Non-Thermal Plasma-Based Technology for Soil Treatment

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Introduction

Modern agricultural methods of production, atmospheric pollution, cultivation, and land clearing can be a factor in the degradation of soil, which results in its erosion and decreases productive capacity. Organic and inorganic matter and microbial contamination of soil not only strongly influences its productivity but could also enhance air and water quality.

Application of electric discharges for sterilization and disinfection of microbiologically contaminated soil has not been widely studied. Sterilization should destroy/eliminate microbial cells whilst retaining the chemical and physical properties and fertility of the soil.

The three main sterilization techniques are based on (1) heat, (2) radiation, and (3) chemicals. Table 1 presents a review of the current methods of soil sterilization together with their advantages and disadvantages. Alternatives to these methods, particularly those based on chemicals, attempt to exploit electrical discharges in the non-equilibrium state.

Plasma-based technologies are already applied, to some extent, in the agricultural and food industry in the following processes: (1) pasteurization and disinfection of pathogenic...
micro-organisms in food, (2) removal or reduction of pesticides in fruits and vegetables, and (3) in corn steeping processes. The use of non-thermal plasma-borne species and radicals (like ozone O₃, nitric oxide NO, and UV radiation) in the above specified processes is advantageous, as sensory quality, nutritional value, and storage life of the agricultural products is improved. In addition, the use of chemical compounds that contain sulfur and chlorine, which can persist in the environment, are eliminated from the process. Benefits of the application of ozone in the agricultural industry are a result of:

i) its properties: ozone has a very short decay time (minutes at ambient temperature) and the soil treatment with ozone will not result in the build-up of any environmentally persistent or toxic compounds as it decomposes into simple diatomic oxygen and is immediately consumed in the process.

ii) manufacture: this must occur on site, so it cannot be stored and its sudden release into the atmosphere is not possible.

iii) minimal toxic effects.

Therefore, gas plasma-assisted methods of agricultural materials sterilization can provide reasonable alternatives to traditional thermal or chemical ones. For environmental applications a variety of non-equilibrium low-temperature discharges and reactors could be considered, like: dielectric barrier discharges (DBDs), atmospheric pressure glow discharges (APGD), radio frequency (RF) and pulse discharges, ferroelectric bad-packed reactors, and quasi-arc discharges. They are environmentally friendly and are already applied on an industrial scale in many emergent technologies.

Dielectric barrier discharges (DBDs), even though commonly applied for the treatment of potable water with ozone almost from the beginning of the last century, are still under investigation to improve the efficiency of ozone generation from air and from oxygen. Novel electrode arrangements, dielectric packing and granular materials introduced into the discharge zone, application of ultrasound fields or micro-hollow cathodes are only some of most recent ideas announced in the literature for the purposes of receiving high concentrations of ozone at reasonable generation efficiency.

New ecological applications of DBDs as a source of a chemically active environment for pollution control, disinfection, sterilization, and bleaching are also being explored.

In this paper, dielectric barrier reactors with a high-voltage electrode of a screw or pyramid form are investigated. The concentration of ozone and nitrogen oxides and the generation efficiency at different flow rates, lengths of the discharge tube, and power supply conditions are measured. The results show that, in the case of air as a process gas, the content of nitrogen oxides depends on the power supply frequency and gas flow rate. The length and form of the high-voltage electrode, together with supply system parameters and gas flow rate, could control the generation efficiency of ozone and its concentration over a wide range.

Table 1. Current methods of soil sterilization.

<table>
<thead>
<tr>
<th>Sterilizing medium</th>
<th>Method</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat</td>
<td>Autoclaving (dry, hot steam)</td>
<td>simple and easy available technique used commonly in agricultural laboratories</td>
<td>could destroy the soil structure and release ammonium-N and amino acids</td>
</tr>
<tr>
<td></td>
<td>Microwaves[3]</td>
<td>rapid and selective heating, pollution-free environment</td>
<td>quite large energy demands for sufficient sterilization</td>
</tr>
<tr>
<td></td>
<td>Solarization</td>
<td>low cost, environmentally friendly and with no risk for consumers</td>
<td>soil should be covered with the transparent plastic film for 1–2 months in the summer time high cost of lasers</td>
</tr>
<tr>
<td>Radiation</td>
<td>UV[4]</td>
<td>chemical free sterilization, ultraviolet germicidal lamps at 254 nm are applied for packaging surfaces, pulse monochromatic light produced by excimer lasers at 248 nm has been considered as efficient at inactivating bacteria</td>
<td>require irradiation facility (60Co source) and presently is limited to commercial use produce toxic for environment chemical residues, methyl bromide is categorized as an ozone-depleting chemical</td>
</tr>
<tr>
<td>Chemical compounds</td>
<td>Gaseous: chloroform, ethylene oxide, bromomethane</td>
<td>commonly used and most effective</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Liquid: hydrogen peroxide</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Solid: mercuric chloride</td>
<td></td>
<td></td>
</tr>
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</table>


