Optimization of the combined sono-photo-Fenton process for the degradation of the Antiepileptic Drug Primidone

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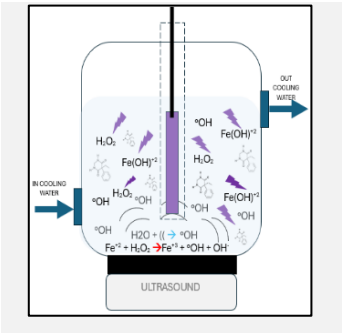

This study reports the degradation of primidone (PRI), an emerging contaminant, by combined sono-photo-Fenton process. Initially, in the combined process, operating parameters such as Fe^{2+} concentration (5 mg L^{-1}) and UVA lamp position inside the reactor (5 cm) were optimized at an ultrasonic power and frequency of 20 W and 578 kHz, respectively. Subsequently, PRI degradation in the combined and individual processes was evaluated, finding that the combined processes (sono-photo-Fenton and sono-Fenton) were faster than the sonolysis process, revealing the following sequence: sonolysis (k_{deg}: 0.013 min^{-1}) < sono-Fenton (k_{deg}: 0.024 min^{-1}) < sono-photo-Fenton (k_{deg}: 0.035 min^{-1}). No photolysis (UVA) or synergistic effect was not observed; however, the addition of Fe and UVA light to the sonochemical process improved PRI degradation from 62% to 93% during 75 min of treatment.

Introduction

Recent concerns about pharmaceutical residues in water bodies, such as Primidone (PRI, an anti-epileptic drug), pose environmental and health risks due to their persistence in water. For example, fish contaminated with antiepileptics have been detected in West Africa (Pra, Narkwa and Volta rivers), posing a direct risk to consumers [1]. In Peru, PRI has been detected in the municipal wastewater (effluents) from Lima and Puno [2]. Their presence in aquatic ecosystems is due to the fact that conventional wastewater treatment plants do not degrade or eliminate them completely. Research suggests that tertiary treatment processes should be incorporated to improve the degradation rates of these pharmaceuticals, so research into effective treatment methods should be encouraged. Advanced Oxidation Processses (AOP) have proven to be effective in eliminating pharmacetutical residues in water, with the high-frequency ultrasound process (US) being a promising and clean technology, as no chemical compounds are added during treatment. The basis of this process is the generation of hydroxyl radicals (•OH) by acoustic cavitation through the interaction of ultrasound waves in aqueous media. In addition, hydrogen peroxide is formed as a by-product of the radical combination. To enhance the process, iron ions and UVA light can be added to the US process to generate an *in situ* (photo-)Fenton reaction producing a hybrid sono-(photo)-Fenton process (US/Fe/UVA or US/Fe) and thus, enhance the degradation efficiency by producing additional OH radicals through (photo)-Fenton reaction. Therefore, understanding the sono-(photo)-Fenton process to find the best optimization of the process could lead to sustainable water treatment solutions for pharmaceutical waste [3].

This study aims to eliminate the antiepileptic drug PRI by combining high-frequency ultrasound with the photo-Fenton process. First, the parameters Fe^{2+} concentration (mg L^{-1}) and UVA lamp position within the reactor (cm) were analyzed on PRI degradation. Subsequently, the effectiveness of the individual processes (sonolysis) and of the combined AOP process (sono-Fenton and sono-photo-Fenton) was evaluated.

Material and Methods

Reagents

Primidone (95% purity, Biosynth Carbosynth); iron(II) sulfate heptahydrate (Sigma-Aldrich); catalase (200-5000 units/mg, Sigma-Aldrich); Acetonitrile (ACN, HPLC grade, Supelco).

Analytical methods

The quantification of primidone was measured using the Agilent 1000 HPLC system with a DAD detector at 210 nm. The mobile phase was ACN:H_2O (22:78), with a flow rate of 0.8 mL/min and a run time of 15 min. Prior to chromatographic analyses, catalase (100 µL) was added to the samples to scavenge residual hydrogen peroxide.

The ultrasonic power was calculated by calorimetry method and the ultrasonic frequency was set at 578 kHz according to previous studies [4]. Iodometric and 1,10-phenanthroline methods were employed to determine the concentrations of hydrogen peroxide and soluble iron, respectively [4].

Experimental Setup:

PRI degradation was carried out in a glass batch reactor (Meinhardt Ultrsonics) at 578 kHz and 66.7 W L^{-1} of ultrasonic frequency and power density, respectively, containing 300 mL of 2.5 mg L^{-1} of PRI dissolved in distilled water at pH 7.0 ± 0.5. A water cooling system was used to control the reactor temperature (18 ± 2 °C). Additionally, the reactor was covered with aluminum foil during exposure to a UVA lamp (maximum emission at 365 nm, 4W). All experiments were conducted at least in triplicate with good reproducibility.

Results and Discussion

Effect of UVA lamp position on PRI degradation

Figure 1a illustrates how the PRI degradation rate constant (k_{deg}, min^{-1}) varies with the UVA lamp position in the sono-photo-Fenton process. The evaluated UVA lamp positions (lengths) in the solution

were 3, 5, and 6 cm. The results indicated that the highest degradation occured at the 5 cm lamp position compared to other positions (k_{deg}: 0.035 min^{-1}), which showed the lowest hydrogen peroxide accumulation rate (r_{H2O2}: 0.86 µmol L^{-1} min^{-1}, Fig. 1b). This can be explained by the fact that in this position of the lamp physical interferences are reduced by promoting a uniform distribution of oxidants (•OH) in the aqueous solution [5], thus favoring the interaction of sonogenerated •OH radicals and improving the PRI degradation.

