Review

Application of Spinel and Hexagonal Ferrites in Heterogeneous Photocatalysis

Zuzanna Bielan 1,*, Szymon Dudziak 2*, Adam Kubiak 3 and Ewa Kowalska 4,*

1 Centre for Plasma and Laser Engineering, The Szewalski Institute of Fluid-Flow Machinery, Polish Academy of Science, Fiszera 14, 80-231 Gdansk, Poland
2 Department of Process Engineering and Chemical Technology, Chemical Faculty, Gdansk University of Technology, G. Narutowicza 11/12, 80-233 Gdansk, Poland; dudziakszy@gmail.com
3 Institute of Chemistry and Technical Electrochemistry, Faculty of Chemical Technology, Poznan University of Technology, Berdychowo 4, 60-965 Poznan, Poland; adam.kubiak@put.poznan.pl
4 Institute for Catalysis (ICAT), Hokkaido University, N21 W10, Sapporo 001-0021, Japan
* Correspondence: zbielan@imp.gda.pl (Z.B.); kowalska@cat.hokudai.ac.jp (E.K.)

Abstract: Semiconducting materials display unique features that enable their use in a variety of applications, including self-cleaning surfaces, water purification systems, hydrogen generation, solar energy conversion, etc. However, one of the major issues is separation of the used materials from the process suspension. Therefore, chemical compounds with magnetic properties have been proposed as crucial components of photocatalytic composites, facilitating separation and recovery of photocatalysts under magnetic field conditions. This review paper presents the current state of knowledge on the application of spinel and hexagonal ferrites in heterogeneous photocatalysis. The first part focuses on the characterization of magnetic (nano)particles. The next section presents the literature findings on the single-phase magnetic photocatalyst. Finally, the current state of scientific knowledge on the wide variety of magnetic-photocatalytic composites is presented. A key aim of this review is to indicate that spinel and hexagonal ferrites are considered as an important element of heterogeneous photocatalytic systems and are responsible for the effective recycling of the photocatalytic materials.

Keywords: heterogeneous photocatalysis; hexagonal ferrites; magnetic separation; spinel ferrites

1. Introduction

Nowadays, increasing global pollution and energy issues constitute the main threats to the natural environment. Therefore, new strategies and approaches have been developed to solve those issues. Among them, materials science might be considered as one of the crucial fields for environmental protection [1]. For example, oxide systems, defined as a material consisting of at least two components (oxides) aimed at improving the application properties of the final product, are becoming more and more popular. The growth of the application potential of oxide systems is due to the synergistic effects between components (e.g., heterojunction, Z-scheme mechanism, etc. [2]) or the formation of mixed crystallographic structures (e.g., ZnTiO$_3$, SrTiO$_3$ [3]). It should be emphasized, however, that apart from the chemical composition, the control of crystallite/particle sizes, in particular at the nano scale, is fundamental for further applications of oxide materials in photoactive processes (photocatalytic, photovoltaic, etc.) [4]. For this reason, the classic approach to materials’ synthesis, where the size of the particles is not the main concern for the process efficiency, is currently one of the crucial issues in modern materials science.

Since the famous publication by Fujishima and Honda in 1972 [5], photocatalysis study using semiconductor materials has received increasing attention [6–9]. Each year, scientists from around the world are developing new photoactive materials, as well as modifying the known ones, in order to overcome their limitations with mass transfer, charge carrier...
recombination, visible-light activity, separation, generation of reactive oxygen species, and effective irradiation [10–15].

Comparing the number of recently published manuscripts in the field of photocatalysis (Figure 1), only about 7% consider the material separation after the reaction, which is considerably less than those focusing on activity increase (84%) and visible-light response (80%). This clearly shows that the recycling and reuse of photocatalysts is still undervalued. Furthermore, it should be mentioned that the study of magnetic separation began relatively late (around beginning of the 21st century) in comparison to the other aspects of heterogeneous photocatalysis.

![Figure 1](image_url)

Figure 1. The number of scientific articles published in 2020 (according to the Web of Science database) for various keywords concerning photocatalysis.

Of course, other types of separation/recycling have been proposed and investigated, such as sedimentation, coagulation, (ultra)filtration, immobilization of photocatalysts on elements of photoreactors (walls [16], quartz protecting tubes of lamps and LEDs [17,18], and optical fibers [19]) or additional supporters (glass beads [16], microspheres [20], balls [21], mesh [22], cloth [22], rings [23], membranes [24–26], and plates/films/foils [27–30]) [31].

The main limitation of simple separation by gravitational sedimentation is caused by the nanometric size of photocatalysts. Kagaya et al. [32] as well as Baran et al. [33] proposed photocatalyst separation by coagulation. The addition of inorganic (FeCl₃ [33], [Al₂(OH)₆Cl₆-n]n [32] and poly-ferric sulfate (PFS) [34]) or organic coagulants (e.g., cationic polyacrylamide (CPAM) [35]) might effectively accelerate the aggregation of photocatalyst nanoparticles (NPs) by modifying their double layer potential. Another method of suspended photocatalyst recovery is ultrafiltration. For example, Xue et al. [36] separated fine titania NPs by both cross-flow ultrafiltration (CFU) and coagulation. It has been found that
titania loses activity during coagulation, in contrast to CFU, which does not cause activity loss. However, the application of ultrafiltration is associated with significantly higher operation costs. In this respect, the immobilization of photocatalysts seems to be a better option. However, it is obvious that worse photocatalytic activity is expected for immobilized than suspended photocatalysts due to (i) mass transfer limitations, (ii) surface area decrease, and (iii) lower number of active sites for photocatalytic reactions. Additionally, the stability of immobilized photocatalysts is challenging, since photocatalyst leakage (detachment from the support [22,24,27]) and the destruction of suspended supports (e.g., microsphere breaking under shear forces inside the photoreactor [31]) have been observed. Accordingly, two different synthesis approaches have been proposed for efficient photocatalyst recovery: (i) mesoporous photocatalysts of micrometer size, thus allowing efficient separation by simple physical methods, i.e., sedimentation or filtration [37–39], and (ii) photocatalysts with magnetic properties. The latter is presented and discussed in this review.

The application of an external magnetic field, proposed as an alternative method of photocatalyst recovery, means that separated material must be bifunctional, i.e., with photocatalytic and magnetic properties. Ferromagnets have been viewed as the most promising magnetic materials to be used for this purpose. Their various combinations with popular semiconductors have been proposed in different configurations, i.e., from disordered mixtures [40], through more complex structures, such as core-shells [41], to advanced multilayered materials [42]. It should be pointed out that ferromagnet-semiconductor composites could also form efficient heterojunctions, since several magnetic oxides exhibit photocatalytic activity themselves [43], and thus the heterojunction composite might be even more active than the sole photocatalyst forming it. However, this might also result in the instability of the composite, as ferrites are not as photostable as typical photocatalysts (mainly titania), and thus dissolution and leakage of active components could occur due to photocorrosion. Accordingly, an insulator interlayer between the photocatalyst and ferrites has been proposed in more advanced structures.

In addition to the above-mentioned issues in the field of photocatalysis, attention should be paid to the fact that scientific knowledge in the subject of ab initio is still insufficient, as pointed out by, among others, Lisovski et al. [44]. Ab initio is a computational chemistry method based on quantum chemistry, and in the case of a photocatalyst, it enables determination of, among others, exciton lifetimes, stability, the redox position of valence and conduction bands, bandgap, and adsorption energies. For example, Hu et al. [45] explained the correlation between the packing factor and photocatalytic activity, whereas Lin et al. [46] successfully investigated the geometric structures and electronic properties of Ni-doped TiO₂ anatase and rutile. The authors described the calculation and simulation by a plane wave pseudopotential method based on density functional theory (DFT). However, the ab initio calculations in the field of photocatalysis are still challenging due to the current problems in computational chemistry; the vast majority of advanced experimental systems cannot be recreated, even by the supercomputer systems [47]. Therefore, it is necessary to further develop this field with regard to photooxidation processes [48] as well as the aspects of the separation of photocatalysts after processing.

This review presents all the aspects, focusing on the newest trends, applied for the use of spinel and hexagonal ferrites (selected groups of ferromagnets) in heterogeneous photocatalysis, as an efficient method for semiconductor recycling.

2. Characterization of Spinel and Hexagonal Ferrite Magnetic Nanoparticles

Ferrites, composite metal oxides containing ferric ions, are magnetic materials that have recently been intensively investigated for various possible applications, including electronic devices [49], gas sensors [50], medical purposes [51,52], water purification and wastewater treatment (adsorbent, catalyst, and Fenton reagent) [53–57], organic reactions (catalysts) [58,59], and heterogeneous photocatalysis [43]. Ferrites adopt mainly the spinel structure, but some exist in hexagonal one. The significant scientific interest in spinel and hexagonal ferrites is likely due to both their properties (magnetic properties, large specific
surface area) and simple and cheap synthesis procedure. Recently, they have also been applied for photocatalytic purposes, as discussed in the next sections.

2.1. Spinel Ferrites

Spinels ferrites with the general chemical formula of MFe$_2$O$_4$, where M states for metallic cation of Fe, Mg, Mn, Co, Zn, Ni, etc., are characterized by a cubic shape crystal structure, as presented in Figure 2. The distribution of M$^{2+}$ and Fe$^{3+}$ in the crystallographic sites (tetrahedral and octahedral) depends mainly on the M-cation radius and its charge, which obviously influence the final material properties [60,61]. In the case of normal spinel structures, M$^{2+}$ cations occupy only tetrahedral sides, leaving octahedral ones for Fe$^{3+}$. Zinc ferrite (ZnFe$_2$O$_4$) is an example of this. In contrast, M$^{2+}$ cations could also occupy only octahedral sides, forcing the partial migration of Fe$^{3+}$ ions into the tetrahedra position, which is known as the inverse spinel structure (Fe$_3$O$_4$, CoFe$_2$O$_4$, NiFe$_2$O$_4$, etc.) [62].

![Figure 2. Spinel ferrite structure (inverse) for Fe$_3$O$_4$, presented along the a direction and as a 3D projection (not marked octahedra for clarity). Reprinted with permission from [63]. Copyright (2021) Creative Commons Attribution.](image-url)

Magnetic properties of spinel ferrites strongly depend on their dimensions, i.e., the bigger the NP is, the higher is the value of magnetization saturation (M$_s$). Furthermore, superparamagnetism appears as a consequence of a decrease in ferromagnetic particle size to the nanometric scale. Usually, this occurs in NPs of the order of several nanometers to several dozens of nanometers, but the critical particle size is different for each material and is conditioned by magnetic anisotropy as well as chemical composition, crystal structure, and morphology of the ferrite [64]. As an example, magnetite NPs become superparamagnetics when their diameter is about 10–12 nm [65]. It should be pointed out that NPs lose their magnetization when the magnetic field is turned off.