Also presented in this paper are some initial results of soil treatment with ozone. The electrical conductivity (EC) and acidity (pH) of the soil are measured, and their time development is discussed.

**Experimental Part**

The experimental stand consisted of two main components: a source of active sterilization agents (O₃, NO), produced by dielectric barrier discharges in air and oxygen, and the processing chamber where the soil samples were exposed to the afterglow of the discharge. Dielectric barrier discharges were generated in reactors of a high-voltage electrode of screw and pyramid type; the pyramid-type electrodes employed were of different heights, 0.8 and 1 mm. All the electrode configurations investigated are presented schematically in Figure 1. The grounded electrode was made of quartz glass tube with externally wound aluminum foil. High-voltage electrodes were made of stainless steel and, together with the grounded electrode, they formed the 1 mm discharge gap (Figure 1a). In the case of the screw electrode reactor, the experiments were carried out for four lengths of the screw sector of the discharge element: 100, 200, 300, and 400 mm. Reactors with screw and pyramid high-voltage electrodes are not commercially available and they were made in our laboratory. As a source of surface discharge, a commercially produced reactor, OP-20W (IWASAKI Corp.) was employed in the experiments. In Figure 1d the co-planar electrode geometry applied in the IWASAKI reactor is presented.

Measurements were made using the system shown in Figure 2. The main components of the system are a power supply inverter of 10 kHz frequency and sine regulated voltage, plasma reactor, measuring system, gas flow system, and ozone and nitrogen oxides monitors. The ozone concentration was measured using a UV Ozone Monitor OZM-7000 GN. Courses of current, voltage, and Lissajous curves were recorded on an oscilloscope.

Figure 1. Electrode configurations: a) discharge element with screw-type electrode; b) pyramid-type electrode; c) pyramid dimensions; d) co-planar element of the surface discharge IWASAKI reactor.

Figure 2. Diagram of the measurement setup.

Conditions of the experiments are gathered in Table 2. The discharge gas consisted of ozone, or a mixture of ozone and nitrogen oxides, and was injected directly through the soil positioned in the treatment chamber as shown in Figure 3. The soil samples filled the inner chamber of 70 mm diameter. The treatment gas was supplied from the top of the chamber and evacuated from the bottom exit tube. The outer chamber of 306 mm diameter operated as a draft high-pressure chamber. An ozone concentration from 100 to 50 000 ppm was injected into the soil samples at different gas flow rates and for varying durations. Vegetable seeds were planted in the treated soil and their growth was observed. At the same time the chemical and biological properties were analyzed by conventional methods and the penetration range of the ozone into the soil sample was measured.

The soil parameters were measured in the system schematically presented in Figure 4. The measuring electrodes were placed in the treatment container at a depth of 15, 2, and 5 cm from the central tube through which the ozone with a concentration of 100 g·m⁻³ at flow rate of 2 L·min⁻¹ was introduced to the soil sample over 60 min. Electrical conductivity (EC) and soil acidity pH were measured in the sandy, muddy, and moderately moist soils during the time of ozone injection and 72 h after treatment at time intervals of 12 h.

**Results and Discussion**

**Air as a Processing Gas**

Measurements using air as a processing gas were performed utilizing the screw-type electrode reactor with geometry

