# Chapter 4 Photocatalytic Degradation of Aqueous Organic Pollutants Using Iron Oxide-Based Photocatalysts



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Abstract Pollution of water bodies arose due to invade of pollutants from various sector of society such as industries, agricultural field and domestic effluent water, etc. Heavy metals, pathogens and recalcitrant organic chemicals are typical examples of deleterious elements that adversely affect the health of aquatic environment. The removal of such pollutants has become an urgent need across the globe, which brings the discovery of various water treatment techniques in order to get clean water. In past few decade, outstanding result has been achieved in the field of water desalination. The application of heterogeneous photocatalysis route for the cleaning of water is reflected as one of the potential and sustainable approach since it makes use of renewable solar light as source of energy. In this chapter, we will discuss the application of iron oxide-based photocatalysts towards the removal of pollutants from aqueous source. Various research approaches progressed to improve the photocatalytic ability of iron oxide will be discussed in detail. The discussion of this chapter particularly focussed on the evolution of composite/heterostructure of iron oxidebased photocatalysts and their photocatalytic applications towards the removal of aqueous pollutants.

**Keywords** Photocatalysis  $\cdot$  Water pollutant  $\cdot$  Solar energy  $\cdot$  Iron oxide nanocomposite

# 4.1 Introduction

The water pollution and its impact on the all life on the earth is a global concern. The discharged water from the chemical and agrochemical industries contains substantially huge amount of toxic and carcinogenic organic chemicals such as VOC, pesticides, dyes, etc., which infused into water bodies. This water pollution is one of the

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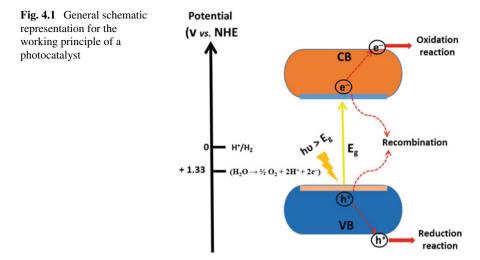
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responsible factor for many water-borne diseases and scarcity of portable water. In this perspective, development of low-cost and high efficient water treatment technologies to treat and recycle the wastewater in a sustainable way is prime importance in order to get portable water for our society. Various methodologies were developed in recent past, which includes wet air oxidation, UV photolysis, adsorption and biodegradation methods are available for wastewater treatment [1-3]. The adsorption or coagulation techniques are among the widely used desalination technique in order to remove organic and inorganic pollutants from contaminated water [2]. However, these techniques simply concentrate the pollutants by transferring them to other phases. Sedimentation, filtration, chemical and membrane technologies are some examples of some conventional water treatment techniques, which suffers with the limitations like high operational cost and could produce toxic by-products into the environment. It is highly essential to develop advanced water treatment technology, which can mineralize the organic pollutants completely by a simple and easy experimentation process, less expense of energy and cost. In this perspective, the complete mineralization of organic pollutants by heterogeneous photocatalytic process using solar light as energy source and semiconductor nanoparticles as catalyst is a sustainable strategy to deal.

### 4.2 Fundamental of Photocatalysis

Photocatalysis is the science, which employed a catalyst and light as energy source to speed up chemical reactions and photocatalyst is a material that is capable of absorbing light, producing electron-hole pairs that enable chemical transformations of the reactants and regenerate after each cycle. When light energy with greater than the band gap energy  $(E_g)$  of the photocatalyst falls on the photocatalyst surface, the electron gets excited to the conduction band (CB) leaving a hole in the valance band (VB). The electron hole migrates to the surface of the photocatalyst and participate in reaction with different substrate. On the other hand, some of the electron hole recombines themselves, which leads to the poor photocatalytic activity of the catalyst (Fig. 4.1). The splitting of water by Fujishima and Honda over TiO<sub>2</sub> surface in the presence of light and electricity put the foundation for the semiconductorbased photocatalysis [4]. Until now TiO<sub>2</sub> is the most widely studied photocatalyst with promising field of applications such as environmental cleaning, self-cleaning surfaces, air and water purification, sterilization, hydrogen evolution, and photoelectrochemical conversion of energy, etc. [4]. TiO<sub>2</sub> is a wide band gap photocatalyst with band gap of 3.2 eV. Although, TiO<sub>2</sub> photocatalyst possess advantages such as high oxidation ability, excellent chemical stability, nontoxicity and inexpensive, it suffers limitations like fast recombination of photogenerated electron-hole pair and poor utilization of solar spectrum [4, 5]. Moreover, the solar spectrum comprises only 5-7% of UV light, while 46% and 47% of the solar spectrum has visible light and infrared radiation, respectively [6].



In recent past, several research efforts has been put in order to design photocatalyst, which can able to absorb visible light of solar spectrum. MoS<sub>2</sub>, CdS, Fe<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>WO<sub>6</sub>,  $Bi_2W_2O_9$ ,  $BiFeO_3$  and bismuth oxyhalides (BiOX, X = Cl, Br, I) are few examples of metal oxide and metal sulphide-based visible light active photocatalyst widely studied for the degradation of a wide range of harmful aqueous organic pollutants into  $CO_2$  and  $H_2O$  [7–13]. The pristine photocatalysts suffers with a poor separation of charge carriers, which leads to a poor photocatalytic efficiency of the photocatalysts. With time, noticeable research attempts have been devoted in order to minimize the recombination process of charge carriers and to enhance the light absorption ability of the photocatalyst, by adopting several strategies such as decoration of noble metal nanoparticles over photocatalyst surface, doping, and composite/heterojunction formation by coupling with suitable a semiconductor [14, 15]. Fe<sub>2</sub>TiO<sub>5</sub>/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/ TiO<sub>2</sub>, α-NiS/Bi<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>S<sub>3</sub>/BiFeO<sub>3</sub>, CuS/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>, Bi<sub>3</sub>S<sub>3</sub>/β-Bi<sub>2</sub>O<sub>3</sub>/ZnIn<sub>3</sub>S<sub>4</sub>, CuS/ BiFeO<sub>3</sub>, CuS/Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>, Bi<sub>2</sub>S<sub>3</sub>/Bi<sub>2</sub>W<sub>2</sub>O<sub>9</sub>, CuS/Bi<sub>2</sub>W<sub>2</sub>O<sub>9</sub>, Bi<sub>2</sub>O<sub>3</sub>/CuBi<sub>2</sub>O<sub>4</sub>, UiO-66/CdIn<sub>2</sub>S<sub>4</sub>, SnS<sub>2</sub>/Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>, CdS/BiOBr/Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> and CdS/Bi<sub>20</sub>TiO<sub>32</sub>/Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> are few examples of recently studied heterojunction photocatalytic systems with improved light absorption and charge carrier separation ability [12, 16-27].

