Non-Thermal Plasma for Microbial Decontamination and Chemical Removal

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Plasma is a quasi-neutral system in a gaseous or fluid-like form that can be artificially generated in an electromagnetic field and a flow of neutral gases such as helium, argon, nitrogen, oxygen, or atmospheric air. It contains a mixture of radicals, H2O2, O3, ultraviolet radiation, charged particles, exited metastable atoms, and electric fields. Non-thermal atmospheric plasma has recently attracted great research interest as an alternative for operative solutions to problems related to safety and quality control. It is a powerful tool for the inactivation of different hazardous microorganisms and viruses, and the effective decontamination of surfaces and liquids has been demonstrated. Additionally, the plasma's active components are strong oxidizers and their synergetic effect can lead to the degradation of toxic chemical compounds such as phenols and azo-dyes.

Keywords: non-thermal atmospheric plasma; microbial decontamination; chemical removal; safety

1. Introduction

Our contemporary society is facing many environmental challenges due to the unprecedented level of industrialization, urbanization, and exponential growth of the human population. The increasing generation and disposal of wastes, environmental pollution, source depletion, biodiversity loss, climate changes, and growing energy demand are global threats to our sustainable development and require a fundamentally new rethinking to reduce the consumer footprint on nature [1][2][3][4]. The transformation of our linear "take-make-waste" system to the cyclic flow of materials and energy is urgent, and this is a key driver for the rapid development and promotion of the circular economy concept. The circular economy has the potential to overcome challenges by following three general principles: "(1) preserve and enhance natural capital by controlling finite stocks and balancing renewable resource flows; (2) optimize resource yields by circulating products, components, and materials in use at the highest utility; (3) foster system effectiveness by revealing and designing out negative externalities" [5][6]. The most widely applicable aspects of the circular economy include ecodesign for sustainability, an extension of the product life cycle, and implementation of "reduce, reuse and recycle" option in waste management [7][8]. However, the closing of loops in different industrial sectors by circulation, reuse, and recycling of materials and products brings to the fore other key issues—those related to safety and the prevention of risks from secondary contamination. Ensuring a high level of uncompromising safety in circular economy practices is a priority task and an important keystone for the achievement of high social acceptance and positive user perceptions and attitudes.

When discussing safety issues, it must be taken into account that safety includes both microbiological and chemical aspects. The context of the circular economy is no exception-we must be sure that the use of waste streams from one industry/sector as a material input for another is completely safe and the possibility for the crossover of chemical or microbiological hazards is eliminated/minimized. The problem is escalating nowadays with the enormous production and use of chemicals, resulting in a global scale of chemical pollution, and the pandemic distribution of unknown viruses and multidrug-resistant bacteria [9][10]. It is clear that we urgently need new advanced approaches ensuring both microbiological safety and the removal of potential chemical residues in different materials and products, with the quick achievement of the high safety level, easy operation, lack of residual toxicity, and wide use with no application restrictions [11][12][13]. Facing these scientific and practical challenges, it seems that one well-known physical phenomenon—plasma—and some recently developed plasma-based technologies can effectively respond to these requirements.

Plasma is a quasi-neutral system in a gaseous or fluid-like form that can be artificially generated in an electromagnetic field and a flow of neutral gases such as helium, argon, nitrogen, oxygen, or atmospheric air. It contains a mixture of radicals, H_2O_2 , O_3 , ultraviolet radiation, charged particles, exited metastable atoms, and electric fields [14][15]. The plasma active components individually are well-known sterilization agents, and as expected, their combination in plasma has a strong synergistic effect and provides high bactericidal efficiency with low costs, timesaving, and non-toxicity.

Based on the temperature of particles, there are two types of plasmas: high-temperature plasmas (fusion plasmas) and low-temperature plasmas (non-thermal or cold plasmas) [14]. Each type of plasma has a specific application and benefits but in the field of biosafety and microbiological control of different materials and products, the leading role of non-thermal main advantage is a simple and less expensive plasma source operating in an open space without thermal damage to treated materials. Non-thermal plasmas may be generated by direct current (DC) discharge, radio frequency discharge, dielectric barrier discharge, pulsed power, and surface wave (microwave) discharge. Microwave plasma is not in equilibrium, the electron energy distribution function is non-Maxwellian, and the temperature of the heavy particles is much lower than the electron temperature [28]. Non-equilibrium, non-thermal atmospheric pressure plasma (also called cold atmospheric plasma—CAP) is suitable to treat living tissues, heat-sensitive materials, foods, and bio-compatible materials, and has wide use in medicine, the agro-food industry, and microbiological control. The use of CAP is not limited to alternative sterilization or therapeutic technique for biomedical application—the plasma-based approach has an important role in the solution of some critical environmental issues. Recent data show its significant potential as an effective tool in pollution control and the treatment of different polluted sources. Looking at the wide field of plasma applications from a different perspective, it is clear that this huge potential can successfully contribute to improving the microbiological and chemical safety of products and materials in the circular economy.

