On the Problem of Optimal Microbiological Decontamination of Air Environment and Surfaces

Yu. A. Boshnyaga\textsuperscript{a}, *, M. K. Bologa\textsuperscript{a}, and E. Yu. Agarval\textsuperscript{b}

\textsuperscript{a} Institute of Applied Physics, Chisinau, MD-2028 Republic of Moldova
\textsuperscript{b} Sulac Theoretical Lyceum, Chisinau, MD-2019 Republic of Moldova
* e-mail: iubosneaga@gmail.com

Received April 5, 2021; revised December 3, 2021; accepted December 7, 2021

Abstract—Modern civilization, providing economic and social progress, at the same time objectively creates—sometimes close to ideal—conditions for the spread of various infections. The catastrophic consequences of the \textit{SARS-CoV-2} pandemic clearly indicate that \textit{homo sapiens} appeared to be unable to effectively resist the onslaught of the coronavirus. The purpose of this publication is an attempt to fill the gap in the development of effective methods and means for microbiological decontamination that are optimal in terms of critical parameters. The observational data indicate that a significant number of \textit{SARS-CoV-2} coronavirus infections occur by air without a direct contact with the source, including over a long time interval. Precipitation helps to cleanse the air from pollutants and viruses, reducing noncontact contamination, which additionally brings up to date the problem of optimal microbiological decontamination of the air environment and surfaces. A thermodynamic approach has been used to optimize microbiological sterilization. It is shown that irreversible chemical oxidation reactions are the shortest way to achieve sterility, and they are capable of providing high reliability of decontamination. It has been established that oxygen is an optimal oxidant, including from the point of view of ecology, since its reactive forms harmoniously fit into natural exchange cycles. The optimal method for obtaining reactive oxygen species for disinfection is the use of low-temperature (\textquotedbl{}cold\textquotedbl{}) plasma, which provides the energy-efficient generation of oxidative reactive forms: atomic oxygen (O), ozone (O\textsubscript{3}), hydroxyl radical (\textit{OH}), hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}), superoxide (O\textsubscript{2}\textsuperscript{−}), and singlet oxygen O\textsubscript{2}(\textit{\textgreek{a}}\Delta\textsubscript{g}). Due to a short lifetime for most of the above forms outside the plasma applicator, objects remote from the plasma generator should be sterilized with ozone (O\textsubscript{3}), the minimum lifetime of which is quite long. It has been substantiated that the microwave method of generating oxygen plasma is optimal for energy-efficient ozone production. A modular principle of generation is proposed for varying the productivity of ozone-generating units over a wide range. The module has been developed on the basis of an adapted serial microwave oven, in which a non-self-sustaining microwave discharge is maintained thanks to ionizers (igniters), including those based on radiating radionuclides-emitters. In case of massive contamination of surfaces, it is advisable—in addition to ozone (O\textsubscript{3}) air disinfecting—to use aqueous solutions of hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}). It is essential that these reactive oxygen species for disinfecting objects remote from the plasma generator are highly efficient and, at the same time, environmentally neutral. Reliable and affordable personal protective equipment is proposed for activities in zones of increased ozone concentration. The considered optimal means of disinfection can be applicable not only in medicine but also adapted for numerous practices in agriculture, industry, and everyday life.

Keywords: coronavirus, optimization of microbiological sterilization, thermodynamic approach, reactive oxygen species, low-temperature plasma, ozone, hydrogen peroxide, microwaves

DOI: 10.3103/S1068375522050039

ON THE RELEVANCE OF OPTIMIZATION OF MICROBIOLOGICAL DECONTAMINATION

In the context of the increasing world population, its rapid urbanization and unprecedented mobility, the risks of an explosive growth in infections are rather high. The anthropogenic degradation of the environment continuously renues (actualizes) microbiological dangers. The economic and social effects due to the \textit{SARS-CoV-2} (\textit{COVID-19}) impact surpassed that due to the previous dangerous epidemics in the 21st century (\textit{atypical pneumonia, Ebola, swine and bird influenza}). A site of infection has turned like lightning (on the epidemiological criteria) into a terrible pandemic because not only the virulence of the \textit{SARS-CoV-2} \textit{“fresh”} coronavirus was underestimated but also this coronavirus infection was mostly treated as a \textit{“disease of dirty hands,”} a result of the direct contact with the source. Thus, the main instrument to prevent the spread of infection was maintaining personal

523
April–May 2021 in relation to the periodic drizzling shows the decline in the coronavirus infections in the Republic of Moldova in April–May 2021. Figure 1 coronavirus infection situation had arisen in the month amount of precipitation is not so important). The rains managed to solve this problem (furthermore, the viruses from the air. Our weather observations showed regularly (periodically) fine contaminations and any formation of oxidizing radicals derived of water (OH and O) because of no nearby molecules of water. Thus, the action of ultraviolet radiation on RNA and other virus components without any perpetuating oxidation is inefficient. We attribute a free spread of coronavirus infection in dry, warm, and sunny weather to this reason: in India, Brazil, the United States in 2020, and in Russia in summer 2021. The problem is solved removing pollutants from the air. Precipitation helps in the case of open areas, and adequate oxidation of infection agents are used in enclosed spaces (see below).

The effect of precipitation deserves some particular attention. At first sight, precipitation can only intensify infestation due to a high humidity and moderate temperatures.

However, it is much more important to remove regularly (periodically) fine contaminations and viruses from the air. Our weather observations showed that light (drizzling) but necessarily regular and long rains managed to solve this problem (furthermore, the month amount of precipitation is not so important). This unique (from the viewpoint of prevention of the coronavirus infection) situation had arisen in the Republic of Moldova in April–May 2021. Figure 1 shows the decline in the coronavirus infections in April–May 2021 in relation to the periodic drizzling (dispersal) precipitation. Please note that such a significant fall in the number of infected people could not be related to the effect of self-restraints due to the bad weather (“stay at home effect”); on the contrary, with a small percentage of vaccinated people, many mass events were held, epidemic restrictions were reduced, and full-time education was resumed in this period. On the other hand, a year earlier (spring and summer 2020) a steady increase in the number of infections was observed against the background of an extraordinary drought and complete absence of periodic drizzling precipitation in the Republic of Moldova (despite the accepted epidemic restrictions). The presented data are circumstantial evidence that a considerable number of the SARS-CoV-2 coronavirus infections occur by air without a direct contact with the source. In addition, it is appropriate to mention the results (published in July 2021) of observation of an accelerated spread of infection in the second half of summer 2020 in the western United States against the background of dry hot weather and widespread forest fires [59]. Thus, people were affected for a long time by smoke with a high content of solid particles (2.5 μm in diameter and less). In this case, the presence of smoke particles is a visual indicator of air flow routes and higher air contamination, including coronavirus. In such a situation precipitation is able to eliminate both kinds of contamination.

Figure 2 presents statistical data for the Republic of India covering the monsoon season of 2021 to confirm the link between precipitation and coronavirus spread rate. (Note that, due to a broad base, the statistical data for India are fairly reliable.) It is obvious that, in the monsoon period of 2021 in India, a considerable (more than by an order of magnitude) decrease in the infection rate per day was observed that can be attributed to a continuous removal of coronavirus from the air due to precipitation.

The resistance of coronavirus to low temperatures in winter and relatively high temperatures in summer facilitates the spread of coronavirus by air [2]. Unlike the above-mentioned respiratory virus epidemics in the 21st century, COVID-19 less depends on the seasonal factors of the environment: no expected significant decrease in infection was observed in 2020 and 2021. It should be noted, however, that daytime ultraviolet radiation from the Sun (mainly in the UV-A and UV-B ranges since UV-C is almost completely absorbed by the atmosphere) is inefficient with respect to the COVID-19 virus.

Any control of the spread of the SARS-CoV-2 coronavirus infection is rather difficult due to the seemingly positive factor—numerous asymptomatic or poorly expressed cases observed in approximately 80 percent of people. (In this regard, it is important to note that vaccination should not serve as a pretext for any unjustified relaxation since it can aggravate this factor and promote the growth in the percentage of
asymptomatic or poorly expressed cases). An infected person in the incubation period of the disease without any clinical manifestations can already be an infection source (latent period at the SARS-CoV-2 coronavirus infection is generally shorter than that of incubation). Consequently, only a small part of infection sources is controlled (in isolation) due to the epidemiological measures, and the coronavirus infection coefficient $R_t$ grows ($R_t > 1$).

Two significantly different situations of infection are observed in practice:

1. Preventive measures (large-scale testing among at-risk groups, adequate quarantine measures, vacci-
nation, etc.) allow the timely identification of infection centers at early stages enabling medics and other state structures to monitor single infections and eliminate the infection spread chains \( \left( R_t < 1 \right) \).

(2) The high rate of infection exceeds the ability of the medical system to control the epidemic, which is continuing to spread \( \left( R_t > 1 \right) \); expenditures and losses increase dramatically.

