

Technological applications of surfatron produced discharge

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The unique properties, which low-temperature plasma offers are frequently used for industrial plasma processing. Plasma surface treatment can lead to changes of free surface energy and also to bactericidal effects. We applied a plasma source of jet type based on surfatron principle for bio-technological experiments - surface activation of plastic materials, plasma sterilisation, increasing of seed germination. The surfatron source was powered by a microwave magnetron generator working at frequency 2.45 GHz with the output power range 0-300 W. Mixtures of Ar (carrier gas) and N₂ or O₂ (reactive gases) were mainly used for treatment of samples. The paper is focused on surface activation of low density polyethylene (LDPE) for the purpose of increasing free surface energy. The critical surface energy was obtained from approximation of experimental data in so-called Zisman plot. Bactericidal effects of Ar/O₂ and Ar/N₂ discharges under open atmosphere were tested on the bactericidal cultures *Neisseria sicca*, *Deinococcus radiodurans*, *Enterococcus faecium* and *Stenotrophomonas maltophilia*. These both discharges were also used for stimulation of germination of Lambs Quarter (*Chenopodium album* agg.) seeds.

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1. Introduction

Low-temperature plasma offers broad range of industrially interesting applications. The main advantage in comparison to other media consists in ability of plasma to produce energy-containing active species which initiate physical changes or chemical reactions, which would otherwise occur only with difficulties or not at all. Frequently the low-temperature plasma treatment of surfaces is intended to change (increase or decrease) the surface energy. Because of its technical and economical advantages the plasma surface treatment is increasingly exploited in the last years [1].

Probably the most important surface-energy-related characteristic of materials is wettability. Many industrial plastics such as polyethylen (PE), polypropylen (PP), polytetrafluorethylen (PTFE) have low surface energy and lacquers, inks and adhesives do not sufficiently wet them. In the work by *Barni et al.* the wettability and dyeability of polyethylen terephthalate (PET) was modified using radio-frequency SF₆ plasma [2]. *Janca et al.* used the dielectric barrier discharge for the activation of oiled polyester (PES) multi-cord sewing threads for tires [3]. The surface discharge was used for several applications e.g. for increasing of wettability of the non-woven PP textiles in [4].

Low temperature plasma is able to produce energetic active species and UV radiation which can initiate specific physical and chemical reactions with sterilisation effects. Plasma sterilisation efficiency is strongly influenced by numerous experimental parameters as described in a large

review work by *Lerouge et al.* [5]. Former experiments demonstrated that oxygen-based plasmas are more efficient in sterilisation process than pure argon (or other pure rare gas) plasmas. For instance in [6,7] is assumed that the sterilisation effect of plasma generated by surfatron in the Ar/O₂ mixture is mainly due to ultraviolet photons and partly also by oxygen atoms. For this purpose the most important oxygen-based plasmas as those based on pure O₂, CO₂ or on mixtures O₂/H₂, Ar/O₂ and CF₄/O₂ have been studied by *Lerouge et al.* in [8]. *Hury et al.* reported the inactivation of spores exposed in Ar/O₂ microwave sustained plasmas at low pressures [9]. Microwave Ar/O₂ flowing post-discharge was also used by *Ricard et al.* with the view of *Escherichia coli* inactivation [10]. In the last years the plant stimulation using physical factors (ionizing radiation, laser, high-power light radiation, high electro-magnetic field etc.) was tried. The main aim of these investigations is a search for methods that would improve the sowing quality of seed. *Dubinov et al.* treated oat (*Avena Sativa*) and barley (*Hordeum Vulgare*) seeds by the air glow discharge with the view to increase their germination under laboratory condition [11]. The seeds were treated in continuous as well as in pulsed regime for several minutes (up to 4 min). The seed was successfully stimulated and the germination increased. Exposure in continuous regime was more effective than in pulsed discharge. *Zivkovic et al.* used for *Paulownia tomentosa* seed stimulation the RF (13.56 MHz) discharge in air and Ar with applied power about 100 W [12]. The experiments were done under reduced pressure (about 10

Pa). Simple tests proved that no affection of germination by vacuum was caused. Plasma exposed on the seed caused increasing of their germination by almost three times - from 25 % up to 75 %. Mechanism of seed stimulation was investigated in detail also by *Volin et al.* [13]. They carried out experiments with CF_4 and ODFD (octadecafluorodecalin) plasma generated by RF driven (13.56 MHz) electrodes in vacuum chamber.

