Synthesis of magnetic CuFe$_2$O$_4$/Fe$_3$O$_4$ core-shell materials and their application in photo-Fenton-like process with oxalic acid as a radical-producing source

Thu Uyen Tran Thi$^{a,b}$, Van Hung Phan$^{a,b}$, Huu Thinh Pham Nguyen$^{a,b}$, The Luan Nguyen$^{a,b}$, An Nang Vu$^{a,b}$ and Tien Khoa Le$^{a,b}$

$^a$Faculty of Chemistry, University of Science, Ho Chi Minh City, Vietnam; $^b$Faculty of Chemistry, University of Science, Vietnam National University, Ho Chi Minh City, Vietnam

ABSTRACT

In this work, we proposed to synthesize CuFe$_2$O$_4$/Fe$_3$O$_4$ core-shell materials with different Fe$_3$O$_4$ contents in order to create new and efficient photo-Fenton-like catalysts for the degradation of methylene blue with oxalic acid as a radical-producing source. The catalysts were prepared through two stages: first, CuFe$_2$O$_4$ was prepared by a hydroxide coprecipitation–annealing method and then, Fe$_3$O$_4$ was immobilized on CuFe$_2$O$_4$ surface by a simple impregnation–annealing procedure. According to the experimental results, our CuFe$_2$O$_4$/Fe$_3$O$_4$ core-shell materials exhibit high photo-Fenton-like catalytic activity for the degradation of methylene blue under both UVA light and visible light, as well as good ferromagnetic properties, which allows them to be easily separated from the solution by a magnet. Among them, the catalyst prepared with the molar CuFe$_2$O$_4$/Fe$_3$O$_4$ ratio of 1:2 showed the best catalytic performance with the rate constant of 2.103 h$^{-1}$ under UVA light and 0.542 h$^{-1}$ under visible light, which were 2 times higher than CuFe$_2$O$_4$ sample. The enhanced catalytic activities of our core-shell materials can be attributed to the high content of surface Fe$^{3+}$ species, high specific surface area and the presence of rod-like Fe$_3$O$_4$ particles on their surface.

1. Introduction

The existence of various dye molecules in textile wastewater has been widely considered as one of major environmental problems that our world is facing today. Due to their toxicity, organic dyes have many negative effects not only on human health but also on aquatic life [Berradi et al. 2019, Hassan et al. 2018, Ito et al. 2016, Lellis et al. 2019]. Therefore, treatment of textile wastewater containing organic dyes has become an urgent need for the environment protection. Unfortunately, the decomposition of organic dyes is usually ineffective since these organic molecules are remarkably resistant to conventional biological methods such as activated sludge or anaerobic digestion [Katheresan et al. 2018]. Over the past decades, homogeneous Fenton processes based on the reactions of Fe$^{3+}$/Fe$^{2+}$ ions and H$_2$O$_2$ were commonly known as a potentially better oxidation approach owing to the generation of highly reactive oxygen species like hydroxyl radicals which can completely mineralize most of organic species [Fenton 1894; Gligorovski et al. 2015, Neamtu et al. 2003, Wang and Xu 2012]. More specially, it was reported that the production of hydroxyl radicals was greatly improved under UV light [Zepp et al. 1992]. However, the homogeneous Fenton and photo-Fenton technologies still present some shortcomings for practical applications. Firstly, Fe$^3+/Fe^{2+}$ ions as homogeneous catalysts are completely dissolved in reaction solution, leading to enormous challenges in catalyst recovery after wastewater treatment. Secondly, for the recovery, these homogeneous catalysts usually require a post-neutralization process, which possibly causes the increase in the treatment cost as well as the formation of ferric sludge as a secondary pollution source [Catrinescu et al. 2003, Hanna et al. 2008].

In order to overcome these obstacles, several magnetic photo-Fenton-like catalysts were developed in the literature [Heidari et al. 2019, Liu et al. 2012, Sharma et al. 2015, Sharma and Singhal 2018] (in general, the photo-Fenton-like reactions are the advanced oxidation processes using oxidants other than H$_2$O$_2$ and transition metals as catalysts other than iron under illumination [Rodriguez-Narváez et al. 2019]). These heterogeneous magnetic catalysts relies on the ferrite materials which belong to the spinel structure with the common formula $M^{2+}Fe^{3+}O_4$ (M = Fe, Mn, Cu, Zn, Ni). Owing to the tunability of their structure and composition, they do not only display promising photo-Fenton catalytic activities but also exhibit highly ferromagnetic properties which help them to be easily separated from the solution after the treatment [Sharma et al. 2015].

