Zinc Ferrite Nanoparticles in Photo-Degradation of Dye: Mini-Review

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Abstract: Organic pollutants are the largest kind of pollutants released into waters and wastewater from the some industry and industrial processes. Photocatalytic degradation is one of the significant and effective methods to remove the dyes and other organic pollutant from water and wastewater. This mini-review presents the application of zinc ferrites and ZnFe\textsubscript{2}O\textsubscript{4}-based composites in the photocatalytic degradation of organic dye. The zinc ferrite nanomaterials are obtained mainly by thermal methods, sol-gel, co-precipitation, and solid-state or hydrothermal route. Zinc Ferrites have good photocatalytic activity, but when exploited as composite photocatalysts, their photocatalytic efficiency were increased. As a critical magnetic material, the ZnFe\textsubscript{2}O\textsubscript{4} spinel structure has been proven to be useful in removal dye, ZnFe\textsubscript{2}O\textsubscript{4} have photocatalytic activity under visible light irradiation. However, it is possible to improve the efficiency of photocatalysis activity of ZnFe\textsubscript{2}O\textsubscript{4} by coupling it with another semiconductor or coupling it with carbon nanotubes and graphene, resulting in enhanced photocatalytic performance.

Keywords: Dye degradation; Zinc ferrite; Nanotechnology; Photocatalysis; Magnetic nanoparticles

Graphical Abstract:

Biography:

Fatemeh Ajormal has completed BS in chemistry in Shahid Chamran University from Ahwaz in 2010. She has Master's degree in organic chemistry from University of Zanjan, at the moment she is a PhD student in organic chemistry. Her area of research interest is synthesis of heterocyclic Compounds, Synthesis of complexes and Application of Catalytic them.
Farzaneh Moradnia has completed her M. Sc. (2013) Degree under the supervision of Dr. Hamid Saeidian in Organic Chemistry from Payame Noor University, IRAN. At present she is following her Ph. D. degree under the supervision of Professor Ali Ramazani in organic chemistry from University of Zanjan, IRAN. Her area of research interest is green synthesis of nanomaterial as catalyst for water splitting, wastewater treatment, and multicomponent synthesis.

Saeid Taghavi Fardood received his M.Sc. degree under the supervision of Professor Gholamhassan Imanzadeh in Organic Chemistry from University of Mohaghegh Ardabili in 2011. Also, he obtained his Ph.D. degree under the supervision of Professor Ali Ramazani in Organic Chemistry from University of Zanjan in 2017. He is currently working as a researcher in chemistry at the University of Zanjan. His research interests include green synthesis of nanomaterial as photocatalysts for wastewater treatment, and application of heterogeneous nano-catalysts in multicomponent synthesis.

Ali Ramazani has completed his Ph.D under the supervision of Professor Issa Yavari in the Department of Chemistry at the Tarbiat Modares University (TMU) in the Tehran-Iran. He currently works as a full professor in Chemistry at the University of Zanjan in the Zanjan-Iran. His studies focused on organic synthesis and nanochemistry and he has published more than 350 papers. He is an Editorial Board Member of the international Journal Nanochemistry Research. He has received several national and international awards, including the 2013 khwarizmi international award, several top-cited author awards and best-paper awards from leading ISI Journals, Best Researcher Awards, and the Best Lecturer Awards at the University of Zanjan.

1. Introduction

Colors are used in large amounts in a multitude of industries to color the products. In reality, the art of using color for cloth has been known to people since 3500 BC. Color is the fundamental attraction of any fabric. WH Perkins, in 1856, discovered the use of synthetic color. However, their harmful nature has become a cause of grave concern to conservationist. The use of synthetic color harms all forms of life. Many colors are poisonous with doubtful mutagenic carcinogenic and carcinogenic effects that influence humans and aquatic biota. Today, more data on the environmental consequences of dyestuff application has become available, and the dye makers, gainer, and government themselves are taking substantial to cure the dye-containing wastewaters [1-15].

