Review Article

Increase of the Photocatalytic Activity of TiO$_2$ by Carbon and Iron Modifications

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Modification of TiO$_2$ by doping of a residue carbon and iron can give enhanced photoactivity of TiO$_2$. Iron adsorbed on the surface of TiO$_2$ can be an electron or hole scavenger and result in the improvement of the separation of free carriers. The presence of carbon can increase the concentration of organic pollutants on the surface of TiO$_2$ facilitating the contact of the reactive species with the organic molecules. Carbon-doped TiO$_2$ can extend the absorption of the light to the visible region and makes the photocatalysts active under visible-light irradiation. It was proved that TiO$_2$ modified by carbon and iron can work in both photocatalysis and photo-Fenton processes, when H$_2$O$_2$ is used, enhancing markedly the rate of the organic compounds decomposition such as phenol, humic acids and dyes. The photocatalytic decomposition of organic compounds on TiO$_2$ modified by iron and carbon is going by the complex reactions of iron with the intermediates, what significantly accelerates the process of their decomposition. The presence of carbon in such photocatalyst retards the inconvenient reaction of OH radicals scavenging by H$_2$O$_2$, which occurs when Fe-TiO$_2$ photocatalyst is used.

1. INTRODUCTION

The photocatalytic process with using TiO$_2$ photocatalyst is very promising for application in the water purification because many organic compounds can be decomposed and mineralized by the proceeding oxidation and reduction processes on TiO$_2$ surface. The most commonly tested compounds for decomposition through the photocatalysis are phenols, chlorophenols, pesticides, herbicides, benzenes, alcohols, dyes, pharmaceutics, humic acids, organic acids, and others.

TiO$_2$ is the most commonly used photocatalyst, because it is nontoxic, chemically stable, cheap, and very efficient. 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 TiO$_2$ 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.

2. TIO$_2$ MODIFIED BY CARBON

2.1. Carbon-doped TiO$_2$ visible ligh-active photocatalysts

Recently, modification of TiO$_2$ by C doping towards obtaining the visible light-active photocatalyst has been reported [1–9]. The narrowing of the bandgap, the anodic shift of the quasi-Fermi potential, the visible-light absorption, and the transfer of photoexcited carriers to the reactive sites at the catalyst surface have been noticed as a result of nonmetal anion doping affecting its visible-light activity.

Sakthivel and Kisch [2] proved that prepared C/TiO$_2$ photocatalyst from TiCl$_4$ and tetrabutylammonium hydroxide was active under artificial solar light and could efficiently decompose tetrachlorophenol with the activity higher than TiO$_2$ and TiO$_2$ doped with nitrogen. In Figure 1, diffuse reflectance spectra of pure and carbon-doped TiO$_2$ are shown [2].
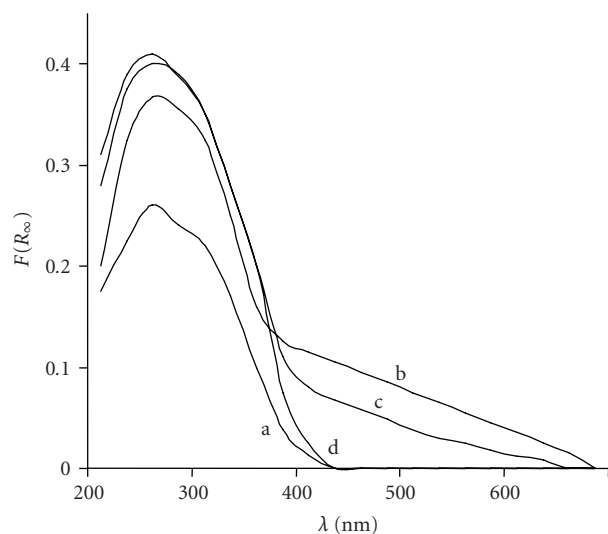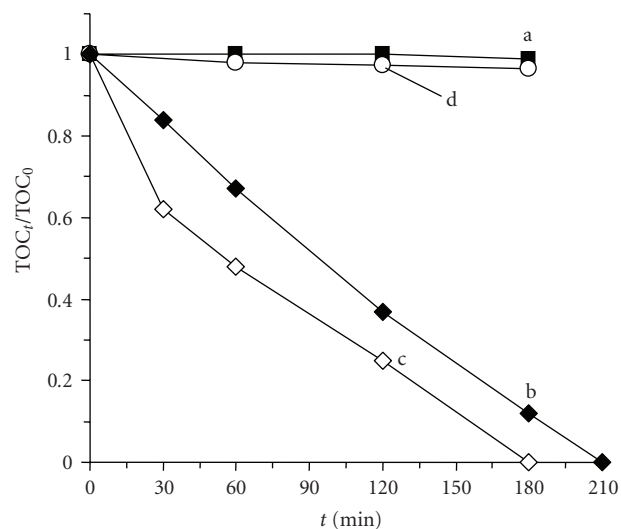
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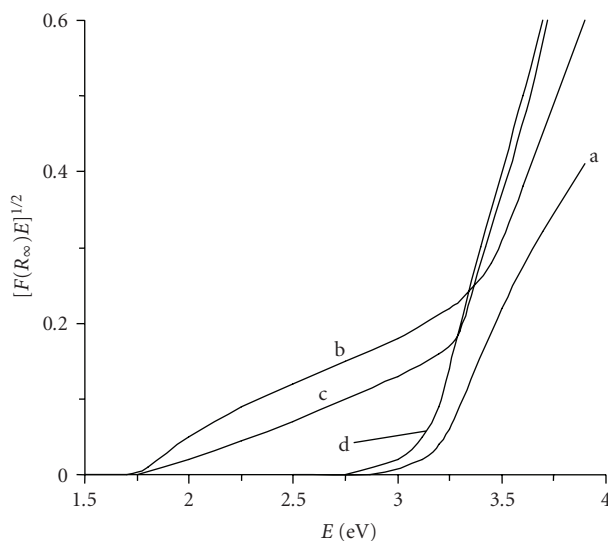
(b)

FIGURE 1: (A) Diffuse reflectance spectra of modified and pure TiO$_2$, (B) plot of transformed Kubelka-Munk function versus the energy of the light absorbed; (a) TiO$_2$, (b) TiO$_2$-2.98%C, (c) TiO$_2$-0.42%C, (d) TiO$_2$-0.03%C.

(a)

(b)

FIGURE 2: (A) Photomineralisation of 4-chlorophenol with artificial visible light ($\lambda = 455$ nm; TOC$_0$ and TOC$_t$ = total organic carbon content at times 0 and t); (B) diffuse indoor daylight degradation of 4-chlorophenol and remazol red on pure and modified TiO$_2$; (a) TiO$_2$, (b) TiO$_2$-2.98%C, (c) TiO$_2$-0.42%C, (d) TiO$_2$-0.03%C.
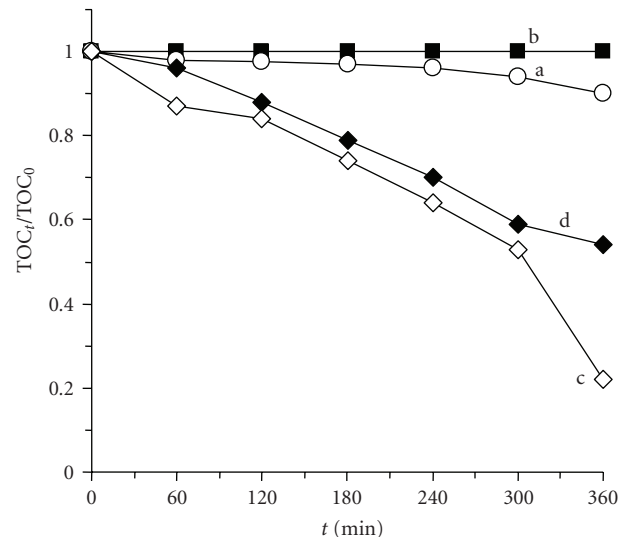
Two absorption maxima on the UV-Vis spectra have been observed, in the range of UV and Vis, showing that these photocatalysts could be excited with the wavelengths in the visible region.

In Figure 2, the mineralisation of the tetrachlorophenol on these samples is presented.