#### 4.3 Iron Oxide-Based Photocatalyst

The iron oxides are composed of Fe and O. Among eight different form of iron oxides, the hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), magnetite (Fe<sub>3</sub>O<sub>4</sub>) and maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) are widely studied oxides due to their unique biochemical, magnetic and catalytic properties. The Fe<sub>2</sub>O<sub>3</sub> exists in three of different crystalline structures, such as hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) and  $\epsilon$ -Fe<sub>2</sub>O<sub>3</sub> [6, 28]. The  $\alpha$ - and  $\gamma$ -phases are extensively studied materials, while  $\beta$ -Fe<sub>2</sub>O<sub>3</sub> phase is less studied material because of

the difficulty in the preparation of single-phase material. Rhombohedral-hexagonal  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is highly stable and has significant potentials in photocatalytic applications, as it is nontoxic, inexpensive, earth abundance, corrosion resistance property with a suitable band gap value ( $E_g = 2.0-2.2 \text{ eV}$ ) to harvest visible light of the solar spectrum, whereas the maghemite is a metastable phase between hematite and magnetite. It has similar crystal structure as magnetite and chemical composition similar to hematite. In the hematite crystal structure, iron occupies the octahedral sites where oxygen is hexagonally close packed. On the other hand in both maghemite and magnetite, iron present in both octahedral and tetrahedral sites and oxygen cubically close packed. The  $\epsilon$ -Fe<sub>2</sub>O<sub>3</sub> is a transition phase between hematite and maghemite, which attract research attention owing to its unique magnetic properties. Seeing the extensively used of both hematite and maghemite form of Fe<sub>2</sub>O<sub>3</sub> than the other polymorphs, this study is focussed on their utilizations in the field of heterogeneous photocatalysis towards the degradation of various persistent organic contaminants from aqueous medium.

Song and co-worker prepare  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanodisks by the assembly of singlecrystalline nanoplates with layered structures by using a silicate-anion-assisted hydrothermal method. The silicate anions believe to adsorb selectively onto the  $\{0001\}$  plane of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoplates and induce the self-assembly of the plates to give the layered nanodisks structure. The  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanodisks display enhanced visible light absorption with excellent photocatalytic activity for the degradation of methylene blue under visible light irradiation [29]. Heidari and co-worker reported the synthesis of porous network-like  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\alpha/\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles by a simple solution combustion method and evaluated the photocatalytic activity towards the degradation of methylene blue (MB) dye under. The Fe<sub>2</sub>O<sub>3</sub> materials calcined at 700 and 800 °C contains diffraction peaks for only  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, where Fe<sub>2</sub>O<sub>3</sub> material obtains after a calcination at 450 °C, which contains both the  $\alpha$  and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> for of Fe<sub>2</sub>O<sub>3</sub>. The higher photocatalytic efficiency of the  $\alpha/\gamma$ -Fe<sub>2</sub>O<sub>3</sub> heterophase material may be account for the formation of junction between  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> phases, which reduced the recombination of photogenerated electrons, and holes [30]. Jing and co-workers studied the photocatalytic activity of pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> as well as phosphatemodified  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. They have employed the simple one-pot water-organic two-phase separated hydrolysis-solvothermal (HST) method for the preparation of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles. The phosphate-modified  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> exhibits high visible photocatalytic activity for the degradation of liquid-phase phenol and gas-phase acetaldehyde. After surface modification with phosphate, the surface -Fe-OH substituted with -Fe-O-P-OH groups, which significantly promote O<sub>2</sub> adsorption over the catalyst surface. The enhanced photocatalytic activity is due to the enhancement in charge carriers separation ability after the modification with phosphate groups [31]. By using electron beam evaporation through a normal thin film deposition and oblique angle deposition (OAD), Fe<sub>2</sub>O<sub>3</sub> thin films and nanorod arrays fabricated by Larsen and co-workers [32]. The growth of the materials aligns towards the (110) direction. Under visible light, the Fe<sub>2</sub>O<sub>3</sub> thin film samples shows more photocatalytic efficiency towards the degradation of methylene blue dye. Whereas the Fe<sub>2</sub>O<sub>3</sub> nanorod inactivate more efficiently to the Escherichia coli O157:H7 bacteria as compared to

