Utilization of Ultraviolet Radiation of Cold Hollow Cathode Glow Discharge Plasma for Water Disinfection

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Abstract. In this proceeding the results of experimental studies of peculiarities of *Escherichia coli* water suspension inactivation by ultraviolet radiation of hollow cathode discharge plasma in different gaseous media are presented. It is shown that efficiency of the inactivation by the discharges on oxygen, mixtures of oxygen with deuterium, and water vapor is essentially higher than that by the discharge on air, as well as the discharges of low and medium pressure mercury lamps.

Keywords: Ultraviolet, plasma, hollow cathode, water disinfection.

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INTRODUCTION

In the last decade ultraviolet (UV) radiation attains growing application as antimicrobial agent at disinfection of water, air, sterilization of packing materials for foodstuffs, etc. Inactivation of microorganisms under action of UV radiation occurs, first of all, due to DNA damage in result of a set of photochemical reactions [1]. Main advantage of UV sterilization and disinfection method, as compared to those using chemical agents (chlorine, hydrogen peroxide, ozone, etc.), consists in fact that at the use of UV radiation no toxic and/or mutagenic residuals are formed. Modern UV systems commonly use low and medium pressure mercury lamps. Advantages of mercury lamps consist in their high energy efficiency, reaching 40% for low pressure lamps, and long service life – up to 10 thousands hours. However, there is essential drawback of using such lamps due to high toxicity of mercury vapor. It results in extra expenses for safety assurance in production and recycling of those lamps. In the experiments on sterilization of medical articles by gas discharge plasma [2] it has been shown that the efficiency of sterilization of *Bacillus subtilis* spores by broad-band (200÷300 nm) UV radiation of hollow cathode discharge (HCD) oxygen plasma is essentially higher than that by monochromatic radiation at 254 nm of low pressure mercury lamp.

Due to that, in the present proceeding the possibility of use of ultraviolet radiation of HCD plasma for water disinfection was studied. For that purpose comparative experiments on the influence on *Escherichia coli* water suspension produced by ultraviolet radiation of both mentioned discharge plasma, and standard low and medium pressure mercury lamps were performed.

DESCRIPTION OF SETUP AND METHODS OF MEASUREMENTS

The experiments on study of the efficiency of water disinfection by UV radiation of HCD plasma were performed at the setup schematically shown in Fig.1. Walls of cylindrical chamber 1 having 400 mm length and 50 mm internal diameter simultaneously served as the discharge cathode. The end of the chamber was closed by window 3 made of quartz of KU-1 type with 4 mm thickness and low bandpass bound about 175 nm. At a time of the experiments, Petri dish made of 2 mm thick KU-1 quartz with water suspension of the test microorganisms was placed on the

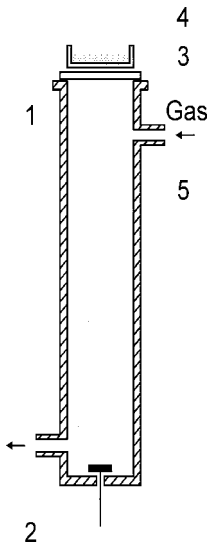

FIGURE. 1. Scheme of experimental setup. 1 – chamber-cathode, 2 – anode, 3 – window of KU-1 quartz, 4 – Petri dish of KU-1 quartz, 5 – discharge plasma.

window 3. Discharge plasma 5 served as volume source of UV radiation. Air, oxygen, deuterium, mixture of oxygen and deuterium with various ratios, and water vapor were used as working gases/mixtures. Working pressure in the chamber was varied in range from 0.1 to 1 Torr depending on type of gas media. Power introduced into the discharge was varied in range of 250÷350 W.

