

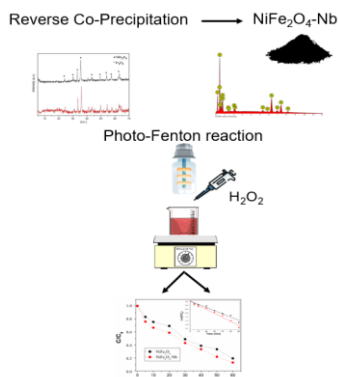
Preparation of Highly Efficient NiFe₂O₄-Nb Doped Photocatalyst for the Degradation of Azo Amaranth Dye from Aqueous Solution

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Ferrites are known as good catalysts for Fenton photo reactions with excellent results. In this context, there are still possibilities for improvements, and niobium appears as an interesting material to add to the ferrite structure. The present work aims to synthesize and characterize a material developed to be used mainly in degrading dyes. The characterization indicates niobium doping in the ferrite structure occurred. The doped material had faster kinetics and greater efficiency decolorization of the solution compared to material without niobium. The reaction rate constants obtained were $31 \times 10^{-3} \text{ min}^{-1}$ ($R^2 = 0.99$) and $25 \times 10^{-3} \text{ min}^{-1}$ ($R^2 = 0.98$) for the NiFe₂O₄-Nb and NiFe₂O₄ catalysts.

Introduction

The natural resources are dwindling at an alarming rate. The constant water pollution, due to industrialization is a major concern to society. As a consequence, organic contaminants, including pharmaceuticals, dyes, and pesticides, pervade water and sewage treatment facilities, where traditional methods often fall short of eradicating these pollutants. This predicament demands adopting advanced water treatment techniques, such as adsorption and Advanced Oxidation Processes (AOPs) [1].

Among the AOPs, the heterogeneous photo-fenton method is seen as effective in decomposing organic contaminants in wastewater, also standing out for the possibility of recycling and reusing the catalyst in future reactions. This process resorts to the use of hydrogen peroxide (H₂O₂), Fe²⁺, and light in an aqueous and acidic environment (pH ≤ 3), resulting in the formation of radicals extremely oxidizing ($\cdot\text{OH}$) [2].

The AOPs field is always in search of new catalysts that possess better properties such as high thermal and electrical conductivity, malleability, ductility, and superior resistance to corrosion, heat, and wear of niobium, giving this metal the ability to improve the properties of materials, making them more efficient [3].

The present work aims to combine the remarkable and promising properties of niobium with those of ferrites, which are already known as effective materials for photo-Fenton reactions, and to evaluate the impact of niobium's presence on the structure of ferrite.

Material and Methods

1) Synthesis: Nanoparticles of NiFe₂O₄ and NiFe₂O₄-Nb were produced by reverse coprecipitation, a route adapted from the study proposed by Zampiva [4]. The oxidizing precursors used were niobium chloride (NbCl₅), iron chloride III (FeCl₃·6H₂O) and nickel chloride II (NiCl₂·6H₂O), and ammonium hydroxide (NH₄OH) was used as a precipitating agent. All reagents were obtained from Merck.

2) Characterization: The crystalline structure of the NiFe₂O₄-Nb composite was characterized using an X-ray diffractometer (XRD, Philips, X'pert MPD), settled at 40 kV, 40 mA, and Cu ($\lambda = 1.54056 \text{ \AA}$) anode at $0.05^\circ \text{ s}^{-1}$. Scanning electron microscopy-energy dispersive X-ray analysis (SEM-EDX).

3) Photo-Fenton reaction: The photo-Fenton reactions were carried out using a glass container containing 100 mL of amaranth azo dye (50 mg L^{-1}) with pH adjusted to 3, in which 50 mg of catalyst was added to the solution under magnetic stirring until reaching equilibrium adsorption. Then, 8 mmol L⁻¹ of H₂O₂ was added and irradiation was started under a fluorescent lamp (85 W, Empalux, luminous flux 5195 lm) located 10 cm above the aqueous surface of the dye. The discoloration of the solution was determined by reading the color on a UV-vis spectrophotometer (Bel Photonics, SP1105), at the wavelength of maximum absorbance, 525 nm. The discoloration kinetics of the solution was expressed as the ratio C/C_0 ($= A/A_0$) as a function of time.

Results and Discussion

Figure 1 shows the diffractograms corresponding to

NiFe₂O₄ (black) and NiFe₂O₄-Nb (red). The diffractogram indicates the presence of NiFe₂O₄ according to the XRD pattern (ICSD database: NiFe₂O₄-158834), however, both samples show the formation of a second phase of iron oxide (Fe₂O₃) (ICSD database: Fe₂O₃-172906). Nb and its oxides were not found in the XRD analysis. Interestingly, in the sample where Nb was doped in the NiFe₂O₄ structure, there is an increase in the intensity of the peaks that correspond to Fe₂O₃, this occurrence may indicate that niobium doping in the ferrite structure occurred. The EDX (Figure 2) helps to support this assumption because it confirms the presence of niobium in the material and of all the other elements that make up the structure of NiFe₂O₄-Nb. The proportions found in the analysis were 45.07% for iron, 24.09% for nickel, 19.09% for oxygen, and 4.06% for niobium.

