Robust photo-Fenton Degradation of Organic Pollutants by MFe₂O₄ ferrite Nanoparticles

Nishesh Kumar Gupta^{a,b}, Yasaman Ghaffari^{a,b}, Kwang Soo Kim^{*a,b}

a. University of Science and Technology (UST), Daejeon, Republic of Korea

b. Department of Land, Water, and Environment Research, Korea Institute of Civil Engineering and Building Technology (KICT), Goyang, Republic of Korea

Abstract

Ferrite nanoparticles, MFe₂O₄ (M = Co, Ni, Cu, and Zn) were synthesized by the surfactant-mediated co-precipitation-oxidation method. The bandgap calculated from UV-Visible diffuse reflectance spectroscopy was found in the range of 1.11–1.81 eV. These nanocatalysts were used for the photocatalytic degradation of organic dyes in a 32 W UV-C/H₂O₂ system at neutral pH. All the four ferrites showed an exceptional degradation rate in the range of 2.065–2.417 min^{−1}. In the optimized condition, NiFe₂O₄ was found to degrade 93%, 92%, 89%, and 78% of methyl orange, bromo green, methylene blue, and methyl red, respectively, in 1 min of irradiation. Nearly 40% of mineralization occurred after 5 min, which reached 60% in 50 min. With remarkable reusability, these photocatalysts could be used for the remediation of dye-contaminated wastewater.

Introduction

Severe contamination of water bodies is considered as a threat to both human beings and other life forms. Organic dyes are one of the major pollutants discharged into the water bodies by textile, printing, and leather industries. Conventional methods like adsorption, microbial degradation, and chemical precipitation have been established for the treatment of dye-contaminated wastewater. These processes suffer due to high sludge production, operational cost, and formation of secondary pollutants. For the complete conversion of organic dyes into non-toxic byproducts, the photocatalytic process is one of the suitable options[1].

Advanced oxidation processes which are based on the generation of hydroxyl radicals are being employed for the degradation of organic pollutants. Among numerous metal-oxide based photocatalysts developed for the purpose, researchers are more focused on spinel ferrites due to their low cost, narrow bandgap, magnetic property, and high stability. Another advantage is that the properties of ferrites could be easily tuned by replacing Fe²⁺ ions with other divalent cations. In the literature, many reports on the application of ferrites are available, but significant issues with these research works were low pH requirement, slow degradation kinetics, and high energy consumption[2].

Considering these drawbacks as challenges, we successfully developed an economical method for the fabrication of spinel ferrites. The prepared photocatalysts were characterized by various microscopic and spectroscopic techniques. These ferrite photocatalysts were found highly efficient in degrading multiple organic dyes at neutral pH in a 32 W UV-C/H₂O₂ system. The kinetic rates observed in this study were the highest ever reported under this set of experimental conditions.

Results

Synthesis: For the synthesis of CoFe₂O₄ (CoF), CoCl₂•6H₂O (4.76 g) and Fe(NO₃)₃•9H₂O (16.16 g) were dissolved in 0.5 L of distilled water (DW) at 60 °C under constant stirring. To it, cetyl trimethylammonium bromide (1.0 g) was added and stirred for 30 min at 60 °C. The solution pH was maintained to 12 by slow addition of 1.0 mol L^{−1} NaOH solution. After stirring for 1 h, the precipitate was separated, washed with DW several times, and dried at 100 °C for 24 h. The dried precipitate was finely grounded before subjecting it to calcination for 24 h at 700 °C. The same protocol was adopted for the synthesis of NiFe₂O₄ (NiF), CuFe₂O₄ (CuF), and ZnFe₂O₄ (ZnF) using NiCl₂•6H₂O (4.75 g), CuSO₄•5H₂O (4.99 g), and Zn(NO₃)₂•6H₂O (5.95 g), respectively along with Fe(NO₃)₃•9H₂O (16.16 g).

Fig. 1. HRTEM images of CoF, NiF, CuF, and ZnF.

Fig. 2. Bandgap energy of ferrite nanocatalysts.