The different methods used to remove the dye, started just with some physical treatments such as equalization and sedimentation to maintain the total suspended solids (TSS), total dissolved solids (TDS), and pH of the discharged water. Other treatments, such as the use of biodegradation or filter and other, the innovation of the activated sludge process (aerobic biodegradation), were applied to treat the dye wastewater. The different methods used to remove the dye. Inorganic materials used as adsorbents in dye removal: clays, metal oxides, nanoparticles, and minerals are used as adsorbents. Photocatalytic degradation of organic pollutants is becoming one of the useful promising green chemistry technologies. Also, today utilization and demand for photo-catalysts can be great for environment pollution monitoring [16-25]. The use of photocatalytic wastewater treatment has many advantages, among which can be mention to degrade pollutants completely. In the beneficial usage of therapy of wastewater using photocatalyst, researchers found a considerable problem. Separation of photocatalyst compound from wastewater and water was hard, high-cost and time-consuming. Among photocatalysis, magnetic nanoparticles have distinctive advantages; the most important is the possibility of separating after photocatalysis is the process by using an external magnetic field. Iron oxide nanoparticles have attracted the researcher’s attention due to their excellent magnetic properties and easy magnetic separation of solids after adsorption, high surface area, high adsorption capacity, nanoparticle size, and great biocompatibility photocatalysis. Also, the iron
nanoparticles are very efficient to remove a wide variety of inorganic and organic contaminants [26-29]. The transfer can be active in removing the pollutants from the surroundings, however, additional treatment and/or disposal of the waste products ultimately is required for complete removal the main advantage of this method is functional degradation of organic pollutants to CO$_2$ and H$_2$O and inorganic constituents with solar energy as an endless energy source [30-32]. Various methods have been employed for improving the photocatalytic activity of semiconductors, such as metal composite, non-metal composite, and heterojunctions. Heterojunctions are one of these effective ways and divided to four main groups [33-35].

1. Multicomponent semiconductors
2. Semiconductor-carbon group (S-C) (graphene, CNT, graphite)
3. Semiconductor-metal (S-M)
4. Semiconductor-semiconductor (S-S).

2. Synthesis Zinc Ferrites

Different methods reported to prepare Zinc ferrites, containing thermal methods, sol-gel, co-precipitation, and many others.

2.1. Co-precipitation Method

Co-precipitation procedure for synthesis of zinc ferrites is similar to thermal methods. Fe(III) and zinc salt are dissolved in water along with oleic acid, surfactant, under stirring and gentle heating. The pH is enhanced to 7–10 to precipitate the zinc ferrite particles. The obtained nanoparticles are filtered and washed with distilled water and ethanol, then dried at oven. Once dried, the nanoparticles can then be calcined at different temperatures to specify the impact of the temperature on the activity of the samples. [36-38]

2.2. Sol-gel Methods

The term ‘sol-gel’ is used for a diverse range of chemistries involve the addition of the metal and iron precursors, along with citric acid, to create a gel. Sol-gel and citrate methods require the addition of the zinc and iron precursors, along with citric acid or another gel, to create a gel. The precursors are dissolved in water or ethanol and stirred vigorously at a specified pH until a gel-like material is developed. The gel is dried and then sintered at determined temperatures at different periods. The sintering time usually is varied and tested to determine the effects on the photocatalytic activity [39-58].

2.3. Hydrothermal method

Hydrothermal synthesis contains the numerous techniques of crystallizing substances from high-temperature aqueous solutions at high vapor pressures. The benefits of the hydrothermal technique over other kinds of crystal growth contain the ability to form crystalline phases that are not stable at the melting point. Also, materials that have a high vapor pressure near their melting points can be grown by the hydrothermal method. This method is also particularly appropriate for the growth of large good-quality crystals while maintaining control over their composition. The grain size of the powder grows with the time and temperature of hydrothermal treatment. [59-61]

2.4. Solvothermal Method

Solvothermal synthesis is the effective methods used to produce magnetic zinc ferrite. This method similar to the hydrothermal route (where the synthesis is conducted in a stainless steel autoclave), the only difference being that the precursor solution is usually not aqueous in compared with the conventional hydrothermal technique, solvothermal synthesis shows better effects on dispersed nanoparticles in a recent study in 2017 by Guangshuo Wang et al. zinc ferrite (ZnFe$_2$O$_4$) nanocrystal clusters were synthesized successfully with a surfactant-assistant solvothermal method and investigated as a potential magnetorheological material. It was found that the ZnFe$_2$O$_4$ nanocrystal clusters showed a definite shape and homogeneous dispersion, as well as improved sedimentation stability. [62-64]

