

Iron doped TiO₂ photocatalysts for environmental applications: fundamentals and progress

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Abstract—Many recent studies have been reported on the photodegradation of the organic compounds in industrial wastewater in the presence of TiO₂ semiconductor as photocatalyst. Heterogeneous photocatalysts using Iron as a dopant metal, so far, have been reported for various environmental applications. This paper highlights the recent advances and applications of Fe-TiO₂ photocatalysis for the degradation of various pollutants, phenols and dyes.

Keywords—wastewater; photocatalyst; iron doped titanium dioxide; dyes

I. INTRODUCTION

One of the most pervasive problems affecting people throughout the world is inadequate access to clean water and sanitation. Problems with water are expected to grow worse in the coming decades, with water scarcity occurring globally, even in regions currently considered water-rich [1]. Many recent studies have been reported on the photodegradation of the organic compounds present in industrial wastewater using TiO₂ semiconductor as photocatalyst [2-4].

A. TiO₂ as a photocatalyst

TiO₂ is the most commonly used photocatalyst and believed to be an ideal photocatalyst because of the ability to completely mineralize the target pollutants. Furthermore, TiO₂ is cheap, abundant, photostable in solution, very efficient and nontoxic in nature. However, it has some disadvantages: one of this is a relatively high value of the bandgap, around 3.2 eV, which limits its using to the UV light, high dispersion in the water which causes difficulties in sedimentation, and sensitivity to the recombination of photoinduced electrons and holes, which decreases its photocatalytic activity. Many efforts of researchers are focused on the enhancing the photoactivity of TiO₂ by improving the separation between free carriers, increasing the adsorption abilities of the photocatalyst surface, or charging one photocatalyst by another when the mixture of two photocatalysts is used [5]. Furthermore, its photocatalytic properties can be limited by stabilization of the charge photocarriers in the bulk of the material, by fast charge recombination either at the bulk or at the surface of the oxide or by its relatively large band gap [6] and [7]. Hole–electron recombination is a serious problem for the development of photocatalytically based technologies since it severely limits the quantum yields achievable[8]. The most common and effective method to reduce the electron–hole recombination

rates and increase photocatalyst efficiency is the doping of titania with transition metal cations [9-17].

According to Di Paola et al. [16] reported that the photoactivity cannot be generally straightforwardly related only to few physical and chemical properties of the photocatalysts. A comparison of the various findings reported in the literature is a difficult task because of different experimental conditions. The experimental conditions include photocatalyst preparation/ synthesis method, type of dopants used, dopant concentration and calcination temperature of the photocatalyst. Furthermore, the experimental conditions under which the photodegradation experiments were carried out, for example; type of irradiation source, reaction temperature, photocatalyst loading, pollutant concentration and pH of the reaction medium. In this review, a comparison among the results reported in literature for iron doped photocatalysts used for wastewater treatment for the degradation of various organic pollutants including photodegradation of Active Yellow XRG [18, 19], phenol [9], Malachite Green (MG) [20], benzoic acid [16], 4-Nitrophenol [16, 17], Nitrite and nitrate ions [21] under UV and visible light irradiation. A comparison among the results reported in the literature for doped samples obtained from various preparations is not easy and the photoactivity cannot be generally straightforwardly related only to few properties because it depends on all of them. In order to compare the photoactivity of variously doped TiO₂ samples, it would be necessary to use the same bare TiO₂ as starting material by scrutinizing carefully the various findings deriving from the characterization results and to evaluate their relative importance [16].

II. DOPING TiO₂ WITH METALS

It is the method of metal ion insertion into the TiO₂ semiconductor by chemical doping through the different preparation methods and photocatalysis using visible light. The metal may be introduced through different ways [22].

- Doping, i.e. molecular combination of metal oxide in the lattice of TiO₂. This process is expected to modify the band gap of the photocatalyst.
- Metallisation, i.e. deposition of noble metal on TiO₂ crystallites.
- Impregnation of TiO₂ with a salt of metal followed by evaporation, i.e. deposition of small amount of salt on TiO₂ surface.

- Addition of low concentrations of transition metal to the solution of substrate to be treated.