Shen et al. [4] prepared C/TiO$_2$ photocatalyst through calcination of TiCl$_4$ in air at 350°C and proved that such prepared photocatalyst was active for decomposition of trichloroacetic acid under visible light. Carbon-doped TiO$_2$ can be prepared also by hydrolysis and calcinations of TiCl$_4$ with tetra-n-butyl ammonium hydroxide [7], and by calci-

nations of TiO$_2$ with urea and thiourea [8] or oxidation of TiC at high temperatures [9]. Choi et al. [9] have investigated carbon-doped TiO$_2$, and they claimed that substitution of C for O in the TiO$_2$ leads to a photocatalytic decomposition of methylene blue under visible-light irradiation. Di Valentin et al. [10] reported a theory of in-building of carbon atom in the structure of TiO$_2$, and they showed that carbon atom could replace oxygen atom or titania atom depending on the concentration of oxygen in the structure of TiO$_2$. Replacing of carbon atom with Ti conducts to form the new states in the bandgap. Some oxygen vacancies are formed, which could be responsible for the extending of the photocatalytic activity
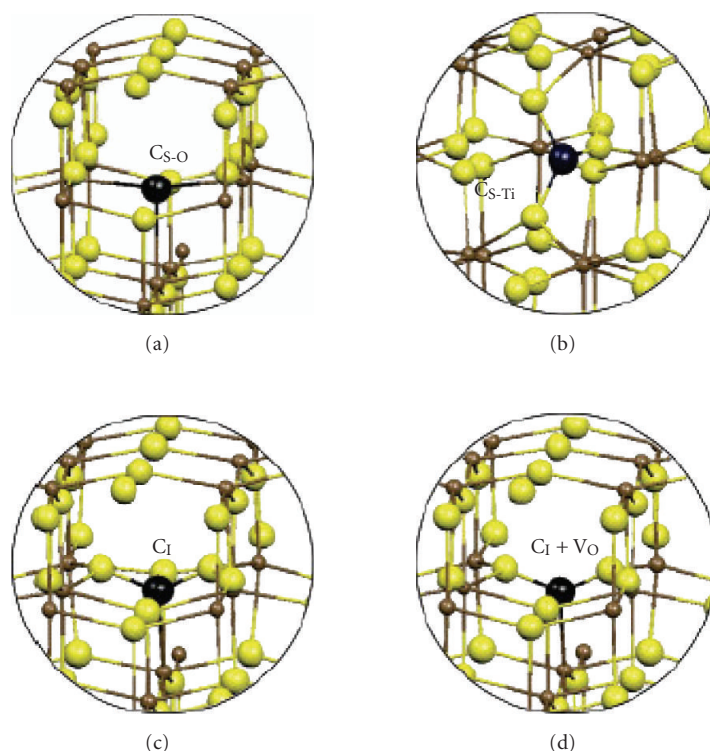
FIGURE 3: Partial geometry of the models for: (a) one substitutional C atom to O (C_{S-O}), (b) one substitutional C atom Ti (C_{S-Ti}), (c) one interstitial C atom (C_I), and (d) one interstitial C atom nearby an oxygen vacancy ($C_I + V_O$) in the anatase TiO_2 supercell; the yellow spheres represent O atoms, the small brown spheres represent Ti atoms, and the black represents the carbon impurity.

of C/TiO_2 to the visible range. The model proposed by Di Valentin et al. is presented in Figure 3 [10].

Preparation of C/TiO_2 photocatalyst by heating of TiO_2 with the vapours of n-hexane [11] and ethanol [12], and by mixing of TiO_2 with liquid ethanol and heating under pressure [13] has been also reported. Enhanced photoactivity of carbon-doped TiO_2 prepared under pressure has been noticed for decomposition of dyes under UV irradiation [13].

Carbon-doped TiO_2 electrodes have been prepared by modified sol-gel method from tetraisopropoxide, 2-propanol, and activated carbon at $600°C$ and were used for electrochemical photooxidation of sodium oxalate; the efficiency of electrode with 5% of doped activated carbon was two times higher than the electrode without carbon doping [14].

Effective photoresponse in the visible-light region was observed in carbon-doped TiO_2 [7, 15]. Carbon-doped TiO_2 nanotube arrays for efficient solar water splitting have been prepared by Park et al. [16]. The synthesised TiO_2-xCx nanotube arrays showed much higher photocurrent densities and more efficient water splitting under visible-light illumination (>420 nm) than pure TiO_2 nanotube arrays.

2.2. TiO_2 and activated carbon (AC) composites

Herrmann et al. [17], Araña et al. [18, 19], and Liu et al. [20] have observed the synergistic effect for the mixture of TiO_2 with activated carbon (AC). Improving the photocatalytic properties of TiO_2/AC composite was explained by the high adsorption of the impurities on the surface of activated carbon and their transfer to TiO_2 surface. Carbon/TiO_2 microsphere has been prepared by Nagaoka et al. [21], and it was successfully used for decomposition of acetaldehyde through the concentration of the pollutant around TiO_2 anchored on the composite surface. In Figure 4, the enhanced photoactivity with using TiO_2/AC composite is presented under both solar and UV irradiations, for photodecomposition of p-nitrophenol [19].

2.3. Carbon-coated TiO_2

Carbon-coated TiO_2 photocatalysts have been prepared by calcination of TiO_2 with carbon precursor such as (polyvinyl alcohol) (PVA), poly (terephthalate ethylene) (PET), or hydroxyl propyl cellulose (HPC) at high temperatures, 700–900°C [22–24], or impregnation of TiO_2 with sacharose 400–600°C [25]. Carbon coating TiO_2 retarded the phase transformation from anatase to rutile, which usually occurs during heating TiO_2 at 700°C and through that improved the crystallinity of anatase phase in TiO_2, which was responsible for its high photoactivity. From the other hand, carbon coating reduced the amount of UV radiation reaching the surface of the TiO_2 particles. A balance among different factors controlled by the carbon layer on the TiO_2 particles was
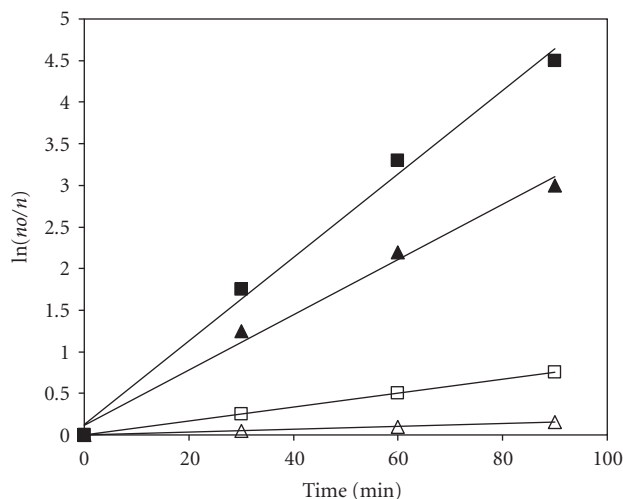
FIGURE 4: Apparent first-order linear transform ln $(n_0/n) = f(t)$ of the p-nitrophenol concentration during its degradation; UV-light: (▲)—bare TiO_2, (■)—13% AC-TiO_2; solar light: (△)—bare TiO2, (□)—13 % AC-TiO2 .

FIGURE 6: Color fading of MB solution under UV irradiation in the presence of carbon-coated TiO_2 sample (10 wt% of carbon) with cycling to use fresh MB solution, concentration of MB = 2.94 × 10^{-5} M.

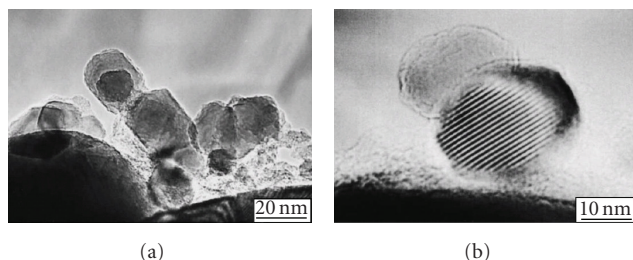(a)   (b)

FIGURE 5: TEM images of carbon-coated TiO_2 prepared from TiO_2 and PVA.

required to get high-photocatalytic activity. On the sample prepared at 850°C with a carbon content of about 3.5 wt%, the highest rate constant for methylene blue decomposition was obtained, in which the transition from anatase to rutile was suppressed, and carbon layer was thin enough to transmit UV rays [24]. The TEM images of carbon-coated TiO_2 are presented in Figure 5 [23].

