Comparison of the photocatalytic efficacy and environmental impact of CdS, ZnFe$_2$O$_4$, and NiFe$_2$O$_4$ under visible light irradiation

Xiaoyu Wang, Susan J. Masten and Elaheh Esfahanian

ABSTRACT

Three photocatalysts (CdS, ZnFe$_2$O$_4$, and NiFe$_2$O$_4$) were synthesized and their ability to photodegrade methylene blue (MB) was evaluated. MB was degraded by both spinel photocatalysts under visible light at room temperature, although their efficacy was less than that for CdS. The photocatalytic efficacies of NiFe$_2$O$_4$ were observed to be much greater than that for ZnFe$_2$O$_4$. All the synthesized nanoparticles absorbed visible light, while CdS had a larger absorption range within the visible light spectra and the most porous surface. Photo-deactivation was observed during the study, which could be due to the chemical adsorption of the degraded products on the catalyst surface. The factors that affected MB removal efficacy include the absorption range of photocatalysts, initial MB concentrations, amount of photocatalysts added, and photoreactor conditions. Life cycle analysis was used to compare the preparation methods of the photocatalysts in terms of energy consumption and environmental impact. The results showed that the hydrothermal method for NiFe$_2$O$_4$ preparation was less energy-intensive than the sol-gel method for CdS and ZnFe$_2$O$_4$ as the hydrothermal method is effective over a wider range of temperatures in aqueous media. Also, as ZnFe$_2$O$_4$, and NiFe$_2$O$_4$ have lower environmental impacts than CdS both show promise as photocatalysts.

Key words | life cycle assessment, photocatalytic degradation, spinel photocatalysts, water purification

HIGHLIGHTS

- CdS, ZnFe$_2$O$_4$, and NiFe$_2$O$_4$ degraded methylene blue.
- Adsorption of photodegradation products likely caused photo-deactivation.
- Life cycle analysis showed that hydrothermal method for NiFe$_2$O$_4$ preparation was less energy-intensive than the sol-gel method for CdS and ZnFe$_2$O$_4$. 

This is an Open Access article distributed under the terms of the Creative Commons Attribution Licence (CC BY-NC-ND 4.0), which permits copying and redistribution for non-commercial purposes with no derivatives, provided the original work is properly cited (http://creativecommons.org/licenses/by-nc-nd/4.0/). 

INTRODUCTION

The effluent of manufacturing industries results in the release of numerous recalcitrant chemicals, including dyes. Physiochemical treatment technologies such as adsorption, coagulation, and membrane filtration simply transfer the target dye compounds from water but do not degrade the molecules (Janus & Morawski 2007; Chaari et al. 2019; Maknakorn et al. 2019). Additionally, the regeneration of adsorptive capacity and the post-treatment of concentrated wastes are expensive (Galindo et al. 2001; El-Dein et al. 2019; Maknakorn et al. 2019). Organic dyes such as methylene blue (MB) are aromatic compounds, and conventional biological treatment methods are not very effective for their degradation (Janus & Morawski 2007). Moreover, as many organic dyes are recalcitrant, conventional biological treatment is ineffective (Janus & Morawski 2007) and energy-intensive (Liu et al. 2004). Ozone and chlorination are used for the removal of dyes; however, operating costs are high (Slokar & Marechal 1998; Venkatesh et al. 2017) and chlorination may result in toxic chlorinated byproducts (Karnik et al. 2005; Oliveira et al. 2006; Vacchi et al. 2013). Therefore, there is a need to develop more cost-effective and environmentally benign methods for the degradation of dye effluents. Developing ways to efficiently remove dyes from wastewater yet minimize energy consumption is of increasing interest (Sun et al. 2014). As such, the development of photocatalysts that utilize solar light energy for the photodegradation of organic compounds present in water and wastewaters is of particular importance.

As photocatalytic degradation of environmental contaminants using UV-light is an energy-intensive process, there has been intense interest in developing semiconductor photocatalysts that utilize solar energy. Fossil fuels are being rapidly consumed resulting in various environmental concerns including climate change, air pollution, etc., while solar energy is safe and abundant (Gasser et al. 2015; Larcher & Tarascon 2015). As mentioned before, conventional wastewater treatment is energy-intensive (Liu et al. 2004).