2.2. Hexagonal Ferrites

Hexagonal ferrites (also referred as hexaferrites) represent a large class of magnetic ceramics with a hexagonal structure, which could be seen as an Fe$_2$O$_3$ network distorted by the presence of larger cations, usually Sr, Ba, or Pb. Compared to their spinel relatives, they generally (i) require higher temperatures to be synthesized, (ii) form larger particles easily, and (iii) exhibit typical hard-ferromagnetic behavior, with a large value of magnetic remanence and coercivity [66]. The hexaferrite family might be classified into six sub-categories, depending on the complexity of their crystal structure: M-type, Z-type, Y-type, W-type, X-type, and U-type ferrites [67]. However, regarding their photocatalytic applications, only M-type materials, with the general formula of MFe$_{12}$O$_{19}$, have been studied so far. Their crystal structure, using barium hexagonal ferrite (BaFe$_{12}$O$_{19}$) as an example, is presented in Figure 3.
3. Single-Phase Magnetic Photocatalysts

3.1. Spinel Ferrites

As presented by Zielińska-Jurek et al., pristine Fe$_3$O$_4$ ($E_g = 0.1$ eV) does not show any photocatalytic activity [68]. Nevertheless, some of MFe$_2$O$_4$ spinel ferrites are photocatalytically active themselves, without any coupling with other semiconductors (see Table 1). For example, Sutka et al. compared five different ferrites in terms of magnetic and photocatalytic properties [69]. It was found that materials with no or low $M_s$ exhibit good photocatalytic activity for degradation of methyl orange (MO). Similarly, Dojcinovic et al. observed that with an increase in the content of doped cobalt in Co$_x$Mg$_{1-x}$Fe$_2$O$_4$ ferrite, the magnetic properties increased, but photocatalytic activity decreased [70]. However, it has also been reported that manganese spinel ferrite (MnFe$_2$O$_4$) with a high $M_s$ value (~60 Am$^2$ kg$^{-1}$) shows high photocatalytic activity (about 56% degradation of Direct Red 81 after 2 h of solar-light irradiation) [71]. It is also worth mentioning that the photocatalytic activity of spinel ferrites seems not to depend on their bandgap energies or on the conduction band (CB) and valence band (VB) positions, as they are similar for a wide range of materials (Figure 4).
Table 1. Summary of photocatalytic activity on spinel ferrites.

| Photocatalyst       | Pollutants    | Experimental Conditions                                                                 | Findings                  | Ref.   |
|---------------------|---------------|----------------------------------------------------------------------------------------|---------------------------|--------|
| MnFe$_2$O$_4$       | Direct Red 81 | Solar light (Indonesia); 0.035 g L$^{-1}$; 15–35 ppm; 120 min                          | 56% deg. (15 ppm)         | [71]   |
| MnFe$_2$O$_4$       | MB            | 500-W Hg lamp; 2–8 g L$^{-1}$; 50 ppm; pH = 2–10; 5–35 min                             | ~70% (35 min, 6 g L$^{-1}$, pH 8.5) | [73]   |
| MFe$_2$O$_4$ (M = Zn, Ni, Mg, Cu, Co) | MO           | 100-W LED; 1 g L$^{-1}$; 10 ppm; 180 min                                              | NiFe$_2$O$_4$ 70% deg., MgFe$_2$O$_4$ ~30% deg., ZnFe$_2$O$_4$ ~15% deg., CoFe$_2$O$_4$ ~0 deg., CuFe$_2$O$_4$ ~0 deg. | [69]   |
| ZnSm$_{x}$Fe$_{2-x}$O$_4$ (x = 0–2) | MO           | Solar light (India); 1 g L$^{-1}$; 10–30 ppm; 80 min                                  | ZnSm$_{1.5}$Fe$_{0.5}$O$_4$ 100% deg. (10 ppm); no activity loss after 5 runs | [74]   |
| Co$_{x}$Mg$_{1-x}$Fe$_2$O$_4$ (x = 0–1) | MB           | Vis halogen lamp (70 mW cm$^{-2}$) or natural sunlight (800–1100 W m$^{-2}$); 0.5 g L$^{-1}$; 10 ppm; 240 min | Co$_{0.1}$Mg$_{0.9}$Fe$_2$O$_4$ ~80% deg. | [70]   |
| Mg$_{1-x}$Ni$_x$Fe$_2$O$_4$ (x = 0.0, 0.6, 1.0) | MB           | HEBER multilamp reactor; 0.1 g; 100 ppm; 2 ml Fenton’s agent; 180 min                  | ~86% deg.; negligible activity loss after 5 runs | [75]   |
| Cu-MgFe$_2$O$_4$    | MB            | UV-lamp; 1 g L$^{-1}$; 25 ppm; 180 min; 2 ml of H$_2$O$_2$                             | 97% deg.; ca. 10% activity loss after 5 runs                                      | [76]   |
| La$_{1-x}$Bi$_x$Cr$_{1-y}$Fe$_y$O$_3$ (x = 0–0.1; y = 0.02–0.12) | RhB        | 200 W Ar lamp/420 nm cut-off filter; 5 g L$^{-1}$; 5 ml of 10% H$_2$O$_2$; 55 min     | 90.8% deg. (La$_{0.06}$Bi$_{0.04}$Fe$_{0.04}$Cr$_{0.08}$O$_3$) | [77]   |

deg.—degradation; MB—Methylene Blue; MO—Methyl Orange; RhB—Rhodamine B.

Figure 4. Bandgap energies of spinel ferrites (NHE, pH = 0 and 14). Reprinted with permission from [72]. Copyright (2021) Elsevier.

3.2. M-Type Hexaferrites

Concerning the photocatalytic activity of single-phase M-type hexaferrites, their efficiency is often much lower than that of known photocatalytic materials, but they can absorb a broad spectrum of visible light, and thus their vis activity is of some interest, as summarized in Table 2. For example, Bibi et al. studied the photocatalytic properties of pure and Nd/Cu co-doped BaFe$_{2}$O$_{9}$ under solar light in Pakistan, using methylene green dye as a probe [78]. Both types of ferrites could remove the target compound, with a final efficiency of 37% and 93% for pristine and doped materials, respectively, after 60 min of
irradiation. It has been proposed that the increased activity of a doped structure is caused by the possible formation of oxygen vacancies (due to the dopants' presence), which results in hindering of electron-hole recombination. Moreover, only a slight decrease in the efficiency from 93% to 91% was observed during five cycles, indicating high reusability of the Nd/Cu co-doped photocatalyst. Interestingly, Raut et al. showed that pristine BaFe$_{12}$O$_{19}$, prepared via the molten salt method, exhibits even higher photocatalytic activity than the well-known P25 TiO$_2$ (famous due to exceptionally high activity for various reactions and thus used as a standard for activity checking [79,80]) under both UV and UV/vis irradiation for degradation of hexahydro-1,3,5-trinitro-1,3,5-triazine (hexogen, RDX) [81]. The highest activity of the ferrite, observed under neutral pH conditions, was explained by efficient light absorption (bandgap of 2.1 eV) and thus an increased number of generated charge carriers. The high reusability of the photocatalyst was confirmed during three cycles, with the efficiency change from 100% to 98%.

Bavarsiha et al. investigated the SrFe$_{12}$O$_{19}$ structure for photocatalytic degradation of methylene blue (MB) under UV irradiation [82]. It was found that 46% of dye could be removed during 120 min of irradiation, but reusability was not determined. Finally, the unique structure of the CdFe$_{12}$O$_{19}$ photocatalyst, both in its non-modified form (with some Fe$_2$O$_3$ impurities) and as a composite with CdTiO$_3$ phase, was investigated by Mahdiani et al. for removal of MB, methyl orange (MO), and methyl violet (MV) dyes under UV irradiation (without recycling analysis) [83]. It was found that the composite (CdFe$_{12}$O$_{19}$/CdTiO$_3$) is more active than a one-component photocatalyst for all the studied dyes, reaching the highest activity for MO—71% degradation during 70 min of irradiation.

**Table 2. Summary of M-type hexaferrite photocatalysts.**

| Photocatalyst | Pollutants | Experimental Conditions | Findings | Ref. |
|---------------|------------|------------------------|----------|------|
| BaFe$_{12}$O$_{19}$ | MG | Pakistan sunlight; 882–890 W m$^{-2}$; 0.05 g·L$^{-1}$; 10 ppm; 60 min | 37% deg. | [78] |
| BaFe$_{12}$O$_{19}$ doped with Nb and Cu | RXD | 250 W Hg lamp ($\lambda_{\text{max}}$ 254 nm); 300 W Hal. lamp (350–1100 nm); pH 3–10; 0.2–1.4 g·L$^{-1}$; 40 ppm; 240 min | 100% deg. (Hg lamp); 90% deg. (Hal. lamp) | [81] |
| SrFe$_{12}$O$_{19}$ | MB | 20 W UV light; 50 ppm; 120 min | 46% deg. | [82] |
| CdFe$_{12}$O$_{19}$ (with Fe$_2$O$_3$ impurity) | MO; MB; MV | 400 W UV light; 1 g·L$^{-1}$; 5 ppm; 70 min | 19% deg. MO; 0% deg. MB; 0 deg. MV | [83] |
| CdFe$_{12}$O$_{19}$/CdTiO$_3$ | CV | Bahawalpur (Pakistan) sunlight (881–892 W·m$^{-2}$); 1 g·L$^{-1}$; 10 ppm; 60 min | ~65.5% deg. | [84] |

**4. TiO$_2$-Based Magnetic Photocatalysts**

Titanium(IV) oxide (TiO$_2$, titania, titanium dioxide) is probably the most broadly investigated semiconductor photocatalyst due to various advantages, including high photocatalytic activity, stability, abundance, low price, and low toxicity [85–89]. However, the wide bandgap of titania, resulting in good redox properties (both oxidation and water reduction capabilities) is not recommended for light harvesting efficiency. Moreover, titania, as all semiconductors, suffers from charge carriers' recombination. In addition, the most active titania, i.e., that used in a particulate form, cannot be easily recycled, as already discussed in the introduction. Accordingly, various methods of titania modification, doping, coupling, and immobilizing have been proposed to improve its photocatalytic performance [14,90–94]. Ferrites have also been proposed as titania modifiers for three
main purposes, i.e., (i) improved activity by hindering the charge carriers’ recombination, (ii) extension of activity towards vis range of solar spectrum, and (iii) easy and cheap recycling, as presented in this Section.

4.1. Spinel Ferrites with TiO2

The coupling of spinel ferrites and titania (pristine or modified) in order to obtain a highly photoactive material with magnetic properties has commonly been reported in the recent literature, as summarized in Table 3.

