Ultrasound-assisted ozonation for the degradation of venlafaxine in hospital wastewater

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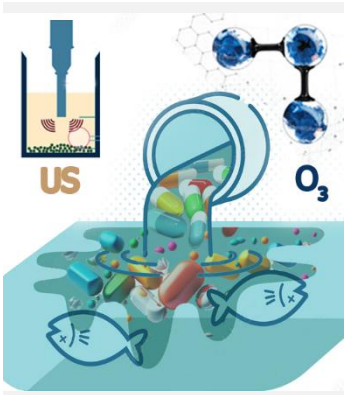

This study proposed ultrasound-assisted ozonation to degrade venlafaxine in real wastewater samples. Venlafaxine is a widely used antidepressant compound commonly found in wastewaters ranging from ng L^{-1} to µg L^{-1}. It was selected to demonstrate the potential of the proposed setup. The coupling of ultrasound (US) radiation with ozonation enhances the mass transfer of ozone from the gas phase to the liquid phase. The physical effects of a cavitation bubble implosion, such as shock waves and micro-jets, induce the fragmentation of ozone bubbles, increasing the contact area of bubbles with the liquid phase. The application of ultrasound during ozonation enhanced the venlafaxine degradation to 90% with ultrasound-assisted ozonation after 60 min. Using O_3 combined with ultrasound increases the efficiency of venlafaxine degradation, reducing the time required for it to remain under ozone bubbling.

Introduction

Environmental contamination by residual pharmaceuticals is a global concern, with an increasing number of studies in recent years due to its occurrence, persistence, and harmful potential for human health and ecosystems [1]. Among the various categories of compounds, psychiatric medications are of environmental significance due to their potent pharmacological activity [2]. These drugs can affect the central nervous system and directly disrupt neuroendocrine signaling. [3]. Changes in reproduction patterns in aquatic species were one of the possible adverse effects reported [4]. The use of psychodrugs, especially antidepressants, has increased considerably due to improvements in diagnoses of psychiatric disorders, the appearance of new medications on the pharmaceutical market, and new therapeutic restrictions on existing psychotropic drugs [5]. Brazil has the highest percentage of the population affected by anxiety-related disorders in the world. In addition, it is the fifth country with the highest rate of depressed people, according to data released in 2017 by the World Health Organization (WHO). As a consequence of the high use, bearing in mind that these drugs are excreted and effluent treatment systems, for the most part, are not effective in removing these compounds, several studies have reported the occurrence of these compounds in different environmental compartments in other parts of the world [6]. Venlafaxine is a member of this class of medications. This psychotropic medication has been detected in various matrices, including hospital effluents, sewage treatment plant effluents, surface water, and potable water sources across different countries, such as the USA, Sweden, Spain, Poland, and Greece, in concentrations from 0.2 ng L^{-1} to up to 1,914 µg $L^{-1.}$ Furthermore, studies report that it is not easily removed in sewage treatment processes, reaching only 50% removal by conventional sewage treatment [7]. There is scarce information about venlafaxine degradation in wastewater. Therefore, the present work aimed to demonstrate the utilization of ultrasound-assisted ozonation for the degradation of venlafaxine in hospital effluent.

Material and Methods

For degradation experiments, real wastewater was collected from the University Hospital of Santa Maria (HUSM), which is located in Santa Maria, Rio Grande do Sul state, Brazil (latitude 29°43′02’S and longitude 53°43′4.2″W). After biological treatment, the effluent is discharged into a watercourse. A total of 20 L of wastewater was collected in polyethylene vessels and stored in the dark at -20°C. Before the experiments, wastewater samples were thawed at room temperature. With a Ti-alloy probe (Q630-0217, Sonics, USA) with a 13 mm diameter and 254 mm long. Degradation experiments in silent condition (i.e., in the absence of US waves) were carried out with a stand homogenizer (PT 3100 D, Kinematica, Switzerland) coupled with a stainless-steel homogenizer tip (PT-DA 12 / 2EC-F154, Kinematica, Switzerland) operating at 3000 rpm. Ozone was produced using a commercial ozone generator (Ozonebras, Brazil) fed with dried air at a flow rate ranging from 1 L min^{-1} to 5 L min^{-1}. Ozone generation was determined using the titrimetric iodometric method described by SMWW (2350 E) [8]. Residual ozone from reactor off-gas was collected in a glass washing bottle with 20 g L^{-1} of KI. Liquid chromatography equipment coupled with a mass spectrometer (LCMS-2020, Shimadzu, Japan) was used. The system consisted of an autosampler, degasser, binary pump, column oven, electrospray ionization source (ESI), and a single quadrupole mass spectrometer. Chromatographic separations were carried out in a C18 column (Shim-pack CLC-

