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Advanced hybrid electro-oxidation & O_3 technology for water reuse in the fruit and vegetable process industry

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ABSTRACT

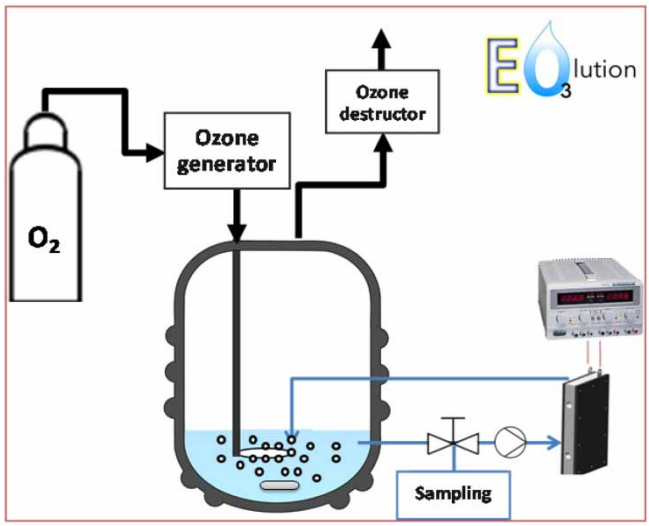
Alternative sanitising agents are required in the fruit and vegetable processing industry, capable of effectively disinfecting both the product and the washing water to increase its reuse, while not producing harmful by-products like chlorine-based agents. In the present work, electro-oxidation (EO) and ozone are proposed for vegetable process water reuse, being optimised for their individual and combined application. The application of hybrid electro-oxidation and ozone achieved 7 log reduction after 15 min of treatment in batch using boron-doped diamond (BDD) as anode material, showing important synergistic effects when compared with the individual treatments. When the process was applied in continuous mode, up to 6 log reduction of total bacteria was achieved using EO alone with Ru as the anode and stainless steel as the cathode, under 11 mA/cm^2 of current density, a cell retention time of 12 s and no addition of chemical reagents (electrolyte). Under these conditions, the absence of microorganisms in water was maintained for more than 24 h, no harmful by-products (chlorate, bromate) were detected and no damage to lettuce seeds were observed when evaluating water reuse potential.

Key words: disinfection, electro-oxidation, fresh-cut vegetables, ozonation, water reuse

HIGHLIGHTS

- EO and O_3 for water reuse in the fruit and vegetable process sector.
- Lettuce washing water was used to test the technology at laboratory scale.
- The novelty lies in the application of the combined treatment for disinfection and water reuse.
- 7 log reduction after 15 min in batch and up to 6 log reduction in continuous mode were achieved.
- Cost reduction in terms of electrode price and durability would allow an easy up-scaling.

GRAPHICAL ABSTRACT



INTRODUCTION

In the fruit and vegetable process industry, washing is designed to remove dirt, pesticide residues and microorganisms responsible for quality loss. With a production above 250,000 tonnes per year in Europe (considering the top four producing countries: United Kingdom, France, Italy, and Spain) (Martin-Belloso & Soliva-Fortuny 2019), the total wastewater produced in this sector exceeds 5–12 million m^3 per year considering 2.4–11 m^3/tonne (Lehto 2020). In order to lessen overall water consumption, water must be reused, the use of disinfectants is necessary for minimising the potential transmission of pathogens from one cleaning cycle to another. Washing with sanitisers is, therefore, important in the fruit and vegetable process industry to clean and hygienise, particularly removing soil and debris, but especially to avoid cross-contamination between clean and contaminated product. According to the US Environmental Protection Agency (USEPA), a good sanitising agent is one that is able to reduce the microbial load in 5 log units in 30 s. Chlorinated agents are used worldwide for disinfecting water and wastewater, due to their ease of use and relative low cost. However, hyperchlorination of water with high total organic carbon (TOC) content may produce unacceptably high levels of disinfection by-products (DBPs) such as trihalomethanes. Accordingly, the use of chlorine is being gradually reduced and, in some countries such as Germany, even banned (Kettlitz *et al.* 2016). Some alternatives to the use of chlorine have been investigated (Gopal *et al.* 2010) but none of them have gained widespread acceptance due to economic competitiveness limitation compared to inexpensive chlorine-based reagents or some limitations that must be overcome. In the present work, electro-oxidation (EO) and ozone (O_3) are proposed. EO is an effective, environmentally sustainable, and versatile technology based on the electro-generation of high reactive species (·OH, H_2O_2, O_3, chloride-derived species, etc.) with high oxidation potentials (2.08 eV for O_3 and 2.8 eV for ·OH) compared to hypochlorite (1.48 eV), resulting in promising technologies for disinfection (Barrera-Diaz *et al.* 2014).

The efficiency of the EO process is highly dependent on the anode materials, which can be manufactured with stainless steel (SS), Pt, PbO_2, SnO_2, IrO_2, RuO_2, Boron Doped Diamond (BDD), etc. Other factors, such as cell design, current density, type of support electrolyte, pH and the conductivity of the aqueous media, temperature, time of reaction, etc. affect not only the efficiency of the EO process but also electrical consumption and thus energy demand (Garcia-Rodriguez *et al.* 2020). Therefore, before applying this technology for water treatment and/or reuse, it is of great importance the optimisation of the previously mentioned parameters. For example, electrolytes such as NaCl are widely used for maximising the process efficiency by increasing water conductivity. However, the presence of chloride in water can lead to the undesirable appearance of chlorinated DBPs during the EO treatment (Yang 2020). Therefore, the necessity of an additional treatment for the removal of undesired by-products generated during the EO treatment may be addressed. Among the different alternatives, ozone has been demonstrated to be an efficient treatment for the abatement of DBPs before/after their formation, since the centres of natural organic matter (NOM) which are responsible for the formation of DBPs are selectively removed (Hua & Reckhow 2007). Furthermore, simultaneous combination of ozonation and electro-oxidation for water treatment

has revealed the existence of synergistic effects which accelerate the chemical oxygen demand (COD) removal rate and reduce the necessity of power consumption, in comparison with ozonation and electrochemical treatment alone (Bergmann 2021).

