Plasma treated water spray: reactors and RONS production

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Abstract: Plasma treated water (PTW) plays a major role in cold plasma research and applications. The experimental reactor designs for PTW production are numerous and variated. Far from being trivial, the comparison between different plasma reactors is an important step to improve the energy efficiency and reduce the operating costs of plasma systems. A comparison between different reactors for the production of PTW is here presented with a focus on systems based on water spray.

Keywords: cold plasma, water, spray, droplet, energy yield, generation rate

1. General

Plasmas in/above/with liquids science and technology at atmospheric pressure have been intensely investigated in the last years, partly due to the very active research activity in the fields of plasma medicine and plasma agriculture [1], [2]. Plasma treated water (PTW) can be regarded as vector of plasma action on biological target. Plasma interaction with water introduces into water several reactive oxygen and nitrogen species. PTW can be produced and stored since the long lived reactive species introduced may last for a relatively long time (days and weeks). The use of PTW is particularly advantageous where a direct contact between target and plasma needs to be avoided or simply is not possible. Another advantage of PTW is the possibility to convert it in a liquid spray allowing to uniformly treat a much larger surface than that usually addressable using a an atmospheric pressure plasma.

In this framework, several scientific works,reviews and references therein [3], [4] provided insights into the non-equilibrium chemistry created at the plasma–liquid interface and addressed the role of liquid and gas reaction pathways. It is safe to affirm that PTW production always requires a direct contact between the water and the plasma phases (or its early afterglow). Thus the plasma-water interface limits the production of reactive species and, thus, process throughput.

Several solutions have been advanced to maximize this interface and overcome the limit of bach processes. Among many, there are configurations based on the treatment of flowing liquid film, bubbling air in the liquid, treatment of aerosol, cavitation inside the liquid, formation of electrospray. At the same time, the electrical parameters, geometry and materials can greatly vary even between reactors based on the same principle. Comparing different reactors is anyway difficult due to the somewhat disperse literature and time to time inconsistencies in the information reported in the scientific papers.

In the present work a comparison between several plasma reactors for the production of PTW is addressed with a special regard to the possibilities offered by spray and aerosols [5]. Details on the key parameters and measurements necessary, as well as some indexes possibly usefull for the comparison are suggested.

2. Materials and Methods

Plasma reactors

The reactors design investigated in this work are schematically reported in figure 1. These configurations are as simple and similar as possible in order to ease the comparisons. All the systems use an high voltage electrode either constituted by a stainless steel needle (G23, Hamilton) or a brass electrode (custom made, brass 4mm diameter). The reactors were all powered either by a micropulsed power supply (2µs, up to +20kV and 20kHz, developed by the GREMI laboratory) or by a DC power supply (+30kV, Ultravolt by Advanced Energy). The operating conditions in each configuration were chosen so to have similar power delivered to the plasma reactor (different than the power consumed by the power supply and the power delivered to the plasma or the target). The jet configurations (Figure 1 c and d) used He as working gas (99.999%). The water pump used in configurations b, d and f is a syringe pump (NE-1000 One). In configuration b and d the film was immediately nebulized through a piezoelectric membrane and collected in a vessel (Fig. 2). In configuration g the water aerosol introduced in the DBD reactor was generated by means of a pneumatic spray nebulizer (BLAM by CHtechnology). For all the tests demineralized water was used as liquid target.

Electrical measurements

The current and voltage waveforms were recorded on the high voltage electrode using high voltage passive probe (P6015, Tektronix) and current (Pearson 6585) probes connected to an oscilloscope (MDO34, Tektronix).

Liquid analysis

The production of long lived reactive species in the PTW was evaluated through colorimetric methods as greiss assay (nitrates), amplex red (hydrogen peroxide) and KI-starch (non specific ROS evaluation). The pH and conductivity of the PTW were also investigated through specific probes (InLab Micro by Mettler Toledo).

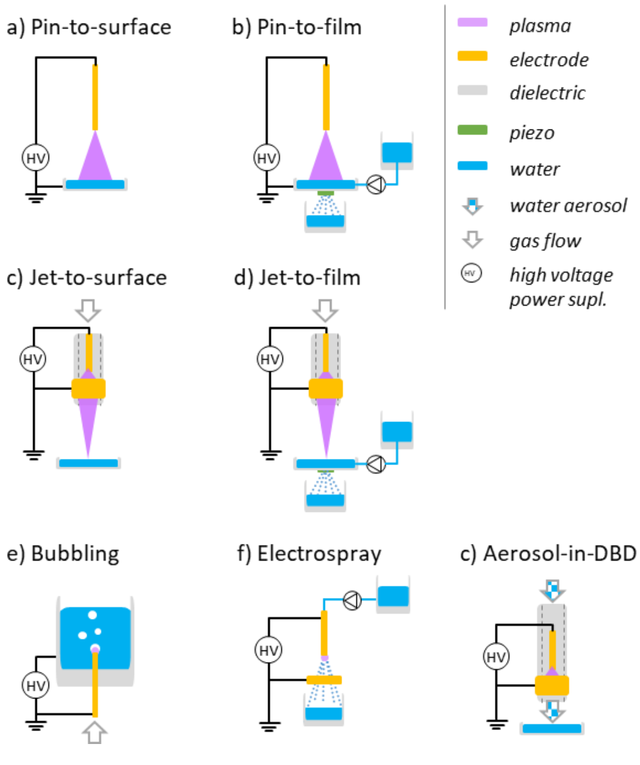


Fig. 1. Schematic of the reactor configurations for plasma treated water production.