Table 3. Summary of TiO2-spinel ferrite photocatalysts.

| Photocatalyst | Pollutants | Experimental Conditions | Findings | Ref. |
|---------------|------------|-------------------------|----------|-----|
| Fe3O4@SiO2/TiO2-M (M = Pt/Cu) | Ph, 4-NPh | 300 W Xe light (UV/vis, 60 W·m−2); 2 g·L−1; 20 ppm (Ph) or 500 μM (4 NPh); 60 min | 10% 4-NPh deg. (Fe3O4@SiO2/TiO2); 100% Ph deg. and 50% TOC removal (Fe3O4@SiO2/TiO2-Pt) | [95] |
| ZnFe2O4/SiO2/TiO2 | ETD | 300 W Xe light (UV/vis or vis; λ > 400 nm); 2 g·L−1; 15 ppm; 30 min | 100% deg. (UV/vis); 40% deg. (vis); 6 cycles | [96] |
| TiO2-Fe3O4-M (M = Ag/Au) | Phenols | 120 W Hg lamp (UV) or 150 W Hal lamp (UV/vis, 350-700 nm); 2 g·L−1; 1 mM; 7 h | ~0.29 mm·h−1 (TiO2-Fe3O4/Ag; UV); ~0.13 mm·h−1 (TiO2-Fe3O4/Ag; vis) | [97] |
| NiFe2O4@TiO2 core@shell | MO | 300 W Xe lamp with cut-off filter (λ > 400 nm); 0.8 g·L−1; 8 ppm; 90 min | 90% deg. (NiFe2O4@40% TiO2) | [98] |
| Co0.5Zn0.25Mn0.25Fe2O4/TiO2 (M = Ni, Cu, Mn, Mg) | MO; MB | 180 W solar simulator; 1 g·L−1; 4·10−5 M; 80 min (MB) or 360 min (MO) | 95% MO deg. (Co0.5Zn0.25Ni0.25Fe2O4/TiO2); 99% MB deg. (Co0.5Zn0.25Mn0.25Fe2O4/TiO2) and Co0.5Zn0.25Mg0.25Fe2O4/TiO2 | [99] |

4-NPh—4-nitrophenol; conv.—conversion; deg.—degradation; ETD—etodolac; Hal.—halogen; MB—Methylene Blue; MO—Methyl Orange; Ph—phenol; TOC—total organic carbon.

It should be underlined that MFe2O4 NPs in TiO2 composites (and in other ferromagnet-photocatalyst materials) can exhibit a dual function. First, as semiconductors with narrower bandgap than UV-active photocatalysts, they could take part in photocatalytic reactions, creating a heterojunction, which might cause both vis activity and efficient charge carriers’ separation [100]. At the same time, their magnetic properties allow easy and cheap recycling of photocatalysts after reactions. However, in some cases, the direct connection between magnetic and photocatalytic materials is not worthwhile, especially when the separation is emphasized. For example, environmental conditions (e.g., acidic pH) and enhanced charge carrier migration (e.g., resulting in photocorrosion) could cause the leaching of iron ions from the composite, thus resulting in the destruction of the spinel ferrite structure. The possible reactions of Fe3O4 oxidation/reduction are presented in Equations (1)–(4) and Figure 5.

\[
\text{Fe}^{3+} (s) + e^- \rightarrow \text{Fe}^{2+} (s) \quad (1)
\]

\[
\text{Fe}_2\text{O}_3 + 6\text{H}^+ + 6e^- \rightarrow 2\text{Fe}^{2+} + 3\text{H}_2\text{O} \quad (2)
\]

\[
\text{Fe}_3\text{O}_4 + 8\text{H}^+ + 2e^- \rightarrow 3\text{Fe}^{2+} + 4\text{H}_2\text{O} \quad (3)
\]

\[
\text{Fe}^{2+} (aq) + \text{h}^+ \rightarrow \text{Fe}^{3+} (aq) \quad (4)
\]
Figure 5. Possible reactions in Fe$_3$O$_4$/TiO$_2$ composite (drawn based on [101]).

Accordingly, the approach of separation between magnetic and photocatalytic parts through an inert interlayer, such as silica [102], polyaniline [103], and carbon [104], has been proposed. The core-interlayer-shell structure (e.g., shown in Figure 6), with a magnetic core, an inert interlayer, and a photocatalytic shell, prevents unfavorable charge transfer, maintaining the photocatalytic and magnetic properties of both composites.

Figure 6. STEM images of Fe$_3$O$_4$@SiO$_2$ (a) and Fe$_3$O$_4$@SiO$_2$/TiO$_2$ (b) combined with Ti, Fe, and Si mapping. Reprinted with permission from [102]. Copyright (2017) Creative Commons Attribution.

4.2. Hexaferrites with TiO$_2$

Although pure hexaferrites have gained moderate attention as photocatalysts, their combination with other photoactive materials have frequently been reported. Among them, titania-based photocatalysts are the most common (see Table 4). For example, BaFe$_{12}$O$_{19}$/TiO$_2$ composites, initially reported by Fu et al. [105] and Lee et al. [106], can be prepared by a simple TiO$_2$ coating on the surface of the ferrite. In both studies, procion red MX 5B was used as a target pollutant decomposed under UV irradiation (no reusability analysis). It was found that though the activity increased with an increase in TiO$_2$ content, it was always lower than that of the P25 reference and/or sole TiO$_2$ NPs. In contrast, Xie et al. found higher activity for the SrFe$_{12}$O$_{19}$/TiO$_2$ composite (0.2/0.8 for Sr-ferrite and TiO$_2$, respectively) than that for single components under UV irradiation [107]. Moreover, reusability was also confirmed in three consecutive cycles, with an activity decrease of ca.
Furthermore, in contrast to pristine TiO$_2$ NPs, the composites also exhibited activity under visible-light (λ ≥ 420 nm) irradiation. In both cases (UV and visible-light irradiation), 100% degradation was observed after approx. 4–5 h of irradiation. It has been proposed that enhanced activity is caused by the possible formation of a n-n type heterojunction between both phases. Another SrFe$_{12}$O$_{19}$-based composite was also prepared by Bavarsiha et al. [108]. This time, three-phase composites, i.e., core/interlayer/shell structure, were prepared using SrFe$_{12}$O$_{19}$, SiO$_2$, and TiO$_2$ as a core, an interlayer, and an outerlayer, respectively. The efficiency of the composite was confirmed during degradation of MB, reaching ca. 80% degradation during 3 h of UV irradiation, with high reusability since only an 8% activity decrease was observed after three cycles. As a reference, SrFe$_{12}$O$_{19}$/SiO$_2$ composite was used, showing negligible photocatalytic activity. Finally, PbFe$_{12}$O$_{19}$/TiO$_2$ composite was also investigated by Lahijani et al. for degradation of Acid Blue 29, Acid Violet 7, and Acid Black 1 dyes [109]. The effective decolorization (based on the presented photographs) was observed for all tested dyes during 20–40 min of UV irradiation, but detailed process kinetics, as well as reusability, were not examined.

### Table 4. Summary of TiO$_2$-hexaferrite photocatalysts.

| Photocatalyst                  | Pollutants      | Experimental Conditions                                                                 | Findings                                                                 | Ref.       |
|-------------------------------|-----------------|-----------------------------------------------------------------------------------------|--------------------------------------------------------------------------|------------|
| BaFe$_{12}$O$_{19}$/TiO$_2$ (10–30% TiO$_2$) | Procion Red MX-5B | 4 × 8 W UV bulbs (λ$_{max}$ 365 nm); 0.2 g·L$^{-1}$ (with respect to TiO$_2$); 10 ppm; 300 min | 75% deg. (BaFe$_{12}$O$_{19}$); 96% deg. (BaFe$_{12}$O$_{19}$/30%TiO$_2$) | [105]      |
| BaFe$_{12}$O$_{19}$/TiO$_2$     |                 |                                                                                         | 60% deg. (BaFe$_{12}$O$_{19}$/30%TiO$_2$ after 500 °C heat treatment); 70% deg. (BaFe$_{12}$O$_{19}$/30% TiO$_2$ without heat treatment) | [106]      |
| SrFe$_{12}$O$_{19}$/TiO$_2$ (70–85% TiO$_2$ content) | MB              | UV light (λ$_{max}$ 254 nm) or vis light (λ > 420 nm); pH 7; 2 g·L$^{-1}$; 10 ppm; 300 min | 95% deg. (UV) and 99% deg. (vis) for SrFe$_{12}$O$_{19}$/80% TiO$_2$ | [107]      |
| SrFe$_{12}$O$_{19}$/SiO$_2$/TiO$_2$ | MB              | 20 W UV light; 50 ppm; 180 min                                                          | 80% deg.                                                 | [108]      |
| PbFe$_{12}$O$_{19}$/TiO$_2$     | ABl; AV; ABk    | 10 W UV light; 20 g·L$^{-1}$; 10 ppm; 60 min                                            | ~100% dec. of all dyes                                        | [109]      |

ABk—Acid Black 1; ABl—Acid Blue 29; AV—Acid Violet 7; dec.—decolorization; deg.—degradation; MB—Methylene Blue.

### 5. Other Magnetic-Photocatalytic Composites

Titania is still the main photocatalytic material used. However, the continuous development of materials science shows that the photocatalytic activity of titania depends on various parameters, including the crystal structure, the presence of surface impurities, the specific surface area, the morphology, etc. [4]. In order to be able to control the above parameters, it is necessary not only to apply innovative synthesis techniques (e.g., microwave route [110]) but also to use morphology-determining agents (e.g., hydrofluoric acid [111]). Despite the undoubted advantages resulting from the high photoactivity of titania, researchers are still looking for novel materials with similar or better parameters than TiO$_2$. However, regardless of the main component of the photocatalytic composite, e.g., ZnO [112], CuO [113], or others, the key aspect is the recovery of the material after the photodegradation process. Therefore, in the next part of this review, the current state of knowledge in the field of ferrite-based composite photocatalysts not containing titania is presented and discussed.

#### 5.1. Spinel Ferrite Composites

The summary of selected materials containing spinel ferrites is presented in Table 5. Despite the semiconductor and ferrite types, all composites (presented in the Table 5) have
revealed high photocatalytic activity, in the range of 96% (ZnS-WO$_3$-CoFe$_2$O$_4$ [114] and Ag$_3$PO$_4$/MnFe$_2$O$_4$ [115]) to even 100% (rGO-based spinel ferrite composites [116,117]). It has also been proven by Abroshan et al. [115] that MB degradation for single-phase manganese spinel ferrites and trisilver phosphates is much lower than that for the composite (58%, 80%, and 96%, respectively), probably due to the formation of a heterojunction between the phases, allowing the effective charge separation.

Additionally, in a large number of research works, the recovery/recycling of the magnetic composites was investigated. The use of external magnetic field allows the genuine separation, and thus the reuse, of the photoactive material in at least three cycles of pollutant degradation. As a prominent example, in the work of Dudziak et al. [118], during eight cycles of carbamazepine photodegradation on the Fe$_3$O$_4$-based Pt-modified composite, 100% efficiency was preserved.

Table 5. Summary of selected spinel ferrite–photocatalyst composites.

| Photocatalyst                  | Pollutants | Experimental Conditions | Findings                                  | Ref.  |
|-------------------------------|------------|-------------------------|-------------------------------------------|-------|
| Ag$_3$PO$_4$/MnFe$_2$O$_4$     | MB; RhB    | Sunlight (Iran, ~185 mW cm$^{-2}$); 2 g L$^{-1}$; 15 ppm; 80 min | 58% MB deg. (MnFe$_2$O$_4$); 80% MB deg. (Ag$_3$PO$_4$); 96% MB deg. (Ag$_3$PO$_4$/MnFe$_2$O$_4$) | [115] |
| Ni$_{0.65}$Zn$_{0.35}$Fe$_2$O$_4$@rGO | MB         | 300 W Xe lamp (vis $\lambda > 420$ nm); 1 g L$^{-1}$; 15 ppm; 48 min | 100% dec.; 5 cycles—10% activity loss | [116] |
| BiFeO$_3$-ZnFe$_2$O$_4$        | MB         | 100 W Xe lamp with cut-off filter ($\lambda > 420$ nm); pH 2; 1 g L$^{-1}$; 15 ppm; 120 min | ~97% deg. (BiFeO$_3$-25 wt% ZnFe$_2$O$_4$) | [119] |
| LaZF@rGO                      | RhB        | UV lamp ($\lambda_{max}$ = 254 nm; 0.6 mW cm$^{-2}$); 1 mM PDS; pH 4.5; 0.25 g L$^{-1}$; 30 ppm; 80 min | 100% dec. (1:1 LaZF@rGO) | [117] |
| ZnS-WO$_3$-CoFe$_2$O$_4$       | MB         | Tungsten-halogen lamp (400–800 nm); 0.05 g; 50 ppm; 180 min | 96% deg.; 4 cycles no activity loss | [114] |
| PANI/BiOBr/ZnFe$_2$O$_4$       | RhB; NB    | HPHgL with cut-off filter ($\lambda > 420$ nm); 1 g L$^{-1}$; 20 ppm (RhB) and 5 ppm (NB); 30 min | 99% RhB deg. & 87% NB red. (7% PANI/BiOBr/ZnFe$_2$O$_4$) | [120] |

dec.—decolorization; HPHgL—high pressure mercury lamp; LaZF—lanthanum-substituted zinc spinel ferrite; MB—Methylene Blue; NB—nitrobenzene; PANI—polyaniline; PDS—peroxydisulfate; red.—reduction; rGO—reduced graphene oxide; RhB—Rhodamine B.