Developing ways to effectively treat wastewater yet minimize energy consumption is of increasing interest (Sun et al. 2014). The application of photocatalytic processes that utilize solar light energy for the photodegradation of organic compounds present in water and wastewaters is particularly important. More than 50 types of organic compounds or waste products that potentially could be photodegraded include organic dyes, sugars, alcohols, aldehydes, ketones, and organic acids (Chen et al. 2010a, 2010b).

Based on previous studies, the efficiency of photocatalysts for the degradation of environmental contaminants is affected by such factors as the type of photocatalyst, illumination time, the particle size of photocatalyst (Xu et al. 2013), band gap, oxidizing agents, calcination temperatures, and catalyst loadings (Daneshvar et al. 2004; Akpan & Hameed 2009). Photocatalytic degradation is an oxidation-reduction reaction. When the catalyst is irradiated and absorbs photons of energy greater than or equal to its bandgap, electrons move from the valence band to the conduction band, resulting in the formation of an electron (e\(^-\)) and holes (h\(^+\)). The electrons (e\(^-\)) are generated at the conduction band and holes (h\(^+\)) are collected at the valence band. The electrons can react with electron acceptors on the surface of catalysts. The generated holes can oxidize the molecules on the photocatalysts surface or oxidize OH\(^-\) and H\(_2\)O into -OH radicals, a strong oxidizing agent that is capable of oxidizing many dyes (Konstantinou & Albanis 2004).

Huang et al. (2020) synthesized Z-scheme heterojunction TiO\(_2\) for enrofloxacino photocatalytic degradation under visible light and proved the efficiency. Pirhashemi & Habibi-Yangjeh (2017) prepared ZnO/Ag/Ag\(_2\)WO\(_4\) nanoparticles by an ultrasonic-assisted method and investigated the photocatalytic degradation of Rhodamine B (RhB) using visible light. The results demonstrated that O\(_2\), h\(^+\)
and OH had a major influence on the degradation reaction, and the degradation ability of O$_2$ was greater than that of h$^+$ and OH species generated using ZnO as a photocatalyst. On the other hand, Daneshvar et al. (2004) studied the photocatalytic degradation of azo dye acid red 14 with ZnO using UV light and found that hydroxyl radicals were the main reactive species and that positive holes were involved in the reactions. Moreover, the results of Daneshvar et al. (2004) also indicated that the degradation efficiency of acid red 14 was affected by illumination time, pH, and the mass of photocatalyst. The rate of photodegradation increased with the addition of hydrogen peroxide but was inhibited with the addition of ethanol. Sapkota et al. (2020) analyzed nanocomposites of copper oxide and single-walled carbon nanotubes for the degradation of methylene blue and the photocatalysts showed great photocatalytic performance.

This study compared the efficacy and kinetics of three photocatalysts (CdS, ZnFe$_2$O$_4$, and NiFe$_2$O$_4$) under solar irradiation. MB was chosen as the model contaminant as its concentration is easily quantified. Cadmium sulfide was chosen as a baseline photocatalyst as it has been extensively studied due to its activity under visible-light and potential to degrade organic contaminants resulting in hydrogen production (Yan et al. 2009; Soltani et al. 2012). ZnFe$_2$O$_4$ and NiFe$_2$O$_4$ were chosen as they are environmentally benign spinel semiconductors minerals. The surface properties and absorption spectrum of the photocatalysts were determined. The impact of the concentration of MB on removal efficiencies was examined. Moreover, the kinetics and photo-degradation properties of CdS as a photocatalyst were studied. Numerous studies have investigated the photocatalytic degradation of a variety of dyes, and various kinds of photocatalysts have been synthesized by different methods. This research quantitatively assesses the photocatalysts and their synthesis methods in terms of energy consumption and environmental impacts. Using the principles of life cycle assessment (LCA), the preparation methods for the photocatalysts can be compared in order to develop and implement new technologies that incorporate green chemistry and are environmentally friendly and sustainable.

**MATERIALS AND METHODS**

**Materials preparation**

All chemical reagents used in this experiment were obtained from Alfa Aesar (Tewksbury, MA, US), and of analytical grade.