CONTACT Tien Khoa Le tkhoa@hcmus.edu.vn Faculty of Chemistry, University of Science, Ho Chi Minh city, Vietnam © 2021 The Author(s). Published by Informa UK Limited, trading as Taylor & Francis Group on behalf of The Korean Ceramic Society and The Ceramic Society of Japan. This is an Open Access article distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/4.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.
Nevertheless, the activity of ferrite catalysts is still limited and needs to be further improved for the practical applications. Recently, Guo et al. proved that the addition of tartaric acid into the H₂O₂-ferrite-photo system could enhance the decolorization of methylene blue from 52% to 92.1% within 80 minutes [Guo et al. 2019]. Unfortunately, it was widely recognized that H₂O₂ is hard to be stocke for a long period because this compound is unstable and easily decomposes to form oxygen gas and water during the storage.

According to our previous reports, the replacement of H₂O₂ by oxalic acid can extend the storage time and notably ameliorate the photo-Fenton performance of these catalysts [Dinh et al. 2017, Ngo TPH and Le TK 2018]. In fact, the ferric species on the surface of ferrite catalysts and oxalic acid dissolved in solution seem to be able to create ferrioxalate complexes which can enhance the photoabsorption of UV-visible light to produce more hydroxyl radicals and thus improve the photo-Fenton efficiency [Liu et al. 2012]. Beside, our previous works also proved that the amounts of different ions on the surface of ferrite catalysts greatly affect their photo-Fenton performance [Ngo TPH and Le TK 2018]. It was observed that the photo-Fenton catalytic activity tends to rise when the surface Fe content of our catalysts gradually increases [Ngo TPH and Le TK 2018]. With that in mind, this work aims to prepare new magnetic photo-Fenton catalysts based on CuFe₂O₄/Fe₂O₃ core-shell materials with different Fe₂O₃ contents on their surface in order to enhance the photo-Fenton catalytic activity. Actually, before our study, the combination of Fe₂O₃ and CuFe₂O₄ was carried out by Silva et al. who used the modified Pechini method to form new heterogeneous α–Fe₂O₃/CuFe₂O₄ catalysts [Silva et al. 2020]. These new mixed oxides exhibited both magnetic behavior and high photo-Fenton catalytic activity for the degradation of methylene blue under visible light. However, since the modified Pechini method is based on the polycondensation between citrate salts and ethylene glycol followed by a pyrolysis at high temperatures, this technique is not only inappropriate to synthesize the core-shell materials but also complicated, requiring a careful control of polymerization and a long reaction time (24 hours). Therefore, in this study, we proposed to apply a facile impregnation–annealing method to synthesize our CuFe₂O₄/Fe₂O₃ core-shell materials with enhanced catalytic activities. Moreover, oxalic acid was used as a stable and effective radical-producing source instead of H₂O₂ to further improve the photo-Fenton performance. The influences of Fe₂O₃ contents on the crystal structure, morphology, surface composition and magnetic properties of our catalysts were also discussed in details.

2. Materials and methods

2.1. Sample preparation

In our work, all chemicals were commercially available and used without further purification. The preparation of CuFe₂O₄/Fe₂O₃ core-shell materials with different Fe₂O₃ contents was effectuated through two stages. In the first stage, CuFe₂O₄ nanoparticles were synthesized by a simple hydroxide coprecipitation – annealing method which used NaOH as the precipitator. Briefly, Cu(NO₃)₂·3H₂O and Fe(NO₃)₃·9H₂O (≥98%, purchased from Sigma Aldrich) in a molar ratio of 1:2 were dissolved in 200 mL distilled water to form a solution containing 0.10 mol.L⁻¹ Cu²⁺ and 0.20 mol.L⁻¹ Fe³⁺. Next, 400 mL solution of 0.40 mol.L⁻¹ NaOH was slowly dropped into the above solution under constant stirring to obtain a brown co-precipitate. This co-precipitate was washed with distilled water, dried at 150°C during 2 hours and then annealed in an electric furnace at 800°C for 2 hours to produce magnetic CuFe₂O₄ nanoparticles.

In the second stage, Fe₂O₃ was immobilized on the surface of CuFe₂O₄ nanoparticles via a facile impregnation – annealing process. Firstly, 1.20 g synthesized CuFe₂O₄ powder was dispersed in 400 mL solution of NaOH (0.225 mol.L⁻¹). The suspension was constantly stirred by a mechanic agitator. In the other hand, a series of aqueous Fe(NO₃)₃ solutions were prepared with different concentrations (0.05, 0.10, 0.15 mol.L⁻¹). These concentrations were calculated following the desired molar CuFe₂O₄/Fe₂O₃ ratios (1:1, 1:2, 1:3, respectively). Then, the aqueous Fe³⁺ solutions were quickly poured into the suspension containing NaOH and CuFe₂O₄ to form a slurry solution. This slurry solution was regularly stirred for 30 minutes. After that, the magnetic powders were separated from the solution by a magnet, dried at 150°C for 1 hour and annealed at 500°C for 2 hours. Finally, the products were washed with distilled water, collected by a magnet and dried again at 150°C for 1 hour. All the samples were named as CuFe₂O₄/Fe₂O₃·X (X = 0, 1, 2 and 3 corresponding to the molar Fe₂O₃/CuFe₂O₄ ratios). Besides, Fe₂O₃ nanoparticles (without magnetic CuFe₂O₄ cores) were also prepared from aqueous Fe(NO₃)₃ and NaOH solutions in the same conditions (annealing at 500°C for 2 hours) in order to compare their photo-Fenton activity with that of our CuFe₂O₄/Fe₂O₃ samples.