Carbon-coated TiO_2 samples showed high adsorption and high photoactivity towards methylene blue decomposition [22–25], however in case of phenol, reactive black 5 or iminoctadine triacetate decomposition was slower than on unmodified TiO_2 [23]. In Figure 6, there is shown a cycling decomposition of methylene blue on carbon-coated TiO_2 prepared from powders of TiO_2 and PVA at 900°C with ratio of TiO_2/PVA = 50/50 in weight [22].

Coating of carbon changes the nature of TiO_2 from hydrophilic to hydrophobic and results in lower adsorption of water on the photocatalyst surface and lower formation of OH radicals in comparison with TiO_2. Probably in case of methylene blue, decomposition is going by the direct oxidation pathway, therefore high adsorption of methylene blue on the carbon-coated TiO_2 improved its photocatalytic activity.
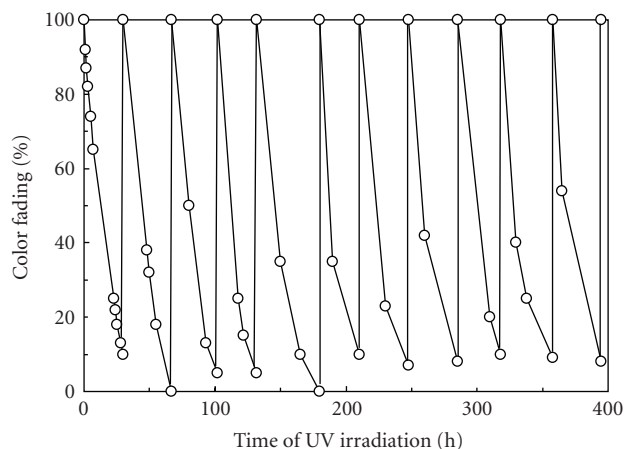
2.4. TiO$_2$ loaded carbon

TiO_2 can be loaded on the activated carbon (AC) [26–35], carbon fibers [36], carbon nanotube [37], exfoliated graphite [38, 39] with efficient adsorption and decomposition of organic compounds such as phenol, 4-chlorophenol, methyl orange, methylene blue, iminoctadine triacetates, oils, dichloromethane, and so forth. In Figure 7, TiO_2 loaded on different carbon structures is presented.

TiO_2 loaded carbon spheres have been prepared by hydrolysis of $TiOSO_4$ under hydrothermal conditions. Adsorption and decomposition of methylene blue on TiO_2 loaded carbon spheres are presented in Figure 8 [28]. It can be observed saturation with methylene blue adsorption on carbon spheres (CS), and no change in methylene blue concentration with UV irradiation, whereas on anatase loaded carbon spheres (Ti/CS) methylene blue could be adsorbed in the dark and decomposed with UV irradiation in the cycles.

Tryba et al. [29] have reported preparation of TiO_2 loaded AC from the tetraorthotitanate solution. Higher removal of organic compounds has been achieved by combination of adsorption, which occurred in the pores of activated carbon, with decomposition on the anatase particles. Decreas in adsorption has been observed after TiO_2 mounting, because mounted TiO_2 particles blocked the entrance to the pores of AC, however these TiO_2 particles could decompose the adsorbed organic molecules in the pores of AC, enhancing the total removal of the pollutant [29].

El-Sheikh et al. [34] have prepared TiO_2 loaded AC by different methods: chemical vapour deposition (CVD), direct air-hydrolysis (DAH), and high-temperature impregnation (HTI), among those methods, CVD gave the best bounding of TiO_2 with the carbon surface; anatase particles were placed in the pores of activated carbon.

Tsumura et al. have mounted TiO_2 on the exfoliated graphite [38]. High sorption of oil and its decomposition under UV irradiation have been observed.
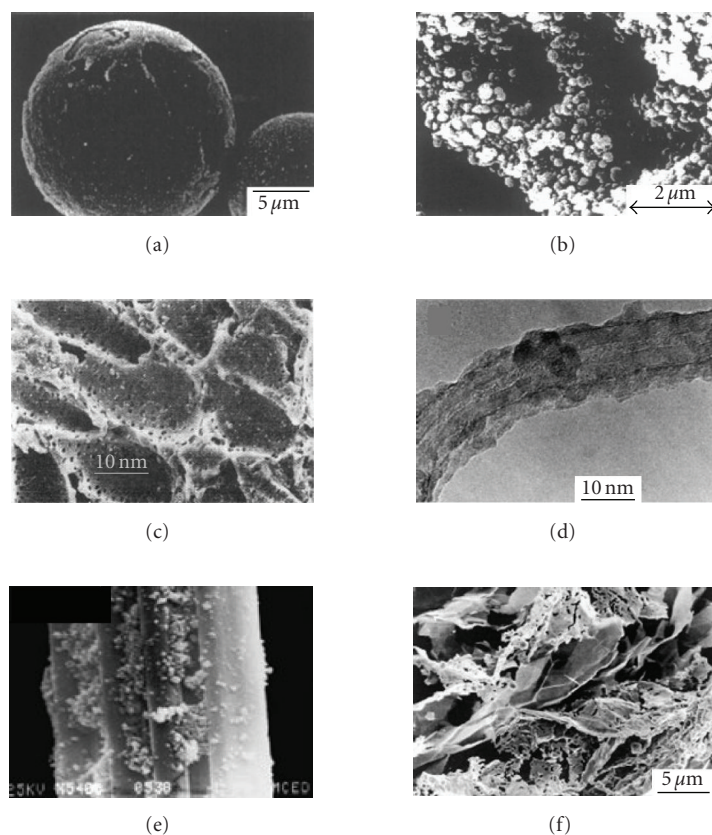
(a)

(b)

(c)

(d)

(e)

(f)

FIGURE 7: TiO_2 loaded on (a) carbon spheres [28], (b) activated carbon [28], (c) granular activated carbon [35], (d) carbon nanotubes [37], (e) carbon fibers [36], and (f) exfoliated graphite [38].

3. TIO$_2$ MODIFIED BY IRON

3.1. Preparation methods

There are few methods of Fe doping to TiO_2. The sol-gel method has been widely used for preparation of Fe-doped TiO_2 from $TiCl_4$ or titania alkoxide and an iron precursor like $FeCl_3$, $Fe(NO_3)_3 \cdot 9H_2O$, or Fe(III)-acetyloacetonate [40–47]. Wang et al. [40] have reported that preferable preparation of Fe-doped TiO_2 to get the uniform distribution of the dopant ions on TiO_2 particles is hydrolysis of a homogeneous mixture of organic titanium and organic iron precursors in isopropyl alcohol. Preparation of Fe-doped TiO_2 by hydrolysis of $TiCl_4$ with $FeCl_3$ appeared to be less favourable than using Fe(III)-acetyloacetonate as an iron precursor. Fe doping from microemulsion of Ti tetraisopropoxide with an aqueous solution of iron and further calcinations has been reported by Adán et al. [48], Fe-doped TiO_2 can be obtained also through the calcination of $FexTiS_2$ [49–51], plasma oxidative pyrolysis [52], one-step flame spray pyrolysis (FSP) [53], coprecipitation and immersion [46], and by the wet impregnation method from Fe(III) acetylacetonate [54] or $Fe(NO_3)_3 \cdot 9H_2O$ [42].

Navío has been reported that impregnation with Fe(III)-acetyloacetonate gives more homogeneous distribution of iron for each mixed oxide sample on the particle surfaces but

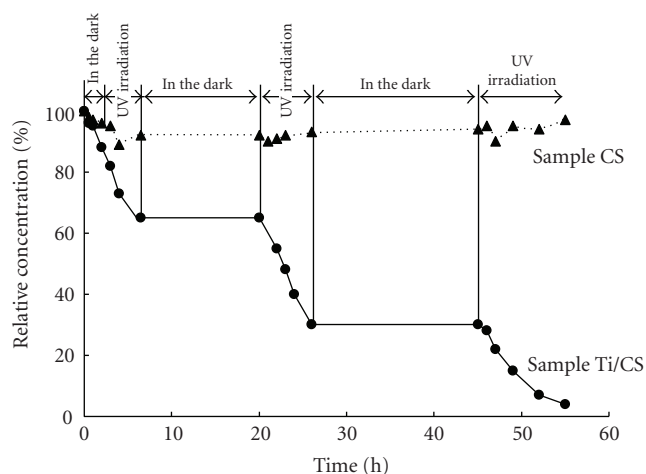FIGURE 8: Changes in relative concentration of MB in the solution in which pristine carbon spheres (CS) and anatase loaded one (Ti/CS) were dispersed.

not between particles in comparison with impregnation with $Fe(NO_3)_3 \cdot 9H_2O$ [54].

