Remediation Of Soils Polluted With Antibiotic Residues By Ozonation Technique

POSTER
Ph.D. Student: N
Journal: ESPR

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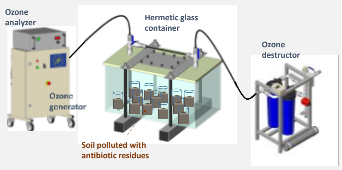

The degradation efficiency of three antibiotic residues (clarithromycim, erythromycim and sulfadiazine) in different soils (S1, S2 and S3) using ozone as treatment method has been investigated at laboratory scale. Degradation experiments were performed with an airtight glass container connected to an ozone generator running at maximum efficacy. An ozone destructor and a BMT964 analyzer were also used. Ozonation treatment led to the removal of the three antibiotic compounds after 6 days of continuous ozone exposure. For all compounds, degradation efficiencies followed the order S1 > S2 > S3, in coincidence with the lesser organic matter content of soils. Results suggest that ozonation treatment could be a useful tool for remediating soils polluted with pharmaceutical residues.

Introduction

Antibiotics, such as macrolide and sulfonamides classes, are available and commonly applied in human and veterinary medicine. Clarithromycim (CLA) and Erythromycim (ERY) are macrolide antibiotics widely used to fight against many serious infections induced by pneumococci, staphylococci and streptococci organisms, as well as to inhibit the growth of Legionella species. Sulfadiazine (SDZ) is a sulfonamide antibiotic with a wide spectrum against most gram-positive and many gram-negative organisms. These compounds have reportedly been detected in water bodies and effluents from wastewater treatment plants. In addition, the reuse of treated wastewater for agricultural irrigation has extended their presence to soils, where they may be accumulated, migrate to crops and be transferred to surface and groundwater courses, leading to dangerous situations for human health and the environment. Advanced Oxidation Processes (AOPs) have been proposed for the degradation of environmental pollutants in soils. Among them, ozonation has awaken a great interest. It is based on the use of ozone, a strong oxidizing agent able to eliminate a wide variety of recalcitrant organic pollutants. Ozone can react directly with organic pollutants or by hydroxyl radicals ($HO^{\bullet}$) formed during ozone decomposition. Additionally, it may degrade organic matter, which would favour pollutants desorption and increase their availability for elimination. This work was aimed at studing the effectiveness of ozonation technique under laboratory conditions on the removal of clarithromycim, erythromycim and sulfadiazine in three different soils.

Material and Methods

Analytical standards of CLA, ERY and SDZ were supplied by Dr. Ehrenstorfer GmbH (Augsburg, Germany). Sodium chloride and acetonitrile were purchased from Scharlab (Barcelona, Spain). The three soils selected for this study were taken from Campo de Cartagena and Águilas areas (Murcia, South-East of Spain). Their main physical-chemical properties are listed in Table 1. After their collection, soils were air-dried, 2-mm sieved and spiked with active ingredients of each compound to reach an individual level of 200 µg kg^{-1}. Soils were introduced in pyrex glass vessels (110 mm long, 80 mm diameter) and then, placed in a hermetically sealed glass container (volume 150 L) connected to an Osmaqua Ozone generator. Ozone concentration inside the glass container was estimated as 4.49 g (O_3) h^{-1} using a BMT 964 analyser. The system was completed with the installation of an ozone destructor at the outlet of the container to guarantee the experiment safeness. Ozonation assays were conducted during 6 days and three replicates of soil samples were taken at scheduled times (0, 0.2, 1, 2, 4, 5 and 6 days). A control experiment was also conducted using soil not exposed to ozonation. The procedure followed for the isolation of antibiotic residues in soil samples was performed as described by Fenoll et al. [1]. Samples were analysed by HPLC-MS^2.

Results and Discussion

Prior to degradation experiment, ozone concentration was optimized. The evolution of antibiotics residues during the experiment is shown in Figure 1. In general, the application of ozone resulted in an increment in antibiotics removal, improving degradation efficiency with the increase of exposure time. Remaining percentages found at the end of the treatment varied from 0.4 to 30.4 % for CLA, 0.2 to 21.6 % for ERY and 0 to 5.8 % for SDZ (in soils S1 and S3, respectively). In soils not exposed to ozone, remaining percentages ranged from 68.8 to 75.3 % for CLA (soils S1 and S3, respectively), 51 to 73.2 % for ERY (soils S2 and S3, respectively), and 7 to 50.2 % for SDZ (soils S1 and S3, respectively). The greater ozonation efficiencies were observed for soil S1, which could be attributed mainly to the differences in organic matter content (OM) of individual soils (0.27, 0.51 and

1.20% for soil S1, S2 and S3, respectively). OM is an essential factor in pollutant–soil interactions. It can decrease/enhance pollutants absorption, making them more or less available for dissipation [2]. In addition, OM lessen the quantity of ozone molecules available for reacting with pollutants, so this competing reaction could be expected to happen in a smaller degree for soil matrices with lower OM content [3].

Table 1. Physical-chemical properties of soils assayed.

Soil	Clay (%)	Silt (%)	Sand (%)	Organic matter (%)	pH (H_2O 1:1)	Electric conductivity (dS cm^{-1})
S1	17.8	15.6	66.6	0.27	7.96	0.92
S2	34.0	26.1	39.9	0.51	7.38	9.11
S3	10.3	27.4	62.3	1.20	8.1	4.8

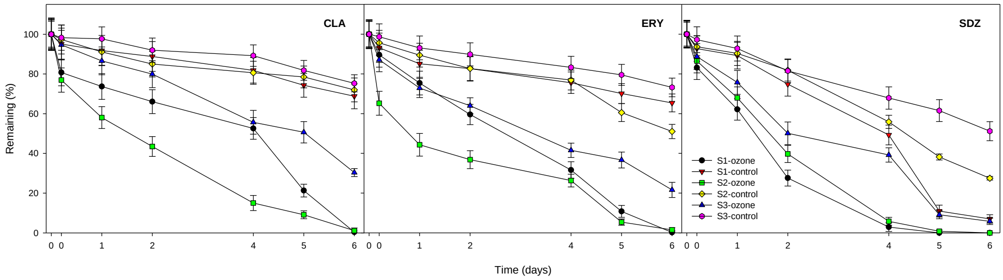

Figure 1. Evolution of clarithromycim (CLA), erythromycim (ERY) and sulfadiazine (SDZ) in the different soils during the experiment.

Conclusions

Results suggest that ozonation treatment could be proposed as a promising technology for removing environmental persistent pollutants from soils.

Acknowledgments

The authors acknowledge financial support received from the from the Ministerio de Ciencia e Innovación (TED2021-129766B-C22 AEI/10.13039/501100011033/ Unión Europea NextGenerationEU/PRTR). M. Aliste thanks the support of the program “Juan de la Cierva” (JDC2022-048225-I), financed by MCIN/AEI/10.13039/501100011033 and by European Union “NextGenerationEU”/PRTR. The authors are grateful to C. Colomer, H. Jiménez, J. Cava, I. Garrido, M.V. Molina and E. Molina for technical support.

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