constants obtained, as well as the S calculated for the two treatments in the two configurations. As

Fig. 3. Variation of Fe^{2+} concentration during ferrioxalate actinometry experiments for a batch and a tubular reactor.

Fig. 2. Influence of the reactor on A) PMS and B) H_2O_2 for the inactivation of *Enterococcus* sp. (solid lines: tubular reactor; dashed lines: batch reactor). Experimental conditions: [PMS] = 0.05 mM; [H_2O_2] = 1.5 mM; pH = natural; Matrix = distilled water; Irradiation = UV-A.

Einstein·L^{-1}·s^{-1}, while this value was 1.19×10^{-6} Einstein·L^{-1}·s^{-1} for the batch reactor, despite using two lamps.

This improvement in treatment efficiency may be due to two different phenomena. The first one is a better activation of the oxidants due to higher incident radiation. The bond dissociation energy of hydrogen peroxide has been estimated to be between 44.1 and 50.72 kcal mol^{-1} (184.51–212 kJ ml^{-1}) [45]. On the other hand, there is no reference value for the PMS bond energy, although it has been estimated to be lower than that of H_2O_2 [46]. This could explain why there is some activation of PMS when using a batch configuration, but not of H_2O_2. On the other hand, although radiation alone has been shown to be not capable of inactivating microorganisms, it could have sufficient power to weaken their structure and promote slight oxidative damage [47], facilitating their subsequent inactivation when reagents are added, either by direct oxidation or through generated radicals. In either case, actinometry results corroborate that, by using a tubular reactor, the greater efficiency of the treatment is a consequence of the fact that this configuration can maximise incident radiation flux. Therefore, this configuration was selected as optimal for the rest of the experiments.

3.2. Effect of the matrix

The selected doses of PMS and H_2O_2 from the optimization phase (Section 3.1) were applied to various aqueous matrices, gradually increasing the complexity of the medium. For this, a saline solution and simulated wastewater were used. The saline solution used has a concentration of 9 g L^{-1}. Although municipal wastewater generally has a lower salt content (< 0.5 g·L^{-1}), saline wastewater can occur for a variety of reasons, such as leaks from landfills or in response to seawater infiltration into sewer systems, which is a common problem during storm surge flooding in coastal areas [48]. On the other hand, it should not be forgotten that NaCl concentrations of up to 760 mM can be found in industrial wastewater [49]. The concentration of salt ions in inorganic industries ranges from 1.5 to 11 g·L^{-1}, and the concentration of total dissolved solids (TDS) can range between 48 and 100 g·L^{-1} depending on the industrial process [50]. Bacteria are well acclimatised to media with a salinity of up to 10 g·L^{-1}, and their survival in more concentrated media is difficult [48]. Finally, it should be noted that the use of a saline concentration of 9 g·L^{-1} is very common in microbiological analyzes to avoid cell death as a consequence of the osmotic difference between the inside and outside of the cell. Therefore, it is important to get insight about the effects of this salt concentration (in terms of NaCl) on the studied disinfection processes.

expected, the highest S was obtained for the H_2O_2/UV-A system in the tubular reactor (11.90), while no interaction between the two treatment elements was observed for the batch configuration. The difference between the S values obtained for the PMS/UV-A system is smaller, although the tubular reactor also favours synergy in this treatment.

Experimental results showed that by changing the reactor configuration used for the treatment, higher efficiencies can be obtained using the same reagent dose. Although it is possible to deduce that this is due, as mentioned above, to a better distribution of the radiation, actinometry experiments have been carried out in both the batch reactor and the tubular reactor to quantify the total incident radiation. Fig. 3 shows Fe^{2+} formation versus time during the two actinometric reactions. The results were linearly fitted to obtain the slope, and, in order to calculate the incident radiation flux, it was divided by the quantum yield of ferrioxalate actinometry, which is known but is dependent on wavelength. Goldstein et al. (2008) estimated this parameter in the range of 205–365 nm, obtaining a weighted average value for the emission spectrum of the lamps used in this work of 1.273 mol/Einstein [44]. The incident radiation calculated for the tubular reactor was 2.23×10^{-6}

Fig. 4A shows that the inactivation of microorganisms was complete in 5 min when the PMS/UV-A system was applied in saline solution. It has been stated that PMS reacts with chlorine-generating HClO/Cl$_2$ species (Eqs. (2)–(3)) [51], responsible for the inactivation of bacteria [20,52]. To confirm the formation of free chlorine, an experiment was carried out in which the free chlorine was monitored. Fig. S2 (supplementary material) illustrates how the generation of free chlorine occurs linearly up to a concentration of 1.6 mg/L. Considering that the initial sodium chloride concentration (9 g·L^{-1}) led to 5.46 g/L of chlorine in the water, 0.3% of the chlorine was transformed into free chlorine.

