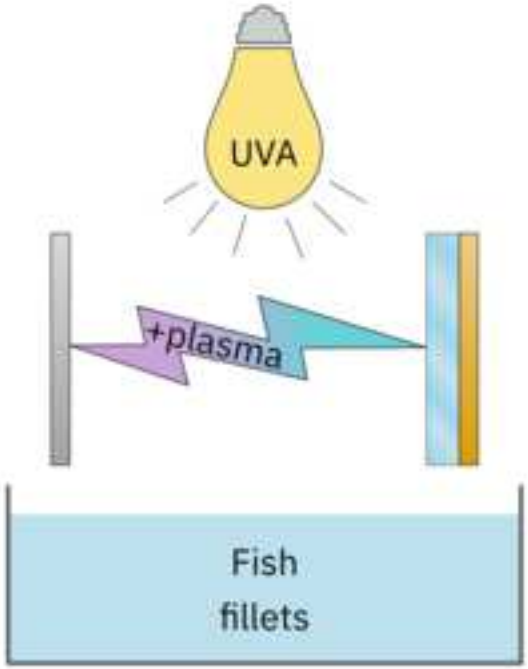
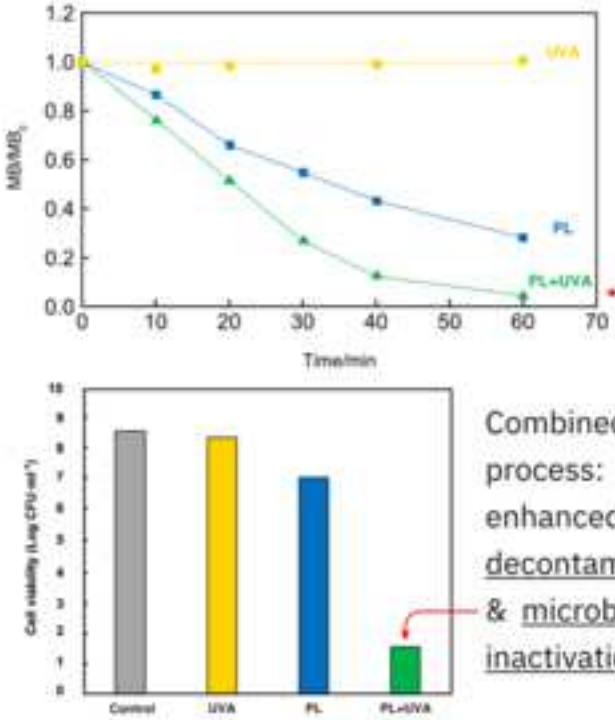
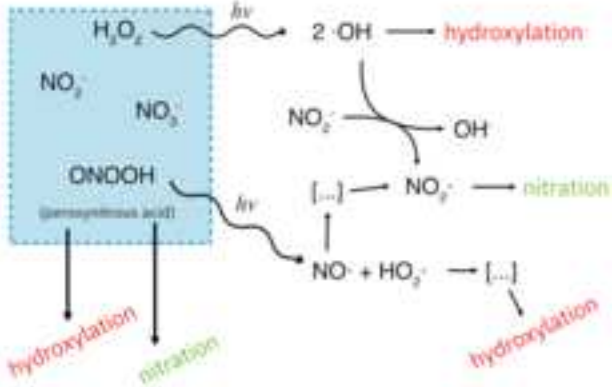
Combined effect of atmospheric gas plasma and UVA light: A sustainable and green alternative for chemical decontamination and microbial inactivation of fish processing water





Combined process: enhanced <u>decontamination</u> & <u>microbial inactivation</u>

Mechanism: photoactive species in plasma-activated water



Highlights

- Cold plasma is a chlorine-free technique for water decontamination and disinfection.
- Coupling cold plasma with UVA irradiation leads to process intensification.
- Synergy explained by the presence of photoactive species in plasma-activated water.
- The treatment does not affect the quality of the food.

Combined effect of atmospheric gas plasma and UVA light: a sustainable and green alternative for chemical decontamination and microbial inactivation of fish processing water

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Abstract

The simultaneous use of UVA light irradiation coupled with low energy cold plasma generated by a dielectric barrier discharge prototype, results in significant enhancement of efficiency of the integrated process with respect to the sole plasma treatment. This effect has been demonstrated both on microbial inactivation of a food-borne pathogen, i.e. *Listeria monocytogenes*, and on the degradation of a compound of biological origin such as phenylalanine. In the latter case, the analysis of its reaction intermediates and the spectroscopic identification and quantification of peroxynitrites, allowed to propose mechanistic hypotheses on the nature of the observed synergistic effects.

Moreover, it has been demonstrated that the process does not affect the quality of trout fillets, indicating its suitability as a chlorine-free, green, and sustainable tool for the decontamination of fish processing water.

Keywords: Food processing water, UVA light; dielectric barrier discharge; process intensification; microbial inactivation; peroxynitrite.

1. Introduction

Fish products represents an important source of both macro and micro nutrients for human consumption, and are considered essential to meet the increasing demand of high valuable protein and long chain omega 3 (n-3) polyunsaturated fatty acids (PUFA) (Sampels, 2014).

Due to its structure and composition, fish is a highly perishable product, which requires careful processing in order to prolong the shelf life and to limit losses. Therefore, fish handling has a big role, from catching and along the supply chain until packaging and eventually human consumption, in the preservation of nutritional properties and hygienic conditions, and in the reduction of postharvest losses (Sefa-Dedeh, 2003).

To this aim, during various stages of processing a high amount of water is required (Murali et al., 2021). Generally, from 5 to 11 m^3 water per ton of fish intake are required for fish filleting and 15 m^3 for canning (Unep, 1999). These operations, in addition to plant cleaning procedures, also generate significant wastewater, which must be, in turn, subjected to treatment processes ruled by stringent liquid effluent regulations (Chowdhury et al., 2010).