**Synthesis of CdS**

CdS was prepared according to the hydrothermal method (Yan et al. 2009). A sodium sulfate (Na$_2$S, 99%) solution (300 mL, 0.14 M) was added slowly to a cadmium acetate (Cd(OAc)$_2$, 99%) solution (300 mL, 0.14 M) under vigorous stirring. A yellow precipitate formed. The mixture was stirred for 24 h, allowed to settle for 1 day, and then filtered through a 20 µm pore size filter. The yellow solid was then suspended in pure water (120 mL) and transferred to a Teflon-lined stainless-steel autoclave (150 mL) and heated at 200°C for 72 h (hydrothermal treatment). The yellow solid was filtered, washed with water and ethanol subsequently, filtered again, and kept in a desiccator in the dark at room temperature until use.

**Synthesis of ZnFe$_2$O$_4$**

ZnFe$_2$O$_4$ was prepared by the sol-gel method (Zhang et al. 2013): 0.016 mol of Fe(NO$_3$)$_3$·9H$_2$O (99.999%) and 0.008 mol of Zn(NO$_3$)$_2$·6H$_2$O (98%) were dissolved in 20 mL deionized water. Citric acid (0.036 mol) was then dissolved in the suspension. While the suspension was magnetically stirred at 60°C, 12 mL ammonia (25% wt ratio) was added dropwise to adjust the pH of the aqueous mixture to 7.0, and the mixture became a sol during this process. After stirring for about 6 h, the sol became a black gel. The gel was then dried at 120°C for 12 h, during which its volume expanded about 10-fold. The dried gel was ground and calcined at 700°C for 4 h until a brown product formed. The product was kept in a desiccator in the dark at room temperature until use.

**Synthesis of NiFe$_2$O$_4$**

Synthesis of NiFe$_2$O$_4$ was carried out by the hydrothermal method in a stainless-steel autoclave. Ni(NO$_3$)$_2$·6H$_2$O (98%) (0.001 mol) and FeSO$_4$·6H$_2$O (reagent grade)(0.002 mol) was dissolved separately in 100 mL of deionized water. Then 0.036 mol of citric acid powder was dissolved in the suspension. The mixed suspension was precipitated with the addition of 1 M NaOH solution until pH was 9.7, followed by the addition of 0.1 g of isopropyl alcohol under constant and vigorous magnetic stirring for 5 min. The suspension was poured into the stainless-steel autoclave for hydrothermal treatment. The temperature was controlled at 100°C for 3 h, and then cooled to room temperature. Finally, the product was washed several times with absolute ethanol and then dried in a desiccator for 24 h to obtain Ni-ferrite nanoparticles.
Photocatalysts characterization

During SEM analysis, the photocatalysts samples were mounted on aluminum stubs using high vacuum carbon tubes (SPI Supplies, West Chester, PA). Samples were coated with iridium to an approximate thickness of 2.7 nm in a Q150T turbo pumped sputter coater (Quorum Technologies, Laughton, East Sussex, England BN8 6BN) purged with argon gas. The size and morphology of the photocatalyst samples were examined in a LEOL 7500F (field emission emitter) scanning electron microscope (JEOL Ltd, Tokyo, Japan) operated at an accelerating voltage of 5 kV. The absorption spectra of the photocatalysts were investigated by a UV–vis spectrophotometer (Shimadzu, UV-2600, Japan) in the wavelength range from 200 to 800 nm and measured every 1 nm.

Evaluation of efficacy of photocatalysts

Photoreactions were performed in a Pyrex glass reactor containing the MB solution. The initial concentration varied between 2 and 20 μmol/L. A selected amount of photocatalyst (CdS, ZnFe2O4, NiFe2O4) was added to the solution. The photoreactor was illuminated using a solar simulator (Abet Technologies’ model 11002 SunLite™, Milford, Connecticut, US), ozone-free Xe Arc Lamp of 100 W, transmitting λ > 420 nm at room temperature, with continuous stirring for 4 h (batch system). Samples (10 mL) were collected at 0 min, 5 min, 10 min, 30 min, 1 h, 1.5 h, 2 h, 3 h, and 4 h. At the end of the experiment, MB concentrations were determined by visible spectroscopy (Shimadzu, UV-2600, Japan) at its absorption peak (665 nm) after centrifugation at 3,200 rpm (Clay ADAMSTM, COMPACT II CENTRIFUGE). The efficacy of all three photocatalysts was evaluated using MB as the target chemical. The absorption peak of MB is 665 nm. The initial concentration of the MB was controlled at 8 μmol/L.