Noble metals, such as Ag, Pt, Ni, Cu, Rh, Pd, have been studied and showed to be very effective for enhancement of TiO₂ photocatalysis. These metals reduce the possibility of electron-hole recombination, causing efficient charge separation and higher photocatalytic reaction rates. Therefore, noble metals with these properties can help electron transfer, leading to higher photocatalytic activity. Many studies of noble metal deposition on TiO₂ have been focused on group VIII metals for UV-irradiated Photocatalytic degradation of organic pollutants and different dyes [23-27]. Figure 1 show the comparison of UV-vis spectra of undoped and iron-doped titania catalysts. Examples of the metal doped TiO₂ photocatalysts used for wastewater treatment are presented in Table I.

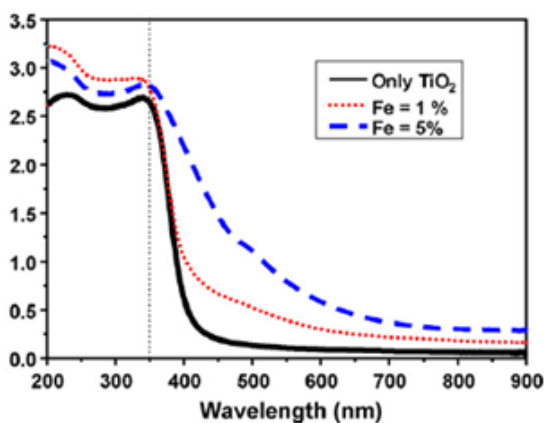


Fig. 1. UV-vis spectra of iron-doped titania catalysts [1]

TABLE I. DOPED TiO₂ PHOTOCATALYSTS USED FOR WASTEWATER TREATMENT

Metal doped TiO ₂	Preparation Method	Photodegradation Study	Ref.
CdS/TiO ₂	Sol-gel	Orange II	[13]
Co, Cr, Cu, Fe, Mo, V & W doped TiO ₂	Impregnation	Benzoic acid and 4-Nitrophenol	[16]
Co, Cr, Cu, Fe, Mo, V & W doped TiO ₂	Impregnation	4-Nitrophenol	[17]
Fe/ TiO ₂	Hydrothermal	Malachite Green	[20]
Ag, Cu and VO/TiO ₂	Impregnation	Orange II and tartrazine	[22]
Cu/TiO ₂	Photo-deposition, sol-gel	Orange II	[28]
Pt/TiO ₂	Impregnation	Orange II, Basic Blue 41 and Basic Red 46	[29]
Pt/TiO ₂	Thermal hydrolysis	Orange II	[30]
ZrO ₂ /TiO ₂	Homogeneous hydrolysis	Orange II	[31]
Zn-Fe/TiO ₂	Sol-gel	Orange II	[32]
CoPcS/TiO ₂	Sol-gel	Orange II	[33]
Pb, Cr, Ag, Fe doped TiO ₂	Hydrothermal, impregnation	Salicylic acid	[34]

III. PHOTOCATALYTIC DEGRADATION OF ORGANIC POLLUTANTS USING Fe DOPED TiO₂

For the previous studies it can be seen that photocatalytic properties of TiO₂ doped photocatalysts can be limited by stabilization of the charge photocarriers in the bulk of the material, by fast charge recombination either at the bulk or at the surface of the oxide or by its relatively large band gap [6] and [7]. Furthermore, electron-hole recombination is a serious problem for the development of photocatalytically based technologies since it severely limits the quantum yields achievable [8]. Many studies have been reported using iron-doped titania photocatalysts for different environmental applications specially for the wastewater treatment, prepared through different preparation methods allowing a good control of the particle size and morphology in the nanoscale range. Fe³⁺ is considered an interesting dopant of titania and it is believed that Fe³⁺ cations can act as shallow traps in the titania lattice although discrepancies appear with respect to their role in enhancing electron/hole recombination properties [6] and [35]. Moreover, modification of the surface properties induced by metal doping can be most relevant to explain the photocatalytic performance.