2.5. Microemulsion Method

The word microemulsion was proposed initially by Schulman et al. (1959). The microemulsion method to be one of the versatile preparation methods which enable to control the particle properties such as mechanisms of particle size control, morphology, geometry, homogeneity, and surface area. A report by R. D. K. Misra and et al. described this technique to produce nanocrystalline zinc ferrites with a narrow size distribution. In general, this potential method is based on the synthesis of zinc ferrite in a controlled environment using conditions that were reported generated in water in oil microemulsion. The technique permits reasonable control of particle size distribution and non-aggregated products. [65-67]

3. Photocatalysts

ZnFe$_2$O$_4$ as a magnetic material with the spinel structure, has been proven to be useful in many applications such as dye removal. According to its visible-light response, excellent photochemical stability, and low cost. ZnFe$_2$O$_4$ has attracted considerable attention in the conversion of solar energy and photochemical hydrogen production from water. Also, the ZnFe$_2$O$_4$ magnetic particles possessed
intrinsic peroxidase-like activity, which could react with H₂O₂ to produce •OH. Zinc ferrite is one of the most important ferrites. ZnFe₂O₄ nanoparticles have a significant photo-response in the visible light region (1.92 eV) with excellent photochemical stability, suggesting their potential uses as the gas sensors and photocatalysts [16,68]. Photooxidation and photoreduction refer to the initiation of oxidation and reduction reactions by light energy. When irradiated with light energy, an electron (e⁻) is excited from the valence band (VB) to the conduction band (CB) of the photocatalyst, leaving a photogenerated hole (h⁺) photogenerated electron and holes are capable of oxidizing/reducing adsorbed substrates. The ZnFe₂O₄ NPs promote a photocatalytic reaction by acting as mediators for the charge transfer between two adsorbed molecules advises in the first, charge transfer at the semiconductor–electrolyte interface follows bandgap excitation of a semiconductor nanoparticle. In the latter case, the semiconductor nanoparticle quenches the excited state by accepting an electron, and either transferring the charge to another substrate or generating photocurrent [60]. In both cases, the semiconductor sensitizer remains, thus it is described as photocatalytic.

The mechanism which is suggested for photocatalyst reaction in the presence zinc ferrite is that the potential of ZnFe₂O₄ to oxidize pollutants in the system is based on the hypothesis, which is presented by Minhua Su et al. [69]. A schematic of the reaction mechanism is depicted in Figure 1, forming holes and electrons by absorbing the photons.

\[
\text{ZnFe}_2\text{O}_4 + \text{hv} \rightarrow \text{ZnFe}_2\text{O}_4 (e^-_{\text{CB}} + h^+_{\text{VB}}) \quad (1)
\]

Oxidation of water holes

\[
h^+_{\text{VB}} + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-
\]

Oxidation of hydroxyl ions by hole

\[
h^+_{\text{VB}} + \text{OH} \rightarrow \text{OH}^-
\]

Oxygen reduction by electron

\[
\text{O}_2 + e^- \rightarrow \cdot\text{O}_2^-
\]

The reaction of hydroxyl radicals created with the dye

dye + \cdot\text{O}_2^- \rightarrow \text{products Degradation}
dye + h^+_{\text{VB}} \rightarrow \text{products Degradation}
\cdot\text{O}_2^- + \text{H}_2\text{O}_2 \rightarrow \text{H}^+ \rightarrow \text{H}_2\text{O}_2 + \text{O}_2
\text{dye} + \text{OH}^- \rightarrow \text{Degradation of the dye}
\]

Fe(III) on the surface of ZnFe₂O₄ can initiate reactions which produce OH⁺ radicals by the fenton reaction.

\[
\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}
\]

\[
\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{HO}^+ + \text{H}^+
\]

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}^-
\]