Consequently, it is necessary to control the spread of infection acting according to p. 1 when \( R_t < 1 \). When the control of the epidemic \( \left( R_t > 1 \right) \) is lost in view of a great number of the interacting factors of infection \( \left[ 3–6 \right] \), the only extremely costly and effective measure so far providing a rapid, operative limitation of the spread of the \( SARS-CoV-2 \) coronavirus infection is a well-reasoned strict quarantine \( \left( lockdown \right) \). As a result, the government structures should regulate the strictness of quarantine balancing between the caused economic damage and threats to public health (committing to the effective control of infections with the infection spread coefficient \( R_t < 1 \)). It is essential to timely and adequately implement a reliable microbiological decontamination in order to reduce the number of infections.

The optimization of microbiological decontamination (particularly, of air and surfaces) in view of an invertible prospect of new epidemic threat becomes a civilizational priority task. The social and economic progress targeted to homo sapiens paradoxically entails more favorable conditions for coexistence (unfortunately, not always harmless) with numerous bacteria and viruses.

It should be noted that the existing measures to combat harmful bacteria and viruses remain generally palliative. Bacteria successively use their natural mechanism of evolution for adaptation to the action of continuously updated antibiotics and become antibiotic-resistant. The excessively wide application of antibiotics inevitably leads to the release of them into the environment where the microorganisms generate and then carry the genetic information of resistance to antibiotics. It is difficult to hinder the adaptation of microorganisms to antibiotics and, thus, the opinion about the inevitable “antibiotic apocalypses” is strengthened. In turn, viruses, the parasitic noncellular (and the most numerous) biological formation on the Earth on the verge of living, periodically test the human immune system with updated strains (mutations). Unfortunately, the acquired immunity (including the result of antiviral vaccination) is of limited validity until the inevitable appearance of another more resistant and aggressive mutation of the virus. Mutations are an immanent property of viruses. Therefore, an unpredictable appearance of a virulent form of the virus that can destroy the extensive, expensive, and continued efforts to develop and introduce vaccines is always probable. The identified strains of \( SARS-CoV-2 \) have not as yet had any catastrophic impact on the course of the pandemic, but they can help the virus to evade the immune system, vaccines, and therapy by antibodies in the future \( \left[ 7 \right] \).

The \( COVID-19 \) pandemic is the root cause for multidimensional socio-economic shocks—the world’s largest recession after the \( Great Depression \) of the 20th century—that predetermines the relevant optimization of microbiological decontamination.

OPTIMIZATION OF MICROBIOLOGICAL DECONTAMINATION

The aim of this article is to propose some methods and means of microbiological decontamination optimal with respect to critical parameters (rapid irreversible universal sterilization; with no time limit; maximum energy efficiency; environmental safety, simplicity, availability, acceptable cost; etc.).

Microbiological decontamination (sterilization) is conventionally presented by a set of classical (standard) physical and chemical methods, including heating, chemicals, irradiation with different frequencies, high pressure, and filtration. In recent years, sterilization plasma systems are getting more and more widespread. However, though there exist numerous sterilization technologies, some serious problems remain unsolved: no 100 percent quality (sterility) guarantee, high cost and complexity of the equipment, harm to personnel and environment, duration of the process, etc. The sterilization of air and surfaces is a particular problem, and it is the main subject of this work. The formation that can replicate itself (with mandatory changes) due to the free energy accumulated from the environment is living. The range of “living” is extremely large: from noncellular prions and viruses to the most complex human body. There is a pattern: the simpler (smaller in size) is the living formation, the less vulnerable it is and, correspondingly, more difficult to detect and dangerous (prions which even do contain any nucleic acids are a typical example). On the other hand, when noncellular formations are damaged, they have no opportunity to repair it since, unlike cellular organisms, they do not possess any appropriate mechanisms.

The thermodynamic (“energy”) approach is applicable and effective to optimize the processes of microbiological sterilization. All the processes near the earth’s surface occur at constant (on average) pressure and temperature. Therefore, it is the \( isobaric-isothermal potential \), or the Gibbs free energy \( G = H − TS \), that characterizes the full potential energy of the thermodynamic system (organism or simpler formation). The input of free (i.e., high-potential high-quality) energy from the environment is a mandatory condition for sustaining life. The Sun is the only significant primary source of free energy on the Earth.

Without any input of free energy from the outside, all systems inevitably spontaneously tend to the mini-
maximum of free energy $G$ due to the enthalpy consumption $H$ and the disorder (disturbance) growth $S$. Thus, the course of the isobaric-isothermal process is determined by two factors: enthalpic factor, related to the change in the system enthalpy ($\Delta H$), and entropic factor ($T \Delta S$) caused by the varied order in the system (varied entropy). The difference between these thermodynamic factors is a function of the system state.

The dynamics of growth (or degradation) of the organism at a prescribed temperature and pressure is characterized by the change in the accumulated free energy:

$$\Delta G = \Delta H - T \Delta S. \quad (1)$$

The increase in free energy in the organism (due to the assimilation of energy from the environment) is an obligatory condition of its existence (growth and multiplication); accordingly, the reduction in free energy means degradation and, finally, death of a living formation (see Fig. 3). Thus, the free energy of a living formation should be reduced (up to a certain limit when there comes a guaranteed nonviability) for decontamination.

With respect to cellular (relatively complex) living organisms, the phenomenon of apoptosis (“cellular suicide”) of unwanted cells can be used for sterilization. The prospects for application of the knowledge about programmed cell death are associated with not only the possibilities of decontamination but also with treatment of oncological, autoimmune, and other diseases. At present, the implementation mechanisms of apoptosis are being investigated, and its regulators and activators are being studied. The following analysis showed that reactive oxygen species should be an optimal inductor of apoptosis. This fact is confirmed experimentally in [8]: hydrogen peroxide ($H_2O_2$) is an effective trigger of apoptosis. However, the problem of a selective impact on target cells remains unresolved.

Unfortunately, the programmed apoptosis mechanism cannot be used in the case if noncellular structures (viruses, prions), and other solutions should be found. Let us show that the reliable and shortest way to sterilization is to ensure irreversible chemical reactions of oxidation of infection agents.

For implementation of nonspontaneous reversible (endothermic) life-sustaining reactions, the change in free energy must necessarily be positive ($\Delta G > 0$), which means the need for the external energy supply. An indicative example of a nonspontaneous endothermic reaction symbolizing life is the photosynthesis reaction for which the absorption of high-potential solar energy is the mandatory condition:

$$6CO_2 + 6H_2O \xrightarrow{\nu} C_6H_{12}O_{6} + 6O_2. \quad (2)$$

On the contrary, reverse reaction (3) (oxidation) is a spontaneous exothermic reaction, and it means the destruction of organic life. The release of low-potential energy (“dead” energy) makes this reaction not reversible (respectively, for it $\Delta G < 0$):

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + Q. \quad (3)$$

In these spontaneous exothermic oxidation reactions, the complete reduction in free energy ($\Delta G < 0$) occurs due to the growth in the entropy (the degree of disorder $\Delta S$) and decrease in the enthalpy (heat content) $\Delta H$, see formula (1).

Thus, the irreversible chemical reactions of oxidation are the shortest method to achieve sterility. They can ensure the 100 per cent reliability of decontamination under the condition of a sufficient decrease (“combustion”) in free energy contained in virulent forms through oxidation and final transformation of organic compounds into a gaseous phase.

The best oxidizer can be chosen using the data of Table 1, which show that the fluorine atom is the strongest oxidizer in nature (fluorine is able to oxidize even oxygen with the formation of oxygen difluoride $OF_2$). However, fluorine is so active that any manipulations with it are extremely dangerous (only diamond and some kinds of glassy carbon are stable against fluorine). And furthermore, the widespread application of fluorine as an oxidizer would upset the balance of nature.

Therefore, atomic oxygen—the second in oxidizing ability (see Table 1)—is a suitable (optimal) oxidizer. The choice of oxygen as an optimal oxidizer is logical and natural: oxygen is the most abundant (in weight) element of the earth crust. Living organisms consist of oxygen by almost 70% in weight and get energy to sustain life due to the biological oxidation by inhaled oxygen of organic accumulations. Thus, oxygen is environmentally perfect as an oxidizer; it harmonically fits into the natural exchange cycles.

Unfortunately, chlorine or its derivatives were chosen and are still the main sterilizing agent in many cases on the base of expediency.

However, it should be noted that that the use of chlorine in water treatment is a necessary measure
particularly applied for long water pipelines typical for mega cities. The oxidizing properties of oxygen are better than those of chlorine (see Table 1); however, atomic oxygen and generated ozone are “perishable” products (ozone disintegrates spontaneously in air and water within several dozens of minutes). Chlorine is less active, it is not prone to self-disintegration, thus maintaining a significant aftereffect and ensuring a certain long microbiological safety. However, when anthropogenic chlorine is used for water treatment, the security is achieved with other threats to public health, because a lot of organochloride compounds, many of which are toxic, such as dioxins, can be formed in the case of chlorination. A long-term exposure to dioxins leads to the suppression of the immune system, the emerging nervous system, the endocrine system, and the reproductive functions.