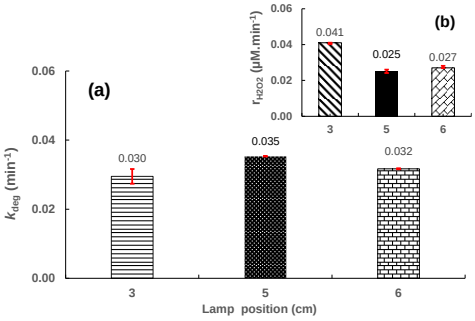

Figure 1. Effect of UVA lamp position (a) and H_2O_2 accumulation rate (b) on Primidone degradation (k_{deg}) by sono-photo-Fenton process at 578 kHz, 20 W and 5 mg L^{-1} Fe^{2+}. [PRI]: 2.5 ppm, V: 300 mL, pH: 7.0 ± 0.5 , T: 18 ± 2 °C.

Effect of Fe dosage on PRI degradation

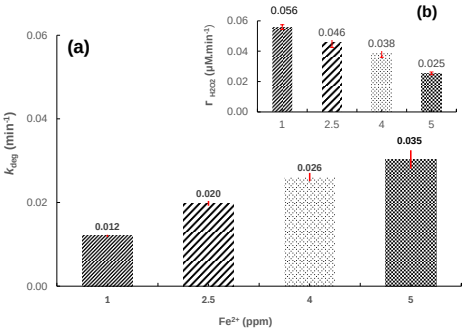

Figure 2. Effect of initial iron concentration (a) and H_2O_2 accumulation rate (b) on PRI degradation (k_{deg}) by sono-photo-Fenton process at 578 kHz, 20W and 5 cm (UVA lamp position). [PRI]: 2.5 ppm, V: 300 mL, pH: 7.0 ± 0.5 , T: 18 ± 2 °C.

Different iron concentrations (1, 2.5, 4 and 5 $mg.L^{-1}$) were evaluated based on the degradation of PRI by the sono-photo-Fenton process (Fig. 2a). The results showed that when the Fe dosage increased, the PRI degradation also increased, while the H_2O_2 accumulation rate (r_{H2O2}) decreased (Fig. 2b). This improvement may be due to the *in situ* (photo-)Fenton reaction occurring in the bulk solution, which contributes to a higher presence of hydroxyl radicals when the Fe dose is increased, resulting in better degradation of primidone.

Evaluation of individual and combined processes

After 75 min of treatment, sono-Fenton and sono-photo-Fenton processes elimined 83% (k_{deg}: 0.024 min^{-1}) and 93% (k_{deg}: 0.035 min^{-1}) of primidone, respectively, compared to sonolytic process (62%, k_{deg}: 0.013 min^{-1}) as can be seen in Fig 3a. This enhancement is atributed to the generation of additional •OH radicals formed by *in situ* (photo-)Fenton reactions, which is suported by the low H_2O_2 accumulation rate obtained in the sono-Fenton (r_{H2O2}: 0.037µMmin^{-1}) and sono-photo-Fenton (r_{H2O2}: 0.025µM min^{-1}) processes (data not shown). No sinergistic effect was observed (S<1), calculated through the % degradation efficiency of the combined process versus individual processes. Pseudo-first order kinetics with good data accuracy were observed in all US-based AOP processes (Fig. 3b).

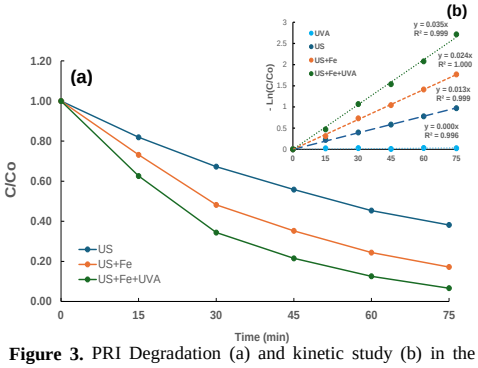

Figure 3. PRI Degradation (a) and kinetic study (b) in the photolysis (UVA), sonolysis (US), sono-Fenton (US/Fe) and sono-photo-Fenton (US/Fe/UVA) processes. [PRI]: 2.5 mg L^{-1}, f: 578 kHz, P: 20W, [Fe]: 5 mg L^{-1}; UVA Lamp position: 5 cm, V: 300 mL, pH: 7.0 ± 0.5, T: 18 ± 2 °C.

Conclusions

The combined sono-(photo-)Fenton process showed an improvement in the elimination of antiepileptic primidone compared to the individual process.

Acknowledgments:

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References

[1] A. Ebo Duncan, C. Adokoh, M. Osei. *J Salud del Agua* 21, (2023), 1703.
[2] J.I. Nieto-Juárez, R. Torres-Palma, A.M. Botero-Coy, F. Hernandez. *Environ. Int.*, 155, (2021), 160.
[3] L.J. Xu, W. Chu, N. Graham. *Chem. Eng. J.*, 255, (2014), 541.
[4] K. Celis – Llamoca (2022). Thesis Faculty of Chemical and Textilr Engineering, Universidad Nacional de Ingeniería.
[5] J. Mierzwa, R. Rodrigues, A. Teixeira, UV-Hydrogen Peroxide Processes,Sao Paulo, Elsevier, (2018), p. 13