We present in this paper our first results on application of surfatron plasma for material surface treatment, processing of seeds before sowing and for sterilisation. Surface of low density polyethylene (LDPE) samples were treated with the aim to increase the surface free energy and hydrophilicity of the material surface. The same experimental conditions - Ar/O_2 and Ar/N_2 discharges at pressure $p = 40$ mbar and power $P = 100$ W - were used for germination stimulation of Lamb's Quarters (*Chenopodium album* agg.) seeds. The sterilisation effects of Ar/O_2 and Ar/N_2 discharges were tested at open atmosphere and microwave power $P = 300$ W on bactericidal cultures *Neisseria sicca*, *Deinococcus radiodurans*, *Enterococcus faecium* and *Stenotrophomonas maltophilia*.

2. Experimental system

Our experiments were carried out with plasma generated by surfatron in microwave range of frequencies. We used commercial (Sairem) surfatron and microwave generator 300 W (GMP 03) in configuration, which can be seen in Fig. 1a. A quartz tube, 6 mm in inner diameter, was inserted into a surfatron cavity and working gas flew through it due to the action of a fast pump. The microwave power was coupled from the surfatron resonator cavity to the plasma via a thin slit and caused ionisation of flowing gas in the quartz tube. Plasma created in this manner was sustained further downstream by a surface wave, which propagated along the plasma column [14].

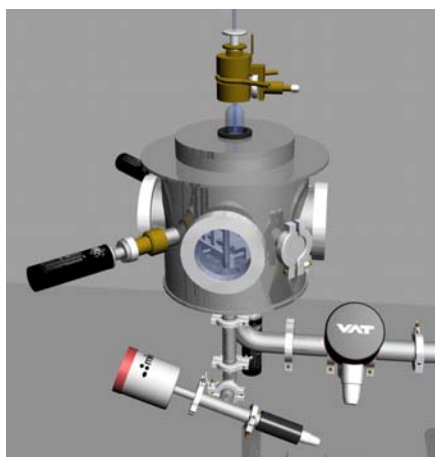


Fig. 1a. General view - experimental setup based on surfatron.

The developed experimental arrangement consisted of a vacuum vessel made of stainless steel. The upper flange of the vessel was made of plastic in order to enable the propagation of the surface wave into the vessel. Four quartz windows were provided in the vessel for the observation and one of the vacuum ports also served as an access for sample replacement. The outlet of the quartz tube protruded into the vessel using silicon O-ring sealed PTFE feed-through. The quartz discharge tube was designed as two coaxial quartz cylinders welded together at the bottom part; the space between both tubes was cooled by compressed air, see Fig. 1b.

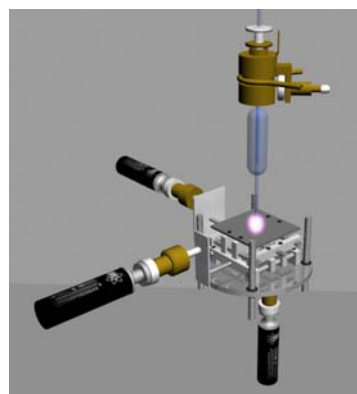


Fig. 1b. Facility inside of the vacuum chamber.

The volume of the vessel was continuously pumped by a large rotary vacuum pump; the ultimate pressure achieved without gas flow was of the order units of Pa. The butterfly VAT valve between the vessel and the pump controlled the pumping speed and thus allowed to set the desired pressure independently of the working gas flow rate. The pressure in the vessel was measured by MKS Baratron. The working gas flow rate was controlled by MKS flow-controller. The total flow rate of working gas mixture was in the described experiments kept constant at 600 sccm. The technical Ar , N_2 and O_2 with purity grade 4.6 were used. The body of the surfatron was cooled by water and compressed air. Table for samples, movable in three dimensions via stepper motors controlled by PC, was situated inside the vacuum chamber, see Fig. 1b.

3. Results and discussion

3a) Activation of low density polyethylene

Surfaces of low density polyethylene (LDPE) samples were activated using Ar/O_2 and Ar/N_2 discharges with the aim to increase the total surface energy and hydrophilicity of this material. The experiments were done at reduced pressure $p = 40$ mbar with input power $P = 100$ W. The gas mixing ratio Ar/O_2 was held constant at 590/10 sccm. Under these conditions the plasma exiting the tube did not create typical "plum-shape" (usually created at the lower pressure

around 0.1 mbar) around the nozzle outlet but it was spread over the sample surface homogeneously in a fog-like form [15]. This discharge behaviour at higher pressures was probably caused by long-lived metastable particles of oxygen or nitrogen.