$$Cl^- + HSO_5^- \rightarrow HClO + SO_4^{2-} \quad (2)$$

$$Cl^- + H^+ + HClO \rightarrow H_2O + Cl_2 \quad (3)$$

On the other hand, the optimized treatment in DW was not enough to inactivate *Enterococcus* sp. in the simulated wastewater, only a 0.5 log reduction of the initial concentration was achieved after 120 min. The higher complexity of the matrix frequently leads to lower degradation or inactivation rates, and dissolved organic matter (DOM) has a documented role as a sink for radicals [53]. The synthetic wastewater used in

this work has a dissolved organic carbon content of 100 mg/L [36], which is responsible for inhibition of treatment. In addition, organic matter can absorb radiation in the UV-A region, thus also preventing the activation of the oxidant. In addition to this, the unstable nature of PMS means that it can react rapidly with almost any component of the matrix [54,55]. Therefore, the higher the complexity of the matrix, the higher the degradation rate of PMS, leaving less available for activation by UV-A. Previous studies have demonstrated that higher doses of PMS would be needed to achieve bacterial inactivation under the same conditions [11].

In Fig. 4B, the efficiency of the H$_2$O$_2$/UV-A system is compared in the three studied matrices. Complete inhibition of treatment was observed when applied in simulated wastewater. As in the PMS/UV-A system, the presence of organic matter could be mainly responsible for inhibition of treatment by absorbing radiation, quenching radicals, and promoting H$_2$O$_2$ degradation, also known for its unstable nature. Although Cédat et al. (2016) determined that the amount of H$_2$O$_2$ used in this work (1.5 mM) is sufficient to remove estrogens [56] from wastewater, UV-C (254 nm) was used in that study to activate H$_2$O$_2$. Hydrogen peroxide has a much higher radiation absorption capacity in the UV-C region than at the wavelength used in this work [57], which explains the difference in activation efficiency. Therefore, a much higher radiation dose would be necessary to achieve the same effect.

The disinfection rates achieved in the saline matrix were similar to those obtained in DW, with the disinfection kinetics slightly higher in SS. In this matrix, the detection limit was reached at 90 min, compared to the 120 min needed to reach the same point when the treatment was applied in distilled water. This differs from the reported results for the removal of organic pollutants. The presence of Cl$^-$ has been shown to have inhibitory effects on the degradation of compounds such as amoxicillin [58], ofloxacin [59], or RhB dye [60] by acting as a scavenger for hydroxyl radicals (Eqs. (4)–(5)) [61]. However, Nihemaiti et al. (2018) stated that the presence of chloride did not influence the degradation of trace organic chemicals [62] as the reaction between chloride and •OH is reversible, the rate constant of the forward reaction (4.3 × 10^9 M^{-1} s^{-1}) being lower than that of the backward reaction (6.1 × 10^9 M^{-1} s^{-1}). Moreover, the chlorine radical formed during these reactions may aid in this case the inactivation of *Enterococcus* sp.

$$\bullet OH + Cl^- \rightarrow ClOH\bullet^- \rightarrow \bullet OH + Cl^- \quad (4)$$