2. Low-Temperature Non-Equilibrium Plasma for Microbial Decontamination

For convenience, the specific fields of CAP where its germicidal effect is used can be generalized as follows: (1) plasma-aided medical therapies, (2) plasma-assisted dentistry, and (3) plasma-based decontamination and sterilization for microbiological control in agriculture, food industry, microbiology, water treatment, etc.

The interaction of CAP with living objects, bacteria, spores, and viruses has been extensively studied in the last decades, and basic principles have been defined [29][30][31][32]. The main attention has been paid to plasma's killing effect on bacteria (both Gram-positive and Gram-negative), bacterial spores, biofilms, and fungi. A significant efficiency of treatment has been gained with different CAP-generated configurations against a large number of pathogens with high-risk profiles: Escherichia Listeria monocytogenes, Salmonella enterica. Staphylococcus sp.. aeruginosa, Bacillus sp.; and spores such as Candida albicans [33][34][35][36][37][38][39][40]. The bactericidal effect of CAP is clearly expressed in the treatment of biofilms on different surfaces and bacterial suspensions in liquids. Viruses and prions have been studied to a lesser extent, but in the last two years, this gap has begun to fill intensively due to the COVID-19 crisis [41][42][43]. Many studies have demonstrated the ability of non-thermal plasma to be an effective virucidal agent. The plasma treatment reduces virus burdens on contaminated surfaces and airborne viruses. and can be applied for successful prevention and interference of virus replication [44].

Some of the hypotheses for the inactivation mechanism of CAP on bacteria are summarized by Fernandez and Thompson as follows $^{[45]}$: the destroying effect of UV irradiation on DNA according to its power density and wavelength range $^{[46]}$; damage from the diffusion of reactive species through membranes and their reaction with cell macromolecules $^{[47]}$; the etching effect on the cell surface by direct bombardment with free radicals $^{[48]}$; erosion of the microorganisms through intrinsic photodesorption by UV $^{[49]}$. The last two lead to a massive leakage of cell content, a strongly negative effect on cell adhesion at biofilm growth, and the interruption or inhibition of biofilm quorum sensing systems $^{[50]}$.

In the field of agriculture and food processing, the search for new promising and effective "cleaning" tools with a multipurpose application based on cold atmospheric plasma has also been the subject of many types of research [16][24][51] [52][53][54][55]. The growing need for "green", un- or less processed food with high quality, safety, and preserved taste and nutrients leads to a very attractive rating of CAP as a powerful non-thermal sterilization technique. The recent studies are aimed at the treatment of food products, food processing devices, packaging materials, functionality modification of food materials, and removal of agrochemical residues [22][56][57][58]. Non-thermal atmospheric plasma is a promising decontamination technology for the inactivation of bacteria, yeasts, molds, and fungal and bacterial spores both on the foods and on the abiotic surfaces of packages or processing equipment [59]. The obtained results reveal promising opportunities to use CAP to ensure safety, especially in the case of the entry of waste streams in different stages of processing. The reuse of composted food wastes or activated sludge as fertilizer in agriculture, for example, may increase microbiological risk, while appropriate plasma treatment of the final product may eliminate the hazard. Additionally, plasma can be used for alternative food processing to obtain the desired color of meat products without adding chemicals, to improve the extraction of essential oils, or to extend the life of some products [27][59].

3. Low-Temperature, Non-Equilibrium Plasma for Removal of Hazardous Chemicals

The growing production, wide use, and subsequent discharge of different toxic and persistent pollutants in the environment are another serious threat to human and ecosystem health. The effective solution of associated environmental problems needs adequate pollution control based on innovative approaches, and plasma technologies are one of the promising new alternatives. Considerable attention of researchers has been focused on plasma-assisted removal of volatile organic compounds from polluted air, and significant results have already been achieved in this area [60][61][62][63]. In the last years, these technologies have been applied for the treatment of gases from animal production to food processing facilities, and a high removal and energy efficiency has been achieved [64]. Solid waste and soil treatment is another area of research interest where the focus is mainly on thermal plasma application, but some types of nonthermal plasmas have been used [65][66]. The efforts in the environmental field of plasma application are related to another target component—water—and its treatment for the removal of organic pollutants. The strong oxidation features of some highly energetic plasma components mean that plasma can be used successfully for the removal of unacceptable organic compounds in wastewater [67][68][69][70][71]. In many advanced strategies for pollution control and management, plasma technologies are considered as one of the options for the substitution of expensive traditional chemical methods in water treatment and the elimination of secondary pollution in treated water. High efficiency has already been achieved in the removal of phenol and a wide range of phenolic derivates [68][71][72][73][74], azo-dyes [65], pharmaceutical and antibiotic compounds [75][76][77], and carbon from plastic waste [78]. Several configurations have been developed and applied for the removal of different organic pollutants during discharge in the gas, liquid, or hybrid liquid-gas phase, such as pulsed highvoltage electrical discharge, glow discharge, and gliding arc [71].

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