the  $Fe_2O_3$  thin films. Bahnemann and co-workers demonstrated the generation of H<sub>2</sub>O<sub>2</sub> species during the photocatalytic oxidations of organic compounds by using  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> photocatalyst. In a comparison study, the ZnO and TiO<sub>2</sub> photocatalysts found to be more active in the generation of  $H_2O_2$  and in the degradation of chlorinated hydrocarbon molecules as compared to the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> photocatalyst [33]. Hameed and co-workers successfully fabricated the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> polymorphs by using a simple surfactant (Triton X) aided hydrogel synthetic route. The photocatalytic properties of both the form of  $Fe_2O_3$  were studied for the mineralization of 2-chlorophenol and 2-nitrophenol pollutants under the visible light as well as under natural sunlight illumination. Both the polymorphs showed a considerably high activity for the degradation of the phenolic compounds under solar light as compared to visible light irradiation. A significant improvement in the photocatalytic activity under visible light was noticed when the polymorphs were preexposed to sunlight preceding to the photocatalytic tests. The higher photocatalytic activity of the exposed polymorphs as compared to the unexposed one is due to the introduction of defects sites which traps the excited electrons during the photocatalysis mechanism [34]. Wang and co-workers fabricated a dodecahedral  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticle with 6 (012) and (104) exposed facets, respectively. The coexistence of these different facets account for a better photocatalytic ability in comparison with the crystals having single exposed facet. They have also demonstrated that the separation of charge carriers between anisotropic facets also has a significant contribution on photocatalytic degradation of Rhodamine B and methylene blue organic dyes [35]. Ramakrishna and co-workers prepared pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> with nanobraids and nanoporous like structures using an electrospinning synthesis method followed by annealing at 500 °C for 5 h. Both of the nanobraids and nanoporous display excellent photocatalytic degradation activity for Congo red dye with 91.2% and 90.2% degradation, respectively after 140 min of irradiation under visible light. They have demonstrated the significant role of porous surface and small particle size of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> towards the excellent photocatalytic activity. The superoxide radicals (O<sub>2</sub><sup>--</sup>), H<sup>+</sup> ion, hydroperoxyl radicals (<sup>•</sup>HO<sub>2</sub>), hydroxyl radicals are generated by the reaction of water and oxygen on the photogenerated hole and electron are responsible for the degradation of Congo red dye over the photocatalyst surface [36]. Zheng and co-workers successfully fabricated dendritic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanostructures with controlled dimension and morphology by a facile solvothermal synthesis method in the presence of 1-N-butyl-3-methylimidazolium benzoate ([Bmim][PhCOO]) ionic liquid. A change in the molar ratio of [Bmim][PhCOO] to K<sub>3</sub>[Fe(CN)<sub>6</sub>] from 0:1 to 2:1, and 5:1 can bring the dendrite structure to hexagonal nanoplates and rods. The ionic liquid plays a crucial role in deciding the formation of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> with different morphologies. The  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> with rod morphology exhibit superior photocatalytic activity towards visible light-induced degradation of Rhodamine B (RhB) dye as compared to the dendrites and plates structured  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials. The degree of crystallinity and exposed crystal facets of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials accounts for improving the photocatalytic activity [37].

Song and co-workers recently fabricated a snowflake-like  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials by using a simple single-step hydrothermal approach and studied there photocatalytic activity towards the degradation of a wide variety of organic pollutants such as crystal violet, Rhodamine 6G, methyl orange, etc. The  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> snowflakes exhibit a superior photocatalytic activity towards degrading cationic organic dyes (crystal violet, Rhodamine 6G) than for the anionic dye (methyl orange) degradation [38]. Shim and co-workers synthesized porous natured Fe<sub>2</sub>O<sub>3</sub> nanorod by a two-step process. First ferrous oxalate dihydrate (FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O) precursor synthesized by a chemical solution processes and second the ferrous oxalate dehydrate on annealing in air at 500 °C for 2 h to get the porous Fe<sub>2</sub>O<sub>3</sub> nanorod. The ferrous oxalate dihydrate nanorods precursor has the length  $3-9 \,\mu m$  and diameter of between 110 and 150 nm. After thermal annealing, the nanorods structured remain intact in the Fe<sub>2</sub>O<sub>3</sub> materials. The Fe<sub>2</sub>O<sub>3</sub> nanorod exhibited excellent photocatalytic degradation ability for a wide range of organic pollutants such as RhB, methylene blue (MB), p-nitrophenol (pNP), eosin B and methyl orange (MO), respectively. The porous structures believe to provide more active reaction sites and also facilitates the efficient separation of photogenerated electrons and holes which is accountable for the excellent photocatalytic efficiency of the prepared porous Fe<sub>2</sub>O<sub>3</sub> nanorods [39]. Zhou and co-workers has prepared  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles with spherical morphology by using an oxidizing environment via a solution synthesis method by changing the pH and reaction temperature. The spherical nanoparticles has a particle size around 17-55 nm and a BET surface area of 14.357  $m^2/g$ . The pH of the reaction media crucially influence the particle size of the nanomaterials. With increase in the pH value from 6 to 12, the particle size also increases. The as-synthesized y-Fe<sub>2</sub>O<sub>3</sub> nanoparticles show potential photocatalytic activity towards the degradation of Orange I dye under UV and visible light illumination. The y-Fe<sub>2</sub>O<sub>3</sub> nanoparticles prepared at pH 6 at a reaction temperature 60 °C with smallest particle size show highest photocatalytic efficiency than other synthesized  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles [40]. Fardood and co-workers synthesized hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) nanoparticles by a simple, environment-friendly and less-expensive sol-gel synthesis method in the presence of a bio template (Arabic gum). The average particle size of the prepared materials is 45-50 nm. The  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials evaluated as a potential photocatalyst with a photocatalytic activity of 90% degradation of Congo red dye after a 90 min of irradiation time [41]. Wang and coworkers fabricated hollow microspherical α-Fe<sub>2</sub>O<sub>3</sub> nanostructure material by ionic liquid-assisted solvothermal method followed by calcination at 250 °C for 6 h. The  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> have a specific surface area up to 220 m<sup>2</sup>/g. The  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> microspheres show excellent photocatalytic activity towards the degradation of Rhodamine B dye. The as-synthesized  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> microspheres exhibit a photocatalytic activity 2–3 times higher than the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles. The higher specific surface area, porous nature and hollow nanostructure play crucial role in the enhanced photocatalytic activity of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> microspheres [42]. Zhu and co-workers prepared hierarchical α-Fe<sub>2</sub>O<sub>3</sub> hollow microspheres using a surfactant-free solvothermal synthesis method and post-thermal treatment at 450 °C for 2 h. The prepared photocatalyst evaluated as a potential catalyst for the degradation of salicylic acid under UV light irradiation [43]. Wang and co-workers fabricated  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanospheres/microsphere by using

