

## Review Article

# Heterogeneous Photo-Fenton Reaction Catalyzed by Nanosized Iron Oxides for Water Treatment

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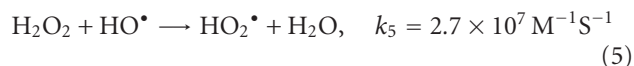
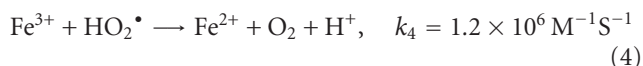
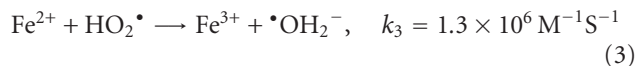
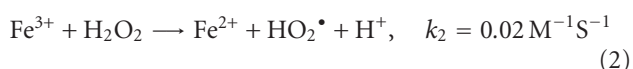
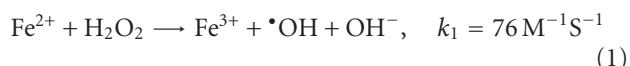
Great efforts have been exerted in overcoming the drawbacks of the Fenton reaction for water treatment applications. The drawbacks include pH confinement, handling of iron sludge, slow regeneration of Fe(II), and so forth. This paper highlights the recent developments in the heterogeneous photo-Fenton reaction which utilizes nanosized iron oxides as catalyst for maximizing the activity due to the enhanced physical or chemical properties brought about by the unique structures. This paper also summarizes the fundamentals of the Fenton reaction, which determine the inherent drawbacks and associated advances, to address the advantages of iron oxides and nanosized iron oxides. Tips for applying this method in water treatment are also provided. Given that the environmental effect of nanosized iron oxides is not yet well established, rapid research growth may occur in the near future to advance this promising technology toward water treatment once it is smartly coupled with conventional technologies.

## 1. Introduction

Large amounts of wastewater from industries, agriculture, and households are produced every day, and organic wastewater has a dominant proportion. The organic content must be reduced to a sufficiently low level acceptable for the receiving waters. Organic pollutants are highly toxic and need to be subjected to physicochemical approaches such as advanced treatment or pretreatment.

The Fenton reaction is frequently investigated as a physicochemical technology because it involves highly oxidative activity of hydroxyl radicals ( $\cdot\text{OH}$ ) with respect to the substrates [1]. The  $\cdot\text{OH}$  is the second most powerful oxidizing species after fluorine in aqueous media, and it is believed to destroy or even mineralize most organic substrates nonselectively in advanced oxidation processes [2–5].

Fenton reaction uses  $\text{H}_2\text{O}_2$  and ferrous ion ( $\text{Fe}^{2+}$ ) to produce  $\cdot\text{OH}$ , as shown in the following reactions [1]:



During the process,  $\text{Fe}^{2+}$  is oxidized to ferric ion ( $\text{Fe}^{3+}$ ) and then reduced back to  $\text{Fe}^{2+}$ . Thus, iron is considered to function as a catalyst. Several studies indicate that  $\text{Fe}^{3+}$  can also mediate the Fenton reaction [6–8]. In practice, an  $\text{Fe}^{2+}$  solution almost inevitably contains  $\text{Fe}^{3+}$ ; thus, the Fenton reaction is actually mediated by the mixture of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ .

Apart from its well-established high efficiency, the Fenton reaction has attracted much attention because of its environmental friendliness, that is, nontoxic products (1)–(6). However, engineers encounter two drawbacks when implementing the Fenton reaction in water treatment. First, the working pH for the reaction is confined to 2.0–4.0, and the highest efficiency of the Fenton reaction occurs at pH 2.8–3.0 [9, 10]. At pH higher than 4.0, the Fenton reaction appears to terminate due to the precipitation of  $\text{Fe}^{3+}$ . Second,

the amount of iron ions decreases because  $\text{Fe}^{3+}$  precipitates after use due to its extremely low solubility product constant even at the pH 4.0.