The present work aims to research and optimise a hybrid EO&O_3 treatment for water reuse in the fruit and vegetable process sector, particularly in the fresh-cut produce industry, using lettuce washing water, generated at laboratory scale simulating the real washing process, as a model. For that purpose, different combinations of both EO and O_3 technologies were tested at laboratory scale, as well as design parameters such as electrode materials and the distance between them, and process conditions such as current density, the use of non-chlorinated electrolyte, ozone dose and retention time in the electrochemical cell. The novelty of the work lies in the application of the combined treatment for disinfection and water reuse using water obtained in a simulated lettuce washing process.

MATERIALS AND METHODS

Studied water

The water used in the experiments was generated at laboratory scale following the lettuce washing procedure of a fresh-cut produce industry. The use of real process water was discarded since the industry used hypochlorite as disinfection treatment, so the effect of the studied technology could not be distinguished from the disinfection effect of the hypochlorite and, additionally, the presence of high concentrations of chlorine would lead to the undesirable appearance of DBPs. For generating water, 900 g of lettuce were washed with 1 L of distilled water during 1 min. Distilled water was used because the model fresh-cut produce industry, located in Valencia (Spain) uses distilled water instead of tap water, due to its high concentration of Ca and Mg. The characteristics of the generated water are shown in Table 1 in comparison with real fresh-cut process water, the generated water presented a microbial content 100 times higher (since no disinfection treatment was still applied), a chloride content four times lower and a trihalomethanes concentration >150 times lower (especially important for chloroform, >220 times lower, while dibromochloromethane and bromoform were found 12.5 and 9 times lower). Turbidity was also found four times lower in the simulated water, but it was mainly due to a higher presence of suspended solids in the real water, which could be separated by a filtration step recommended before the application of the oxidation treatment. The water was always generated just before its treatment, to have a more controlled microorganisms' population.

Experimental set up

The experimental set up, represented in the graphical abstract, was formed by: (i) a 5 L volume glass hermetically closed reactor agitated at 200 rpm by means of a magnetic plate (IKA C-MAG MS10), with an external chamber to control the temperature by a Huber Pilot One heat bath; (ii) Heidolph 5006 peristaltic pump for recirculating the water between the reactor and the electrochemical cell, with adjustable flow velocity: (iii) ozone generator (Hidro GH 15) fed with pure oxygen at 1 bar, obtaining an O_3 concentration of 30–35 g/m^3; ozone analyser (MINI-HICON SMC 900), connected to the O_3 generator to monitor O_3 concentration, with a reading range of 0–100 g/m^3; (iv) O_2/O_3 flow controller to regulate the O_3 dose; (v) ozone catalytic destructor (Ingenieria del Ozono SL DC-PVC-01) receiving the outlet air from the reactor; (vi) electrochemical cell (manufactured at Leitat Technological Center), detachable to change electrodes, which should have a surface of 37.2 cm^2 and (vii) SORENSEN DCS40-70E Switchable Power Supply (1.2 kW with voltage range 0–70 V and current levels up to 40 A). The set up was modified for the continuous mode experiments by adding a buffer tank previous to the 5 L glass reactor (i) and changing the exit from the electrochemical cell (vi) so the treated water was not recirculated to the reactor.

Operational conditions

Experiments were carried out at 21 °C (ambient temperature) and pH around 7.5 (no pH modification), using 1 L of water coming from lettuce wash. First, 30 min batch experiments were carried out to optimise EO and ozonation separately, measuring total bacteria at 5, 15 and 30 min. For the EO batch experiments, carried out with a recirculation flow of 35 L/h, the following variables were studied: anodic and cathodic material (including BDD, Ti and stainless steel), distance between electrodes (6 and 10 mm), current density (17 and 29 mA/cm^2) and the addition of electrolyte (Na_2SO_4 up to a conductivity of 550 μS/cm). For the ozonation batch experiments, two variables were studied: ozone dose (3 and 10 mg/min) and reactor diameter (10 and 20 cm). Both technologies were later applied in combination, comparing the results of the combined treatment with the individual application of the technologies (synergistic effects), and evaluating the influence of the addition of

Table 1 | Characteristics of the studied simulated water and real fresh-cut process water