The valence band edge of ZnFe₂O₄ is located at ca. 0.38 eV vs. SCE while the conduction band is at −1.54 eV vs. SCE. In the presence of light, holes (h₂o) are produced, which can oxidize pollutant molecules. Holes may also oxidize water to form 'OH.

\[
h^+_{\text{VB}} + \text{OH} \rightarrow \text{OH}^- + \text{H}^+
\]

Importantly, H₂O₂ in the system can capture electrons, thus diminishing the recombination of holes and electrons, which can enhance the photocatalytic performance of ZnFe₂O₄ in the presence of H₂O₂ and visible light. Furthermore, the capturing of electrons produces 'OH radical.

\[
\text{H}_2\text{O}_2 + e^- \rightarrow \text{OH}^- + \text{OH}^-
\]

The combined effects of there are thus expected to enhance the degradation of pollutants. [70,71]

4. Coupling two Semiconductor Systems

ZnFe₂O₄ is a magnetic semiconductor material. Therefore, ZnFe₂O₄-based composites particularly afford a potential benefit for repeated magnetic separation purposes.

Many nanoparticles, discovered by chemists (such as ZnO and β-AgVO₃) are considered as a significant breakthrough in the field of visible-light-driven photocatalysts and removal dye more accurately, their shows an extremely high quantum efficiency of approximately in water oxidation with the mater as a scavenger. However, as there are light-sensitive and slightly soluble in aqueous solution, it will be decomposed dye to during the photocatalytic reaction process without any sacrificial electron acceptor. This process not only destroys the structure of nanoparticles, but also can reduce its light absorption efficiency, inevitably influencing its photocatalytic activity and stability [72; 73]. So, it is possible to improve the effectiveness of the photoinduced charge separation in ZnFe₂O₄ by coupling it with another semiconductor, resulting in enhanced photocatalytic performance. Electrons photo induced on the conduction band of a
### Table 1. Dye degradation by zinc ferrite nanoparticles

