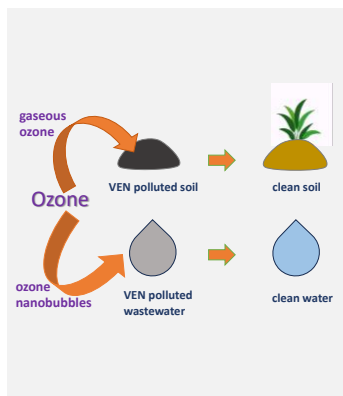


Degradation Of Venlafaxine In Wastewater And Soil Using Ozonation Processes

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This work is aimed to study the degradation of venlafaxine residues in wastewater and soils using ozonation as a remediation technique. For wastewater treatment, ozone was delivered as nanobubbles. For soil ozonation treatment, samples were introduced in a hermetic glass chamber and ozone was supplied in gaseous state. In both cases, ozone was previously generated from ambient air using an Osmoqua ozone generator running at maximum efficiency. Our results suggest that ozonation using both delivery methods could be proposed as an efficient technology for eliminating persistent pharmaceutical compounds in water and soils.

Introduction

In last years, emerging compounds (ECs) have frequently been found in the environment. Once released in the environment, they can be discharged into wastewater treatment plants (WWTPs) [1], which are not capable of completely mineralizing some ECs from sewage water. Venlafaxine (VEN), 1-[2-(dimethylamino)-1-(4-methoxyphenyl)-ethyl]cyclohexanol is an antidepressant drug for the therapy of the clinical depression and anxiety disorder [2]. VEN has been included in the 3rd and 4th EU Watch List to assess the Europe-wide distribution and hazard to the aquatic environment [3,4] due to detection in WWTP effluents. In addition, VEN can be accumulated in soil if these waters are used for irrigation crops. Under this perspective, advanced oxidation processes (AOPs) can be considered an effective solution for the elimination of many pharmaceutical compounds [4]. Another fact to be considered is the formation of transformation products (TPs) which may be generated in the environment. In this work, VEN was chosen as model compound for the ozonation study in wastewater and soil. Ozonation uses ozone as reagent for the elimination of organic contaminants. It can react in a selective way through molecular ozone, or in a non-selective mode through hydroxyl radicals formed during ozone decomposition. This technique has been widely examined in water treatments but its application to soils is not so advanced, probably because of ozone is normally delivered through water. In both cases is presented the same drawback, ozone fast decomposition in the aqueous phase (its lifespan is less than one hour) which limits the treatment efficiency. Other approaches, such as ozone delivery as nanobubbles or its application in gaseous state (for water and soil remediation, respectively) have been explored to increase ozone stability and overcome this limitation. In this work we have evaluated the efficiency of ozonation technique for the elimination of venlafaxine residues in wastewater and soils, using nanobubbles and gaseous

ozone, respectively, as delivery methods.

Material and Methods

VEN analytical standard (95%) was purchased by Toronto Research Chemicals Inc. (Toronto, Canada). For wastewater ozonation WWTP effluent (pH 7.7; conductivity 1.1 dS m⁻¹; dissolved organic carbon (DOC) 2.6 mg L⁻¹; total nitrogen 1.8 mg L⁻¹; Ca²⁺ 67 mg L⁻¹; Mg²⁺ 46 mg L⁻¹; Na⁺ 99 mg L⁻¹; K⁺ 6.0 mg L⁻¹; SO₄²⁻ 263 mg L⁻¹; Cl⁻ 150 mg L⁻¹; HCO₃⁻ 122 mg L⁻¹; NO₃⁻ 1.9 mg L⁻¹; NO₂⁻ < 0.01 mg L⁻¹; PO₄³⁻ < 0.2 mg L⁻¹) was taken from a modular AT-8 WWTP supplied by AugustSpain (Alicante, Spain). 50 L of water spiked at 1 µg L⁻¹ were maintained in continuous agitation and exposed to ozonation during 30 min. Experiment was conducted in triplicate and water samples were collected at scheduled times (0, 1, 2, 5, 10, 20 and 30 min). For soil ozonation, different soils were assayed: soil S1 texture (18% sand, 16% silt, 34% clay), pH 7.9, OM 0.27% (w/w), EC 0.92 dS m⁻¹; soil S2 texture (34% sand, 26% silt, 40% clay), pH 7.4, OM 0.51% (w/w), EC 9.11 dS m⁻¹; soil S3 texture (10% sand, 27% silt, 62% clay), pH 8.1, OM 1.20% (w/w), EC 4.8 dS m⁻¹. Soils were spiked at 200 µg kg⁻¹ of VEN active ingredient. Samples were weighed in pyrex glass vessels (110 mm long, 80 mm diameter), introduced in the container and exposed to gaseous ozone during 6 days and three replicates were collected at scheduled times (0, 4, 24, 48, 96, 120 and 144 hours). In both assays a control experiment (without ozone exposure) was also conducted. Wastewater and soil ozonation treatments were performed using a tank (50 L) and an airtight glass container (volume 150 L), respectively, connected to an Osmoqua Ozone generator. For wastewater ozonation, ozone was delivered as nanobubbles using a nanobubbles generator. Ozone concentration was about 2 mg L⁻¹ in the aqueous solution. Samples were analysed by HPLC-MS² using an analytical column Zorbax Eclipse XDB-C8.