At carrying out comparative experiments, low pressure (LP) mercury lamp of DB-30 type generating practically monochromatic UV radiation with ≈ 254 nm wavelength, and medium pressure (MP) mercury lamp of PRK-400 type producing broadband UV radiation in 200÷300 nm wavelength range were used. In the experiments mercury lamps were placed inside devices consistent with requirements described in [3, 4]. Petri dishes were placed at the ends of collimating tubes having 300 mm length and 40 mm internal diameter closed by windows made of quartz of KU-1 type.

Spectroscopic measurements were performed with the use of automated setup based on 0.6 m monochromator of MDR-23 type with 1200 lines/mm diffraction grating (inverse linear dispersion 1.3 mm/nm). Radiation intensity at the monochromator output was measured by photomultiplier tube of FEU-39A type, and the signal was supplied to the input of measuring-processing system developed by the authors.

The integral intensity of UV radiation in the plane of sample irradiation was measured by DAU-81 radiometer before and after each record of spectrum intensity distribution, and respective average value allowed to link together the sets of experimental data obtained in spectroscopic and medical-biological researches.

Escherichia coli 1257 strain received from Scientific Research Institute of Standardization and Control of Medical Biological to. 3 ml of *Escherichia coli* water suspension with density of 10^6 CFU/ml was placed into the Petri dish with 32 mm diameter resulting in layer thickness of about 3 mm. After UV irradiation for predetermined time, required aliquot of the suspension or its dilution was introduced into Endo medium, survived bacteria were incubated for 18-24 hours at 37^0 C temperature, and colony count was performed. On a basis of obtained data, bacteria survival curves, that is dependencies of a number of survived bacteria on UV radiation doze, were built.

Due to fact that experimental studies of sterilization efficiency of *Escherichia coli* water suspension were performed with the use of UV radiation with essentially different spectrum shape, in this proceeding the method of determining effective irradiation dose for studied sample was used which enabled correct comparison of the results obtained with the use of mentioned UV sources. Essence of the method consisted in "weighing" spectrum distributions of intensity absolute values for each used type of UV radiation.

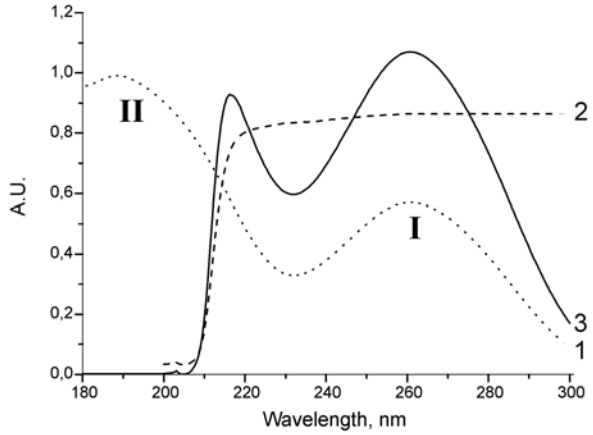

FIGURE. **2**. 1 - DNA absorption spectrum; 2 – transmission curve of BaF2 filter with 3 mm thickness; 3 - "weighing" curve, obtained by multiplying DNA absorption spectra and transmission curve of BaF2 filter.

At determination of "weighing" function, first of all, results of works [5-7] devoted to studies of DNA molecule absorption and efficiency of bactericidal action of UV radiation on the microorganisms in dependence on the radiation frequency were taken into account. It has been shown in [5] that DNA absorption spectrum in considered wavelength range (≈180÷300 nm) represents superposition of broad absorption bands having maxim at about 190 nm and 260 nm (bands II and I, curve 1 in Fig.2) due to electron excitation of diene and triene fragments of DNA molecule chain. In experiments with *Bacillus subtilis* spores [6] and *Escherichia coli* bacteria [7] it has been shown that at long enough wavelength ($\lambda >$ 230 nm) curves of dependencies of absorption and bactericidal efficiency on λ practically coincide, and

