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Pilot-scale regeneration of wastewater through intensified sulfate radical-based advanced oxidation processes (PMS/UV-A, PMS/H_2O_2/UV-A, and PMS/O_3): Inactivation of bacteria and mechanistic considerations

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ABSTRACT

This research addresses the application of advanced oxidation processes (AOPs) for wastewater reclamation at pilot scale, one of the main limitations usually observed in this type of technology. Although interest in sulfate radical-based AOPs (SR-AOPs) has increased considerably in recent years, pilot-scale application studies are very scarce. The generation of free radicals by activation of peroxymonosulfate (PMS) can be enhanced by the introduction of UV-A radiation, or other oxidants such as hydrogen peroxide (H_2O_2) or ozone (O_3), increasing the efficiency of the processes with lower reagent consumption.

The combination of 0.5 mM PMS and 0.25 g·h^{-1} O_3 was the fastest process in inactivation of *Enterococcus faecalis*, achieving inactivation in less than 45 min. Significant synergies were also observed for the combination of PMS, H_2O_2 and UV-A radiation, achieving total inactivation in less than 120 min, a performance significantly lower than that of the PMS/O_3 system. Mechanistic studies showed that the sulfate radical ($SO_4^{\bullet-}$) was responsible for bacterial inactivation in the PMS/O_3 system, while in the PMS/H_2O_2/UV-A system the predominant species varies according to the molar ratio of the oxidants. Thus, the hydroxyl radical ($^{\bullet}OH$) is predominant in a 1:1 ratio, and $SO_4^{\bullet-}$ is predominant in a 1:3 ratio. This phenomenon occurs because an excess of PMS acts as a sink for radicals, preventing their interaction with bacteria.

The treatments studied have been shown to be effective in the simultaneous elimination of several pathogenic microorganisms such as *Enterococcus faecalis*, *Escherichia coli,* and *Staphylococcus aureus*, making this technology an alternative to conventional disinfection treatments.

1. Introduction

Population growth, changing consumption patterns, and economic development have led to a six-fold increase in water use over the last 100 years. Estimates predict that this increase will continue at a steady pace, so that by 2050 water consumption will have increased by up to 30% over the current level [1], and it is expected that by 2050 more than 52% of the world's population will live in regions strained by water [2]. A third problem that adds to existing is the declining quality of available water, with an estimate that more than 80% of wastewater (WW) is discharged into the environment untreated [3].

Reclaimed wastewater is considered a nonconventional water resource and can be used for industrial, urban, environmental, or recreational purposes. Spain is among the 10 countries in the world that reuse the most water [4], thanks to the high purification capacity available, which was 8,130 hm^3·yr^{-1} (2.15 billion of gallons·yr^{-1}) in 2017 [5]. Although Spain is one of the few European countries with national legislation on the reuse of reclaimed water (Royal Decree 1620/2007), this must be modified, because recently it was approved a European Regulation (EU) 2020/741 established minimum requirements for water reuse, with the aim of promoting water reuse in all member states. This new legislation has been in force since June 2020, but will only be applicable as of June 26, 2023.

In recent years, advanced oxidation processes (AOPs) have become a plausible tertiary treatment for wastewater treatment plants (WWTPs) by achieving high efficiency in the removal of organic and microbiological pollutants from wastewater [6,7]. Furthermore, the formation of significant concentrations of disinfection by-products (DBP) has not

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been observed in oxidation processes dominated by hydroxyl radicals ($HO^{\bullet}$) [8] as in conventional disinfection processes, such as in chlorination. Sulfate radical-based advanced oxidation processes (SR-AOPs) are proving to be a good alternative due to the numerous advantages of sulfate radicals ($SO_4^{\bullet-}$) with respect to $HO^{\bullet}$ [9], such as a higher oxidation potential (2.5–3.1 V), they are more selective and efficient, react efficiently with organic compounds over a wide pH range of 2–8, and the half-life of sulfate radicals is 30–40 μs, which allows them to have a more stable mass transfer and better contact with target compounds [10].

Peroxymonosulfate (PMS; HSO_5^-) is the most effective specie for the formation of sulfate radicals. Activation of PMS involves the generation of both $SO_4^{\bullet-}$ and $HO^{\bullet}$ [11]. One of the most efficient processes for PMS activation is energy delivery through radiation application, including UV, gamma, and ultrasound [12–15]. Although UV radiation is the most effective way to activate (especially using a wavelength of 254 nm) [16], recently, an increasing number of studies are investigating the activation of PMS by solar radiation, in which case the wavelengths used vary between UV-A and visible radiation [17,18].

On the other hand, the combination of PMS with other oxidants to generate radicals has also given good results. In recent years, the application of the PMS/O_3 system has been studied in the degradation of various pollutants that are recalcitrant to ozone treatments [19–26], or in the inactivation of microorganisms [27]. In this case, degradation has been observed due to the generation of $SO_4^{\bullet-}$ and $HO^{\bullet}$, in addition to the simple effect of ozone [28]. Some authors have also reported synergies when combining PMS and H_2O_2 [29–31]. Despite this, very few articles have reported the application of this system to wastewater treatment, so more research is needed to gain an in-depth understanding of the reactions that take place in this system, as well as its feasibility.

Although SR-AOPs have gained interest in the scientific community in recent years, their development is practically limited to laboratory-scale studies. This makes it a less mature technology than other AOPs, such as the Fenton process. Although recent years have seen a shift in the focus of SR-AOP research towards more concrete and specific cases [32], there are still very few pilot or full-scale applications [13,33–37].

The main objective of this study is to evaluate the efficacy in the elimination of pathogenic microorganisms through the application of advanced pilot-scale oxidation processes based on the generation of sulfate radicals. Under these conditions, different treatments have been evaluated that combine the use of PMS in combination with radiation and with other oxidants (H_2O_2 and O_3) have been evaluated. In the first approach, optimisation of the treatments and operating conditions is proposed on simulated wastewater samples inoculated with *Enterococcus faecalis,* determining the main species involved in the processes.

2. Materials and methods

2.1. Chemicals

Potassium peroxymonosulfate (PMS) was used as the central oxidant in the research, using concentrations between 0.01 mM and 1.5 mM. This compound is marketed by Sigma-Aldrich as a triple potassium salt ($KHSO_5$-0.5$KHSO_4$-0.5K_2SO_4; Oxone®). Hydrogen peroxide (H_2O_2, 30% v/v; Chem-Lab) at concentrations ranging from 0.1 to 3 mM was also evaluated.

Radical scavengers were used to give an idea of the reactive species involved in the treatments studied. Methanol (MeOH, CH_3OH, Chem-Lab) was used as radical scavenger of $HO^{\bullet}$ and $SO_4^{\bullet-}$ and *tert*-Butyl alcohol (TBA, $C_4H_{10}O$, Scharlau) as the $HO^{\bullet}$ [38,39]. These compounds were used at concentrations ranging from 1 to 30 mM, depending on the concentration of the oxidant used in the treatment. The influence of scavengers on the survival of bacteria was previously tested at the concentrations under study, and no effect on the bacterial population was observed (results not shown).

