Synthesis of Iron-Based Nanomaterials for Pharmaceutical Degradation in Water

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Introduction

The increase in human activity has had a significant impact on the environment. Among the most commonly found contaminants of emerging concern (CECs) in surface and groundwater are pharmaceutical compounds.[1] Conventional water treatment methods are not effective in removing these contaminants, highlighting the need to develop new technologies for their remediation.[2]

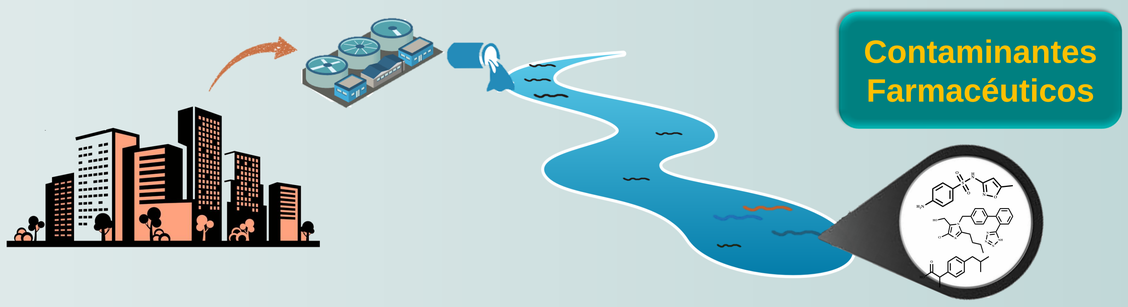


Figure 1. Issue: Water Pollution by Pharmaceutical Products

Various studies have utilized ferrites, iron-based nanomaterials, as catalysts for the degradation of different contaminants.[2,3] In this work, the synthesis of three ferrites is proposed: $CoFe_2O_4$, $MnFe_2O_4$, and $CuFe_2O_4$, for their use as photocatalysts in the degradation of pharmaceutical contaminants through the Heterogeneous Photo-Fenton process.[4]

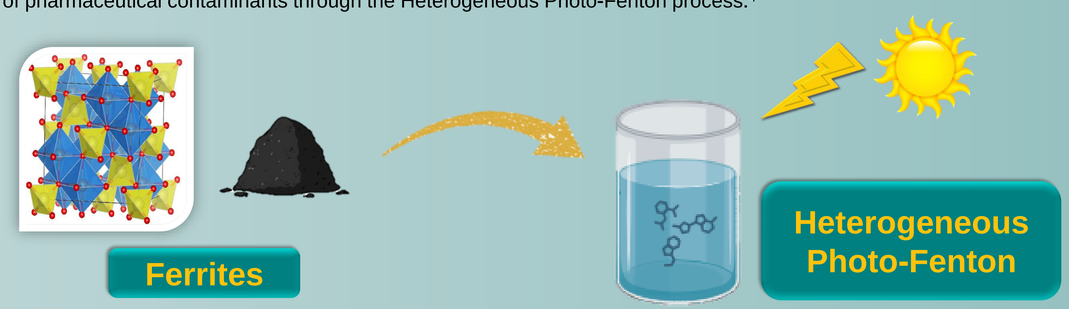


Figure 2. Proposal: Degradation of Pharmaceutical Contaminants via the Heterogeneous Photo-Fenton Process Using Ferrites as Catalysts.

Methodology

The synthesis of ferrites was carried out based on a modification of the method proposed by Cruz and collaborators, using metal chlorides as inorganic precursors and water with natural organic matter (NOM).[5] Additionally, other synthesis tests were performed with different reducing agents to compare the obtained nanomaterials. The other reagents used were oleic acid, citric acid, sodium borohydride, and a plant extract *(moringa oleifera)* as a green methodology.