Parameter	Simulated water	Real water
pH	7.40	6.31
Conductivity	88 μS/cm	1,176 μS/cm
Turbidity	22.5 NTU	95.1 NTU
Chemical oxygen demand (COD)	172 mg O_2/L	140 mg O_2/L
Dissolved total organic carbon (TOC)	149 mg/L	43 mg/L
Dissolved total nitrogen (TN)	7.9 mg/L	5.5 mg/L
Chloride	<70 mg/L	253 mg/L
Total chlorine	0.19 mg/L	0.55 mg/L
Free chlorine	0.18 mg/L	0.44 mg/L
Chlorate	<1 mg/L	<1 mg/L
Bromate	<0.1 mg/L	<0.1 mg/L
Trihalomethanes		
Chloroform	0.448 μg/L	99.213 μg/L
Dibromochloromethane	0.095 μg/L	1.478 μg/L
Bromodichloromethane	0.124 μg/L	1.223 μg/L
Bromoform	<0.01 μg/L	<0.01 μg/L
Total	0.667 μg/L	101.49 μg/L
Total bacteria (kit)	10^6–$5{\cdot}10^6$ CFU/100 mL	$6.5{\cdot}10^4$ CFU/100 mL
Total bacteria count	$1.85{\cdot}10^6$ CFU/100 mL	$6.5{\cdot}10^4$ CFU/100 mL
Total coliforms	Absence	Absence
Escherichia coli	Absence	Absence
Salmonella	Absence	Absence
Legionella	Absence	Absence
Listeria monocytogenes	Absence	Absence
Mesophilic aerobic bacteria	$3.8{\cdot}10^5$ CFU/100 mL	Absence
Enterobacteria	$3{\cdot}10^3$ CFU/100 mL	Absence

electrolyte to the combined treatment, the type of combination (sequential EO-O_3, sequential O_3-EO and hybrid EO + O_3) and the recirculation flow (13 and 35 L/min, corresponding to cell retention times of 6 and 2 s, respectively). Continuous experiments were also carried out for the combined treatment, studying different cell retention times (6, 12 and 23 s, corresponding to 13, 7 and 3.5 L/h of treatment time), distance between electrodes (3 and 6 mm) and anodic material (BDD, Pt and Ru). EO alone was finally also evaluated in continuous mode, studying different anode materials (BDD and Ru), distance between electrodes (3 and 6 mm) and cell retention times (3, 6 and 12 s). With the aim of studying the effect of the treated water on tissues, lettuce leaves were washed with the treated water (contact time of 1 min, 1 L of water per 900 g of lettuce), evaluating the results by visual observation after 24 h. Moreover, lettuces were left in the treated water for a contact time of 24 h, evaluating the results by visual observation after 96 h. All the treatment experiments were carried out in duplicate (Figures show mean values), while the experiments to evaluate the effect of the treated water on tissues were performed in triplicate.

Analytical methods

Conductivity and pH were measured by potentiometry (multimeter Crison MM41), while a turbidimeter LaMotte 2008 was used to measure turbidity following UNE-EN ISO 7027:2001. Dissolved TOC and TN were analysed using a Shimadzu TOC-V CSH E200 V ASI-V TNM-1, and COD was measured using kits (Hach Lange LCK614) and a spectrophotometer (Hach LANGE DR 3900). Trihalomethanes were analysed by gas chromatography/mass spectrometry (VARIAN SATURN MS/MS). The water treatment processes were optimised by measuring total bacteria using kits (MICROBIOL) with tryptone

soya agar with triphenyltetrazolium chloride (TSA-TTC) culture medium. Once the operational conditions were optimised, the treated water was evaluated in terms of chloride (Hach Lange LCK311), total chlorine and free chlorine (Hach Lange LCK310), chlorate and bromate (Ionic Chromatography, DIONEX ICS-3000), total bacteria count (ISO6222), total coliforms (ISO9308), *E. coli* and *Legionella* (ISO11731), *Salmonella* (ISO6579:2002), *L. monocytogenes* (ISO11290-1:1997), mesophilic aerobic bacteria (ISO4833-2:2013), Enterobacteria (ISO2128-2:2004) and affect on lettuce tissues.

RESULTS AND DISCUSSION

Batch assays

Optimisation of electro-oxidation

The results of the optimisation of EO treatment are shown in Figure 1, comparing different materials for electrodes, distances between them, current densities, and the elimination of Na_2SO_4 as electrolyte. For the comparison of electrode materials, the other variables were set as 10 mm (distance of electrodes), 29 mA/cm^2 of current density and Na_2SO_4 as electrolyte in concentration up to 550 μS/cm of conductivity. When comparing cathodes (Figure 1(a)), results were similar for stainless steel (SS) and BDD, achieved 3 log of bacteria reduction. These results were expected, since disinfection through EO is mainly due to the *in situ* production of ·OH (or active chlorine species in the presence of chloride ions) at the anode (Bruguera-Casamada *et al.* 2017). In the case of the anodic material (Figure 1(b)), BDD showed better efficiency (almost 1 log more of bacteria removal after 30 min), which has also been reported: it is known that BDD produces higher quantities of oxidant species such as ·OH and O_3 compared with other materials based in Pt and Ti (Jeong *et al.* 2009). In addition, the inactivation of *E. coli* using BDD occurs mainly by reaction with ·OH, while with other materials such as Pt, the main mechanism is the direct transfer of electrons (Jeong *et al.* 2009). Considering the different prices of the studied materials (30, 500 and 800 €/dm^2 for SS, Ti and BDD, respectively) along with the obtained results, stainless steel was selected as the cathode and BDD as the anode, since the difference in prize with Ti electrodes did not justify their lower performance. This cell configuration was used for the study of the optimal distance between electrodes (Figure 1(c)), resulting in a better efficiency when 6 mm was employed. The indirect correlation between bacteria removal efficiency and distance between electrodes agrees with other EO studies, not only for disinfection (*E. coli* removal of 10^2–10^3 CFU/mL with 2 cm between electrodes reported by Rezaee *et al.* (2011), when testing 2, 2.5, 3 and 3.5 cm) but also for other EO applications such as dyes removal (Khosravi *et al.* 2017). In consequence, the study continued using 6 mm as the distance between electrodes, this time evaluating different current densities (Figure 1(d)). A clear decrease in the disinfection capacity (more than 2 log after 30 min) can be observed