Therefore, the use of chlorine in water treatment should be minimized replacing it by ozone. Certainly, it is reasonable to use ozone in water treatment within compact autonomous systems. With regard to long water system with necessarily used chlorination, for food purposes it is expedient to consume ozonated water from alternative sources (ozonated water scarcely contains any toxins) or to filter water through a layer of a high-quality adsorbent. It is important to note that boiling of chlorinated water only stimulates the formation of toxic organochlorine compounds. The prospect of sustainable development is associated with a complete exclusion of chlorine from the process of microbiological decontamination due to the improvement of oxidation by ozonation (being an optimal solution as the result is achieved at minimal free energy consumption $\Delta G$).

The nonequilibrium (“cold”) oxygen plasma, which generates reactive oxygen species, is an optimal sterilization means with respect to the microbiological decontamination of air and surfaces. This conclusion follows from the fact that most traditional physical and chemical methods of decontamination (thermal sterilization, chemicals, high pressure, ultrasonic, filtration) have limited reliability at high costs, “work” in the restricted volume, and they are ineffective in relation to spatially distributed objects. The exceptions are different types of electromagnetic radiation—ultraviolet light, X-rays and gamma rays—as well as irradiation with subatomic rays (for example, electron beams). These high-energy ionizing effects cause “endother-

### Table 1. Atom (molecule) constants which determine oxidizing properties [9–11]

| Molecules | $F_2$ | $Cl_2$ | $O_2$ | $O_3$ | $N_2$ |
|-----------|-------|--------|-------|-------|-------|
| Binding (dissociation) energy of molecules, eV (kJ/mole) and maximum wavelengths λ<sub>max</sub> dissociation limit | 1.61 (155.0) | 2.52 (242.6) | 5.12 (493.6) | 1.11 (107.0) | 9.81 (945.3) |
| $F_2 + \nu \rightarrow F + F$ | $Cl_2 + \nu \rightarrow Cl + Cl$ | $O_2 + \nu \rightarrow O + O$ | $O_3 + \nu \rightarrow O_2 + O$ | $N_2 + \nu \rightarrow N + N$ |
| Electron affinity, eV (kJ/mole) | 3.45 (332.7) | 3.61 (348.7) | 1.47 (141.5) | 2.26 (217.9) | $-0.21 (-20)$ |
| (for atom F) | (for atom Cl) | (for atom O) | (for molecule $O_3$) | (for atom N) |
| Energy of ionization (of atoms, molecules), eV | 17.42 | 12.96 | 13.62 | 12.52 | 14.53 |
| $(F + \nu \rightarrow F^+ + e)$ | $(Cl + \nu \rightarrow Cl^+ + e)$ | $(O + \nu \rightarrow O^+ + e)$ | $(O_3 + \nu \rightarrow O_2^+ + e)$ | $(N + \nu \rightarrow N^+ + e)$ | $(N_2 + \nu \rightarrow N_2^+ + e)$ |
| Electronegativity of atoms (according to L.Pauling, eV<sup>-1/2</sup>) | 3.98 | 3.16 | 3.50 | 3.50 | 3.05 |
| Electronegativity of atoms (according to [11], dimensionless) | 4.00 | 3.50 | 3.78 | 3.78 | 3.56 |
| Covalent radius of atoms, nm | 0.064 | 0.099 | 0.066 | 0.066 | 0.074 |
mic” structural damages (at which $\Delta G > 0$) and lead to the formation of free radicals, including ionized radicals. Furthermore, the radiation decomposition of oxygen and water molecules means the generation of strong oxidizers—atomic oxygen and hydroxyl radical (O and OH), respectively—favoring the decontamination of the object. However, there are parallel processes of repairing and forming some mutations—viable (virulent) forms. (Note that, in the case of microbiological decontamination with the nonequilibrium oxygen plasma, the mutagenesis is absolutely impossible). The above-mentioned features of the physical methods of sterilization (X-rays and gamma rays, irradiation with accelerated particles) are rather expensive and complex in their safety maintenance; thus, they are persistent obstacles to the use for decontamination of air and surfaces.

The ultraviolet spectrum of electromagnetic radiation deserves additional consideration due to its relatively higher safety, availability, and incidence. Artificial generators of ultraviolet for industrial and domestic applications (mainly based on gas discharge lamps) provide close ($UV-A$, $\lambda = 315–400$ nm, $E_{hv} = 3.10–3.94$ eV), average ($UV-B$, $\lambda = 280–315$ nm, $E_{hv} = 3.94–4.43$ eV), and far ultraviolet ($UV-C$, $\lambda = 100–280$ nm, $E_{hv} = 4.43–12.4$ eV) spectra. The energy of ultraviolet quanta in the range $UV-C$ is sufficient for the photodissociation of biological molecules (in particular, DNA, RNA, and proteins), but it is insufficient for practical ionizations. Please note that the extreme ultraviolet ($E-UV$, $\lambda = 10–121$ nm, $E_{hv} = 10.25–124$ eV) has a significant ionizing power; however, it is not in demand due to its complex and expensive generation (at present usually laser). The range $UV-C$ has an important advantage with regard to decontamination—since the energy of its quanta is sufficient for photodissociation of oxygen (O$_2$) and water (H$_2$O) molecules with the formed oxidizing radicals atomic oxygen (O) and hydroxyl (OH):

$$
O_2 + hv \rightarrow O + O (\Delta H = 493.6 \text{ kJ/mole});
$$

$$
H_2O + hv \rightarrow H + OH (\Delta H = 498.7 \text{ kJ/mole}). \quad (4)
$$

The oxidizing radicals (O and OH) are formed both in the air and wet surface layers (with the penetration depth of the $UV-C$ photons of some micrometers) favoring the irreversible decontamination and preventing mutations. Thus, the presence of oxygen and moisture is the necessary condition for an effective decontamination with $UV-C$ ultraviolet. It is significant that, in an anhydrous and oxygen-free environment, the sterilizing ability of ultraviolet of any hardness is reduced. In 2020, Japanese research workers proved experimentally that the granules of dried bacteria, stuck to the external wall of the station (ISS), can survive in space during 3 years [12]. There is no doubt that, under the action of hard space ultraviolet, some repeated photodissociation of the dry bacteria components took place; however, the absence of oxidizers in the cosmic vacuum caused the recovery (recombination) of broken bonds.

Solar radiation in the $UV-C$ range is almost completely absorbed by the atmosphere (mainly in the ozone layer); therefore, there is no considerable daily solar decontamination owing to the natural ultraviolet. No effect in shaded places is an important immanent drawback of ultraviolet radiation that is eliminated in the case of sterilization with diffusing oxidizing agents generated in the gaseous plasma.

In general terms, it may be noted that the independent use of ultraviolet is not an optimal and reliable option of decontamination of air and surfaces, though it is useful due to the reduction in the infection dose (viral load). In this case, the erosion of microorganisms due to photodissociation with ultraviolet is a much less efficient mechanism than direct etching (oxidation of surface layers) with reactive oxygen species.

NONEQUILIBRIUM ("COLD") OXYGEN PLASMA GENERATING REACTIVE OXYGEN SPECIES—OPTIMAL MEANS OF MICROBIOLOGICAL DECONTAMINATION OF AIR AND SURFACES

The fourth aggregate state of substance—plasma generated at gas discharges—serves as the source of the reactive oxygen species. The range of applications of gaseous plasma generated with electrophysical methods continuously expands from aerospace technologies to medicine and food industries [13–53]. Low-temperature (nonequilibrium, “cold” plasma) at atmospheric pressure is of particular interest due to its energy efficiency and relative simplicity of widespread implementation.

Gas plasma is a high energy, quasi-neutral state of gas (with a certain share of ionization of components as well as the dissociation of molecules with formed high chemically active radicals). A continuous external supply of free (highly potential) energy is necessary in order to create and maintain the nonsteady (nonequilibrium) plasma state of gas; thus, the condition for the existence of plasma coincides with the condition for the existence of life. Accordingly, the energy balance is maintained by the continuous relaxation (recombination) radiation of plasma, which is the main manifestation to determine the properties of plasma—ionization balance, temperature, density and content of elements. With no supply of high-potential energy, the time of plasma “quenching” under atmospheric pressure is fractions of a second. Thus, plasma is a “perishable” product and must be generated for application in situ.

For the purposes of microbiological decontamination, only low temperature ("cold") oxygen plasma is suitable for reasons of energy efficiency during generation as well as the necessary decontamination of the
thermolabile surfaces. This plasma is considerably nonequilibrium, the average kinetic energy of electrons is much higher than that of gas molecules and ions ($T_e \gg T_g$, respectively). It is impossible to achieve plasma nonequilibrium by the thermal method—kinetic energy is efficiently transferred only to massive molecules, and then to electrons. The problem of the selective transfer of kinetic energy to electrons is solved with the help of an alternating electric field. It is clear a priori that, for the generation of nonequilibrium plasma, it is necessary to affect the gas by an alternating electric field with the maximum frequency and intensity (naturally, exceeding the breakdown intensity). Furthermore, positive ions (being thousands of times more massive) almost stay in place and do not acquire any kinetic energy, and light electrons (with times more massive) almost stay in place and do not contract. Because of the contact with the third particle. Therefore, the microwave field frequency $f \sim 2.45$ GHz applied in industry is optimal according to a number of features (available generation sources, relatively simple realization of breakdown and essential plasma nonequilibrium, and prevention of discharge contracting).