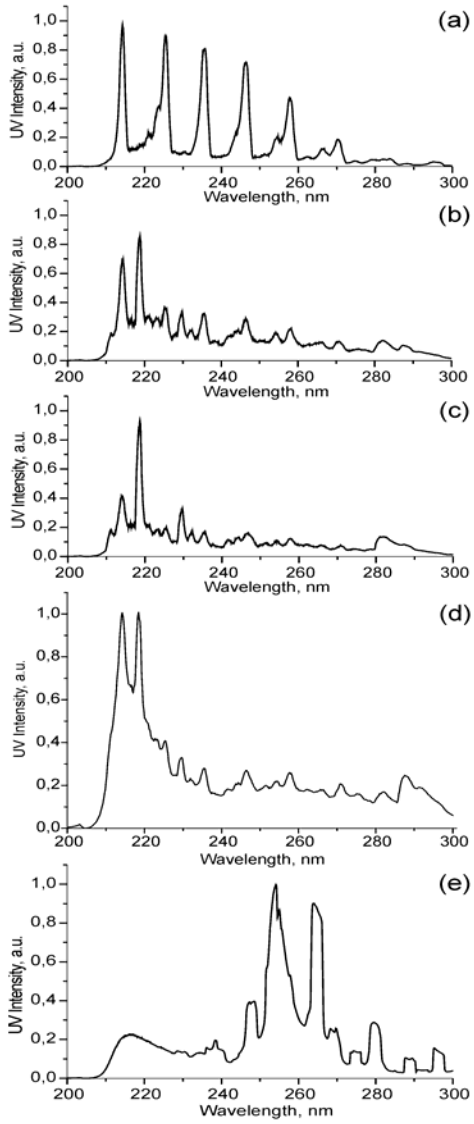

FIGURE. 3. Distributions of "weighed" intensity of UV radiation over spectrum for hollow cathode discharge plasma on different working media and for MP mercury lamp. a) air, pressure 0.2 Torr, b) oxygen, pressure 0.1 Torr, c) water vapor, pressure 0.1 Torr; d) mixture 0.35 Torr D2 + 0.08 Torr O2; e) MP mercury lamp

both of them reach maximum at λ≈260 nm. At shorter wavelength (λ ≤ 220 nm) the dependencies diverge – absorption curve goes up with wavelength decrease, whereas bactericidal efficiency rapidly decreases. (Such difference is most likely due to strong absorption of short wavelength radiation by the structures surrounding DNA – cell walls, plasma membranes, cytoplasm, etc.). In the present experiments it was founded that bactericidal action of radiation of the discharge used by us on studied *Escherichia coli* culture remained completely unchanged at introduction of additional filter made of BaF_2 with low pass boundary λ = 215 nm, that is, in our case radiation with wavelength λ ≤ 215 nm did not provide essential effect on vital functions of the microorganisms. On another side, this fact enabled expression of "weighing" function in form of a product of spectrum dependencies of factors of BaF_2 filter transmission(curve 2 in Fig.2) and DNA absorption obtained in [5]. Resulted "weighing" function normalized by 1 at λ=254 nm is presented by curve 3 in Fig.2. At short λ it was actually determined by factor of the filter transmission, and at longer λ - by factor of DNA absorption. Thus, we used the portion of radiation transmitted by the filter and absorbed by DNA for defining irradiation dose at survival curves of the microorganisms presented below.