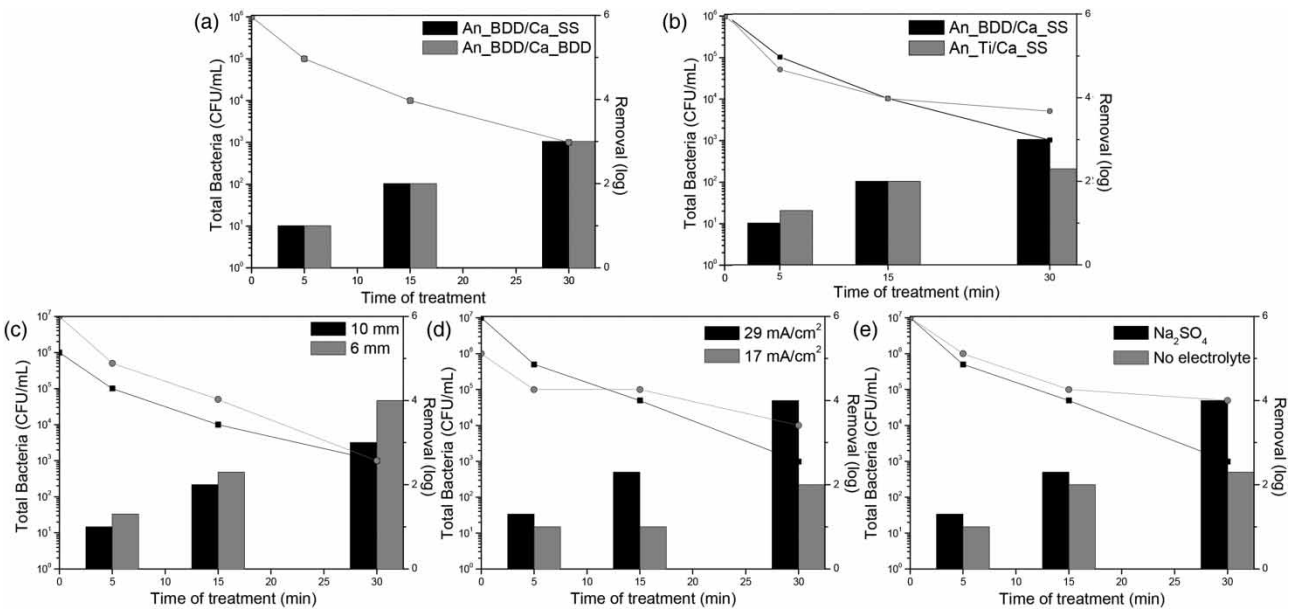


Figure 1 | Time evolution of Total Bacteria (scatter) and the corresponding bacteria removal (bars) during the optimisation of EO treatment. Comparison of different cathodes (a), anodes (b), distances between electrodes (c), current densities (d) and use of electrolyte (e).

when current density was reduced, being necessary to apply 29 mA/cm^2 to achieve an effective treatment (4 log removal in 30 in). These results are in accordance with the ones reported by Bruguera-Casamada *et al.* (2016), that obtained 3 log *E. coli* removal after 30 min of EO treatment of a 10^6 CFU/mL solution at pH 7 using BDD/SS (anode/cathode), 33.3 mA/cm^2 of current density and 7 mM NaSO4 (corresponding to a conductivity of 1.59 mS/cm). Disinfection capacity increased up to 6 log after 60 min of treatment under the mentioned conditions It is important to consider that using low current densities avoids the appearance of dangerous DBPs such as perchlorate and trihalomethanes (Cano *et al.* 2012), so current densities above 29 mA/cm^2 were avoided in the present work, and DBPs were analysed once the technology was totally optimised, ensuring their absence in the treated water. Figure 1(e) shows the influence of the electrolyte. Water conductivity highly affects the EO process: treating water with 100 μS/cm instead of 550 μS/cm caused an increase in voltage from 40 to 75 V (therefore increasing electricity consumption) and a decrease of almost 2 log in disinfection capacity This observation corresponds to previous recommendations which suggest that electro-oxidation leads to better disinfection yields and lower electricity consumption when treating waters that have moderate to high conductivity (Hand & Cusick 2021). Therefore, optimal conditions for EO batch experiments were set as follows: stainless steel and BDD as cathode and anode, respectively, with 6 mm of distance between them, using a current density of 29 mA/cm$_2$ and Na_2SO_4 as electrolyte up to a conductivity of 550 μS/cm.

Optimisation of ozonation

Figure 2 shows the results obtained for the optimisation study of ozonation, in which O_3 dose and reactor diameter were evaluated as variables. An enhancement of more than 2 and 4 log was observed after 15 and 30 min of ozonation when the dose was increased to 10 mg O_3/min. However, no changes were observed when a column reactor (10 cm diameter, same volume) was used to increase the height of the water column and, therefore, the contact time between ozone and water. These results may be due to good homogenisation in the reactor, allowing the achievement of the saturation concentration of ozone in the water. Ozonation has been previously studied for the disinfection of lettuce at pilot scale by Nahim-Granados *et al.* (2020), reporting >5 log reduction of *E. coli* and *S. enteritidis* in less than 10 min with an ozone dose <8.6 mg/L. From the different operational conditions tested by this author, the simplest condition (i.e., ozonation at natural pH) allowed the higher kinetics rates, compared to ozonation at basic pH and peroxone. Moreover, ozone treatment allowed up to 85% of organic microcontaminants removal, which represents an extra benefit of applying this treatment to fresh-cut wastewater.