2.2. Wastewater sample

Simulated wastewater (SWW) with physicochemical characteristics similar to those of the secondary effluents of WWTP was used in this research. The composition of SWW was meat peptone (Scharlau; 32 mg/L), meat extract (Scharlau; 22 mg/L), urea (Scharlau; $CO(NH_2)_2$; 6 mg/L), NaCl (Scharlau; 7 mg/L), $CaCl_2{\cdot}2H_2O$ (Scharlau; 4 mg/L), $MgSO_4{\cdot}7H_2O$ (Scharlau; 2 mg/L), K_2HPO_4 (Scharlau; 28 mg/L) and tap water. This poses a risk, as the residual chlorine present in tap water could contribute to the elimination of bacteria, making it impossible to know the real effect of the treatments used. To avoid this, tap water was collected in 100 L drums and left to stand for 24 h. To ensure complete evaporation, the free chlorine concentration was measured using a multiparametric photometer (Hanna HI83399), using HI93701-F reagent kits of the same brand. The main physicochemical characteristics of the SWW samples are summarised in Table S1 (supplementary material).

2.3. Microbiological analysis

During the investigation, different species of microorganisms were used to inoculate SWW samples to reach a concentration of around 10^6 $CFU{\cdot}mL^{-1}$. Three different bacteria, two Gram-positive and one Gram-negative, were used. For this purpose, commercial strains of *Enterococcus faecalis* (ATCC® 29212TM), *Escherichia coli* (ATCC® 25922TM) and *Staphylococcus aureus* (ATCC® 6538TM) were purchased in the form of MiStraCon®Swabs2 microorganism pellets (Scharlau). Commercial strains of *E. faecalis*, *E. coli* and *S. aureus* stored in cryovials in a freezer, were individually growth in 50 mL of Luria Bertani broth (Scharlau; Spain) and incubated for 24 h (37 °C). After this time, each bacterial suspension was centrifuged for 15 min at 4200 rpm and the pellets were resuspended in the same volume of saline solution (NaCl 0.9%) and stored in the refrigerator for later use.

The concentration of bacteria during the treatments was determined using the drop plate method [40] through a serial 10-fold dilution in sterile saline solution (NaCl 0.9%), and when needed, followed by the spread plate method (*Standard Method 9215C*) to increase the detection limit (DL), i.e., 100 CFU/mL and 10 CFU/mL, respectively. *Quantification of E. faecalis* was performed on selective culture medium Slanetz & Bartley agar (Condalab; Spain), *E. coli* on MacConkey agar (Scharlau; Spain), and *S. aureus* on hypersaline Mannitol agar (Scharlau, Spain). Finally, the determination of total aerobic bacteria was made using Plate Count Agar (Scharlau, Spain). The colonies formed were counted after incubation at 37° C for 24 h for *Escherichia coli* and 48 h for the rest of the microbiological parameters. The analyses were performed in triplicate and the standard deviation of the results was calculated, plotted as error bars.

2.4. Pilot plant

In this work a pilot plant model Photobench LED275-0.8/LED365-16/450-16a developed by the company APRIA Systems has been used. Figure S1 (Supplementary Material) shows a scheme and front and back pictures of the plant. The system has a single feed pump (CM 1–3; Grudfos), whose main function is to establish continuous flow inside the installation. Therefore, the pump is fed with water from the feed tank (50 L; Etatron) and drives it through the different modules for treatment. This equipment has a nominal flow rate of 1,700 $L{\cdot}h^{-1}$ and a maximum operating pressure of 16 bar. To optimise the efficiency of treatment and protect the most sensitive parts of the system, the installation has a safety filter (NW25, Cintropur) placed downstream of the feed pump that prevents the passage of solids with a diameter greater than 25 μm.

The main elements of the plant are the two ring photoreactors arranged in parallel. Both photoreactors consist of two concentric tubes, with the LED lamps located in the inner tube, while the water to be treated flows through the outer tube. One of them has an LED lamp that

emits ultraviolet radiation in the UV-C region, while the other has an LED lamp that emits both ultraviolet radiation in the UV-A region and in the visible spectrum (vis). The UV-C LED lamp consists of a total of 80 LEDs ($\lambda = 265–285$ nm, $\lambda_{peak} = 275$ nm, $I_{rad} = 10.5$ mW·LED^{-1}) arranged in 4 rows. The UV-A/Vis LED lamp consists of 20 UV-A LEDs ($\lambda = 365–370$ nm, $I_{rad} = 1{,}200$ mW) and 20 Vis LEDs, arranged alternately in 4 rows. Thus, the theoretical maximum radiation emitted by the UV-C, UV-A, and Vis lamps is 93 W·m^{-2}, 1,973 W·m^{-2} and 2,969 W·m^{-2}, respectively. However, the total irradiated power is not a fixed value but can be regulated in each test. Both reactors are made of borosilicate glass and are protected by a black polylactic acid housing. In addition, they also include an air-cooling system at the top equipped with a temperature probe, which preserves the irradiation potential and prolongs the lifetime of the LEDs. Due to the low resistance of glass, the maximum recommended operating flow rate in both reactors is 650 L·h^{-1}, with an associated maximum pressure of 1 bar. As it has the lowest maximum allowable pressure in the whole installation, it was this unit that limited the working flow rate during the treatments. Considering that the illuminated volume in the reactor is 500 mL, the hydraulic retention time is 2.77 s. However, it should be noted that this is a treatment carried out in continuous recirculation, so the residence time is equal to the duration of the treatment.

The installation also has an ozone generation unit. This offers the possibility of incorporating an ozonisation stage prior to photochemical treatment (regardless of the type of radiation selected), as well as using ozonisation alone as the main treatment. The ozonisation system consists of an ozone generation unit and a Venturi tube for in-line dosing of the generated ozone. The ozone generator (GHBZO3-E, ZonoSistem) produces an adjustable ozone dose, with a maximum flow rate of 2.5 g·h^{-1}. The output water from this unit can be sent to the photochemical reactors or directly back to the feed tank if a second treatment is not desired. Similarly, this unit may not be used if only a photochemical treatment is desired. To control the gases generated during this process, the plant also has an in-line air extractor with a Kosner activated carbon filter (model KE-100). This filter is located above the feed tank and allows for a maximum air flow of 198 m^3·h^{-1} (working at 2,200 rpm).

The installation also includes: (i) a temperature control system consisting of a heat exchanger, a thermostatised bath, and an external temperature probe. The plant has a programmable logic controller (PLC) to monitor, control and regulate the temperature and power consumed by the LED lamps. And (ii) an on-line controller consisting of a pH and temperature probe and an analytical transmitter that displays the value collected by the probe (both Mettler-Toledo).

3. Results and discussion

3.1. Baseline operating conditions

PMS has an oxidising capacity and therefore the ability to inactivate microorganisms at certain concentrations, even under dark conditions. Therefore, to select the working PMS concentration under these new conditions, different concentrations of oxidant were evaluated in darkness in the pilot plant and using SWW samples, obtaining the results shown in Fig. 1. For the lowest concentrations evaluated (0.10 and 0.25 mM) no significant effect on the bacterial population was observed. A certain disinfectant power starts to be appreciated when increasing the reagent dose to 0.50 mM, achieving an inactivation rate of almost 4 logarithmic reduction value (LRV) after two hours of treatment when the concentration evaluated was 1.50 mM. Apparently, no noticeable differences are observed between the different concentrations of PMS used, especially in the first 60 min of reaction because, although PMS is a strong oxidant, with a redox potential of 1.82 V, it reacts directly with pollutants with a low reaction rate [11]. Thus, during the first reaction times, no appreciable changes can be seen, even if the concentration is high, and it is with the passage of time that the differences between concentrations can begin to be appreciated.