Carbon-based materials, i.e., containing graphene, reduced graphene oxide (rGO), carbon nanotubes (CNT) or graphitic carbon nitride, have recently been widely used for photocatalytic reactions. After coupling them with spinel ferrite NPs, an efficient composite with both photocatalytic activity and magnetic separability can be obtained. What is more important, the photogenerated electrons can migrate only from ferrite to carbon material. In this regard, the main shortcoming of a ferrite-based photocatalyst, i.e., photobleaching, is inhibited [63].

The schematic mechanism of heterojunction for non-carbon-based ferrites is shown in Figure 7, where ZnFe$_2$O$_4$ NPs and BiFeO$_3$ represent the group of p-type and n-type materials, respectively. It has been proposed that during visible-light irradiation, the excited electron from CB of ZnFe$_2$O$_4$ could migrate to CB of BiFeO$_3$. At the same time, the created holes are transferred between the valence bands, in the opposite direction, due striving for the equilibrium state. Accordingly, this separation of charge carriers might effectively improve the photoactivity of the composite [119].
5.2. Hexaferrite Composites

Similar to spinel ferrites, hexaferrites have also been combined with different carbon-based materials, especially for possible visible-light response, as summarized in Table 6. For example, Mahdiani et al. investigated the photoactivity of PbFe$_{12}$O$_{19}$/graphene and PbFe$_{12}$O$_{19}$/CNT composites for degradation of methyl orange under UV irradiation and acidic conditions (pH 2–3) [121]. An increased activity of the composite in comparison to the simple PbFe$_{12}$O$_{19}$ structure, especially for the graphene-based photocatalyst, was explained by the inhibition of charge carriers’ recombination, resulting from the separation of the π-π* orbitals of graphene due to the interactions with the 2p oxygen orbitals from the ferrite structure. Ultimately, 75% degradation efficiency was observed for PbFe$_{12}$O$_{19}$/graphene after 70 min of irradiation. A unique approach was proposed by Ismail et al., where BaFe$_{12}$O$_{19}$/g-C$_3$N$_4$ photocatalysts were used to reduce Hg(II) ions [122]. Although the photocatalysts contained only 1–4 mass% of Ba-ferrite, a significant activity increase was observed with respect to the sole BaFe$_{12}$O$_{19}$ and g-C$_3$N$_4$ materials. It was proposed that enhanced activity could be caused by charge carrier migration and cumulation on different components, i.e., electrons and holes on g-C$_3$N$_4$ and ferrite, respectively. The best activity was obtained for 3%-BaFe$_{12}$O$_{19}$ composite under vis irradiation (λ > 420 nm), reaching 100% reduction of Hg$^{2+}$ ions within 30 min. Reusability of the composite was also tested, and a slight decrease in activity (from 100% to 90%) after five consecutive cycles was ascribed to be caused by the blocking of the surface active sites (no photocatalyst loss). Furthermore, Wang et al. also investigated BaFe$_{12}$O$_{19}$/g-C$_3$N$_4$ composites, using them as catalysts in the photo-Fenton process of rhodamine B degradation under visible-light irradiation [123]. Again, a synergistic effect was observed, with the highest activity achieved for 16.8 wt% of BaFe$_{12}$O$_{19}$. It was also proposed that charge separation between phases is responsible for the activity increase. However, in the contrast to the report by Ismail et al. [122], it was proposed that excited electrons react with H$_2$O$_2$ on the surface of BaFe$_{12}$O$_{19}$, whereas holes migrate to g-C$_3$N$_4$, as shown in Figure 8. Scavenger-based experiments have confirmed an active role of *OH, h$^+$ and *O$_2^-$ on the degradation efficiency. Reusability tests during four cycles showed a slight decrease in activity, from 98% to 91% degradation, during 100 min of irradiation. Quaternary composite SrFe$_{12}$O$_{19}$/SiO$_2$/TiO$_2$/GO was also proposed by Abd Aziz et al. towards direct sunlight-driven photocatalytic degradation of 2,4-dichlorophenol

![Figure 7. The schematic illustration of charge carriers’ migration in BiFeO$_3$-ZnFe$_2$O$_4$ composite. Reprinted with permission from [119]. Copyright (2018) Creative Commons Attribution.](image-url)
(2,4-DCP) [124]. An increased activity of 4-phase composite in comparison to pristine TiO$_2$ and TiO$_2$/GO nanostructures was explained by the possible charge transfer between TiO$_2$ and GO and increased specific surface area of the composite. It was proposed that the ferrite contribution to the photocatalytic mechanism is insignificant because of its coverage with an insulating layer (SiO$_2$). Moreover, it was shown that photocatalysts could be efficiently reused, as complete degradation of 2.4-DCP was observed during three cycles within 2.5–5 h (depending on the light intensity) of sunlight irradiation.

![Figure 8](https://via.placeholder.com/150)

**Figure 8.** The schematic illustration of the proposed mechanism for the photocatalytic degradation of Rhodamine B on BaFe$_{12}$O$_{19}$ ferrite/g-C$_3$N$_4$ composite. Reprinted with permission from [123]. Copyright (2017) Elsevier.

Finally, hexagonal ferrites, combined with other photocatalysts, have also been intensively studied. For example, Xie et al. proposed a double-magnetic composite of ZnFe$_2$O$_4$/SrFe$_{12}$O$_{19}$ as a visible-light active photocatalyst towards the degradation of MB [125]. It was proposed that the composite exhibits both improved magnetic and photocatalytic performance, i.e., (i) SrFe$_{12}$O$_{19}$ enhances the magnetic properties of ZnFe$_2$O$_4$, which are quite weak for the pure spinel phase (M$_S$ value of ca. 1.75 and 39 Am$^2$kg$^{-1}$ for the pure ZnFe$_2$O$_4$ and the composite, respectively), and (ii) substitution of Fe$^{3+}$ by Zn$^{2+}$ ions at the 2a sites of the M-ferrite structure results in enhanced photocatalytic activity when compared to pristine ZnFe$_2$O$_4$. This substitution caused a presence of Fe$^{2+}$ in the composite, and the resulting Fe$^{2+}$/Fe$^{3+}$ interactions could be responsible for an increased e$^-$ transport and a further increase in photocatalytic activity of the composite. However, reusability tests showed a constant decrease in activity between the first and fifth cycle (from 95% to 70% degradation), connected with possible photocatalyst loss between the cycles as well as surface blocking and partial destruction of the composite mesostructured. Another photocatalyst was designed by Sobhani-Nasab et al., who prepared a BaFe$_{12}$O$_{19}$/Sm$_2$Ti$_2$O$_7$ structure in its bare and Ag-decorated forms [126]. It was found that Ag has a positive impact on the activity, resulting in 100% degradation of MB during 150 min of vis irradiation (400–770 nm). It should be pointed out that the positive effect of noble metals has been well known and intensively investigated for more than forty years, as they usually work as an electron scavenger, inhibiting charge carriers’ recombination [127–130]. Unfortunately, recycling causes a slight activity decrease (as in many ferrite-based photocatalysts), to 90% degradation after four cycles.

Another visible-light active structure was proposed by Xie et al., who prepared a SrFe$_{12}$O$_{19}$/BiOBr 2D-2D nanocomposite for the degradation of Rhodamine B (λ > 420 nm) [131]. An increase in the activity of BiOBr was noticed for samples with 3 wt% and 5 wt% Sr-ferrite, probably because of increased charge carrier separation, where electrons migrate
to BiOBr and holes to the SrFe$_{12}$O$_{19}$. The highest removal efficiency of 97% after 30 min of visible-light irradiation was achieved for the sample with 5 wt% of SrFe$_{12}$O$_{19}$. Similar to other ferrite photocatalysts, an activity loss (97% to ca. 90%) was observed during five cycles of degradation. Finally, scavenger-based experiments showed that •OH radicals play a less significant role in the examined system than e$^-$ and •O$_2^-$, which might suggest that the oxidative potential of h$^+$ at the ferrite surface might be too low to effectively oxidize water to •OH.

An interesting approach was suggested by Xu et al., in which BaFe$_{12}$O$_{19}$ ferrite was coupled with Ag$_3$PO$_4$ photocatalysts to create an in situ Fenton-like photosystem for degradation of bisphenol A under visible light ($\lambda \geq 420$ nm) [132]. It is known that Ag$_3$PO$_4$ is able to generate H$_2$O$_2$ due to 2-electron oxygen reduction (photocatalytic reaction); then, H$_2$O$_2$ is responsible for further degradation of organic pollutants [133]. An approach proposed by Xu et al. not only utilized BaFe$_{12}$O$_{19}$ as a magnetically separable part of the composite, but also enabled further conversion of photogenerated H$_2$O$_2$ to other reactive oxygen species (ROS), such as a •OH and •O$_2^-$. The quantification of generated H$_2$O$_2$ for pristine Ag$_3$PO$_4$ and Ag$_3$PO$_4$/BaFe$_{12}$O$_{19}$ composite, as well as ESR-DMPO experiments for the observation of •OH and •O$_2^-$ radicals, were used for the mechanism clarification. For 10% Ba-ferrite composite, the amount of both radicals was significantly increased, whereas the concentration of H$_2$O$_2$ was ca. three times lower than that of Ag$_3$PO$_4$. Unfortunately, the stability tests showed an efficiency decrease from 80% to ca. 60% after four cycles of 30 min of irradiation. Much worse stability was observed for pristine Ag$_3$PO$_4$, where a decrease in activity from 50% to ca. 5% was noticed (Photocorrosion of Ag$_3$PO$_4$ and Ag$_4$P$_2$O$_7$ is a well-known problem [134,135]). As another example of BaFe$_{12}$O$_{19}$ ferrite combined with an Ag-based photocatalyst, Xie et al. proposed a BaFe$_{12}$O$_{19}$/AgBr composite for visible-light degradation of 2-mercaptobenzothiazole—MBT ($\lambda \geq 420$ nm) [136]. Again, the synergistic effect between both phases was observed, with the highest degradation efficiency (100% during 30 min) observed for the photocatalyst containing 10% BaFe$_{12}$O$_{19}$ ferrite. However, XPS analysis showed the presence of zero-valent silver (Ag$^0$), thus indicating the formation of a BaFe$_{12}$O$_{19}$/AgBr/Ag ternary structure. The charge transfer and separation between these three components was recognized as a main reason behind the increased activity of the composite. Based on the combined Mott-Schottky and ESR-DMPO experiments, a Z-scheme heterojunction was proposed with (i) Ag$^0$ acting as an “intermediate” for electron transfer between BaFe$_{12}$O$_{19}$ and AgBr, (ii) oxygen reduction to •O$_2^-$ on AgBr, and (iii) H$_2$O oxidation to •OH on BaFe$_{12}$O$_{19}$. The proposed mechanism is presented in Figure 9. The slight activity loss was observed during recycling, i.e., 90% degradation after four 30 min cycles (but still almost 100% for a 1 h process).
Figure 9. The schematic illustration of the proposed mechanism for degradation of 2-mercaptobenzothiazole over the ternary BaFe$_{12}$O$_{19}$/Ag/AgBr nanocomposite. Reprinted with permission from [136]. Copyright (2020) Elsevier.