a surfactant and template-free two-step synthesis procedure, hydrothermal treatment followed by a thermal decomposition. The  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanospheres/microsphere composed of interlinked elongated nanoparticle and nanospheres/microsphere has a diameter around 5  $\mu$ m, and the elongated particle size is below 30 nm. The  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanospheres/microsphere is mesoporous in nature, with a pore size distribution between 2 and 50 nm with specific surface area of 20  $m^2/g$ . The photocatalytic activity of the as-synthesized  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanospheres/microsphere evaluated for the degradation of Rhodamine 6G dye under visible light illumination. The  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanospheres/microsphere exhibit a photocatalytic efficiency 2 times that of nanosized  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles and around 12 times higher than the micron-sized particles. The higher photocatalytic activity of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanospheres/microsphere was due to combined contribution of the high specific surface area and the porous architecture [44]. Wang and co-workers develop a facile solvothermal route to prepare 3D porous flower-like  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanomaterial with hierarchical architecture without using any structural templates. Two-dimensional  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanopetals organize themselves in a hierarchical fashion in order to give the 3D porous flower-like structure. The depth morphological analysis reveals that the nanopetals has a thickness between 20 and 50 nm and width of 300-500 nm; moreover, these nanopetals composed of nanobricks with 100 nm in length and 30 nm in diameter. The 3D  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials has high specific surface area ( $\sim 52.51 \text{ m}^2/\text{g}$ ) with the presence of numerous mesopores and macropores that facilitate the efficient transportation of the substrate during the catalytic reaction. The photocatalytic activity of the 3D  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanomaterial explored by the mineralization of Rhodamine B dye under UV light irradiation [45]. Geng and co-workers prepared  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> with flue-like 3D porous nanoarchitectures by using a Ni<sup>2+</sup>/surfactant-assisted solvothermal method at 200 °C for 24 h. The  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> material has a specific surface area of 88.82 m<sup>2</sup>/g with potential photocatalytic activity towards the degradation of methylene blue dye under visible light. They have closely demonstrated the influence of the Fe<sup>3+</sup> and Ni<sup>2+</sup> ion ratio on the morphology of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials. At a molar ratio of Fe<sup>3+</sup> to Ni<sup>2+</sup> ion at 1:2 in the solution gives rise to a micro-balls constituted of fine  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanorods, while at molar ratio of 1:3 gives the 3D flue-like structure and the micro-balls structure again regain on further changing in the molar ratio to 1:4. The 3D flue-like  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> shows highest photocatalytic ability for the degradation of methylene blue dye as compared  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles and P25 photocatalyst under visible light illumination [46]. The pristine Fe<sub>2</sub>O<sub>3</sub> photocatalyst has some limitations such as rapid recombination of photogenerated electron-hole pair and poor response to solar spectrum, which result in poor photocatalytic performances. Within short span of time, a lot of research effort have been devoted to prepare novel hybrid materials such as modification with noble metal, doping and formation of binary and ternary composite/heterojunction material. These strategies believe to suppress the recombination process of charge carriers and enhance the light photocatalytic efficiency as a whole. In the subsequent text, we will discussed the hybrid, doped and noble metal-modified  $Fe_2O_3$ photocatalyst and their photocatalytic applications.

Generally, doping of foreign elements (metal or non-metal) significantly alter the physical parameters, chemical reactivity and redox behaviour of the host material. The doping with non-metal such as nitrogen and sulphur widely studied. The main purpose of non-metal doping in  $Fe_2O_3$ , TiO<sub>2</sub> or with metal oxide photocatalysts is to alter the band gap value by mixing the oxygen 2p orbital with that of non-metal. The doping of non-metals believe to creating a trap state (separate band) in between the valence band and conduction band which controls the electron-hole recombination and delay the recombination process so that the photogenerated electron-hole pair could be available for the redox reaction. Parida and co-workers prepare  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> material co-doped with S and N by using co-precipitation method. They have used thiourea both as precipitating agent and as the sulphur and nitrogen source. The S and S-N co-doping induced growth along the (104) plane, whereas the N doping induced along the (110) crystal plane. After S and N doping, the specific surface area increases significantly than the un-doped pristine  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>; on the other hand, the highest surface area has been noticed for the S–N co-doped sample  $(57.85 \text{ m}^2/\text{g})$ . This observation indicates the significant contribution of minute amount of sulphate ion in the samples. The doped sample shows improved visible light response than the pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> sample. The photocatalytic activity of the un-doped and doped sample was evaluated for the degradation of Rhodamine B dye under natural sunlight. A maximum degradation efficiency of 95% was obtained after a reaction time of 4 h [47]. Almazroai and co-workers prepared S-doped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanomaterial by microwave irradiation (300 W for 20 min) using thiourea as sulphur precursor. The crystallinity of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanomaterial has found to decrease after S doping on the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> lattice. After the sulphur-doping enhancement in the visible light absorption, intensity was noticed with a small decrease in the band gap value. This enhancement in the absorbance intensity of the doped photocatalyst can be attributed to the charge transition between the p-orbitals of the S atom and the conduction band (CB) of the α-Fe<sub>2</sub>O<sub>3</sub> nanomaterial. The S-doped α-Fe<sub>2</sub>O<sub>3</sub> nanomaterial display improved photocatalytic degradation efficiency than the pristine  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanomaterial [48]. Suganthi and co-workers fabricated metal (M = Cu, Ni and Co)-doped iron oxide ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) nanoparticle by chemical precipitation followed by calcination. The specific surface area and mesoporosity of the  $Fe_2O_3$  increases after doping with metal was observed. The metal-doped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> exhibits higher photocatalytic activity than the pristine  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanomaterial towards the degradation of Acid Red-27 organic dye under visible light illumination. Among the metal-doped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials, the Cu-doped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> exhibits highest photocatalytic activity [49]. Gao and co-workers prepared multiple metal-doped Fe<sub>3</sub>O<sub>4</sub>@Fe<sub>2</sub>O<sub>3</sub> nanoparticles from Waelz slag, an iron containing hazardous waste. They have employed acidolysis, sol-gel and calcination in order to prepare the multiple metal (Al, Zn, Cu and Mn)-doped Fe<sub>3</sub>O<sub>4</sub>@Fe<sub>2</sub>O<sub>3</sub> nanoparticles from the waste slog. The photocatalytic activities of the synthesized multiple-metal-doped Fe<sub>3</sub>O<sub>4</sub>@Fe<sub>2</sub>O<sub>3</sub> nanoparticles as well as the pristine Fe<sub>2</sub>O<sub>3</sub> nanoparticles were compared for the photocatalytic degradation of methyl orange dye under UV and simulated sun light irradiation. It was observed that all of the doped Fe<sub>3</sub>O<sub>4</sub>@Fe<sub>2</sub>O<sub>3</sub> nanoparticles shows improved photocatalytic activities as compared

to the pristine Fe<sub>2</sub>O<sub>3</sub> [50]. So far, TiO<sub>2</sub> and ZnO are widely studied UV-active photocatalyst. However, there UV light response and poor separation of charge carriers limits their practical utility. Hence, a lot of research effort has been made in recent past in order to make heterojunction and composite by combining with different suitable visible light active semiconductor photocatalyst.  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is a narrow band gap visible light active photocatalyst and its suitable band alignment makes  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> an ideal candidate to combine with other wide band gap semiconductor with improved light absorption and charge carrier separation ability. In the subsequent text, we will discuss the research progress in the preparation of composite/heterojunction of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> with various semiconducting photocatalytic materials.