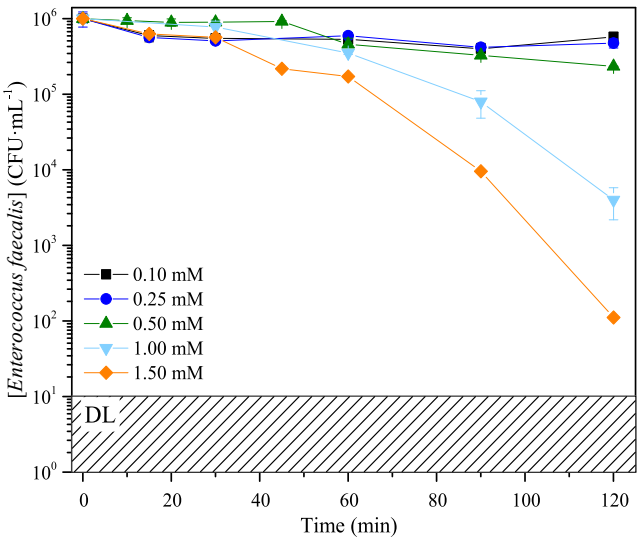

Fig. 1. Influence of PMS concentration on the inactivation of *E. faecalis* at the pilot scale. Experimental conditions: Matrix = SWW; pH ≈ 7. DL: Detection Limit.

The disinfectant power of PMS is explained by its direct interaction with the cell wall, which is able to oxidise its components. On the other hand, Berruti et al. [7] also proposed the possibility of sulfate penetrating through the cell membrane, facilitating its reaction with the metals naturally present inside the cell. From this, sulfate and hydroxyl radicals can also be generated intracellularly, damaging the internal components of the cell.

Following a review of the literature, it was confirmed that the concentrations of PMS used in treatments such as the one proposed here are very disparate, with good disinfection or contaminant removal results obtained for concentrations ranging from a few μmol·L^{-1} [41,42] to doses as high as 32 mM [43]. However, the reagent doses most frequently used are in the range of 0.5 to 2 mM [44–46], so it was decided to discard the two smallest concentrations, evaluating photochemical activation for all others.

The first PMS activation method evaluated was photochemical activation by UV-A radiation. Although PMS does not have a significant absorbance in the UV-A region, it has been shown to be effective for wastewater treatment.

On the other hand, the influence of radiation on microbial viability is well known and cannot be discarded as a potential factor of inactivation. Therefore, the mere effect of radiation intensities from 60 to 1,900 W·m^{-2} emitted by the LED lamps on the population of *E. faecalis* was assessed. Fig. 2 shows the results obtained, and none of the intensities evaluated had a significant disinfectant effect on the population, with a decrease in the concentration of *E. faecalis* of 0.5 log units after two hours of treatment at the maximum intensity and, therefore, selecting 1,900 W·m^{-2} as the working intensity for PMS activation. This result is consistent with other studies in the literature, demonstrating that wavelengths in the UV-A spectrum are not effective in the inactivation of other microorganisms such as *E. coli*, *S. aureus,* or *B. mycoides* [47–49]. This is because, unlike UV-C radiation, emission in the UV-A range is not absorbed by the DNA of bacteria, although it is possible to inactivate microorganisms by damaging their proteins or generating internally reactive oxidant species [50]. This is why it has been observed that the doses used are not sufficient to disinfect, although it is expected that over the course of the treatment it will affect the cell membrane.

The results derived from the combination of PMS with UV-A are shown in Fig. 3. As can be seen, the PMS/UV-A system did not generate obvious synergies for the 1.00 mM and 0.50 mM concentrations. However, the result was different when increasing the dose to 1.50 mM, as its combination with UV-A resulted in a treatment capable of reducing the

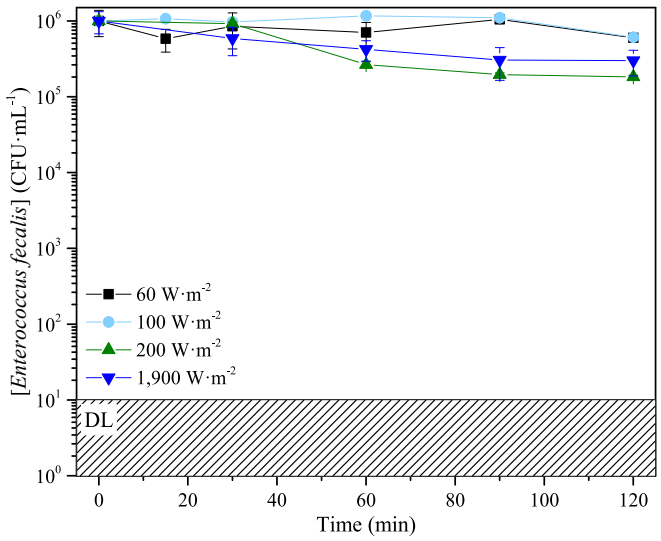

Fig. 2. Influence of UV-A radiation intensity on the inactivation of *E. faecalis* at a pilot scale. Experimental conditions: Matrix = SWW; pH ≈ 7. DL: Detection Limit.

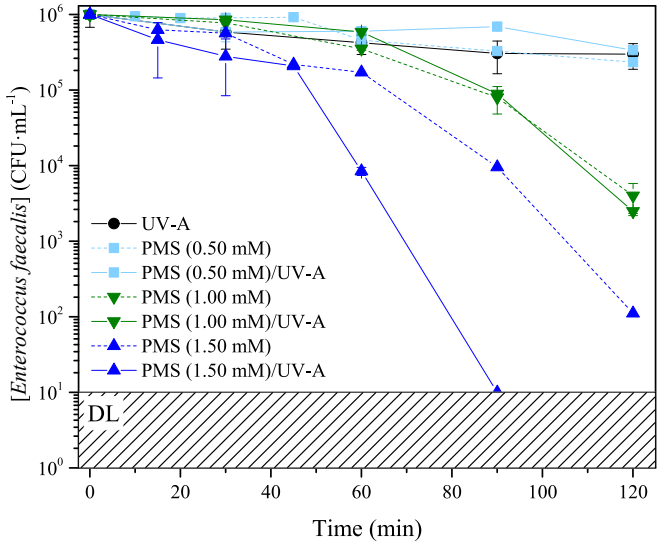

Fig. 3. Influence of PMS concentration on the inactivation of *E. faecalis* by PMS/UV-A system applied at pilot scale. Experimental conditions: Matrix = SWW; pH ≈ 7; Radiation intensity = 1,900 W·m^{-2}. DL: Detection Limit.

bacterial population to DL in 90 min. This result is slightly better than that obtained by Venieri et al. [49] for the elimination of *E. coli* and *E. faecalis*, although in that work PMS was not used as an oxidant but persulfate (PS). A 1.10 mM concentration of this compound, combined with UV-A radiation, allowed the inactivation of 10^6 CFU·mL^{-1} to the DL of both species in 180 min. After two hours of treatment, the bacterial population was reduced by approximately 1-LRV, compared to the almost 3-LRV eliminated in this work at the same time using a 1.00 mM concentration of PMS of 1.00 mM. However, this is due to the lower disinfectant power of PS compared to that demonstrated for PMS.