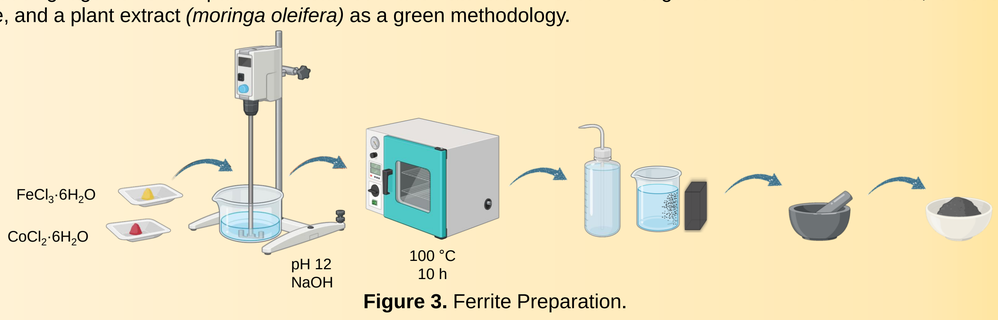
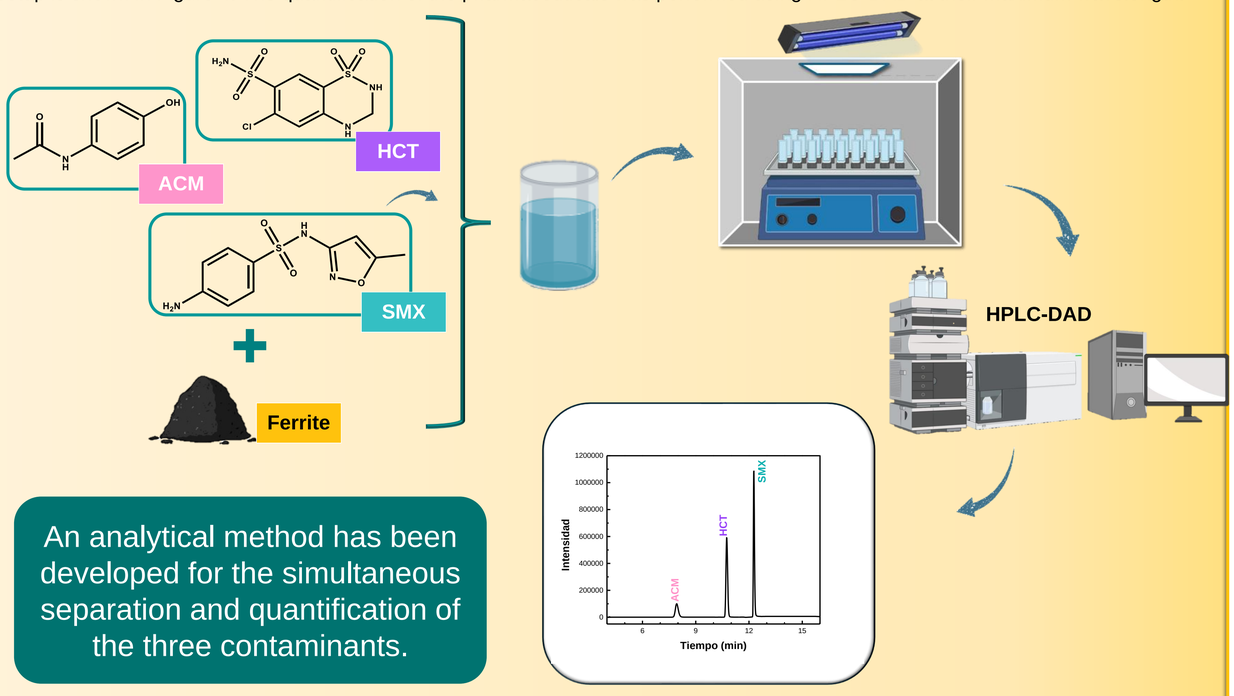


Figure 3. Ferrite Preparation.

The physicochemical characterization of the synthesized materials was performed using:

Field Emission Scanning Electron Microscopy (FESEM)	Transmission electron microscopy (TEM)	Morphological Characterization
X-ray diffraction (XRD)	X-ray Photoelectron Spectroscopy (XPS)	Chemical Composition
Ultraviolet-Visible-Near Infrared Spectroscopy (UV-Vis-NIR)		Band Gap Determination
Specific Surface Area measured by the BET method (SBET)		Surface Area
Raman Spectroscopy		Microcrystalline order

The pharmaceutical degradation experiments were carried out using the Heterogeneous Photo-Fenton process. The experimental setup is shown in Figure 4. The quantification of the pharmaceuticals was performed using HPLC-DAD at their maximum wavelength.