Omri and co-workers recently fabricated α-Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> nanocomposite material containing 10 and 50 mol% of TiO<sub>2</sub> by using a simple precipitation method. The  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> nanocomposite materials were characterized using various analytical instruments and studied as photocatalyst to degrade methylene blue dye (MB) under visible light. A maximum of 92% of MB dye degradation was recorded after 120 min of irradiation by using  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> composite material 50 mol% of TiO<sub>2</sub>, whereas the pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> exhibited relatively lower photocatalytic efficiency than the composite materials. Under the visible light, the  $TiO_2$  material is unable to generate electron-hole pair, whereas the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> material produce electron-hole pair. After material contact, the excited electron from the conduction band (CB) of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> migrate to the CB of TiO<sub>2</sub>, whereas the hole accumulate in the valance band (VB). This process minimize the recombination process of photogenerated electron-hole pair. The improved visible light absorption and charge carrier separation properties are account for the higher photocatalytic activity of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> nanocomposite material [51]. Qu and co-workers prepared α-Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> dendritic heterostructure nanomaterials in a two-step processes, first TiO<sub>2</sub> nanofiber prepared by electrospinning method and in second step the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanomaterial deposited over the TiO<sub>2</sub> nanofiber by hydrothermal method. Four different sets of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> dendritic heterostructure materials were prepared containing different amount of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. From morphology, it is clearly seen that the heterostructure are comprises of TiO<sub>2</sub> nanofiber (diameter 70 nm) and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanorods (length 100–200 nm and diameter ~ 30 nm), and the TiO<sub>2</sub> nanofibers are homogeneously covered by the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanorods giving a typical branched and dendritic heterostructure configuration. The heterostructure materials exhibit enhanced visible light absorption feature. The photocatalytic activity of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> dendritic heterostructure nanomaterials demonstrated towards the degradation of a wide range of organic dye pollutants such as Congo red (CR), methylene blue (MB), methyl orange (MO) and eosin red (ER). All the heterostructure materials show enhanced degradation efficiency than the parent TiO<sub>2</sub> and commercial  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials. The enhanced photocatalytic activity of the heterostructured material is due to improved visible light response, charge carrier separation and efficient generation of hydroxyl radical [52]. Fu and co-workers fabricated magnetic y-Fe<sub>2</sub>O<sub>3</sub> nanosheets/mesoporous black TiO<sub>2</sub> hollow spherical heterojunctions material by employing a metal-ion intervened hydrothermal process followed by high-temperature hydrogenation technique. The hybrid  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/b-TiO<sub>2</sub> hollow structure material have high specific surface area of  $\sim 63 \text{ m}^2/\text{g}$  and a pore size of 10.5 nm. The resulting hybrid material contains oxygen vacancies which influence the recombination process of electron-hole pairs and extend the lifetime of the charge carriers, by this means improving the photocatalytic performance of the photocatalyst. The photocatalytic activity of the hybrid  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/b-TiO<sub>2</sub> heterojunctions material has been studied by degrading tetracycline pollutant. The hybrid  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/b-TiO<sub>2</sub> display the photocatalytic degradation efficiency about three times greater than that of the pristine photocatalyst. The high photocatalytic property of hybrid  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>/ b-TiO<sub>2</sub> heterojunctions is account to the narrow bandgap nature which extending the photo response from visible light to near infrared regions and the efficient separation and trapping of charge carrier due to generation of vacancies [53]. Jeevanandam and co-workers have synthesized TiO<sub>2</sub>@a-Fe<sub>2</sub>O<sub>3</sub> core-shell nanoheterostructured material by using a simple thermal decomposition technique. Microscopic studies confirm the deposition of the uniform  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> shell on the surface of TiO<sub>2</sub> spheres. The photocatalytic application of the  $TiO_2@\alpha$ -Fe<sub>2</sub>O<sub>3</sub> core-shell nanoheterostructured material was explored towards the degradation of RhB dye under sunlight illumination. The nanoheterostructured material displays enhanced photocatalytic ability than the pristine TiO<sub>2</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials. This enhanced photocatalytic activity of the heterostructured material can be ascribed to the facile transfer of electrons from TiO<sub>2</sub> and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> phase, which reduce the recombination processes of electron-hole pair over the photocatalyst surface [54].

The zinc oxide (ZnO) is an n-type wide band gap semiconductor, low price and non-toxic nature and a very good photocatalyst photocatalysis. Zhang and coworkers fabricate of magnetic 3D y-Fe<sub>2</sub>O<sub>3</sub>@ZnO core-shell nanomaterial by using hydrothermal sintering followed by atomic layer deposition (ALD) method. ZnO shell layer was uniformly deposited on the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> core. The band alignment of the y-Fe<sub>2</sub>O<sub>3</sub> and ZnO photocatalyst are so aligned in a manner to give the characteristic feature of a type-II heterojunction photocatalyst. The photocatalytic activity of the synthesized core-shell nanomaterial was evaluated for ciprofloxacin degradation under simulated sun light illumination. The hydroxyl radical and the hole contribute significantly on the degradation of ciprofloxacin is noticed. The y-Fe<sub>2</sub>O<sub>3</sub>@ZnO core-shell nanomaterial displays enhanced photocatalytic efficiency than the pristine y-Fe<sub>2</sub>O<sub>3</sub> and ZnO counterpart. The improved photocatalytic activity of the heterostructured material is due to the formation of type-II heterojunction and the core-shell structure, which facilitate the efficient migration and separation of the charge carrier [55]. Carmalt and co-workers fabricate α-Fe<sub>2</sub>O<sub>3</sub>/ZnO heterojunction films by using aerosol-assisted chemical vapour deposition technique. The band alignment and electron migration gives a characteristic feature of a type-I heterojunction system. The prepared  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/ZnO heterojunction films exhibit remarkably improved photocatalytic efficiency towards the degradation of stearic acid under UVA light, which is 16 times higher than that of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and 2.5 times than that of the ZnO photocatalysts. Upon irradiation photogenerated electrons migrate from the CB of ZnO layer to the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> layer that increase the life time of the electron which is responsible for the enhanced photocatalytic property of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/ZnO heterojunction films [56]. Mohapatra and co-workers fabricated a ternary α-Fe<sub>2</sub>O<sub>3</sub>/ZnFe<sub>2</sub>O<sub>4</sub>/