Several green technologies such as photocatalysis and ozonation have been proposed for water treatment purposes (Miklos et al., 2018) but their large-scale application is still limited (Wang et al., 2021; Wang et al., 2022). On the other hand, sanitizers are used in industry to assure the microbial quality of the washing water, and to avoid cross contamination. For instance, based on its efficacy towards bacteria, chlorine was extensively employed in different food processing units, from fruits

and vegetables to meat. However, the chemical risk associated with the formation and accumulation, both in process water and products, of chlorine disinfection intermediates such as trichloromethane and other carcinogenic and mutagenic chlorinated compounds, (EFSA Journal, 2019) is of great concern. For this reason, the use of chlorine is now prohibited in several European countries (Gil et al., 2009).

Among the novel techniques proposed to tackle this issue, "cold plasma" produced under atmospheric conditions allows to inactivate pathogenic agents and to decontaminate water, due to formation of strong oxidants such as ozone (O_3) and reactive oxygen (ROS) and nitrogen (RNS) species produced when air acts as the working gas (Oehmigen et al., 2010; Berardinelli et al., 2016). These reactive species are responsible of cell membrane damages, which further enable cell penetration, consequent DNA damages, and eventually death of the pathogen microorganism (Bourke et al., 2017). It is known that reactive molecules production is affected by the applied energy level, the nature of the gas mixture used to generate the discharge, (Moreau et al., 2008) while the characteristics of the substrate and the microorganism type, load, and physiological state highly affect the efficacy of the treatment (Berardinelli et al., 2012; Guo et al., 2015). In particular, the decontamination efficacy of the atmospheric gas plasma technique was evidenced towards Gram-negative and Gram-positive bacteria, spores, yeasts, molds, and viruses (Montie et al., 2000).

Differently from other food sectors, few studies have been dedicated to the application of this non-thermal treatment for the processed fish. The bactericidal effect of a dielectric barrier discharge (DBD) prototype was evidenced in mackerel fillets by Trevisani et al. (2021) in terms of viability and histamine-producing activity of psychrotrophic bacteria, also in combination with sodium dodecyl sulphate and lactic acid. The potentiality of the technique for ensuring the microbiological quality and safety of seafood have been recently evidenced in the reviews proposed by Kulawik and Kumar Tiwari (2018), Ekonomou and Boziaris (2021), and Andoni et al. (2021).

If cold plasma reactive species generated in gas phase can diffuse into a water-based environment or can be generated underwater, a series of complex reactions involving the formation of biologically active species such as nitric/nitrous acid, hydrogen peroxide (H_2O_2), superoxide radical anion ($O_2^{-\cdot}$), and peroxynitrite ion ($ONOO^-$) or peroxynitrous acid (ONOOH) can occur (Oehmigen et al., 2010). However, the interaction between gas and liquid phases or the underwater generation of these species is not well understood (Jiang et al., 2016) and require further fundamental investigation.

The use of UVC light (wavelength, λ, ranging between 100 and 280 nm), also known as "cold pasteurization" is another well-established method to reduce or eliminate pathogens and to extend the shelf life of fresh-cut fruits and vegetables. However, UVC light is highly energetic and represents an expensive investment in terms of both initial set-up and operating costs. Irradiation at lower energy (such as UVA, with λ between 320 and 400 nm) would be desirable, but generally ineffective for the required tasks (EPA Research, 2016). In a previous paper (Berardinelli et al. 2021), we investigated the features of a treatment combining cold plasma discharge and photocatalysis for water decontamination in order to assess the existence of process intensification between the two technologies, similarly to other cases in the relevant literature. Preliminary results suggested that afterglow species, e.g. hydrogen peroxide and/or peroxynitrous acid could be activated by UVA light irradiation, producing hydroxyl radicals in the liquid phase and that TiO_2 limited this effect by acting as UVA screen barrier material. Even if the decontamination efficiency of photocatalysis under certain conditions could be higher than that obtained with plasma systems, no synergistic effects between plasma and photocatalysis could be proved in this case.

In the present paper, we focus at providing novel insights on the synergistic effect between plasma and UVA irradiation, reported in our previous study for methylene blue as a model pollutant, and to extend it for a compound of biological origin such as phenylalanine, and for bacterial inactivation. The identification and quantification of active species such as peroxynitrous acid and the detection of particular reaction intermediates in plasma activated water, allowed us to propose some

mechanistic hypotheses on the nature of the observed synergistic effects, which is still under debate in literature. Finally, tests on microbial inactivation of a food-borne pathogen and on the quality of fish fillets subjected to the integrated process have been carried out, in order to highlight possible changes in colors and sensorial attributes of the fish flesh. The information hereby presented, deriving from interdisciplinary but complementary research efforts, indicates that the combination of cold plasma and UVA irradiation could be suggested as a sustainable and chlorine-free tool for the decontamination of fish processing water.

2. Materials and methods

2.1 Experimental set-up

The dielectric barrier discharge (DBD) gas plasma device consisted of two parallel plate electrodes made of brass (28 mm × 15 mm × 2 mm) and stainless steel (10 mm × 18 mm × 1.5 mm), respectively. The brass electrode was covered by a thin sheet of glass (30 mm × 40 mm × 5 mm) working as dielectric barrier. A fan was mounted at about 40 mm over the electrodes in order to facilitate the transport of the plasma induced species to the reacting solution. The solution (200 mL) was contained in a cylindrical reactor (inner diameter 120 mm; height 60 mm) made of Pyrex, placed within the chamber, and the free surface was at about 20 mm below the discharge (filling height of the reactor about 3 cm) (Fig. 1).