High-resolution transmission electron microscopy (HRTEM) showed single crystals for all the four ferrites with cubic morphology (**fig.1**). The bandgap calculated for CoF, NiF, CuF, and ZnF, i.e., 1.11 eV, 1.59 eV, 1.55 eV, and 1.81 eV, respectively which were found significantly lower than those reported in the literature (**fig.2**)[3].

Fig. 3. Photo-Fenton degradation of MB dye over ferrite nanocatalysts (plot of $\ln(C/C_0)$ versus time (in inset)).

In the absence of photocatalyst, 8% and 10% of MB dye were degraded with H₂O₂ and UV/H₂O₂. In the dark condition, nearly 14% of dye was adsorbed onto NiF after 5 min of contact time. Thus, the contribution of adsorption in photocatalytic degradation of dye would be even lesser due to faster degradation kinetics. The photo-Fenton degradation of organic dye over ferrite photocatalysts showed rapid decolorization at neutral pH. More than 90% of dye degraded within 75 s of irradiation (**fig.3**). The calculated rate constant (k_{app}) value was 2.141 min^{−1}, 2.417 min^{−1}, 2.065 min^{−1}, and 2.069 min^{−1}, for CoF, NiF, CuF, and ZnF, respectively. The kinetic rate of degradation of ferrite photocatalysts in this study was found significantly higher than those reported in the literature[4]. A 40% mineralization was recorded after 5 min, which increased to 60% after 50 min. Thus, MB dye could be effectively mineralized into residual organic molecules.

Fig. 4. Fluorescence spectra of 2-hydroxyl terephthalic acid (TAOH) (dye degradation efficiency of ZnF in the presence of scavengers (in inset)).

In the presence of scavengers, the dye degradation performance followed the trend: tert-butanol > KI > EDTA > K₂Cr₂O₇ > *p*-benzoquinone > no scavenger. The presence of tert-butanol severely hindered the photocatalytic process, suggesting that the generated •OH radicals were the primary active species. The performance decreased from ~89% to ~54% in the presence of EDTA, confirming the involvement of *h*⁺ (photogenerated in the valence band of ZnF) directly in the degradation of MB dye. The non-fluorescent TA molecule reacts with an •OH radical to form fluorescent TAOH. The fluorescent intensity of TAOH is proportional to the concentration of •OH radicals in the reaction. In the presence of ZnF, the fluorescence intensity enhanced with the irradiation time. Thus, it was concluded that the formation of •OH radicals drove the dye degradation process.

Conclusion

We have demonstrated enhanced photocatalytic activity of MFe₂O₄ nanoparticles synthesized by the surfactant-mediated co-precipitation-oxidation method. All the ferrites absorbed effectively in the UV-Vis-NIR region with low bandgap energy. In the optimized experimental conditions, NiF showed an extraordinary MB degradation rate of 2.417 min^{−1}, which decreased to 2.065 min^{−1} for ZnF. The degradation mechanism in the UV/H₂O₂/ferrite system was primarily driven by •OH radicals and holes, which was further confirmed by scavenger studies and fluorescence spectroscopy. From this study, it was concluded that these ferrites have the potential to be used for the affordable treatment of dye-contaminated wastewater without pH adjustment under low power UV-C irradiation.

Acknowledgement

Authors are grateful for the funds [Project # 20190151-001] provided by the “Korea Institute of Civil Engineering and Building Technology” (KICT), Rep. of Korea.

Reference

- Zhu, M. X., Lee, L., Wang, H. H. & Wang, Z., J. Hazard. Mater. 149, 735-741 (2007).
- Dhiman, M., Goyal, A., Kumar, V. & Singhal, S., New J. Chem. 40, 10418-10431 (2016).
- Sharma, R., Bansal, S. & Singhal, S., RSC Adv. 5, 6006-6018 (2015).
- Saha, M., Mukherjee, S., Kumar, S., Dey, S. & Gayen, A., RSC Adv. 6, 58125-58136 (2016).