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ZnO nanohybrid material by using a microwave-assisted co-precipitation and coprecipitation and thermal annealing synthesis technique. The co-precipitation method gives raise to nanoparticle where microwave-assisted synthesis gives nanodisks like morphology of the ternary photocatalyst. The ternary  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/ZnFe<sub>2</sub>O<sub>4</sub>/ZnO photocatalyst materials were examined as photocatalyst towards the degradation of methylene blue and malachite green dyes under solar light. The material prepared by using microwave-assisted synthesis shows highest photocatalytic activity than the material obtained by co-precipitation method. A maximum of 93.2% of MB degradation noticed after 32 min of irradiation using the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/ZnFe<sub>2</sub>O<sub>4</sub>/ZnO nanodisks. The hydroxyl radical plays a crucial role in the degradation of the organic dyes which was confirmed from the radical scavenger experiment. They have proposed a cascade movement of electron across the CB band of the three component of the ternary photocatalyst, which efficiently reduce the recombination rate of the photogenerated charge carriers. This property may accountable for the improved photocatalytic activity of the synthesized ternary photocatalytic material [57]. Hota and co-workers have fabricated Fe<sub>2</sub>O<sub>3</sub>/ZnFe<sub>2</sub>O<sub>4</sub>, ZnFe<sub>2</sub>O<sub>4</sub>/ZnO and Fe<sub>2</sub>O<sub>3</sub>/ZnFe<sub>2</sub>O<sub>4</sub>/ZnO binary and ternary composite photocatalyst systems by using a simple hydrothermal method followed by calcination at 500 °C. All the synthesized nanocomposite materials display improved visible response as compared to the  $Fe_2O_3$  material. The  $Fe_2O_3/$  $ZnFe_2O_4/ZnO$  ternary composite material has the highest specific surface area of 49.464 m<sup>2</sup>/g, which is much higher than that of the pure  $Fe_2O_3$  and the binary composite material. The photocatalytic activity of the synthesized composite materials was evaluated for the degradation of malachite green (MG) dye under natural sunlight. A maximum of 96.92% of degradation of MG dye was achieved after 90 min of irradiation using the Fe<sub>2</sub>O<sub>3</sub>/ZnFe<sub>2</sub>O<sub>4</sub>/ZnO ternary composite material. They have proposed a cascade migration of electron across the CB of the different component of the ternary photocatalyst, which significantly reduce the recombination process of charge carriers [58].

Graphic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) has been emerged as a potential visible light active photocatalyst with a band gap of 2.7 eV due to high chemical stability, suitable band alignment, natural abundance and easy synthesis. However, low specific surface area, moderate band gap value and poor separation of photogenerated charge carriers limits its practical applications. So many research approaches have been made in recent past in order to prepare composite and heterojunction with Fe<sub>2</sub>O<sub>3</sub>, which has a suitable band alignment to prepare hybrid material with improved visible light response and charge carrier separation properties. Lu and co-workers has recently fabricated a series of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> hybrid materials and studied their photocatalytic activity towards tetracycline degradation under visible light. The  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/ g-C<sub>3</sub>N<sub>4</sub> hybrid materials were prepared by the calcination of Fe-based metal organic framework (Fe-MOF) and melamine. They have demonstrated the uniform distribution of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles (3–5 nm) over the porous g-C<sub>3</sub>N<sub>4</sub> nanosheet. The existence of close microscopic contact between these two phases further confirmed from the TEM analysis. The  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> hybrid material displays higher photocatalytic activity than the bulk  $g-C_3N_4$  photocatalyst. The band alignment of both the component of the hybrid  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> material are aligned in a type-II fashion, and this is responsible for the enhanced charge carrier separation and photocurrent density. The improved visible light absorption, greater specific surface area and efficient charge carrier separation property of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> hybrid material are responsible for the enhanced photocatalytic activity [59]. Prakasam and co-workers prepared g-C<sub>3</sub>N<sub>4</sub>/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> hybrid nanocomposites material by changing the mass ratio of both the components by using a simple one-step hydrothermal method. The photocatalytic activity of the hybrid material evaluated by degrading Congo red (CR) and malachite green (MG) dye under visible light. The FESEM study of g-C<sub>3</sub>N<sub>4</sub>/  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> composite material clearly indicates the incorporation of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles over the  $g-C_3N_4$  nanosheet. The absorption edge of both the pristine  $g-C_3N_4$ and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> materials commence around 455 and 460 nm, respectively. A considerable red shift in the absorption edge was observed for the hybrid material indicating the better visible light absorption and decrease in the band gap value of the photocatalyst. The hybrid material exhibits 87 and 95% of CR and MG dyes degradation after 100 min of irradiation time, which is around 2 times higher than that of the pristine  $g-C_3N_4$  photocatalyst. The type-II nature of the electron-hole migration in the heterojunction is responsible for the higher photocatalytic activity of the hybrid photocatalyst [60]. Li and co-workers prepared a cocoon-shaped magnetic  $Fe_2O_3/$  $g-C_3N_4$  nanocomposite material by two-step hydrothermal synthesis. The cocoonshaped Fe<sub>2</sub>O<sub>3</sub> dispersed uniformly over the porous and layered g-C<sub>3</sub>N<sub>4</sub> surface. The  $Fe_2O_3/g-C_3N_4$  composite photocatalyst exhibits better photocatalytic efficiency for the degradation of Rhodamine B dye than the pristine Fe<sub>2</sub>O<sub>3</sub> and g-C<sub>3</sub>N<sub>4</sub> counterpart [61]. Li and co-workers prepared a Z-scheme  $g-C_3N_4/\alpha$ -Fe<sub>2</sub>O<sub>3</sub> heterojunction photocatalytic system with enhanced charge carrier separation and photocatalytic activity. They have demonstrated the establishment of the Fe-O-C bond in the heterojunction system, which believe to induce facile migration of electron across the grain boundary. The improved visible light response and facile migration of electron makes the heterojunction photocatalyst a better one than the pristine counterpart towards visible light-induced degradation of methylene blue dye [62]. Due to narrow band gap nature and suitable band alignment of the Fe<sub>2</sub>O<sub>3</sub> semiconducting nanoparticle, it is not only involve in making hybrid photocatalyst with  $TiO_2$ , ZnO and g-C<sub>3</sub>N<sub>4</sub> but also a lot of new Fe<sub>2</sub>O<sub>3</sub>-based hybrid materials with improved photocatalytic activity that has been evolved with time. The Fe<sub>2</sub>O<sub>3</sub>-based hybrid materials, their synthesis method, photocatalytic application and their photocatalytic efficiency is presented in Table 4.1.

