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Advanced oxidative processes in caffeine degradation: CWPO and photocatalysis

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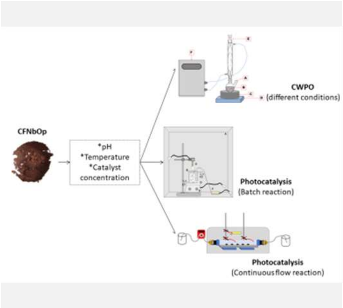

This study aims to investigate efficient methods for caffeine degradation through photocatalysis and CWPO (catalytic wet peroxide oxidation), which are promising for this purpose. The research highlights the potential of magnetic nanocatalysts from orange waste, indicating convincing results in caffeine degradation. Suggesting a more sustainable and effective initiative for the treatment of contaminated water, helping to reduce the effects of caffeine pollution.

Introduction

Caffeine is becoming one more emerging pollutant because the high ingestion daily of this compound (by drinks, foods, drugs, among others). Of course, coffee is not the only product that is caffeine-containing, but only this consume is around 2.25 billion cups of coffee are consumed in the world daily [1]. The high consumption of this substance has been gaining ground in the problem of emerging contaminants, as it is being detected in rivers and drinking water. In Brazil, the average concentration is between 0.08 and 6.5 $\mu g.L^{-1}$ in rivers [2], and around 0.22 $\mu g.L^{-1}$ in drinking water [3].
Like other emerging pollutants, it involves research to know different ways to degrade it [4]. One way is using advanced oxidation processes (AOPs), which produces free radicals which have a high oxidizing capacity, promoting the degradation of various pollutants efficiently [5].
Photocatalysis and CWPO (catalytic wet peroxide oxidation) reactions are examples of the AOPs. CWPO is a process by which organic pollutants in water bodies can be degraded. The decomposition of hydrogen peroxide over an appropriate catalyst generates hydroxyl (·OH) and hydroperoxyl (HO_2·), radicals that enable degradation[6]. While in photocatalysis, hydroxyl radicals (·OH), those responsible for degrading polluting substances, are formed on the catalyst surfaces by activating light [7].
This work aims to compare the efficiency of caffeine degradation by different advanced oxidative processes, such as CWPO and photocatalysis, using the same catalyst.

Material and Methods

In this research, magnetic nanocatalysts synthesized with orange peel, cobalt ferrite and niobium pentoxide (CFNbOp)[7] were applied to the degradation of Caffeine (~20 ppm concentration), Figure 1 by CWPO (Catalytic Wet Peroxide Oxidation) under several conditions of pH (1.95 to 10.00), catalyst concentration (302 to 1698 $mg.L^{-1}$), and temperature (299 to 367 K), Table 1.

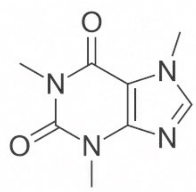

Figure 1. Caffeine molecule. Souce: NCBI (2024)[8]

The best pH and catalyst concentration conditions were repeated in caffeine degradation under photocatalysis, both batch and continuous flow reactions.
Finally, all obtained results were compared to establish the best way to degrade caffeine using the catalyst proposed.

Results and Discussion

Previous studies have already shown that caffeine can be degraded under different pH conditions by Fenton, photo-Fenton, UV/H_2O_2 and UV/Fe^{3+} processes. The degradation percentage varied between 1% to 98% [4].
Caffeine already degraded using other catalyst materials upon functionalization with TEOS and EDTA by pseudo-first power-law rate equations [6].
However, the catalyst CFNbOp had not yet been tested with this pollutant. Actually tests that reveal interesting results, with more than 70% of degradation. This catalyst is more sustainable than previously used with TEOS and EDTA. Making the result even more advantageous.

Table 1. Desing of experiments proposed in CWPO reaction to degradation of caffeine.[a]

Run	Ph	Temperature (K)	Catalyst Concentration (mg.L-1)	Degradation (%)
A	7.00	333	302	3%
B	1.95	333	1000	71%
C	4.00	353	1415	61%
D	10.00	353	1415	3%
E	4.00	353	585	68%
F	12.05	333	1000	29%
G	4.00	313	1415	14%
H	4.00	313	585	8%
I	10.00	353	585	13%
J	10.00	313	585	7%
K	10.00	313	1415	8%
L	7.00	367	1000	2%
M	7.00	299	1000	4%
N	7.00	333	1698	10%
O	7.00	333	1000	4%
P	7.00	333	1000	4%

[a] Source: authors (2024)

Conclusion

We can conclude with this work that the degradation of emerging pollutants needs to be studied before the problems increase by the discards of it. Advanced oxidation processes are suitable for this type of degradation study by CWPO and photocatalysis. Future work is intended to combine these processes to evaluate the performance of the combined degradation.

Acknowledgments

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References

1. Driveresearch. *2024 Coffee Consumer Report - Consumption Habits , Preferences , & Spending*. (2024).
2. de Sousa, D. N. R., Mozeto, A. A., Carneiro, R. L. & Fadini, P. S. Electrical conductivity and emerging contaminant as markers of surface freshwater contamination by wastewater. *Sci. Total Environ.* 484, 19–26 (2014).
3. Mokh, S., El Khatib, M., Koubar, M., Daher, Z. & Al Iskandarani, M. Innovative SPE-LC-MS/MS technique for the assessment of 63 pharmaceuticals and the detection of antibiotic-resistant-bacteria: A case study natural water sources in Lebanon. *Sci. Total Environ.* 609, 830–841 (2017).
4. de Almeida, L. N. B. *et al.* Process Comparison for Caffeine Degradation: Fenton, Photo-Fenton, UV/H2O2 and UV/Fe3+. *Water, Air, Soil Pollut.* 232, 147 (2021).
5. Preethi *et al.* Recent progress in mineralization of emerging contaminants by advanced oxidation process: A review. *Environ. Pollut.* 341, 122842 (2024).
6. Diaz de Tuesta, J. L. *et al.* Kinetic insights on wet peroxide oxidation of caffeine using EDTA-functionalized low-cost catalysts prepared from compost generated in municipal solid waste treatment facilities. *Environ. Technol. Innov.* 24, 101984 (2021).
7. Oliveira, J. R. P. *et al.* Green Magnetic Nanoparticles CoFe2O4@Nb5O2 Applied in Paracetamol Removal. *Magnetochemistry* 9, 200 (2023).
8. National Center for Biotechnology Information. Compound Summary for CID 2519, Caffeine. https://pubchem.ncbi.nlm.nih.gov/compound/Caffeine.