In another study, Chen et al. prepared a SrFe$_{12}$O$_{19}$/MoS$_2$ heterostructure as the visible-light active photocatalysts for MB and methyl orange (MO) degradation under simulated sunlight [137]. The highest activity was observed for the composite with 1:2 mass ratio of Sr-ferrite:MoS$_2$, reaching ca. 100% and 70% degradation of MB (120 min) and MO (60 min). A possible charge separation between both phases was suggested, with electron and hole migration to SrFe$_{12}$O$_{19}$ and MoS$_2$, respectively, generating ROS (•OH and •O$_2^-$). During six subsequent cycles of MB degradation, a decrease in activity to 82% was observed. However, XRD and XPS analyses did not reveal any significant change in the composite structure. Furthermore, SrFe$_{12}$O$_{19}$ was also coupled with Bi$_2$O$_3$ for MB degradation under visible-light irradiation (λ > 420 nm) [138]. It was found that an increase in Sr-ferrite content between 30% and 40% caused a photocatalytic activity increase, with a maximum efficiency obtained for 35% of SrFe$_{12}$O$_{19}$. The most important finding was the stable activity (100% degradation of MB during 4 h of irradiation) for three subsequent cycles. It was proposed that increased photocatalytic activity of the composite could be caused by three possible factors: (i) charge separation between both phases, with electrons accumulating on the Bi$_2$O$_3$ phase, (ii) increased mobility of the charge carriers inside the SrFe$_{12}$O$_{19}$ structure due to its remanent magnetic field, and (iii) increased light absorption efficiency by SrFe$_{12}$O$_{19}$ (when compared to pristine Bi$_2$O$_3$). Other composites utilizing different Bi-based photocatalysts were also investigated by Wang et al., combining SrFe$_{12}$O$_{19}$ ferrite with Bi$_4$O$_5$Br$_2$ and Bi$_3$O$_4$Cl [139,140]. During both studies, the composites were tested for degradation of Rhodamine B (10 ppm) under UV/vis irradiation (Xe lamp). The synergistic effect was observed between Sr-ferrite and Bi$_4$O$_5$Br$_2$ when the composite contained 5 wt% of SrFe$_{12}$O$_{19}$. However, there was no synergy between the components in the case of the SrFe$_{12}$O$_{19}$/Bi$_3$O$_4$Cl photocatalyst. Ultimately, the 5 wt% Sr-ferrite/Bi$_4$O$_5$Br$_2$ was found to be the most active sample in both studies. It was proposed that an activity increase was caused by the charge carriers’ separation, with electrons accumulating on the ferrite phase. Scavenger-based studies have shown the dominant role of •O$_2^-$ radicals and an insignificant contribution of •OH. The latter might relate to the unsuitable position of the valence band edge for both components. The reusability tests for five consecutive cycles indicated a constant activity decrease (from 100% to 85% of degradation). Although it has been proposed that an activity decrease is caused by the composite loss during the
recovery, the constant change in the reaction rates between the cycles might also suggest that some damage could occur directly during the process.

Moreover, a novel structure, based on SrFeO$_{12}$ ferrite, carbon quantum dots (CQDs) and CeO$_2$, was proposed by Wang et al. [141]. The ternary composite allows an increase in both the adsorption efficiency of pollutants (here MB) and photocatalytic efficiency under simulated sunlight (AM1.5), when compared to pristine CeO$_2$, CeO$_2$/CQDs, and SrFeO$_{12}$/CeO$_2$ materials. It was proposed that the formation of II-type heterojunction between Sr-ferrite and Ce$_2$O is responsible for enhanced photocatalytic activity. Ternary composite could decompose 90% of MB during 4 hours of irradiation, but a decrease in activity to 65% was observed after four subsequent cycles.

Finally, hexagonal ferrites have also been combined with conjugated polymers, such as polyaniline (PANI) and polythiophene (PTh). For example, Mesdaghi et al. prepared two composite systems using Zn,Co,Sn-co-doped BaFeO$_{12}$ ferrite with either multiwall carbon nanotubes (MWCNTs) or polyaniline [142]. The composites, tested towards degradation of MB under irradiation with an Hg lamp ($\lambda > 400$ nm), showed increased activity in comparison to the pure ferrite; however, MWCT-based composite slightly outperformed the PANI-based one. In both cases, a decrease in degradation efficiency was observed after the three degradation cycles. A similar study was also performed by Khandani et al., who combined Ce,Nd-co-doped SrFeO$_{12}$ with polythiophene [142]. Again, the combination of ferrite with polymer increased the degradation efficiency (MB) by ca. two times. However, it should be noted that, during both studies, the composition of both phases was not optimized, and the mechanism of the photocatalytic reaction was not examined in detail.

| Photocatalyst | Pollutants | Experimental Conditions | Findings | Ref. |
|--------------|------------|-------------------------|---------|-----|
| CdFeO$_{12}$/CdTiO$_3$ | MO; MB; MV | 400 W UV light; 1 g L$^{-1}$; 5 ppm; 70 min | 71% deg. MO; 61% deg. MB; 55% deg. MV | [83] |
| PbFeO$_{12}$/GN and PbFeO$_{12}$/CNT | MO | UV light; pH 2–3 | 75% deg. (PbFeO$_{12}$/GN); 50% deg. (PbFeO$_{12}$/CNT) | [121] |
| BaFeO$_{12}$/g-C$_3$N$_4$ (10.1–35.5% wt. of Ba-ferrite) | Hg$^{2+}$ | Xe lamp ($\lambda > 420$ nm; 425 W m$^{-2}$); pH 4; 0.4–2 g L$^{-1}$; 100 ppm; 30 min | 100% red. of Hg$^{2+}$ ions | [122] |
| SrFeO$_{12}$/SiO$_2$/TiO$_2$/GO | 2,4-DCP | Kuala Lumpur sunlight; 482–776 W m$^{-2}$; 2 g L$^{-1}$; 50 ppm; 170–300 min | 100% deg.; time depending on sunlight intensity (180 min—776 W m$^{-2}$; 300 min—482 W m$^{-2}$) | [124] |
| SrFeO$_{12}$/ZnFe$_2$O$_4$ | MB | 500 W Xe lamp; pH 7; 2 g L$^{-1}$; 10 ppm; 300 min | 97% deg. | [125] |
| BaFeO$_{12}$/Sm$_2$Ti$_2$O$_7$/Ag (0–20% Ag salt) | MB | 400 W lamp (400–770 nm); 10 ppm; 150 min | 45% deg. (BaFeO$_{12}$/Sm$_2$Ti$_2$O$_7$); 100% deg. (BaFeO$_{12}$/Sm$_2$Ti$_2$O$_7$/20% Ag) | [126] |
| SrFeO$_{12}$/BiOBr (3–15% wt. of Sr-ferrite) | RhB | 300 W Xe lamp, filter ($\lambda > 420$ nm); 0.5 g L$^{-1}$; 10 ppm; 30 min | 55% deg. (15% SrFeO$_{12}$/BiOBr); 97% deg. (5% SrFeO$_{12}$/BiOBr) | [131] |
6. Conclusions and Future Perspectives

The literature review reflects the recent need to search for innovative combinations of semiconductors with ferrite NPs for heterogeneous photocatalysis. Various studies have been carried out at multiple research centers worldwide, being largely focused on the choice of appropriate ferromagnets to produce advanced magnetic photocatalytic systems. Based on the presented literature, it was found that spinel and hexagonal ferrite magnetic NPs, despite their magnetic properties enabling easy separation, have received moderate attention as the main photocatalytic material, probably because of lower activity than well-known photocatalysts (e.g., TiO$_2$) and stability concerns. However, they could be an interesting component of photocatalytic materials, with a possible synergistic effect, resulting in increased activity under UV light and the appearance of visible response. However, their stability (even though, in many cases, it is much better than single-component photocatalysts) should be improved for possible commercialization, as most lose activity during recycling.

Moreover, though ferrites have proven to be a suitable choice for the separation of the multi-phase photocatalysts, there are still some unknown aspects of their operation in the photocatalytic systems. Above all, the ability of the ferrite materials to generate reactive oxygen species by themselves; as well, further identification of the main ROS and the positions of CB and VB edges of such ferrite materials are usually missing. This leads
to confusing results reported in different studies. For example, opposite charge transfers between the same components was claimed (e.g., BaFe fifteen O nineteen /g-C three N four [122,123]) or the oxidative role of *OH radicals in the presence of Ba-ferrite [78,81] was suggested, whereas other studies excluded such mechanisms [131,137]. Since water purification from organic pollutants remains the most investigated application of the magnetic photocatalysts, these details, as well as the possible factors that affect them, are considered as crucial for further studies to better understand the interactions between hexaferrites, other photocatalysts, and pollutants. Moreover, the surface structure of the magnetic materials is usually not considered, though many reports on other photocatalysts have proven how important it is for efficient photocatalytic performance [111,144]. In this regard, surface-based studies of such materials are highly recommended as another direction for further research.

It is also thought that the mechanism of ferrite-based photocatalysts needs further investigation, as only a few studies discussed the possible mechanism in detail (showing direct proof instead of speculation). Moreover, though the use of dyes is very convenient for fast and easy activity testing (and important for environmental purification), it is not recommended for mechanism discussion due to the additional mechanisms of photocatalyst sensitization (barely discussed in the presented papers).

Even though there are many unsolved issues and unknown aspects, it is thought that the study of the creation of a new generation of ferromagnetic-photocatalytic systems will grow as a result of evolving strategies for environmental protection, since easy and inexpensive separation of photocatalysts for reuse is highly important.

**Author Contributions:** Writing—original draft preparation, S.D., A.K., Z.B. and E.K.; Writing—review and editing, S.D., A.K., Z.B. and E.K. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Data are available in a publicly accessible repository.