Combination of EO and O_3

Figure 3 shows the comparison between the individual EO and O_3 treatments and their application in combination using (Figure 3(a)) or not (Figure 3(b)) Na_2SO_4 as electrolyte, the different possible combinations (including sequential and hybrid application, Figure 3(c)) and the influence of the recirculation flow velocity (Figure 3(d)). Optimal conditions obtained for both EO and O_3 processes were used. The combined application of EO and ozonation showed synergistic effects at 5 min

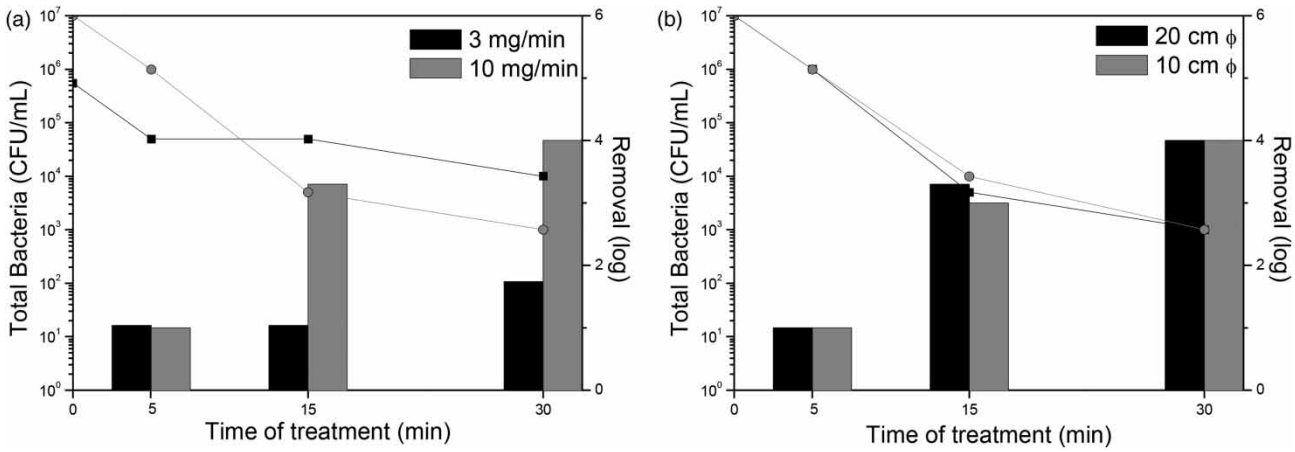


Figure 2 | Time evolution of Total Bacteria (scatter) and the corresponding bacteria removal (bars) during the optimisation of the ozonation treatment. Comparison of different O_3 doses (a) and reactors configurations -diameters- (b).

