Plasma treatment of pesticide-contaminated water: assessment of toxicity and possible use in irrigation

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Abstract: The effect of 2,4-dichlorophenoxyactic acid solution treated in a coupled plasma-ozonation system on the growth and development of *Solanum lycopersicum* L. was studied. While the presence of the compound has a significant negative impact on the plants, its complete removal, achieved for treatment times above 20 minutes, reduces the toxicity and improves growth.

Keywords: non thermal plasma, 2,4-dichlorophenoxyactic acid, irrigation, agriculture, auxin

1. Introduction

Organic water pollutants, such as pesticides, pharmaceuticals and personal care products and others, pose a high risk for the environment [1], [2]. The intense use of organic chemicals at a global scale has drastic effects on the biodiversity, with the maximum impact on aquatic ecosystems [3]–[5].

The study of advanced water treatment methods has thus became imperative for eliminating these contaminants before they enter the environment and exert their toxic effects on life. Different advanced oxidation processes have been investigated for this purpose, such as electro-peroxone [6], catalysis [7], ozonation [8] and plasma treatment [9], [10].

2,4-dichlorophenoxyacetic acid (2,4-D) is an auxin-like herbicide frequently used worldwide. In small concentrations, it can stimulate auxin response pathways in plant cells [11], [12]. Larger concentrations produce damaging effects on plants growth and development [13] and the toxicity extends even to non-target organisms [14]. Degradation by-products such as 2,4-dichlorophenol can exhibit higher toxicity than the parent compound [15].

In this work, the toxicity of 2,4-D solutions treated by plasma-ozonation was investigated using tomato seeds as the study organism. Employing this combined method maximises the contact of plasma generated oxidative species with the treated solution, leading to a synergic action in the degradation of the target compound [9].

In recent years plasma activated water (PAW) has become increasingly investigated. One of its main applications is the improvement of seed germination and plant growth [16]. This suggests that contaminated water treated by plasma could also be reused in agriculture for the purpose of irrigations if toxicity is removed.

2. Experimental

The experimental set-up was comprised of a corona plasma reactor with multi-wire to plate geometry coupled with an ozonation reactor, as previously described in [17]. The discharge was generated in oxygen (flow rate 300 mL/min), at atmospheric pressure, above the liquid surface. The effluent gas containing plasma generated ozone was bubbled through the solution in the ozonation reactor.

The electrical circuit, described in detail in [18] is based on a pulse forming line. High voltage pulses of negative polarity were used, with amplitude of 17 kV, duration of 110 ns (FWHM), rise time of 11 ns and repetition rate of 25 Hz. The amplitude of the current was 140 A and the average power in the discharge was 5.4 W.

2,4-D solutions (concentration 25 mg/L, conductivity 300 µS/cm) prepared in tap water were used in these experiments (330 mL per experiment). During the experiment the solution was circulated between the plasma reactor and the ozonation reactor.

The presence of bicarbonate and carbonate ions in tap water allow for little variation in the pH (7.9-8.6) of the solution during treatment. When measuring the chlorine levels resulting from 2,4-D degradation, the experiments were carried out in distilled water and the conductivity was adjusted using $NaHCO_3$.

The treatment time was varied between 5 and 120 minutes. A second experiment with tap water alone and 60 min treatment was employed to assess the effect of the process in the absence of the contaminant.

The degradation of 2,4-D was assessed using high performance liquid chromatography (HPLC) on a Varian ProStar equipped with a Zorbax SB-C18 column (4.6 mm × 250). The mineralization of the compound was measured by total organic carbon (TOC) analysis.

The effect of the plasma-ozonation treated samples on seeds germination and growth was assessed using tomato seeds (*Solanum lycopersicum* L.).

For each sample (2,4-D: control and treated for 5, 10, 20, 60, 120 min; tap water: control and 60 min treatment) 35 seeds were placed in petri dishes on filter paper along with 3 mL solution and sealed.

They were monitored for seven days after planting, measuring the root length. After that period they were weighed both wet and dry.

3. Results and discussion

The results on 2,4-D degradation in the plasma-ozonation system are shown in Fig. 1.