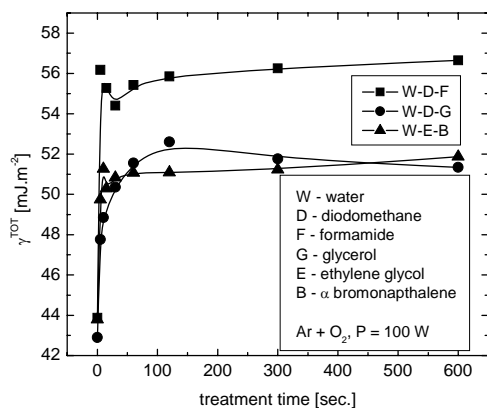


Fig. 2. The dependence of γ^{TOT} on time estimated from different liquid combinations.

The total surface energy was estimated by means of the sessile drop technique using the SeeSystem equipped by a CCD camera [16]. Images of liquid drops on sample surface were registered by the camera and contact angles were subsequently measured from the solid-liquid meniscus. The total surface free energy γ^{TOT} of the samples was calculated using regression methods according to Lifshitz-van der Waals/acid-base theory from the contact angles of at least three different polar and apolar liquids; water (W), glycerol (G), diodomethane (D), ethylene glycol (E) and α -bromnaphthalene (B) were used in our case [16]. The total surface energy γ^{TOT} is a sum of its apolar γ^{LW} and polar γ^{AB} components, $\gamma^{\text{TOT}} = \gamma^{\text{LW}} + \gamma^{\text{AB}}$ where LW indicates the dispersive, i.e. apolar, Lifshitz-van der Waals interaction and AB refers to acid-base or electron-acceptor/electron-donor interaction.

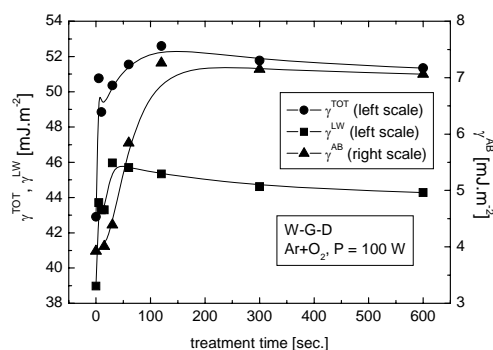


Fig. 3. The dependence of γ^{TOT} as well as both, apolar γ^{LW} and polar γ^{AB} component on time.

The dependences of total surface γ^{TOT} calculated from different liquids combinations (W-D-F, W-D-G, W-E-B)

on the treatment time are depicted in Fig. 2. The γ^{TOT} reaches energies about 51 mJ.m^{-2} for the W-D-G and W-E-B liquid combinations. The energy calculated from W-D-F gave the energy by about a few percent higher. The cause of this difference is probably connected with the choice of liquid combination; this problem is in detail discussed by Navratil et al [17].

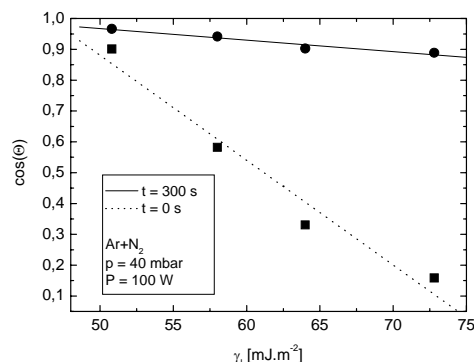


Fig. 4. The Zisman plot for four different liquids: water, glycerol, formamide, methylene iodide. The critical surface energy $\gamma^c = 48.75 \text{ mJ.m}^{-2}$