$$ClOH\bullet^- + H^+ \rightarrow Cl\bullet + H_2O \quad (5)$$

3.3. Enterococcus sp. inactivation mechanisms

3.3.1. Identification of main radical species

To know more about reactive species involved in the inactivation process, a set of experiments using radical scavengers has been conducted in DW and SWW. These experiments have not been carried out on real wastewater due to the low treatment performance achieved in the said matrix. The use of scavengers is a good qualitative approach for the identification of free species; however, further analysis using more complex analytical technologies such as electron paramagnetic resonance (EPR) should be performed to confirm the results. MeOH has been used as a scavenger for hydroxyl and sulfate radicals, while TBA has been used as a scavenger for hydroxyl radicals only. Furthermore, singlet oxygen (^{1}O$_2$) can also play an important role in the elimination of pollutants in AOPs, so FFA has been used as a scavenger of this species. MeOH is known to scavenge SO$_4$•$^-$ and •OH at a rate of 3.2·10^6 M^{-1} s^{-1} and 9.7·10^8 M^{-1} s^{-1}, respectively [63]. On the contrary, TBA reacts only with •OH at a rate of 6 × 10^8 M^{-1} s^{-1}, three orders of magnitude faster than SO$_4$•$^-$ (8.0 × 10^5 M^{-1} s^{-1}) [63]. FFA reacts with ^{1}O$_2$ at a rate of 1.2 × 10^8 M^{-1} s^{-1}, but it should also be noted that FFA is also an efficient quencher for •OH (1.5 × 10^{10} M^{-1} s^{-1}). Thus, if •OH was the dominant reactive species, TBA and FFA should have similar inhibitory effects [64].
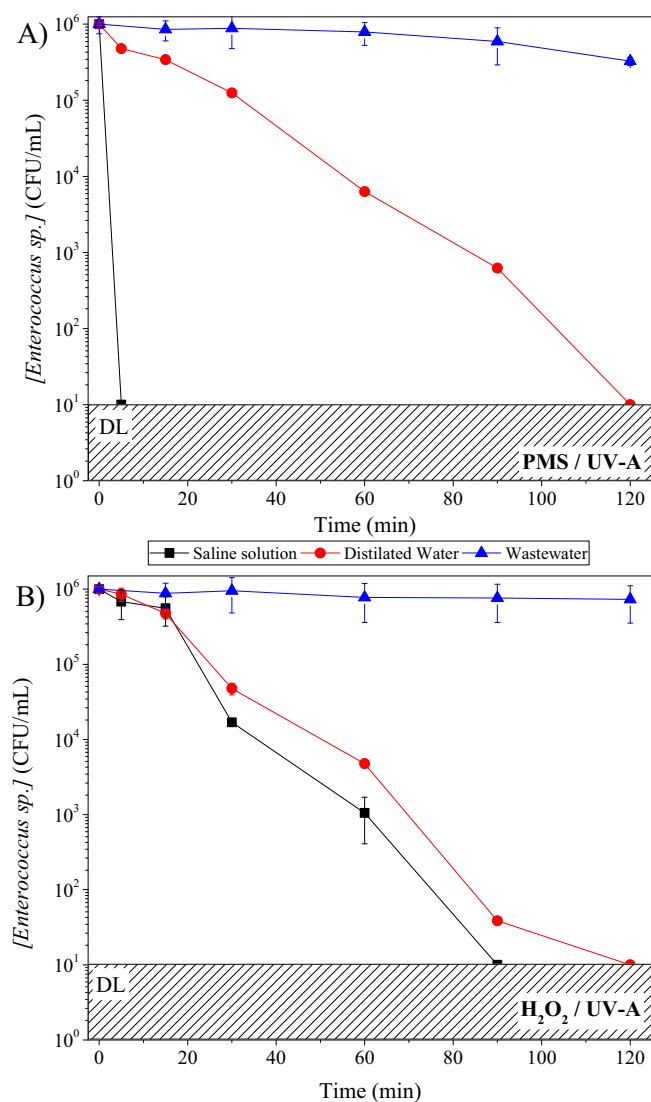

Fig. 4. Influence of the matrix on the photoactivation of PMS (A) and H$_2$O$_2$ (B) for the inactivation of *Enterococcus* sp. Experimental conditions: [PMS] = 0.05 mM; [H$_2$O$_2$] = 1.5 mM; pH = natural; Reactor = tubular reactor; Irradiation = UV-A.

All scavengers had a similar effect on the activation of PMS in DW. The efficiency of the treatment was reduced so that, after two hours, the concentration of microorganisms was only reduced by 1–2 log units (Fig. 5A). This shows that the •OH radical is mainly responsible for bacterial inactivation in this scenario, as it is the only radical that reacts with all the scavengers used. However, since inhibition is not complete, there is part of the disinfection that is not due to the action of any of the radicals studied, which could indicate the combination with non-radical pathways. Qi et al. (2020) obtained the same result when combining PMS and UV-A radiation for the inactivation of *Escherichia coli* [65]. Some [53] consider the existence of nonradical mechanisms for the disinfection or degradation of contaminants as one of the advantages of using PMS, as these mechanisms are less sensitive to scavenging by organic matter.

Performing scavenger experiments on the saline matrix confirmed that, as stated in Section 3.2, inactivation in this scenario is mainly a consequence of the generation of chlorinated species [Eqs. (1)–(2)]. Fig. 5B shows that none of the scavengers resulted in a pronounced decrease in the efficacy of the treatment, revealing that the reactive species studied play a minor role in disinfection. A closer look at the inactivation curves shows that all the scavengers slightly increased the time needed to complete the treatment from 5 to 15 min, with the use of FFA resulting in the slowest inactivation. Wen et al. (2019) also stated the greater involvement in chlorinated species disinfection compared to radicals in their study on the inactivation of fungi by a PMS/Cl$^-$ system [20].