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Method synthesis</th>
<th>Dye (mg/L)</th>
<th>Amount of Catalyst (g/L)</th>
<th>Irradiation source</th>
<th>Irradiation time (min)</th>
<th>Degradation (%)</th>
<th>Dye</th>
<th>Ref.</th>
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<tr>
<td>1</td>
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<td>Sol-gel method</td>
<td>25</td>
<td>5</td>
<td>&gt; 400 nm</td>
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<td>[78]</td>
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<tr>
<td>2</td>
<td>0.5μm</td>
<td>Co-precipitation</td>
<td>10</td>
<td>4</td>
<td>&gt; 400 nm</td>
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<td>2 layers</td>
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<td>[80]</td>
</tr>
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<td>37</td>
<td>ZnFe₂O₄, Size 75-105 nm</td>
<td>Co-precipitation</td>
<td>10</td>
<td>Sunlight</td>
<td>50</td>
<td>99</td>
<td>Methyl Orange</td>
<td>[91]</td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>ZnFe₂O₄, Size 9 nm</td>
<td>Colloidal mill and hydrothermal method</td>
<td>20</td>
<td>72W Halogen Lamp</td>
<td>360</td>
<td>97</td>
<td>Acid Oran Ge-II</td>
<td>[87]</td>
<td></td>
</tr>
</tbody>
</table>
Table 2. Dye degradation by zinc ferrite nanocomposites.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Compound</th>
<th>Method synthesis</th>
<th>Dye (mg/L)</th>
<th>Catalyst (g/L)</th>
<th>Irradiation source</th>
<th>Irradiation time (min)</th>
<th>Degradation (%)</th>
<th>Dye</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ZnFe₂O₄/ZnO molar ratio%50</td>
<td>electrospinning and subsequent calcination process</td>
<td>10</td>
<td>0.5</td>
<td>solar irradiation 500 W Xenon</td>
<td>150</td>
<td>99%</td>
<td>Rhodamine B</td>
<td>[92]</td>
</tr>
<tr>
<td>2</td>
<td>ZnO/ZnFe₂O₄</td>
<td>reverse micelle system size 20 and 35 nm</td>
<td>60</td>
<td>0.2</td>
<td>670 nm</td>
<td>60</td>
<td>&gt;95</td>
<td>Methylene Blue</td>
<td>[84]</td>
</tr>
<tr>
<td>3</td>
<td>ZnO/ZnFe₂O₄+H₂O2</td>
<td>co-precipitation</td>
<td>10</td>
<td>0.2</td>
<td>365</td>
<td>360</td>
<td>&gt;95</td>
<td>Methyl Orange</td>
<td>[93]</td>
</tr>
<tr>
<td>4</td>
<td>ZnO/ZnFe₂O₄+H₂O2</td>
<td>co-precipitation</td>
<td>10</td>
<td>0.2</td>
<td>380&gt;</td>
<td>360</td>
<td>47</td>
<td>Methyl Orange</td>
<td>[93]</td>
</tr>
<tr>
<td>5</td>
<td>graphene oxide-ZnFe₂O₄</td>
<td>co-precipitation</td>
<td>10</td>
<td>0.2</td>
<td>800 under NIR</td>
<td>360</td>
<td>68</td>
<td>Methyl Orange</td>
<td>[93]</td>
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<td>Hydrothermal</td>
<td>1.8</td>
<td>0.5</td>
<td>400</td>
<td>210</td>
<td>35</td>
<td>Malachite Green</td>
<td>[94]</td>
</tr>
<tr>
<td>7</td>
<td>graphene oxide-ZnFe₂O₄+H₂O₂</td>
<td>Hydrothermal</td>
<td>1.8</td>
<td>0.5</td>
<td>dark</td>
<td>210</td>
<td>&gt;97</td>
<td>Malachite Green</td>
<td>[94]</td>
</tr>
<tr>
<td>8</td>
<td>ZnFe₂O₃/MWCNTs</td>
<td>Hydrothermal</td>
<td>10</td>
<td>1</td>
<td>&gt; 420 nm</td>
<td>360</td>
<td>99</td>
<td>Methylene Blue</td>
<td>[83]</td>
</tr>
<tr>
<td>9</td>
<td>ZnFe₂O₃/MWCNTs + H₂O₂</td>
<td>Hydrothermal</td>
<td>10</td>
<td>1</td>
<td>&gt; 420 nm</td>
<td>360</td>
<td>95</td>
<td>Methylene Blue</td>
<td>[83]</td>
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<tr>
<td>10</td>
<td>ZnFe₂O₃/MWCNTs + H₂O₂</td>
<td>Hydrothermal</td>
<td>10</td>
<td>1</td>
<td>Dark</td>
<td>360</td>
<td>67</td>
<td>Methylene Blue</td>
<td>[83]</td>
</tr>
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<td>11</td>
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<td>Hydrothermal</td>
<td>10</td>
<td>1</td>
<td>&gt; 420 nm</td>
<td>360</td>
<td>67</td>
<td>Methylene Blue</td>
<td>[83]</td>
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<tr>
<td>12</td>
<td>ZnFe₂O₃/graphene + H₂O₂</td>
<td>Solvothermal</td>
<td>20</td>
<td>0.5</td>
<td>553</td>
<td>120</td>
<td>100</td>
<td>Rhodamine B</td>
<td>[86]</td>
</tr>
<tr>
<td>13</td>
<td>ZnFe₂O₃/graphene + H₂O₂</td>
<td>Solvothermal</td>
<td>20</td>
<td>0.5</td>
<td>464</td>
<td>120</td>
<td>96</td>
<td>Methyl Orange</td>
<td>[86]</td>
</tr>
<tr>
<td>14</td>
<td>ZnFe₂O₃/graphene + H₂O₂</td>
<td>Solvothermal</td>
<td>20</td>
<td>0.5</td>
<td>664</td>
<td>120</td>
<td>100</td>
<td>Methylene Blue</td>
<td>[86]</td>
</tr>
<tr>
<td>15</td>
<td>Meso-ZnFe₂O₄+H₂O₂</td>
<td>Hydrothermal</td>
<td>200</td>
<td>0.5</td>
<td>&gt; 400 nm</td>
<td>120</td>
<td>≈100</td>
<td>Acid Orange II (Aoii)</td>
<td>[16]</td>
</tr>
<tr>
<td>16</td>
<td>ZnFe₂O₄/graphene oxide-ZnFe₂O₄</td>
<td>solvothermal</td>
<td>10</td>
<td>0.5</td>
<td>664 nm</td>
<td>120</td>
<td>99.23</td>
<td>Methylene Blue</td>
<td>[95]</td>
</tr>
<tr>
<td>17</td>
<td>ZnO/ZnFe₂O₄</td>
<td>Hydrothermal</td>
<td>10</td>
<td>0.5</td>
<td>750 nm</td>
<td>140</td>
<td>&gt;94</td>
<td>Methyl Orange</td>
<td>[96]</td>
</tr>
<tr>
<td>18</td>
<td>ZnO/ZnFe₂O₄</td>
<td>Hydrothermal</td>
<td>10</td>
<td>0.5</td>
<td>750nm</td>
<td>70</td>
<td>&gt;92</td>
<td>Malachite Green</td>
<td>[97]</td>
</tr>
<tr>
<td>19</td>
<td>ZnO/ZnFe₂O₄</td>
<td>Hydrothermal</td>
<td>10</td>
<td>0.05</td>
<td>500</td>
<td>360</td>
<td>98</td>
<td>Methylene Blue</td>
<td>[98]</td>
</tr>
<tr>
<td>20</td>
<td>ZnO/ZnFe₂O₄</td>
<td>Co-Precipitation</td>
<td>20</td>
<td>0.05</td>
<td>500</td>
<td>300</td>
<td>99</td>
<td>Methyl Orange</td>
<td>[98]</td>
</tr>
</tbody>
</table>
higher level semiconductor get injected into the lower level semiconductor’s conduction band. However, coupling semiconductors does not always increase photocatalysis by charge separation. They are usually determined by multitude of factors, including defect density, surface area, crystallinity, and quantum size effects. [26; 74-76] a schematic of the reaction mechanism is depicted in Figure 2.