Energy and environmental impact analysis of three photocatalysts

Life cycle assessment (LCA) was used to evaluate the energy costs and environmental impacts of the preparation of the three photocatalysis to explore the sustainability during the process. Laboratory instruments and equipment such as glassware, magnetic stirrer, and oven were not included within the system boundary. No transportation costs were considered as all synthesis chemicals were assumed to be bought from the same manufacturer. One gram of photocatalyst was selected as the functional unit, and the flows and processes involved were normalized to the functional unit accordingly. For chemical inputs not included in proprietary Life Cycle Inventory (LCI) databases, precursor chemicals that were included in proprietary LCI databases were used in the analyses. For example, Fe(NO3)2·6H2O, Ni(NO3)2·6H2O, and Zn(NO3)2·6H2O were assumed to be prepared by dissolving ferrite, nickel or zinc in nitric acid and then combining the product with formaldehyde and ammonia (Papadaki et al. 2017). The cumulative energy demand method was used to quantify energy consumption. The Eco-indicator method was applied to normalize the impact analysis and present the result quantitatively.

RESULTS

SEM analysis

The SEM images of CdS, ZnFe2O4, and NiFe2O4 are shown in Figure S1 in the supplementary materials. The particle size for CdS ranged from 50–400 nm (Figure S1(a)). ZnFe2O4 was mainly composed of spherical grains with sizes of 50–400 nm (Figure S1(b)), and the majority of particles were in the range of 75–190 nm. NiFe2O4 particles ranged in size from 50–700 nm (Figure S1(c)). The surface of the NiFe2O4 appeared to be more porous, and small particles adhered to large irregular particles, probably due to the magnetic characteristics of NiFe2O4, resulting in a wide variety of particle sizes.

UV–vis analysis

UV–vis spectroscopy was used to investigate the absorptive properties of the catalysts. The results are shown in Figure S2 in the supplementary materials. All photocatalysts absorbed light in the visible range. The absorption peaks of synthesized CdS, ZnFe2O4, and NiFe2O4, were at 512 nm, 564 nm, and 291 nm, respectively. The absorption edges of CdS and ZnFe2O4 were at ~770 nm, and that of NiFe2O4 was at ~500 nm, respectively. CdS and ZnFe2O4 nanoparticles had the widest absorption range. NiFe2O4 had a relatively narrow visible light absorption range with most absorption occurring at wavelengths less than 500 nm.

The spectra also showed that the formulated CdS and ZnFe2O4 had excellent absorption in the wavelength range...
from 210 to 800 nm. According to Lv et al. (2010), the transition of photoexcited electrons from the 2p level of O into the 3d level of Fe can explain the absorption of visible light with ZnFe$_2$O$_4$, with the assumption that the O 2p orbital serves as the valence band and the Fe 3d orbital acts as the conduction band. For NiFe$_2$O$_4$, Ni$^{2+}$ and Fe$^{3+}$ also occupy the tetrahedral and octahedral sites (Ceylan et al. 2008).

Photocatalytic degradation of MB

MB removal efficiencies by different photocatalysts

The amount of photocatalyst used in this set of tests was controlled at 1.0 g/L. The kinetics of disappearance of MB by various photocatalysts are shown in Figure 1. During illumination, MB concentrations decreased rapidly initially; the rate decreased after 100 min. The decrease in reaction rate is consistent with the hypothesis that as products are formed, they also absorb light, resulting in a reduction in the rate of photolysis of MB.