In gas discharge (the ionization threshold exceeded), there is collisional ionization by the electron impacts with formation of molecular ions and electron multiplication:

$$O_2 + e^- \rightarrow O_2^+ + 2e^-; \quad N_2 + e^- \rightarrow N_2^+ + 2e^-.$$  \hspace{1cm} (5)

Dynamic ionization balance is maintained by the electron volumetric recombination which occurs at low temperature mainly in a dissociative way:

$$O_2^+ + e^- \rightarrow O + O; \quad N_2^+ + e^- \rightarrow N + N.$$  \hspace{1cm} (6)

Recombination of electrons with molecular ions takes place mainly dissociatively, since no participation of the third particle is necessary in this case.

The mechanism of dissociative adhesion of electrons to the molecules of oxygen for which there is the energy threshold $\sim 4$ eV (this estimate follows from the data presented in Table 1) also operates:

$$O_2 + e^- \rightarrow O^- + O.$$  \hspace{1cm} (7)

However, not a large number of dissociations (less than 15%) occur according to this mechanism.

The factor of mostly dissociative recombination is crucial for the sterilization features of plasma when atomic oxygen (O) (highly active oxidizer) is generated as a result. The reverse reactions of association (recovery of molecules $O_2$ and $N_2$) are possible, but the course of them in the undesired reverse direction is hindered due to the contact with the third particle absorbing the association energy:

$$O + O + M \rightarrow O_2 + M^*; \quad N + N + M \rightarrow N_2 + M^*.$$  \hspace{1cm} (8)

Any molecule or atom of the gaseous mixture (including molecular oxygen $O_2$ and nitrogen $N_2$) can act as the third particle.

Highly reactive and, as a consequence, short-lived atomic oxygen (O) generated due to reactions (6), (7) are of the greatest interest for decontamination. It is a three-particle reaction with molecular oxygen producing ozone $O_3$:

$$O + O_2 + M \rightarrow O_3 + M^*.$$  \hspace{1cm} (9)

The reaction takes place with the mandatory participation of the third particle receiving relatively little binding energy of an oxygen atom in the ozone molecule (Table 1: $E = 1.11$ eV, or 107.0 kJ/mole). So little binding energy predetermines the comparative instability of the ozone molecule, which increases with the growth in temperature. On the other hand, this low energy of the separation of the atom O from the molecule $O_3$, together with a high affinity to $O_3$ (Table 1: $E = 2.26$ eV, or 217.9 kJ/mole), determines the high oxidizing ability of ozone necessary for decontamination. The lifetime of ozone under favorable conditions is dozens of hours [55]; thus, the decrease in its concentration at night in the protective ozone layer in the stratosphere is insignificant, which secures the conditions of life on Earth (since ozone absorbs the harmful day solar ultraviolet radiation in the range $\lambda = 200–310$ nm). The sufficient stability of gaseous ozone can be considered as an invaluable gift of nature ensuring organic life and permitting the accumulation and delivery of the chemical energy of oxidation necessary for decontamination to the right place. (However, unfortunately, the problem of the long safe storage (accumulation) of highly concentrated ozone defies a solution even for the case of liquid or solid (cryogenic) state of ozone because of the danger of the spontaneous avalanche-like heat release according to the reaction with the explosive evolution $\Delta H = -285$ kJ/mole).

The optimal composition of the plasma-forming gas should contain molecular oxygen whose dissociation in the discharge ensures, finally, the maximum oxidation of microbiological forms.

In equations (5)–(6) there is also molecular nitrogen ($N_2$) that involves the use of air as the most suitable (cheap) plasma-forming agent. The highly active atomic nitrogen $N$ formed according to equation (6) reacts to form nitrogen oxides $NO_x$ (mainly, monoxide NO and dioxide $NO_2$). Both nitrogen oxides contribute directly and indirectly to the reduction of ozone formation in the discharge:

$$O_3 + NO \rightarrow O_2 + NO_2; \quad O + NO_2 \rightarrow O_2 + NO.$$  \hspace{1cm} (10)

There are other possible reactions of violation of ozone formation in the discharge plasma with participating nitrogen oxides, for example:
\[ \text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2; \]
\[ \text{O} + \text{NO}_3 \rightarrow \text{O}_2 + \text{NO}_2. \]  

(11)

According to the total negative effects due to the presence of nitrogen in the plasma-forming gas there follows: despite the increasing cost of the process because of the necessary preliminary separation of oxygen, nitrogen should be excluded from the gas mixture. (The positive dynamics of improvement and widespread adoption of available oxygen concentrators from the ambient air up to household appliances ensuring the acceptable oxygen concentration up to 95% should be noted).

Please note that, even without decreasing ozone formation of nitrogen simultaneously with the target reaction of ozone synthesis (9), the undesired reaction \( \text{O} + \text{O} + M \rightarrow \text{O}_2 + M^* \) takes place in plasma with the mandatory participation of the third participle \( M \) absorbing a substantial energy of association (Table 1: 5.12 eV, or 493.6 kJ/mole) and transforming it into useless heat. However, fortunately, at the high concentration of molecular oxygen in plasma, the atomic oxygen forms ozone much more likely than recombines, and the process energy efficiency remains high.

Let us consider the water vapor wetting (saturation) of oxygen supplied into the plasmotron to generate hydrogen peroxide \( (\text{H}_2\text{O}_2) \) along with ozone. As a result of shock ionization by electrons (the ionization energy of molecule \( \text{H}_2\text{O} = 12.61 \text{ eV} \), or 1217.1 kJ/mole according to [10]), there appear molecular ions of water:

\[ \text{H}_2\text{O} + e^- \rightarrow \text{H}_2\text{O}^+ + 2e^- . \]  

(12)

The competitive process of recombination of electrons with water ions takes place mainly through its dissociation since the probability of collisions with the suitable third body in the recombination process itself is not high:

\[ \text{H}_2\text{O}^+ + e^- \rightarrow \text{H} + \text{OH}. \]  

(13)

The energy consumed for dissociation \( (\Delta H = 496.7 \text{ kJ/mole according to [10]}) \) is close to that for the oxygen ion \( \text{O}_2^- \) \( (\Delta H = 493.6 \text{ kJ/mole according to Table 1}) \); the remaining kinetic energy is carried away by radicals formed due to the dissociation.

Highly reactive radicals OH participate in three-particle reaction forming hydrogen peroxide \( (\text{H}_2\text{O}_2) \):

\[ \text{OH} + \text{OH} + M \rightarrow \text{H}_2\text{O}_2 + M^* . \]  

(14)

The kinetic energy of association \( (\Delta H = 214.2 \text{ kJ/mole [10]}) \) carried away by the particle \( M \) significantly exceeds that in the case of ozone generation \( (\Delta H = 107.1 \text{ kJ/mole according to Table 1}) \) which reflects greater losses due to the useless heating of gas. The molecule of hydrogen peroxide \( \text{H}_2\text{O}_2 \), more durable in comparison with the molecule of ozone, demands higher energy of activation for the oxidation reaction. Thus, the results presented in works [56–58] indicate better impact of ozone applied to decontaminate air and surfaces in comparison with hydrogen peroxide. Nevertheless, hydrogen peroxide has its own priority application areas:, which is, above all, the prevention of surface decontamination. Furthermore, the efficiency of gaseous disinfectants depends on the infection concentration (degree of surface contamination). Their precleaning before gas disinfection with hydrogen peroxide (existing aqueous solution) to reduce the viral load is the optimal eco-friendly version: the remains of hydrogen peroxide \( \text{H}_2\text{O}_2 \), as well as ozone \( \text{O}_3 \), unlike other chemical reagents, leave no traces, except water \( \text{H}_2\text{O} \), oxygen \( \text{O}_2 \), and heat generations according to the following reactions:

\[ 2\text{O}_3 \rightarrow 3\text{O}_2 (\Delta H = -285 \text{ kJ/mole}); \]
\[ 2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2 (\Delta H = -196 \text{ kJ/mole}). \]  

(15)

A considerable virtue of hydrogen peroxide is its possible relatively simple (as compared with ozone) accumulation and long storage thanks to a higher stability of the molecule \( \text{H}_2\text{O}_2 \). At present, other methods than gas discharge plasma are optimal and widely used.

We can make a conclusion that the nonequilibrium (“cold”) plasma-generating ozone in pure oxygen is the optimal energy-saving means of microbiological decontamination of the air environment and extended surfaces. The application of aqueous solutions of hydrogen peroxide \( (\text{H}_2\text{O}_2) \) is expedient to be used when there is massive pollution in addition to the disinfecting effect of ozone \( (\text{O}_3) \).