Recently, doping of Fe to TiO_2 by the ultrasonic-induced hydrolysis reaction of tetrabutyl titanate ($Ti(OC_4H_9)_4$) in a ferric nitrate aqueous solution has been reported in [55].

The mechanical alloying on the solid state reaction of hematite, Fe_2O_3, and titanium has been also sufficiently used for introducing of iron to TiO_2 lattice [56].

TiO_2/Fe thin film has been prepared by metal (Fe) plasma ion implantation [57, 58] and by magnetron sputtering method [59].

Using a simple sol-gel method, a novel magnetic photocatalyst was produced by immobilisation of TiO_2 nanocrystal on Fe-filled carbon nanocapsules. TiO_2-coated Fe-CNC displayed good performance in the removal of NO gas under UV exposure [60].

Fe-doped TiO_2 nanotubes with small diameter of 10 nm were obtained by hydrothermal method [61].

3.2. Visible-light activity of fe-doped TiO_2

It has been found that the addition of transition metals to TiO_2 can improve the photocatalytic activity of the photocatalyst by UV irradiation and extend its use in the visible region of the electromagnetic spectrum. It has been observed the red shift in the UV-Vis spectra due to the introduction of the 3d electron state of Fe^{3+}, $3d^5$, in the conduction band of TiO_2 [40, 44, 48, 49, 58, 59, 62–65].

The absorbance of visible light is higher for higher amount of doped iron, as it is presented in Figure 9 [48].

This implies that iron-doped TiO_2 may be photocatalytically reactive under visible-light irradiation. Navío et al. have reported that the photodegradation of oxalic acid under visible irradiation, not occurring with TiO_2, could be observed for Fe-doped TiO_2 using 5% Fe-containing samples [54]. Nahar et al. reported that Fe-doped TiO_2 was responsive to the visible-light activity of phenol degradation [49]. Teoh et al. have reported that by flame spray pyrolysis a stable Fe-TiO_2 photocatalyst can be prepared and at the ratio of Fe/Ti = 0.05 it has high activity towards oxalic acid mineralisation under visible light [53]. Wang et al. have reported that for Fe(III) doping in TiO_2 > 0.05 at.%, decomposition of methyl orange under UV irradiation has been lower than on undoped TiO_2, but under visible-light irradiation the Fe(III)-doped TiO_2 with an intermediate iron doping concentration of ≈1 at.% had the highest photocatalytic reactivity due to the narrowing of bandgap so that it could effectively absorb the light with longer wavelength [52]. Chen and Peng have reported the preparation of magnetic-nanometer titanium dioxide/ferriferous oxide (TiO_2/Fe_3O_4) composite photocatalyst with the particles size of 30–50 nm, which appeared to be very active under visible light and highly effective in discoloring of wastewater [66].

It has been investigated that Fe/TiO_2 particles had a higher hydrophilic property compared with TiO_2 [65, 67].

TiO_2/Fe thin film has been demonstrated to have antimicrobial activity after being irradiated with visible light [68].

3.3. Enhancement of photocatalytic activity of TiO_2 by iron doping

It is generally accepted that Fe(III) centres form shallow charge trapping sites within the TiO_2 matrix as well as on the particle surface through the replacement of Ti(IV) by Fe(III)
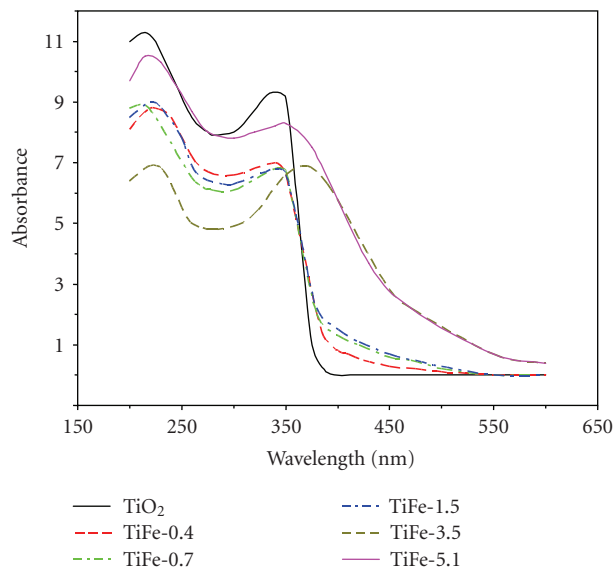

FIGURE 9: UV-Vis spectra of Fe-doped TiO_2 with different iron content.
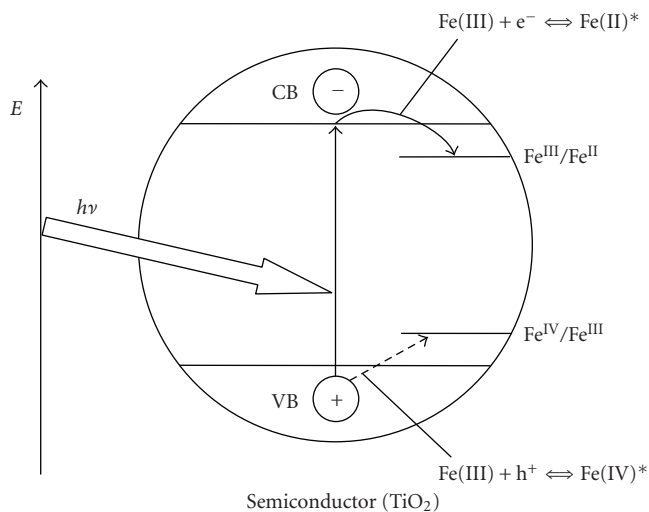
FIGURE 10: Scheme of mechanism of TiO_2 photocatalysis with modifications by Fe(III) ion doping (CB—conduction band, VB—valence band).

[69]. Based on the favourable energy levels, Fe(III) centres may act either as an electron or a hole trap (see Figure 10); so that photogenerated charge carriers are temporarily separated more effectively [40].

Wang et al. [40] have reported that enhancement of the quantum yield by Fe(III) doping TiO_2 can be explained by assuming that the Fe(III) centre acts predominately as a shallow electron trap from which the electron is transferred to molecular oxygen more rapidly than the undoped TiO_2.

However, it was proved that the photoactivity of Fe/TiO_2 catalyst is dependent on the way of preparation and the amount and state of iron.

Wang et al. [40] have reported that the highest quantum yield has been obtained when Fe(III)-acetyloacetonate precursor was used and for the optimal doping levels 0.25 and 0.5 atom %. They have also reported that above-mentioned optimal doping level, some of the Fe(III) dopants might act as shallow hole traps leading to an enhanced recombination of the trapped charge carriers.

Navío et al. [42] have also observed that at the some conditions and for the certain quantity of Fe(III), the dopant can be a center of recombination. They prepared Fe/TiO$_2$ by an impregnation of TiO$_2$ with Fe(NO$_3$)$_3\cdot$9H$_2$O and by the sol-gel method from TiCl$_4$ and Fe(NO$_3$)$_3\cdot$9H$_2$O. They have been reported that Fe/TiO$_2$ prepared by the sol-gel method was less active than TiO$_2$ due to the fact that dopants acted more as recombination centres than a trap sites for charge transfer and the obtained photocatalysts had the lower amount of surface hydroxyl groups and a lower anatase-to-rutile ratio compared with TiO$_2$ precursor sample. They proved that the existence of separated hematite or pseudobrookite (Fe$_2$TiO$_5$) phases in samples containing more than 2% iron could decrease the activity [42]. It has been also proved that the excess of deposited iron on TiO$_2$ can form Fe(OH)$^{2+}$, which has the greater adsorption to the incidence light than TiO$_2$ in the range of 290–400 nm, and can cause decreasing of the Fe/TiO$_2$ photoactivity [69]. The low temperature of calcinations, such as 300°C in Fe/TiO$_2$ preparation appeared to be favoured taking into account its photoactivity [70].

Different amount of doped Fe(III) to TiO$_2$ has been reported to affect the enhanced photoactivity of photocatalyst, dependent on the way of preparation and degradation compound.