The evolution of γ^{TOT} as well as its apolar γ^{LW} and polar components γ^{AB} with the Ar/O₂ discharge treatment time can be seen in Fig. 3. The depicted results were computed from the W-G-D liquid combination. The total surface energy was about $\gamma^{\text{TOT}} = 40 \text{ mJ.m}^{-2}$ at the beginning of the process, i.e. before plasma treatment. Surface treatment caused steep increase of total surface energy to a maximum located at about 52 mJ.m^{-2} during first 100 s. After this time the γ^{TOT} was almost constant. The apolar component γ^{LW} with maximum value about 45 mJ.m^{-2} , is a major component of total surface energy γ^{TOT} . It can be seen in the Fig. 3 that both γ^{TOT} and γ^{AB} have similar time evolution. Polar component reaches energy in order of unit mJ.m^{-2} . The bigger scatter of both energies γ^{TOT} and γ^{AB} during the interval 10-25 sec is most probably caused by instability of the surfatron discharge just after ignition. Discharge cannot be sufficiently well stabilized at the beginning of the experiment, and that limits the time resolution of measurements during the initial time period after discharge ignition. The points acquired in shorter treatment times are therefore loaded with bigger experimental error than those acquired at longer ones.

The critical surface free energy γ^c can be estimated from so-called Zisman plot. The term "critical" is used because any liquid on the Zisman plot whose surface tension is greater than the "critical surface tension" makes a finite contact angle with the substrate. Critical surface tension values are useful empirical values that characterize relative degrees of surface energy of polymer substrates. Zisman noticed that a plot of cosine Θ (with Θ being the contact angle between the drop edge and the surface) versus the surface tension of the liquid of the sessile drop

γ_1 is often linear. Hence, the Zisman plot method is based on the determination of the dependence of $\cos\Theta$ on γ_1 . With linear extrapolation (for $\cos\Theta \rightarrow \gamma_1$) we can obtain the critical surface energy γ^C . There were used four liquids, water, glycerol, formamide, methylene iodide, for building the Zisman plot in Fig. 4. The value of critical surface free energy for low density polyethylene obtained from linear extrapolation was estimated as $\gamma^C = 48.75 \text{ mJ.m}^{-2}$. From the previous results we can consider that after plasma treatment when $\gamma^{\text{TOT}} > \gamma^C$ the sample is well wettable.

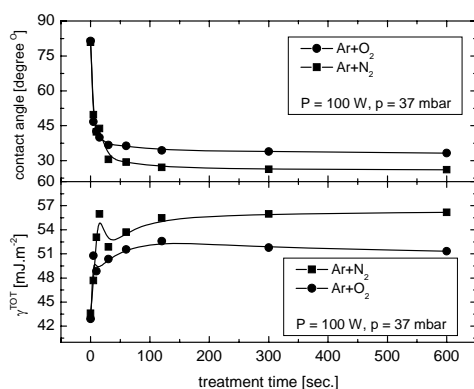


Fig. 5. Comparison of the dependences of the contact angle Θ and of the total surface energy γ^{TOT} (bottom panel) on treatment time for two different discharges.

Correspondence of surface hydrophilicity and total surface energy γ^{TOT} , after plasma treatment by means of two different gas admixtures O_2 and N_2 , can be assessed in Fig. 5. The contact angle was measured for distilled water drop with volume $8 \mu\text{l}$. Contact angle of non-treated LDPE sample was about $\alpha \approx 85^\circ$ and quickly fell down to less $\alpha \approx 30^\circ$ during the first 50 seconds of the treatment. The discharge in the Ar/N_2 mixture has been found more effective than that in Ar/O_2 ; it yielded higher total surface energy and, consequently, smaller contact angle within the same treatment time. Irregularities were not observed in decreasing contact angle curves, see Fig. 5. The small total energy descent followed by re-rise observed during first 50 seconds in both types of discharges was probably due to the discharge instability in the initial time period after ignition as described above.

3b) Plasma sterilization

We decided to test the bactericidal effects of the plasma generated by the described surfatron-based experimental system. The suspension of sterile water and the defined bacteria culture was inoculated on the cultivating medium (agar) in appropriate concentration. The gram-negative *Neisseria sicca*, *Deinococcus radiodurans* and the gram-positive *Enterococcus faecium*, *Stenotrophomonas maltophilia* were used as model

bacterial cultures. The concentration of bacteria on the cultivating medium was approximately 600 cm^{-2} to get the continuous overlay of bacterial coat on the sample.

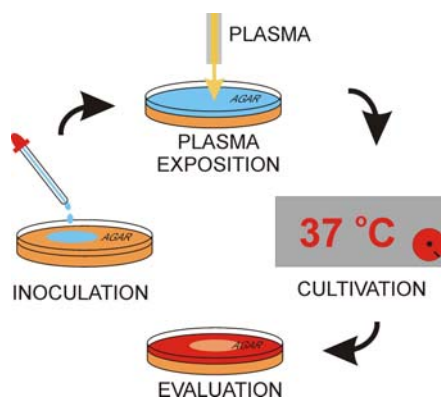


Fig. 6. Sterilisation procedure consists of four basic steps: inoculation by sterile water and bacterial culture, exposition in plasma, cultivation and evaluation.