Amongst a variety of transitional metals, iron has been considered to be an appropriate candidate due to the fact that the radius of Fe³⁺ (0.69 Å) is similar to that of Ti⁴⁺ (0.745 Å), so Fe³⁺ can be easily incorporated into the crystal lattice of TiO₂. Furthermore, Fe³⁺ can provide a shallow trap for photo-generated electron and hole because the energy level of Fe²⁺/Fe³⁺ lies close to that of Ti³⁺/Ti⁴⁺, favoring the separation of photo-generated electron-hole pair, and consequently resulting in the improvement of quantum yield [15].

IV. FACTORS AFFECTING THE PHOTODEGRADATION OF ORGANIC POLLUTANTS USING Fe DOPED TiO₂

The main challenges in the heterogeneous catalysis is to achieve the proper physico-chemical properties, maximum dispersion of the active species onto the photocatalysts support. From the previous work it has been concluded that the main factors that determine the photocatalytic activity of the photocatalysts are the physic-chemical properties and the dispersion of the doped species onto the support [36]. A reasonable approach towards the solution of this problem is related with the selection of different photocatalysts synthesis parameters and reaction parameter. Some of the factors regarding the photocatalytic degradation of the organic pollutant using iron doped TiO₂, discussed in this review are: an appropriate methodology of preparation, effect of metal ion dopant concentration and the optimal photocatalysts loading

A. Effect of photocatalysts preparation method

The photocatalytic and photoelectrochemical properties of TiO₂ and doped TiO₂ photocatalysts are directly associated with the synthesis technique because it can affect various characterizations of the nanomaterials [36]. Many recent studies have been reported for the preparation of photocatalysts using different preparation materials. Different preparation methods may result in different defect structures and surface

morphologies, affecting the photocatalytic activity. Table 2 represent the Fe/TiO₂ photocatalyst prepared via different preparation methods and their application for photocatalytic degradation of different organic compounds present in industrial wastewaters.

Most of these metal doped TiO₂'s reported in the literature are prepared by co-precipitation and incipient wet impregnation method. In the impregnation method, substitution of metal ions in the bulk TiO₂ crystallites is not likely to occur, and at best, substitution may take place on the surfaces [16, 37]. In the co-precipitation method, post-heat processing of mixed metal hydroxides yields metal doped TiO₂. This high temperature, long time heating may separate out the dopant metal ions into respective metal oxides and in many cases they segregate on the surfaces [38]. The hydrothermal synthesis has become a good doping method, because dopant ions precursor distributes uniformly in reaction system during the whole hydrothermal process. Hydrothermal method has been applied to synthesize nanosized materials due to the advantage that the products prepared by this method have well crystalline phase, which benefits to thermal stability of the nanosized materials. Kominami et al. [39, 40]. have synthesized nanosized titanium (IV) dioxide in the anatase form by hydrolysis of titanium (IV) alkoxide in the toluene with water that was dissolved from the gas phase at high temperatures (150–300 °C) [39] and [40].

Di Paola et al. [16], reported photocatalytic oxidation reactions of aliphatic and aromatic organic compounds having different acid strengths, i.e. methanoic acid, ethanoic acid, benzoic acid and 4-nitrophenol, under 25 W medium pressure Hg lamp were carried out in aqueous systems by using polycrystalline TiO₂ powders doped with various transition metal ions (Co, Cr, Cu, Fe, Mo, V and W) prepared using incipient wet impregnation method.

Zhu et al. [18], reported that Iron-ion-doped anatase titanium (IV) dioxide (TiO₂) photocatalysts prepared using hydrothermal hydrolysis, exhibited higher photoactivity for the decolorization of Active Yellow XRG dye diluted in water under both UV and visible light irradiation compared to the undoped TiO₂. Fe²⁺/Fe³⁺ doped TiO₂ was reported to have high specific surface areas and small crystal sizes. Furthermore, TiO₂ doped with FeCl₃ was found to have better catalytic activity for the degradation of XRG than those doped with FeCl₂. It was also reported that UV-Vis diffuse reflectance spectra showed a slight shift to longer wavelengths and an extension of the absorption in the visible region for almost all the ion-doped samples, compared to the non-doped sample. The photocatalytic activity of those catalysts was investigated for the liquid phase photocatalytic degradation of active yellow XRG dye diluted in water under UV and visible light irradiation. Zhu et al. [19] further reported that Fe³⁺-doped TiO₂ prepared using sol-gel method, extends its absorption to longer than 500 nm, which leads to an obvious photocatalytic activity under visible irradiation. From XRD, EPR, AAS and XPS, it was found that Fe exist in trivalent ionic state substituting Ti⁴⁺ in TiO₂ lattice and its concentration decreases from the surface to the center of doped TiO₂.