OSD, 5 µm, 150 × 4.6 mm, Shimadzu, Japan) kept at 35° C. The mobile phase consisted of (A) 5 mmol L^{-1} ammonium formate and (B) acetonitrile, both acidified with formic acid (0.1 % w/w). The chromatographic gradient program was carried out for 15 min: 0 min 10% B, 6 min 75%, 7 min 75%, 10 min 10%, 15 min 10%. The mobile phase flow rate was set to 0.4 mL min^{-1}, and the injection volume was 10 µL.

Results and Discussion

Experiments were carried out with ultrasound alone (US), ozone alone (O_3), and a combined process of ultrasound and ozone (O_3 + US). The degradation of venlafaxine was evaluated for each process, and the results are shown in Figure 1.

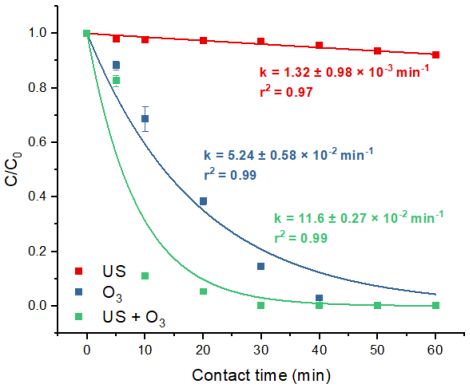

Figure 1. Degradation of venlafaxine in different reaction systems. Symbols represent experimental data, and a continuous line represents the pseudo-zero-order or pseudo-first-order reaction kinetic model for venlafaxine degradation. Experimental conditions: C_0 = 5000 µg L^{-1}, initial pH = 7.0, C_{ozone} = 63 ± 6 mg O_3 L^{-1}, Pw = 61 W L^{-1}, T = 25 ± 0.3°C.

Several factors influence the degradation of venlafaxine in a complex matrix such as real wastewater. Besides venlafaxine initial concentration, the presence of scavengers (NO^{3-}, PO_4^{3-}, HCO_3^-, CO_3^{2-}, humic substances, and other compounds) and changes on the mass transfer can affect the efficiency of ozone attack. Additionally, alterations in the stoichiometry of the equation resulting from variations in venlafaxine concentration can also influence the reaction order, resulting in pseudo-first-order reaction kinetics at lower concentrations. Comparing the values of pseudo-zero order kinetic constants for the experiments with an initial venlafaxine concentration of 5000 and 2500 µg L^{-1}, no significant difference was observed ($p < 0.05$). No significant difference was observed when comparing the pseudo-zero order kinetic constants for the experiments with an initial venlafaxine concentration of 5000 and 2500 µg L^{-1} ($p < 0.05$). Ozone is a powerful oxidant widely applied to organic pollutant degradation in water and wastewater. However, the main drawback of ozone application in wastewater treatment is the mass transfer of ozone from the gas phase to the liquid phase. The shear force and micro-jets formed in bubble cavitation implosion can increase the mass transfer of ozone to the aqueous phase. Furthermore, ozone can undergo pyrolysis reactions in the inner parts of cavitation bubbles, contributing to •OH formation. Comparing the values of the pseudo-zero order kinetic constant for venlafaxine degradation, it is possible to observe an increase from k = 5.24 ± 0.58 10^{-2} mol min^{-1} for O_3 process to k = 11.6 ± 0.27 10^{-2} mol min^{-1} for O_3+US process, representing a two-fold increase in the constant. Regarding the percentage of venlafaxin degradation, the removal increased up to 90% for the O_3+US process after 60 min of contact time. Therefore, O_3+US was chosen as the optimal degradation system for optimizing venlafaxin degradation.

Conclusion

Using O_3 combined with ultrasound increases the efficiency of venlafaxine degradation, reducing the time required for it to remain under ozone bubbling.

Acknowledgments

CNPq, Capes and Fapergs

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