**Conflicts of Interest:** The authors declare no conflict of interest.

**References**

1. Roberts, B.A.; Strauss, C.R. Toward Rapid, “Green”, Predictable Microwave-Assisted Synthesis. *ChemInform* 2005, 36, 653–661. [CrossRef]
2. Janczarek, M.; Kowalska, E. On the Origin of Enhanced Photocatalytic Activity of Copper-Modified Titania in the Oxidative Reaction Systems. *Catalysis* 2017, 7, 317. [CrossRef]
3. Siwińska-Stefańska, K.; Kubiak, A.; Piasecki, A.; Dobrowolska, A.; Czaczyk, K.; Motyleńko, M.; Rafaja, D.; Ehrlich, H.; Jesionowski, T. Hydrothermal synthesis of multifunctional TiO$_2$-ZnO oxide systems with desired antibacterial and photocatalytic properties. *Appl. Surf. Sci.* 2019, 463, 791–801. [CrossRef]
4. Kubiak, A.; Siwińska-Cieszylczyk, K.; Jesionowski, T. Titania-Based Hybrid Materials with ZnO, ZrO$_2$ and MoS$_2$: A Review. *Materials* 2018, 11, 2295. [CrossRef]
5. Fujishima, A.; Honda, K. Electrochemical Photolysis of Water at Semiconductor Electrode. *Nature* 1972, 238, 37–38. [CrossRef] [PubMed]
6. Herrmann, J.M.; Disdier, J.; Pichat, P. Photoassisted platinum deposition on TiO$_2$ powder using various platinum complexes. *J. Phys. Chem.* 1986, 90, 6028–6034. [CrossRef]
7. Di Paola, A.; Marci, G.; Palmisano, L.; Schiavello, M.; Uosaki, K.; Ikeda, S.; Ohtani, B. Preparation of polycrystalline TiO$_2$ photocatalysts impregnated with various transition metal ions: Characterization and photocatalytic activity for the degradation of 4-nitrophenol. *J. Phys. Chem. B* 2002, 106, 637–645. [CrossRef]
8. Zhang, L.; Baumanis, C.; Robben, L.; Kandiel, T.; Bahnemann, D. Bi$_2$WO$_6$ Inverse Opals: Facile Fabrication and Efficient Visible-Light-Driven Photocatalytic and Photoelectrochemical Water-Splitting Activity. *Small* 2011, 7, 2714–2720. [CrossRef]
9. Sclafani, A.; Palmisano, L.; Davi, E. Photocatalytic degradation of phenol in aqueous polycrystalline TiO$_2$ dispersions: The influence of Fe$^3+$, Fe$^{2+}$ and Ag$^+$ on the reaction rate. *J. Photochem. Photobiol. A Chem.* 1991, 56, 113–123. [CrossRef]
10. Hitoki, G.; Takata, T.; Kondo, J.N.; Hara, M.; Kobayashi, H.; Domen, K. An oxynitride, TaON, as an efficient water oxidation photocatalyst under visible light irradiation ($\lambda \leq 500$ nm). *Chem. Commun.* 2002, 2, 1698–1699. [CrossRef]
11. Tomita, O.; Nitta, S.; Matsuta, Y.; Hosokawa, S.; Higashi, M.; Abe, R. Improved photocatalytic water oxidation with Fe$^{3+}$/Fe$^{2+}$ redox on rectangular-shaped WO$_3$ particles with specifically exposed crystal faces via hydrothermal synthesis. Chem. Lett. 2017, 46, 221–224. [CrossRef]

12. Buchalska, M.; Kunczewicz, J.; Świątek, E.; Labuz, P.; Baran, T.; Stochel, G.; Macyk, W. Photoinduced hole injection in semiconductor-coordination compound systems. Coord. Chem. Rev. 2013, 257, 767–775. [CrossRef]

13. Kowalska, E.; Abe, R.; Ohtani, B. Visible light-induced photocatalytic reaction of gold-modified titanium(IV) oxide particles: Action spectrum analysis. Chem. Commun. 2009, 2, 241–243. [CrossRef]

14. Mitoraj, D.; Kisch, H. The nature of nitrogen-modified titanium dioxide photocatalysts active in visible light. Angew. Chem. Int. Ed. 2008, 47, 9975–9978. [CrossRef]

15. Ghosh, S.; Kouamé, N.A.; Ramos, L.; Remita, S.; Dazzi, A.; Deniset-Besseau, A.; Beauquier, P.; Goubard, F.; Aubert, P.H.; Remita, H. Conducting polymer nanostructures for photocatalysis under visible light. Nat. Mater. 2015, 14, 505–511. [CrossRef]

16. Dijkstra, M.F.J.; Michorius, A.; Buwalda, H.; Panneman, H.J.; Winkelman, J.G.M.; Beenackers, A.A.C.M. Comparison of the efficiency of immobilized and suspended systems in photocatalytic degradation. Catal. Today 2001, 66, 487–494. [CrossRef]

17. O’Neal Tugaoen, H.; Garcia-Segura, S.; Hristovski, K.; Westerhoff, P. Compact light-emitting diode optical fiber immobilized TiO$_2$ reactor for photocatalytic water treatment. Sci. Total Environ. 2018, 613–614, 1331–1338. [CrossRef]

18. Kubiak, A.; Zółtowska, S.; Bartkowiak, A.; Gabala, E.; Sacharczuk, N.; Zalas, M.; Siwińska-Ciesielsczyk, K.; Jesionowski, T. The TiO$_2$-ZnO Systems with Multifunctional Applications in Photactive Processes—Efficient Photocatalyst under UV-LED Light and Electrode Materials in DSSCs. 2014, 14, 6003. [CrossRef]

19. Song, Y.; Ling, L.; Westerhoff, P.; Shang, C. Evanescent waves modulate energy efficiency of photocatalysis within TiO$_2$ coated optical fibers illuminated using LEDs. Nat. Commun. 2021, 12, 4101. [CrossRef] [PubMed]

20. Marques, A.C.; Vale, M.; Vicente, D.; Schreck, M.; Tervoort, E.; Niederberger, M. Porous Silica Microspheres with Immobilized Titania Nanoparticles for In-Flow Solar-Driven Purification of Wastewater. Glob. Chall. 2021, 5, 2000116. [CrossRef]

21. Verma, A.; Dixit, D.; Toor, A.; Srivastava, J. Highly Photocatalytic Degradation of 2-chloro-4-Nitrophenol Using Slurry and Fixed Bed Reactor. Environ. Prog. Sustain. Energy 2015, 34, 380–386. [CrossRef]

22. Villacres, R.; Ikeda, S.; Torimoto, T.; Ohtani, B. Development of a novel photocatalytic reaction system for oxidative decomposition of volatile organic compounds in water with enhanced aeration. J. Photochem. Photobiol. A Chem. 2003, 160, 121–126. [CrossRef]

23. Zielinska-Jurek, A.; Klein, M.; Hupka, J. Enhanced visible light photocatalytic activity of Pt/I-TiO$_2$ in a slurry system and supported on glass packing. Sep. Purif. Technol. 2017, 189, 246–252. [CrossRef]

24. Molinari, R.; Mungari, M.; Drioli, E.; Di Paola, A.; Loddo, V.; Palmisano, L.; Schiavello, M. Study on a photocatalytic membrane reactor for water purification. Catal. Today 2000, 55, 71–78. [CrossRef]

25. Mozia, S.; Tomaszewska, M.; Morawski, A.W. A new photocatalytic membrane reactor (PMR) for removal of azo-dye Acid Red 18 from water. Appl. Catal. B Environ. 2005, 59, 131–137. [CrossRef]

26. Argurio, P.; Fontananoova, E.; Molinari, R.; Drioli, E. Photocatalytic membranes in photocatalytic membrane reactors. Processes 2018, 6, 162. [CrossRef]

27. Byrne, J.A.; Eggins, B.R.; Brown, N.M.D.; McKinney, B.; Rouse, M. Immobilisation of TiO$_2$ powder for the treatment of polluted water. Appl. Catal. B Environ. 1998, 17, 25–36. [CrossRef]

28. Chen, D.; Ray, A.K. Photocatalytic kinetics of phenol and its derivatives over UV irradiated TiO$_2$. Appl. Catal. B Environ. 1999, 23, 143–157. [CrossRef]

29. Arabatzis, I.M.; Stergiopoulos, T.; Bernard, M.C.; Labou, D.; Neophytides, S.G.; Falaras, P. Silver-modified titanium dioxide thin films for efficient photodegradation of methyl orange. Appl. Catal. B Environ. 2005, 42, 187–201. [CrossRef]

30. Markowska-Szczupak, A.; Rokicka, P.; Wang, K.; Endo, M.; Morawski, A.W.; Kowalska, E. Photocatalytic water disinfection under solar irradiation by D-glucose-modified methyl titania. Catalysts 2018, 8, 316. [CrossRef]

31. Kowalska, E.; Rau, S. Photoreactors for Wastewater Treatment: A Review. Recent Pat. Eng. 2010, 4, 242–266. [CrossRef]

32. Kagaya, S.; Shimizu, K.; Arai, R.; Hasegawa, K. Separation of titanium dioxide photocatalyst in its aqueous suspensions by coagulation with basic aluminum chloride. Water Res. 1999, 33, 1753–1755. [CrossRef]

33. Baran, W.; Makowsky, A.; Wardas, W. The separation of catalyst after photocatalytic reactions conducted in the presence of TiO$_2$/FeCl$_3$/UV. Chemosphere 2005, 59, 853–859. [CrossRef]

34. Wang, H.; Qi, J.; Keller, A.A.; Zhu, M.; Li, F. Effects of pH, ionic strength and humic acid on the removal of TiO$_2$ nanoparticles from aqueous phase by coagulation. Colloids Surf. A Physicochem. Eng. Asp. 2014, 450, 161–165. [CrossRef]

35. You, Z.; Zhuang, C.; Sun, Y.; Zhang, S.; Zheng, H. Efficient Removal of TiO$_2$ nanoparticles by enhanced flocculation-coagulation. Ind. Eng. Chem. Res. 2019, 58, 14528–14537. [CrossRef]

36. Xue, X.D.; Fu, J.F.; Zhu, W.F.; Guo, X.C. Separation of ultrafine TiO$_2$ from aqueous suspension and its reuse using cross-flow ultrafiltration (CFU). Desalination 2008, 225, 29–40. [CrossRef]

37. Chang, Y.; He, P.; Wei, Z.; Chen, Y.; Wang, H.; Wu, C.; Zhou, Z.; Huang, H.; Kowalska, E.; Dong, S. Three-dimensional monodispersed TiO$_2$ microsphere network formed by a sub-zero sol-gel method. Mater. Lett. 2020, 268, 127592. [CrossRef]