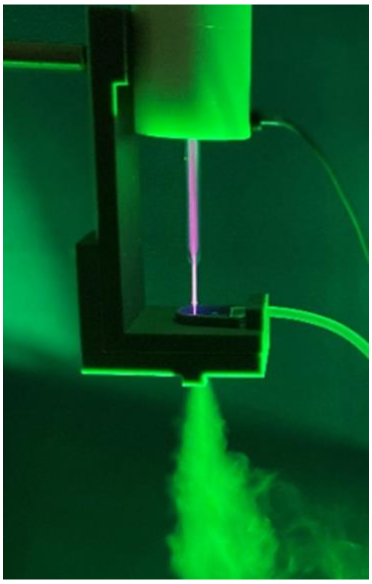


Fig. 2. Picture of configuration *d* during operation. (receiving vessel removed)

Optical diagnostics

The morphology of the plasma discharge and its interface with the water phase was investigated by means of a combination of iCCD (Pimax 3 by Princeton Instruments) and high speed cameras (MiniAX by Photron) as well as conventional photography (Canon 6D).

3. Discussion

For non-thermal plasma applications to become a reality in the treatment of seeds and plants, it is necessary for them to meet the application specific goals (e.g. reduce bacterial load, improve crop yield) and the economical requirements demanded by the industry. In this sense, a good indicator for comparison of different treatments should take into account both aspects. Plasma reactors may greatly differ from one another but all require electrical power to operate. Similarly, plasma is useful only if it produce the desired effect on the target. The type of target and effect is necessarily defined by the application. In this work we take as an example the production of H_20_2 and NO_2 in PTW.

The performance of a plasma system for PTW production could then be evaluated in terms of the following quantities:

- G : Treated volume or generated amount of compound per treatment (i.e. L of PTW or g of the desire compound)
- t : Treatment time (in seconds)
- E : Total input energy to the plasma reactor (i.e. kWh). It is supposedly equal to the power consumed by the high voltage power supply minus the losses.
- C : Total input resource cost (i.e. €/s from energy consumption including auxiliary, gases and other input reactants)

Measuring or estimating these quantities it is possible to calculate three suitable and complementary indicators to evaluate plasma treatments:

Energy yield $$\alpha = \frac{G}{E} \qquad \left[\frac{L \text{ or } g}{kWh}\right]$$

α is representative of the energy efficiency of the plasma process. It express the amount of good that can be produced (or treated) with 1 kWh worth of plasma. The proposed expression of α is similar to yield formulas already adopted in other related fields such as in agriculture for crops yield (i.e. tons/hectare) and ozone generators for ozone yield (i.e. kg of O_3/kWh). The same energy yield has also been adopted in other plasma applications such as for hydrogen peroxide production from water [6] and decomposition of pollutants [7], [8].

Generation rate $$\beta = \frac{G}{t} \qquad \left[\frac{L \text{ or } g}{min}\right]$$

β is representative of the generation rate essential to appreciate the scale of the system and its applicability to real size applications as well as for considerations on the possible scale up [6]. It must be paid particular attention to the definition of the required time for indirect treatments. The time should be considered from the entry of the fresh reactants into the system (e.g. water, air) to the delivery of the final desired output (e.g. PTW, decontaminated water, treated seeds). If a "plasma off" period (when there is no power delivered to the reactor) is part of the process and is used to leave the plasma generated species act on the targe, this should be counted too. Storage time, during which for example PTW is not used or alterated, is not to be taken into account instead. The quantities G and t should refer to steady state regime of the system.

Treatment total cost $$\gamma = \frac{C}{G}\, t \qquad \left[\frac{€}{L\ or\ g}\right]$$

γ will help determining the economical attractiveness of the technology taking into account also input resources different from electrical energy such as gas and liquid inputs and added chemical compounds. This simple indicator is important to be able to compare plasma technology with other standard techniques for the same application.

These three indicators are somehow sparsely used in the dedicated plasma literature but hardly in a constant and uniform way. The adoption of these indicators, or equivalent ones, in a more consistent way would greatly foster the comparisons between plasma solutions and prompt the adoption of plasma technology in agriculture.