A series of nanosized iron-doped anatase TiO₂ catalysts with different iron content (between 0.4 and 5.1 wt.%) were

prepared by a microemulsion method and examined with respect to their behavior for UV photocatalytic degradation of aqueous phenol [9]. An enhancement of the photocatalytic activity is observed for doping levels up to ca. 1 wt.% which is attributable to the effective introduction of Fe³⁺ cations into the anatase structure along with associated modifications of the surface acid/base properties. Achievement of relatively high levels of surface segregation of oxidic iron-containing amorphous phases for higher doping levels results however detrimental to the photoactivity [9].

Nano-sized Fe-doped and undoped TiO₂ particles, synthesized by hydrothermal process at low temperature were reported for degradation of Malachite Green (MG) dye in aqueous solution under UV and visible light irradiation [20]. Fe doping has an effect on the crystallization on TiO₂ and may prevent particle agglomeration, forming well-defined nanocrystalline particles with high surface area. Asiltürk et al. [20] further reported that the crystallite size and the particle size of the Fe³⁺-doped TiO₂ are smaller than those of UTiO₂ (without doping), which can signify that the presence of Fe³⁺ in the reaction media might be used to control the particle and crystallite sizes of the oxides. Moreover, increasing the Fe³⁺ ion concentration decreases the particle size. Reduction in the particle size caused by doping Fe³⁺ ion led to larger surface area and higher surface area may be benefit to their high photocatalytic performance, due to enhanced adsorption of photons and dye molecules.

TABLE II. Fe/TiO₂ PHOTOCATALYST PREPARED VIA DIFFERENT PREPARATION METHODS AND THEIR APPLICATION FOR PHOTOCATALYTIC DEGRADATION OF DIFFERENT ORGANIC COMPOUNDS IN WASTEWATERS

Pollutant	Preparation method	Reaction parameters	Ref.
Phenol	Microemulsion	Phenol photooxidation under high-pressure Hg lamp (500 W)	[9]
benzoic acid and 4-Nitrophenol	Impregnation	Photocatalytic oxidation of methanoic acid, ethanoic acid, benzoic acid and 4-nitrophenol, under 25 W medium pressure Hg lamp	[16]
4-Nitrophenol	Impregnation	Photodegradation of 4-nitrophenol under 125 W medium-pressure Hg lamp	[17]
Active Yellow XRG	Hydrothermal	Photocatalytic degradation of active yellow XRG dye under UV (300 W high-pressure Hg lamp) and visible light irradiation	[18]
Active Yellow XRG	Sol-gel	Photocatalytic degradation of XRG under UV (using a 300 W high-pressure Hg lamp) and visible light irradiation	[19]
Malachite Green	Hydrothermal	Degradation of Malachite Green (MG) dye under UV and visible light irradiation	[20]
Nitrite and nitrate ions	Coprecipitation and the sol-gel	Photocatalytic reduction of nitrite and nitrate ions using a 450 W Xe lamp	[21]

B. Effect of dopant concentration

The relative efficiency of a metal ion dopant depends on whether it serves as a mediator of interfacial charge transfer or as a recombination center, which is related to the preparation method, the dopant concentration, the energy level of the dopant within the TiO_2 lattice, its d electronic configuration, the distribution of the dopant within the particles [15].