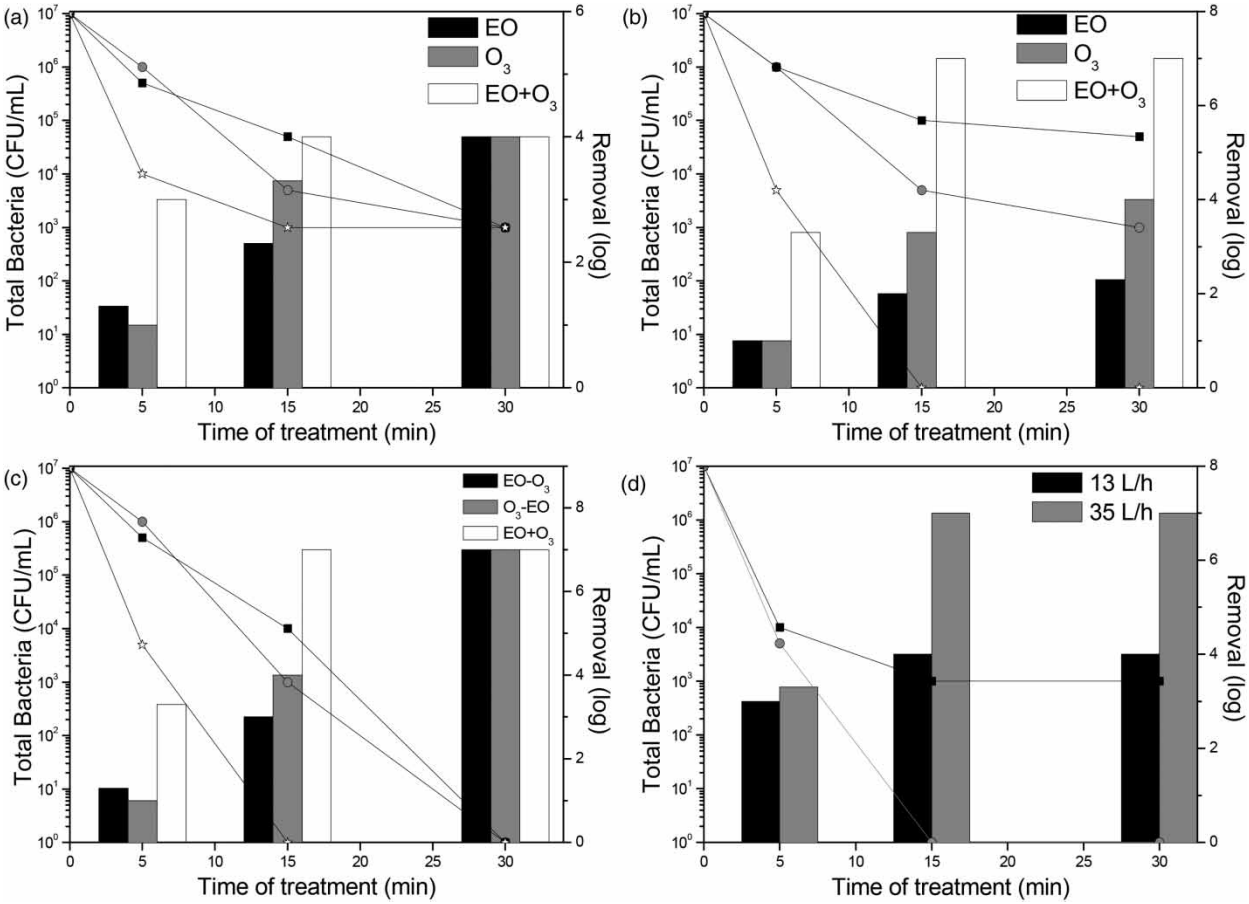


Figure 3 | Time evolution of Total Bacteria (scatter) and the corresponding bacteria removal (bars) during the optimisation of the combined EO and ozonation treatment. Comparison of the individual EO and ozonation treatments vs. hybrid treatment with electrolyte (a) and without it (b), different combinations sequential/hybrid (c) and recirculation flow velocities (d).

when electrolyte was used (Figure 3(a)) and at any time of treatment in absence of electrolyte (Figure 3(b)), since the bacteria removal obtained for the combined treatment was higher than the addition of the resultants applying the individual treatments. The efficiency of the combined treatment in absence of electrolyte was clearly higher than that observed adding Na_2SO_4, achieving total disinfection (7 log removal) after 15 min of treatment, corresponding to a treatment capacity of 4 L/h with the laboratory set up. In this case, the increase of voltage derived from the application of the same current (0.4 A) in a medium with less conductivity (from 35 to 40 V in presence of Na_2SO_4 to up to 75 V in absence of Na_2SO_4), improved the disinfection efficiency. This effect has been previously observed for disinfection (Feng *et al.* 2004) and water treatment (Zhang *et al.* 2015). Moreover, according to Amado-Piña *et al.* (2017), combined EO and ozone enhances by 2.5 times the mineralisation of phenol when compared to O_3 alone and reduces by half the time to achieve a phenol mineralisation >90%, results that highlight the synergistic effects. In the combined process, disinfection (or oxidation of organic compounds) does not occur mainly at the anode surface via hydroxyl radicals as in the case of the EO treatment. In this case, the high oxidation power of BDD allows the concurrent formation of several side products: hydrogen peroxide (from the recombination of ·OH radicals or from the oxygen reduction at the cathode), peroxodisulphate (formed by the oxidation of sulfate) and ozone (that might be generated from water oxidation at the anode) (Amado-Piña *et al.* 2017). Moreover, the reaction between the peroxodisulphate with the electrons generated in the cathode forms the radical $SO_4{\cdot}-$, a better oxidant than persulphate and oxygen and which can also generate hydroxyl radicals when reacting with water (Amado-Piña *et al.* 2017). Disinfection by EO is based not only in the production of ·OH as an indirect process but also for a direct effect of the electrical pulse: microorganisms' membrane is more permeable after exposure to an electrical field, swelling the cells and even breaking the cellular membrane (Ghernaout 2017). Furthermore, the existence of synergistic effects

when combining ozonation and electrochemical treatments has been also reported, being possible to increase the COD removal rate and decrease the electrical consumption in comparison with their individual application (Bergmann 2021). Other examples have been disclosed for phenol removal (reduction of the time of treatment from 120 to 60 min reported by Torres *et al.* (2014)), *p*-nitrophenol elimination (TOC mineralisation from 20% -EO- and 44% -O_3- up to 91% for the combined treatment according to Qiu *et al.* (2014)) and the treatment of industrial wastewaters (reduction of the time of treatment from 120 to 60 min, achieving a 99% of COD removal reported by García-Morales *et al.* (2013)).

When comparing different combinations of EO and ozonation (Figure 3(c)), it can be observed that a 7 log reduction can be obtained after 15 min of hybrid treatment, while applying a sequential treatment would require, for both EO-O_3 and O_3-EO configurations, 30 min. These results reinforce the appearance of synergistic effects when hybrid treatment is applied. Figure 3(d) shows the influence of the recirculation flow, which affects the cell retention time and the number of 'steps by cell' that the water passes through. For a recirculation flow of 13 L/h, the water passed 6.5 times through the cell, with a retention time of 6 s, while for 35 L/h, 17.5 steps by cell were performed with 2 s each one. A decrease in the disinfection efficiency was observed when lowering the recirculation flow, therefore indicating that the number of steps by cell is more decisive on the disinfection efficiency than the cell retention time under the studied operational conditions.

Continuous assays

Combined EO and O_3

The optimal operational conditions obtained in batch experiments for the combined EO and ozonation treatment were further studied under continuous flow experiments, passing the ozonated water just one time by the electrochemical cell. Experiments were carried out under optimised conditions of ozone dose (10 mg/min), cathode material (SS) and current density (29 mA/cm^2), evaluating different cell retention times (6, 12 and 23 s, corresponding to treatment capacities of 13, 7 and 3.5 L/h, respectively), distance between electrodes (3 and 6 mm) and anode materials (BDD, Pt and Ru) (Figure 4). In this case, at least 12 s of cell retention time (equivalent to a treatment capacity of 7 L/h, 1.75 times higher than the achieved in batch experiments) were needed to reach total disinfection (6 log reduction), as can be seen in Figure 4(a). When the distance between electrodes was reduced up to 3 mm maintaining the treatment capacity in 7 L/h, that is only 6 s retention time (Figure 4(b)), the disinfection efficiency decreased up to 2.7 log. Finally, different materials were evaluated under optimal conditions (6 mm, 12 s, 7 L/h), achieving total disinfection for both BDD and Ru (6 log) while Pt was discarded since only 2 log removal was observed (Figure 4(c)). Ru was therefore selected as the optimal anode for continuous operation since this material is around six times less expensive than BDD and its durability is 3–5 times longer.