**OPTIMAL METHODS AND DEVICES TO GENERATE AND APPLY NONEQUILIBRIUM OXYGEN PLASMA**

Plasma state is characterized by the fact that a significant part of gas molecules (atoms) are ionized. As follows from Table 1, the ionization energies of molecules (atoms) significantly exceed the energy of their dissociation. Thus, reactive radicals (neutral, agitated, and ionized) necessary for decontamination must be present as a result of the dissociative recombination of molecular gases in plasma. The mean free path of electrons in the air at atmospheric pressure are of the micrometer fractions. The minimal energy necessary for dissociation of the target molecule of oxygen \( (\text{O}_2) \) is 5.12 eV, and it is 12.08 eV for its ionization (Table 1). Consequently, the minimum intensity of the electric field \( E \) required to generate plasma in the air at atmospheric pressure is some kilovolts per centimeter \( (E \sim n \times \text{ kV/cm}) \), i.e., it is necessary to realize a high-voltage discharge. However, in order to create a high-voltage discharge at atmospheric pressure with a significant duration (comparable with the time of the electron avalanche development in gas discharges) between flat conducting electrodes, one deals with the discharge
contraction, that is, with a quick transition of it into a spark discharge, and then into a destructive arc discharge. The contraction can be overcome with the help of corona discharge (where the current is limited by a small area of corona electrodes), barrier discharge (where stabilization is achieved arranging dielectrics on the electrodes with supply of an alternating voltage), and due to the used sufficiently short pulses (nanosecond, with $T \sim 10^{-9}$ s as follows from above). It is reasonable to use the listed types of discharges as independent generators of ozone with relatively low productivity (because of their low energy efficiency and high cost).

In our opinion, the application of the electrodeless microwave (ultrahigh frequency—UHF) discharge is the optimal solution to the problem of ozone generation [60]. The absence of electrodes means not only convenient production of the applicator but also the elimination and possible dissipation of heat losses on the electrodes. In the ultrahigh frequency discharge, the coefficient of the electric energy transformation into a plasma state achieves large values (more than 80%) unattainable for other kinds of discharge. This occurs due to the fact that positive ions thousands times more massive scarcely have enough time to accumulate any significant kinetic energy during short half-periods of oscillations (less than $T \sim 10^{-9}$ s), and the total kinetic energy is got by the incomparably lighter electrons. Quick but light electrons poorly transfer the energy by massive particles that leads to the significant nonequilibrium of the microwave plasma with $T_e \gg T_x$. The risk of contraction is reduced due to the volumetric character of the UHF discharge and short period of oscillations ($T \sim 10^{-9}$ s is small in comparison with the time of the electron avalanche development: $\sim 10^{-7} - 10^{-3}$ s). The highest density and, correspondingly, the reaction ability of the UHF plasma are also unavailable for other kinds of discharge. Relatively high density of the UHF discharge plasma (correspondingly higher concentration of free electrons) ensures an efficient absorption of microwave energy [61]. The listed advantages of the nonequilibrium microwave plasma are particularly important at the decontamination of large volumes of air and extended remote surfaces.

The highest reaction capacity is observed directly in the UHF plasma torch and also depends on the working mixture composition. Naturally, moving away from the torch the concentration of the reactive particles decreases sharply. Therefore, the reactionary potential of the microwave plasma was fully achieved only with regard to relatively small surfaces directly contacting with plasma.

The working mixture composition is determined by the aims at the plasma action. For example, the presence of monoatomic helium (He) in the plasma-forming gas allows us to expect the generation of the hardest ultraviolet since the energy of the first ionization of the inert gas He (the highest among all the atoms) is 24.59 eV [10]. Pure oxygen plasma consists of neutral molecules $O_2$ as well as atomic oxygen $O$, ozone $O_3$, superoxide $O_2^–$, and electrons. Positive ions (mainly $O_2^+$) quickly recombine by means of dissociation. The listed molecules, atoms, and ions can also be in the excited state. The UHF plasma is a productive source of atomic particles (atomic oxygen in this case), and the release of them depends on the presence of other particles. The presence of water vapors ($H_2O$) in oxygen provides the generation of all oxidizing reactive oxygen species: atomic oxygen ($O$), ozone ($O_3$), hydroxyl radical (-OH), hydrogen peroxide ($H_2O_2$), superoxide (oxygen molecule with unpaired electron $O_2^–$), singlet oxygen-agitated state of oxygen $O_2(a^1Δg)$, with a half-life under normal conditions of 72 min. Due to the generation of the listed reactive oxygen species, the nonequilibrium (“cold”) plasma is the optimal means of local microbiological decontamination. Note that there is no information that any microorganisms can confront the devastating impact of the oxidizing low-temperature plasma.

It would be fair to say that the “patent” for the use of optimal reactive oxygen species belongs to nature: in support of this, it is shown in [62] that even such strong oxidizers as ozone ($O_3$) and hydrogen trioxide ($H_2O_3$) from the singlet oxygen and water are synthesized in the human body when it is necessary.

In our opinion, the application of ozone generated in situ in the microwave (UHF) oxygen plasma is optimal to decontaminate large volumes of air and extended remote surfaces. An additional argument for this solution is the widespread use of microwave heating technology at home and at work, including generators of sufficient capacity (many millions of microwave resonator-type ovens have been produced and are in service in the world). The microwave oven can be simply developed preserving the basic purpose in order to give it an additional option (function) of a plasma generator of reactive oxygen species, including ozone. It is preferable but not necessary to use a microwave oven with a dissection, which provides a better uniform distribution of the microwave field in the volume and a varied frequency (variable frequency microwave oven). This is desirable since the electromagnetic field of standing waves is nonuniform in the resonators (even in multimode ones): the neighboring nodes and antinodes are situated at a distance of a quarter of the wavelength $Λ$.

To exclude any formation of toxic nitrogen oxides ($NO_x$) in plasma, it is desirable to clean up the air as much as possible from nitrogen or to use medical oxygen.

The microwave discharge can be initiated in the microwave oven applicator using different igniters: flames of different origin (flames of household, gas lighter, alcohol lamp, etc.), subsidiary electric dis-
ON THE PROBLEM OF OPTIMAL MICROBIOLOGICAL DECONTAMINATION

533

Charges (for example, corona), and special design passive metal antenna concentrators of an electric field. When ignited, this discharge can function independently (Fig. 4).

In order to ensure the most reliable ignition, as well as to guarantee a stable operation of the generator of the reactive oxygen species at a variable load, it is necessary to use in the microwave oven a nonindependent microwave discharge (i.e., which proceeds using an additional ionizer) maintained continuously by specially selected ionizers, including the irradiating radionuclide-emitters. The maximum energy efficiency of generation is an additional advantage when using radionuclides.

Radionuclides used when generating cold (non-thermal) plasma should have a number of properties: the emitter half-life \( t_{1/2} \) must be long enough to provide energy release (ionization) with a relatively constant time during a reasonable period of time (at least, during some months).

In addition, the specific energy (measured in W/g)—the quantity of energy released (and consumed for ionization) per unit time by the unit of the radionuclide weight—is important. The power density (specific power) is inversely proportional to the half-life and directly proportional to the energy released at every act of emission of this radionuclide.

Table 2 presents the most suitable radionuclides for the generation of plasma. The isotope of polonium Po\(^{210}\) should be recognized as a preferable radionuclide for the generation of cold plasma due to its total characteristics. Its extremely high specific power (Table 2: \( P_s \sim 140 \text{ W/g} \)), which ensures the generation of sufficiently concentrated (dense) plasma, is particularly attractive. The application of a thin (as possible, monomolecular) Po\(^{210}\) layer as an emitting surface is an obligatory condition for a high energy efficiency due to the reduced useless volumetric heat dissipation. (This is because the specific power of Po\(^{210}\) is extremely large, and the Po\(^{210}\) compact capsule only 0.5 g by weight under normal conditions achieves a temperature over 500°C owing to the absorbed kinetic energy of \( \alpha \)-particles in the radionuclide volume.) At normal atmospheric pressure in the air, the \( \alpha \)-particles radiated by Po\(^{210}\) completely loses its energy (\( \sim 5.49 \text{ MeV} \)) on the path of \( \sim 4.14 \text{ cm} \) (as found by William H. Bragg). This characteristic path length of \( \alpha \)-particles is important for the optimization of the structures of suitable applicators.

