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Centre of Research on Food Safety and Control - CRESCA UPC

Polytechnic University of Catalonia (UPC), Terrassa Campus

SUBJECT:

Evidence of safety for humans of Advanced Oxidation Processes (AOP) based on the emission of OH· radicals for disinfecting indoor air and surfaces.

To whom it may concern:

Since 2012, the Centre of Research on Food Safety and Control of the Polytechnic University of Catalonia (CRESCA-UPC) has developed several studies and work protocols for the validation of the efficacy and safety of advanced oxidation processes through Hydroxyl radicals (OH·) that have concluded with a publication in April 2020 entitled: Evidence of OH· radicals disinfecting indoor air and surfaces in a harmless for humans method (M.Vimbert et al, 2020).

In the aforementioned report, it is concluded that advanced oxidation through hydroxyl radicals (OH·) is a fast, efficient, safe and harmless method for humans; with proven biocidal efficacy on some types of gram+, gram- bacteria, covered and uncovered viruses and fungi under different relative humidity conditions.

The Advanced Oxidation Processes (AOP) based on the emission of hydroxyl radicals (OH·) are a harmless environmental sanitation method, which has demonstrated a high biocidal efficacy for the elimination of pathogenic microorganisms and volatile organic compounds (VOCs), degrading them to mineral forms or harmless organic compounds.

The results of different studies show that OH· radicals rapidly destroy different microorganisms with a concentration of 0.8 mg/L and a spray density of 21 µL/m² in 4 seconds.

Compared to chemical disinfectants, advanced oxidation technology, based on the emission of OH· radicals, has several advantages:

- 1) Lack of selectivity; it can kill any pathogenic microorganism in low lethal doses due to its strong oxidative character.
- 2) The processing time for OH· radicals is very short; The reason is that the chemical reaction rate of OH· radicals is greater than 10⁹ L mol⁻¹ second⁻¹, which is 10⁷ times greater than in other oxidants such as O₃, H₂O₂, Cl₂, etc.
- 3) As a green oxidant, OH· radicals decompose into H₂O and O₂ without residual oxidants after their biochemical reactions.

The technological objective is based on the milestone of achieving a technology capable of producing OH· radicals in sufficient quantities through an innovative system that guarantees their efficacy and safety for human beings. The Wadu02© system is a device by which an oxygen reactive specie (ORS) such as hydrogen peroxide (H₂O₂) or a terpene such as d-limonene evaporates. This evaporation will react with an internal ozone emission below a concentration of 0.050 ppm (0.1 mg/m³), the ozone exposure limit established in the regulations issued by the WHO in the environmental limit values (ELV) of the year 2000 for the general public in exposures of up to 8 hours, taken as an

international benchmark for safety in ozone emission and thus obtain a constant and non-harmful production of OH· radicals.

The ozone emission of the Wadu02© system, certified in active mode and night mode in parameters less than 0.020 ppm (0.012 - 0.015 ppm without filters and 0.015-0.016 ppm with filters, respectively) was lower than all international standards with respect to safety in prolonged exposures to ozone.

The production of OH radicals through the oxidation of H₂O₂, under controlled conditions, was evaluated and the results indicate that the average oxidative capacity of a H₂O₂ at 0.5% purity is equivalent to the oxidative capacity offered by the Wadu02© system, with a maximum production of 0.9 mg/m³ (0.64 ppm), which is approximately 64.2% of the current occupational exposure limit (OEL) set at 1.4 mg/m³ (1 ppm).

The threshold concentration for the acute irritant effects of hydrogen peroxide gas in the respiratory tract is 10 mg/m³ (equivalent to 7 ppm) in humans, while the corresponding values for the skin are 20 mg/m³. With respect to its prolonged exposure, hydrogen peroxide has not been found to cause teratogenic or carcinogenic effects in humans. Neither mutagenic nor chromosomal effects have been observed.

It was also verified, as an alternative to the high natural reactivity that hydrogen peroxide presents, the replacement of the cartridge charge with d-limonene for its antiviral and antibacterial properties and the advanced oxidation process was analysed under the same conditions of low ozone emission (less than 0.02ppm) with the Wadu02© system, to compare the efficacy already proven with hydrogen peroxide.

The total consumption of d-limonene in the Wadu02© system was determined to be of the order of 0.4 g/24h. Depending on the functionality of this device and the average evaporation of the measurements recorded in the laboratory, the Wadu02© system emit a cloud containing d-limonene with a concentration of approximately 1.84 ppm, which in a 60m² (180m³) room can result in a maximum concentration lower than 2 ppb. This concentration is significantly lower than the Swedish and German Occupational Exposure Limit (OEL) levels which are 27ppm and 10 ppm, respectively.

Once it was verified that the total consumption of d-limonene and hydrogen peroxide does not exceed the limits that are considered teratogenic and carcinogenic in humans and that the ozone emission is lower than in international regulations, the effectiveness in reducing formaldehydes was evaluated in the advanced oxidation of limonene with Wadu02©. The results indicate that the reduction of formaldehyde in ozonolysis reactions with emissions less than 0.020 ppm and with low concentrations of d-limonene with an evaporation of 0.4 g/24h equivalent to 1.84 ppm is significant and reaches values of 19% with gel and 41% with liquid d-limonene cartridge.

These results show that, despite the high reactivity of d-limonene with ozone for the formation of formaldehyde, the controlled emission of ozone below 0.02ppm and the evaporation of d-limonene below 2 ppb in a space of 60m² is a reaction safe and harmless.

Finally, it is determined that the biocidal function of OH· radicals is based on the advanced oxidation process. This mechanism of cellular stress is generated by the phenomenon of "respiratory explosion" through a cascade of reactions due to the release of reactive oxygen species:

- 1) The OH· radical is the most reactive species in biology (half-life 100 picoseconds)
- 2) Hydrogen peroxide can pass through biological membranes.



3) The hypochlorite ion modifies and degrades all biological molecules. It is a product of the respiratory explosion (similar to the mitochondrial).

The application of OH· radicals in different studies has shown that their application in advanced oxidation processes, standardized as a safety measure performed by Wadu02© are safe, innocuous and effective in the control of pathogenic microorganisms, elimination of suspended particles, formaldehyde and VOC (Volatile Organic Components).

The evidence on the efficacy of OH· radicals as a biocide shows us that their use is supported by being a strong oxidant, capable of eliminating microorganisms in low concentrations (0.8 mg/L) equivalent to 10 thousandths of the dose of conventional chemical disinfectants. Its spray density dispersion is 22 ml/cm², which represents one thousandth of other disinfectants, its constant high reaction rate 10⁹ L/mol·s in OH· radical processing is less than 4 seconds, which is one thousandth of chemical disinfectants.

Finally, the damage that has been observed to pathogens under a microscope is irreversible.

The results show that the use of OH· radicals in the advanced oxidation process produced by the Wadu02© purifier is a new safe and effective method to rapidly eliminate pathogenic microorganisms in large spaces.

The inclusion of equipment for the disinfection of air and surfaces through the emission of hydroxyl radicals within their standard work procedures for cleaning and disinfection of a space does not constitute a process that replaces the disinfection and cleaning protocols already implemented, but will make them safer and more effective due to the evidence of the effectiveness of these advanced oxidation processes.

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