The escape of iron ions can be prevented and the range of the working pH can be widened once the Fenton reaction evolves into a heterogeneous Fenton reaction that utilizes solid iron oxides as a catalyst instead of free iron ions [10, 11]. A light source can also elevate the reaction efficiency by enhancing the generation of  $\cdot\text{OH}$  and recycling  $\text{Fe(II)/Fe(III)}$ . Nanosized iron oxides further exhibit improved catalytic activity because of their large surface area, which potentially provides more active sites for the generation of  $\cdot\text{OH}$  [12–19].

This review focuses on the heterogeneous photo-Fenton reaction catalyzed by nanosized iron oxides. Iron oxides are commonly found in nature and can be easily prepared in the laboratory. They are commonly considered to be nontoxic, environmentally friendly compounds similar to free iron ions, in contrast to other Fenton-like ions such as cobalt ions [20, 21]. In particularly, the nanosized iron oxides have been acknowledged to have unique properties including stronger adsorptive and catalytic activities. Moreover, the solid iron oxides are subjected to manipulate to achieve special physical and chemical structures, which serve to bring added advantages to the target reactions. Consequently, the Fenton reaction using nanosized iron oxides should be paid, as it is, great attention. Besides, UV-based technologies [22–24] have also been widely tested and already implemented in wastewater treatment plants. Thus, the utilization of a light source in the heterogeneous photo-Fenton reaction, which aids to enhance the Fenton reaction by generating more radicals, is expected to be widespread as it has already been. From an economic point of view, once the solid iron oxides become reusable, the operation cost of the Fenton reaction can be considerably reduced. However, the heterogeneous photo-Fenton reaction is rarely studied compared with other types of Fenton reactions, and thus deserves further investigations. To arouse the attention of readers regarding the importance of heterogeneous photo-Fenton reaction using the nanosized iron oxides for water treatment, this review starts with the brief development of the Fenton reaction, then has a special interest in the iron oxides as catalysts for the heterogeneous Fenton reaction, emphasizing the nanosized iron oxides including their preparation, associated Fenton matrix, and working mechanism. After that, the reusability of nanosized iron oxide and coupling of heterogeneous Fenton reaction with conventional water treatment technologies are addressed because the two topics are significant in real applications. Ahead of the concluding remarks, the potential environmental effect of nanoiron oxides is covered.

## 2. Developments of the Fenton Reaction

The classic Fenton process begins with the production of short-lived, extremely reactive  $\cdot\text{OH}$  with a potential of 2.8 V [1] from the interaction between  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  (1).  $\cdot\text{OH}$  then attacks the substrate, which results in substrate decomposition [1, 25].

$\cdot\text{OH}$  generation occurs with the concurrent transformation of  $\text{Fe(II)}$  to  $\text{Fe(III)}$ , whose kinetics relies on the pH, partial pressure of oxygen, and initial concentration of  $\text{Fe}^{2+}$ , as expressed in the following equation [26]:

$$\frac{d[\text{Fe}^{2+}]}{dt} = k[\text{OH}^-]^2 P_{\text{O}_2} [\text{Fe}^{2+}] \quad (6)$$

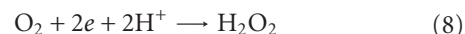
This indicates that the pH plays an important role in  $\text{Fe(II)}$  transformation, and a high pH favors  $\text{Fe(II)}$  oxidation. pH higher than 4.0 induces  $\text{Fe(II)}$  oxidation and its subsequent rapid precipitation, which adversely terminates the Fenton reaction. Therefore, the classic Fenton reaction is limited by a narrow pH range.

Under the narrow pH range, iron must be separated from water after use by adding alkali to form iron sludge, which is an awkward process in real applications. Thus, a heterogeneous Fenton reaction using solid iron oxides to extend the pH range and prevent the formation of iron sludge was needed.