After 4 h, the removal efficiencies of MB were greatest for CdS > NiFe$_2$O$_4$ > ZnFe$_2$O$_4$. A direct comparison of the removal efficiency of the photocatalysts after 4-h treatment can be found in the supplementary material. The reason for the greater photocatalysis rate with CdS was likely due to the wide visible absorption range of CdS. As such, during irradiation, CdS nanoparticles could utilize a wider range of photon energy than the other photocatalysts. The surface properties of the photocatalysts also affected photocatalysis removal efficiency. In this case, CdS had a relatively higher removal efficiency comparing with ZnFe$_2$O$_4$ and NiFe$_2$O$_4$, while CdS had a wider visible light absorption range, and more porous surfaces, resulting in a larger surface:volume ratio and a greater surface area, with more positions for MB adsorption and oxidation. When comparing NiFe$_2$O$_4$ and ZnFe$_2$O$_4$, although ZnFe$_2$O$_4$ had a wider absorption range based on UV-vis analysis, the surface of the NiFe$_2$O$_4$ appeared to be more porous. As a result, it is likely that the MB molecules were more easily attached to the surface, thereby increasing the degradation efficiency of NiFe$_2$O$_4$.

Our results showed significantly higher removal efficiencies for MB compared to that of Chen et al. (200a, 200b) who synthesized ZnFe$_2$O$_4$ (size at 15 nm) using hydrothermal method and obtained removal efficiencies for MB under visible light of 8%. However, Abazari & Mahjoub (2017) developed a route for the synthesis of quite spherical $\beta$-AgVO$_3$/ZnFe$_2$O$_4$ and obtained an efficiency for MB removal at 70%, suggesting that alternative preparation methods could result in significant improvement in the removal efficiency of MB. Similarly, Singh et al. (2017) prepared magnetic NiFe$_2$O$_4$ photocatalyst supported on nitrogen doped graphene and observed >90% removal efficiency for MB. This suggests significant promise for the spinel photocatalysts when prepared using these alternative methods.

Effect of the initial concentration of MB on removal efficiencies

The effect of the initial concentration of MB was determined by varying the initial concentration of MB between 2 and 20 $\mu$mol/L using ZnFe$_2$O$_4$ as photocatalyst. The mass of ZnFe$_2$O$_4$ photocatalyst remained constant at 1 g/L. The pH of the solutions was at 7.7 ± 0.32. The solutions contained only MB and photocatalysts; no pH buffer was added. ZnFe$_2$O$_4$ was chosen for this experiment since it had the lowest removal efficiency at 8 $\mu$mol/L and we sought to determine how the removal efficiency depended on initial concentration.

As shown in Figure 2, the efficacy of photodegradation decreased as MB concentration increased. As the MB concentrations were increased, the concentration of photocatalysts available to provide the electron loop necessary for oxidation became rate-limiting. Moreover, higher concentrations of photocatalysts increased the turbidity of the solution, which decreased the light penetration in the system, and affected photon utilized efficiency. The lowest concentration (2 $\mu$mol/L MB) had the highest removal efficiency (31.5%), and it was twice that observed when the
initial MB concentration was 20 μmol/L. Since the turbidity increased with initial concentration, similar results would be anticipated for both CdS and NiFe₂O₄ photocatalysts.

The effect of reactor size and the concentration of photocatalysts on MB removal efficiency

Since the removal of MB was greatest with CdS, further studies were conducted with it. The effect of reactor size was studied using two Pyrex glass reactors with two different diameters (9.8 cm outside diameter (OD) and 8.6 cm OD). The initial MB and CdS concentrations were 8 μmol/L and 1 g/L, respectively. All other conditions were the same. The photoreactors were illuminated with continuous stirring for 4 h. As Figure 3(a) shows, the removal efficiency was significantly greater in the reactor with a smaller diameter. The reason for this is that light is more effectively transmitted through the annular space of the smaller diameter reactor.

The effect of different amounts of CdS (1 g/L and 0.5 g/L) under visible light illumination with continuous stirring for 4 h (batch system) was investigated. As shown in Figure 3(b), 0.5 g/L CdS nanoparticles resulted in higher removal efficiency of MB under visible light as compared to 1 g/L of the same nanoparticles. Although the availability of active sites increased as the mass of CdS increased, there was a concomitant increase in the turbidity and a decrease in photon penetration as a result of increased scattering effect, resulting in a decrease in photodegradation activity, consistent with the findings of Kartal et al. (2001) and Gonçalves et al. (1999).