2.2. Characterization

The structural and phase analyses of CuFe₂O₄ and CuFe₂O₄/Fe₂O₃ samples were performed by powder X-ray diffraction (XRD) using a BRUKER-Binary V3 X-ray diffractometer with monochromatic Cu Kα source (λ = 1.5406 Å) operated at 40 kV and 40 mA. The phase identification and the Rietveld refinement were carried out using Joint Committee on Powder
Diffraction Standards database (JCPDS cards) and Fullprof 2009 software, respectively. The surface morphology of our samples were characterized via field emission scanning electron microscopy (FE-SEM) images taken on a HITACHI SU8000 with an accelerating voltage of 5 kV. The specific surface area (S\text{BET}) of samples was measured through nitrogen adsorption-desorption isotherms recorded at 77 K using a NOVA 1000e analyzer (Quantachrome Instruments).

The Fourier transform infrared studies (FT-IR) for all our samples were carried out in KBr matrix using Bruker VERTEX 70 spectrometer. The FTIR spectra were recorded at the wavenumber resolution of 4 cm\(^{-1}\) and in the wavenumber range of 4000–400 cm\(^{-1}\). The surface atomic composition of our samples was also investigated by low voltage energy-dispersive X-ray spectroscopy (EDX) on a HITACHI SU8000 instrument operated at 5 kV (corresponding to the penetration depth of 50 nm [Takano 2011]).

The magnetic properties of CuFe\(_2\)O\(_4\) and CuFe\(_2\)O\(_4\)/Fe\(_2\)O\(_3\)\(\cdot\)2 samples were measured at room temperature using a vibrating sample magnetometer PPMS6000 (Quantum Design) in the magnetic field range varying from −11 kOe to 11 kOe. The saturation magnetization (M\(_s\)), the remanent magnetization (M\(_r\)) and the coercivity (H\(_c\)) of each sample were determined from the obtained corresponding hysteresis loops.

### 2.3. Catalytic tests

The photo-Fenton-like catalytic activities of CuFe\(_2\)O\(_4\), Fe\(_2\)O\(_3\), and CuFe\(_2\)O\(_4\)/Fe\(_2\)O\(_3\) samples with H\(_2\)C\(_2\)O\(_4\) as a radical-producing source were evaluated through the degradation of methylene blue (MB, purchased from Merck) under UVA light and visible light illumination. The typical experiments were conducted in a batch-type reactor based on a glass beaker containing a solution of MB (2 × 10\(^{-5}\) mol.L\(^{-1}\)) and H\(_2\)C\(_2\)O\(_4\) (10\(^{-3}\) mol.L\(^{-1}\)). Firstly, 0.125 g of catalytic powder was dispersed into this solution, which was then constantly stirred by a mechanic agitator in the dark for 60 minutes until the MB adsorption-desorption equilibrium was established. The solution temperature was maintained at about 30°C by a circulation system of water. Next, for photo-Fenton-like reactions, the suspension was irradiated by a visible light (VIS) lamp (9 W Osram Dulux S with the visible-light intensity of 12.5 W.m\(^{-2}\)) or an ultraviolet A (UVA) light lamp (9 W Radium 78 with the UVA-light intensity of 33.0 W.m\(^{-2}\)) fixed 10 cm above the solution surface. The light intensity of both lamps was measured by an Ocean Optics USB4000 spectrometer. It should be noted that MB has the maximum absorption at 664 nm whereas the light spectra of both our UVA and visible lamps (Figure 1, measured by a StellarNet spectrometer USB4C00211) does not show any peak around this wavelength. Furthermore, the capacity of our lamps is only 9 W, much lower than that of other works [Liu et al. 2012, Sharma et al. 2018], which allows us to avoid the self-sensitization of MB molecules. At given time intervals, aliquots (5 mL) of solution were collected, followed by the separation of catalytic powder from the solution by a magnet. Finally, the concentrations of remaining dye were analyzed using a Helios Omega UV–VIS spectrophotometer.

![Figure 1](image-url)  
*Figure 1. The light spectra of our UVA and visible light lamps.*
(Thermo Fisher Scientific, USA) at 664 nm. The total organic carbon (TOC) of the solution was also determined by Shimadzu TOC-VPCH analyzed. The calibration curve was prepared using potassium hydrogen phthalate (99.99%, purchased from Merck).