The synergies observed in the PMS/UV-A system could be due to the generation of $HO^{\bullet}$ and $SO_4^{\bullet-}$ radicals. Both have a strong oxidative capacity, capable of oxidising lipids from the cell membrane and destroying their proteins [51]. In addition, as mentioned above, UV-A radiation causes stress in the cell that could allow reactive species to penetrate through the membrane and reach the cytoplasm, potentially causing oxidation of cytoplasmic proteins and causing bacterial death. However, to determine which mechanism actually takes place, an in-depth assessment is needed, using, among other things, scavenger assays, as shown below.

3.2. Evaluation of PMS/H_2O_2/UV-A system

The addition of H_2O_2 to the system PMS/UV-A has been proposed to evaluate whether the interaction between the two oxidants can increase the disinfection kinetics. Although the combination of both compounds is not very widespread, research by Amanollahi et al. [29] shows that this system promotes synergies for the elimination of ammonia, also allowing the inactivation of bacteria present in the treated sample. On this basis and taking as reference the optimised PMS concentration of the previous section, a concentration of 1.50 mM H_2O_2 was selected so that a 1:1 M ratio between the two reagents was evaluated. Furthermore, to check the suitability of this choice, tests were carried out by evaluating different molar ratios, which confirmed that the 1:1 M ratio is the one that allows the best disinfection results to be obtained (Figure S2, Supplementary Material). Fig. 4 shows that at the selected working concentration, H_2O_2 does not show a disinfectant effect in the dark or under UV radiation. However, when the two oxidants are combined in the dark, a synergistic effect is produced that allows the inactivation of 5-LRV from *E. faecalis* (reaching the DL), compared to the 4-LRV obtained by PMS.

As shown in Equation (4), PMS and H_2O_2 can not only be activated by excitation by ultraviolet radiation (eq. 1–3) but are likely to react with each other giving rise to both sulfate and hydroxyl capable radicals, responsible for the subsequent inactivation of the microorganisms [29].

$$H_2O_2 + UV - A \rightarrow 2HO^{\bullet} \quad (1)$$

$$HSO_5^- + UV - A \rightarrow SO_4^{\bullet-} + HO^{\bullet} \quad (2)$$

$$SO_4^{\bullet-} + H_2O \rightarrow HO^{\bullet} + SO_4^{2-} \quad (3)$$

$$HSO_5^- + H_2O_2 \rightarrow SO_4^{\bullet-} + 3HO^{\bullet} \quad (4)$$

The efficacy of the treatment increases again when carried out under UV-A radiation, reducing the time needed to reach the DL from 120 to 60 min. Given the good results obtained when evaluating the PMS/H_2O_2/UV-A system, the possibility of reducing the PMS concentration

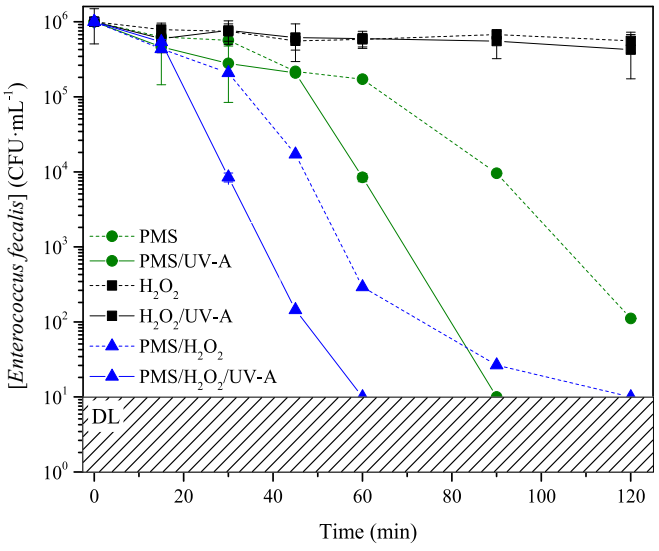

Fig. 4. Inactivation of *E. faecalis* by a combination of PMS, H_2O_2, and UV-A radiation at pilot scale. Experimental conditions: [PMS] = [H_2O_2] = 1.50 mM; Matrix = SWW; pH ≈ 7; Radiation intensity = 1,900 W·m^{-2}. DL: Detection Limit.

used was studied. As seen in the previous section, a dose of 0.5 mM PMS does not have a significant effect on the microbiological population. On the contrary, Fig. 5 shows how its combination with hydrogen peroxide and UV-A radiation inactivates bacteria up to the detection limit after two hours. Since none of the three elements individually has a relevant disinfectant power, it is possible to state that this combination provides the strongest synergistic effect.

Although complete inactivation of *E. faecalis* is achieved under these conditions, it cannot be overlooked that the time required to complete the treatment is significantly high compared to other treatments that reach complete disinfection in a few minutes, such as the use of UV-C radiation [34] or the combination of persulfates with some catalyst [52,53]. However, the reduction to one third of the PMS concentration could justify this increase in the duration of the process and, therefore, of the associated energy expenditure. Therefore, after completing this second stage of optimisation, three of the treatments evaluated have been selected as viable, as they are capable of inactivating *E. faecalis* up to the DL in less than two hours. PMS/UV-A with an oxidant concentration of 1.50 mM, PMS/H_2O_2/UV-A with concentrations of both reagents of 1.50 mM and, finally, PMS/H_2O_2/UV-A using a PMS concentration of 0.50 mM and three times H_2O_2.

3.3. Evaluation of PMS/O_3 system

PMS activation was also assessed in combination with ozone in the pilot plant. The process is carried out in the absence of UV-A radiation, because the results obtained initially with UV-A there was no significant improvement in performance to justify the increased energy cost of LED lamps (data not shown), so its incorporation into the process is discarded. A preliminary assessment of the disinfecting power of ozone was performed individually at three different doses, and the results obtained are shown in Fig. 6.

For all the flow rates evaluated, ozone is capable of inactivating, in less than 30 min, the bacteria present in the matrix up to the DL. As expected, an increase in dose implies a reduction in the time required, the treatment being completed in 15 min when the flow rate of O_3 injected was 1.25 g·h^{-1}. Since the objective of this section is to evaluate its combination with PMS, the lowest flow rate provided by the equipment (0.25 g·h^{-1}) was selected as the working flow rate and, under these conditions, the concentration of dissolved O_3 in the water was monitored. These results are shown in Figure S3 (Supplementary Material), in

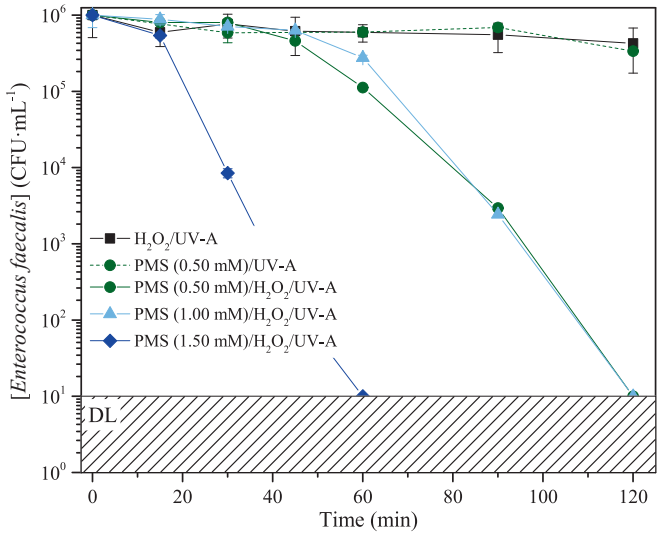

Fig. 5. Influence of PMS concentration on the inactivation of *E. faecalis* by PMS/H_2O_2/UV-A system at pilot scale. Experimental conditions: [H_2O_2] = 1.50 mM; Matrix = SWW; λ = 365 nm; Radiation intensity = 1,900 W·m^{-2}. DL: Detection Limit.