MB degradation kinetics by CdS

The kinetics of the photodegradation of MB by CdS occurred via a two-stage reaction (Xu & Wang 2011). During the first stage (0–10 min), there is a rapid degradation according to zero-order kinetics with a reaction rate of 0.022 ± 0.00297 M/min. The initial conditions for the MB solution was with 8 μmol/L of MB with 0.5 g/L CdS as the photocatalyst. The reaction rate should not be dependent on the concentration of MB, but on the number of available ‘holes’ on the surface of the catalyst. During this stage, it is likely that the catalyst absorbed energy from photons and formed e⁻ and h⁺. The rate of photodegradation is determined by the number of ‘holes’ generated on the surface of the catalyst. After 10 min, a first-order reaction and a lower reaction rate were observed, with a reaction rate constant of 0.0095 ± 0.00176 min⁻¹. In the second stage, the degradation reaction rate depends on both the number of available ‘holes’ and the concentration of MB. While a sufficient number of ‘holes’ would likely have
been generated at the catalyst surface, the degradation rate is limited by the rate of attachment of the MB molecules to the catalyst surface.

**Proposed MB photodegradation routes**

The proposed mechanism of MB degradation by the CdS photocatalyst is shown below. Electrons in the valence band are activated by the absorption of a photon with sufficient energy and ‘jump’ to the conduction band. Electrons and holes are then generated in the conduction band and valence band, respectively. As mentioned, there are two possible routes for MB degradation: MB molecules attach to the surface of the photocatalyst are oxidized (as reaction (1) shows), or MB reacts with hydroxyl radicals that are produced by a Fenton process in the solution (as reactions (2) and (3) show). To investigate the oxidation process, tert-butyl alcohol was added as a hydroxyl radical scavenger. The initial concentrations of MB and tert-butyl alcohol were both 8 µmol/L. The concentration of tert-butyl alcohol was measured by UV-vis at its maximum peak (290 nm). The photodegradation spectra from before and after the 4-h test are shown in Figure S3 in the supplementary materials. The absorption peak of MB occurred at 665 nm, and that of t-butyl alcohol at 290 nm. After 4 h of treatment, the absorbances of both MB and t-butyl alcohol peak (at 665 and 290 nm, respectively) decreased, and a significant increase showed in the absorbances of both chemicals at ~200 nm, presumably due to the byproducts formed during the process.

\[
\begin{align*}
\text{CdS} + h\nu & \rightarrow e_{CB}^- + h_{VB}^+ \\
R + h^+ & \rightarrow R^+ \rightarrow \text{degradation} \\
(H_2O \leftrightarrow H^+ + OH^-) + h^+ & \rightarrow H^+ + OH^- \\
R + OH^- & \rightarrow R'(\text{degraded}) + H_2O \\
(O_2)_{\text{ads}} + e^- & \rightarrow O_2^- \\
O_2^- + H^+ & \rightarrow HO_2^- \\
2HO_2^- & \rightarrow H_2O_2 + O_2 \\
H_2O_2 + e^- & \rightarrow OH^- + OH^- \\
R + OH^- & \rightarrow R'(\text{degraded}) + H_2O
\end{align*}
\]

Figure 4 shows the effects of radical scavenger (8 µmol/L tert-butyl alcohol) on the degradation of MB with CdS as the photocatalyst. Based on the removal efficiency during the time, 0–10 min, the MB degradation rate was unaffected by the addition of tert-butyl alcohol. This result is consistent with the hypothesis that during the first stage of reaction, MB molecules are oxidized predominantly by the $h^+$ on the surface of CdS nanoparticles. However, after 30 min, the degradation of MB slowed and was inhibited by the presence of t-butanol. At the end of the 4 h experiment, MB removal efficiency decreased from 91.7% to 61.0%, indicating that about 30% of MB degradation by CdS was oxidized by hydroxyl radicals in the solution.