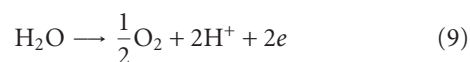
The Fenton reaction is sustained by the redox recycling of the  $\text{Fe(II)/Fe(III)}$  couple, although  $\text{Fe}^{3+}$  can also initiate a Fenton-like reaction [27]. Equations (1) and (2) suggest that the reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  occurs much more slowly than the backward process. Thus, any measure to accelerate the  $\text{Fe(II)}$  regeneration is desired in the Fenton-based reaction. The phototreatment of solid iron oxides can accelerate the recycling of  $\text{Fe(II)/Fe(III)}$ , as illustrated by [28]



Thus, the heterogeneous photo-Fenton reaction is established [29]. Given the difficult transportation and storage of  $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{O}_2$  is produced electrochemically instead of chemically. The in situ electrochemical production of  $\text{H}_2\text{O}_2$  is performed via the cathodic reduction of oxygen from ambient air to establish the electro-Fenton reaction [25, 30–34]:



At the same time, the anodic reaction occurs to produce oxygen:



$\text{H}^+$  consumption (cathodic reaction) and production (anodic reaction) is an equilibrium process. Liu et al. [35] utilizes this inherent consumption and production of  $\text{H}^+$  to adjust the pH automatically for the Fenton reaction instead of chemical addition.

Following the fundamental research of Fenton reaction, remarkable developments have been made to advance its application in water treatment [13, 26, 36]. A variety of Fenton reactions are outlined in Table 1.

Table 1 shows that the efforts exerted to develop the Fenton reaction focused on pH extension, in situ supply of  $\text{H}_2\text{O}_2$  via the cathodic reduction of oxygen, in situ supply of  $\text{Fe}^{2+}$  via the electrochemical anodic oxidation of elemental iron, avoidance of iron loss, and  $\text{Fe(II)}$  regeneration by

TABLE 1: Varieties of Fenton reactions.

	Reagents	pH	Iron loss	Light
Classic Fenton	H <sub>2</sub> O <sub>2</sub> , Fe <sup>2+</sup>	2–4	Yes	No
Fenton-like	H <sub>2</sub> O <sub>2</sub> , Fe <sup>3+</sup>	2–4	Yes	No
Photo-Fenton	H <sub>2</sub> O <sub>2</sub> , iron complex, free iron ions	Acidic to neutral	Yes	Yes
Heterogeneous Fenton	H <sub>2</sub> O <sub>2</sub> , solid iron oxide	Wide range	No	No
Electro-Fenton	Electrogenerated H <sub>2</sub> O <sub>2</sub> , free iron ions; H <sub>2</sub> O <sub>2</sub> , electrogenerated Fe <sup>2+</sup>	2–4	Yes	
Heterogeneous photo-Fenton	H <sub>2</sub> O <sub>2</sub> , solid iron oxide	Wide range	No	Yes
Heterogeneous photoelectro-Fenton	Electrogenerated H <sub>2</sub> O <sub>2</sub> , solid iron oxide	Wide range	No	Yes

illuminating the sludge iron sources [37]. Although all these modifications of the classic Fenton reaction cannot be coupled in one system, the heterogeneous photo-Fenton reaction unifies most of them and poses a promising Fenton-based technology. Obviously, it overcomes the pH limitation, prevents the iron loss after use like that in the reaction using free iron ions as the iron sources, and utilizes light to favor Fe(II) generation from Fe(III). The in situ supply of electrogenerated H<sub>2</sub>O<sub>2</sub> can also be coupled into this system to form a photoelectro-Fenton system [31, 33]. Fe-oxalate can also be utilized in a heterogeneous photo-Fenton system by fixing the Fe ions on silica fabric [37]. Therefore, the heterogeneous photo-Fenton reaction covers almost all developments of the Fenton reaction and has certainly attracted much attention in recent years.

### 3. Iron Oxides as Catalysts for the Heterogeneous Fenton Reaction

Iron oxides are found abundantly in nature and easily synthesized in the laboratory. There are some iron oxides that exist in nature, hematite, magnetite (Fe<sub>3</sub>O<sub>4</sub>), maghemite,  $\beta$ -Fe<sub>2</sub>O<sub>3</sub>,  $\epsilon$ -Fe<sub>2</sub>O<sub>3</sub>, goethite, ferrihydrite, lepidocrocite, and wüstite (FeO). Oxide-hydroxides can be dehydroxylated to their oxide counterparts under specific conditions such as thermal treatment. In most iron oxides, iron is present in the trivalent state, and three compounds of green rusts, magnetite, and wüstite contain Fe(II).

Although all iron oxides are crystalline, their degrees of structural order and crystallinities differ depending on the conditions for crystal formation. Ferrihydrite and schwetmannite are poorly crystalline. The structures of the iron oxides are well defined [38], and particularly interesting, determine the activities for the degradation of organic substrates.

