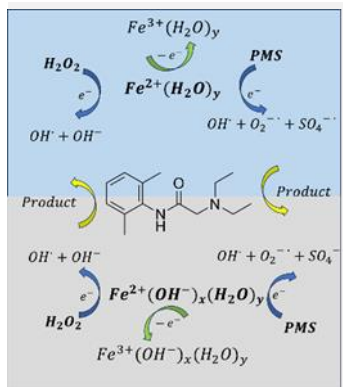


The effect of basic pH on Lidocaine degradation with PMS and H₂O₂ in the presence of iron ions.

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This study aims to evaluate the effect of conducting the Fenton reaction at basic pH using Lidocaine as the target molecule, a compound employed in the pharmaceutical industry as a local anesthetic. By comparing the Fe(II) species present in the system when reacting with two types of inorganic peroxides (hydrogen peroxide-H₂O₂ and peroxymonosulfate-PMS). It was experimentally found that the Fe(II) species remaining in solution undergo degradation of the target compound but with a reaction kinetics lower than that obtained in the presence of Fe(II)-hydroxy complexes when exposed to the different types of peroxide. The removal of the drug is greater in the Fe(II) system with the presence of hydroxy-complex precipitates, when it is treated with hydrogen peroxide.

Introduction

Among the advanced oxidation methods for treating pharmaceuticals in water, the Fenton reaction stands out as a methodology that has demonstrated high efficiency in removing refractory compounds. However, one of the limitations of the Fenton reaction is pH effects; due to its better working pH is typically acidic (traditionally performed at pH ~3). This is due to the convenient Fe(II) species are present in the solution, making it available for the reaction. Likewise, modifications to the Fenton reaction, known as Fenton-like reactions, have been reported [1],[2]. These systems involve adding compounds that allow for the chelation of metal ions and modifying the reaction conditions to enable pollutant degradations at pH levels above 3. This opens the possibility of conducting the Fenton reaction at basic pH and evaluating the contribution of Fe(II) that remains in solution due to the complexation with pharmaceuticals and the participation of hydroxy-complexes [1],[2]. On the other hand, sulfate radicals (SO₄•⁻, which has an oxidizing potential ranging from 2.50 to 3.10 V vs SHE), can be formed in Fenton-like processes and enhance the degradation of pollutants.

In this work, the Fenton reaction at basic pH, Lidocaine hydrochloride (Lido) with H₂O₂ and peroxymonosulfate (PMS) [3],[4] was evaluated, analyzing the role of the peroxide bond in the oxidation process for this organic molecule (which is widely as anesthesia [5]).

Material and Methods

The quantification of Lido was performed using high-performance liquid chromatography with a diode array detector (HPLC-DAD). A Phenomenex Luna® C18 column with dimensions of 300x3.9 mm was employed, maintained at a temperature of 35 °C, and with a flow rate of 1.2 mL/min. The mobile phase consisted of sodium acetate buffer at pH 3.6 with a ratio of acetonitrile (ACN) 74:26. Injection volume was 5 µL. The water used in the buffer preparation was Type I, Milli-Q water obtained from Thermo Scientific purification equipment. For analysis of peroxides effects, 2 mL of a 500 mM mother solution of PMS was used in the Lido-Fe(II)-PMS systems, resulting in a reaction concentration of 11.11 mM. Similarly, for the Lido-Fe(II)-H₂O₂ systems, a 500 mM mother solution was prepared, and 2 mL was added to the reaction system. Samples were taken at 0, 3, 5, 10, 20, 30, 45, 60, and 90 minutes, taking a 700 µL aliquot and transferring it to a 2 mL vial containing 300 µL of an 80 mM metabisulfite solution to stop the reaction.