The hydroxyl radical is mainly responsible for the inactivation of *Enterococcus* sp. in the scenario DW/H_2O_2/UV-A. When MeOH and FFA were added to the treatments, very similar results were obtained (Fig. 6A). Treatment was inhibited so that, when using MeOH, the disinfection ratio was 0.6 log after 90 min. A slightly stronger inhibition was observed when using FFA as a scavenger, as only 0.5 log units decreased the concentration of microorganisms. This indicates that $^1O_2$ also plays a role in treatment, although less than •OH. Most studies reporting the use of H_2O_2/UV-A for the removal of pollutants overlook the possible effect of radicals other than •OH. In fact, a recent study by Kim et al. (2021) addressed the occurrence of unknown reactive species in UV/H_2O_2 systems, and the presence of singlet oxygen was reported
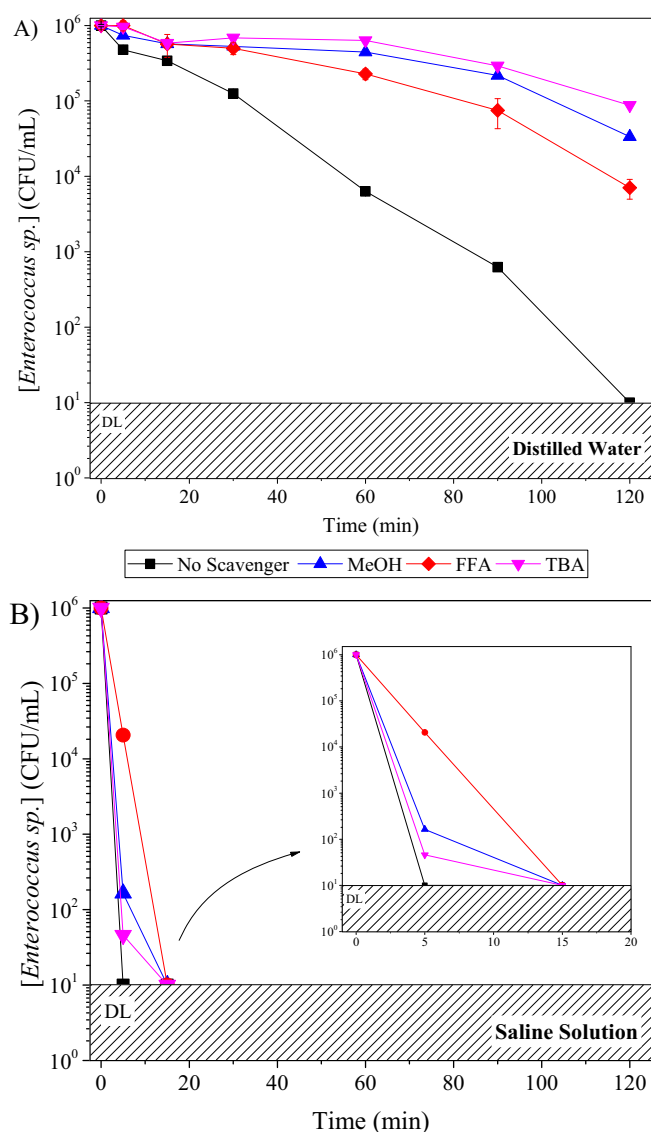

Fig. 5. Influence of radical scavengers on PMS-driven *Enterococcus* sp. inactivation in A) distilled water and B) saline solution. Experimental conditions: [PMS] = 0.05 mM; [PMS]: [Scavenger] = 1:20; pH = natural; Irradiation = UV-A; Reactor = Tubular reactor.
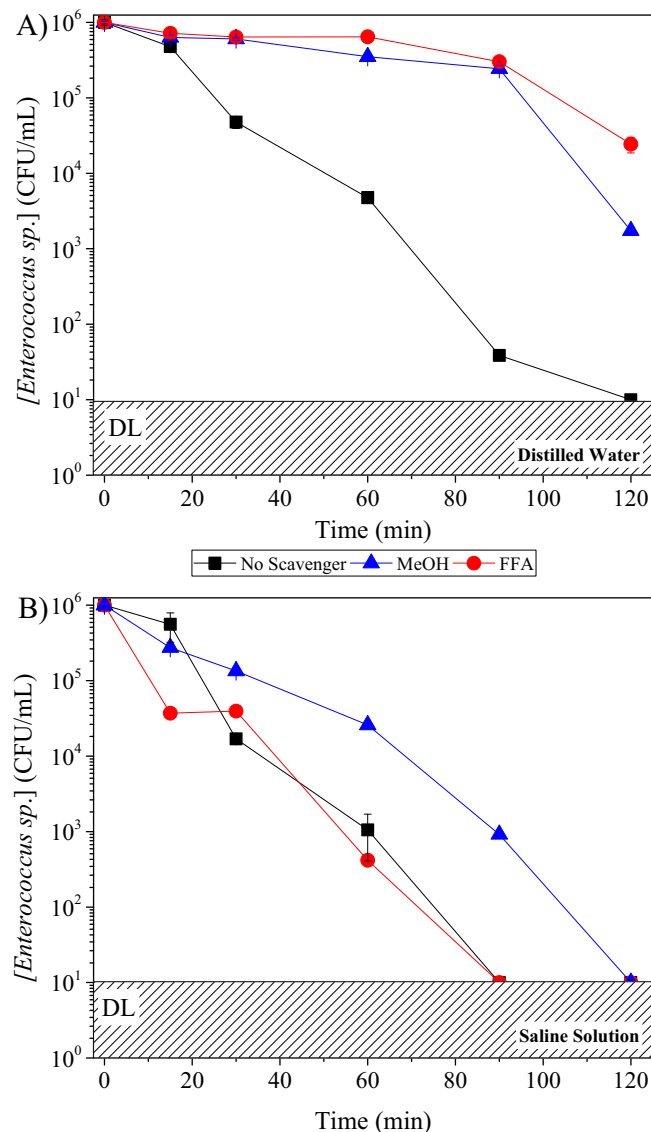
Fig. 6. Influence of radical scavengers on H_2O_2-driven inactivation of *Enterococcus* sp. in A) distilled water and B) saline solution. Experimental conditions: [H_2O_2] = 1.5 mM; [H_2O_2]: [Scavenger] = 1:20; pH = natural; Irradiation = UV-A; Reactor = Tubular reactor.