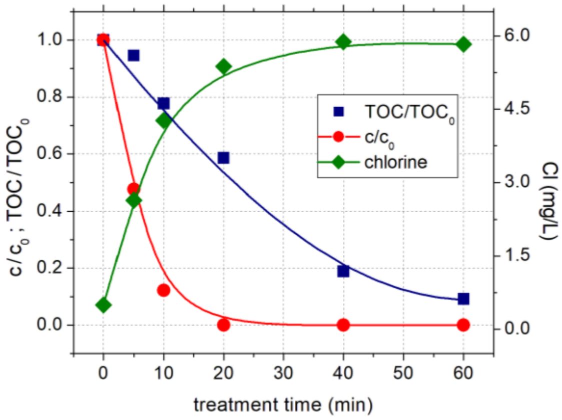

Fig. 1. Evolution of 2,4-D removal (c/c_0), mineralization (TOC/TOC_0) and chlorine levels as a function of treatment time

Almost complete removal of the target compound was achieved after 20 min treatment. The release of chloride ions in the solution was similarly fast, suggesting that dechlorination of 2,4-D represents the first step of the degradation process. The mineralization is definitely slower, but still reached over 90% after 60 min treatment.

Photographs of tomato seeds after 6 days of incubation with 2,4-D solutions and with tap water are shown in Figure 2.

Comparing the seeds grown in untreated 2,4-D solution (Fig. 2A) with those in tap water (Fig. 2G), it is observed that 2,4-D inhibits the elongation of the root and the formation of absorbent hairs. This is due to its auxin-like interaction with the biochemical processes in plants [13], [19]. Solutions treated for 5 and 10 min, containing lower amounts of 2,4-D, allow the growth of root hairs at the root tip (Figs. 3B,C). The seeds grown in 2,4-D solutions treated for longer times (Fig. 3.D-F) are characterised by both root elongation and root hairs growth with an even distribution on the surface. It is also observed that the presence of 2,4-D is associated with larger root diameter, which can be explained by induction of xylogenesis (i.e. the formation of new vessels) [6].

The mean root length, averaged from measurements done by ImageJ software, is shown in Fig. 3, starting with the fourth day after planting.

The mean root lengths of the seeds grown in samples of untreated pesticide or treated by plasma for 5 and 10 minutes show little variation between them. The values range between 1 and 2 mm in the fourth day after planting and reach 4-5 mm in the seventh day. The roots of seeds grown in solutions treated for 20 minutes or more (where 2,4-D was completely removed) were 2-3 times longer, reaching 11-13 mm after seven days of cultivation. These samples are comparable from the point of view of root length with the ones grown in tap water. However, tap water treated by plasma-ozonation significantly enhances plant growth, the roots being 50-60% longer than the ones with untreated tap water.

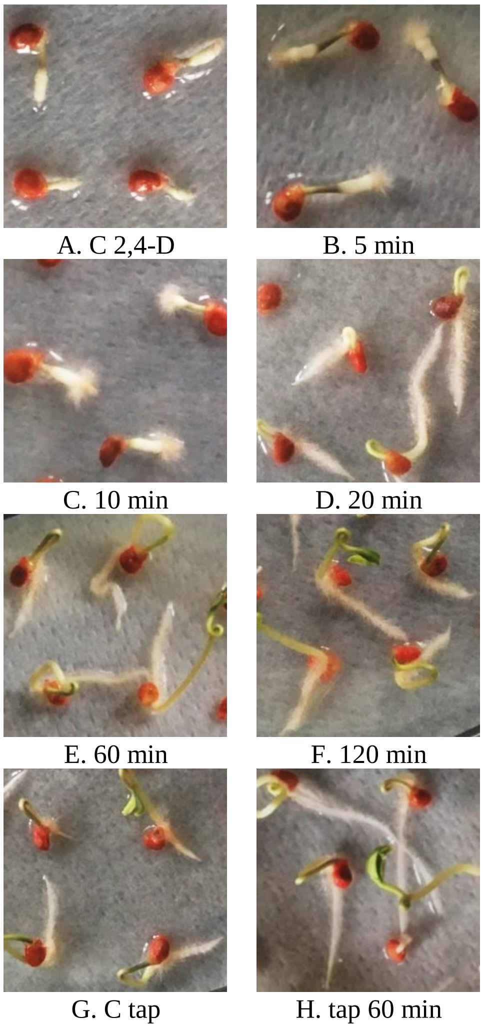

Fig. 2. Photographs of Solanum lycopersicum seeds after 6 days of incubation in different water samples (A: 2,4-D untreated, B-F: 2,4-D treated for 5-120 min, G tap water untreated; H: tap water treated for 60 min)