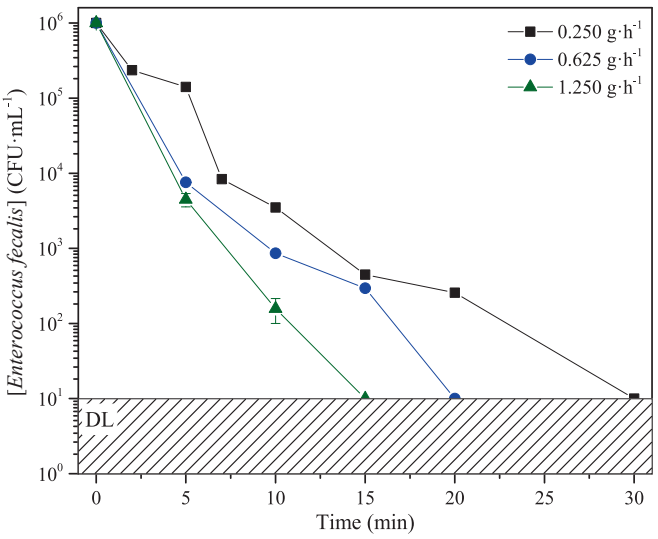

Fig. 6. Inactivation of *E. faecalis* by injection of different O_3 flow rates. Experimental conditions: Matrix = SWW; pH ≈ 7. DL: Detection Limit.

which during the first minutes of treatment, the concentration of ozone increases almost linearly and then stabilises at 0.6 mg·L^{-1} (12.5 μM).

The combination of ozone with PMS reduces the time required for disinfection by 10 min, reaching DL in 20 min (Fig. 7). The concentrations of PMS that provided the best results in previous sections, 0.5 and 1.5 mM, were selected for this study. As can be seen in Fig. 7, an increase in dose is not reflected in a higher inactivation rate, with the same results obtained for the two PMS concentrations evaluated.

Few studies are available in the literature assessing the influence of PMS dose. Excess PMS can react with the radicals generated in the interaction between PMS and O_3, acting as a scavenger and thus causing fewer reactive species. However, some authors have reached conclusions similar to those reached in this work. Gholikandi et al. [54] evaluated the application of PMS/O_3 for the stabilisation of the sludge and, increasing the dose of PMS used beyond 0.30 mM, observed a slight decrease in the removal efficiency of volatile solids. Also, Wu et al. [55] noted that, although for low PMS doses, increasing the PMS dose leads to an increase in the efficiency of prometon degradation, this trend is broken when doses exceed 0.30 mM (or 100 mg·L^{-1}).

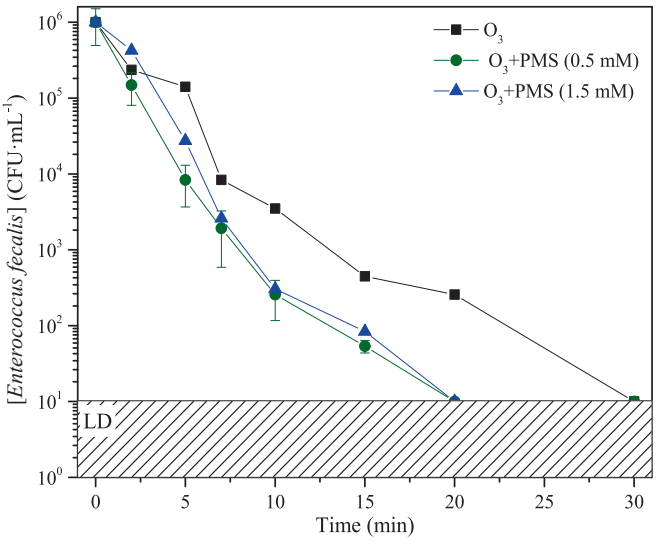

Fig. 7. Inactivation of *E. faecalis* by PMS/O_3 system applied at pilot scale. Experimental conditions: Matrix: = SWW; pH ≈ 7; O_3: 0.25 g·h^{-1}. DL: Detection Limit.

It is relevant to compare the results obtained with conventional treatments used in water disinfection, such as chlorination. Assuming that chlorination is not the ideal technology for wastewater disinfection due to the high amount of trihalomethanes that can be generated as a result of the reaction with organic matter. However, considering chlorination as a disinfection technology for drinking water treatment, the recommended chlorine doses range from 1 to 5 mg/L depending on the physicochemical characteristics of the water to be treated (turbidity, suspended solids, organic matter, etc.). To achieve a residual chlorine concentration between 0.3 and 0.5 mg/L, a contact time of 30 to 50 min is necessary, which would also ensure total inactivation of fecal bacteria [56].

Comparatively, the processes proposed in this research, especially the PMS/O_3 process, achieve complete elimination of *Enterococcus faecalis* in 20 min of contact time, with an ozone dose of 0.38 mg·L^{-1} and PMS dose of 0.5 mM. At first glance, the proposed systems are competitive in terms of efficiency compared to conventional chlorination systems, although comparative studies should be conducted under the same operating conditions (same water matrix, same experimental setup, etc.), but economic aspects should also be considered. It should be noted that the cost of PMS is relatively high ($1.36/mol) [33], and ozone generation requires energy consumption. In addition, residual effect studies of the PMS/O_3 system would need to be conducted, which, at first glance, would be much lower than what chlorination can provide.

3.4. Qualitative identification of radicals involved in treatments.

A series of tests were carried out with the aim of identifying the radicals involved in the different processes investigated. To this end, TBA and MeOH were used as scavengers and the results are shown in Fig. 8.

The addition of TBA during treatment using the PMS/UV-A system has not led to a significant variation in the inactivation kinetics of the bacteria, although in Fig. 8a it can be seen how this compound causes an increase of 30 min in the time required to reach DL. The addition of MeOH to the treatment has a greater effect. Although, again, the DL is reached after 2 h, the concentration of bacteria decays more slowly throughout the treatment.