[66]. Disinfection increases significantly during the last part of the treatment, achieving an inactivation rate of 2.9 log and 1.9 log at 120 min when using MeOH and FFA, respectively.

Although the disinfection result is similar in the two matrices, the scavenger study reveals that the disinfection mechanism is different when treating water with the presence of Cl⁻. In this case, hydroxyl radicals do not play such a relevant role in treatment because, although the disinfection rate is slightly lower compared to the reference treatment when using MeOH as a scavenger, after 120 min the result achieved is the same.

3.3.2. Proposed inactivation mechanisms

Based on both the above findings and a critical revision of the scientific literature, an outline of mechanistic processes that might play a role on the inactivation of *Enterococcus* sp. have been proposed.

The effect of UV light on bacteria inactivation differs according to the UV source. In contrast to UV-C radiation, the emission in the UV-A range is not absorbed by bacteria' DNA but is capable of inactivating microorganisms by damaging their proteins or through the generation of internal reactive oxidant species [67]. In tests using radiation alone, it has been observed that the dose used is not sufficient to disinfect on its own, although it is expected that throughout treatment it will affect the cell membrane.

By combining UV-A with H_2O_2, hydroxyl radicals can be generated in the extracellular environment and are capable of attacking and destroying the cell membrane, leading to leakage of intracellular material and the death of bacteria. It has been confirmed by scavenger experiments, which suggests that •OH is mainly responsible for the inactivation of *Enterococcus* sp. in the H_2O_2/UV-A system. Additionally, the cell structure might be weakened due to UV-A exposure. It would allow diffusion of inactivated H_2O_2 into the cell, which can produce an intracellular Fenton reaction with the iron naturally present inside the cell. It might leads to an enhancement of bacterial inactivation [29]. This is reflected in an increase, in the last few minutes, of the disinfection rate (Fig. 6A) that is not dependent on generated radicals, as seen previously. Moreover, this effect is accentuated by increasing the incident radiation flux, which explains why this effect was not observed in the batch reactor.

Something similar might happens in the PMS/UV-A system. Again, it has been seen that the most influential radical in microorganism inactivation is •OH, although some involvement of the sulfate radical must also be assumed. Like •OH, SO_4•⁻ has a strong oxidative capacity, capable of oxidizing cell membrane lipids and destroying their proteins [68]. As mentioned above, UV-A radiation causes stress on the cell that allows reactive species to penetrate through the membrane and reach the cytoplasm, resulting in the oxidation of cytoplasmic proteins and causing the death of bacteria [65]. In addition to radicals, there are other ways to oxidize the cytoplasmic membrane that can be related to other forms of PMS action. On the one hand, direct oxidation of PMS on the components of the cell wall is possible [69]. On the other hand, Berruti et al. (2021) also propose the possibility of sulfate penetration through the cell membrane, facilitating its reaction with the metals naturally present inside the cell. From this, sulfate radicals can also be generated intracellularly, damaging internal cell components. This approach is based on the fact that sulfate (SO_4^{2-}), which is present in Oxone (PMS source used in the present study), is one of the preferred sources of sulfur for cells and its uptake occurs through well-defined membrane protein transporters [69].