On the basis of the Po\(^{210}\) \( \alpha \)-radiation, one can easily receive plasma with a desired density due to a simple increase in the area of emitting surfaces. The cost (availability) of radionuclides for the generation of cold plasma is a crucial parameter for their widespread economically viable application. Po\(^{210}\) is usually produced artificially by bombarding the almost stable \( T_{1/2} \sim 1.9 \times 10^{19} \text{ years} \) isotope of bismuth by neutrons in the nuclear reactors:

\[
{^{83}\text{Bi}}^{209} + \gamma h^1 = {^{83}\text{Bi}}^{210}. \tag{16}
\]

The radioactive Bi\(^{210}\) is then transformed into the target Po\(^{210}\) as a result of the spontaneous \( \beta \)-disintegration (with a half-life period of only 5 days):

\[
{^{83}\text{Bi}}^{210} = {^{84}\text{Po}}^{210} + e^- . \tag{17}
\]

This method of production and practical use of Po\(^{210}\) to generate plasma has already been introduced; however, it can apparently be supplemented. The compet-

### Table 2. Most suitable radioactive nuclides to generate cold plasma

| Radioactive nuclides | Half life, \( t_{1/2} \) | Specific power, W/g | Structure of radiated energy | Protection requirements | Methods of producing |
|----------------------|-------------------------|--------------------|-----------------------------|-----------------------|---------------------|
| Po\(^{210}\)          | 138.376 days            | 149                | Practically pure \( \alpha \) rad. \( \sim 5.49 \text{ MeV} \) (insignif. \( \gamma \) or X-ray radiation) | Minimal               | Subsoil (including extraction of CH\(_4\)) Nuclear reactors |
| Pu\(^{238}\)          | 87.6 years              | 0.56              | Practically pure \( \alpha \) rad. (with low level of \( \gamma \) and \( n \)) | Minimal               | Processing of SNF   |
| Am\(^{241}\)          | 432.2 years             | 0.114             | \( \alpha \)-Radiation and \( \gamma \) | Average               | Processing of SNF   |
| Sr\(^{90}\)           | 28.8 years              | 0.46              | Practically pure \( \beta \), but with secondary braking radiation | High                  | Processing of SNF   |
| Cs\(_{137}\)          | 30.17 years             | -0.8              | \( \beta \)-rad. and \( \gamma \) (not pure \( \beta \) rad.) | Maximal               | Processing of SNF   |

Fig. 4. Configuration of plasma area (foreground of microwave oven converted into plasma generator).
ing method based on the possible utilization of the radioactive isotope of radon Rn\(^{222}\) naturally coming from the bowels with its subsequent disintegration up to Po\(^{210}\) is being studied. The gaseous radon Rn\(^{222}\) with a half-life period of only \(t_{1/2} \approx 3.8\) days migrates from the source (from the bowels) to the surface due to the diffusion on the path being disintegrated mainly into lighter isotopes of other elements. As a result, there is only approximately \(N_R \approx 6.02 \times 10^{23}\) of radon atoms in the ground layer in the Earth’s atmosphere due to their large weight. The dynamic equilibrium is maintained by new portions of radon migrating from the depth. It is obvious that it is possible by mining radon at the depth to relieve simultaneously the environmental problem. Radon and its derivatives are the key factor of the lung cancer risk; thus, the World Health Organization initiated the International Radon Project. The urgent topic to neutralize radon by its utilization goes beyond this article.

Masks, protective suits, gloves, and other individual means of protection against infections are passive elements. On the basis of the oxidizing nonequilibrium plasma produced by radionuclides, it is possible to implement a portable autonomous active system to decontaminate the inhaled air designed for safe work of personnel in an infected zone.

The use of radionuclides to generate cold plasma is an example of an effective direct transformation of nuclear energy into a high-potential energy of the nonequilibrium plasma.

A module principle of generation (with increasing number of needed microwave generators activated in parallel) is convenient to widely vary the performance of the installation to generate microwave plasma and, consequently, ozone.

In Fig. 4, the plasma region is limited by the rectangular applicator. However, the whole volume of the oven can be utilized if necessary to generate plasma and sterilize thermolabile dielectric materials along with the simultaneous production of relatively stable ozone to use it on-site or the subsequent transportation into other places of consumption.

The efficiency of a microwave oven as a plasma sterilizer can be shown on the example of the disinfection of masks and respirators. Synthetic materials of filters are thermolabile, and detergents and disinfectants react with polypropylene that damages filters and results in the passage of dangerous fine aerosols. The same effect occurs in the case of boiling, hard washing, detergents, and disinfectants. Therefore, the use of the low temperature oxidizing microwave plasma to sterilize these materials is the optimum variant, which allows for 100% sterilization during the shortest time. One should remember about fire safety: the temperature should nowhere be over room temperature; in particular, this means that the metal retainer for the nose should not be treated in the microwave oven.

The oxidation reactions are certainly exothermic, which means the possible development of the avalanche-like process of burning, particularly against the background of the rising temperature. The implementation of molecular oxygen as a potential oxidizer demands a strict compliance with the known fire-safety rules, such as no flame and sparkles, sufficiently low temperature, and no contact with flammable substances and oils. However, the generation of the strongest oxidizers (such as atomic oxygen and ozone) in the oxygen plasma calls for an additional analysis. The concentration of ozone used for decontamination far from the plasmotron is not more than 25–30 ppm. This means that, due to ozone treatment, the number of reactive particles in the hypothetical fire zone is increased only for \((0.25–0.30) \times 10^{-6}\%\), which has only a negligible impact on the ignition process. Thus, the fire safety measures, when using ozone for decontamination far from the plasmotron, little differ from those at the work with molecular oxygen. However, to prevent ignition of the materials under treatment in the plasmotron volume, it is crucial to maintain a sufficiently low temperature of the gas (plasma) which is the major factor in order to prevent any development of the avalanche-like process of burning. It is possible to achieve the desired plasma temperature using various methods to decrease the feed gas temperature (up to the cryogenic temperature when necessary).

Significantly, Po\(^{210}\) is a relatively fusible material \((T_i \approx 254^\circ C)\); thus, it should not be exposed to elevated temperatures.

It is not necessary to use harmonic high frequency oscillations to generate the nonequilibrium (nonthermal) plasma. The same effect can be received applying short (nano- and, theoretically possible, picosecond) high voltage pulses. High voltage pulses can be considered as the same (in comparison with microwaves) mode of action because the periodic nanopulses can be presented as the sum of oscillating functions, namely, \(\sin (\omega t)\) and \(\cos (\omega t)\) with the frequencies \(\omega\) within the “microwave” range (as a result of the expansion in the Fourier series). When applying nanosecond pulses, the plasma parameters can be controlled via the signal amplitude, duration, and ratio. The main differences lie in the equipment design (see Fig. 5).

At first sight, the “pulse” variant is simpler. However, the widespread perfected “microwave” variant presently surpasses the “pulse” one due to the complexity and high cost of the powerful pulse high voltage sources (that do not exclude any change in the situation in future).

With regard to the generation of large quantities of the homogeneous low temperature microwave plasma, the application of the radial line is attractive where the absorption of microwave energy by plasma is compensated by the thickening of power lines of the electric field with the wave propagation to the center (see Fig. 6). An additional adjustment of the micro-
wave field strength is carried out if it is necessary to correct the radial line profile. The use of radionuclides in the radial variant is also desirable since it contributes to the energy efficiency and sustainable generation.

Summarizing the above-mentioned information, we should note that there is a set of certified generators of nonequilibrium plasma with relatively low productivity that can produce ozone for the decontamination of the air environment and extended surfaces. To improve the energy efficiency of disinfection (being particularly important at large volumes), the promising microwave generators of low-temperature plasma and ozone should be further developed and certified.

Ozone—as an optimal oxidizer for decontamination—should certainly be used in the premises, in the absence of people, in the concentrations and durations providing 100% disinfection. In these cases, the limitations on the concentration and duration of ozone application is usually connected to the damage of materials sensitive to oxidation (the allowable mole fraction is determined experimentally; it is approximately 25–30 ppm in a first approximation). The same rigorous regimes are applicable for disinfecting masks, clothes, and other potentially infected objects. The repeated, safe and, if necessary, impersonal use of expensive protective components, tools, etc. ensures an important economic effect that is achieved due to the ozone oxidation at minimal cost.

Microorganisms have no protection (which is shown not to appear) against the ozone oxidation. Unlike all living creatures unarmed against ozone, homo sapiens, with a proper desire, can create such a protection. Thanks to abstract thinking, the man can ensure a gain in free energy $\Delta G$ required for sustaining life (that means in this particular case the creation of efficient means to fight against the pandemic).

To prevent any harmful effect of ozone you should use its strong point: a high reaction capacity. Unlike a classic gas mask, a complex (separate) protection of eyes, nose, and mouth—the organs sensitive to ozone—is proposed. Special glasses or contact lenses are sufficient to protect eyes.

The protective mask-respirator should be greatly modernized. In most cases, the full-face protective mask-respirator equipped with a carbon filter is functionally redundant and, accordingly, too expensive when massively applied. Following the complex principle of mass protection, it is suggested to ensure, if necessary, the possibility of an independent (separate) protection for nose and mouth since it is evidently typical for safer eating and drinking. The mask-respirator for breathing through the nose and mouth should then be aggregate, i.e., it should consist of several replaceable layers-masks. The outer (external) layer-mask containing effective neutralizers of ozone (and simultaneously other poison gases) based on activated carbon must be put on at the entrance to the zones with an increased ozone content. In a critical epidemic situation, these zones can be not only specialized COVID-centers but also shopping areas, transport, etc. Outside the ozonation zones, the use a mask-neutralizer of ozone is undesirable, and its expenditure potential should be preserved with the help of a sealed package.