3. Results

3.1. Crystal structure and phase composition

XRD characterization was used to determine the crystal structure of our magnetic CuFe₂O₄ powder and CuFe₂O₄/Fe₂O₃ core-shell materials (Figure 2). From their patterns, the quantitative analysis of phase composition was carried out by using Fullprof 2009 program and the results are given in Table 1. Accordingly, the pattern of CuFe₂O₄ sample shows the characteristic diffraction peaks at 18.2°, 30.0°, 35.3°, 36.9°, 43.0°, 53.2°, 56.8° and 62.2°, corresponding to the crystallographic planes of CuFe₂O₄ cubic spinel phase (space group Fd3m, JCPDS No.34–0425) [Gupta et al. 2020]. These peaks were found to be symmetric and intense, indicating the high crystallinity and high content of CuFe₂O₄ spinel phase (92.0%). A weak peak was also detected at 38.7°, which can be indexed to the CuO tenorite phase (space group C2/c, JCPDS No. 05–0661) as the minor impurity phase (8.0%). When different contents of Fe₂O₃ were applied on the surface of CuFe₂O₄ nanoparticles, a new series of diffraction peaks was observed at 24.1°, 33.1°, 40.9°, 49.5°, 54.1° and 64.1°. These peaks can be attributed to the α-Fe₂O₃ hematite phase (space group R-3 c, JCPDS No. 86–0550) [Ghaffari et al. 2020, Gupta et al. 2020], suggesting the successful combination of two components, CuFe₂O₄ and Fe₂O₃, in our core-shell materials. Moreover, as shown in Table 1, the amount of hematite phase gradually increases with the content of Fe₂O₃ used in the preparation of CuFe₂O₄/Fe₂O₃ samples.

3.2. Morphology and surface specific area

The FE-SEM images of CuFe₂O₄ and CuFe₂O₄/Fe₂O₃ core-shell samples are represented in Figure 3. It can be seen that the CuFe₂O₄ sample is composed of agglomerated cubic particles with their size range between 80 and 200 nm (Figure 3a). In contrast, all CuFe₂O₄/Fe₂O₃ core-shell materials show the formation of rod-like particles which nearly covered the entire surface of cubic CuFe₂O₄ particles. The rod-like particles are likely to be assigned to Fe₂O₃ nanoparticles since they were grown on the surface of magnetic

![Figure 2](image-url)  
Figure 2. XRD patterns of CuFe₂O₄, CuFe₂O₄/Fe₂O₃-1, CuFe₂O₄/Fe₂O₃-2 and CuFe₂O₄/Fe₂O₃-3 samples.
core during the synthesis process. Interestingly, the FE-SEM observation (with magnification of 100 K) also showed the evolution of particle size when the content of Fe$_2$O$_3$ increased. For CuFe$_2$O$_4$/Fe$_2$O$_3$-1 sample, the rod-like particles are about 100 nm in length and 40 nm in diameter (Figure 3b). This length tends to increase to 150 nm whereas the diameter tends to decrease to 25 nm for the core-shell material prepared with the molar CuFe$_2$O$_4$/Fe$_2$O$_3$ ratio of 1:2 (Figure 3c). However, when the molar CuFe$_2$O$_4$/Fe$_2$O$_3$ ratio was up to 1:3 (Figure 3d), the rod-like particles were strongly shortened (60–70 nm in length). More specially, in this sample, some rod-like particles seems to be transformed to spherical particles with the size of about 60 nm. This result suggests that loading a very large quantity of Fe$^{3+}$ ions on the surface of CuFe$_2$O$_4$ may reduce the available surface area for the development of Fe$_2$O$_3$ seeds, as a consequence, hindering the growth of rod-like Fe$_2$O$_3$ nanoparticles.

Besides, we also noticed the difference in surface texture between CuFe$_2$O$_4$ and CuFe$_2$O$_4$/Fe$_2$O$_3$-2 samples via FE-SEM images with higher magnification (×200 K). Owing to the presence of randomly distributed rod-like particles, the surface of CuFe$_2$O$_4$/Fe$_2$O$_3$-2 sample (Figure 3f) becomes roughness with more porosity than CuFe$_2$O$_4$ surface (Figure 3e), likely resulting in higher surface area for core-shell materials. In order to better investigate the effect of loading Fe$_2$O$_3$ on the surface morphology of CuFe$_2$O$_4$, the nitrogen adsorption-desorption isotherms analysis was carried out. For CuFe$_2$O$_4$/Fe$_2$O$_3$-2 sample, the BET specific surface area was found to be 11.498 m$^2$g$^{-1}$, which is about ten

| Phase          | CuFe$_2$O$_4$ | CuFe$_2$O$_4$/Fe$_2$O$_3$-1 | CuFe$_2$O$_4$/Fe$_2$O$_3$-2 | CuFe$_2$O$_4$/Fe$_2$O$_3$-3 |
|----------------|--------------|-----------------------------|----------------------------|----------------------------|
| CuFe$_2$O$_4$  | 92.0         | 57.8                        | 46.4                       | 34.2                       |
| CuO (C2/c)    | 8.0          | 7.1                         | 7.1                        | 7.9                        |
| α-Fe$_2$O$_3$  | 35.1         | 46.5                        | 57.9                       |                            |
| CuFe$_2$O$_4$ (R-3c) |            |                             |                            |                            |