Iron oxides are semiconductors. For instance, stoichiometric hematite is an n-type semiconductor, with the conduction band composed of empty Fe<sup>3+</sup> d orbitals and the valence band consisting of full 2t<sub>2g</sub> orbitals. Photocatalysts such as n-type TiO<sub>2</sub> with a bandgap of 3.2 eV that outputs holes and electrons upon UV excitation have been frequently investigated [39–41]. During the TiO<sub>2</sub> photocatalytic process to decompose organic substrates, photogenerated holes can attack H<sub>2</sub>O molecules to produce  $\cdot$ OH, which further oxidizes the organic substrates. Likewise, the bandgap of stoichiometric hematite is commonly considered to be 2.2 eV [42]; thus, it can be photoexcited by light for the decomposition of organic pollutants in waters [43–45] and the splitting of H<sub>2</sub>O to extract hydrogen energy [46] or disinfect the water [47]. Apparently, poorly crystalline iron oxides release iron ions more readily than their good-crystalline counterparts particularly in acidic media.

### 4. Nanosized Iron Oxides as Catalysts for the Heterogeneous Photo-Fenton Reaction

Under sunlight irradiation, iron minerals are known to undergo reductive dissolution into Fe<sup>2+</sup> species with the concomitant oxidation of organic compounds on solid-liquid surfaces [48]. These heterogeneous photo-Fenton reactions with iron oxides as catalysts can be mimicked and applied in water treatment. Some mineral iron oxides such as Fe<sub>3</sub>O<sub>4</sub> and FeO [49] have been reported to mediate the photo-Fenton reaction. To obtain desired properties, iron oxides are often prepared artificially; thus, extensive efforts have been exerted to the synthesis of iron oxides in the last decade.

Iron oxides are readily prepared using different methods, and their size, orientation, dimensionality, and morphology can be manipulated. Table 2 shows that, in recent years, various interesting architectures of nanoparticles, nanorods, nanoplates, nanosheets, and nanotubes for potential electronic, magnetic, optoelectronic, biomaterial, and catalytic applications have been developed. Nanoparticles have at least one dimension in size of less than 100 nm, and the activity of solid catalysts depends on their particle size and fine structure. With decreased catalyst particle size to the nanometer scale, the particles exhibit unique catalytic activity due to their increased surface areas and number of active sites.

Nanoiron oxides have also been intensively fabricated, and the nanostructures of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, and Fe<sub>3</sub>O<sub>4</sub> have attracted remarkable interest due to their potential applications in nanodevices. Among iron oxides, nanohematite is the most widely prepared probably because of its scientific and technological importance as the most stable iron oxide under ambient conditions. Several methods for hematite preparation are listed in Table 2.

For the large-scale production of nanoiron oxides, a low operational cost is highly expected. Generally, the hydrothermal method involves high pressure and temperature, and is thus an energy-intensive route. A method that utilizes a template or substrate to control direct growth often suffers from high cost, heterogeneous impurity, and complexity. For

TABLE 2: Preparation methods of iron oxides.

Nomenclature	Chemical	Preparation methods	Reference
Nanorod, nanosphere, and nanohexagon	$\alpha\text{-Fe}_2\text{O}_3$	Hydrothermal	[50]
Nanohematite	$\alpha\text{-Fe}_2\text{O}_3$	Hydrothermal	[51, 52]
—	$\alpha\text{-Fe}_2\text{O}_3$	Chemical precipitation	[53]
—	—	High-energy ball milling	[54]
Nanocomposite	$\text{Fe}_2\text{O}_3/\text{SiO}_2$	Sol-gel method	[16, 55]
Maghemite (7-8 nm)	—	Microemulsion method	[56]
Fe/SBA-15	Hematite	Two solvent impregnation technique	[57]
	$\alpha\text{-Fe}_2\text{O}_3$	Solvent thermal	[45]
Flower-like hierarchical $\alpha\text{-Fe}_2\text{O}_3$	$\alpha\text{-Fe}_2\text{O}_3$	Vapor-solid growth	[58]
	$\alpha\text{-Fe}_2\text{O}_3$	Solution-combustion	[59]
Flower-like hematite	—	Complexation-mediated oxidation-hydrolysis	[60]
Nanocrystals	$\alpha\text{-Fe}_2\text{O}_3$	Convenient organic phase process	[61]
Nanoparticle	$\alpha\text{-Fe}_2\text{O}_3$	conducting controlled oxidation reactions	[62]
Nanocube	$\alpha\text{-Fe}_2\text{O}_3$	—	[63]
Nanospindle	$\alpha\text{-Fe}_2\text{O}_3$	—	[64]
Nanorod	$\alpha\text{-Fe}_2\text{O}_3$	Ethylenediamine-(EDA-) assisted method	[65, 66]
Nanowire	$\alpha\text{-Fe}_2\text{O}_3$	Oxidation of pure iron	[67]
Nanotube	—	Solutionphase approach	[52, 68]
Nanobelt	$\alpha\text{-Fe}_2\text{O}_3$	Direct thermal oxidation	[69]
Nanoflake	$\alpha\text{-Fe}_2\text{O}_3$	Deposition	[70]