38. Golabiewska, A.; Checa-Suárez, M.; Paszkiewicz-Gawron, M.; Lisowski, W.; Raczk, E.; Klimczuk, T.; Polkowska, Z.; Grabowska, E.; Zaleska-Medyńska, A.; Łuczak, J. Highly Active TiO$_2$ Microspheres Formation in the Presence of Ethylammonium Nitrate Ionic Liquid. Catalysts 2018, 8, 279. [CrossRef]
39. Shamaila, S.; Sajjad, A.K.L.; Chen, F.; Zhang, J. Study on highly visible light active Bi₂O₃ loaded ordered mesoporous titania. *Appl. Catal. B Environ.* 2010, 94, 272–280. [CrossRef]
40. Kubiak, A.; Kubacka, M.; Gabala, E.; Dobrowska, A.; Synoradzki, K.; Siwińska-Ciesielczyk, K.; Czaczek, K.; Jesionowski, T. Hydrothermally assisted fabrication of TiO₂-Fe₃O₄ composite materials and their antibacterial activity. *Materials* 2020, 13, 4715. [CrossRef]
41. Li, Z.-D.; Wang, H.-L.; Wei, X.-N.; Liu, X.-Y.; Yang, Y.-F.; Jiang, W.-F. Preparation and photocatalytic performance of magnetic Fe₂O₃@TiO₂ core-shell microspheres supported by silica aerogels from industrial fly ash. *J. Alloys Compd.* 2016, 659, 240–247. [CrossRef]
42. Li, W.; Deng, Y.; Wu, Z.; Qian, X.; Yang, J.; Wang, Y.; Gu, D.; Zhang, F.; Tu, B.; Zhao, D. Hydrothermal Etching Assisted Crystallization: A Facile Route to Functional Yolk-Shell Titane Microspheres with Ultrathin Nanosheets-Assembled Double Shells. *J. Am. Chem. Soc.* 2011, 133, 15830–15833. [CrossRef]
43. Casbeer, E.; Sharma, V.K.; Li, X.Z. Synthesis and photocatalytic activity of ferrites under visible light: A review. *Sep. Purif. Technol.* 2012, 87, 1–14. [CrossRef]
44. Lisovski, O.; Piskunov, S.; Bocharov, D.; Kenmoe, S. 2D Slab Models of Nanotubes Based on Tetragonal TiO₂ Structures: Validation over a Diameter Range. *Nanomaterials* 2021, 11, 1925. [CrossRef]
45. Hu, L.; Xu, C.; Peng, L.; Gu, E.L.; Yang, W. Photocatalytic activity and the radiative lifetimes of excitons via an ab initio approach. *J. Mater. Chem. A* 2018, 6, 15027–15032. [CrossRef]
46. Lin, Y.-M.; Jiang, Z.-Y.; Zhu, C.-Y.; Hu, X.-Y.; Zhang, X.-D.; Fan, J. Visible-light photocatalytic activity of Ni-doped TiO₂ from ab initio calculations. *Mater. Chem. Phys.* 2012, 133, 746–750. [CrossRef]
47. Bocharov, D.; Piskunov, S.; Zhukovskiy, Y.F.; Evarestov, R.A. Ab Initio Calculations on the Electronic Structure and Photocatalytic Properties of Two-Dimensional WS₂ (001) Nanolayers of Varying Thickness. *Phys. Status Solidi Rapid Res. Lett.* 2018, 13, 1800253. [CrossRef]
48. Eidsvåg, H.; Bentouba, S.; Vajeeston, P.; Yohi, S.; Velauthapillai, D. TiO₂ as a photocatalyst for water splitting—An experimental and theoretical review. *Molecules* 2021, 26, 1687. [CrossRef]
49. Kefeni, K.K.; Msagati, T.A.M.; Mamba, B.B. Ferrite nanoparticles: Synthesis, characterisation and applications in electronic device. *Mater. Sci. Eng. B* 2017, 215, 37–55. [CrossRef]
50. Šutka, A.; Gross, K.A. Spinel ferrite oxide semiconductor gas sensors. *Sens. Actuators B Chem.* 2016, 222, 95–105. [CrossRef]
51. Sharifi, I.; Shokrollahi, H.; Amiri, S. Ferrite-based magnetic nanofluids used in hyperthermia applications. *J. Magn. Magn. Mater.* 2012, 324, 903–915. [CrossRef]
52. Amiri, M.; Salavat-Niasari, M.; Akbari, A. Magnetic nanocarriers: Evolution of spinel ferrites for medical applications. *Adv. Colloid Interface Sci.* 2019, 265, 29–44. [CrossRef]
53. Reddy, D.H.K.; Yun, Y.-S. Spinel ferrite magnetic adsorbents: Alternative future materials for water purification? *Coord. Chem. Rev.* 2016, 315, 90–111. [CrossRef]
54. Tatarchuk, T.; Palijchuk, N.; Bitra, R.B.; Shlychuk, A.; Naushad, M.; Mironyuk, I.; Ziółkowska, D. Adsorptive removal of toxic Methylene Blue and Acid Orange 7 dyes from aqueous medium using coal-based zinc ferrite nanoadsorbents. *Desalin. Water Treat.* 2019, 150, 374–385. [CrossRef]
55. Tatarchuk, T.; Myslin, M.; Mironyuk, I.; Bououdina, M.; Pędzwiatrz, A.T.; Gargula, R.; Bogacz, B.F.; Kurzyzdło, P. Synthesis, morphology, crystallite size and adsorption properties of nanostructured Mg–Zn ferrites with enhanced porous structure. *J. Alloys Compd.* 2020, 819, 152945. [CrossRef]
56. Wang, Y.; Zhao, H.; Li, M.; Fan, J.; Zhao, G. Magnetic ordered mesoporous copper ferrite as a heterogeneous Fenton catalyst for the degradation of imidacloprid. *Appl. Catal. B Environ.* 2014, 147, 534–545. [CrossRef]
57. Guan, Y.-H.; Ma, J.; Ren, Y.-M.; Liu, Y.-L.; Xiao, J.-Y.; Lin, L.; Zhang, C. Efficient degradation of atrazine by magnetic porous copper ferrite catalyzed peroxymonosulfate oxidation via the formation of hydroxyl and sulfate radicals. *Water Res.* 2013, 47, 5431–5438. [CrossRef]
58. Kharisov, B.I.; Dias, H.V.R.; Kharissova, O.V. Mini-review: Ferrite nanoparticles in the catalysis. *Arab. J. Chem.* 2019, 12, 1234–1246. [CrossRef]
59. Goyal, A.; Bansal, S.; Singhal, S. Facile reduction of nitrophenols: Comparative catalytic efficiency of MFe₂O₄ (M = Ni, Cu, Zn) nano ferrites. *Int. J. Hydrog. Energy* 2014, 39, 4895–4908. [CrossRef]
60. Pham, T.N.; Huy, T.Q.; Le, A.T. Spinell ferrite (AFe₂O₄) based heterostructured designs for lithium-ion battery, environmental monitoring, and biomedical applications. *RSC Adv.* 2020, 10, 31622–31661. [CrossRef]
61. Sergy, V.; Burne, R.; Maiorov, M.; Krumina, A.; Skaužiūnas, R.; Zarkov, A.; Kareiva, A.; Popov, A.I. Impact of Gadolinium on the Structure and Magnetic Properties of Nanocrystalline Powders of Iron Oxides Produced by the Extraction-Pyrolytic Method. *Materials* 2020, 13, 4147. [CrossRef]
62. Tatarchuk, T.R.; Bououdina, M.; Palijchuk, N.D.; Yaremiy, I.P.; Moklyak, V.V. Structural characterization and antistructure modeling of coal-substituted zinc ferrites. *J. Alloys Compd.* 2017, 694, 777–791. [CrossRef]
63. Janczarek, M.; Endo-Kimura, M.; Wei, Z.; Bielan, Z.; Mogan, T.R.; Khedr, T.M.; Wang, K.; Markowska-Szczupek, A.; Kowalska, E. Novel Structures and Applications of Graphene-Based Semiconductor Photocatalysts: Faceted Particles, Photonic Crystals, Antimicrobial and Magnetic Properties. *Appl. Sci.* 2021, 11, 1982. [CrossRef]
64. Gu, F.; Leshuk, T.; Linley, S. Superparamagnetic Photocatalytic Microparticles. U.S. Patent No. US 2014/0131288 A1, 17 May 2012. pp. 1–25.

65. Zhang, S.; Zhao, X.; Niu, H.; Shi, Y.; Cai, Y.; Jiang, G. Superparamagnetic Fe₃O₄ nanoparticles as catalysts for the catalytic oxidation of phenolic and aniline compounds. J. Hazard. Mater. 2009, 167, 560–566. [CrossRef]

66. Dudziak, S.; Ryzynska, Z.; Bielan, Z.; Rył, J.; Klimeczuk, T.; Zielinska-Jurek, A. Pseudo-superparamagnetic behaviour of barium hexaferrite particles. RSC Adv. 2020, 10, 18784–18796. [CrossRef]

67. Pullar, R.C. Hexagonal ferrites: A review of the synthesis, properties and applications of hexaferrite ceramics. Prog. Mater. Sci. 2012, 57, 1191–1334. [CrossRef]

68. Zielińska-Jurek, A.; Bielan, Z.; Wysocka, I.; Strychalska, J.; Janczek, M.; Klimczuk, T. Magnetic semiconductor photocatalysts for the degradation of recalcitrant chemicals from flow back water. J. Environ. Manag. 2017, 195, 157–165. [CrossRef]

69. Sutka, A.; Millers, M.; Vanags, M.; Joost, U.; Maiorov, M.; Kisand, V.; Pärna, R.; Juhnevica, I. Comparison of photocatalytic activity for different co-precipitated spinel ferrites. Res. Chem. Intermed. 2015, 41, 9439–9449. [CrossRef]

70. Dojcimovic, M.P.; Vasiljevic, Z.Z.; Pavlovic, V.P.; Barisic, D.; Pajic, D.; Tadic, N.B.; Nikolic, M.V. Mixed Mg–Co spinel ferrites: Structure, morphology, magnetic and photocatalytic properties. J. Alloys Compd. 2021, 855, 157429. [CrossRef]

71. Rahmayeni, R.; Oktavia, Y.; Stadi, Y.; Arief, S.; Zulhadji, Z. Spinel ferrite of MnFe₂O₄ synthesized in Piper betle Linn extract media and its application as photocatalysts and antibacterial. J. Dispers. Sci. Technol. 2021, 42, 465–474. [CrossRef]

72. Sonu; Sharma, S.; Dutta, V.; Raizada, P.; Hosseini-Bandegharaei, A.; Thakur, V.; Nguyen, V.; Vanle, Q.; Singh, P. An overview of heterojunctioned ZnFe₂O₄ photocatalyst for enhanced oxidative water purification. J. Environ. Chem. Eng. 2021, 9, 105812. [CrossRef]

73. Ata, S.; Shaheen, I.; Majid, F.; Bibi, I.; Ijaz-Ul-Mohsin; Jilani, K.; Slimani, Y.; Iqbal, M. Hydrothermal route for the synthesis of manganese ferrite nanoparticles and photocatalytic activity evaluation for the degradation of methylene blue dye. Z. Phys. Chem. 2021, 235, 1381. [CrossRef]

74. Rashmi, S.K.; Bhoja Naik, H.S.; Jayadevappa, H.; Viswanath, R.; Patil, S.B.; Madhukara Naik, M. Solar light responsive Sm-Zn ferrite nanoparticles as efficient photocatalyst. Mater. Sci. Eng. B Solid-State Mater. Adv. Technol. 2017, 225, 86–97. [CrossRef]

75. Ajeebah, T.; Ashwini, A.; George, M.; Manikandan, A.; Mary, J.A.; Slimani, Y.; Almessiere, M.A.; Baykal, A. Nickel substituted MgFe₂O₄ nanoparticles via co-precipitation method for photocatalytic applications. Phys. B Condens. Matter 2021, 606, 412660. [CrossRef]

76. George, M.; Ajeebah, T.L.; Manikandan, A.; Manantheram, A.; Jansi, R.S.; Kumar, E.R.; Slimani, Y.; Almessiere, M.A.; Baykal, A. Evaluation of Cu–MgFe₂O₄ spinel photocatalysts for photocatalytic and antimicrobial activates. J. Phys. Chem. Solids 2021, 153, 110010. [CrossRef]