Adán et al. [48] reported the enhancement of photocatalytic activity of Fe-doped TiO$_2$ for doping levels up to ca. 1 wt%, which was attributable to the introduction of Fe^{3+} cations into the anatase structure. Nahar et al. [49] reported that the molar ratio of 0.005 Fe content in Fe-doped TiO$_2$ was the optimum for degradation rate of phenol under both the UV and visible-light irradiations. Hung et al. [44] also found that 0.005 mol% of iron ions can enhance the photocatalytic activity, while too great an amount will make the iron ions become recombination centres for the electron-hole pairs and reduce the photocatalytic activity. Chen et al. [47] and Feng et al. [71] have found the highest photocatalytic activity of Fe-doped TiO$_2$ for 0.05 at.% Fe(III). The photocatalytic decomposition of Rhodamine B. on the nanosize Fe(III)-doped TiO$_2$ catalysts prepared by the hydrothermal method with TiCl$_4$ as the precursor was higher than on TiO$_2$, and the optimal results have been obtained for the 0.1% Fe(III)-doped TiO$_2$ [72]. For photocatalytic oxidation of nitrite to nitrate, the most photoactive sample was found to be TiO$_2$ doped with 0.5 wt% of iron [73]. The mesoporous nanocrystalline Fe-doped TiO$_2$ samples prepared by ultrasonic method exhibited enhanced photocatalytic activity towards oxidation of acetone in air at a small amount of doped Fe^{3+} ions in TiO$_2$ particles. The found optimal atomic ratio of Fe to Ti was 0.25 The high activities of the Fe-doped TiO$_2$ powders could be attributed to the results of the synergetic effects of Fe-doping, large BET specific surface area, and small crystallite size [55]. Zhang et al. [74] reported that the films with low-iron concentrations performed better photocatalytic activity than the pure TiO$_2$ film, and the best doped iron concentration was 0.58 at.%.

Wang et al. have reported that the formation of surface defects in Fe-doped TiO$_2$ affects the high-photocatalytic activity of this photocatalyst [43, 75]. They reported that when the Fe content increased in Fe-doped TiO$_2$ prepared by the sol-gel method, the isolated Fe$_2$O$_3$, Fe$_3$O$_4$, and FeO species were observed and Ti-O-Fe species were formed, which increased the surface defects of the Ti/Fe particles and led to the higher activity of the catalyst than bare TiO$_2$ for the degradation of tetracycline [75]. They also reported that the concentration of titanium defects remained almost constant below 400°C but decreased as the calcination temperature was higher than 600°C due to the decrease of the hydroxyls in the crystalline structure. Below 400°C of calcination, all the samples had some brookite and a majority of anatase phase. when the temperature was 800°C , Fe$_2$TiO$_5$ was produced in the sample containing 5 wt% Fe by a reaction between interstitial iron ions and lattice titanium ions, and in the 10 wt% Fe sample through a reaction of hematite with titania phases. [43].

Egerton et al. have investigated that photoelectrocatalytic disinfection of Escherichia coli by an iron doped TiO$_2$ sol-gel electrode was more efficient than disinfection by the corresponding undoped electrode. The optimum disinfection rate corresponded to the replacement of $\approx$0.1% of the Ti atoms by Fe [76].

Some researchers have been observed that doping Fe to TiO$_2$ can be detrimental or not affect the enhancement activity of the photocatalysts [77, 78].

Fe$_2$O$_3$ can work as a photocatalyst and can decompose some organic compounds like aniline [79]. However, the mixture of Fe$_2$O$_3$ and TiO$_2$ has been reported to be less active than original TiO$_2$ [80, 81].

3.4. Mechanisms of organic compounds decomposition by Fe-doped TiO$_2$

Wang et al. [82] detected by cryo-TEM that Fe(III)-doped TiO$_2$ prepared by hydrolysis of TiCl$_4$ with Fe(III)-acetyloacetonate as an iron precursor forms three-dimentional networks with nanoparticles of 2–4 nm, which act as antenna systems in photocatalysis, leading to an enhanced photocatalytic activity of the colloidal preparation. HRTEm image of such prepared particles is shown in Figure 11, and the scheme of this working system is presented in Figure 12 [82].

Once the energy has reached the particle with the adsorbed target molecule, the latter will act as a hole trap thus inducing the separation of the original excitation [82].

Araña et al. [83] have studied the photocatalytic degradation of maleic acid by using Fe-doped TiO$_2$ (0.15, 0.5, 2, and 5% w/w in Fe) catalysts. They observed that catalysts with the lowest Fe content (0.15 and 0.5%) showed a considerably better catalytic behaviour than nondoped TiO$_2$ and catalysts with higher Fe contents. Maleic acid molecules interacted with the surface of the lowest Fe-containing catalysts and as a consequence; iron atoms were extracted from the catalyst surface as photoactive Fe^{3+-} maleic acid complexes.
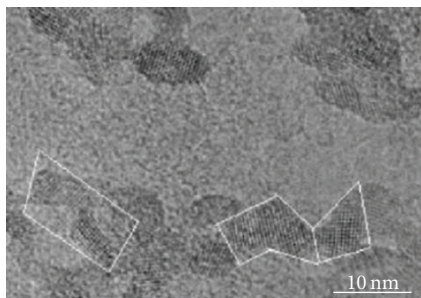
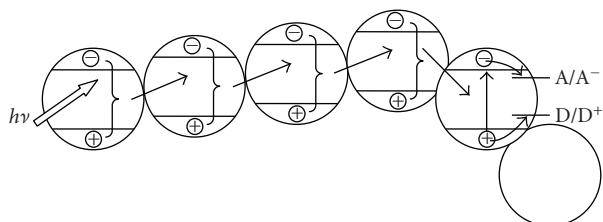FIGURE 11: HRTEM image of 0.5 at % Fe(III)-doped TiO$_2$ nanoparticles.

FIGURE 12: The scheme of increased photocatalytic activity through energy/exciton transfer in aggregated photocatalyst particles (antenna effect). A and D represent electron and hole scavengers, respectively.

When this complex was degraded, the resulting Fe^{2+} ions reacted with TiO$_2$ holes (h+) and the iron return to the catalyst surface as Fe$_2$O$_3$. In catalysts with low-Fe content (0.15 and 0.5% w/w in Fe), this process occurs in a fast way. On the contrary, in catalysts with high-Fe content (2 and 5% w/w in Fe), the formation of less photoactive complexes seems to predominate [83].

These authors have studied also the photocatalytic degradation of formic acid by Fe-doped TiO$_2$ calcined at 773 and 1073 K [84]. For 773 K calcined catalyst, results suggested that Fe was extracted through the formation of a [Fe-OOCH]$^{2+}$ complex by which formic acid degrades. Fe^{2+} ions that remain in solution after formic acid degradation went back to the catalyst surface and were oxidised by photogenerated holes. In this way, the catalyst was reactivated becoming ready for a new degradation process. The formation of hydrogen-carbonates on the TiO$_2$ catalyst through OH radicals insertion was inhibited, and the formation of [Fe-OOCH]$^{2+}$ complex was favoured. A markedly lower capacity for the formic acid degradation has been determined for the 1073 K calcined catalysts, because of its lower surface area and the major presence of lower-active phases such as rutile and Fe$_2$TiO$_5$ [84].

The formation of intermediate products over the photocatalytic decomposition was found to be important in the further oxidation processes.