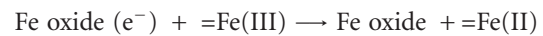
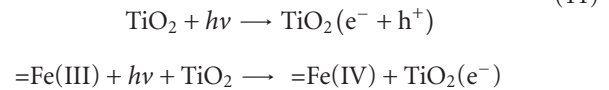
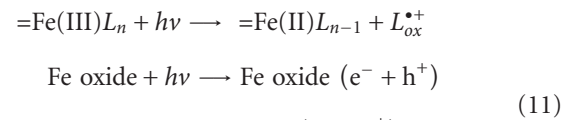
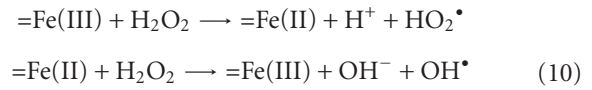
example, in hematite nanotube preparation using an  $\text{Al}_2\text{O}_3$  anodic membrane, the hard template needs to be removed by chemical etching in aqueous NaOH, an extremely basic solution [68].

To overcome the disadvantages of the conventional hydrothermal and template methods for the synthesis of nanosized iron oxides, Zhou and Wong [71] reported a facile synthesis of  $\alpha\text{-Fe}_2\text{O}_3$  hierarchical nanoarchitectures by a solvent thermal process (isopropyl alcohol-mediated self-assembly) without any template or matrix. The formation of 3D porous flower-like  $\alpha\text{-Fe}_2\text{O}_3$  involves a few sequential steps, including nucleation and aggregation, secondary growth (self-assembly), further growth (also self-assembly), and Ostwald ripening (coarsening) [45]. Similarly, Wang et al. [72] prepared flower-like porous hematite nanoarchitectures by annealing the iron oxide precursor formed via the oxidation-hydrolysis reaction between Fe(II) ions and Tris(hydroxymethyl) aminomethane (Tris). They proposed

a formation mechanism of “complex-assembly-aggregation-etching,” wherein as-prepared flower-like nanostructures are nucleated by the self-assembly of Fe(II)-Tris complexes via hydrogen bonds. A simple solution-combusting method to prepare nano- $\alpha\text{-Fe}_2\text{O}_3$  particles has been reported. Using a mixture solvent of ethanol and ethyleneglycol,  $\text{FeCl}_3$  as iron source, and atmospheric oxygen gas as oxidant, nano- $\alpha\text{-Fe}_2\text{O}_3$  particles can be rapidly obtained in one step. This method is cost effective, safe, easily reproducible, and high yielding [72].

Aside from one-component iron oxides, iron oxides with two or more components can be prepared [12] with each component having its specialized function. The composite iron oxides exhibits unique chemical and physical properties.