A very different scenario appears in the PMS/UV-A/Cl⁻ system, where all disinfection is a consequence of the chlorine compounds generated. Wen et a. (2019) studied the effect of the PMS/Cl⁻ system on the inactivation of various fungal species, determining that the cell membrane is destroyed in treatment, with the intracellular material discharged into the medium [20]. Chemical compounds with high oxidative potential (such as free chlorine) have been shown to break the chemical bonds in the molecules that make up the cells [68].
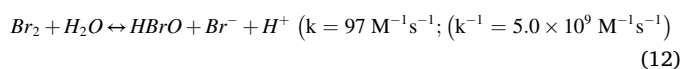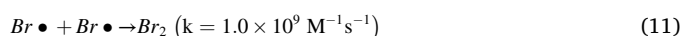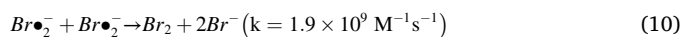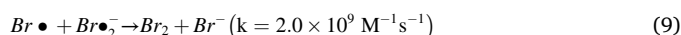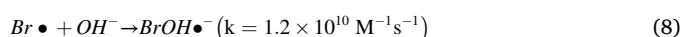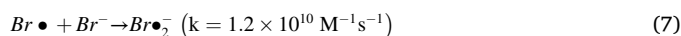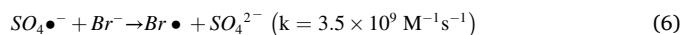
During treatment with H_2O_2/UV-A/Cl⁻ it is also observed that hydroxyl radicals do not play any or only a residual role in the inactivation of microorganisms. As with PMS, in this treatment, chlorinated compounds might play a role in bacterial inactivation. However, on this occasion, their generation is conditional on the prior generation of hydroxyl radicals, as explained in Section 3.2. It would explain why a slower disinfection rate is observed than in the PMS/UV-A scenario, where PMS can directly react with chlorides, what is not possible with H_2O_2. Therefore, it can be expected that inactivation will occur via two routes: direct oxidation from ClOH•⁻ (Eqs. (4) and (5)) and intracellular oxidation, as previously explained.

In Fig. 7, an attempt has been made to synthesise the inactivation mechanisms proposed for the different scenarios studied.

3.4. Influence of inorganic anions

The composition of the matrix in which the treatments take place has been shown to have a great influence on their effectiveness. The presence of certain compounds, such as organic matter or carbonates, which are easily found in municipal wastewater, has been extensively studied [31]. However, there is little to no information on the implications of the presence of other inorganic compounds that frequently appear in industrial wastewater at high concentrations. In addition, most studies on the influence of the matrix have evaluated the degradation of pollutants, but it is also necessary to study the effect of inorganic ions on the inactivation of microorganisms. For this reason, the influence of five anions at the same concentrations of 5 mM (NO_2^-, NO_3^-, F⁻, Br⁻, PO_4^{3-}) has been analysed for optimized treatments. The concentration of 5 mM for each anion was selected as the minimum concentration necessary to observe positive or negative effects in the selected treatments. Tests were carried out to verify that these compounds are not harmful to microorganisms in the concentration used (data not shown).

Fig. 8A shows the influence of the anions on the activation of PMS for the inactivation of *Enterococcus* sp. A large increase in the efficiency of the process was observed when treated with 5 mM Br⁻ in water. While in the reference treatment (DW) the detection limit was reached after 120 min, the presence of bromides in the matrix increased the reaction rate so that the detection limit was reached in half an hour. This behaviour resembles that observed in the presence of chlorides. A study by Xie et al. revealed that both SO_4•⁻ and PMS can transform Br⁻ into bromine radicals, free bromine, and other brominated species such as HBrO (Eqs. (6)–(12)) [70]. These newly generated reactive species are responsible for such a rapid inactivation of the bacteria. However, the presence of this new species can lead, in the presence of organic matter, to the formation of potentially harmful DBPs. In these circumstances, the use of AOPs loses one of its main advantages, the nonformation of DBPs.

$$SO_4 \bullet^- + Br^- \rightarrow Br \bullet + SO_4^{2-} \; \left(k = 3.5 \times 10^9 \; M^{-1}s^{-1}\right) \tag{6}$$

$$Br \bullet + Br^- \rightarrow Br \bullet_2^- \; \left(k = 1.2 \times 10^{10} \; M^{-1}s^{-1}\right) \tag{7}$$

$$Br \bullet + OH^- \rightarrow BrOH \bullet^- \left(k = 1.2 \times 10^{10} \; M^{-1}s^{-1}\right) \tag{8}$$

$$Br \bullet + Br \bullet_2^- \rightarrow Br_2 + Br^- \left(k = 2.0 \times 10^9 \; M^{-1}s^{-1}\right) \tag{9}$$

$$Br \bullet_2^- + Br \bullet_2^- \rightarrow Br_2 + 2Br^- \left(k = 1.9 \times 10^9 \; M^{-1}s^{-1}\right) \tag{10}$$

$$Br \bullet + Br \bullet \rightarrow Br_2 \left(k = 1.0 \times 10^9 \; M^{-1}s^{-1}\right) \tag{11}$$

$$Br_2 + H_2O \leftrightarrow HBrO + Br^- + H^+ \left(k = 97 \; M^{-1}s^{-1}; \left(k^{-1} = 5.0 \times 10^9 \; M^{-1}s^{-1}\right)\right) \tag{12}$$