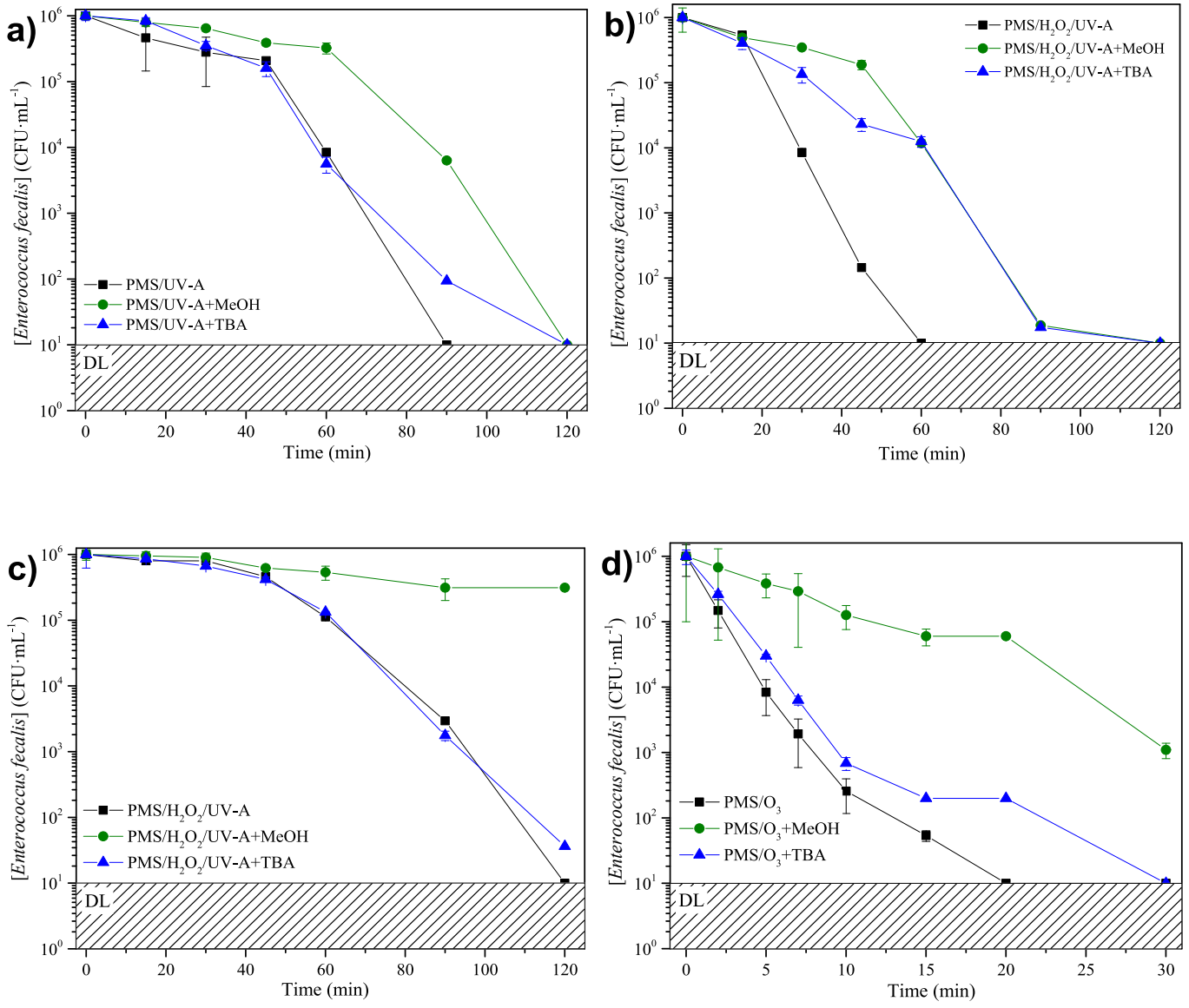

Fig. 8. Influence of scavengers on *E. faecalis inactivation* applied on a pilot scale using the system: a) PMS/UV-A ([PMS] = 1.5 mM; [MeOH] = [TBA] = 30 mM); b) PMS/H_2O_2/UV-A ([PMS] = [H_2O_2] = 1.5 mM; [MeOH] = [TBA] = 30 mM); c) PMS/H_2O_2/UV-A ([PMS] = 0.5 mM; [H_2O_2] = 1.5 mM; [MeOH] = [TBA] = 30 mM); d) PMS/O_3 ([PMS] = 0.5 mM; O_3: 0.25 g·h^{-1}; [MeOH] = [TBA] = 10 mM). Common experimental conditions: Matrix = SWW; pH ≈ 7; Radiation intensity = 1,900 W·m^{-2}; DL: Detection Limit.

These results indicate the presence of $SO_4^{\bullet-}$ in the system, while $HO^{\bullet}$ does not contribute significantly to the process. However, despite the slowing of disinfection kinetics, it cannot be overlooked that neither scavenger is able to completely inhibit treatment. From this it can be deduced that an important part of the inactivation is taking place, in this treatment, due to non-radical mechanisms. As can be seen in Fig. 1, PMS (even if not activated) has a non-negligible oxidising power. Therefore, when a high dose of this compound is used, an important part of disinfection is produced by direct oxidation. However, the existence of synergies with radiation indicates that PMS is not solely responsible for inactivation. UV-A radiation, although not capable of inactivating microorganisms on its own, may weaken or damage their cell membrane, thus facilitating their subsequent inactivation. Not surprisingly, this is the basis for solar disinfection treatments or SODIS [57,58].

Several authors have observed phenomena for the degradation of pollutants, such as those seen in this work. Cui et al. [42] evaluated the activation of PMS by radiation for the removal of sulfonamides, concluding that only 33% of the degradation was produced by radical action, the contribution of $SO_4^{\bullet-}$ being higher than that of $HO^{\bullet}$. Similarly, a study on the degradation of anatoxin-a found that more than 75% of the degradation achieved was due to mechanisms other than $SO_4^{\bullet-}$ or $HO^{\bullet}$ [59]. In both works, the existence of non-radical mechanisms, as well as the possible presence of other reactive species, is raised as a response to this effect. In the case of disinfection, previous studies [7] suggest that PMS has the ability to penetrate the cell membrane, react with the metals present within it, and facilitate their inactivation. This mechanism would explain the percentage of inactivation that responds to non-radical mechanisms. Finally, the existence of non-radical mechanisms has also been verified by other researchers during the degradation of organic pollutants (such as BPA [60]) by catalytic activation of PMS, so it is possible to claim that it is not exclusively related to the use of radiation.

The situation varies when 1.5 mM H_2O_2 is added to the treatment, maintaining the PMS concentration. As shown in Fig. 8b, the two scavengers used achieve a similar inhibition of the treatment, doubling the time required for complete inactivation of *E. faecalis*. The disinfection curves described when one compound is added or the other are very similar, indicating a predominance of the $HO^{\bullet}$ in the bacterial inactivation process. However, despite a slightly higher involvement of radicals than that observed for the PMS/UV-A system, the contribution of non-radical mechanisms to disinfection is still very significant.

There are very few references in the literature discussing the simultaneous application of PMS and H_2O_2 for water treatment, so there are still many uncertainties about the mechanism of action of this dual oxidation system. However, in the study by Zhong et al. [30] for the removal of chloramphenicol, a majority presence of $HO^{\bullet}$ was also detected, although it should be noted that this work evaluates this system in combination with a catalyst, so the results are not necessarily comparable. Furthermore, Amanollahi et al. [29] detected a higher importance of $HO^{\bullet}$ radicals during removal of ammonia nitrogen, although a significant contribution of $SO_4^{\bullet-}$ was also reported.