![Figure 2](image)

Figure 2. Schematic illustration of charge transfer in a coupled semiconductor system.

Carbon nanotubes (CNTs) have a significant electron-storage valence (one electron for every 32 carbon atoms) [26]. Photon-generated e−/h+ pairs usually take about 10−9s to recombine, therefore they may accept photon-excited electrons in nanoclusters and thus retard or hinder e−/h+ pair recombination [77]. In Figure 3, schematic of the reaction mechanism reveals the reduced graphene oxide-ZnFe2O4 composite with high photocatalytic performance under visible light irradiation.

![Figure 3](image)

Figure 3. The reduced graphene oxide-ZnFe2O4 composite which shows for the high photocatalytic performance under visible light irradiation.

As can be seen in Table 1 and 2, zinc ferrites react to degrade organic dyes; however, in most cases complete degradation occurs in the presence of composite photocatalyst or oxidizing agent, H2O2.

5. Conclusion

Zinc ferrites were considered as effective photocatalysts to achieve oxidation processes in visible light region. Diverse preparation procedures affect the size, form, and overall structure, all of which can alter the photocatalytic activity. The photocatalysts lead to formation of the reactive radical species, which may degrade pollutants. To further enhance the production of reactive radical species, oxidants such as H2O2 can be added to generate a Fenton-type system. The mixture of zinc ferrites with other photocatalysts displayed a synergistic effect that produces enhanced photocatalytic activity. Zinc ferrites react to degrade organic dyes; however, in most cases, complete degradation only happens in the presence of composite photocatalyst or oxidizing agent, H2O2. OH, the enhancing the photocatalytic activity of the ZnFe2O4 and ZnFe2O4-composites is the effective separation of electron-hole pairs and the formation of •OH. Because of magnetic properties, zinc ferrite nanocatalyst can be simply recovered from reaction and reused up to multiple runs almost without loss of catalytic activity.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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[9] Sorbini, M., Shayegan Mehr, E., Ramazani, A., & Taghavi Fardood, S. (2018). Biosynthesis of Ag, ZnO and bimetallic Ag/ZnO alloy nanoparticles by aqueous extract of oak fruit hull (Jaft) and investigation of photocatalytic activity of ZnO and bimetallic Ag/ZnO for degradation of basic violet 3 dye. Journal of Materials Science: Materials in Electronics, 29(4), 2806-2814.


