

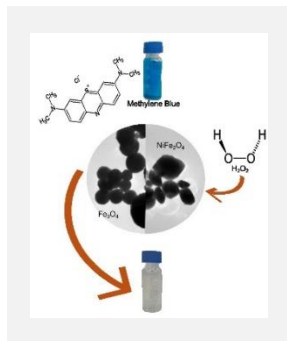
Iron and nickel ferrites as heterogeneous catalysts for the Fenton-like oxidation of methylene blue

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Iron ferrite or magnetite (Fe_3O_4) and nickel ferrite (NiFe_2O_4) were synthesized by the hydrothermal route. X-ray powder diffraction revealed the formation of a single-phase cubic spinel structure for Fe_3O_4 and the formation of NiFe_2O_4 alongside with hematite as secondary phase. Transmission electron micrographs show that Fe_3O_4 particles are spherical while NiFe_2O_4 particles are quasispherical. The specific areas of Fe_3O_4 and NiFe_2O_4 were $6 \text{ m}^2\text{g}^{-1}$ and $32 \text{ m}^2\text{g}^{-1}$, respectively. Both ferrites were used as heterogeneous Fenton catalysts for the degradation of methylene blue (MB) as an organic contaminant. Fe_3O_4 achieved a MB removal of 78% while NiFe_2O_4 reached 97%. Fe and Ni leaching was less than 0.3% after 300 min of reaction. These materials were separated from the reaction media easily by external magnets.

Introduction

Fenton processes are extensively employed advanced oxidation processes for treating organic pollutants. Heterogeneous Fenton promises advantages over homogeneous Fenton which operates only in a narrow pH range (1-3) and produces iron sludge at the end of the process [1]. Various iron oxides and hydroxides have been used as Fenton catalysts, yet often with weak catalytic activity and challenges in stability and reusability. Spinel ferrites are a type of mixed iron oxides with the general formula MFe_2O_4 ($\text{M} = \text{Ni}^{2+}, \text{Fe}^{2+}, \text{Cu}^{2+}$) which exhibit excellent magnetic properties, low toxicity, and chemical stability [2]. Ferrites have been used as adsorbents and catalysts for eliminating harmful dyes, phenols and antibiotics from water [3]. In fact, contaminants such as rhodamine B [1] and 4-Chlorophenol [4] have been treated by heterogeneous Fenton using ferrites. The performance of ferrites at removing contaminants depends on their properties which can be controlled by the synthesis method [1,4].

Methylene blue (MB) is a cationic dye extensively used in coloring paper, wool, silk, and cotton. However, it poses persistent hazards as a toxic, carcinogenic, and mutagenic contaminant [5]. The presence of these types of contaminants in wastewater has a potentially dangerous impact on the environment and human health. Therefore, it is necessary to look for simple contaminant removal methods [3]. The aim of this work is to study the synthesis, characterization, and behavior of magnetite (Fe_3O_4) and nickel ferrite (NiFe_2O_4) for the oxidation of contaminants in water by heterogeneous Fenton.

Material and Methods

The following reactants were used without further purification. Iron nitrate nonahydrate (Merck, 100%), ferric chloride hexahydrate (Fisher Chemical, 100%), sodium acetate (Loba Chemie, 99%), sodium hydroxide (Merck, >99%), ethylene glycol (Mallinckrodt, 99.8%), nickel nitrate hexahydrate (Alfa Aesar, 98%), hydrogen peroxide (Merck, 30% w/w) and methylene blue (Fisher, 92%). Fe_3O_4 was prepared according to Sun, et al. [7] with modifications. Precisely, 1.4 g of iron nitrate was dissolved in 20 ml of ethylene glycol. Then, 3.6 g of sodium acetate were added into the solution, and the mixture was stirred for 30 min. This solution was sent for hydrothermal synthesis heated at $200 \text{ }^\circ\text{C}$ for 6 h. The autoclave was cooled down at room temperature, and the solid product was washed with deionized water (DI) and ethanol and dried at $60 \text{ }^\circ\text{C}$ for 2 h. NiFe_2O_4 was synthesized according to Kennaz, et al. [8] with modifications. Precisely, 20.2 g of iron nitrate were dissolved in 50 ml of DI, and 7.4 g of nickel nitrate were dissolved in 50 ml of DI. Then, 20 ml of each solution were mixed and stirred for 30 min. A 2 M NaOH solution was added dropwise until the pH reached 12. The mixture was sent for hydrothermal synthesis at $180 \text{ }^\circ\text{C}$ for 24 h. The product was washed, dried at $110 \text{ }^\circ\text{C}$ for 2 h, and calcined at $350 \text{ }^\circ\text{C}$ for 3 h. The crystalline structure of the samples was investigated through XRD analysis. A Bruker D8 ADVANCE equipment with Cu K α radiation (1.54 \AA) was operated at 40 kV. The textural properties were evaluated with a Quantachrome Instruments Nova4200e equipment. The Brunauer-Emmett-Teller (BET) model was applied to determine the specific surface area. The