Application of EO alone

In order to lower treatment costs, the application of EO in continuous was evaluated without ozone addition. Experiments were carried out under optimised conditions of cathode material (SS) and current density (29 mA/cm^2), evaluating different cell retention times (3 s, 6 s, and 12 s, corresponding to treatment capacities of 26, 13, and 7 L/h, respectively) and distance between electrodes (3 and 6 mm). As can be seen in Figure 5(a), EO alone was not enough for disinfecting the water (only 2.7 log reduction) when using BDD as anode. In contrast, Ru shown a higher disinfection capacity (Figure 5(b)), achieving

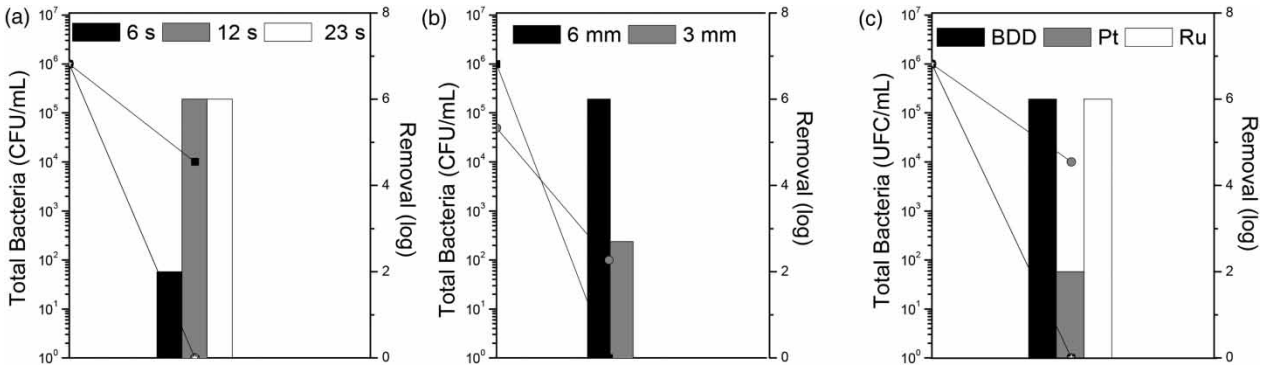


Figure 4 | Total Bacteria (scatter) and corresponding bacteria removal (bars) after the treatment by means of combined EO and ozonation in continuous mode. Comparison of cell retention times (a), distances between electrodes (b) and anode materials (c).

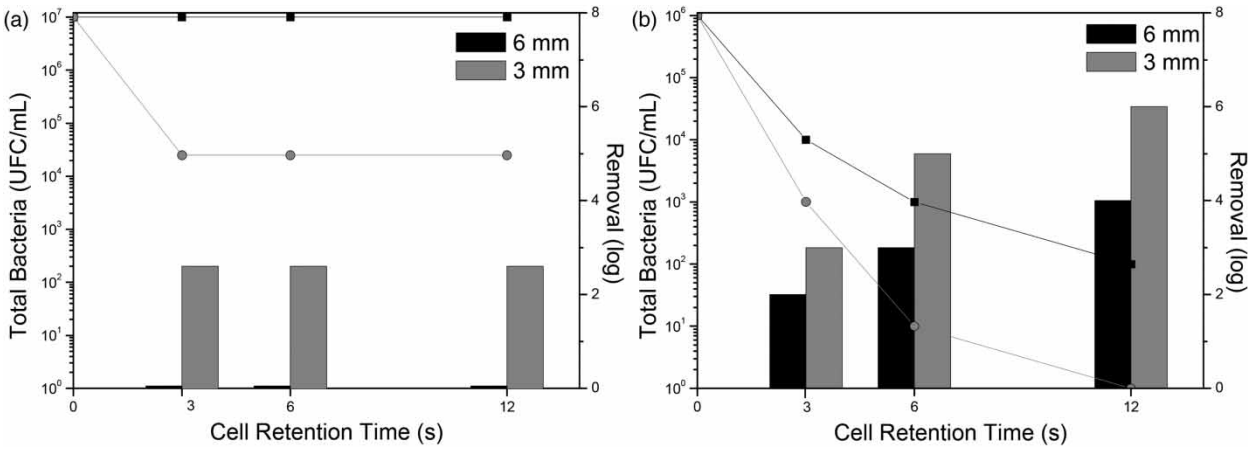


Figure 5 | Total Bacteria (scatter) and corresponding bacteria removal (bars) under different cell retention times and distances between electrodes for EO in continuous mode using BDD (a) and Ru (b) anodes.

total disinfection (6 log) with 12 s of cell retention time and 3 mm distance between electrodes. These results are in accordance with literature (Bruguera-Casamada *et al.* 2017), reporting faster disinfection when using IrO_2- or RuO_2-based anodes compared to BDD. According to this author, this phenomenon is explained by the greater adsorption of microorganisms onto their surface of IrO_2- or RuO_2-based anodes, which enhances their reaction with electrogenerated physisorbed M(•OH). It must be also noted that, in the case of Ru, reducing the distance between electrodes was favourable, unlike of what was observed for BDD. This fact, along with the evidence that disinfection using Ru was much less affected than BDD when O_3 was not applied, suggests that EO with Ru as anode is based mainly on the direct effect of the electrical pulse while using BDD involves ·OH production as major disinfection mechanism. Therefore, for disinfection purposes, the use of Ru instead of BDD can be recommendable, although for other purposes (focused on removal of organic matter and/or pollutants such as pesticides, that may be present in the fresh-cut washing water), BDD is foreseen to provide better results than Ru (Contreras *et al.* 2020).