Araña et al. [85] have proved that the mechanism of ethanol decomposition on Fe-TiO$_2$ was gone by the formation of ethoxides on the catalyst surface that were oxidised to acetate by radicals O$^{2\bullet-}$ and $^\bullet$OH. However, the forma-
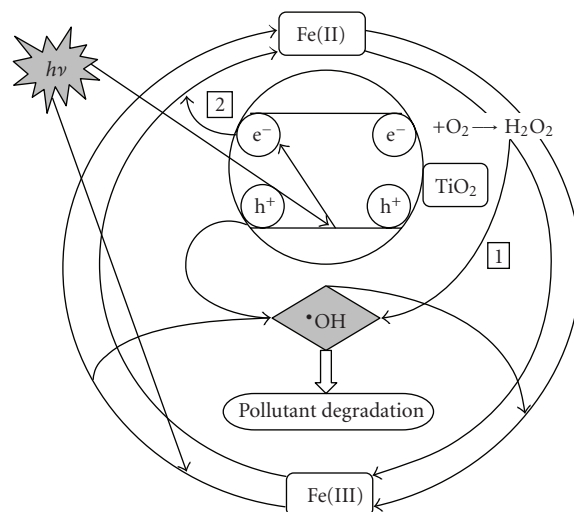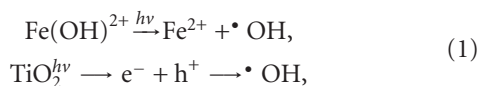

FIGURE 13: Photochemical cycle of combined system iron-TiO$_2$.

tion, an acetaldehyde as an intermediate product, caused that their catalytic activity progressively decreased over time, whereas on Pd-TiO$_2$ and Cu-TiO$_2$, formed ethyleneglycol caused faster degradation [85].
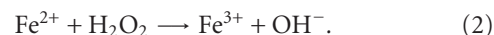
It has been also reported that the formation of a ternary compound HQ-Fe-H$_2$O$_2$ in phenol decomposition or formation of an intermediate, highly-oxidised and unstable form of Fe [Fe(IV)] in the case of chlorophenol decomposition were responsible for fast degradation of phenol and chlorophenol, respectively [86, 87].

The synergistic effect has been observed when a mixture of TiO$_2$ and iron has been used for oxidative photodegradation of monuron (3-(4-chlorophenyl)-1,1- dimethylurea). In a suspension of TiO$_2$ (24 mg L-1) with addition of Fe(III) (3 $\times$ 10^{-4} mol L-1), the measured rate constant was similar to that obtained in a suspension of TiO$_2$ with a concentration more than 20 times higher (500 mg L-1). The optimisation of the photocatalytic systems was obtained when each photocatalyst plays a specific role: Fe(III) as a main OH radicals source and TiO$_2$ as an oxidizing agent of Fe(II) to Fe(III) favouring the photocatalytic cycle Fe(III)/Fe(II). This proposed mechanism is presented in **Figure 13** [88].

The following are photochemical reactions conducted to production of OH radicals:

$$\begin{aligned} \text{Fe(OH)}^{2+} &\xrightarrow{h\nu} \text{Fe}^{2+} + ^\bullet\text{OH}, \\ \text{TiO}_2 &\xrightarrow{h\nu} \text{e}^- + \text{h}^+ \longrightarrow {}^\bullet\text{OH}, \end{aligned} \quad (1)$$

and the reaction occurring in the dark (Fenton reaction):

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \longrightarrow \text{Fe}^{3+} + \text{OH}^-. \quad (2)$$

It has been already established that the formation of H$_2$O$_2$ is negligible in homogeneous photocatalysis with Fe(III). The reactions between iron and TiO$_2$ appear to be essential:

$$\text{Fe}^{\text{II}} + \text{HO}_2^\bullet + \text{H}^+ \longrightarrow \text{Fe}^{\text{III}} + \text{H}_2\text{O}_2, \quad (3)$$

$$\text{Fe}^{\text{II}} + {}^\bullet\text{OH} \longrightarrow \text{Fe}^{\text{III}} + \text{OH}^-. \quad (4)$$
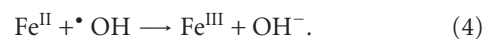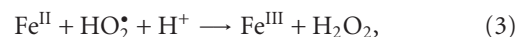
The reaction (4) is detrimental for pollutant degradation. It has been reported that Fe(III) could easily adsorb on the surface of TiO_2, and Fe(II) cations were not adsorbed, therefore the reoxidation of Fe(II) by holes is unlikely. In the absence of oxygen Fe(III), cations react with the electron at the surface of TiO_2, allowing the formation of the active species h^+ and $^\bullet OH$. However, it was proved that $^\bullet OH$ radicals are more efficiently formed via the photodissociation of $Fe(OH)^{2+}$, which was found to be responsible for fast degradation of monuron [88].

Ranjit and Viswanathan [45] reported that the photocatalytic activity of the iron-doped catalysts could be explained in terms of the heterojunction formed between the Fe/TiO_2 and α-Fe_2O_3 phases for the sol-gel-derived catalyst.

4. TiO$_2$ MODIFIED BY CARBON AND IRON

As it was described above, carbon-coated TiO_2 showed high photoactivity towards decomposition of methylene blue but the other organic compounds were poorly decomposed on these photocatalysts, therefore the preparation of carbon-coated TiO_2 has been modified to obtain carbon-coated TiO_2 with doped iron. For this purpose, poly(ethylene terephthalate) (PET) was impregnated with oxalic acid solution (FeC_2O_4) and then was mixed with powder TiO_2 and heat treated at different temperatures, 400–800°C, under flow of Ar [89]. The obtained samples are consisted from anatase phase, contained carbon from 7.5 to 15.5 wt%, and an iron from 0.34 to 0.67 wt%, mostly in the form of Fe(II) [89]. Such prepared samples did not show the enhanced photocatalytic activity towards phenol decomposition under UV irradiation, even though the sample prepared at 400°C exhibited high adsorption of phenol on its surface, around $30 \cdot 10^{-5}$ mol/g, which was much higher than on the other samples, which showed adsorption of phenol in the range of 3–$5 \cdot 10^{-5}$ mol/g. However, high acceleration of the phenol decomposition has been observed on the sample prepared at 400°C, when 0.03 mol/L, H_2O_2 was added to the reaction mixture; see Figure 14 [89]. This could be caused by occurring photo-Fenton reactions, in which Fe^{2+} is oxidised to Fe^{3+} with H_2O_2 yielding in OH radicals. Increase of OH radicals production after H_2O_2 addition on samples contained iron was confirmed by OH radicals measurements [89–91].

The high-decomposition rate of phenol was obtained only on the sample, which showed high adsorption of phenol, although this sample contained the lowest content of Fe(II) in comparison with the other samples. Increase of OH radicals formation on samples with iron was not proportional to the decomposition rate of phenol under UV irradiation with H_2O_2. It has been proved that, in case of the sample prepared at 400°C, some complexes were formed, which were responsible for fast degradation of phenol [91]. The FTIR studies indicated that hydroquinone was more likely adsorbed on Fe-C-TiO_2 and could play a key role in the process of phenol decomposition, as reported by Chen and Pignatello [86] that some hydroquinones formed in the phenol decomposition could reduce iron and accelerate in this way the rate of phenol decomposition by the formation of a ternary HQ-Fe-H_2O_2 complex [93]. Cycling decomposi-
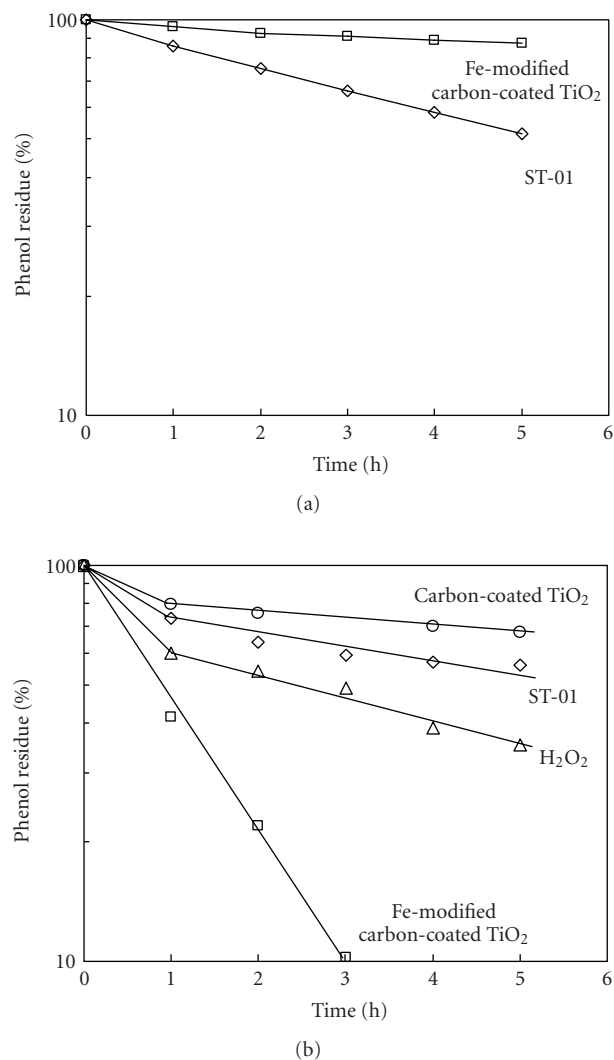

(a)

(b)

FIGURE 14: Phenol decomposition on commercial TiO_2-ST-01 and modified TiO_2 by carbon and iron at 400°C, (a) under UV irradiation and (b) under UV with addition of H_2O_2.

tion of phenol under UV and H_2O_2 was performed on Fe-modified carbon-coated TiO_2 photocatalyst heat treated at 400°C. For those measurements, photocatalyst was mounted on the adhesive tape and fixed to the metal grid, which was placed inside the reactor. For cycling performance, the metal grid with fixed photocatalyst each time was put to the fresh phenol solution with concentration of $2.1 \cdot 10^{-4}$ mol/L; the results are presented in Figure 15.