**Photo-deactivation**

Photo-deactivation tests were performed in the same reactor as photoreactions. The initial concentration was controlled at 8 µmol/L for all dark controlled tests, illumination tests, first and second illumination tests. The photocatalysts (CdS, ZnFe$_2$O$_4$, NiFe$_2$O$_4$) were added to the MB solution at a concentration of 0.5 g/L. For each 4-h test, the experiment process was the same as that earlier except as noted herein. For all photocatalysts deactivation tests, Group 1 was set as a control group. During the first 240 mins, the Group 1 test was conducted without illumination. After adjusting the initial MB concentration to 8 µmol/L and the temperature to the room temperature (25 °C), as the first run, the second 4-h test was conducted under illumination. For Group 2 test, there were two sequential tests at 240-min illumination treatment (three sets of tests when ZnFe$_2$O$_4$ was used as photocatalysts). Between each test, MB concentrations were adjusted back to 8 µmol/L. The removal efficiency at each time point is shown below in Figure 5.

Photocatalysis deactivation happens when electron excitation is inhibited, the target contaminant cannot contact...
the surface of photocatalysts, or the formation of hydroxyl radical is interrupted. The chemical adsorption of MB molecules onto photocatalysts has been reported to be a crucial intermediate step during photocatalysis degradation (Zhang et al. 2014). Figure 5(a) shows the degradation of MB during sequential treatment. It is obvious that during the second illumination treatment, there was a significant decrease in degradation efficiency. Moreover, the deactivation of CdS happened only after the first illumination. Stirring for 4 h in the dark did not affect the MB photodegradation removal efficiency. During the second illumination treatment, the rapid decrease in the first few minutes was not observed. Degradation occurred according to first-order kinetics with the reaction rate constant of $0.0032 \pm 0.0014$ min$^{-1}$. The decrease in reaction rate and efficiency could be due to the chemical adsorption of the degraded products, which blocked the sites of the catalyst surface. For NiFe$_2$O$_4$, as Figure 5(b) shows, there was MB degradation in the dark, which means there was not only photodegradation for MB and NiFe$_2$O$_4$ but also other reactions between them. Moreover, during the second 4-h illumination tests, there were obvious decreases in removal efficiency. The surface of NiFe$_2$O$_4$ was porous, according to SEM scanning, so the removal of MB was probably due to adsorption. The kinetics of MB removal by NiFe$_2$O$_4$ showed a Langmuirian type absorption. As Figure 5(c) shows, after two run tests, the removal efficiency of MB by ZnFe$_2$O$_4$ was maintained during the third test, which suggests that ZnFe$_2$O$_4$ is comparatively stable as a photocatalyst (compared to NiFe$_2$O$_4$).

**Surface comparison of before and after photo-treatment**

Before treatment, CdS particles appeared spherical while NiFe$_2$O$_4$ particles were more like needle-shaped particles that aggregated together. The photocatalysts after treatment were collected through centrifugation and filtration. By comparing the SEM images of photocatalysts before and after MB degradation treatment, it turned out that there was no major structural change in the smaller CdS nanoparticles. The larger particles were pulverized after 4-h treatment, probably because of the friction force during stirring. The cracks shown in the after-treatment images were formed during suction filtration. The SEM images of CdS and NiFe$_2$O$_4$ before and after 4 h of illumination treatment are shown in the supplementary material S7.
Energy-dispersive X-ray spectroscopy (EDS) was used to analyze element composition after photo-treatment of mixed photocatalysts, as Figure 6 shows. Lacey carbon tape was not applied during sample preparation for EDS. According to EDS analysis, in addition to the elements of which the photocatalysts were comprised, there was carbon detected on the surface of photocatalysts, possibly from absorbed degradation products from MB. This supports the hypothesis that the decreases in reaction rate and efficiency could be due to the chemical adsorption of the degraded products, which blocked the sites on the catalyst surface.

**Energy costs and environmental impacts**

The preparation of CdS, ZnFe$_2$O$_4$, and NiFe$_2$O$_4$ photocatalysts was examined for their energy costs and environmental impact, respectively. The energy consumption of the CdS, ZnFe$_2$O$_4$, and NiFe$_2$O$_4$ photocatalysts during preparation, which was evaluated by the cumulative energy demand method, whereas the normalized environmental impacts of the three photocatalysts were calculated by eco-indicator method. Figure 7 shows the results of the energy cost analysis using 1 g of the photocatalyst as the functional unit. Figure 7 shows the normalized environmental impacts of the three photocatalysts calculated by eco-indicator. Normalized results transformed values by the selected reference values, and higher normalization numbers mean greater impacts.