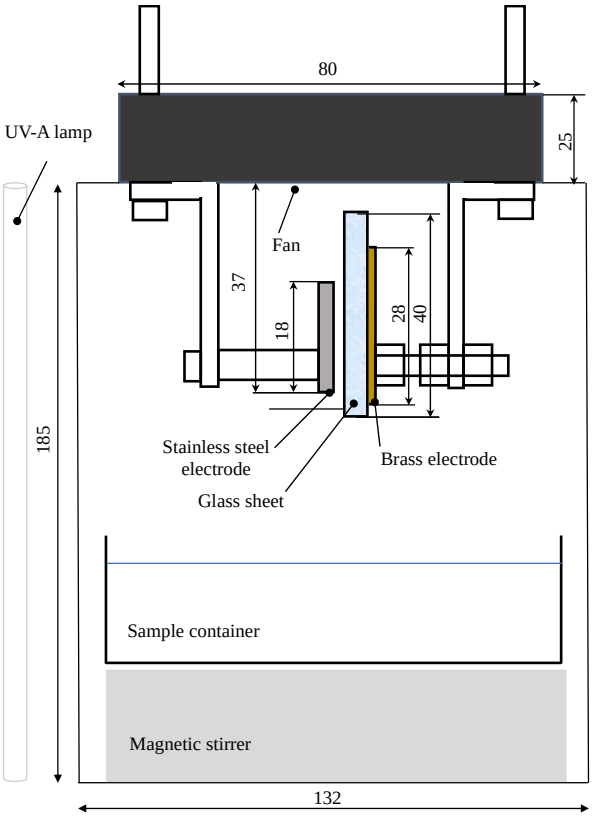


Fig. 1. Scheme of the experimental set up consisting of the dielectric barrier discharge (DBD) device in a Pyrex chamber surrounded by UVA lamps.

The electrodes, the fan, the reacting medium and the stirrer were confined in a Pyrex chamber (132 mm × 185 mm) externally irradiated by means of six actinic Mercury UVA lamps (Philips, nominal power 14 W each, emission peak centered at 365 nm as shown in Fig. S1, radiation power absorbed per unit volume of the solution about 0.7 mW mL^{-1}) surrounding the chamber in hexagonal geometry. High voltage transformers and power switching transistors supplied by a stabilized DC power supply (Elektro-Automatik GmbH & Co.KG, EA-PS 2042-06B) were used to drive the discharge operating at 19.15 V (3.15 ± 0.5 A) and by using air as working gas. The voltage output was characterized by a like-shaped sinusoidal waveform with a peak to peak value of 13.8 kV (fundamental frequency of oscillation around 12.7 kHz). The gas plasma device absorbed around 60 W (the active power at the electrode is around 17 W).

After 10 minutes of plasma treatment the temperature inside the glass chamber reached 33 ± 1°C (starting from ca. 26 °C) and was constant during the treatment (by coupling plasma with UVA, a small temperature increases of about 3°C was measured at the end of treatment). Ozone production within the chamber in the presence of the discharge has been elsewhere reported (about 0.017 mg L^{-1} in the gas phase after 2.5 min of discharge duration in a 0.19 m^3 volume chamber) as well as the nitrites (95 mg L^{-1}) and nitrates (7.5 mg L^{-1}) levels after 60 minutes in a 150 mL of 0.9% NaCl deionized water (Ragni et al., 2016).

2.2 Microbiological tests

Microbiological tests were performed in Petri dishes (90 mm of diameter) containing 26 milliliters of a cell suspension (filling height: 0.6 cm) of a 20-hours old culture of *Listeria monocytogenes* 56Ly, previously centrifuged and resuspended in saline solution (0.9% w/v) (final cell load of 8.66 ± 0.33 Log CFU mL^{-1}).

Cell viability and the pH of the cell suspensions were evaluated immediately after 60 minutes of each treatment (performed without stirring the samples) by plate counting onto agarized Brain Heart Infusion media (Oxoid) and by a pH-meter Meter Basic 20 (Crison), respectively. Each treatment was

performed in triplicate and samples analyzed in duplicate. Data are expressed as means and standard deviations. Microbiological inactivation and chemical degradation tests were carried out for (i) gas plasma treatment, (ii) UVA light irradiation, and (iii) integrated gas plasma and UVA light process.

2.3 Phenylalanine and methylene blue degradation

The degradation tests of phenylalanine (Sigma-Aldrich, p.a.) and methylene blue (Sigma-Aldrich, p.a.) were carried out at an initial concentration of 1 mM and 0.025 mM, respectively. The solution was stirred inside the reactor for 10 minutes and then the plasma discharge and/or UVA light were turned on. Three test sets were carried out, in the presence of plasma only, only under UVA irradiation, and under simultaneous plasma and UVA irradiation. Each test was carried out three times and the deviation of each experimental point was within ±5%. Samples were taken at regular intervals of time by using a syringe, and analyzed by means of a HPLC Shimadzu Prominence equipped with a Shimpack GWS C18, 5 μm, 150 × 4.6 mm column and a diode array UV–vis detector. The eluent was a mixture of 95% aqueous buffer solution (monosodium phosphate/ disodium phosphate) and 5% acetonitrile by volume, circulating at a flow rate of 1 mL min^{-1}. The quantification of the reaction intermediates was performed through calibration, by using standards (pro analysis grade) purchased from Sigma-Aldrich.

2.4 Quantification of peroxynitrous acid

The amount of peroxynitrous acid generated in bidistilled water has been measured under sole UVA irradiation, sole plasma discharge, and integrated plasma and UVA irradiation. By taking into account that the pH of the plasma activated water solution decreases to ca. 3 after ca. 10 minutes from switching on the discharge, and that the pKa of peroxynitrous acid is reported to be 6.8 (Pryor and Squadrito, 1995), peroxynitrous acid is present in the plasma activated water in its protonated form. However, the latter is highly reactive and needs to be stabilized before spectroscopic quantification. To this aim, and to avoid the uncertainties associated with a manual operation, the apparatus hereby