A good performance of the phenol decomposition with cycling suggests that an iron present in the sample could follow the processes of oxidation and reduction, being reused in Fenton reactions and photodegradation of phenol. It is worth to add that in this case no pH adjustment was needed as it is usually applied in photo-Fenton process, and not any leaching of iron occurred.

In the further investigations on TiO_2 modified by carbon and iron photocatalysts, the preparation method was changed, the powder of TiO_2 was impregnated with FeC_2O_4
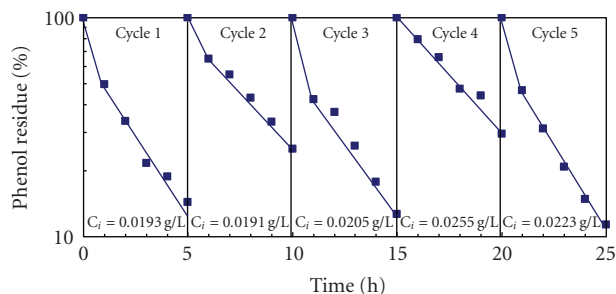
FIGURE 15: Cycling decomposition of phenol under UV irradiation and H_2O_2 on Fe-modified carbon-coated TiO_2 photocatalyst heat treated at 400°C.

solution and heated at 400–800°C under flow of Ar, but not any polymer was added. The obtained Fe-C-TiO_2 samples contained a residue carbon, 0.2–3.3 wt%, which came from the carbonisation of oxalate [90]. A residue carbon did not prevent the transformation of anatase to rutile, which occurred at 700°C, with increasing the heat treatment temperature FeTiO$_3$ phase (ilmenite) appeared. The highest photoactivity for phenol decomposition under UV and H_2O_2 had the sample prepared at 500°C, which contained 2.4 wt% of residue carbon, 0.70 wt% of Fe(II), 0.96 wt% of Fe(III), and did not have FeTiO$_3$ phase. The phenol decomposition on this sample was much faster than in the case of previous experiments, in which PET was used for preparation, phenol was decomposed after 2 hours of UV irradiation, and after 3 hours of UV irradiation not any ring products of phenol decomposition were detected [90, 91].

It was proved that in case of TiO_2 modified by FeC_2O_4 and heated at 550°C in air (Fe-TiO_2), FeTiO$_3$ phase is formed, which exhibits higher photocatalytic activity than pure TiO_2 for phenol decomposition under UV irradiation, but with H_2O_2 addition this activity decreases, proportional to the decreasing of OH radicals formation, due to the scavenging effect:

$$H_2O_2 + {}^{\bullet}OH \longrightarrow HO_2^{\bullet} + H_2O. \qquad (5)$$
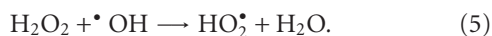
Formed in this reaction, HO$_2^{\bullet}$ radicals are known to have lower potential of oxidation than $^{\bullet}$OH [91]. This scavenging effect has been observed to occur also on TiO_2. In Figure 16, formation of OH radicals on TiO_2, Fe-TiO_2, and Fe-C-TiO_2 samples is presented [91].

In Figure 17, phenol decomposition on these samples is presented [91].

It can be observed that phenol decomposition is going through the radical reaction on TiO_2 and Fe-TiO_2 photocatalysts, whereas by the surface reactions on Fe-C-TiO_2.

The cycling decomposition of phenol on Fe-C-TiO_2 sample prepared at 500°C has been performed in the circulated flow reactor [94]. For this purpose, the photocatalyst has been pasted on the cotton material with a suspension of the powdered photocatalyst with aqueous solution of sodium silicate (Na$_2$SiO$_3$) and was placed inside the reactor on the inner walls, along the UV lamp. Circulated phenol solution was

(a)
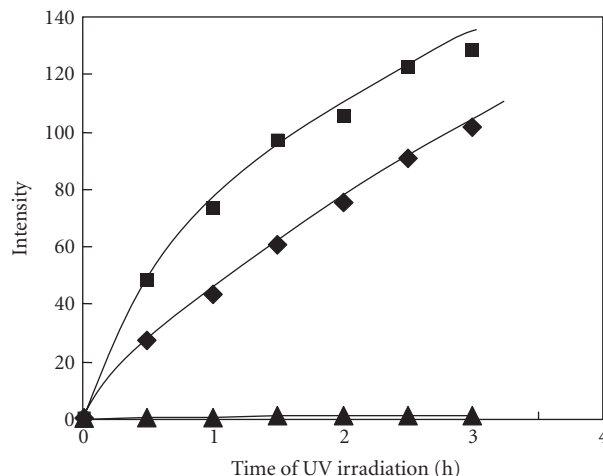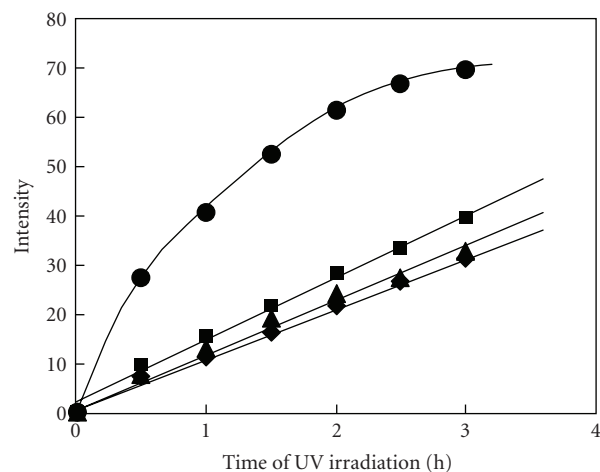
(b)

FIGURE 16: Formation of OH radicals on TiO_2, Fe-TiO_2, and Fe-C-TiO_2 prepared at 500°C, (a) under UV and (b) under UV with H_2O_2.

irradiated with UV for some cycles, and with UV and H_2O_2, as shown in Figure 18 [94].

Adsorption and following decomposition of phenol on immobilised Fe-C-TiO_2 photocatalyst can be observed under UV irradiation, but under UV with addition of H_2O_2 acceleration of phenol decomposition is observed with stable amount of decomposed phenol, over 90% and mineralisation degree around 50% [94].

It has been proved that preparation of Fe-C-TiO_2 from the other TiO_2 precursor of anatase structure at the same conditions as described above gives similar results; the highest photocatalytic activity under UV irradiation with H_2O_2
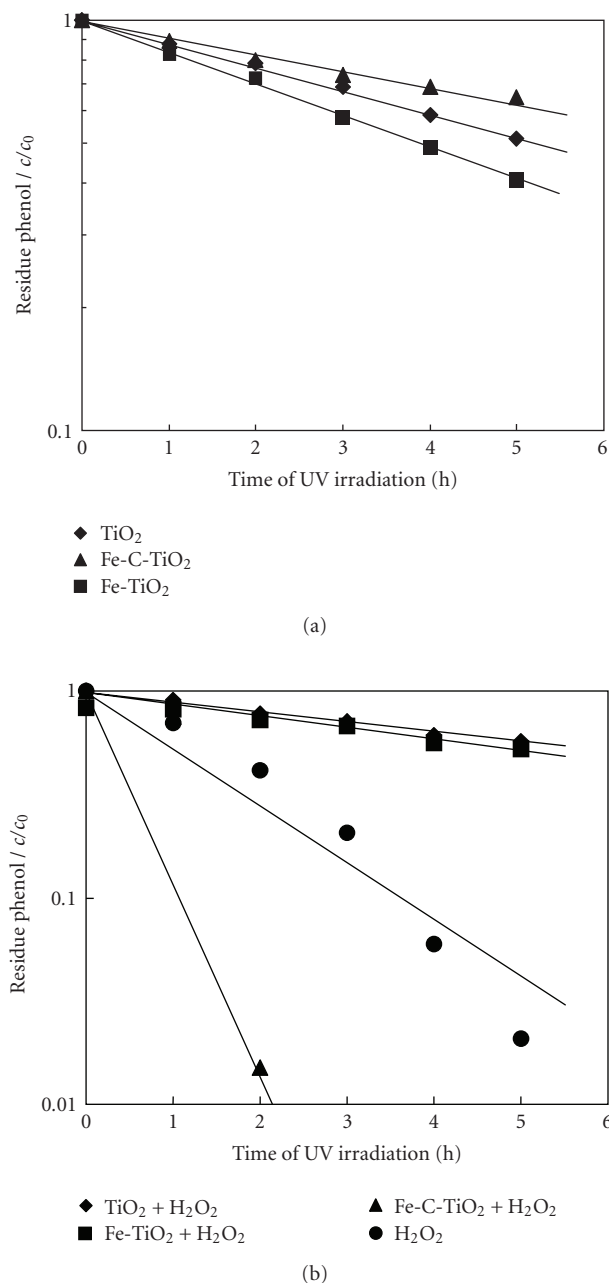
FIGURE 17: Phenol decomposition on TiO_2, Fe-TiO_2, and Fe-C-TiO_2 prepared at 500°C, (a) under UV and (b) under UV with H_2O_2.