Table 4.1 Photocatalytic applications of different Fe <sub>2</sub> O <sub>3</sub> -based photocatalyst	s of different Fe2O3-based photo	ocatalyst		
Materials	Methods	Photocatalytic application	Photocatalytic performance	References
TiO <sub>2</sub> /Fe <sub>2</sub> O <sub>3</sub> /CNTs	Sol-gel and calcination	Tetracycline degradation	89.41% in 90 min	[63]
SiO <sub>2</sub> /TiO <sub>2</sub> /Fe <sub>2</sub> O <sub>3</sub>	Mechanochemical	Methylene blue degradation	97% in 22 h	[64]
$Ag_3PO_4-TiO_2-Fe_2O_3$	Solid state blending	Orange II	86.71% in 30 min	[65]
$Fe_2O_3/g-C_3N_4 @ N-TiO_2$	Electrochemical anodization, calcination	Bisphenol-A degradation	100% in 80 min	[66]
$\mathrm{Fe_2O_3} @\mathrm{SiO_2} @\mathrm{TiO_2} \\$	Solvothermal, layer-by-layer assembly	Phenol degradation	100% in 1 h	[67]
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> @TiO <sub>2</sub> core-shell	Hydrothermal synthesis	Acid orange 7 degradation	98.6% in 90 min	[68]
$Fe_2O_3-TiO_2$	Template-assisted dipping/ adsorbing-calcining strategy	Methyl blue degradation	95% in 25 min	[69]
$g-C_3N_4/\gamma-Fe_2O_3/TiO_2$	Sol-gel	Cefixime trihydrate degradation	98.09% in 90 min	[70]
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> @TiO <sub>2</sub> core-shell	Hetero-epitaxial growth	Rhodamine B degradation	60% in 5 h	[71]
Fe <sub>2</sub> O <sub>3</sub> @TiO <sub>2</sub> @nanometal (Au, Ag)	Sol-gel	Methylene blue degradation	92% in 2 h	[72]
TiO <sub>2</sub> /Au/Fe <sub>2</sub> O <sub>3</sub>	Metal-organic framework (MOF) route	2,4 dichlorophenol	94% in 90 min	[73]
TiO_2 and $\gamma$ -Fe <sub>2</sub> O <sub>3</sub> @ GO/PANI-NT	Co-precipitation, hydrolysis-calcination	Rhodamine B degradation	94% in 140 min	[74]
Carbon/TiO2/Fe2O3	Hydrolysis and hydrothermal procedures	Methylene blue degradation	97% in 100 min	[75]
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> -TiO <sub>2</sub> /fly ash	Sol-gel	Rhodamine B degradation	100% in 1 h	[76]
$Fe_2O_3/TiO_2$	Sol-gel	4-chlorophenol degradation	100% in 180 min	[77]
$Fe_2O_3/ZnO/ZnFe_2O_4$	Hydrothermal and annealing	Rhodamine B degradation	95.7% in 60 min	[78]
CuO/Fe <sub>2</sub> O <sub>3</sub> /ZnO	Sol-gel combustion	Bisphenol A degradation	97.5% in 180 min	[79]
Zeolite-supported ZnO/Fe2O3/MnO2	One-step impregnation method Methylene blue degradation	Methylene blue degradation	93% in 120 min	[80]
				(continued)

Table 4.1 (continued)					66
Materials	Methods	Photocatalytic application	Photocatalytic performance	References	
Fe <sub>2</sub> O <sub>3</sub> /ZnO	Solution-combustion technique	Rhodamine 6G degradation	100% in 4 h	[81]	
Cu-Fe <sub>2</sub> O <sub>3</sub> /Ni-ZnO	Hydrothermal, precipitation and calcination	Tetracycline degradation	94% in 2 h	[82]	
y-Fe <sub>2</sub> O <sub>3</sub> /g-C <sub>3</sub> N <sub>4</sub>	Thermal heating and hydrothermal treatment	Tetracycline degradation	73.8% in 120 min	[83]	
g-C <sub>3</sub> N <sub>4</sub> -Fe <sub>2</sub> O <sub>3</sub>	Calcination	Methyl orange degradation	99% in 120 min	[84]	
BaTiO <sub>3</sub> /α-Fe <sub>2</sub> O <sub>3</sub>	Thermal annealing	Rhodamine B degradation	> 95% in 120 min	[85]	
KNbO <sub>3</sub> / $\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	Hydrothermal method	Methylene blue degradation	89% in 90 min	[86]	
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> /RGO	Hydrothermal method	Phenol degradation	62% in 150 min	[87]	
α-Fe <sub>2</sub> O <sub>3</sub> /CdS	Wet-chemical method	Methylene blue degradation	86.7% in 120 min	[88]	
$SnO_2/\alpha$ -Fe <sub>2</sub> O <sub>3</sub>	Chemical vapour deposition	Methylene blue degradation	100% in 2.5 h	[89]	
SnO <sub>2</sub> /\alpha-Fe <sub>2</sub> O <sub>3</sub> -PB (Prussian blue) thin films	Electrochemical and annealing	Rhodamine B and Congo red degradation	$\sim 80\%$ CR and $\sim 82\%$ RhB in 120 min	[06]	
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> /Ag/AgX (X = Cl, Br, I)	In-situ oxidation reaction and self-assembly process	Rhodamine B degradation	100% in 60 min	[91]	
α-Fe <sub>2</sub> O <sub>3</sub> /rGO	Hydrothermal method	Rhodamine 6G degradation	90.5% in 4 h	[92]	
CaFe <sub>2</sub> O <sub>4</sub> /Fe <sub>2</sub> O <sub>3</sub>	Hydrothermal and co-precipitation method	Methyl orange degradation	99% in 60 min	[93]	
NiO-Fe <sub>2</sub> O <sub>3</sub> -CdO	Precipitation and calcination	Methyl orange degradation	84.25% in 60 min	[94]	Ţ
ZnS/Fe <sub>2</sub> O <sub>3</sub> /Ag	Hydrothermal method	Eosin blue degradation	93% in 60 min	[95]	Y. P.
$Fe_2O_3/Mn_2O_3$	Sol-gel method	Parathion degradation	90% in 15 min	[96]	Bh
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> @rGO/PAN	Hydrothermal method	Methylene blue degradation	98.5% in 2 h	[97]	oi ai
Ag/AgBr@Fe2O3	Solvothermal method	Methyl orange degradation	94.4% in 12 min	[88]	nd V
				(continued)	V. Hu