Focusing on treatment costs, those derived from the use of SS (cathode) and Ru (anode) instead of BDD electrodes have been already mentioned (30, 135 and 800 €/dm^2 for SS, Ru and BDD, respectively). Moreover, performing the disinfection treatment without ozonation would allow savings of around 1.31 €/m^3 (Nahim-Granados *et al.* 2020). Considering electricity expenses, under optimised conditions, the EO treatment consumed 45 V at 0.4 A (18 W) for 3.2 L/h, which corresponds to 5.6 kWh/m^3. Assuming 0.07 €/kWh, the proposed technology would present operational costs of around 0.4 €/m^3 (maintenance costs are not included).

With the aim of further studying the disinfection treatment with EO in continuous use of Ru as the anode, a more exhaustive analysis of parameters was performed, including not only microbiological but also chemical (presence of halogenated by-products) and physical (lettuce tissues affection) criteria. Additionally, the treated water showed no bacteria presence even after 24 h of storage at ambient temperature. For the exhaustive microbial analysis, it must be noted that, in this case, initial water showed a higher total bacteria count (9 log) than the one used in previous experiments (7 or 6 log), maybe due to a variable microbial content in the lettuce, since the washing procedure was always the same. In these conditions, a 4.09 log reduction was achieved for total bacteria count, 3.96 log reduction for mesophilic aerobic bacteria (initial concentration of 8.46 log) and 3.86 log reduction for total coliforms (6.86 log initial concentration). Enterobacteria, *E. coli, Salmonella, Legionella* and *L. monocytogenes* were absent in the water before and after the treatment. The variability of bacteria present in the water is of great importance, based on different strains. According to Bruguera-Casamada *et al.* (2016), the electrochemical disinfection (with BDD) was very effective for Gram-negative bacilli like *E. coli* and *P. aeruginosa* and Gram-positive ones like *B. atrophaeus*, whereas Gram-positive cocci *S. aureus* and *E. hirae* were more resistant. These results highlight the importance of performing disinfection experiments with real (or simulated) wastewaters instead of inoculated solutions of specific strains (usually *E. coli*, which could not be a good indicator of disinfection if other, more resistant, species are present in the water). The treated water also presented a concentration of chlorate and bromate under the detection limit (<0.1 mg/L and <0.01 mg/L, respectively). Attending to other chlorine forms, chloride concentration was reduced from

13.5 mg/L to 10.8 mg/L, while total chlorine was maintained under 0.4 mg/L at 0.3 mg/L of free chlorine (starting concentrations of 0.259 and 0.243 mg/L, respectively).

In order to study the effect of the treated water on tissues, lettuce leaves were washed with the treated water (contact time of 1 min, 1 L of water per 900 g of lettuce). No damage (colour changes, spots, loss of tissue) was observed even 24 h after washing (assays carried out by triplicate). In addition, no damage was observed in the lettuce leaves after 24 h of contact with the treated water, while after 96 h brown spots started to appear regardless of the type of water used (tap water or treated water).

CONCLUSIONS

The present work demonstrates the viability of combined EO and ozonation for water disinfection for its reuse for vegetable washing, achieving 7 log reduction after 15 min of treatment in batch using BDD as anode material and stainless steel as cathode, with 6 mm of distance between them, using a current density of 29 mA/cm_2 and adding Na_2SO_4 as electrolyte up to a conductivity of 550 μS/cm. When the process was applied in continuous mode, up to 6 log reduction of total bacteria was achieved using EO alone with Ru as anode and stainless steel as cathode, both separated by 3 mm, under 11 mA/cm^2 of current density, a cell retention time of 12 s (corresponding to a treatment capacity of 3.5 L/h with the laboratory set up −37.2 cm^2 of electrodes-) and no addition of chemical reagents (electrolyte). Therefore, under these conditions, the EO technology results in a promising sanitising agent fulfilling USEPA requirements (5 log in 30 s), not generating harmful by-products (chlorate and bromate) and not damaging lettuce tissues. Consequently, the use of ozone as a treatment reinforcement was discarded in this case, even though synergistic effects were observed in batch assays when the hybrid process was applied. However, to avoid cross-contamination, the authors recommend an additional chemical aid to achieve residual disinfection effect in the process water (e.g., O_3), since a treatment based only in EO would have no residual effect on the wash water. Moreover, as already mentioned, the application of O_3 in combination with EO leads to synergistic effects which can be of great importance for the mineralisation of pesticides that may be present in the fresh-cut washing water. Such treatment could be used in parallel to the washing line, for improving the microbial and chemical quality of the wash water. In the present work, aiming at lowering implementation and operation costs, it was concluded that EO alone was enough to achieve the required quality for the treated water. The reduction of costs in terms of electrode prize and durability (Ru anode versus BDD) would allow an easy up-scaling of the technology.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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