Table 1. Phase composition of CuFe$_2$O$_4$, CuFe$_2$O$_4$/Fe$_2$O$_3$-1, CuFe$_2$O$_4$/Fe$_2$O$_3$-2 and CuFe$_2$O$_4$/Fe$_2$O$_3$-3 samples.
times higher than that of CuFe$_2$O$_4$ sample (only 1.159 m$^2$·g$^{-1}$). The enhanced surface area was also observed for ZnO/Fe$_2$O$_3$ hollow nanospheres [Li et al. 2014] and MgFe$_2$O$_4$@SiO$_2$ core shell nanocomposites [Tiwari and Kaur 2020]. These FE-SEM and BET results reinforce the fact that Fe$_2$O$_3$ nanoparticles were successfully bound to the surface of CuFe$_2$O$_4$, making the material surface rougher, thereby increasing the specific surface area.

3.3. Surface functional groups

Figure 4a reveals the FTIR spectra of CuFe$_2$O$_4$ and CuFe$_2$O$_4$/Fe$_2$O$_3$ core-shell materials. The spectrum of CuFe$_2$O$_4$ sample contains a large band at around 3541 cm$^{-1}$ and a weak peak at 1675 cm$^{-1}$, which can be attributed to the stretching and bending vibrations of surface hydroxyl groups, respectively [Huang et al. 2007]. The intensities of these peaks were dramatically reduced for CuFe$_2$O$_4$/Fe$_2$O$_3$ samples, indicating the impacts of Fe$_2$O$_3$ immobilization upon the surface of magnetic core. Furthermore, since CuFe$_2$O$_4$ exhibits an inverse spinel-type structure in which Cu$^{3+}$ ions only occupy octahedral sites whereas Fe$^{3+}$ ions can occupy both tetrahedral and octahedral sites, the FTIR spectrum of our CuFe$_2$O$_4$ sample also shows two peaks in the fingerprint region, corresponding to the metal-oxygen bonds in tetrahedral sites (M$_{tetra}$–O, 596 cm$^{-1}$) and the metal-oxygen bonds in octahedral sites (M$_{octa}$–O, 436 cm$^{-1}$) [Aliyan et al. 2017, Zaki and Dawoud 2010]. However, different from the high intensity of M$_{tetra}$–O peak, the M$_{octa}$–O peak is extremely low. Only when Fe$_2$O$_3$ nanoparticles were introduced, the intensity of the M$_{octa}$–O peak was greatly improved. According to the FTIR absorption spectra (Figure 4b), among different samples, the CuFe$_2$O$_4$/Fe$_2$O$_3$-2 sample shows the most intense M$_{octa}$–O peak, suggesting the highest content of octahedral metal ions on the surface. In addition, when combining Fe$_2$O$_3$ and CuFe$_2$O$_4$, it appears that the M$_{octa}$–O peak shifts to higher wave-numbers (453–457 cm$^{-1}$) whereas the M$_{tetra}$–O peak shifts to lower wavenumbers (539–545 cm$^{-1}$). The results demonstrate that the coating of Fe$_2$O$_3$ on CuFe$_2$O$_4$ can strongly affect the surface functional groups of our materials.

3.4. Magnetic properties

The magnetic hysteresis curves of our samples are depicted in Figure 5a. From these curves, the magnetic parameters such as saturation magnetization, remnant magnetization and coercivity are determined and shown in Table 2. All samples were found to follow the soft ferromagnetic behavior at room temperature with the coercivity values inferior to 100 Oe. Among them, CuFe$_2$O$_4$ sample presents the highest saturation magnetization (42.0 emu·g$^{-1}$) but the lowest coercivity (68.4 Oe). In contrast, CuFe$_2$O$_4$/Fe$_2$O$_3$ core-shell materials exhibit lower M$_{s}$ values and higher H$_{c}$ values, which can be attributed to the presence of antiferromagnetic α-Fe$_2$O$_3$ [Bhowmik and Saravanan 2010] on the surface of CuFe$_2$O$_4$. However, the magnetic properties of our core-shell materials are still good enough to make them easily be separated from the solution by a magnet (Figure 5b).