As Figure 7 shows, the preparation of CdS and ZnFe$_2$O$_4$ was more energy-intensive than that of the NiFe$_2$O$_4$. The figure also shows that most of the energy required to prepare ZnFe$_2$O$_4$ was due to length of time it must be heated (700 °C for 4 h) to achieve calcination, which was used to improve
the crystallinity and therefore the photoactivity of the material (Zhang et al. 2000). Since a lower temperature was used during the preparation of NiFe2O4, less energy was required than for the preparation of the other photocatalysts. Most of the energy consumed during photocatalyst preparation was due to electricity production. Energy consumption due to materials extraction was only a small portion of that required for photocatalyst preparation (6.49%, 1.31%, and 2.82% for CdS, ZnFe2O4, and NiFe2O4, respectively). CdS materials had a higher environmental impact than the other two photocatalysts.

Figure 8 illustrates the environmental impact of the three photocatalysts. As shown in the figure, the preparation of CdS had an overall higher normalized environmental impact than that for either ZnFe2O4 and NiFe2O4, with higher impacts due to acidification and eutrophication, carcinogenic chemicals, climate change, and respiratory effects. NiFe2O4 had the highest environmental impact of the three photocatalysts for mineral extraction. For the preparation of all three photocatalysts, the impacts of respiratory effects and mineral extraction were greater than the other impacts due to acidification, eutrophication, carcinogenic chemicals, and climate change. While nickel is an essential trace element in animals, it has the disadvantage of being toxic and has a drinking water maximum contaminant level of 0.1 mg/L in the United States. Zinc ferrite has the advantage of being comprised of earth-abundant materials, it does not corrode easily, and Fe and Zn are both essential nutrients and relatively non-toxic to humans (Plum et al. 2010), making them ideal semiconductor photocatalysts. Based on the results, the photocatalytic efficiency of CdS was the greatest compared with ZnFe2O4 and NiFe2O4, however, it had a higher environmental impacts. As the primary task of photodegradation was to reduce the potential pollution due to textile dyes such as MB, with lower energy, economic and environmental costs, the CdS usage would not be recommended. NiFe2O4 and ZnFe2O4 are recommended for further study in a pilot treatment system because of its degradation efficiency and lower environmental impacts. Moreover, ZnFe2O4 had a great stability compared to CdS and NiFe2O4.

CONCLUSIONS

In this study, CdS, ZnFe2O4, and NiFe2O4 materials were synthesized by the hydrothermal method and the sol-gel method. MB was successfully decolorized and degraded by all three photocatalysts under visible light at room temperature with an order of degradation of CdS > NiFe2O4 ≥ ZnFe2O4. CdS had the widest absorption range, compared to NiFe2O4 and ZnFe2O4, with a more porous surface, which allowed each nanoparticle to have more positions for MB adsorption and oxidation. About 30% of MB degradation by CdS was oxidized by hydroxyl radicals produced by photocatalysis and 70% of MB molecules were directly oxidized by electron transfer on the surface of the photocatalysts. The efficacy of MB removal was also affected by the initial concentrations of MB, the amount of photocatalyst added, and photoreactor design. The removal efficiency of MB decreased as MB concentration increased, so when designing photodegradation systems, it is important to not only consider the photocatalyst, but also the concentration.
of contaminants in the feed water, shape and size of the photocatalyst, and amounts of nanoparticles added. In terms of energy cost and environmental impacts, the hydrothermal method was less energy-intensive than the sol-gel method as the hydrothermal method is effective over a wider range of temperatures in aqueous media. Moreover, based on the results of this study, as ZnFe2O4 and NiFe2O4 have lower environmental impacts than CdS, both show promise as photocatalysts.

ACKNOWLEDGEMENTS

The research was supported by the MSU Discretionary Funding Initiative; MSU College of Engineering; Department of Civil and Environmental Engineering.

DATA AVAILABILITY

All data, models, and code generated or used during the study appear in the submitted article.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES


First received 3 July 2020; accepted in revised form 18 January 2021. Available online 1 February 2021.