EXPERIMENTAL RESULTS AND CONSIDERATIONS

"Weighed" spectrum distributions of UV radiation power for HCD on used working media and that for PRK-400 lamp are presented in Fig.3. Radiation spectrum for low pressure lamp is not shown in the figure because it represents narrow triplet at λ≈254 nm. As it follows from analysis of these spectra, at work on air (Fig.3a) main contribution to UV radiation of the plasma is made by that of γ system NO ($A^2\sum^+ - X^2\Pi$), and at work on oxygen (Fig.3b) – by radiation of secondary negative system (SNS) of molecular ions O_2^+ ($A^2\Pi_u - X^2\Pi_g$). At work on water vapor (Fig.3c) main contribution to total UV radiation also is made by SNS of O_2^+. The shape of radiation spectrum for the discharge plasma on mixture of deuterium with oxygen essentially depends on ratio of these components. At the discharge glowing on pure deuterium, the spectrum is continuous and has a maximum at λ≈220 nm. With oxygen added (Fig.3d), continuous spectrum of deuterium is superimposed by radiation of the bands of SNS of O_2^+. In case of MP mercury lamp the UV radiation is represented by continuous spectrum in 210÷230 nm range and spectral lines in remaining part of considered wavelength range (Fig.3e). One can see from the figure that in case of the use of oxygen, deuterium (or mixture deuterium with oxygen) and water vapor main "weighed" UV radiation power is concentrated in ≈215÷230 nm spectrum range, whereas at air use it is spread over several bands in 210÷260 nm range. In case of medium pressure mercury lamp major power of UV radiation is concentrated in 240÷270 nm wavelength range.

In Fig.4 bacteria survival curves are presented which have been obtained at treatment of *Escherichia coli* water suspension having density of $2 \cdot 10^6$ CFU/ml by UV radiation of LP and MP mercury lamps and that of hollow cathode discharge plasma on air, oxygen, water vapor, and mixture of deuterium with oxygen (N_0 and N_S are initial

number and that of survived bacteria, respectively). Each point in the figure represents data averaged for three to six separate experiments. Bacteria survival curve for D_2+O_2 mixture is obtained by averaging separate curves for cases of the use of pure deuterium and two mixture deuterium with oxygen. (In spite of certain difference in UV spectrum intensity distributions for these media, the bacteria survival curves practically coincide).

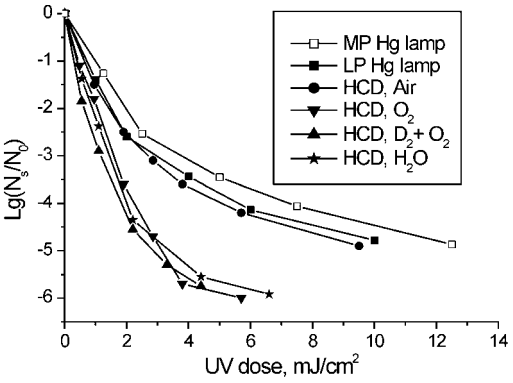

FIGURE. 4. Survival curves obtained at treatment of Escherichia coli water suspension with $2 \cdot 10^6$ CFU/ml density by UV radiation of mercury lamps DB-30, PRK-400, and by the radiation of HDC plasma on air, oxygen, water vapor and mixtures of deuterium with oxygen.

One can see from the figure that bacteria survival curves obtained at the use of plasma UV radiation from discharges on oxygen, water vapor, and mixtures of deuterium with oxygen practically coincide. Curves obtained at the use of UV radiation of mercury lamps and that of the discharge plasma on air are also close to each other, however, they are located above the first set of the curves. Such essential difference in behavior of the curves gives undoubted evidence to fact that bactericidal features of UV radiation in 215÷300 nm wavelength range depend not only on radiation dose absorbed by DNA (as it was observed in the case of monochromatic radiation), but as well on shape of the radiation spectrum. Comparison of spectra of radiation absorbed by DNA for the discharges on different gases shows that maximum efficiency is provided by the discharges with radiation having maximum intensity in 215 to 230 nm spectrum range. High efficiency of UV radiation having maximum in range $\lambda \approx 215 \div 230$ nm (which is located at region of II band of DNA absorption, Fig.2) may be presumably due to:

1) difference in nature of DNA damage caused by UV radiation in mentioned wavelength range, as compared to that occurring at the use of radiation with wavelength matching I band of DNA absorption;

2) stronger damage caused by radiation in mentioned wavelength range to other biological molecules, particularly, enzymes which are responsible for reparation of damaged DNA [8].

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