Both the presence of fluorides and the presence of nitrites seem to have the opposite effect, decreasing the efficiency of the treatment. After 120 min, the concentration of microorganisms was reduced by only 2.51 log in the presence of NO_2^-. Although Jaemin Chai et al. (2021) reported
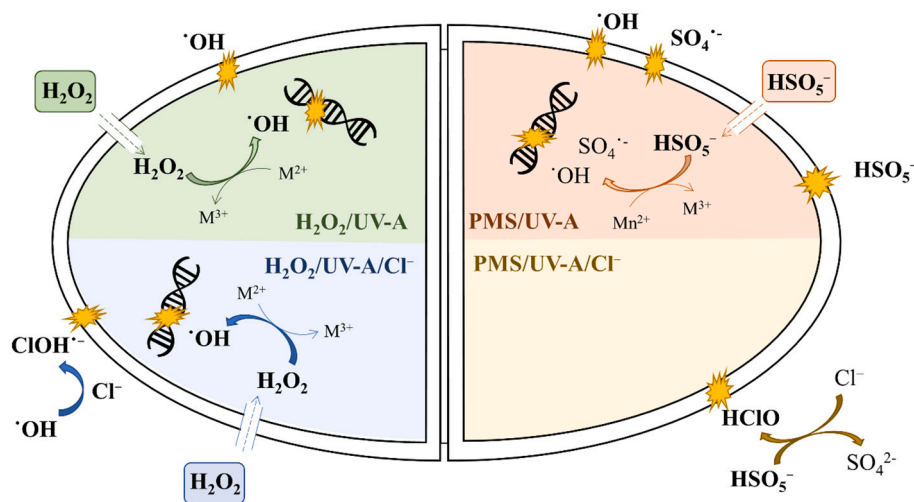
Fig. 7. Mechanisms proposed for inactivation of *Enterococcus* sp. through the treatments studied.

that low concentrations of this ion can promote radical generation in catalytic processes [71], the presence of excess NO_2^- ions can act as a scavenger of sulfate radicals (k = $8.8 \times 10^8 M^{-1} s^{-1}$) [23]. More notable was the decrease in the presence of F^- since, at the same time, the initial concentration is reduced by only 1.68 log. To our knowledge, no research has yet studied the interaction of PMS or sulfate radicals with F^-. From the observed response, it can be deduced that fluorides compete with microorganisms for radicals, thus decreasing the effectiveness of the treatment.

Finally, neither PO_4^{3-} nor NO_3^- had a considerable effect on the treatment. In the study of the catalytic activation of PMS, phosphates, as well as nitrates and nitrites, have been found to have an inhibitory effect on treatment [72]. However, this negative effect is attributed to the competition of anions for active centers on the surface of the catalyst used, and not by radical reaction due to the low reaction rate between NO_3^- and $SO_4^{\bullet-}$ (k = $2.1 M^{-1} s^{-1}$) [23]. On the other hand, Ao et al. (2018) [73] determined that the removal of ciprofloxacin by PMS/UV-A was enhanced by the presence of NO_3^-. This serves to illustrate that it is necessary to study each specific case to know how the pollutant and matrix components would interact.

The results show that the treatment based on H_2O_2 activation is less affected by variations in matrix composition (Fig. 8B). No differences were observed from the reference (DW) when the treatment was carried out in the presence of Br^-, F^-, or PO_4^{3-}. Efficiency again decreased in the presence of nitrites. A slowdown in bacterial inactivation was observed during the first part of the treatment, but the same result was achieved in the reference treatment after 120 min, reaching the detection limit. High concentration of NO_2^- also led to a lower degradation of ibuprofen in the study by Wang et al. (2021) [74]. This ion reacts with the hydroxyl radical (k = $1 \times 10^{10} M^{-1} s^{-1}$) leading to the less reactive $NO_2^\bullet$ radical. On the contrary, an improvement in bacterial inactivation was observed with the addition of 5 mM NO_3^-, reaching the detection limit in 90 min in the H_2O_2/UV-A system. These inorganic species have been reported to generate $^\bullet OH$ and $NO_2^\bullet$ under direct UV photolysis (Eqs. (13)–(17)), consequently increasing the degradation of some compounds [75]. Although this process can occur in both systems studied, the results show that it is enhanced in the H_2O_2/UV-A system.

$$NO_3^- + h\nu \rightarrow NO_2^- + O \tag{13}$$

$$NO_3^- + h\nu \rightarrow NO_2^\bullet + O^\bullet - \tag{14}$$

$$O + H_2O \rightarrow 2\dot{O}H \tag{15}$$

$$O^{\bullet-} + H_2O \rightarrow \dot{O}H + HO - \tag{16}$$

$$2NO_2^\bullet + H_2O \rightarrow NO_2^- + NO_3^- + 2H^+ \tag{17}$$

These results suggest that the H_2O_2/UV-A system may be less dependent on matrix composition than PMS-based treatments, with the presence of nitrites being a contraindication to the application of either process. Furthermore, the use of advanced oxidation processes based on the formation of sulfate radicals would also be contraindicated for waters with a high concentration of bromides, despite the higher inactivation rate.