According to Di Poala et al. [17] dopants can affect negatively the photoreactivity of TiO_2 , changing the number of active sites, the type or surface groups, and the acid–base properties. The different behavior of the various samples is also related to the solubility of the transition metal in the support, which depends strongly on the radius and the charge of the corresponding ion. Any variation in the electronic structure of the surface is reflected in the adsorption characteristics. Dopants contents on photocatalytic activity of photocatalysts have been investigated [6, 9, 16–18, 34].

Zhu et al. [18] revealed that 0.09% $\text{FeCl}_3\text{-TiO}_2$ and 0.09% $\text{FeCl}_2\text{-TiO}_2$ have high specific surface areas and small crystal sizes, which are of benefit to efficient photocatalytic reactions and Fe acting as both hole and electron traps can enhance photocatalytic activity of TiO_2 . An enhancement of the photocatalytic activity is observed for doping levels up to ca. 1 wt.% which is attributable to the effective introduction of Fe^{3+} cations into the anatase structure along with associated modifications of the surface acid/base properties [9]. Zhu et al. [18], further reported that the amount of doped iron ion plays a significant role in affecting its photocatalytic activity and iron doped with optimum content can enhance photocatalytic activity, especially under visible light irradiation. Fe dopant acts as charge traps retarding electron–hole recombination and enhancing interfacial charge transfer to degrade the XRG dye adsorbed on the surface of the particles within the suitable concentration range of dopant. When the dopant concentration is too high, the recombination rate will increase because the distance between trapping sites in a particle decreases. In addition, by EPR analysis there may be some undesirable microenvironments of doped iron in excessively doped samples. It is believed that the crystal sizes and the specific surface areas of the catalysts, which were modified by doping iron ion, must play a significant role in determining the photocatalytic decolorization of XRG.

For the photocatalysts prepared via hydrothermal method, 0.3FeTiO₂ sample with low iron content showed a constant absorption in the visible region (Figure 2) which is higher than UTiO_2 . Asiltürk et al. [20] also reported that Fe doped TiO_2 powders had enhanced absorption characteristics in region of 450–650 nm, and this enhancement increases as the doped Fe is increased, accompanying with the change of powder color from primrose yellow to dark cream. It seems that photocatalytic activity under visible light depends on the addition of iron.

The results of 4-nitrophenol photodegradation have shown that loading TiO_2 with Co, Cr, Cu, Fe, Mo, and V causes a decrease of the photocatalytic activity of TiO_2 and this effect was more significant as the amount of loaded metal increased [17]. The diffuse reflectance spectra reveal a red shift in the band gap transition, which can be explained by the introduction

of energy levels of the transition metal ions into the band gap of TiO_2 [15]. According to [15] and [6] the presence of energy levels below the conduction band edge and above the valence band edge influences the photoreactivity of TiO_2 since the metal ions can act as electron (or hole) traps altering the electron–hole pair recombination rate.

The role of the dopant ion is primarily to improve the charge separation of the photoproduced electron-hole pairs via a permanent electric field. Ranjit and Viswanathan [21] reported the photocatalytic reduction of nitrite and nitrate ions over 100 mg of Fe-doped TiO_2 catalyst prepared by coprecipitation and the sol-gel method under the irradiation of 450 W Xe lamp. They further reported that the anatase to rutile phase transformation is dependent on the nature of the precursor used. Sol-gel-derived iron-doped catalysts show the presence of rutile and pseudobrookite phases, whereas coprecipitated catalysts show only the anatase phase. The photocatalytic activity of the iron-doped catalysts can be explained in terms of the heterojunction formed between the Fe/TiO_2 and $\alpha\text{-Fe}_2\text{O}_3$ phases for the sol-gel-derived catalyst. The summary of the results for the influence of the dopant concentration on photocatalytic activity of iron doped TiO_2 photocatalysts is given in Table 3.