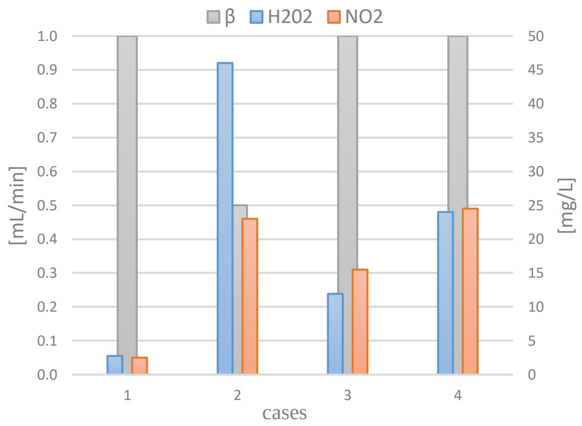
As an example, we here report the comparison between four cases obtained with the reactor configurations *c* and *d* (Figure 1). The reactors were compared over the treatment of 5 mL of water according to the parameters reported in Table 1.

Table 1. Investigated cases preliminary assessed in this work

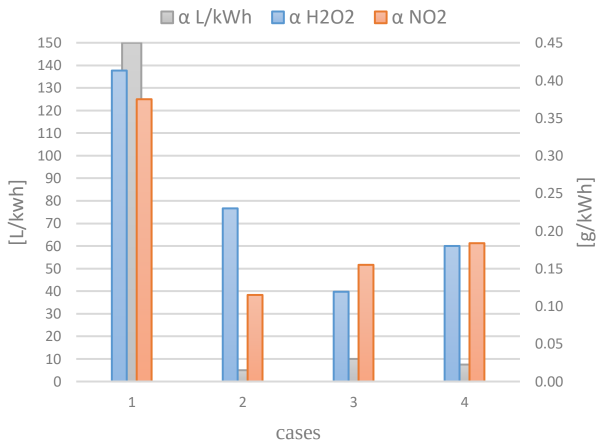
Case	Config	Volt. [kV]	Freq. [kHz]	He [L/min]	Time [s]	Energy [μJ/pulse]	Power [W]
1	c	10	2	0.5	300	200	0.4
2	c	10	20	1	500	300	6
3	d	10	20	1	300	300	6
4	d	15	20	1	300	400	8

For the conditions using configuration *d* the water film was flowing at 1 mL/min. The high voltage power supply and core reactor were the same for the four cases and the variation in the energy delivered to the reactor per pulse are only due to different applied voltage and He flow. The water treated in these conditions presented the concentration of H_2O_2 and NO_2^- reported in Graph 1 together with the index of generation rate β.

The values reported in Graph 1 clearly highlight several differences in the PTW generated in the four cases. For both plasma configurations (c and d) is observable an increase of the concentration of both H_2O_2 and NO_2^- for increased power consumption.



Graph 1. Generation rate (left axis) and concentration of H_2O_2 and NO_2^- (right axis) in PTW



Graph 2. PTW production energy yield (left axis) and energy yield for the production of H_2O_2 and NO_2^- (right axis) in PTW.

Case 2 achieves the highest concentration of H_2O_2 but it is also characterized by the lowest β. Case 4 produces the highest concentrations of NO_2^- but also has the highest power consumption.

Further insight in the comparison can be achieved through the evaluation of the energy yield (α) for three different objectives: production of PTW (α L/kWh), production of H_2O_2 (α g/kWh) and production of NO_2^- (α g/kWh). These values are reported in Graph 2.

Through the energy yield index it is clearly visible that case 1 has the highest production per kWh compared to the other cases. It is interesting also to compare between case 2 and 3 that use the same plasma parameters but either on a static sample (case 2) or a flowing thin film (case 3). The flowing film leads to an higher energy yield rate of NO_2^- while it reduces that of H_2O_2. Case 4, that is the same configuration of case 3 except for an higher voltage and power, see an overall increase in the energy yield of both species compared to case 3..

4. Conclusions and perspectives

The comparison of plasma configurations is certainly far from being trivial but at the same time represents an important step for the advancement of this technology. As plasma reactors configurations can be tailored for each specific application so they should be evaluated according to each specific purpose. Anyway, the availability of comprensive data on the energy and resources as well as the generation rate and characteristic of the final outpuy for any proposed configuration in published scientific papers would greatly help this comparison.

The few examples here presented were chosen to demontrate the proposed comparison method. In the final presentation a larger set of configurations and parameters will be compared with special focus on the potential of spray based reactor designs. The presented results will show how the comparison between palsma configuration can help in the selection of the better option for a specific goal. The detailed characterization of liquid-discharge interplay and liquid recirculation are also valuable for a better understanding of key phenomena and parameters and therefore an optimization of PTW reactors.

Future perspective will be oriented to the comparison of a wider number of configurations for some specific applications (e.g. decontamination of seeds, degradation of pollutants).

5. Acknowledgments

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