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Setting used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrode length, mm</td>
<td>100, 200, 300, 400</td>
</tr>
<tr>
<td>Electrode form</td>
<td>Screw type</td>
</tr>
<tr>
<td></td>
<td>Pyramid type (0.8 mm, 1 mm)</td>
</tr>
<tr>
<td>Frequency, Hz</td>
<td>10 000</td>
</tr>
<tr>
<td>Flow rate, L·min⁻¹</td>
<td>1, 2</td>
</tr>
<tr>
<td>Gas pressure, atm</td>
<td>1</td>
</tr>
<tr>
<td>Discharge gap, mm</td>
<td>1</td>
</tr>
<tr>
<td>Material gas</td>
<td>air, oxygen (purity 99.9%)</td>
</tr>
</tbody>
</table>
presented in Figure 1a. Figure 5 shows the results of O₃, NO, and NOₓ concentration in the afterglow of the dielectric barrier discharge in air measured at 1 atm pressure of gas with two flow rates, 1 and 2 L·min⁻¹, as a function of input power. In the case of a gas flow rate equal to 2 L·min⁻¹ the concentrations of NO and NOₓ are negligible in the afterglow, while at 1 L·min⁻¹ they increase with input power; at 30 W the concentrations are equal to 300 and 500 ppm, respectively. The O₃ concentration at the lower flow rate clearly reaches a maximum equal to 1 g·m⁻³ near 20 W, while at the flow rate of 2 L·min⁻¹ the O₃ concentration is still increasing with power and the maximum is not observed in the investigated range of input power. For a fixed value of input power, the higher gas flow rate (Figure 5b) results in larger concentrations of O₃, while nitrogen oxide concentration are almost immeasurable.

**Oxygen as a Processing Gas**

The ozone concentration obtained from oxygen, and its generation efficiency versus power for different lengths of the discharge tubes of the screw-type reactor, are presented in Figure 6a and b, respectively.

As can be seen, the influence of discharge tube length on the ozone generation efficiency (Figure 6b) is rather small, whereas a distinct increase of ozone concentration with increasing discharge tube length is observed (Figure 6a), as is displacement of the concentration maximum to higher powers. For the reactor with an electrode length of 400 mm, the maximum ozone concentration is still not attained in the investigated range of power, and for 55 W it is equal to 25 (g O₃)·m⁻³. The relation of ozone-generation efficiency versus ozone concentration is also influenced by the form and length of the electrodes, as shown in Figure 7. For the ozone-generation efficiency equal to 150 g·kWh⁻¹, the measured ozone concentration is the highest in the case of a screw electrode of 100 mm length and is equal to 20 g·m⁻³. For the pyramid electrode of 1mm length, the concentration for the same efficiency does not exceed 5 g·m⁻³ (Figure 7a). The influence of the discharge tube length on the discussed relation is not so obvious, but the highest efficiency, together with high ozone concentration, is measured in a 100 mm length reactor (Figure 7b). Increasing the length of the electrode generally makes it possible to obtain a greater ozone concentration at a lower generation efficiency. From the point of view of generation efficiency...
of ozone, the DBDs reactor with a screw-type high-voltage electrode of 100 mm length represents the best performance.

The comparison of ozone concentration–voltage controllability in the dielectric barrier discharges of different high-voltage electrode forms with surface discharges produced in commercially available reactor is shown in Figure 8.

Although the measured ozone concentrations from oxygen in the surface discharge reactor are up to 4–6 times greater than in the DBD reactor, depending on the supply voltage, its controllability is limited to voltages greater than 3 kV and is rather rough. Therefore, a small increase in the value of supply voltage causes a relatively large change in ozone concentration (Figure 8b).

The typical courses of discharge current in the dielectric barrier reactor with a screw- or pyramid-type high-voltage electrode are shown in Figure 9. The discharge is of filamentary structure and the discharge current consists of pulses statistically distributed per half cycle. The number of current pulses and their intensity depends on the value and frequency of power supply, and on the length and form of the high-voltage electrode. Generally the current pulses are not evenly distributed between positive and negative half cycles of the supply voltage. They are more intense but less densely dispersed when the screw electrode is the instantaneous cathode, which is clearly seen in the case of a longer discharge tube. For a fixed length of the discharge tube, an increase of supply voltage usually contributes to a more even distribution of current pulses between half cycles.

The form of the high-voltage electrode, for the fixed values of supply voltage and reactor length, influences the discharge current waveform considerably, as is shown in Figure 9a and b. For the pyramid-type DBD, a larger number of microdischarges with a lower intensity have been observed in comparison to the screw–electrode reactor at the same applied voltage. Although the increase of the number of current pulses promotes the generation of ozone through oxygen decomposition, the rapid decomposition reaction of...
the generated ozone simultaneously occurs upon contact with microdischarges. Hence, the ozone concentration for the pyramid-type electrode is lower than that in the case of screw-type electrode. Another reason is that the increase in temperature of the quartz tube, caused by high frequency dielectric heating, destroys the generated ozone. These results show that the pyramid-type DBD is suitable to generate a lower ozone concentration for soil sterilization and that the screw type is useful for soil treatment requiring a higher ozone concentration.