Results and Discussion

Ozone optimal dosage was previously studied. Figure 1 depicts the evolution of VEN residues during the experiments. For wastewater treatment (Fig. 1A), VEN was completely degraded after 30 min of nano-ozone bubbles exposure. Ozone nanobubbles present rapid mass transfer rates and longer lifespan in water, which improves the dissolved ozone concentration and hence, increases removal efficiency [6]. For soil ozonation (Fig. 1B), the residual levels found at the end of the treatment were 10.4,

2.26 and 58.1 $\mu\text{g kg}^{-1}$ for soils S1, S2 and S3, respectively. Thus, the lower degradation was found for soil S3, in coincidence with its higher OM content. Besides increasing the sorption of pollutants, OM can act as OH[•] scavenger, competing with pollutants in radical reactions and resulting in decreased degradation [7]. In both, wastewater and soil, treatments conducted without ozone exposure, degradation was found to be negligible. Finally, the occurrence of transformation products of VEN was also studied by HPLC-MS².

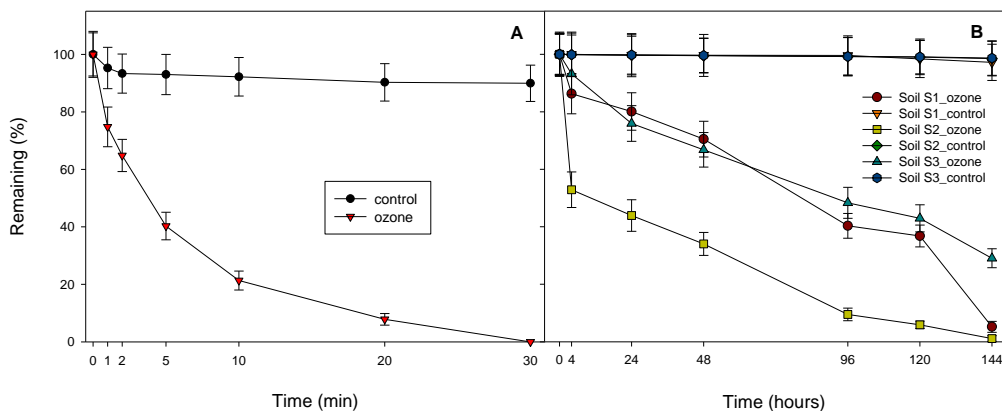


Figure 1. Evolution of venlafaxine residues during ozonation experiments (A: wastewater treatment with ozone nanobubbles; B: ozonation treatment in different soils). Error bars denote standar deviation.

Conclusions

Results indicate that both delivery methods are suitable for venlafaxine removal in WWTP effluents and soils, and could be proposed as a remediation approach for water and soils polluted with other pharmaceutical compounds.

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References

- [1] F. Costa, A. Lago, V. Rocha, O. Barros, L. Costa, Z. Vipotnik, B. Silva, T. Tavares, *Environ. Sci. Technol.* 53 (2019) 7185.
- [2] M. Tzanakaki, M. Guazzelli, I. Nimatoudis, N.P. Zisis, *Int. Clin. Psychopharmacol.* 15 (2000) 29.
- [3] European Commission Decision (EU) 2020/1161. *Off J Eur Union L* 257 (2020) 32.
- [4] European Commission Decision (EU) 2022/1307 *Off J Eur Union* 65(2022) 117.
- [5] A.Y.C. Tong, R. Braund, D.S. Warren, B.M. Peake, *Cent. Eur. J. Chem.* 10 (2012) 989.
- [6] L. Hu, Z. Xia, *J. Hazard. Mater.* 342 (2018) 446.
- [7] C.M. Martínez, I. Garrido, P. Flores, P. Hellín, F. Contreras, J. Fenoll, *Chem. Eng. J.* 446 (2022) 137182.