The samples were placed on the table, distanced 3 cm from the nozzle outlet and have been exposed to the plasma burning in open atmosphere. At such high pressure the highest power $P = 300 \text{ W}$ had to be delivered. The plasma was generated in two mixtures of working gases. The mixtures of Ar (mass flow 590 sccm) with O_2 or N_2 (mass flow 10 sccm in both cases) have been used. The exposition time has varied from 30 seconds up to 8 minutes. After exposition in the plasma the samples were cultivated for the appropriate time and the bactericidal effect of particular experimental conditions was evaluated from the area of the zone of inhibition X_i in dependence on the treatment time t . Detailed description of the methodology can be found in [18]. The sterilisation procedure is depicted in Fig. 6.

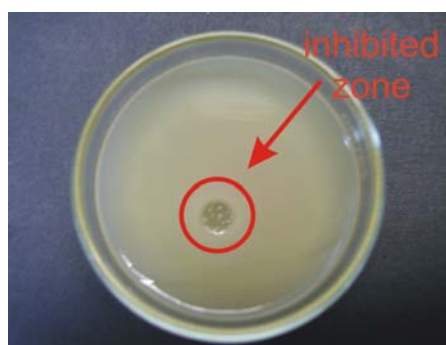


Fig. 7. Example of evaluated surface of the cultivating medium. The zone of inhibition is separated from the continuous coat of bacteria.

Described experiments were done and the area of the zones of bacteria inhibition was evaluated.

Table 1. The areas of the inhibition zones $X_{0.5-8}$ of bacteria exposed to the discharge for 0.5, 1, 2, 4 and 8 minutes for two gas-mixtures – Ar/O₂ upper part, Ar/N₂ lower part of the table.

Gas mixture Ar/O ₂ (590/10 sccm)					
Bacteria	X _{0.5} [mm ²]	X ₁ [mm ²]	X ₂ [mm ²]	X ₄ [mm ²]	X ₈ [mm ²]
<i>Neisseria Sicca</i>	0	34	67	110	165
<i>Deinococcus radiodurans</i>	0	0	69	109	123
<i>Enterococcus faecium</i>	0	0	0	0	0
<i>Stenotrophomonas maltophilia</i>	0	30	64	113	176
Gas mixture Ar/N ₂ (590/10 sccm)					
Bacteria	X _{0.5} [mm ²]	X ₁ [mm ²]	X ₂ [mm ²]	X ₄ [mm ²]	X ₈ [mm ²]
<i>Neisseria Sicca</i>	0	0	0	30	77
<i>Deinococcus radiodurans</i>	0	0	0	50	98
<i>Enterococcus faecium</i>	0	0	0	0	0
<i>Stenotrophomonas maltophilia</i>	0	0	0	15	58

The example of one inhibition zone can be seen in Fig. 7. Results for the evaluated area of the zone of bacteria inhibition in dependence on time of exposition are shown in Table 1. It is evident from the table that the efficiency of bactericidal effect is not the same for all the used gas-mixtures and all the bacteria cultures. For Ar/O₂ gas-mixture the bactericidal effect became visible already after 1 minute of exposition for gram-negative bacteria. For gram-positive bacteria *Deinococcus radiodurans* the effect became visible after 2 minutes of the exposition and for the *Enterococcus faecium* the bactericidal effect was not detectable even after 8 minutes of exposure. For Ar/N₂ gas-mixture the bactericidal effect became visible after 4 minutes of exposition for both gram-negative bacteria and gram-positive bacteria *Deinococcus radiodurans*. For gram-positive bacteria *Enterococcus faecium* the bactericidal effect was not detectable even after 8 minutes of exposure, like in the previous case.

3c) Plasma stimulation of seed germination

The Lamb's Quarters (*Chenopodium album* agg.) seed was stimulated by plasma discharge with the aim to increase germination. The experimental conditions were set in such a way that the fog-like form of discharge was created (pressure $p = 40$ mbar, input power $P = 100$ W, Ar/O₂ or Ar/N₂ discharge gases with mixing ratio 590/10 sccm). The seed, placed on petri dish distanced 3 cm from the nozzle outlet, was treated for relatively long time, up to 50 minutes. Afterwards the germination was tested by standard ways and statistical methods under laboratory conditions. The results are summarised in Fig. 8. Only the percentages of total amount of successfully germinated seeds after 8 days are depicted in the graph.