catalytic activity of ferrites was tested in the oxidation of MB. All tests were performed at room temperature under dark conditions. For the adsorption test, 50 mg of the catalyst was added to 50 ml of the 10 mg l^{-1} MB solution and aliquots were taken at different times. The catalyst was separated, the MB concentration was measured by UV-vis spectroscopy. For the oxidation tests, the previous process was repeated except that 2 ml of H₂O₂ was added at the beginning of the test, such that the mass ratio of H₂O₂/MB/ferrite was kept at 5:66.6:1.

Results and Discussion

The XRD patterns of Fe₃O₄ and NiFe₂O₄ are shown in Figure 1. The black pattern is indexed as a single-phase of Fe₃O₄ according to JCPDS card no.19-0629. The cubic spinel structure of NiFe₂O₄ was verified by the presence of characteristic peaks which matched with standard JCPDS card no. 01-086-2267. Hematite (Fe₂O₃) was detected as an impurity in this diffraction pattern.

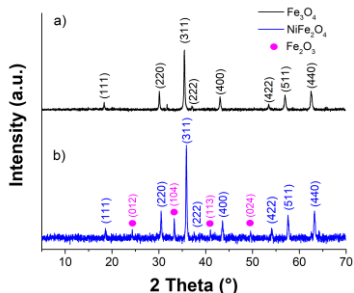


Figure 1. XRD patterns of (a) Fe₃O₄ and (b) NiFe₂O₄

TEM micrographs of Fe₃O₄ and NiFe₂O₄ (Figure 2) reveal their very different morphology. Fe₃O₄ particles are smoother than the NiFe₂O₄ particles, this is due to the use of ethylene glycol as a solvent in Fe₃O₄ synthesis. The particle shape of Fe₃O₄ is spherical whereas the particle shape of NiFe₂O₄ is quasispherical, and both materials show

agglomeration due to their magnetic nature.

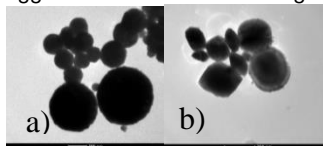


Figure 2. TEM images at 200 nm, (a) Fe₃O₄, (b) NiFe₂O₄

The SSA of Fe₃O₄ and NiFe₂O₄ was determined by applying the BET model, and they correspond to 6 m²g⁻¹ and 32 m²g⁻¹, respectively. Ferrites were tested in the oxidation of MB, but first, an adsorption study in the dark without H₂O₂ was performed. As seen in Figure 3, around 20% of MB was adsorbed using ferrite (iron or nickel) after 300 min. 60% of MB was removed adding only H₂O₂. The removal of MB increased with the use of heterogeneous Fenton, which consisted of both H₂O₂ and ferrites, compared to only ferrite or only H₂O₂. In fact, Fe₃O₄ and H₂O₂ reached 78% MB removal, while NiFe₂O₄ and H₂O₂ reached 97% MB removal under the same conditions. The lower catalytic activity of Fe₃O₄ compared to NiFe₂O₄ could be explained due to surface passivation, which has been observed in previous works [6]. The leaching of Fe was negligible in all tests; however, the leaching of Ni was less than 0.1% in the adsorption test, while in the NiFe₂O₄ + H₂O₂ test, the leaching reached 0.3%. This demonstrates the stability of the catalysts during the Fenton process.

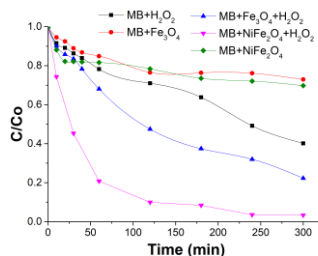


Figure 3. Oxidation tests of MB in the presence of ferrite

Conclusions

Fe₃O₄ and NiFe₂O₄ were successfully synthesized by hydrothermal method, and they demonstrated to behave as heterogeneous Fenton-like catalysts in the oxidation of methylene blue. NiFe₂O₄ exhibited the highest specific surface area of 32 m²g⁻¹, and it was the most active for methylene blue oxidation reaching 97% removal. There was no significant leaching of Ni and Fe, and the magnetic properties of the catalysts eased their separation from the reaction media.

References

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