Wearing a mask not only obstructs the respiratory tract but also deteriorates the quality of inhaled air (a certain part of the used air with an increased content of carbon dioxide CO2 remains inside the mask). Besides, at low temperatures the condensation of moisture can occur on the mask. A fundamental solution of these problems works optimally at low temperatures (since it is accompanied by the release of heat), and it is based on the unique property of superoxides to accumulate and release oxygen. In the presence of water, the superoxides absorb the exhaled carbon dioxide CO2 and release abundantly oxygen O2. By the example of potassium superoxide, the total reaction of the carbon dioxide CO2 substitution for more molecules of oxygen O2 has the form:

$$4\text{K}_2\text{O}_2 + 2\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O} + 2\text{K}_2\text{CO}_3 + 3\text{O}_2. \quad \text{(18)}$$

![Diagram of microwave plasma installation in comparison with high-voltage pulse version.](image1)

![In a radial line, absorption of microwave energy by plasma is compensated by field concentration.](image2)
The implementation of this method to enrich the inhaled air with oxygen in the case of mask respirators is facilitated by the fact that the mentioned principle of the conversion of carbon dioxide into oxygen has been already used at the orbital stations and submarines.

The improvement of masks (respirators) is the focus of many researchers largely because of the SARS-CoV-2 coronavirus pandemic. The development and implementation of an intelligent mask [63], a peculiar i-mask, which allows one to determine the presence of SARS-CoV-2 coronavirus in the host has been launched. The functions of an intelligent mask will certainly increase. For example, a rapid diagnostics of coronavirus concentration in air both in premises and in open spaces is a pressing issue.

The problem of adequately disposing an astronomical amount of produced masks arises. In our opinion, the optimal method to dispose the used masks is high temperature pyrolysis with further recycling of activated carbon (including production of new masks) as well as residual hydrocarbons (see Fig. 7). High temperatures ensure microbiological safety of the pyrolysis products irrespective of the character and degree of their decontamination.

The SARS-CoV-2 coronavirus pandemic identified the shortcomings and requires the improvement of microbiological safety at every level, including household.

For example, infusion systems (droppers), wherein the substitution of the liquid injected into the vein for the air taken directly from the room, are commonly used in medicine for intravenous infusion. This practice is unacceptable in the situation of the pandemic since the coronavirus which is probably present in any room is able to easily enter directly into the patient’s blood provoking nosocomial (hospital-acquired) infection. This problem can be solved using many methods, including the application of a filter on the basis of the low temperature plasma. However, the usage of a thin film ballast vessel filled with a sterile gas is more available and operative (see Fig. 8). This gas can be medical oxygen available in any hospital, which is injected directly into blood and is not just harmless but usually even beneficial.

The coronavirus pandemic emphasized the importance of modernizing the air-conditioning systems in premises.

To ensure microbiological safety, the widely used centralized conditioning systems must be supplemented with the means of reliable decontamination both for fresh air and exhaust air released into the atmosphere. At the same time, it should be noted that the centralized conditioning systems are inertial and not able to respond quickly to the dramatic changes in weather, contingent, and virus load in specific critical places. Therefore, these places (operating rooms, hospital reception departments, waiting rooms, etc.) should have a mobile local conditioning system combined with the controlled decontamination. In our opinion, only the basic load with the mandatory possibility to correct conditioning with local means is the optimal variant that must be ensured at large facilities.

Evidently, it is easier to take into account (together with other local factors) the virus load and, if necessary, to vary the parameters of conditioning and the disinfection intensity in the local conditioning systems. But the term “local system” does not mean that its closure is acceptable (split-systems are almost closed without any significant air renewal). An imminent shortcoming of split-systems is the internal air recirculation with no proper supply of fresh air (as well
as the removal of polluted air). The local conditioning split-systems, even equipped with filters and cold plasma, are categorically contraindicated in the institutions with a large contingent (hospitals, schools, libraries, etc.). For these objects, energy-optimized air-conditioning systems with adequately high multiplicity of air exchange and controlled decontamination of the supply and exhaust air are necessary. Without exaggeration, the design of these systems is one of the most vital challenges related to power engineering and ecology, and it is additionally stimulated by increased microbiological threats. Please note that the task (component) of decontamination at air conditioning is solved within the defined complex problem, as mentioned above, by the use of low temperature (“cold”) plasma for the energy-efficient generation of the reactive oxygen species. The filtration of dust from the air before decontamination is important not only for air conditioning but also for the reduction in the oxidizing load (organic dust particles usually consume a lot of oxidizer).

In this work, the critical epidemiological situation because of the SARS-CoV-2 pandemic determines the focus mainly on the decontamination of extended and remote objects. However, the considered optimal methods and means of decontamination are used not only in medicine but also can be adapted for many applications in agriculture, industry, and household. These commonly compact applications make it possible to implement in full the capabilities of the oxidizing low temperature (“cold”) plasma: to vary the composition of plasma-forming gases, to maintain the optimal pressure (vacuum) and temperature in the applicator, to combine decontamination and final drying, etc.

CONCLUSIONS

The optimization of microbiological decontamination is a priority taking into account the inevitable prospect of new epidemic threats. The irreversible chemical reactions of oxidation are the shortest way to achieve sterility at the highest reliability of decontamination. Furthermore, oxygen is optimal as an oxidizer, including ecology, as it and all its reactive species are advantageously integrated into the natural cycles of exchange. The best way to generate the reactive oxygen species for disinfection is the application of the low-temperature (“cold”) plasma ensuring an energy-efficient generation of oxidizing reactive species: atomic oxygen (O), ozone (O_3), hydroxyl radical (·OH), hydrogen peroxide (H_2O_2), superoxide (O_2^-), and singlet oxygen O_2(Δ°). Because of the short life time of the most above-mentioned species outside the plasma applicator far from the plasma generator, the objects are sterilized by ozone (O_3) since its minimum lifetime is rather long (some minutes). The microwave method of oxygen plasma generation is the best for the energy-efficient production of ozone.

In the case of an extensive contamination of surfaces, it is appropriate to use aqueous hydrogen peroxide (H_2O_2) in addition to the disinfecting ozone (O_3). It is important that these reactive oxygen species for the decontamination of the objects far from the plasma generator possess a high efficiency and are environmentally safe.

To exclude any damage to a human body when using ozone, it is important to solve the problem of the refinement and certification of the modern multifunctional mask-respirator. The energy-efficient systems of air conditioning with the adequate decontamination of the inhaled and exhaust air are also topical.

The considered optimum means of disinfection can be used not only in medical practice but also adapted for many modernizations in agriculture, industry, and in household.

It should be emphasized that no microorganisms can resist the devastating impact of ozone and other oxidizing components of low-temperature plasma.

FUNDING

This work was performed in the framework of the ANCD project no. 20.80009.5007.06 (2020–2023) “Intensification of the Processes of Transfer and Treatment in Electric, Electromagnetic, Cavitation Fields; Practicality.”

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

1. Menebo, M.M., Temperature and precipitation associate with Covid-19 new daily cases: A correlation study between weather and Covid-19 pandemic in Oslo, Norway, Sci. Total Environ., 2020, vol. 737, p. 139659. https://doi.org/10.1016/j.scitotenv.2020.139659

2. Vinoj, V., Gopinath, N., Landu, K., Behera, B., et al., The COVID-19 spread in India and its dependence on temperature and relative humidity, Preprints, 2020, p. 2020070082. https://doi.org/10.20944/preprints202007.0082.v1

3. Rahimi, N.R., Fouladi-Fard, R., Aalii, R., Shahryari, A., et al., Bidirectional association between COVID-19 and the environment: A systematic review, Environ. Res., 2021, vol. 194, p. 110692. https://doi.org/10.1016/j.envres.2020.110692

4. Dbouk, T. and Drikakis, D., Weather impact on airborne coronavirus survival, Phys. Fluids, 2020, vol. 32, p. 093312. https://doi.org/10.1063/5.0024272

5. Bhadrwaj, R. and Agrawal, A., Likelihood of survival of coronavirus in a respiratory droplet deposited on a solid surface, Phys. Fluids, 2020, vol. 32, p. 061704.

6. Hridoy, A.E.E., Mohiman, M.A., Tusher, S.M.S.H., Nowraj, S.Z.A., et al., Impact of meteorological pa-
15. Rogez-Kreuz, C., Yousfi, R., Soufflet, C., Quadrio, I.,
14. Misra, N.N., Patil, S., Moiseev, T., Bourke, P., et al.,
16. Pekárek, S., Non-thermal plasma ozone generation,

21. Moisan, M., Barbeau, J., Moreau, S., Pelletier, J.,
et al., Low-temperature sterilization using gas plasmas: A review of the experiments and an analysis of the inactivation mechanisms, Int. J. Pharm., 2001, vol. 226, nos. 1–2, p. 1.