174 described and schematized in the Supporting Information (Fig. S2) has been devised. The reacting
175 solution was transferred through a tube (inner diameter 0.5 mm) by means of a vacuum pump to a
176 two neck round flask sealed with a rubber cap, containing 1 mL of NaOH solution (pH = 12.5). In
177 this way a controlled amount of reacting solution could be sampled and immediately mixed with a
178 NaOH solution in a reproducible way. The sample was then collected and analysed by means of an
179 UV-9000 Shimadzu UV-vis spectrophotometer. The same procedure was then repeated at fixed
180 intervals of time during the run. UV-vis spectra were deconvoluted by means of Origin software
181 (2022) to correctly evaluate the concentration of peroxynitrite through Lambert Beer law, by
182 considering a molar extinction coefficient at 302 nm of 1670 L mol^{-1} cm^{-1} (Hughes and Nicklin,
183 1968). The fitting of the spectra was satisfactory, as shown in Fig. S3 in the Supporting Information.
184
185 *2.5 Fish fillet quality assessment*
186 In order to assess possible negative effects of the proposed treatments on fish quality properties, fresh
187 rainbow trout fillets (*Oncorhynchus mykiss*) were purchased from a local producer in the Trentino
188 province (Italy).
189 Fish fillet samples (about 40 mm × 30 mm) were obtained from a total of 10 fillets. 12 samples were
190 treated with gas plasma and 12 samples with integrated gas plasma and UVA light process for 60
191 minutes (for both treatments). The tests were performed in a cylindrical reactor (inner diameter 120
192 mm; height 60 mm) in Pyrex positioned within the above described chamber and containing 200 mL
193 of distilled water. A number of 12 non-treated fillets immersed for 60 min in distilled water was also
194 considered as control samples. For each treatment type, quality properties were assessed on 12 fillet
195 samples before and immediately after the treatments, and at 1, 3 and 5 days of storage at 4°C. Color
196 measurements of the pulp were conducted by means of a Minolta ChromaMeter CR-400 reflectance
197 colorimeter (Minolta, Milan, Italy). For each acquisition, an average value of three measurements
198 was calculated. According to the CIELab system, L^*, a^* and b^* coordinates were analyzed (CIE, 1976)
199 and the Chroma values were calculated as $C^* = \sqrt{a^{*2} + b^{*2}}$.

On the same fillet fish samples, a sensory evaluation was conducted by means of a trained sensory panel according to a method developed by Cárdenas Bonilla et al. (2007) for fresh cod *Gadus morhua* fillets and adapted for trout fillet (Table 1). Increments in the demerit score refer to increments in the fish deterioration.

Table 1. Demerit score scheme for sensory evaluation.

Flesh quality parameter	Description	Demerit score
Texture	Firm	0
	Rather soft	1
	Very soft	2
Odour	Fresh, neutral	0
	Seaweedy, marine, grass	1
	Sour milk	2
	Acetic, ammonia	3
Colour	White, greyish	0
	Some yellowish, a little pinkish	1
	Yellow, over all pink	2
Bright	Transparent, bluish	0
	Opaque	1
	Milky	2
Range of the total demerit scores		(0-9)

Within the same treatment, possible significant differences in color attributes (L* and C*) were identified before, after the treatment, and during the storage by the analysis of variance (ANOVA) and Post Hoc Tukey. For demerit scores, the same significant differences were explored by Kruskal-Wallis test followed by Dwass-Steel-Critchlow-Fligner pairwise comparisons (jamovy Desktop, ver. 2.2.5).

3. Results and discussion

Fig. 2 reports cell counts of *Listeria monocytogenes* 56Ly following UVA, plasma and the combined treatment, along with the results of a control experiment.

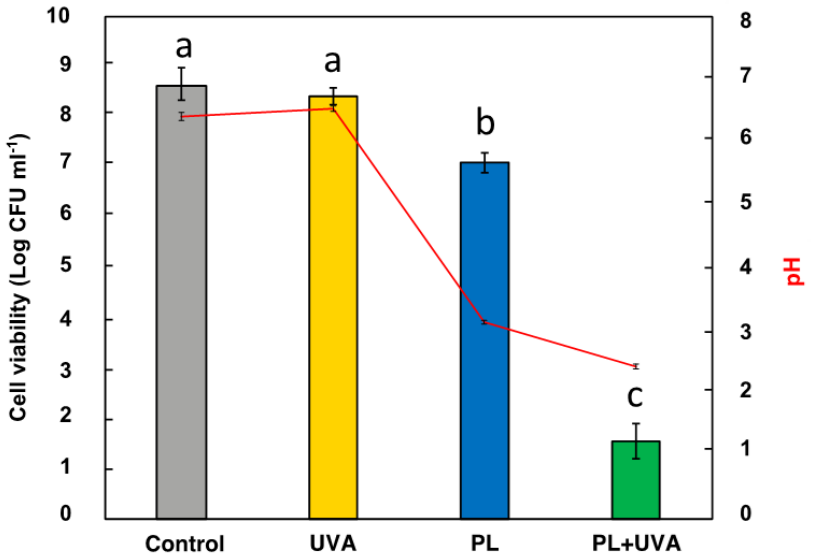


Fig. 2. Cell viability of *Listeria monocytogenes* 56Ly cells in saline solution and pH values of the solutions after exposure for 60 min to UV light (UVA), cold plasma (PL), and integrated UV light – cold plasma (PL + UVA) treatments. Values represent means ± standard deviations of values from three separate experiments. Different letters indicate significant differences among treatments ($p < 0.05$, ANOVA, post hoc Tukey).

While UVA irradiation for 60 minutes was ineffective in decreasing cell viability, exposure to plasma discharge had a significant ($p < 0.05$) effect resulting in 1.4 Log unit inactivation. By contrast, when the UVA light and plasma were simultaneously applied, the overall effect was remarkably enhanced, thus showing a synergistic effect of the combined treatments. In fact, the level of surviving cells did not exceed 1.5 Log CFU mL^{-1} being the Log reductions increased by four times compared to the plasma alone.