77. Ghafoor, A.; Bibi, I.; Ata, S.; Majid, F.; Kamal, S.; Rehman, F.; Iqbal, S.; Aamir, M.; Slimani, Y.; Iqbal, M.; et al. Synthesis and characterization of magnetically separable La₁₋ₓBiₓCr₀.₅₋₄Fe₂O₃ and photocatalytic activity evaluation under visible light. Z. Phys. Chem. 2021, 235, 1747. [CrossRef]

78. Bibi, F.; Iqbal, S.; Sabeen, H.; Saleem, T.; Ahmad, B.; Nadeem, M.; Shakir, I.; Aadil, M. Ambreen kalsoom Evaluation of structural, dielectric, magnetic and photocatalytic properties of Nd and Cu co-doped barium hexaferrite. Ceram. Int. 2021, 47, 30911–30921. [CrossRef]

79. Ohtani, B.; Prieto-Mahaney, O.O.; Li, D.; Abe, R. What is Degussa (Evonic) P25? Crystalline composition analysis, reconstruction from isolated pure nanoparticles and photocatalytic activity test. J. Photochem. Photobiol. A Chem. 2010, 216, 179–182. [CrossRef]

80. Wang, K.; Wei, Z.; Ohtani, B.; Kowalska, E. Interparticle electron transfer dehydrogenation on platinum- loaded titania particles prepared from P25. Catal. Today 2018, 303, 327–333. [CrossRef]

81. Raut, S.S.; Adpa, S.K.; Jambhale, A.; Abhyankar, A.C.; Kulkarni, P. Enhanced photocatalytic activity of magnetic BaFe₁₂O₁₉ nanoplatelets than TiO₂ with emphasis on reaction kinetics, mechanism, and reusability. Ind. Eng. Chem. Res. 2018, 57, 16192–16200. [CrossRef]

82. Bavarsa, F.; Montazeri-Pour, M.; Rajabi, M. Effect of Non-aqueous Media on Nano-crystalline SrFe₁₂O₁₉ Particles Produced by Co-precipitation with Metal Chlorides and Evaluation of Their Magnetic and Photocatalytic Properties. J. Inorg. Organomet. Polym. Polym. Mater. 2020, 30, 2386–2396. [CrossRef]

83. Mahdian, M.; Sobhani, A.; Salavati-Niasari, M. The first synthesis of CdFe₁₂O₁₉ nanocrystals and nanocomposites and considering of magnetic, optical, electrochemical and photocatalytic properties. J. Hazard. Mater. 2019, 367, 607–619. [CrossRef]

84. Bibi, I.; Muneer, M.; Iqbal, M.; Alwadai, N.; Almuqrin, A.H.; Alottowyan, A.S.; Alshammar, F.H.; Almuslem, A.S.; Slimani, Y. Effect of doping on dielectric and optical properties of barium hexaferrite: Photocatalytic performance under solar light irradiation. Ceram. Int. 2021, 47, 31518–31526. [CrossRef]

85. Bahnemann, D.; Henglein, A.; Lilie, J.; Sønsh, L. Flash photolysis observation of the absorption spectra of trapped positive holes and electrons in colloidal TiO₂. J. Phys. Chem. 1984, 88, 709–711. [CrossRef]

86. Pruden, A.L.; Ollis, D.F. Photoassisted heterogeneous catalysis: The degradation of trichloroethylene in water. J. Catal. 1983, 82, 404–417. [CrossRef]

87. Sclafani, A.; Palmisano, L.; Schiavello, M. Influence of the preparation methods of TiO₂ on the photocatalytic degradation of phenol in aqueous dispersion. J. Phys. Chem. 1990, 94, 829–832. [CrossRef]

88. Markowska-Szczupak, A.; Endo-Kimura, M.; Paszkiewicz, O.; Kowalska, E. Are titania photocatalysts and titanium implants safe? Review on the toxicity of titanium compounds. Nanomaterials 2020, 10, 2065. [CrossRef]
98. Ohtani, B.; Osaki, H.; Nishimoto, S.; Kagiya, T. A Novel Photocatalytic Process of Amine N-Alkylation by Platinized Semiconductor Particles Suspended in Alcohols. *J. Am. Chem. Soc.* 1986, 108, 308–310. [CrossRef]

99. Zaleska, A. Doped-TiO$_2$: A Review. *Recent Pat. Eng.* 2008, 2, 157–164. [CrossRef]

100. Wang, K.; Bielan, Z.; Endo-Kimura, M.; Janczarek, M.; Zhang, D.; Kowalski, D.; Zielinska-Jurek, A.; Markowska-Szczupak, A.; Ohtani, B.; Kowalska, E. On the mechanism of photocatalytic reactions on Cu$_2$O@TiO$_2$ core–shell photocatalysts. *J. Mater. Chem. A* 2021, 9, 10135–10145. [CrossRef]

101. Tryba, B.; Tsumura, T.; Janus, M.; Morawski, A.W.; Inagaki, M. Carbon-coated anatase: Adsorption and decomposition of phenol in water. *Appl. Catal. B Environ.* 2004, 50, 177–183. [CrossRef]

102. Baran, T.; Macyk, W. Photocatalytic oxidation of volatile pollutants of air driven by visible light. *J. Photochem. Photobiol. A Chem.* 2012, 241, 8–12. [CrossRef]

103. Desario, P.A.; Pietron, J.J.; Devantier, D.H.; Brintlinger, T.H.; Stroud, R.M.; Rollison, D.R. Plasmonic enhancement of visible-light water splitting with Au-TiO$_2$ composite aerogels. *Nanoscale* 2013, 5, 8073–8083. [CrossRef]

104. Kowalska, E.; Dudziak, S.; Wang, K.; Ohtani, B.; Zielinska-Jurek, A. Mono- and bimetallic (Pt/Cu) titanium(IV) oxide core–shell photocatalysts with UV/Vis light activity and magnetic separability. *Catal. Today* 2021, 361, 198–209. [CrossRef]

105. Fu, W.; Yang, H.; Li, M.; Chang, L.; Yu, Q.; Xu, J.; Zou, G. Preparation and photocatalytic characteristics of core-shell structure magnetic photocatalyst. *Sci. Total Environ.* 2020, 724, 1–12. [CrossRef]

106. Lee, S.W.; Drwiega, J.; Wu, C.Y.; Mazyck, D.; Sigmund, W.M. Anatase TiO$_2$ nanoparticles: A multifunctional heteroarchitecture for Photocatalysis and Energy Storage. *Ind. Eng. Chem. Res.* 2012, 51, 11700–11709. [CrossRef]

107. Zielińska-Jurek, A.; Bielan, Z.; Dudziak, S.; Wolak, I.; Sobczak, Z.; Kluczczuk, T.; Nowaczyk, G.; Hupka, J. Design and application of magnetic photocatalysts for water treatment. The effect of particle charge on surface functionality. *Catalysts* 2017, 7, 360. [CrossRef]

108. Sibi, M.G.; Verma, D.; Kim, J. Magnetic core–shell nanocatalysts: Promising versatile catalysts for organic and photocatalytic reactions. *Catal. Rev.* 2019, 62, 163–311. [CrossRef]

109. Zhang, Q.; Meng, G.; Wu, J.; Li, D.; Liu, Z. Study on enhanced photocatalytic activity of magnesium ferrite nanocomposites with core—Shell nanostructure NiFe$_2$O$_4$@TiO$_2$ for photocatalytic degradation of methyl orange dye. *J. Chem. Soc. Pak.* 2020, 42, 531–541.

110. Ciocarlan, R.G.; Seftel, E.M.; Mertens, M.; Pui, A.; Mazaj, M.; Novak Tutar, N.; Cool, P. Novel magnetic nanocomposites containing quaternary ferrites systems Co$_{0.5}$Zn$_{0.5}$M$_{0.25}$Fe$_{2}$O$_{4}$ (M = Ni, Cu, Mn, Mg) and TiO$_2$-anatase phase as photocatalysts for wastewater remediation under solar light irradiation. *Mater. Sci. Eng. B Solid-State Mater. Adv. Technol.* 2018, 230, 1–7. [CrossRef]

111. Fu, Y.; Chen, Q.; He, M.; Wan, Y.; Sun, X.; Xia, H.; Wang, X. Copper Ferrite-Graphene Hybrid: A Multifunctional Heteroarchitecture for sustainability under solar light. *Sep. Purif. Technol.* 2015, 149, 265–278. [CrossRef]

112. Bielan, Z.; Kowalska, E.; Dudziak, S.; Wang, K.; Ohtani, B.; Zielinska-Jurek, A. Mono- and bimetallic (Pt/Cu) titanium(IV) oxide core–shell photocatalysts with UV/Vis light activity and magnetic separability. *Catal. Today* 2021, 361, 198–209. [CrossRef]

113. Kowalska, E.; Dudziak, S.; Wang, K.; Ohtani, B.; Zielinska-Jurek, A. Mono- and bimetallic (Pt/Cu) titanium(IV) oxide core–shell photocatalysts with UV/Vis light activity and magnetic separability. *Catal. Today* 2021, 361, 198–209. [CrossRef]
139. Wang, H.; Xu, L.; Liu, C.; Jiang, Z.; Feng, Q.; Wu, T.; Wang, R. A novel magnetic photocatalyst Bi$_3$O$_4$Cl/SrFe$_{12}$O$_{19}$: Fabrication, characterization and its photocatalytic activity. *Ceram. Int.* **2020**, *46*, 460–467. [CrossRef]

140. Wang, H.; Xu, L.; Wu, X.; Zhang, M. Eco-friendly synthesis of a novel magnetic Bi$_4$O$_5$Br$_2$/SrFe$_{12}$O$_{19}$ nanocomposite with excellent photocatalytic activity and recyclable performance. *Ceram. Int.* **2021**, *47*, 8300–8307. [CrossRef]

141. Wang, S.; Gao, H.; Fang, L.; Hu, Q.; Sun, G.; Chen, X.; Yu, C.; Tang, S.; Yu, X.; Zhao, X.; et al. Synthesis of novel CQDs CeO$_2$/SrFe$_{12}$O$_{19}$ magnetic separation photocatalysts and synergic adsorption-photocatalytic degradation effect for methylene blue dye removal. *Chem. Eng. J.* **2021**, *404*, 100089. [CrossRef]

142. Mesdaghi, S.; Yousefi, M.; Hossaini sadr, M.; Mahdavian, A. The effect of PANI and MWCNT on magnetic and photocatalytic properties of substituted barium hexaferrite nanocomposites. *Mater. Chem. Phys.* **2019**, *236*, 121786. [CrossRef]

143. Khandani, M.; Yousefi, M.; Afghahi, S.S.; Amini, M.M.; Bikhof Torbat, M. Sr(CeNd)$_x$Fe$_{12-2x}$O$_{19}$/polythiophene nano-particles: Structural investigation, magnetic properties and photocatalytic activity. *Inorg. Chem. Commun.* **2020**, *121*, 108214. [CrossRef]

144. Kowalkińska, M.; Dudziak, S.; Karczewski, J.; Ryl, J.; Trykowski, G.; Zielinska-Jurek, A. Facet effect of TiO$_2$ nanostructures from TiOF$_2$ and their photocatalytic activity. *Chem. Eng. J.* **2021**, *404*, 126493. [CrossRef]