When the PMS dose was reduced to 0.5 mM, an absolute change in system behaviour was observed (Fig. 8c). On this occasion, the use of MeOH as a scavenger results in almost complete inhibition of treatment, while no major variations in kinetics are observed when TBA is used, again indicating that disinfection takes place almost exclusively due to $SO_4^{\bullet-}$ generation. The large difference from the result obtained when applying a higher concentration of PMS shows the great relevance of the ratio between both oxidants in determining the disinfection mechanism, a fact that has not been discussed in the literature to date. One of the possible explanations for this is that PMS, if present in excess, can act as a sink for reactants by reacting with $HO^{\bullet}$ and $SO_4^{\bullet-}$ (eq. 5–6) [29], a phenomenon that is avoided by reducing the concentration of the oxidant. Moreover, this is the first scenario among those evaluated in which no relevant contribution from non-radical mechanisms is observed. This is probably because a PMS concentration of 0.5 mM is not sufficient to cause significant disinfection, which is the case when the concentration used is 1.5 mM, as shown in Fig. 1.

$$HSO_5^- + HO^{\bullet} \rightarrow SO_5^{\bullet-} + H_2O \quad (5)$$

$$HSO_5^- + SO_4^{\bullet-} \rightarrow SO_4^{2-} + SO_5^{\bullet-} + H \quad (6)$$

In the case of ozone treatment, as other authors have shown, both ozone (by direct oxidation) and $HO^{\bullet}$ are the main reactive species when performing an ozonation treatment [26,61]. In fact, depending on the pH of the water, the radical pathway will act or not. Therefore, under working conditions (pH ≈ 7–8) during the treatment evaluated here, the presence of $HO^{\bullet}$ is expected to be relevant, as alkaline conditions favour the decomposition of O_3 [62,63]. On the other hand, when this treatment is combined with PMS, it is expected that $SO_4^{\bullet-}$ radicals or other sulfur species are generated. According to the mechanism proposed by Yang et al. [61], it would be the dissociated form of PMS that would react directly with ozone, triggering a series of reactions that would end with the generation of $SO_4^{\bullet-}$ and $HO^{\bullet}$ radicals following Equations 7–11.

$$HSO_5^- \rightarrow SO_5^{2-} + H^+ \quad (7)$$

$$SO_5^{2-} + O_3 \rightarrow SO_8^{2-} \quad (8)$$

$$SO_8^{2-} \rightarrow SO_5^{\bullet-} + O_3^{\bullet-} \quad (9)$$

$$O_3^{\bullet-} + H_2O \rightarrow HO^{\bullet} + HO- + O_2 \quad (10)$$

$$SO_5^{\bullet-} + O_3 \rightarrow SO_4^{\bullet-} + 2O_2 \quad (11)$$

Fig. 8d shows that, with the addition of MeOH, there is a significant inhibition of disinfection treatment. In addition, slowing of the process is also observed when TBA is used as a radical scavenger, although the inhibitory effect is significantly lower. Therefore, it is possible to affirm that in the PMS/O_3 system both $SO_4^{\bullet-}$ and $HO^{\bullet}$ are generated, although the involvement of the former in bacterial inactivation is higher. This conclusion is the same as that reached by other authors who have studied the application of this system for the degradation of organic pollutants [26,61,64].

Therefore, it has been found that although the disinfection result does not differ greatly when using ozone alone or in combination with PMS, the inactivation mechanisms are very different, which could have important implications for determining the generation (or not) of disinfection by-products, as well as the toxic nature of the by-products. However, all results should be confirmed using electronic spin resonance (ESR) technology, because although qualitative determinations with scavengers are useful, they also have certain drawbacks [60,65].

In Fig. 9, an attempt has been made to synthesise the inactivation mechanisms proposed for the different scenarios studied, including in a larger font size the predominant species for each case, and taking into account the entry of oxidising species into the cellular interior, causing the generation of free radicals intracellularly [66].

3.5. Simultaneous inactivation of other bacterial species

Having established the most effective treatments for the elimination of *E. faecalis* within the established treatment time (less than120 min), as well as their mechanisms of action, their behaviour has been evaluated in the face of a greater complexity of the aqueous matrix to be treated. For this purpose, the simulated effluent was inoculated with bacteria of three different species (*E. coli*, *E. faecalis* and *S. aureus*).

Among the three species of bacteria evaluated during the treatments, *E. coli* has been shown to be the most sensitive for all systems studied, having reached the detection limit after half an hour for all systems evaluated (Fig. 10). Of the three bacteria, this species is the only one of the Gram-negative types. Bacteria with these characteristics have been shown on other occasions to be more sensitive to AOPs than Gram-positive bacteria, one of the possible reasons being the difference in

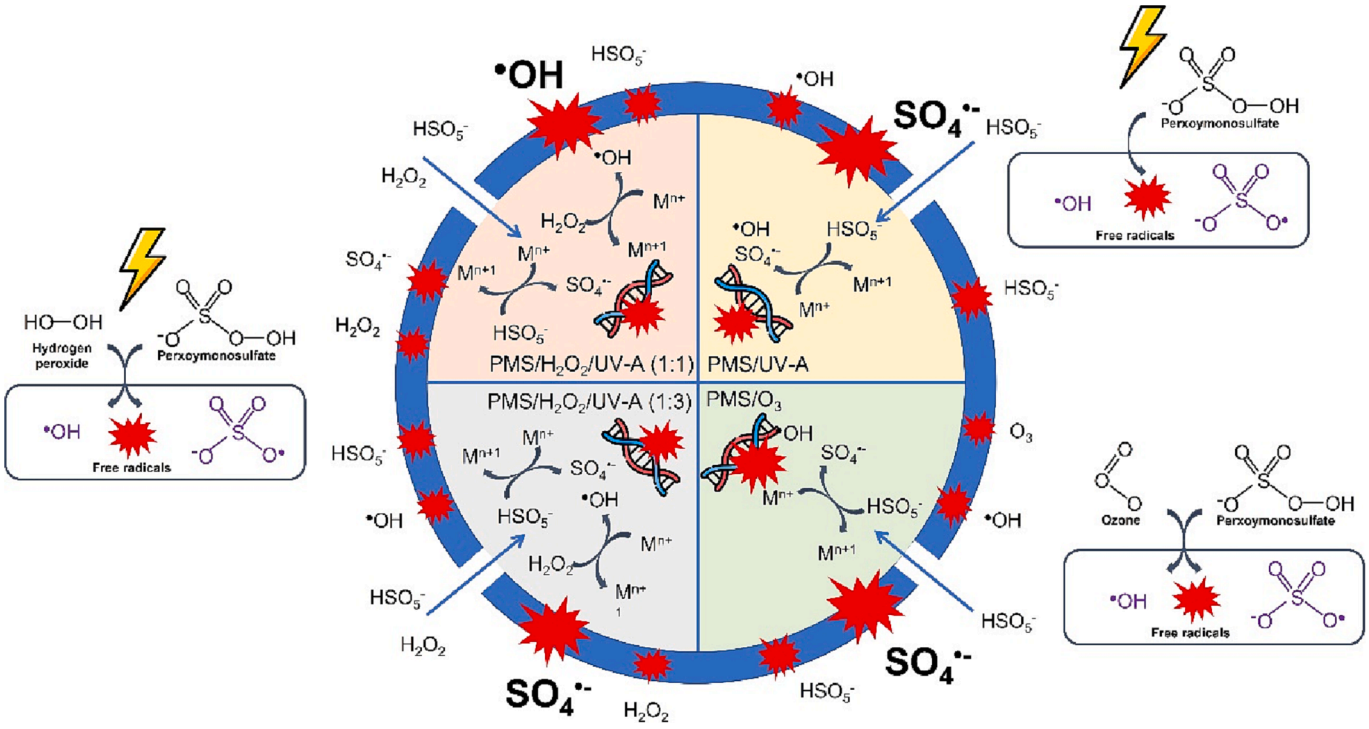

Fig. 9. Mechanisms proposed for the inactivation of *Enterococcus faecalis.* through the treatments studied.