As reported in Fig. 2, acidification of the solution occurred during plasma treatment. However, as widely recognized in literature, the pH decrease does not influence the viability of the microbial cells (Dezest et al., 2017). Similarly, literature reports confirm that the sole UV irradiation does not play a major role in microbial inactivation process, at least when air is used as the operating gas (Guo et al., 2015; Probst-Rüd et al., 2017), as in the present case. To enhance UVA efficacy against different food-borne pathogens some authors successfully tested its use in combination with chemicals including silver ions, antimicrobials and food preservatives (curcumin, acetic or fumaric acids), thus ensuring safety of food and waters (Jeon and Ha, 2020). A synergistic interaction when treating bacterial suspensions of *Escherichia coli* with high-power plasma followed by UVA treatment was reported also by Pavlovich et al. (2013) Authors identify nitrite ions as the most important plasma-associated species responsible for the synergistic effect. In order to test this hypothesis in a more controllable way, i.e. to avoid the biological effects of the nitrite ions on the cells, we performed the degradation of methylene blue (MB) under sole UVA irradiation and UVA in the presence of nitrite ions (1 mM). It is worth to mention that MB was chosen because it is a widely used model pollutant whose photochemical behavior and photodegradation path is well known. Moreover, it presents an absorption minimum between 350 and 450 nm, i.e. at the maximum emission (365 nm) of the irradiation source hereby used. Therefore, photoinduced processes driven by its excited triplet state such as photosensitized singlet oxygen generation are minimized (Mitoraj et al., 2018). Results are reported in Fig. 3, along with the MB degradation under sole plasma and coupled plasma-UVA treatments.

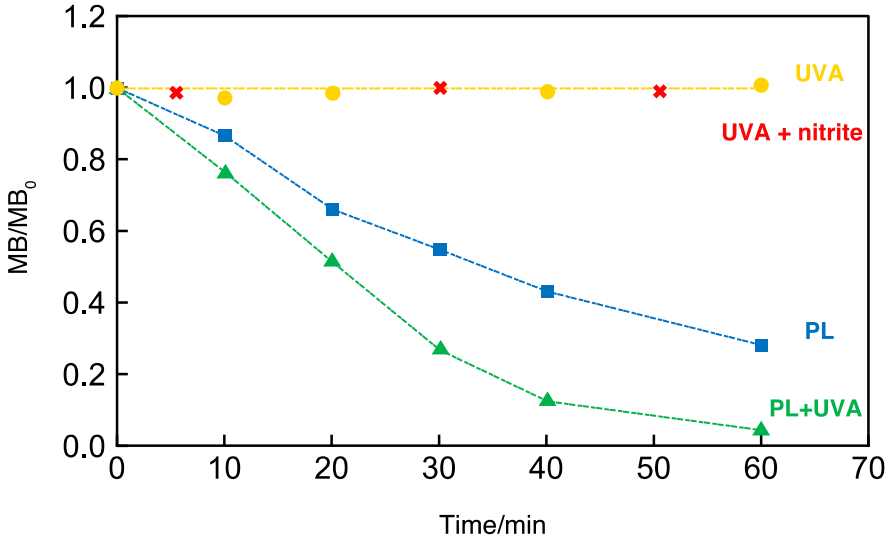


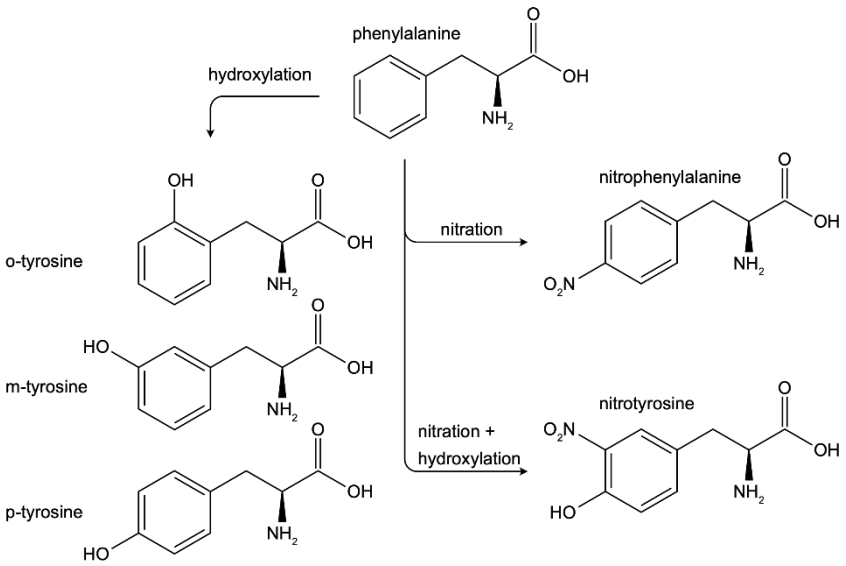
Fig. 3. Normalized concentration of methylene blue (MB) during UVA light (UVA, circles), UV light in the presence of 1 mM sodium nitrite (UVA+nitrite, X marks), cold plasma (PL, squares), and integrated UVA light – cold plasma (PL + UVA, triangles) treatment. Each reaction was performed three times and the standard deviation was ±5%. Significant differences among treatments were observed at each treatment time ($p < 0.05$, Mann-Whitney test).

UVA light does not result in degradation of MB both in the presence and in the absence of nitrite ions. Therefore, the synergistic effect observed in UVA irradiated plasma activated water, cannot be ascribed to the sole presence of nitrite ions. Notably, the synergistic effect observed for the biological tests is also taking place for the MB degradation. In fact, in the presence of the plasma discharge and in the absence of external irradiation, the concentration of MB decreases reaching 44% degradation after 30 minutes. On the other hand, MB degradation almost doubled (ca. 73%) after the same time when the solution was simultaneously irradiated. Also in this case, the pH of the solution decreased to ca. 3 after 10 minutes of discharge. The sole plasma discharge is reported to produce ozone, hydroxyl radicals, reactive oxygen and nitrogen species (Perinban et al., 2019). Hydroxyl radicals in the liquid suspension during plasma treatment in the absence of UVA light could not be detected through benzoic acid-based trapping methods (Vione et al., 2010; Berardinelli et al. 2021). Production

of ozone has been elsewhere reported for this system in the dark (Ragni et al., 2016). Therefore, plasma induced oxidation of MB can be at this stage of investigation tentatively attributed to ozone or to ROS and RNS dissolved in solution.