Chemically, the combination of two oxides exerts a synergistic effect that outweighs the sum of the effects of all individual components. Mazille et al. [73, 74] prepared polymer films that contain titanium oxide and iron oxide ( $\text{PVF}^f\text{-TiO}_2\text{-Fe}$ ). Experiments on the photocatalytic degradation of a few organic substrates (e.g., phenol, nalidixic acid, pesticide mixtures, etc.) demonstrated that the composite oxides have synergistic photocatalytic activity at neutral pH. The high activity is attributed to the photo-Fenton reaction (10) and photocatalytic reaction (11) occurring both on the iron oxide and  $\text{TiO}_2$  surfaces. In particular, the synergistic activity (12) between the two components is believed to accelerate Fe(II) regeneration, which is the rate-determining step in the Fenton reaction [75]. The simplified mechanism can be outlined as follows:



In all the above equations,  $=\text{Fe(II)}$  and  $=\text{Fe(III)}$  are iron species in the solid phase or at the solid-liquid interface.

In some circumstances, the cocomponent assists the immobilization and dispersion of fine particles of iron oxides, which are not trivial tasks. Rasoulifarda et al. [76] prepared nanosized  $\text{Fe}_2\text{O}_3/\text{SiO}_2$  composites by the sol-gel method and calcination.  $\text{Fe}_2\text{O}_3$  induces the photo-Fenton decolorization of azo dye from contaminated water, and  $\text{SiO}_2$  immobilizes the iron oxides. Ho et al. [77] applied solid waste comprising iron oxides that is immobilized on  $\text{SiO}_2$  in the photo-Fenton degradation of reactive black B in a fluidized reactor.  $\text{SiO}_2$  also ensures the recovery of the catalyst with continued activity after three successive tests. Chhabra et al. [51] used a single SBA-15 silica with a mesopore diameter of 7.1 nm and two solvent impregnation techniques to



deposit the iron ions into silica pores. Interesting, a spatial location of the iron oxides are observed to be trapped inside the silica pores or dispersed outside silica grains. The external hematite particles are significantly less active and react less rapidly than the internally trapped iron species in the photo-Fenton decomposition. Wang et al. [78] observed that, the dispersion of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> on silica minimizes particle growth during the sintering process. Fe<sub>2</sub>O<sub>3</sub> crystallites also have larger surface areas and smaller sizes of around 8 nm than unsupported Fe<sub>2</sub>O<sub>3</sub> (>30 nm). They also observed through X-ray diffraction that the phase transformation from  $\beta$ -FeOOH to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> upon thermal treatment is inhibited on silica. In the presence of silica, newly formed ferric (hydr)oxides via photodissolution are preferably redeposited onto the silica instead of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> due to the negatively charged surface. Ferric (hydr)oxides are mostly amorphous and less photoactive; thus,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> is more photoactive than  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.

Another type of two-component iron oxide is formed by the modification of iron oxides using a metal such as gold. Gao et al. [46] described an Au/Fe<sub>2</sub>O<sub>3</sub> aerogel for the photodegradation of azo dye. Due to the addition of gold species to the Fe<sub>2</sub>O<sub>3</sub>, the light absorption spectrum shifts toward the red visible region and reduces the band gap energy. Accordingly, enhanced photocatalytic activity is obtained.

Sometimes, coexisting organic substance, such as organic acids, especially oxalic acid, serves as an indispensable component of the heterogeneous Fenton reaction. The organic acid interacts with the iron oxide under the excitation of photoenergy to produce a series of radicals including hydroxyl radicals, and then the target substrates are decomposed [79–81].

## 5. Reuse of NanoIron Oxides

In the photo-Fenton process, the use of Fe(II)/Fe(III) as a homogeneous catalyst suffers from a major disadvantage, that is, the need to remove the iron sludge after water treatment. This drawback can be overcome by solid iron oxides. The development of nanosized iron oxides increases their activity in the heterogeneous photo-Fenton reaction, whereas the fine particles of nanosized iron oxides necessitate catalyst reusability. The process of separating nanosized particles from the aqueous phase after the reactions is also complicated [82].

For easy separation, magnetic iron oxides [83] that can settle at the bottom of a reactor by the aid of a magnetic field placed under the reactor have been designed. Obviously, this separation method is limited to iron oxides with magnetic force. For other types of nanosized iron oxides without magnetic force, the separation of fine particles from aqueous solution must resort to an alternative technology.

A simple and effective alternative to the prevention of runoff of nanosized catalysts is the immobilization of fine particles on a support. There are various available materials that can serve as supports, such as silica [77, 84, 85], polymer [86, 87], SBA [57], zeolitic Fe(III)-Y and Fe(II)-3X materials [88], alumina [89], and pillared clays [90].