Results and Discussion

Table 1 presents the results for Lido degradation under the different considered systems. When comparing the results, it is observed that the degradation of Lidocaine due to the presence of PMS is not significant, similar to the case when only Fe(II) is present, remaining comparable to the blank sample. In the presence of H₂O₂, after 90 minutes of

degradation, it fails to degrade more than 20%. When comparing the systems with only Fe(II) in solution, upon reaction with peroxides, it is observed that the system with PMS and H₂O₂ are very similar, with both systems degrading approximately 35%. The greatest difference observed when comparing them is the presence of iron hydroxy complexes formed in solution at pH 10. In the Lido-Fe(II)(OH)_x(H₂O)_y-PMS system, a synergistic effect is evident, degrading 59% of Lidocaine, while the system with Lido-Fe(II)(OH)_x(H₂O)_y-H₂O₂ achieves complete degradation of Lidocaine after 3 minutes, showing a synergistic effect. It was observed a differentiated degradation depending on the peroxide type, and it is more favored in the case of H₂O₂.

Systems evaluating only the presence of peroxide degraded a very low portion of the compound. When Fe(II) is present in the system with the peroxide, a higher percentage of degradation is observed because the presence of Fe(II) promotes the formation of hydroxyl radicals

encuentra el origen de la referencia.[1],[3],[4]. Additionally, the precipitation has some contribution to the target pollutant removal.

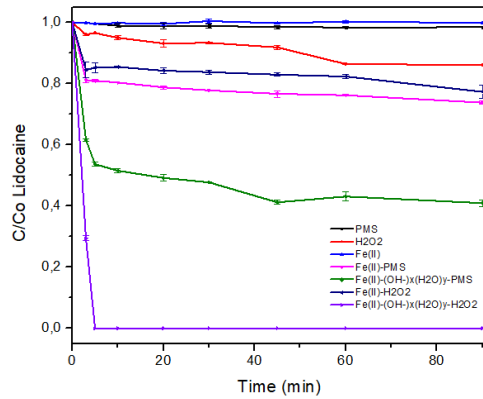


Figure 1. Percentage of Lidocaine recovery as a function of treatment time.

Table 1. Results of Lidocaine degradation at pH 10 after 90 minutes of treatment.^a

Lidocaine HCl	% Lido	%Removal	v (μM ⁻¹ .s ⁻¹)	k (s ⁻¹)	Synergy*	Synergy**
-	100,00	0,0	-	-	-	-
PMS	98,47	1,53	0,2	0,0002	-	-
H ₂ O ₂	86,12	13,88	2,2	0,0015	-	-
Fe(II)	99,86	0,14	0,1	0,0	-	-
Fe(II)-PMS	73,81	26,19	10,5	0,0019	16,8	15,7
Fe(II)-H ₂ O ₂	77,37	22,63	8,6	0,0016	12,5	13,6
Fe(II)-(OH) _x (H ₂ O) _y -PMS	40,93	59,07	15,9	0,0064	31,0	35,4
Fe(II)-(OH) _x (H ₂ O) _y -H ₂ O ₂	0,0	100,0	39,2	0,0043	16,3	7,1

^a Synergy calculated at 30 minutes of treatment. **Synergy calculated at 90 minutes of treatment

Conclusions

When evaluating the effect of basic pH on Fenton-based systems for the degradation of the target compound (Lidocaine), it was observed that the presence of the hydroxy complexes formed by Fe(II) at pH 10 enhances its degradation, unlike when only Fe(II) coordinated remains in solution. The best system for Lidocaine degradation at pH 10 is the Lido-Fe(II)(OH)_x(H₂O)_y-H₂O₂ system, achieving complete degradation of the drug after 3 minutes of treatment, acting as a synergistic system; which can be associated.

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References

- [1] C. Bao, H. Wang, *Journal of Hazardous Materials*, 441 (2023) 129922
- [2] Q. Wu, H. Yang, *Applied Catalysis B: Environmental*, 263 (2020) 118282.
- [3] I. Ijaz, A. Bukhari, Z. Author, *Journal of Environmental Chemical Engineering*, 12 (2024) 112838.
- [4] H. Ibargüen-López, B. López-Balanta, L. Betancourt-Buitrago, *Journal of Environmental Chemical Engineering*, 9 (2021) 106233
- [5] R. Karnina, *Annals of Medicine and Surgery*, 69 (2021) 102733.