On the other hand, the degradation rate enhancement observed when plasma and UVA light operate simultaneously, can be attributed to dissolved species absorbing in the emission range of the UVA lamps. Even if the effect of ozone in the dark cannot be neglected (Camera Roda et al., 2019), it cannot be responsible for the light induced enhancement as it presents an absorption shoulder centered at 254 nm, while wavelengths shorter than 300 nm are cut off by the Pyrex walls of the discharge chamber. Therefore, the intensification effect of the coupled UVA-plasma treatment must be related to the presence of ROS and/or RNS generated through plasma discharge, which are photoactive in the UVA range.

In order to unveil the nature of the synergistic effects between plasma and UVA irradiation, we carried out plasma, UVA, and combined plasma-UVA treatments in the presence of phenylalanine (PA). The choice of this compound relies firstly on its biological nature, which makes it suitable for the purposes of this investigation. Moreover, phenylalanine is a known trap molecule for ROS and RNS species (Oeckl and Ferger, 2009), producing three major hydroxylation (o-, m-, p-tyrosine) and two major nitration products (nitrophenylalanine, nitrotyrosine) as shown in Fig. 4. In particular, the presence of these reaction intermediates has also been used in literature to infer the presence of peroxynitrous species (van der Vliet et al., 1994).



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290

291 **Fig. 4.** Products of nitration and/or hydroxylation of phenylalanine (PA).

292

293 Fig. 5a shows the normalized concentration of PA during time for UVA, plasma and coupled UVA-
294 plasma treatment, while Fig. 5b and 5c report the formation of tyrosine (TYR) and para-
295 nitrophenylalanine (NPA), respectively, for the same runs. The concentration of tyrosine is calculated
296 as the sum of the concentrations of the three isomers (ortho, meta and para). No nitrotyrosine could
297 be detected during the 60-minute runs. In addition, during the PA degradation tests in the presence of
298 cold plasma, the pH of the solution decreased to ca. 3 after 10 minutes from switching on the
299 discharge.

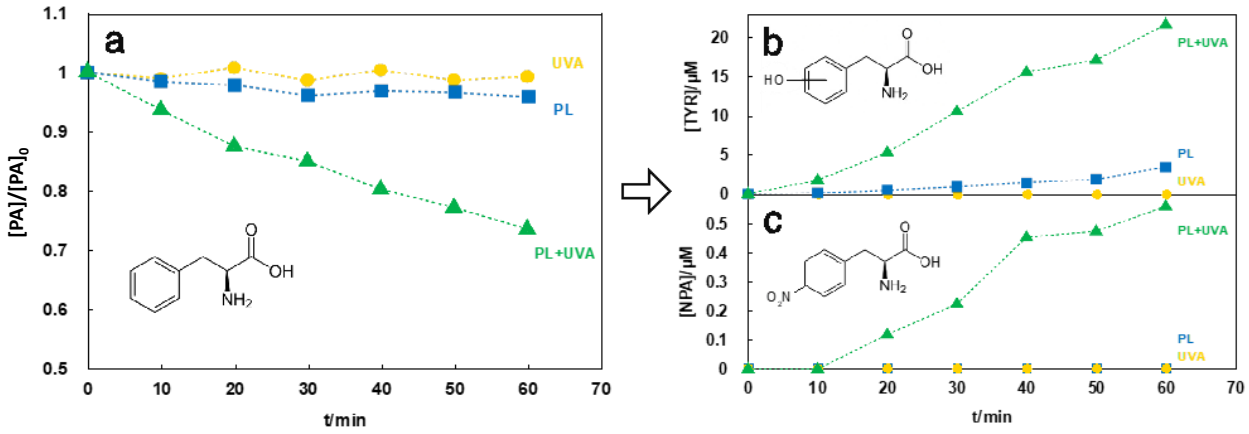

Fig. 5. Normalized concentration of phenylalanine (a), concentration of generated tyrosine (b) and nitrophenylalanine (c) during UV light (UVA, yellow circles), cold plasma (PL, blue squares), and integrated UV light – cold plasma (PL + UVA, green triangles) treatment. Each reaction was performed three times and the standard deviation was ±5%.

Sole UVA irradiation does not produce degradation of phenylalanine and, accordingly, no reaction products were detected in this case. This result is in agreement with the fact that PA does not absorb at wavelengths longer than 300 nm. In the presence of the sole plasma discharge, phenylalanine degradation proceeds to a certain extent, and formation of tyrosine could be observed. In this case traces of nitrophenylalanine could be detected only after 120 minutes of plasma treatment (not reported in Fig. 5c). When combining cold plasma and UVA irradiation, significant degradation of phenylalanine can be observed and, accordingly, the production of tyrosine is increased seven-fold with respect to the case of sole plasma treatment. Moreover, under these conditions formation of nitrophenylalanine could be also observed already during the first 60 minutes of treatment (Fig. 5c). Results show that formation of hydroxylation and nitration intermediates is greatly amplified when UVA and plasma processes act simultaneously. Notably, the observed effect holds also in terms of energy consumption, as shown in Fig. S4 (Supporting information). The faster degradation retrieved

also on a per-unit energy basis is relevant in perspective for a possible scale-up of the process, as recently highlighted in literature (Wang et al., 2021; Wang et al., 2022).