Once immobilized onto support materials, the associated catalytic efficiency may decrease even if there is a synergetic effect. Generally, nanosized iron oxides in powder form can ensure fine contact between light and iron oxide particles. The illumination of the iron oxide surface is a prerequisite for Fe(II)/Fe(III) recycling to sustain the Fenton reaction. Unfortunately, after the particles of iron oxides are immobilized onto a support, particularly onto a porous one, adequate illumination enjoyed by a naked particle system, may be impeded. To date, whether such illumination loss actually occurs is not known.

In TiO<sub>2</sub> photocatalysis, Li et al. [82] reported a type of TiO<sub>2</sub> microspheres fabricated from TiO<sub>2</sub>-nanosized particles and their sol precursor. They observed that the microspheres possess larger pore volumes and surface areas, and consequently, comparable activity with the nanosized particle counterpart. Microspheres with sizes of 30–160  $\mu$ m can also be suspended readily by air bubbling to ensure sufficient illumination. These microspheres can settle quickly at the bottom of the reactor when the air supply stops after use for easy separation from the aqueous solution and reuse. This design concept also appears to be applicable in the heterogeneous photo-Fenton system with nanosized iron oxides.

On the other hand, support materials sometimes have adverse effects on the photo-Fenton reaction. For example, after the support of iron oxides on zeolite, the iron exchange of iron species within the zeolite framework slows down and the stability decreases compared with those in unsupported iron oxides, and some supports such as Nafion are very costly because perfluorosulphonic polymer is used [91]. Thus, its large-scale application in water treatment is hindered.

## 6. Coupling of Iron Oxide-Based Heterogeneous Photo-Fenton Technology with an Integrated Process of Water Treatment

Effluents discharged from industrial processes usually contain recalcitrant pollutants that are nonbiodegradable and destroyed only by chemical approaches. Fenton-based processes are highly effective chemical means that offer simple and cost-effective sources of  $\cdot$ OH to decompose recalcitrant pollutants [92–94]. The heterogeneous photo-Fenton reaction addresses the drawbacks that arise from the classic Fenton reaction, and it is a promising chemical technology for destroying and mineralizing recalcitrant pollutants. Following the successful development of the heterogeneous photo-Fenton technology with iron oxides as catalyst, an incorporation of this technology into an overall process for water treatment becomes essential, given that any individual technology has its own inherent disadvantages and compatible conditions. Water purification demands the coupling of diverse technologies to achieve an integrated process.

Technically, the heterogeneous photo-Fenton process is applicable when two prerequisites are satisfied. One is the transparency of water that ensures the transmission of light. The other is the nonbiodegradability of water that has to be treated by the abiotic method. This method is expected to

improve the biodegradability of water as a pretreatment unit or to decompose recalcitrant pollutants as an advanced unit.

Along with the heterogeneous photo-Fenton process are conventional technologies that work together to purify the polluted influent. At the front-end of the integrated process, the influent can be pretreated by a physical unit such as filtration or grilling to separate the solids present in it. A physicochemical process such as coagulation is subsequently performed to remove colloidal substances. A biological process such as aerobic or anaerobic oxidation is performed to degrade most of the biodegradable organic molecules. Thus, the water quality is usually improved in terms of indices such as chemical oxygen demand (COD) and  $\text{NH}_3\text{-N}$ . If the effluent requires further purification to destroy nondegradable organic pollutants, the heterogeneous photo-Fenton technology follows the biological process. Advanced treatment is believed to increasingly important with the increased requirement of wastewater reclamation.

Alternatively, heterogeneous photo-Fenton technology is used prior to the biochemical process to improve biodegradability for better biological oxidization of the organic substrates in the subsequent process. In this regard, the organic pollutants are highly toxic to the biotas; thus, they are decomposed by the heterogeneous photo-Fenton technology [91].

If the heterogeneous photo-Fenton process is followed by another process, further measures must be taken in some cases. For example, if there is  $\text{H}_2\text{O}_2$  residue (even in small amounts) in the effluent and a membrane process follows for further treatment, the residual  $\text{H}_2\text{O}_2$  must be decomposed to protect the membrane from oxidation.