**Soil Treatment with Ozone**

Typical results of soil ozone treatment with an ozone concentration of 5 000 ppm, a time exposure equal to 30 min at gas flow rate of 1 L·min⁻¹ are shown in Table 3 and 4. An almost 98% decrease of bacteria content in the soil, from initial value of 3.8 × 10⁷ to 8.5 × 10⁵, and 87% decrease of fungi content (Table 4) after ozone treatment is observed. Among them are those species responsible for forming nitrates, therefore, an increase of nitrogen content indica-

<table>
<thead>
<tr>
<th>Soil sample</th>
<th>Moisture</th>
<th>EC</th>
<th>pH</th>
<th>NH₄–N</th>
<th>NO₃–N</th>
</tr>
</thead>
<tbody>
<tr>
<td>untreated</td>
<td>30.7</td>
<td>34</td>
<td>6.5</td>
<td>14.9</td>
<td>0.5</td>
</tr>
<tr>
<td>treated</td>
<td>23.7</td>
<td>79</td>
<td>5</td>
<td>18</td>
<td>22</td>
</tr>
</tbody>
</table>

a) Treatment conditions: 5 000 ppm, 30 min, 1 L·min⁻¹.
tors, NH₄–N and NO₃–N, is also observed. The mineral content in the soil does not change significantly after ozone treatment, as is shown in Table 4. The change in soil acidity after ozone treatment with various doses of ozone related to 100 g of soil is measured and their results are presented in Figure 10. The soil acidity and electrical conductivity depend on its moisture content and the treatment conditions—duration, dosage, and ozone penetration depth, as it is presented in Figure 11. Measurements presented in Figure 11 are made in a moderately moist soil with pF = 2.6 and they demonstrate a slight increase in the soil electrical conductivity (from 29 mS·m⁻¹ before treatment to 32 mS·m⁻¹ after 72 h) and acidity (pH from 6.2 to 6.0) with time.

The seeds of melon and lettuce were planted in the treated and untreated soil and their growth was observed. Initial observations demonstrated that soil treatment with ozone had resulted in decreasing the content of bacteria that control the plant growth.

**Conclusion**

The main purpose of this investigation was to check the suitability and controllability of the dielectric barrier discharges produced in a screw- or pyramid-type high-voltage reactors as a source of an active environment for soil treatment.

<table>
<thead>
<tr>
<th>Soil type</th>
<th>Total bacteria (cfu·cc⁻¹)</th>
<th>Filamentous fungus (cfu·cc⁻¹)</th>
<th>Minerals (mg·(100 g)⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>P₂O₅</td>
</tr>
<tr>
<td>untreated</td>
<td>3.8 × 10⁷</td>
<td>1.8 × 10⁵</td>
<td>674</td>
</tr>
<tr>
<td>treated</td>
<td>8.5 × 10⁵</td>
<td>2.7 × 10⁴</td>
<td>700</td>
</tr>
</tbody>
</table>

Presented results show that the application of a high-voltage electrode in the form of a screw or pyramid allows the production of a relatively high ozone concentration at reasonable generation efficiency from air or oxygen, and both parameters could be controlled by the value of the supply voltage, geometry of the reactor (length and form), and gas flow rate. Our next task is to determine the geometry of the dielectric barrier discharge reactor that would be suitable for soil treatment and could operate at a considerably low value of applied voltage to facilitate voltage supply directly from a solar cell on site.

The process of soil treatment assisted by low-temperature plasma is very complex as it involves both soil properties (composition, nutritive value, contaminants, and microbiology), plasma species (electrons, excited atoms of oxygen and nitrogen, ozone, nitrogen oxides, radicals, UV radiation), and parameters (pressure, temperature, moisture content, time of exposure), all of which play a role in the process.

Nitrogen oxides, present in soil because of the microbial activity of nitrate-forming bacteria and fertilization processes, can react with ozone and nitrogen compounds produced in the discharge, and this process can strongly influence the physical and chemical characteristics of the soil, its fertility, and plant growth. Initial findings obtained here confirm the influence of ozone on the chemical and biological properties of soil and plant growth.
A non-thermal plasma-based technology for soil sterilization seems to be a reasonable alternative to traditional methods and further investigations should be undertaken.

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