Among the post discharge species formed in plasma activated water, peroxynitrous acid is reported in literature along with hydrogen peroxide, ozone, nitrate and nitrite ion, and superoxide radical (Perinban et al., 2019). However, while plenty of information are available in literature on the latter species, quantitative data on peroxynitrous acid formation have been rarely reported (Tarabova et al., 2019). In order to get direct and quantitative evidence of the presence of peroxynitrous acid in plasma activated water, with and without UVA irradiation, we performed the measurement as described in the experimental part. Results are shown in Fig. 6.

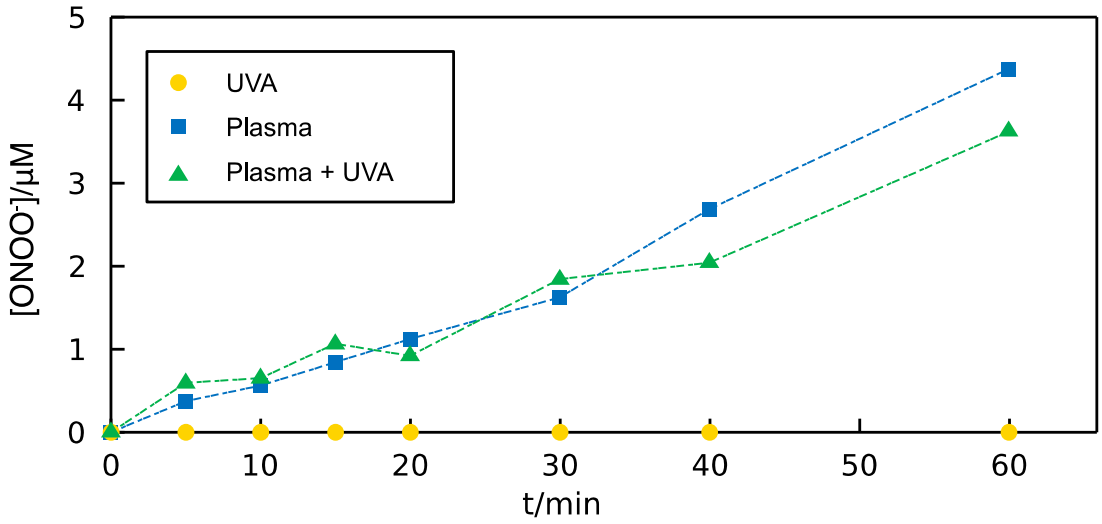

Fig. 6. Time dependence of the concentration of peroxynitrous acid in plasma activated water (measured as peroxynitrite ion upon alkalinization of the sample) in the absence (blue squares) and in the presence (green triangles) of UVA irradiation. Results under sole UVA irradiation are also reported (yellow circles). Each test have been performed three times and the standard deviation was ±5%.

The concentration of peroxynitrous acid in plasma activated water increases almost linearly during the discharge, reaching a concentration of ca. 4 µM after 60 minutes of plasma glowing. It is worth

to mention that this value could underestimate the real concentration in plasma activated water, due to the few seconds needed to transfer the solution into the NaOH solution. However, the error results systematic, due to the standardized procedure of measurement. Notably, formation of peroxynitrous acid does not depend on the simultaneous UVA irradiation. Even if apparently this result seems to disagree with the intensification effect observed, we have to consider that the measurement is carried out in distilled water. In fact, peroxynitrous acid is a transient species, whose concentration is the result of equilibria greatly influenced by the presence of dissolved molecules such as phenylalanine. However, the direct evidence of the formation of peroxynitrous acid in plasma activated water, along with the results of the biological and chemical tests described above, allows to propose some mechanistic insights on the observed synergistic effects.

Peroxynitrous acid (ONOOH) is an unstable isomer of nitric acid, which can be produced through reaction of superoxide radicals and nitrogen oxide (Eq. (1)) (Pryor and Squadrito, 1995), or by reaction of hydrogen peroxide and nitrous acid (Eq. (2)) (Saha et al., 1998).

$$HO_2 + NO \rightarrow ONOOH \quad (1)$$

$$H_2O_2 + HNO_2 \rightarrow ONOOH + H_2O \quad (2)$$

All of the reactants in Eqs. 1-2 are reported to be post discharge species present in plasma activated water (Perinban et al., 2019). By taking into account that the pH of plasma activated water reaches a value of ca. 3 after few minutes, peroxynitrous acid is present mainly in its protonated form (ONOOH, pKa = 6.8) (Pryor and Squadrito, 1995).

Despite decades of research, a complete understanding of the chemistry of peroxynitrous acid has proved to be elusive (Koppenol et al., 2012). Peroxynitrous acid is reported to quickly isomerize to nitric acid. However, in the presence of suitable substrates such as phenylalanine, is reported to give rise to hydroxylation and nitration directly (Goldstein et al., 1996), or indirectly after homolytic rupture of the O-O bond and consequent formation of hydroxyl radical and nitrogen dioxide (Eq. (3)),

which in turn can initiate hydroxylation and nitration reactions, respectively (Pryor and Squadrito, 1995).

$$ONOOH \rightarrow OH^{\cdot} + NO_2 \quad (3)$$

Even if the homolysis of ONOOH and the mechanism of isomerization to nitric acid are still under debate in literature (Koppenol et al., 2012), there is agreement on the hydroxylating and nitrating capability of peroxynitrous acid.

It shall be mentioned that another pathway of decomposition of peroxynitrous acid has been reported (Eq. (4)), where the products are oxygen and nitrite

$$ONOOH + ONOO^- \rightarrow O_2 + H^+ + 2NO_2^- \quad (4)$$

However, the kinetics of this mechanism is negligible at a pH below 4 (Coddington et al., 1999), which is the case of the present experimental conditions.

The formation of small amounts of tyrosine and traces of nitrophenylalanine observed with the plasma treatment in dark conditions can be hardly attributed to the sole action of peroxynitrous acid. The limited extent to which phenylalanine was converted suggests that the action of peroxynitrous acid is relatively modest. The short life of peroxynitrous acid can readily account for that, as confirmed by the relevant amount of nitrate detected in plasma activated water. Moreover, several other post-discharge reactions could be responsible for the tyrosine formed after plasma discharge under dark conditions. Primarily, hydroxylation can be induced by hydroxyl radicals directly generated by plasma, or formed by known reaction of superoxide radicals (HO_2) in water (Parrino et al., 2015) (Eqs. 5-6).