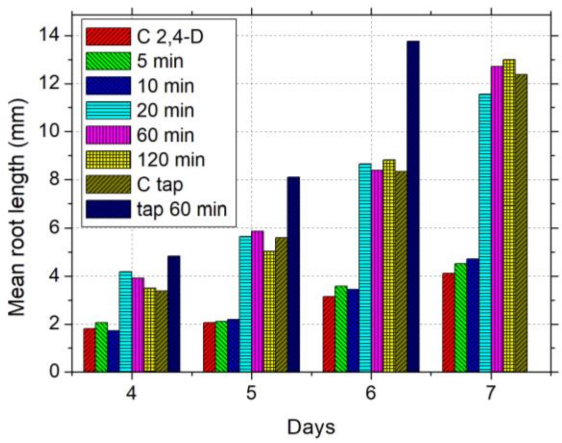

Fig. 3. Temporal evolution of the mean root length for the control and treated 2,4-D and tap water samples

The considerable increase in length for the longer treatment times, where 2,4-D removal has already been achieved is in accordance with the study [12] that associates 2,4-D levels over 2.2 µg/L with a rapid decrease in root length of *Arabidopsis thaliana*. There is no statistically significant difference between root lengths of the seeds cultivated in tap water and in pesticide solution treated for more than 20 min. This finding promotes the hypothesis that the plasma degradation by-products of 2,4-D have little effect on plant growth and development at this stage.

After 7 days of cultivation the plants were weighed (fresh and dry) and the results are shown in Fig. 4.

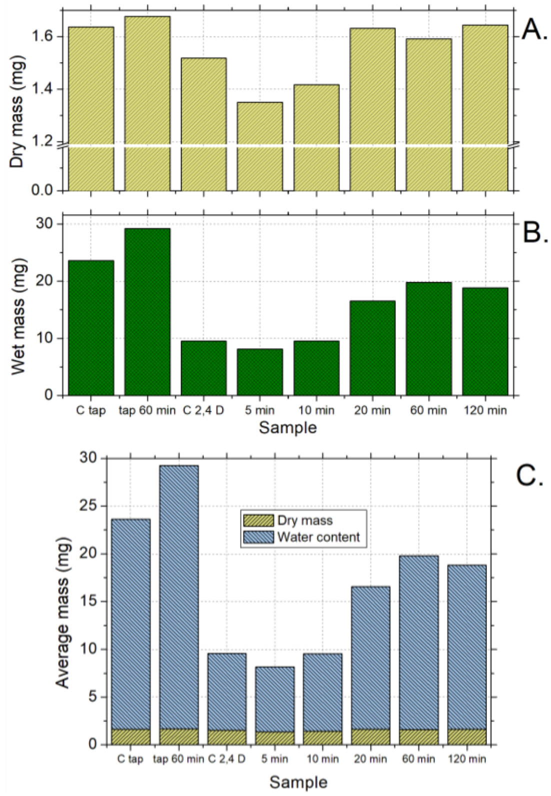

Fig. 2. Graphic representation of the mean dry (A) and wet mass (B) of the plants after 7 days of growth and the mean water content in different samples (C)

The same difference between samples still containing 2,4-D and the ones where the compound was completely removed can be observed. A slight decrease in dry mass is noticed in the presence of the contaminant (1.35-1.52 mg / plant), while the solutions treated for longer times do not significantly affect the plant mass (1.59-1.67 mg), which remains similar to the values obtained for tap water and plasma-treated water (Fig. 4A).

The variations in wet mass are larger for all 2,4-D treated samples, as compared to the tap water control (23.6 mg) and treated water (29.23 mg). The wet mass of plants grown in solutions still containing the pesticide (C 2,4-D, 5 min, 10 min) ranges between 8.2 and 9.6 mg, while the maximum value after 2,4-D complete removal is 19.8 mg, reached for 60 min plasma treatment (Fig. 4B).

The water content of plants grown in the presence of the pesticide is greatly reduced as compared to those cultivated in tap water (to less than 50%). Complete removal of the pollutant (i.e. plasma treatment time above 20 min) leads to higher water levels, but still slightly below the tap water control. An opposite behaviour is observed for the treated tap water, which induces an increase in the water content of plants.

4. Conclusions

Complete removal of 2,4-D in water was obtained after 20 min. plasma-ozonation treatment. High mineralization requires extended treatment time, to at least 60 min. The negative effect of 2,4-D on plant growth was significant. The main parameters affected by the presence of the contaminant were the root length and the water content, while small variations were also observed regarding the dry mass of the plants.

Complete removal of the contaminant leads to improvement in root length and water content as well as in dry mass. Little to no variation as compared to the tap water control was observed. This implies a lack of toxicity from the degradation by-products on the plants used in the experiment, making it suitable for irrigation. The treatment of tap water alone improves plant growth.

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5. References

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