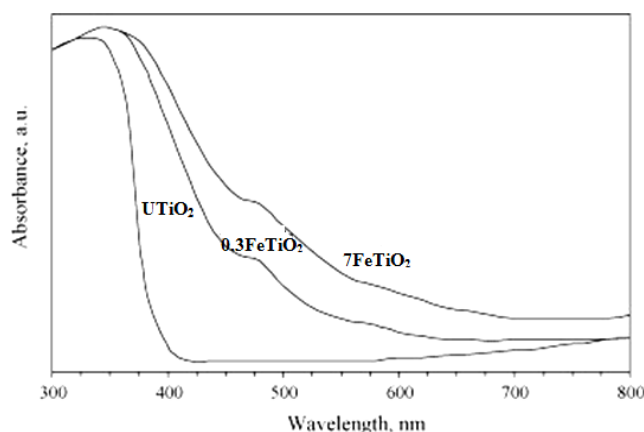


Fig. 2. UV-Vis absorption spectrum of undoped and Fe doped- TiO_2 particles[20]

TABLE III. THE INFLUENCE OF DOPANT CONCENTRATION ON PHOTOCATALYTIC ACTIVITY OF Fe/TiO_2 PHOTOCATALYST

Pollutant	Doping (%)	Optimum doping (%)	Ref.
Phenol	0.4–5.1	1.0	[9]
benzoic acid and 4-Nitrophenol	1.0	1.0	[16]
4-Nitrophenol	0.3–5.0	1.0	[17]
Active yellow XRG	0.03–0.15 %	0.09%	[18]
Active Yellow XRG	0.05–0.5	0.15	[19]
Malachite Green	0.3–0.7	-	[20]
Nitrite and nitrate ions	0.11–1.76	1.48	[21]

C. Effect of photocatalyst loading

For the photocatalytic degradation of organic substances, the optimal photocatalysts loading is very important. From the previous studies it is generally believed that an increase in catalyst concentration increases the number of active sites on the photocatalyst surface, which in turn increase the number of hydroxyl and superoxide radicals. But further increases in the catalyst concentration no longer increases the number of active sites produced by light illumination and, instead, results in agglomeration of catalyst particles and interception of the light by the suspension; hence, part of the catalyst surface becomes unavailable for photon absorption, and the degradation rate decreases. The optimal value of catalyst concentration is also associated with the nature of the pollution and intensity of light [36, 41]. The summary of the finding for the effect of photocatalyst amount required on photocatalytic activity of iron doped TiO₂ photocatalysts is given in Table 4.

TABLE IV. THE EFFECT OF PHOTOCATALYSTS LOADING ON PHOTOCATALYTIC ACTIVITY OF Fe/TiO₂ PHOTOCATALYST

Pollutant	Pollutant concentration (mg/L)	Photocatalyst loading (g/L)	Light source	Ref.
Phenol	50	1	Visible	[9]
Benzoic Acid, 4-Nitrophenol	20	0.7	UV	[16]
4-Nitrophenol	20	1.4	UV	[17]
Active Yellow XRG	100	0.06	UV/Visible	[18]
Active Yellow XRG	100	1.0	UV/Visible	[19]
Malachite Green	2.5	2.5-5.0	UV/Visible	[20]
Nitrite, nitrate ions	20	0.1	UV	[21]
Salicylic Acid	-	1.0	UV	[34]

CONCLUSIONS

Based on the studies reported, this review focuses on the role of various operating parameters on the photocatalytic degradation of various dyes and phenols, and reports the main advances. TiO₂ has been suggested to be efficient for the degradation and mineralization of various toxic organic pollutants, e.g., phenols and dyes in water in the presence of UV and visible light.

- The role of the dopant ion is primarily to improve the charge separation of the photoproduced electron-hole pairs via a permanent electric field.
- The findings also suggest that various operating parameters such as type of photocatalyst, different photocatalyst preparation methods, light source, pollutant types, initial concentration of pollutants, dopant concentration and photocatalyst loading.

- An increase in dopant ion content favors electron-hole separation and in turn enhances the photoactivity. For an optimum dopant value maximum photoactivity can be achieved but beyond a certain level, the photoactivity might be reduced due to the space charge layer becomes thicker, and the probability of carrier recombination is increased.
- There is an optimal value for the dopant concentration and photocatalyst loading at which the photoactivity reaches a maximum.
- Although this review is not exhaustive in the scope of photocatalytic degradation of organic pollutants using Fe/TiO₂ photocatalysts; however, it addresses the fundamental principles and recent applications in this area.

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