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \quad (5)$$

$$H_2O_2 + HO_2 \rightarrow \cdot OH + H_2O + O_2 \quad (6)$$

It shall be mentioned that generation of hydroxyl radicals is also reported through reaction between ozone and hydrogen peroxide (known as the *peroxone* process). However, this reaction requires deprotonated hydrogen peroxide (pKa ~12) (Merényi et al., 2010), thus is inefficient at acidic pH values (Ding et al., 2019). Finally, the plasma discharge emits some UV radiation. Therefore, it cannot be excluded that some of the reactions discussed below under UVA irradiation could take place even under nominal dark conditions.

Under external UVA irradiation of plasma activated water, both hydroxylation and nitration products are formed, and faster degradation of phenylalanine is observed (Fig. 5). Hydroxyl radicals can be formed directly through photolysis of hydrogen peroxide, occurring at wavelengths shorter than 400 nm (Eq. (7)). On the other hand, hydroxyl radicals can be indirectly produced through photolysis of peroxynitrous acid (at $\lambda < 355$ nm) to nitrogen oxide and hydroperoxyl radical (Eq. (8)). Accordingly, Sturzbecher et al., 2009 reports that photolysis of peroxynitrous acid occurs primarily (95%) through fast homolytic rupture of the N-O bond with a rate constant of 1.6×10^{10} M^{-1} s^{-1}. Hydroperoxyl radicals (OH_2) in turn, produce hydrogen peroxide according to Eq. (5), thus becoming a further source of hydroxyl radicals (Eq. (6)-(7)).

$$H_2O_2 \xrightarrow{h\nu} 2 \cdot OH \quad (7)$$

$$ONOOH \xrightarrow{h\nu} NO^{\cdot} + HO_2^{\cdot} \quad (8)$$

Therefore, hydroxyl radicals are eventually generated by photolysis of hydrogen peroxide, deriving directly from plasma discharge or indirectly from photolysis of peroxynitrous acid (Eq. (5)-(6), (8)). The presence of nitrophenylalanine, detected after the first minutes of reaction only in the UVA-plasma integrated process, suggests that the contribution of peroxynitrous acid to the process intensification observed under UVA irradiation of plasma activated water is not negligible. In fact, the sole plasma discharge produces only traces of nitrophenylalanine, indicating that the direct nitration through peroxynitrous acid reported in literature (van der Vliet et al., 1994) is a secondary

path also under UVA irradiation. On the other hand, it seems more plausible to consider nitrogen oxide produced upon photolysis of peroxynitrous acid (Eq. (8)) as a source of NO_2, which is a known nitrating agent (Beckman and Koppenol, 1996). In fact, NO_2 can be easily produced by reaction of nitrogen monoxide with either oxygen (Eq. (9)) or ozone (Eq. (10)) (Fontijn et al., 1970).

$$2NO^{\cdot} + O_2 \rightarrow 2NO_2^{\cdot} \quad (9)$$

$$NO^{\cdot} + O_3 \rightarrow NO_2^{\cdot} + O_2 \quad (10)$$

Finally, a further source of NO_2 under UVA irradiation could be the reaction of hydroxyl radicals with nitrite ions (Eq. (11)) (Coddington et al., 1999).

$$NO_2^- + \cdot OH \rightarrow OH^- + NO_2^{\cdot} \quad (11)$$

This path could contribute to nitration under UVA irradiation due to the enhanced production of hydroxyl radicals above mentioned. However, the rate constant reported in literature for this reaction is almost one order of magnitude lower than the photolysis of peroxynitrous acid (Eq. (8)) which, therefore, seems to play a key role, together with hydrogen peroxide, in the intensification effect observed when irradiating plasma activated water.

In order to test if plasma treatment alone or under simultaneous UVA irradiation affects the quality parameters of fish fillet, we investigated color and sensorial attributes during storage for five days. Main results are reported in the Supporting Information (Table S1) in terms of L* and C* values and demerit scores mean values and standard deviations.

In general, for both color attributes, slight differences (p-level < 0.05) between the control sample and sample means characterized by different storage days were observed for both plasma and plasma with UVA treatments. A slight increase in lightness was observed immediately after the treatments and for the control samples. This result was probably because all samples (treated and control) were immersed in 200 mL of distilled water (Trevisani et al., 2021). This last effect was not appreciated in terms of demerit score that, as expected, increases by increasing the storage days due to degradative mechanisms normally observed during fish fillet shelf life (Cheng et al., 2015).

Main results suggest that the proposed treatments do not induce appreciable modifications in the quality attributes with respect to a control sample during the shelf life of five days at 4°C.

4. Conclusions

Low energy "cold plasma" generated in a confined chamber through dielectric barrier discharge has been demonstrated to degrade chemical compounds and to reduce *L. monocytogenes* in aqueous solution. UVA light alone, being far less energetic than the commonly used germicidal UVC light, does not provide neither chemical degradation nor bacterial inactivation. However, the simultaneous irradiation of the reacting substrate with UVA light irradiation significantly enhances the efficiency of chemical degradation and microbial reduction, in the integrated process with respect to the sole plasma treatment. Degradation tests with phenylalanine, a known peroxynitrous acid trap and the quantitative evaluation of the amount of peroxynitrous acid produced during plasma treatment allowed to highlight the role of peroxynitrous acid in the synergistic effect observed. The integrated plasma-UVA process does not affect the quality parameters of fish fillet samples subjected to the treatment. Therefore, these results could potentially boost a commercial diffusion of plasma devices for food applications in liquid phase, which have been up to now hindered by the limited penetration of short living gaseous reactive species into the deeper layers of bulky food products.

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