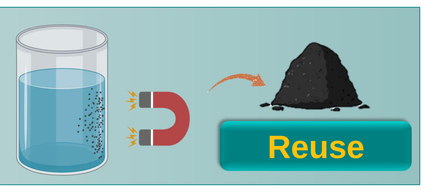


An analytical method has been developed for the simultaneous separation and quantification of the three contaminants.

Figure 4. Experimental setup scheme.

Advantages

The principal advantage is that, due to the magnetic character of ferrites, they can be easily removed from water after the degradation of contaminants, thus preventing the remediation method itself from becoming a new source of contamination. They can also be reused in several degradation cycles. Additionally, ferrites contain metals with two valence states, +2 and +3, allowing for the interconversion of M^{2+} and M^{3+} within the same structure.



Preliminary Experiments

Characterization

The XRD diffractograms were obtained for each of the synthesized ferrites. These diffractograms show the characteristic peaks of a ferrite, corresponding to the planes (220), (311), (400), (422), (511), and (440). These planes align with the reference JCPDS patterns numbers 22-1086, 74-2403, and 34-0425, corresponding to the face-centered cubic spinel structures with space group **fd3m** of cobalt, manganese, and copper ferrites, respectively.[6-8]

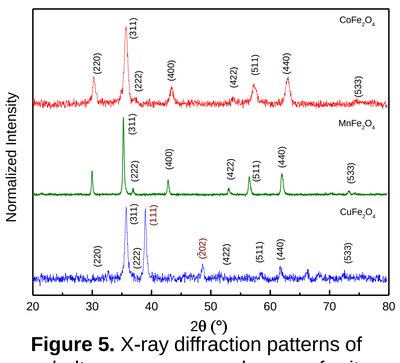


Figure 5. X-ray diffraction patterns of cobalt, manganese, and copper ferrites.

This confirms the successful synthesis of each ferrite. Additional characterizations were performed to study the morphology (SEM and TEM). Moreover, the average particle size was determined using the TEM micrographs and the ImageJ software, confirming a nanometric size for each ferrite, **Figure 6.**