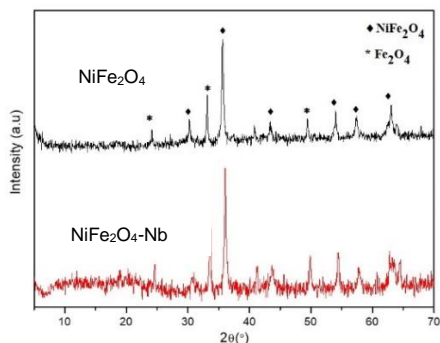


Figure 1. XRD diffractograms of NiFe₂O₄ and NiFe₂O₄-Nb

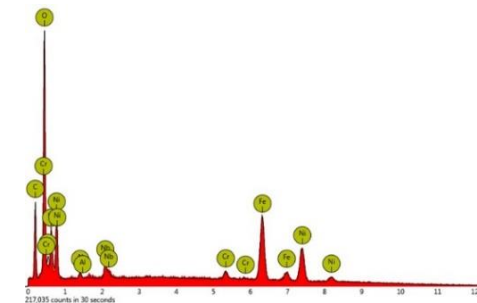


Figure 2. EDX spectrum of NiFe₂O₄-Nb.

Conclusion

Both materials show significant results in the degradation of amaranth dye in the photo-Fenton reaction. However, an increased rate and superior compliance were observed with niobium ferrite, further studies will be carried out with this material to explore its full catalytic power.

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References

- [1] D.M.Druzian, L.R.Oviedo, S.N.Loureiro, R.D.Wouters, B.S.Vizzotto, E.O.Pinto, N.J.S.de Vanconcellos, Y.P.M.Ruiz, A.Galembeck, G.Pavoski, D.C.R.Espinosa, C.dos Santos, W.L.da Silva, *Journal of Photochemistry and Photobiology A: Chemistry*, 442 (2023) 114773.
- [2] J.S.de Oliveira, F.C.Halmenschlager, S.L.Jahn, E.L.Foletto, *Matéria (Rio de Janeiro)* 24 (2019) e12498.
- [3] C.Nico, T.Monteiro, M.P.F.Graça, *Progress in Materials Science*, 80 (2016) 1-37.
- [4] R.Y.S.Zampiva, L.H.Acauan, L.M.dos Santos, R.H.R.de Castro, A.K.Alves, C.P.Bergmann, *Ceramics International*, 43 (2017) 16225-16231.
- [5] I. L. O. Brasileiro, V. S. Madeira, C. P. de Souza, A. L. Lopes-Moryama, M. L. R. A. Ramalho, *Journal of Photochemistry and Photobiology A: Chemistry*, 388 (2020) 112199.

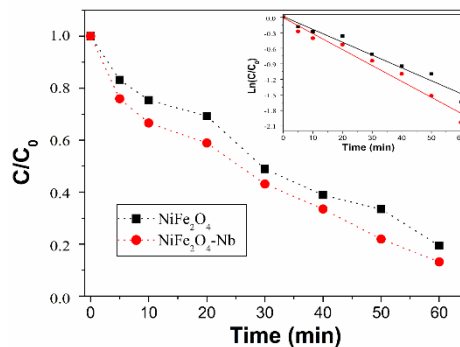


Figure 3. Decolorization efficiency and Kinetics (in detail).

Figure 3 gives the kinetical behavior for both materials. It was found that the NiFe₂O₄-Nb presents a higher degradation rate in comparison with the Fe₂O₄, indicating that the application of niobium is promising for the Fenton process. It is expected that the Nb changes the electronic state increasing the OH radical available during the reaction [5]. The pseudo-first-order kinetic rate constants for the azo amaranth dye degradation using the NiFe₂O₄ and NiFe₂O₄-Nb catalysts were estimated by linear regression from the ln (C/C₀) versus time plots, as shown in Figure 3. Both the plots were obtained from the linearized kinetic equation (Eq. 1).

$$\ln\left(\frac{C}{C_0}\right) = k_d t \quad (1)$$

Where, k_d is the apparent rate constant for the amaranth dye decolorization, which is obtained from the slope of the respective linear plots. The reaction rate constants obtained were $31 \times 10^{-3} \text{ min}^{-1}$ ($R^2 = 0.99$) and $25 \times 10^{-3} \text{ min}^{-1}$ ($R^2 = 0.98$) for the NiFe₂O₄-Nb and NiFe₂O₄ catalysts. Therefore, the doped material promoted greater catalytic activity and a faster reaction rate.