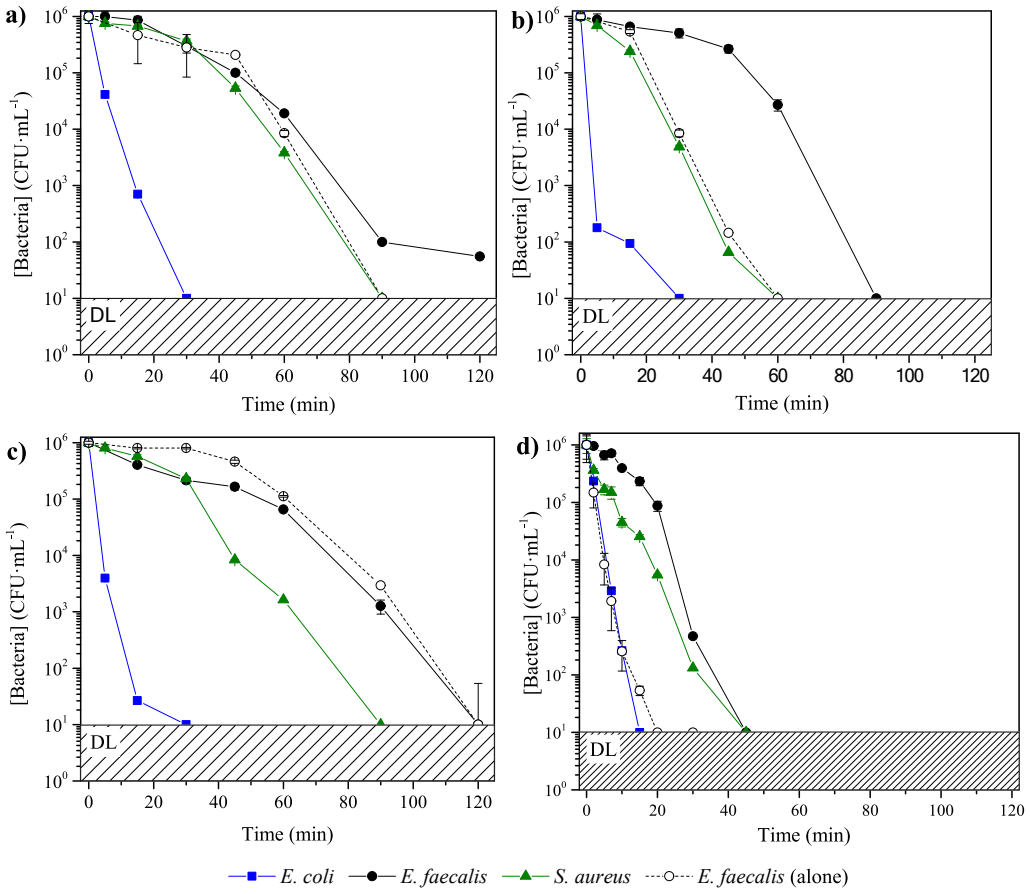

Fig. 10. Simultaneous removal of *E. coli*, *E. faecalis,* and *S. aureus* by a) PMS (1.5 mM)/UVA; b) PMS (1.5 mM)/H_2O_2/UV-A; c) PMS (0.5 mM)/H_2O_2/UV-A; d) PMS (0.5 mM)/O_3. Experimental conditions: [H_2O_2] = 1.5 mM; O_3: 0,25 g·h^{-1}; Matrix = SWW; pH ≈ 7; Radiation intensity = 1,900 W·m^{-2}. DL: Detection Limit.

the structure of their cell wall, with a peptidoglycan layer of less thickness than those belonging to the second group.

Precisely Gram-positive are the two remaining species evaluated. Among them, *S. aureus* is the most rapidly inactivated, while *E. faecalis* is the most resistant. In view of these results, it is confirmed that the choice of this bacteria as a faecal indicator is a good one, as its elimination guarantees the inactivation of other bacteria commonly present in the simulated wastewater.

In addition, it is very interesting to compare the new scenario with the inactivation rate observed when only one type of bacteria is removed. As expected, due to the increased complexity of the matrix, a slowing of the E. faecalis inactivation rate is generally observed, when *E. coli* and *E. faecalis are removed simultaneously,* as described in previous work [67]. This phenomenon is especially noticeable in the PMS/H_2O_2/UV-A treatment in a 1:1 ratio and for the PMS/O_3 treatment.

Furthermore, when applying the PMS/O_3-based treatment, *E. coli* is the least resistant species (Fig. 10d). Furthermore, the time required for the elimination of *E. faecalis* varies significantly in this scenario, increasing from 20 to 45 min.

4. Conclusions

Among the treatments evaluated in simulated pilot-scale wastewater, the combination of PMS (0.5 mM) and O_3 (0.25 $g{\cdot}h^{-1}$) was the fastest in inactivating microorganisms (less than 45 min). Experiments with scavengers confirmed the generation of $SO_4^{\bullet-}$ in the process, which is largely responsible for the bacterial inactivation.

The existence of synergies in the combination of PMS, H_2O_2 and UV-A has also been confirmed, optimising three treatments capable of inactivating 10^6 $CFU{\cdot}mL^{-1}$ of *E. faecalis* in less than 120 min. The addition of scavengers during the treatments allowed different inactivation mechanisms to be observed depending on the molar ratio between the two reagents: $HO^{\bullet}$ is predominant when treatment is carried out in a 1:1 ratio, while practically all inactivation is due to the generation of $SO_4^{\bullet-}$ when the PMS concentration decreases (1:3 ratio). This phenomenon occurs because an excess of PMS acts as a sink for radicals, preventing their interaction with the bacteria.

Therefore, the application of this treatment on a pilot scale for the elimination of different pathogenic microorganisms in complex water matrices has been demonstrated. However, there is still a long way to go and the applicability of the system needs to be further developed. It is important to highlight the limitations of the present work, which in turn allows future lines of work to be addressed. First, it must be considered that the work has been carried out on simulated wastewater. The application of the treatments should be tested in real water to know the real potential of the treatments. In addition, the mechanisms presented are carried out qualitatively by using scavengers. In this sense, the use of technologies for the quantitative determination of oxidant species, such as electron paramagnetic resonance (EPR), should be used to confirm the proposal. Finally, toxicity studies and determination of DBPs should be performed, as well as a techno-economic and environmental impact study of the developed technology by means of life cycle analysis.

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.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2023.143859.

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