3.5. Photo-Fenton catalytic activity

The photo-Fenton catalytic performance of CuFe$_2$O$_4$, Fe$_2$O$_3$ and CuFe$_2$O$_4$/Fe$_2$O$_3$ core-shell materials was evaluated through the MB degradation under UVA light and visible light (Figures 6a and 6b, respectively). The apparent rate constant (k) for each sample is calculated using the pseudo-first-order Langmuir-Hinshelwood kinetic model (Figures 6c and 6d). Without our catalysts, the MB concentration remains almost unchanged up to 60 min of UVA irradiation and 3 hours of visible-light irradiation, confirming that MB is resistant to self-photolysis by UVA light and visible light. Additionally, the photocatalytic test without using oxalic acid (only using CuFe$_2$O$_4$/Fe$_2$O$_3$-2 sample) also demonstrated the stability of MB under both UVA light and visible light despite the presence of our catalyst, which suggests that our sample can not act as an effective photocatalyst in the experimental conditions. The photo-Fenton degradation of MB was only observed when our catalysts were combined with oxalic acid. In fact, as shown in Table 3, with oxalic acid as the radical-producing source, CuFe$_2$O$_4$ sample exhibited the rate constants of 0.962 h$^{-1}$ under UVA light and 0.271 h$^{-1}$ under visible light. When CuFe$_2$O$_4$ was replaced by CuFe$_2$O$_4$/Fe$_2$O$_3$ catalysts, the rate constants greatly increased and reached the best values for the CuFe$_2$O$_4$/Fe$_2$O$_3$-2 sample (k = 2.103 h$^{-1}$ and 0.542 h$^{-1}$ under UVA and visible light, respectively). However, when the Fe$_2$O$_3$ content was further enhanced, the rate of MB degradation tended to decrease. These results prove that the photo-Fenton-like catalytic activity of our samples is able to be controlled by the CuFe$_2$O$_4$/Fe$_2$O$_3$ ratios used in catalyst preparation. Moreover, the UV-light-induced catalytic activity is always higher than the visible-light-induced catalytic activity for all catalysts, indicating that the light energy is also a factor affecting their catalytic performance.

In order to verify the stability and the reproducibility of our catalysts, the leaching test and the reuse tests for the CuFe$_2$O$_4$/Fe$_2$O$_3$-2 sample were carried out as follows: after the first photo-Fenton catalytic run with our CuFe$_2$O$_4$/Fe$_2$O$_3$-2 sample and oxalic acid under UVA light or visible light, the catalyst was removed from the solution by a magnet, washed with distilled water and dried at 150°C for 1 hour. Then, the catalyst
Figure 4. FTIR spectra of CuFe\textsubscript{2}O\textsubscript{4}, CuFe\textsubscript{2}O\textsubscript{4}/Fe\textsubscript{2}O\textsubscript{3}-1, CuFe\textsubscript{2}O\textsubscript{4}/Fe\textsubscript{2}O\textsubscript{3}-2 and CuFe\textsubscript{2}O\textsubscript{4}/Fe\textsubscript{2}O\textsubscript{3}-3 samples: (a) transmission mode and (b) absorption mode in the fingerprint region.
was reused for four next consecutive runs in the same conditions. Besides, the iron concentration in the solution of the first run was evaluated by atomic absorption spectrometry (AAS) using Shimadzu AA-6300 spectrometer. Within 0.5 hour under UVA light or 3 hours under visible light, the catalytic performance of the CuFe2O4/Fe2O3-2 sample was only slightly reduced after four-time reuses (Figure 7a). The FE-SEM image also displays that rod-like and spherical Fe2O3 nanoparticles still cover nearly the entire surface of this sample after 5 consecutive catalytic tests (Figure 7b), indicating the reproducibility and the potential of this catalyst for practical applications. Furthermore, the AAS result shows a very low concentration of leached Fe3+ ions (1.56 mg.L−1), suggesting that our heterogeneous catalyst is stable in the experimental conditions and the dissolution of iron species by oxalic acid can be neglected.

**Table 2.** Magnetic parameters of CuFe2O4, CuFe2O4/Fe2O3-1, CuFe2O4/Fe2O3-2 and CuFe2O4/Fe2O3-3 samples.

| Sample                  | Ms (emu.g−1) | Hc (Oe) | Mr (emu.g−1) |
|-------------------------|--------------|---------|--------------|
| CuFe2O4                 | 42.0         | 68.4    | 4.1          |
| CuFe2O4/Fe2O3-1         | 22.3         | 82.1    | 2.5          |
| CuFe2O4/Fe2O3-2         | 19.6         | 82.1    | 2.8          |
| CuFe2O4/Fe2O3-3         | 18.9         | 92.6    | 2.1          |

**Figure 5.** Magnetic hysteresis of CuFe2O4, CuFe2O4/Fe2O3-1, CuFe2O4/Fe2O3-2 and CuFe2O4/Fe2O3-3 samples at room temperature.

**Figure 6.** Comparison of MB degradation on different catalysts: MB degradation curves as a function of time under UVA light (a) and visible light (b), Ln (Ct/C0) versus time plot of MB degradation under UVA light (c) and visible light (d). C is the MB concentration (mol.L−1) at time t and C0 is the initial MB concentration (mol.L−1).
Table 3. Comparison of MB degradation rate constants on different catalysts under UVA light and visible light in the presence of oxalic acid.

| Sample          | CuFe₂O₄ | CuFe₂O₄ | CuFe₂O₄ | CuFe₂O₄ |
|-----------------|---------|---------|---------|---------|
| CuFe₂O₄         | O₄      | O₄      | O₄      | O₄      |
| Rate constant of MB degradation k (h⁻¹) under UVA light | 0.962   | 1.832   | 2.103   | 1.761   | 3.285   |
| Rate constant of MB degradation k (h⁻¹) under visible light | 0.271   | 0.340   | 0.542   | 0.330   | 0.655   |

Finally, Figure 8 compares the TOC evolution versus irradiation time of CuFe₂O₄ and our core-shell CuFe₂O₄/Fe₂O₃-2 sample. It was observed that CuFe₂O₄/Fe₂O₃-2 sample always showed the better TOC removal than CuFe₂O₄ under UVA light and visible light. Nevertheless, for both samples, the TOC removal is slower than the discoloration of MB solution, which indicates that most MB molecules were effective broken by the highly reactive oxygen species but small organic intermediates produced from the MB degradation are difficult to be removed from the solution.

