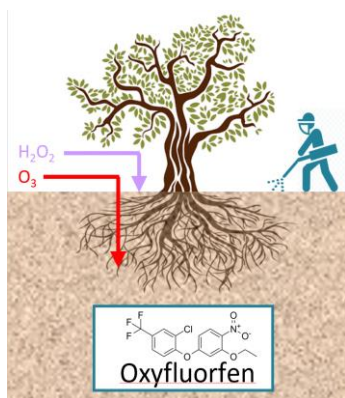


Removal of pesticides in olive soils using electrochemically generated oxidants

ORAL
Ph.D. Student: NO
Journal: JECE

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In this work, we present the main results obtained in the treatment of herbicides of olive orchards. To achieve this aim, we propose the use of hydrogen peroxide and ozone electrochemically produced as oxidants that we introduce in the soil to remove pesticides. Both oxidants are produced by electrochemical technology successfully and presented a good performance in the removal of oxyfluorfen from real spiked soils. For example, using a current density of 170 mA cm^{-2} , the ozone production achieved values of 0.26 mg min^{-1} , and reach a degradation of oxyfluorfen between 40 and 80 % along the 15 cm depth mock-up. In the case of hydrogen peroxide we achieved a production of 0.13 mg min^{-1} , reaching removal percentages between 5-12 % along the mock-up.

Introduction

One of the challenges that faced today's society is the pollution of agricultural soils due to the increase in the amount of food demand. Among them, olive (*Olea europaea* L.) is the most prominent and the most socioeconomically important fruit tree in Europe, especially in Mediterranean countries [1]. Pesticides represent the main pollution in olive soil and their direct application can produce pollution not only in soil, but in surface and groundwater. In olive orchards, the most extensively applied agrochemicals are insecticides, herbicides, and fungicides. The use of these compounds can affect to the sensorial and chemical properties of olives and olive oil.

Regarding herbicides, farmers use them with the objective of remove weeds due to the perception of the competence of them with olive trees for water and nutrients [2]. The main herbicides use in traditional and intensive olive orchard are triazines, phenylurea diuron and phenylether oxyfluorfen. These compounds remain in the top 5- 15 cm of the soil.

With the aim of remove these compounds, the in-situ chemical remediation of soil appears as a good alternative for the removal of organic. In this sense, the application of oxidants can favor the removal of pollution with the production of harmless by-products and a low environmental impact. Among them, hydrogen peroxide and ozone highlight due to the reduction products are oxygen and water. These oxidants can be produced electrochemically from the reduction or oxidation of oxygen dissolved in water. In this work, we propose the use of hydrogen peroxide and ozone produced electrochemically with the aim of remove oxyfluorfen from soil, as target compounds.

Material and Methods

Ozone production have been carried out by a CabECO® cell (supplied by Condias GmbH, Germany) equipped with 4 boron-doped diamonds lattice electrodes (BDDs, 24 cm^2) assembled in a Membrane Electrode Assembly (MEA) configuration using Nafion® proton exchange membrane. The electrolyte used was 1 mM of HClO_4 . Different current densities are evaluated for the production of ozone ($40\text{-}170 \text{ mA cm}^{-2}$). The ozone was introduced in a 3D printed cylinder mock-up design with the objective of dose ozone in a depth of 13 cm (Figure 1a).

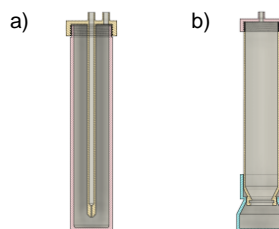


Figure 1. a) Ozone and b) Hydrogen peroxide dosage mock-up.

Hydrogen peroxide was produced in an electrochemical cell previously studied in our group [3]. The cathode (10.9 cm^2) used to produce H_2O_2 is a carbon paper (Freudenberg H23C2) and the anode was commercial DSA (Tianode). Two different electrolytes were use in the production of H_2O_2 (sodium nitrate and sodium bicarbonate). The H_2O_2 produced was introduced in a 3D printed cylinder mock-up design to dose it in the upper surface, in order to percolate the solution and being collected in a recipient situated in the lower part of the mock-up

(Figure 1b).

Results and Discussion

Figure 2 shows the production of ozone at steady state for different current densities. As can be seen, the higher the current density used, the higher the ozone production. For further experiments with spiked soil with oxyfluorfen we set the current density at 170 mA cm^{-2} .

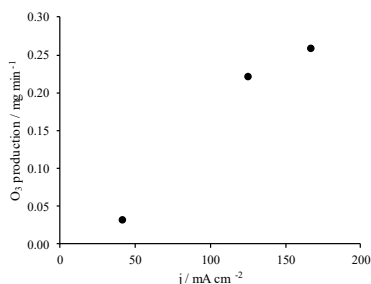


Figure 2. Ozone gaseous production (mg min^{-1}) with CabECO cell (1 mM of HClO_4).

The production of H_2O_2 can be seen in Figure 3. The influence of the electrolyte used was not relevant in the production of H_2O_2 , obtaining similar values with both compounds. Regarding the continuous flow used, it can be settling that the production increases considerably when the flow increases from 0.38 to 1.14 mL min^{-1} . For that reason, for the degradation experiments in the spiked soil with oxyfluorfen, we selected sodium bicarbonate as electrolyte due to its low toxicity; and a continuous flow of 1.14 mL min^{-1} because it produces a higher H_2O_2 production.

Table 1 shows the removal achieved with H_2O_2 and O_3 in a real soil spiked with oxyfluorfen ($1500 \mu\text{g/kg}$) at three different depths. When the gaseous O_3 electrochemically generated at a current density of 170 mA cm^{-2} was introduced, it rose to the surface

Conclusions

In this work, it is evaluated successfully the use of ozone and hydrogen peroxide produced electrochemically in the removal of oxyfluorfen contained in soil. Removals as high as than 80% have been achieved using ozone with a removal ratio of $85 \mu\text{g}_{\text{oxyfluorfen}} \text{ g}_{\text{ozone}}^{-1}$.

Acknowledgments

This project has received funding from the European Union's Horizon Europe research and innovation program under grant agreement No 101091255..

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through the polluted soil, degrading the organic compounds. On the other hand, the hydrogen peroxide was introduced by percolation through the surface to the bottom of the soil mock-up (15 cm).

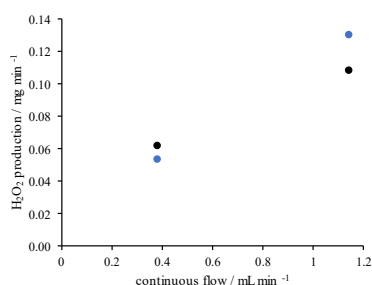


Figure 3. H_2O_2 production (mg min^{-1}) using 50 mM of sodium nitrate (black) and sodium bicarbonate (blue).

The removal of oxyfluorfen was higher using O_3 than with H_2O_2 . As seen, the higher degradation in both cases is in the zone of the dosage (the deeper zone in the case of O_3 ($10\text{-}15 \text{ cm}$) and the upper zone ($0\text{-}5 \text{ cm}$) with H_2O_2) being close to 15 and 80% for H_2O_2 and O_3 , respectively.

Table 1. Oxyfluorfen removal in spiked soil (oxyfluorfen: $1500 \mu\text{g/kg}$, O_3 dosis = 30 mg , H_2O_2 dosis = 3 mg).

Depth	Oxyfluorfen removal (%)	
	H_2O_2 treatment	O_3 treatment
A (0-5 cm)	13.34	36.93
B (5-10 cm)	4.39	59.51
C (10-15 cm)	8.88	80.29