FIGURE 18: Cycling decomposition of phenol on immobilised Fe-C-TiO_2 prepared at 500°C. (a) under UV, (b) under UV with H_2O_2.

cling. The EPR spectra of Fe-C-TiO_2 samples prepared from anatase and FeC_2O_4 [95] are presented in Figure 19.

In obtained EPR spectra, some peaks can be observed, in anatase type TiO_2 a maximum at 344 MT, g = 1.93, which is assigned to Ti^{3+} ions associated to oxygen vacancies [96, 97], this peak was also observed in Fe-C-TiO_2 samples and was higher intensity in samples heated at higher temperatures. Some peaks assigned to Fe^{3+} ions were observed: in Fe-C-TiO_2 samples prepared from anatase at temperature 500 and 600°C, a broad peak with maximum at around 434 MT, g = 1.53 assigned to paramagnetic Fe^{3+} ions, peaks with maximum at around 330 and 310 M (g ≈ 2) assigned to Fe^{3+} ions in octahedral symmetry in anatase [48, 96], and two broad peaks at the range of 133 to 272 MT assigned to Fe^{3+} ions substituting for Ti^{4+} in the TiO_2 rutile lattice [96].

5. SUMMARY

Modification of TiO_2 by carbon can enhance its photocatalytic activity: doped C can extend the light absorption to the visible range and give photocatalytic activity under visible light by the narrowing of the bandgap; carbon coated

has the sample prepared at 500°C [95]. The high photoactivity of Fe-C-TiO_2 sample prepared at 500°C has been found for decomposition of phenol, humic acids, and different dyes, like acid red, methylene blue, and reactive black 5. It has been found that $FeTiO_3$ phase is detrimental in photocatalytic activity of Fe-C-TiO_2 photocatalysts under UV with H_2O_2, and the low temperatures of preparation such as 500°C led to obtain the samples with high amount of paramagnetic iron on the surface, not built in TiO_2 lattice, which probably facilitates proceeding of the photo-Fenton reactions, in which iron is oxidised and reduced with cy-
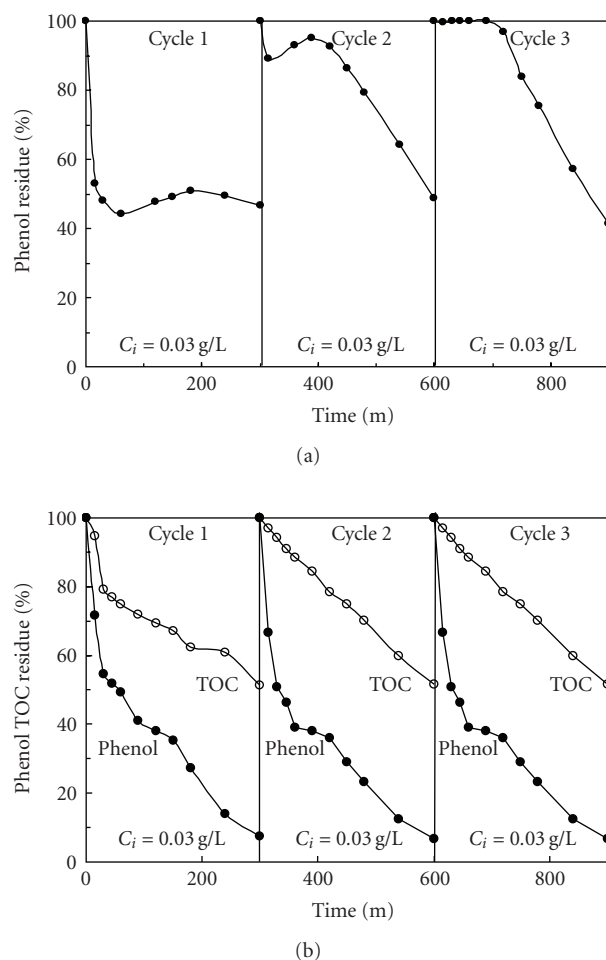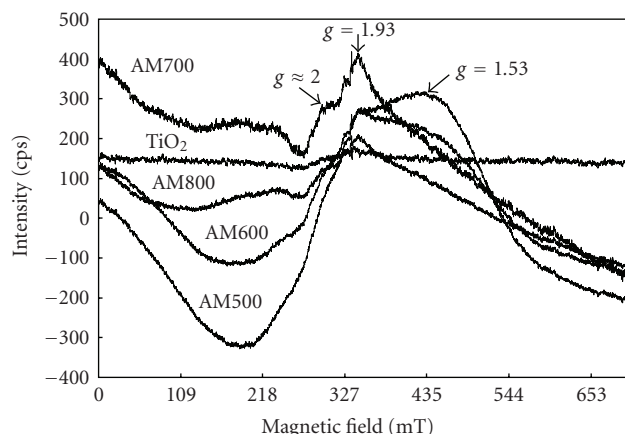
FIGURE 19: EPR spectra of TiO_2 and Fe-C-TiO_2 samples prepared from anatase and Fe-C_2O_4 at 500–800°C.

TiO_2 as well as TiO_2/AC composites can enhance the concentration of the organic compounds on the surface of the photocatalyst and accelerate the process of their decomposition through the transfer of the adsorbed molecules to the TiO_2 surface; TiO_2 loaded carbon can also work as a photocatalyst, on which the molecules are adsorbed in the pores of carbon and then they undergo the photocatalytic decomposition with UV irradiation.

Doping Fe(III) to TiO_2 causes formation of shallow charge trapping sites within the TiO_2 matrix and on the particle surface through the replacement of Ti(IV) by Fe(III). Fe(III) centres may act either as an electron or a hole trap. At high concentration of Fe(III) in Fe-doped TiO_2 Fe(III), ions can act as a recombination centres. The photocatalytic activity of Fe-doped TiO_2 has been found to depend strongly on the preparation method, iron precursor, and the amount and state of iron, generally insignificant amount of doped iron has a positive effect in the enhancement of the photocatalytic activity of Fe-doped TiO_2, whereas amount of doped iron >2 wt% has been detrimental. It has been observed the red shift in the UV-Vis spectra of Fe-doped TiO_2 photocatalysts due to the introduction of the 3d electron state of Fe^{3+}, $3d^5$, in the conduction band of TiO_2, what makes these photocatalysts active under visible light.

TiO_2 modified by carbon and iron can work in both photocatalysis and photo-Fenton processes, when H_2O_2 is used, enhancing markedly the rate of the organic compounds decomposition. The photocatalytic decomposition of organic compounds on TiO_2 modified by iron and carbon is going by the complex reactions of iron with the intermediates, what significantly accelerate the process of their decomposition. A good performance of cycling decomposition of phenol has been obtained on immobilised Fe-C-TiO_2 photocatalyst, what suggests that an iron present in the sample could follow the processes of oxidation and reduction, being reused in Fenton reactions and photodegradation of phenol. The additional advantage of using this photocatalyst for the decomposition of organic compounds is the fact that no pH adjustment is needed, and it was observed that there was not any leaching of iron from this photocatalyst.

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