The synthesized materials are of nanometric size

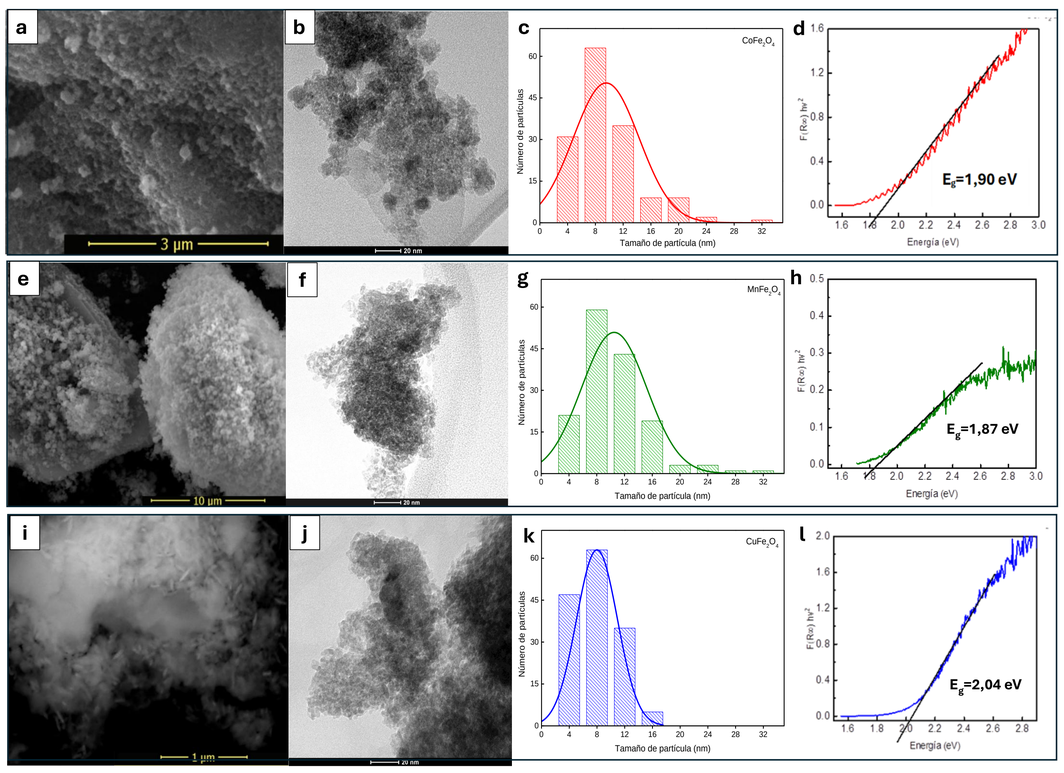


Figura 6. SEM micrographs, HRTEM micrographs, particle size distribution, and band gap determined using the Tauc graphical method for cobalt ferrite (a-d), manganese ferrite (e-h), and copper ferrite (i-l), respectively.

Finally, the band gap value for each ferrite was determined using the Tauc plot method, and these values fall within the expected range for these photocatalysts.[9]

Degradation example

The **Figure 7** presents the degradation of a contaminant, sulfamethoxazole (SMX), in the presence of each ferrite. The best degradation percentage was achieved with copper ferrite, reaching 80% degradation within one hour of treatment.

The system successfully achieves the degradation of sulfamethoxazole, demonstrating its suitability for removing pharmaceutical contaminants from water

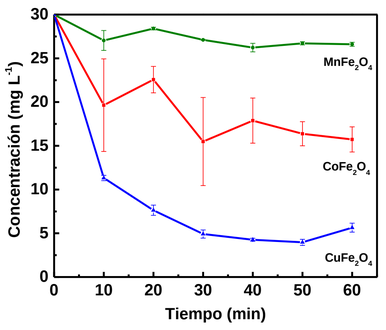


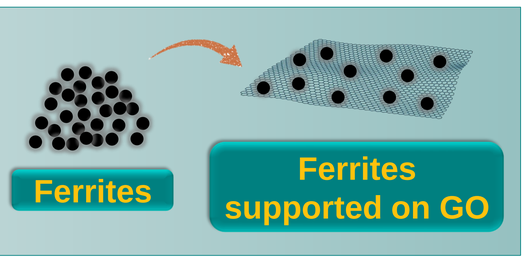
Figure 7. Degradation curves of 30 mg L^{-1} SMX over 60 minutes using cobalt (■), copper (●), and manganese (▲) ferrites. Experimental conditions: $[H_2O_2]$ = 15 mM, 10 mg of catalyst, 365 nm ultraviolet light.

Relation to Green Chemistry

This thesis aligns with several principles of green chemistry by focusing on the development of environmentally friendly and sustainable solutions for water remediation. Nanoparticles are synthesized using water as a solvent and natural, non-toxic reactants such as river water or plant extracts, minimizing the use of hazardous chemicals. The materials are magnetic, enabling easy removal from water post-treatment to prevent secondary contamination. Efforts to optimize the synthesis processes and improve material properties include supporting the nanoparticles on graphene oxide, a breakthrough achieved during a research internship in Mexico. These materials are applied to degrade pharmaceutical pollutants in water, addressing the toxic impact of these contaminants on living organisms. By employing sustainable synthesis methods, reusability, and targeting environmental pollutants, this research embodies the core objectives of green chemistry: reducing waste, minimizing toxicity, and promoting the design of safer materials and processes

Future Directions

To further enhance the properties of the synthesized ferrites, future work will focus on supporting them on graphene oxide (GO). This strategy aims to improve their catalytic performance by increasing their surface area, optimizing their electronic properties, and enhancing their stability during degradation processes. The incorporation of graphene oxide is expected to provide a synergistic effect, making the ferrite-based materials more efficient and versatile for applications in environmental remediation and beyond.[10]



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Acknowledgments

This work was financially supported by the FONDECYT Regular Project No. 1220077, the ANID National Doctoral Scholarship (Folio 21211517), and the Millennium Nucleus Catalytic Processes Towards Sustainable Chemistry (CSC).
Part of this work was also carried out at the Centro de Investigación en Materiales Avanzados, Cimav, Subsede Monterrey, México