The seed was stimulated and the germination increased roughly three-times, from 15 % up to 50 % after treatment in the Ar/O₂ surfatron discharge. In the interval 0-20 minutes the germination increased almost linearly. For longer treatment times the germination remained more

or less constant; slight fluctuations are probably due to statistical error.

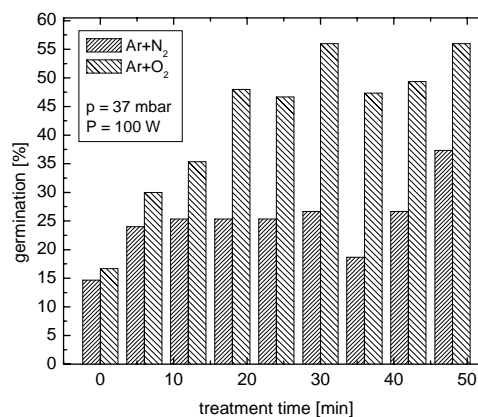


Fig. 8. Dependence of seed germination on plasma treatment time for the Lamb's Quarters seeds. The fluctuations of germination percentage for plasma treatment times longer than 20 min are probably due to statistical error.

In our opinion the plasma stimulation of seeds might be caused by two major effects: (i) by erosion processes of seed protective coat and (ii) by germicidal effect of Ar/O₂ discharge. Indeed, the oxygen plasma can erode the protective seed-coat and growth of seeds is easier. This presumption is supported by the experimentally observed dynamics of germination: the plasma-treated seeds started to grow as early as after several hours (approximately after 5 hours) while non-treated seeds as far as after several days (2-3) days. Bactericidal effects of oxygen mixture plasma were confirmed earlier (see previous chapter). In this way the surfatron-generated discharge could remove bacteria off the seed protective coat. This effect was also supported by the experimental observation: the treated

seeds (unlike sometimes the untreated ones) did not become mouldy during germination under laboratory condition. Ar/O₂ discharge seems to be more efficient than Ar/N₂ discharge which supports both the above mentioned stimulation mechanisms.

4. Conclusions

Surfatron-generated plasma was used for material surface treatment, for sterilisation and for processing of seeds before sowing. The microwave discharge generated in Ar/O₂ and Ar/N₂ mixtures was used for this purpose. The surface of LDPE was treated by plasma with the idea to increase its free surface energy (increase hydrophilicity). The critical surface energy of the low density polyethylene was experimentally estimated using the so-called Zisman plot; $\gamma^C = 48.75 \text{ mJ.m}^{-2}$. The total surface energy calculated according the Lifshitz-van der Waals/acid-base theory was determined experimentally (W-G-D liquid combination), $\gamma^{\text{TOT}} = 52 \text{ mJ.m}^{-2}$. We concluded that the surface of LDPE material became hydrophilic after plasma treatment. This characteristic was also confirmed by measurements of contact angles between plastic material and sessile water drop (see Fig. 5). The Ar/N₂ discharge seems to be more efficient for this type of LDPE surface modification.

The bactericidal effect of plasma generated by surfatron in the Ar/O₂ and Ar/N₂ mixtures was assessed. The defined bacteria cultures were exposed to the generated plasma and the areas of inhibition zones were measured. Preliminarily, it can be concluded that the bactericidal agent generated by the surfatron-plasma is more effective for the gram-negative bacteria. For the gram-positive bacteria the sterilisation efficiency is lower or the process is non effective at all.

The bactericidal effect of Ar/O₂ discharge probably plays significant role also in stimulation process of seed germination. The germination increased after plasma treatment by more than three times from 15 % up to 50 %. The percentage of successfully germinated seeds was calculated by standard statistical methods from large amount of seeds. The second effect which influences seed germination after plasma treatment might be the erosion of the seed protective coat by the plasma treatment.

From the presented preliminary results one can conclude that the surfatron generated plasma is a promising tool for bio-technological applications. Other, more advanced experiments are needed in the future that would help to better explain the mechanisms of the observed effects and to find the optimum experimental conditions for real applications in practice.

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