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Materials	Methods	Photocatalytic application	Photocatalytic performance	References
SrTiO <sub>3</sub> /Fe <sub>2</sub> O <sub>3</sub>	Hydrothermal and electrospinning technique	Tetracycline degradation	82.7% in 140 min	[66]
Ag3PO4/α-Fe2O3	Hydrothermal method	Rhodamine B degradation	95% in 10 min	[100]
Fe <sub>2</sub> O <sub>3</sub> /Cu <sub>2</sub> O	Hydrothermal method	Rhodamine B degradation	91.25% in 120 min	[101]
$Fe_2O_3$ @WO_3	Hydrothermal method and precipitation	Rhodamine B degradation	98% in 75 min	[102]
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> /Ag <sub>6</sub> Si <sub>2</sub> O <sub>7</sub>	Wet chemical method	Methylene blue degradation	98% in 30 min	[103]
Fe <sub>2</sub> O <sub>3</sub> /CuBi <sub>2</sub> O <sub>4</sub>	Hydrothermal method	Tetracycline degradation	80% in 120 min	[104]
$Fe_2O_3/Ag_3VO_4$	Solvothermal and precipitation method	Rhodamine B degradation	96.1% in 60 min	[105]
CeO <sub>2</sub> /Fe <sub>2</sub> O <sub>3</sub>	Co-precipitation method	Eosin yellow degradation	98% in 25 min	[106]
Fe <sub>2</sub> O <sub>3</sub> /BiOCl	Hydrothermal method	Methyl orange-Rhodamine B mixed dye degradation	90% in 30 min	[107]
$CuO/\alpha$ -Fe <sub>2</sub> O <sub>3</sub> / $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	Precipitation method	Methyl orange degradation	98% in 240 min	[108]
SnO <sub>2</sub> -Fe <sub>2</sub> O <sub>3</sub> -rGO	Hydrothermal method	Crystal violet degradation	96.3% in 120 min	[109]
α-Fe <sub>2</sub> O <sub>3</sub> /BiVO <sub>4</sub>	Hydrothermal method	Tetracycline degradation	> 80% in 120 min	[110]
$Fe_2TiO_5/\alpha$ - $Fe_2O_3/TiO_2$	Combustion synthesis	Methylene blue degradation	> 95% in 120 min	[16]
$\alpha$ -Fe <sub>2</sub> O <sub>3</sub> /BiFeO <sub>3</sub>	Hydrothermal method	Rhodamine B degradation	60% in 4 h	[111]
FeWO <sub>4</sub> /Fe <sub>2</sub> O <sub>3</sub> di-modified WO <sub>3</sub>	Hydrothermal method	Methylene blue degradation	95% in 10 min	[112]
$\gamma$ -Fe <sub>2</sub> O <sub>3</sub> @ SiO <sub>2</sub> @ AgBr:Ag	Solvothermal, Stöber method	Acid orange 7 degradation	> 90% in 20 min	[113]
α-Fe <sub>2</sub> O <sub>3</sub> -doped Ti <sub>3</sub> C <sub>2</sub> MXene	Ultrasonic assisted self-assembly method	Rhodamine B degradation	98% in 120 min	[114]
α-Fe <sub>2</sub> O <sub>3</sub> @UiO-66	Wet chemical method and calcination	Methylene blue degradation	> 95% in 60 min	[115]
$Fe_2O_3/Bi_2S_3$	Hydrothermal method	Methylene blue degradation	$\sim 90\%$ in 5 h	[116]
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Materials	Methods	Photocatalytic application	Photocatalytic performance	References
			1 A	
$\gamma$ -Fe <sub>2</sub> O <sub>3</sub> /BiOI	Sol-gel, microwave hydrothermal method	Methyl orange degradation	86.3% in 120 min	[117]
$Ag_2CO_3/\alpha$ -Fe $_2O_3$	Precipitation and hydrothermal Malachite green degradation method	Malachite green degradation	$\sim 90\%$ in 120 min	[118]
ZnS/Fe <sub>2</sub> O <sub>3</sub>	Hydrothermal method	Methylene blue degradation	90.17% in 4 h	[119]
$C_3N_4$ @ CoFe <sub>2</sub> O <sub>4</sub> /Fe <sub>2</sub> O <sub>3</sub>	Hydrothermal and calcination Tetracycline degradation method	Tetracycline degradation	99.7% in 80 min	[120]
P3HT/a-Fe2O3	Electrophoretic deposition	Tetracycline degradation	97% in 90 min	[121]

# 4.4 Conclusions

In this chapter, we emphasized the photocatalytic applications of iron oxide and iron oxide-based materials towards the degradation of various persistent aqueous organic pollutants such as dyes, pesticides and phenolic compounds. In terms of synthesis, this chapter provides an overview of morphology control preparation of phase pure iron oxide as well as single-step and multiple-step preparation of iron oxide-based hybrid materials. We believe that this chapter gives an idea in order to prepare iron oxide-based hybrid materials and their applications in the emerging field of research such as electronic, energy and environment.

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