The smart coupling of the heterogeneous photo-Fenton technology with conventional technologies results in an integrated process for water treatment. The enhanced degradation of polycyclic aromatic hydrocarbons by biodegradation combined with a modified Fenton's reaction [95] is expected to have progress based on a comprehensive assessment of technique and economic feasibility. A pilot-scale test is extremely necessary to verify such data because related reports are very limited.

## 7. Potential Environmental Effect of Nanoiron Oxides

Nanoparticles are increasingly used for industrial and commercial purposes due to their unique characteristics, such as large specific surface areas and unique surface structures that cause high surface reactivity. The widespread use of nanoparticles leads to their inevitable release into the environment during manufacturing, transportation, use, and/or disposal. Therefore, the potential health and environmental risks posed by nanoparticles have drawn significant attention in recent years [96]. In aqueous environments, many nanoparticles such as nano- $\text{TiO}_2$  [97, 98] and nano- $\text{Al}_2\text{O}_3$  have been confirmed to pose biological risks. Consequently, the bioaccumulation of nanoparticles in aquatic organisms is a very important process that affects the overall toxicity of nanoparticles in a realistic environment.

Iron oxides are commonly considered to be nontoxic, whereas some studies suggest that *C. dubia* significantly accumulate on nano- $\text{Fe}_2\text{O}_3$  through ingestion and that nano- $\text{Fe}_2\text{O}_3$  serves as a carrier of As(V) to enhance As(V) toxicity [99]. Some studies reported the cytotoxicity of nano- $\text{Fe}_2\text{O}_3$  toward different types of cell lines, such as human MSTO cells [100] and PC12 cells [101], or toward different bacteria, such as *Escherichia coli* [102]. Katsnelson et al. also observed that at equal mass doses,  $\text{Fe}_3\text{O}_4$  nanoparticles possess considerably higher systemic toxicity than microparticles [103].

Nanoiron oxides can also be formed via secondary formation. For example, nanoscale zerovalent iron that is often used for groundwater remediation because of its reducing ability can be oxidized over time to magnetite, maghemite, hematite, and goethite. Such surface oxidation tends to reduce the activity, agglomeration, sedimentation rate, and toxicity to mammalian cells [104].

Primary tests on the toxicity of nanoiron oxides indicate that great care must be taken when handling nanosized iron oxides during their life cycle from manufacturing to disposal. When used in water treatment, nanoiron oxides can be reused by gravity-induced settlement and immobilization onto a support material that enables their fast separation. Although long-term utilization is possible under illumination, the nanoparticles may undergo photocorrosion and escape from the system into the aquatic environment. In this case, further efforts are recommended to improve the photostability of the iron oxides for the heterogeneous photo-Fenton reaction.

## 8. Concluding Remarks

The heterogeneous photo-Fenton reaction combines most efforts to overcome the drawbacks of the classic Fenton reaction. This combination extends the working pH range using a solid iron source instead of free iron ions. The method also prevents the formation of iron sludge by immobilizing iron oxides, accelerates Fe(II) regeneration by light illumination, and enables the reusability of iron oxides after separation by rapid settlement. The preparation and utilization of nanosized iron oxides pave the way for technological advancement by allowing the manipulation of their architectures and chemical compositions. Consequently, unique physical and chemical properties are exhibited by these nanoiron oxides.

Following the successful development of the heterogeneous photo-Fenton process, a smart coupling of this technology with conventional ones such as filtration, coagulation, biological oxidation, and membrane technology becomes essential. Thus, pilot-scale and field tests are necessary to develop a well-established integrated water treatment process that involves the heterogeneous photo-Fenton reaction and determine technical and economical parameters.

Research on the heterogeneous photo-Fenton process is expected to grow rapidly in the near future prompted by the increasing amount of released recalcitrant pollutants. Future investigations may center on the fabrication of finer physical architectures and well-defined chemical compositions of

nanosized iron oxides. The degradation pathway of organic substrates and evolution of toxicity during the treatment process should be determined. Attention must also be paid to the potential environmental effect of nanosized iron oxides. The mechanism that governs the catalytic reactions occurring on the surface or in the pores of nanosized iron oxides remains to be elucidated as well.

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