Figure 7. (a) Degradation of methylene blue on CuFe₂O₄/Fe₂O₃-2 catalyst in five consecutive experiments, (b) FE-SEM image of CuFe₂O₄/Fe₂O₃-2 sample after five consecutive catalytic tests.

Figure 8. TOC changes measured during the photo-Fenton catalytic tests of CuFe₂O₄ and CuFe₂O₄/Fe₂O₃-2 samples under UVA light (a) and visible light (b).

4. Discussion

As shown in Figure 6 and Table 3, Fe₂O₃ nanoparticles (without magnetic CuFe₂O₄ cores) exhibited great photo-Fenton catalytic activities for MB degradation (k = 3.285 h⁻¹ under UVA light and k = 0.655 h⁻¹ under visible light). However, since these nanoparticles are antiferromagnetic and well dispersed in the solution, they are difficult to be recovered and reused. In contrast, although CuFe₂O₄ and other ferrite materials can be easily recovered owing to their ferromagnetic properties, their catalytic performance was not high enough for practical applications due to the limited iron species on their surface. Therefore, the combination of Fe₂O₃ and CuFe₂O₄ can be a promising solution for the improvement of magnetic photo-Fenton catalysts. On the other hand, it should be reminded that our catalysts did not display photocatalytic activities in the experimental conditions (using a 9 W Osram Dulux S lamp as visible light source and a 9 W Radium 78 lamp as UVA light source) although in some studies, the authors reported the photocatalytic activity of CuFe₂O₄ materials. For these studies, the authors usually used a 500 W xenon lamp [Zhu et al. 2013] or a 150 W xenon arc lamp [Ismael et al. 2020]. Their
capacity is much higher than that of our lamps (only 9 W). There are also some works on CuFe₂O₄ photocatalysts using a 8 W lamp, but this lamp emits the light in the UVC region [Gupta et al. 2020] whereas our study only uses the UVA lamp and visible lamp. Hence, the photocatalytic activity of our samples can be excluded from this study.

According to the experimental results, via the immobilization of Fe₂O₃ onto CuFe₂O₄ particles, we really improved the photo-Fenton-like catalytic activity of CuFe₂O₄ for the degradation of MB under both UVA light and visible light. This enhancement of activity should be explained by various factors including the change in phase composition, the evolution of morphology and the variations of functional groups on the surface of our catalysts. In fact, the growth of Fe₂O₃ nanoparticles on the surface of magnetic CuFe₂O₄ cores did not only increase the hematite phase in the structure of samples but also modified the distribution of metallic ions on their surface. As displayed in the FTIR spectra, the magnetic CuFe₂O₄ powdered shows an extremely weak M₆octa−O peak, indicating a very limited presence of surface octahedral metal ions (Cu²⁺ and Fe³⁺). In contrast, when the surface of CuFe₂O₄ was coated by Fe₂O₃ nanoparticles, the intensity of this peak remarkably increased, which can be associated with the fact that our Fe₂O₃ nanoparticles crystallize in the corundum structure and contain all Fe³⁺ ions in octahedral sites [Krauschofer et al. 2018, Li et al. 2016]. Interestingly, the M₆tetra−O peak of these CuFe₂O₄/Fe₂O₃ core-shell catalysts contain the high amounts of both tetrahedral and octahedral Fe³⁺ ions on their surface, which can be considered as the main reason for the improvement of photo-Fenton-like catalytic performance. Among all our catalysts, the CuFe₂O₄/Fe₂O₃-2 sample seems to show the highest content of surface Fe³⁺ ions owing to the most intense M₆octa−O and M₆tetra−O peaks in its FTIR spectrum. The enhanced Fe content on the surface of our core-shell catalysts is also supported by the EDX study. In fact, Table 4 shows the surface elemental composition of CuFe₂O₄ and CuFe₂O₄/Fe₂O₃-2 samples taken by EDX spectra recorded at 5 kV. The Fe quantity of CuFe₂O₄ is found to be only 16.60 at% while the Fe content of CuFe₂O₄/Fe₂O₃-2 reaches 23.05 at%. Moreover, when Fe₂O₃ was immobilized on CuFe₂O₄ surface, the surface Cu content was dramatically reduced, from 12.06 at% for CuFe₂O₄ to 0.90 at% for CuFe₂O₄/Fe₂O₃-2. Since all our samples still show the ferromagnetic properties of CuFe₂O₄ particles, we believe that these results support the core-shell structure of our CuFe₂O₄/Fe₂O₃ catalysts.