30. Laroussi, M., Lu, X., and Keidar, M., Perspective: The role of humidity and UV-C emission in the inactivation of B. subtilis spores during atmospheric-pressure dielectric barrier discharge treatment, J. Phys. D: Appl. Phys., 2020, vol. 53, p. 295201.

https://doi.org/10.1088/1361-6463/ab77ec

29. Brayden, M., Ranieri, P., Smirnova, T., Hewitt, P., et al., Measuring plasma-generated OH and O atoms in liquid using EPR spectroscopy and the non-selectivity of the HTA assay, J. Phys. D: Appl. Phys., 2021, vol. 54, no. 14, p. 145202.

https://doi.org/10.1088/1361-6463/ab94a6

23. Shimizu, T., Steffès, B., Pompl, R., Jamitzky, F., et al., The role of humidity and UV-C emission in the inactivation of B. subtilis spores during atmospheric-pressure dielectric barrier discharge treatment, J. Phys. D: Appl. Phys., 2020, vol. 53, p. 295201.

https://doi.org/10.1088/1361-6463/ab77ec

22. Berezhetskaya, N.K., Gritsinin, S.I., Kop’ev, V.A., Kossyi I.A., et al., Long-lived plasmoids generated by surface microwave discharges in chemically active gases, Plasma Phys. Rep., 2005, vol. 31, p. 886.

https://doi.org/10.1134/1.2101976

21. Moisan, M., Barbeau, J., Moreau, S., Pelletier, J.,
et al., Low-temperature sterilization using gas plasmas: A review of the experiments and an analysis of the inactivation mechanisms, Int. J. Pharm., 2001, vol. 226, nos. 1–2, p. 1.

36. Ruiling Lv, Donghong Liu, and Jianwei Zhou, Bacteri-
sistance and inactivation mechanisms, *Curr. Opin. Food Sci.*, 2021, vol. 42, p. 31.

37. Graves, D.B., Low temperature plasma biomedicine: A tutorial review, *Phys. Plasmas*, 2014, vol. 21, no. 8, p. 080901. https://doi.org/10.1063/1.4892534

38. Foster, J.E., Plasma-based water purification: Challenges and prospects for the future, *Phys. Plasmas*, 2017, vol. 24, no. 5, p. 055501. https://doi.org/10.1063/1.4977921

39. Laroussi, M. and Lu, X., Room-temperature atmospheric pressure plasma plume for biomedical applications, *Appl. Phys. Lett.*, 2005, vol. 87, no. 11, p. 113902.

40. Ionescu, A.C., Brambilla, E., Manzoli, L., Orsini, G., et al., Aerosols modification with H2O2 reduces airborne contamination by dental handpieces, *J. Oral Microbiol.*, vol. 13, no. 1, p. 1881361. https://doi.org/10.1080/20002297.2021.1881361

41. Basaran, P., Basaran-Akgul, N., and Oksuz, L., Elimination of *Aspergillus parasiticus* from nut surface with low pressure cold plasma (LPCP) treatment, *Food Microbiol.*, 2008, vol. 25, no. 4, p. 626.

42. von Woedtke, Th., Reuter, S., Masura, K., and Weltmann, K.-D., Plasmas for medicine, *Phys. Rep.*, 2013, vol. 530, no. 4, p. 291.

43. Chen, Z., García, G., Arumugaswami, V., and Wiz, R.E., Cold atmospheric plasma for SARS-CoV-2 inactivation, *Phys. Fluids*, 2020, vol. 32, no. 11, p. 111702. https://doi.org/10.1063/5.0031332

44. Tiwari, S., Caiola, A., Bai, X., Lalsare, A., et al., Microwave plasma-enhanced and microwave heated chemical reactions. A review, *Plasma Chem. Plasma Process.*, 2020, vol. 40, no. 1, p. 1. https://doi.org/10.1007/s11090-019-10040-7

45. Domonkos, M., Tichá, P., Trejbá, J., and Demo, P., Applications of cold atmospheric pressure plasma technology in medicine, agriculture and food industry, *Appl. Sci.*, 2021, vol. 11, no. 11, p. 4809. https://doi.org/10.3390/app11114809

46. Cvelbar, U., Walsh, J., Černák, M., de Vries, H., Reuter, S., et al., White paper on the future of plasma science and technology in plastics and textiles, *Plasma Processes Polym.*, 2019, vol. 16, no. 1, p. 1700228.

47. Monrolin, N., Plouraboué, F., and Praud, O., Electrohydrodynamic thrust for in-atmosphere propulsion, *AIAA J.*, 2017, vol. 55, no. 12, p. 4296.

48. Miotk, R., Hrycak, B., Czyżkowski, D., Dors, M., et al., Liquid fuel reforming using microwave plasma at atmospheric pressure, *Plasma Sources Sci. Technol.*, 2016, vol. 25, no. 11, p. 035022.

49. Uhm, H.S., Kim, J.H., and Hong, Y.C., Disintegration of water molecules in a steam-plasma torch powered by microwaves, *Phys. Plasmas*, 2007, vol. 14, p. 073502.

50. Uhm, H.S., Hong, Y.C., and Shin, D.H., A microwave plasma torch and its applications, *Plasma Sources Sci. Technol.*, 2006, vol. 15, no. 2, p. S26.

51. Xu, H., He, Y., Strobel, K.L., Gilmore, C.K., et al., Flight of an airplane with solid-state propulsion, *Nature*, 2018, vol. 563, no. 7732, p. 532.

52. Isikber, A.A. and Athanassiou, C.G., The use of ozone gas for the control of insects and microorganisms in stored products, *J. Stored Prod. Res.*, 2014, vol. 64, p. 139. https://doi.org/10.1016/j.jspr.2014.06.006

53. Megahed, A., Aldridge, B., and Lowe, J., The microbial killing capacity of aqueous and gaseous ozone on different surfaces contaminated with dairy cattle manure, *PLoS One*, 2018, vol. 13, no. 5, p. e0196555. https://doi.org/10.1371/journal.pone.0196555

54. Fizicheskaya entsiklopediya (Physical Encyclopedia), Moscow: Bol’shaya Ross. Entsiklopediya, 1998.

55. Smyshlyaev, S.P., Gontsov, Ya.A., and Khoreva, E.I., Estimates of the residence time of chemically active anthropogenic gases in the atmosphere, *Uch. Zap. Ross. Gos. gidrometeorol. Univ.*, 2011, no. 22, p. 195.

56. Tanaka, N., Biswal, M., Kumar, A., Edvin, A., et al., Hydrogen peroxide vapour for decontaminating air-conditioning ducts and rooms of an emergency complex in northern India: Time to move on, *J. Hosp. Infect.*, 2011, vol. 78, no. 3, p. 200. https://doi.org/10.1016/j.jhin.2011.02.013

57. Falagas, M.E., Thomaidis, P.C., Kotsantis, I.K., Sgouros, K., et al., Airborne hydrogen peroxide for disinfection of the hospital environment and infection control: A systematic review, *J. Hosp. Infect.*, 2011, vol. 78, no. 3, p. 171. https://doi.org/10.1016/j.jhin.2010.12.006

58. Pottage, T., Richardson, C., Parks, S., Walker, J.T., et al., Evaluation of hydrogen peroxide gaseous disinfection systems to decontaminate viruses, *J. Hosp. Infect.*, 2010, vol. 74, no. 1, p. 55. https://doi.org/10.1016/j.jhin.2009.08.020

59. Kiser, D., Elhanan, G., Metcalf, W.J., Schneider, B., et al., SARS-CoV-2 test positivity rate in Reno, Nevada: Association with PM2.5 during the 2020 wildfire smoke events in the western United States, *J. Exposure Sci. Environ. Epidemiol.*, 2021, vol. 31, p. 797. https://doi.org/10.1038/s41370-021-00366-w

60. Azharonok, V., Filatova, I., Bosnega, Iu., Bologa, M., et al., Non-thermal plasma sterilization in RF and MW discharges, *Rom. J. Phys.*, 2011, vol. 56 Suppl., p. 62.

61. Bosnega, Iu., Bologa, M., and Agarwal, E., Intensification of electro-magneto-hydrodynamic effects using radionuclides, *Proc. 12th Int. Conf. Modern Problems of Electrophysics and Electrohydrodynamics (MPEE-2019)*, Peterhof, Russia, 2019, p. 189.

62. Babior, B.M., Takeuchi, C., Ruedi, J., Gutierrez, A., et al., Investigating antibody-catalyzed ozone generation by human neutrophils, *Proc. National Academy of Sciences of the United States of America (PNAS)*, 2003, vol. 100, no. 6, p. 3031. https://doi.org/10.1073/pnas.0530251100

63. Nguyen, P.Q., Soenksen, L.R., Donghia, N.M., et al., Wearable materials with embedded synthetic biology sensors for biomolecule detection, *Nat. Biotechnol.*, 2021, vol. 39, p. 1366. https://doi.org/10.1038/s41587-021-00950-3