4. Conclusions

Both the PMS/UV-A and H_2O_2/UV-A systems have been proven to successfully inactivate *Enterococcus* sp. A higher incident radiation flux is achieved in the tubular reactor compared to the batch configuration, enhancing treatment performance.

Optimized treatments in distilled water are effective when applied in a saline matrix. However, they have not been successful in transferring said processes to wastewater. This corroborates the belief that it is necessary to study the behaviour of the treatments directly in wastewater, and optimization in a simpler matrix may be unnecessary, as the results obtained are, in many cases, not reproducible in more complex matrices.

The use of scavengers confirms that, when a PMS treatment is applied in a medium with a high content of chlorides, the effect of radicals is minor. In a simpler medium, without the presence of ions, the predominant main radical involved in disinfection with UV-A activated PMS is $^\bullet OH$. The same applies to the H_2O_2/UV-A system. Although the presence of chloride has been reported to inhibit the degradation of contaminants, its interaction with hydroxyl radicals results in more selective species that could enhance the disinfection efficiency.

Although the presence of high concentrations of Br^- leads to very rapid bacteria inactivation, this is due to the formation of free bromine that, in the presence of organic matter, can give rise to potentially hazardous by-products. Furthermore, the presence of F^- and NO_2^- negatively affects the performance of the treatment based on sulfate radicals. Therefore, in these three scenarios, the use of H_2O_2-based treatments is recommended. However, the PMS concentration needed to achieve complete disinfection is lower than that of H_2O_2. Therefore, when applying these treatments under real conditions, more economic and environmental studies would be necessary to determine the most appropriate treatment in each situation.
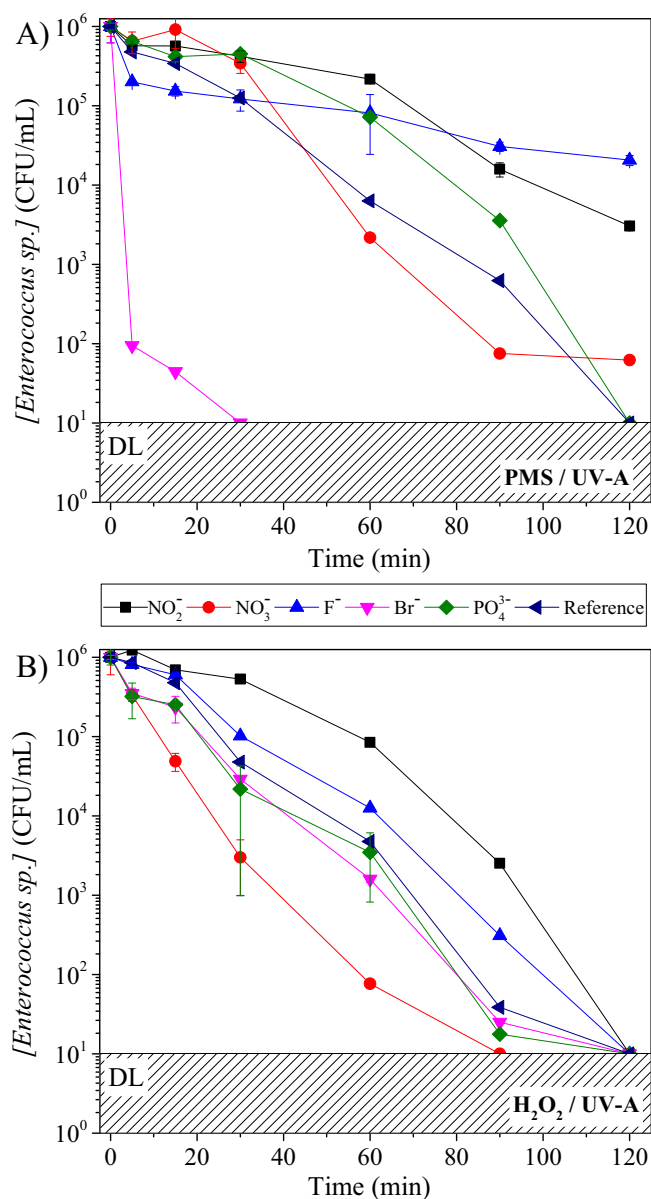
Fig. 8. Influence of the presence of inorganic anions on PMS (A) and H_2O_2 (B) photoactivation for *Enterococcus* sp. inactivation. Experimental conditions: [PMS] = 0.05 mM; [H_2O_2] = 1.5 mM; pH = natural; Matrix = DW; Reactor = tubular reactor; Irradiation = UV-A.

Declaration of competing interest

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.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jwpe.2022.102740.

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