Generally, the enhanced content of Fe³⁺ ions on the surface of our CuFe₂O₄/Fe₂O₃ catalysts can promote the formation of surface ferrioxalate complexes via the reaction between surface ↔Fe³⁺ ions and H₂CO₃ [Jeong and Yoon 2005, Liu et al. 2012, Ngo TPH and Le TK 2018]. Then, due to light irradiation, these ferrioxalate complexes will be excited to produce numerous radicals such as C₂O₄−²⁻, O₂− and OH (eq. 1–4) [Liu et al. 2012, Mulazzani et al. 1986], which are both highly reactive and thus able to degrade effectively MB molecules in solution. Therefore, the best performance of CuFe₂O₄/Fe₂O₃-2 catalyst is likely attributed to the highest surface Fe³⁺ content of this sample.

\[
\begin{align*}
\text{[Fe(C₂O₄)₂]}^3+ + \text{hv} & \rightarrow \text{Fe}^{2+} + C₂O₄^- (1) \\
C₂O₄^- + O₂ & \rightarrow O₂^- + 2CO₂ (2) \\
\text{Fe}^{3+} + O₂^- + H₂O & \rightarrow \text{Fe}^{2+} + H₂O₂ + \text{OH}^- (3) \\
\text{Fe}^{2+} + H₂O₂ & \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}^- (4)
\end{align*}
\]

Secondly, when Fe₂O₃ nanoparticles were combined with CuFe₂O₄, the specific surface area of our catalysts was strongly enhanced (about ten times higher than that of CuFe₂O₄). This can increase the reactive sites on their surface, leading to the enhancement of their photo-Fenton-like activity. Moreover, we also noticed a sound correlation between the shape of Fe₂O₃ particles and the catalytic activity. Depending on the molar CuFe₂O₄/Fe₂O₃ ratios, the Fe₂O₃ particles could be transformed between the spherical shape and the rod-like morphology. It seems that the rod-like Fe₂O₃ particles in CuFe₂O₄/Fe₂O₃-1 and CuFe₂O₄/Fe₂O₃-2 samples showed the better performances than the spherical Fe₂O₃ particles in CuFe₂O₄/Fe₂O₃-3 catalyst. Although the reason for the enhanced activities of rod-like particles is still unclear and needs to be further studied, this phenomena was also observed in some previous works [Chaudhari et al. 2012, Liang et al. 2015]. Chaudhari et al. compared the peroxidase mimic activity of hematite iron oxides with different nanostructures, including hexagonal prism, cube-like and rod-like particles, and found that the rod-like particles showed the best activity [Chaudhari et al. 2012]. Likewise, Liang et al. reported that the photocatalytic degradation of rhodamine B can be improved when using X-shaped α-Fe₂O₃ nanocrystals which are composed of two rod-

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**Table 4. Surface elemental composition of CuFe₂O₄ and CuFe₂O₄/Fe₂O₃-2 samples.**

| Surface elemental composition (atomic %) | C | O | Fe | Cu |
|----------------------------------------|---|---|----|----|
| CuFe₂O₄                               | 7.80 | 63.55 | 16.60 | 12.06 |
| CuFe₂O₄/Fe₂O₃-2                       | 12.28 | 64.58 | 23.05 | 0.09 |
5. Conclusion

In summary, we successfully developed a new and effective magnetic photo-Fenton-like catalysts based on the immobilization of Fe$_2$O$_3$ nanoparticles on the surface of CuFe$_2$O$_4$ particles. These core-shell materials exhibited excellent activities for the degradation of methylene blue in the presence of oxalic acid under both UVA light and visible light. Among them, the CuFe$_2$O$_4$/Fe$_2$O$_3$-2 catalyst show the best catalytic performance, which can be assigned not only to the highest surface Fe$^{3+}$ content of this sample but also to the high specific surface area and the presence of Fe$_2$O$_3$ rod-like particles immobilized on the surface of its magnetic CuFe$_2$O$_4$ cores. Moreover, owing to the presence of magnetic CuFe$_2$O$_4$ cores, our core-shell catalysts can be easily separated from the solution and recovered by using a magnet, making them suitable for practical applications.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Availability of data and materials

Not applicable.

Conflict of interest

The authors declare that they have no conflict of interest.

Authors’ contributions

All authors are individually mentioned in the author contribution statement. Thu Uyen Tran Thi prepared the samples and the manuscript. Van Hung Phan estimated the catalytic activity of samples. Huu Thinh Pham Nguyen analyzed the FTIR spectra and FESEM images of samples. The Luan Nguyen analyzed the XRD results and interpreted the data. An Nang Vu measured the magnetic properties of samples. Tien Khoa Le developed the ideas and was a major contributor in organizing the manuscript. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Disclosure Statement

No potential conflict of interest was reported by the author(s).

Funding

This research is funded by Vietnam National University, Ho Chi Minh City (VNU-HCM) under grant number C2020-18-08.

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