The Effect of Fe-Loading and Calcination Temperature on the Activity of Fe/TiO$_2$ in Phenol Degradation

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ABSTRACT: *In this research work, iron modified titanium dioxide photocatalyst was synthesized by the sol-gel method. The catalyst is characterized by FT-IR, XRF, and TGA techniques. Since the activity of Fe/TiO$_2$ is highly affected by the loading of Fe, our major purpose of this work was focused on the role of this factor. Moreover, the effect of calcination temperature, which was also of high importance, was studied in this work. FT-IR results indicated the existence of a peak in the range of 1100-1200 corresponding to Ti-O-Fe bonds. The intensity of this peak is proportional to the amount of iron, which is incorporated into the TiO$_2$ lattice. Optimum Fe-loading was specified by FT-IR and it was measured by XRF. In order to evaluate the catalytic activity of Fe/TiO$_2$, a synthetic wastewater of phenol was irradiated by the UV lamp (757.38 mW/cm^3), Fe/TiO$_2$ with the dosage of 0.5 g/L was applied as the catalyst and H$_2$O$_2$ (12.5 mL, 30% wt. /wt.) was added as an oxidizing agent. Experimental results proved, the optimum condition for phenol degradation process over Fe/TiO$_2$ is as follows: Fe loading in the TiO$_2$ lattice: Fe$_2$O$_3$/TiO$_2$ is 0.27%, calcination temperature: 600°C, and irradiation time of 600 min. Under this circumstance, 98.26% of the phenol in water was decomposed.*

KEYWORDS: *Photocatalyst; Fe/TiO$_2$; Fe- loading; Phenol degradation.*

INTRODUCTION

Titanium dioxide has the potential to be applied in the decomposition of many organic pollutants due to its optical and electrical properties, low cost, chemical stability, and nontoxicity [1]. Numerous methods are available for preparation of photocatalysts. Among them sol-gel methods are interesting. They have benefits such as synthesis of nano-sized crystallized powder at low temperature, preparation of composite materials, and possibility of stoichiometry control over the process [2, 3]. Recently, considerable efforts have been made to develop TiO$_2$ catalyst to improve their catalytic behaviors. *Hung et al.* [4] synthesized TiO$_2$ and Fe-TiO$_2$ by the sol-gel method and tested their photocatlytic activity for dichloromethane degradation in the gaseous phase [4]. *F. Akhlaghian* and *S. Sohrabi* prepared Fe/TiO$_2$ catalyst and investigated the effect of catalyst dosage, H$_2$O$_2$ amount, and pH on the photocatalytic phenol degradation. The obtained optimum values are as follows: catalyst dosage=0.5g/L, H$_2$O$_2$ amount =12.5mL, pH=9. [5]. Metallic nanoparticles such as Pt [6], Pd [7, 8], Au [9], Ag [10–13], Ru [14], and Fe [17–19] have been used to enhance the photocatalytic activity of TiO$_2$ by retarding the recombination behaviors. The effects of silver doping on titanium photocatalyst properties

were evaluated in [10]. Two "green" photocatalytic reactions were chosen for photocatalytic experiments: photocatalytic reduction of CO_2 and photocatalytic oxidation of 4-chlorophenol (4-CP) water solution. Both photocatalytic reactions were carried at mild conditions [10].

Ag/titanium dioxide (TiO_2)-coated silicon catheters were easily fabricated with Ag nanoparticles deposition on both the inside wall and the outside wall of TiO_2 coated catheters by TiO_2 photocatalysis. This is an application of the silicon catheters coated with TiO_2, which possess a self-sterilizing and self-cleaning property combining with UV light illumination [11].

The inactivation of *Escherichia coli* (*E. coli*) in water was investigated systematically with Ag-coated TiO_2 thin film under UV-C irradiation. Compared with UV-C irradiation alone, the inactivation of *E. coli* by the UV/Ag-TiO_2 process was enhanced and the photoreactivation of the bacteria was much repressed [12]. Ag–TiO_2 multiphase nanocomposite thin films were prepared on quartz substrates by the Liquid Phase Deposition (LPD) method from a mixed aqueous solution of ammonium hexafluouotitanate, silver nitrate and boric acid under ambient temperature and atmosphere followed by calcination at 500 °C for 1 h [13]. The photocatalytic activity of the Ag–TiO_2 multiphase nanocrystal composite thin films prepared by this method exceeded that of pure TiO_2 thin films. This was attributed to the fact that there were many hetero-junctions, such as anatase/rutile, anatase/brookite, Ag/anatase, Ag/rutile and so on, existed in the Ag–TiO_2 multiphase nanocomposite films [13].

The rates of photocatalytic oxidation of gaseous formic acid, acetic acid, acetaldehyde and toluene over N-doped TiO_2 ($TiO_{2-x}N_x$) loaded with Fe, Cu or Pt were determined under visible light irradiation (>410 nm). It was found that the loading of Fe, Cu or Pt resulted in similar rates of enhancement of acetaldehyde oxidation, and that Cu and Pt gave the highest rates of acetic acid and toluene oxidation, respectively [15].

Modeling and optimization of phenol degradation over copper modified titaniumdioxide nano-structured catalyst (Cu/TiO_2) was investigated using response surface methodology. High values of the determined R^2 coefficients of the model (>0.99) confirm that the model fits the experimental data accurately [16].

Al and Fe co-doped TiO_2 nanotubes were successfully synthesized using the hydrothermal method. The effect of the optimal co-doped TiO_2 nanotubes catalyst on the HAs removal efficiency through O_3/UV/co-doped TiO_2 process was investigated. The highest HAs removal efficiency (79.4%) that exhibited a pseudo-first-order rate constant of 0.172 min^{-1} was achieved [17].

Q. Sun et al., investigated the effect of surface Fe_2O_3 clusters on the photocatalytic activity of TiO_2 for phenol degradation in aerated aqueous suspension. The relevant rate constant (k_{obs}) of phenol loss over 0.10 Fe/TiO_2 was 0.0225 min^{-1}, which was about 70% larger than that over TiO_2 (0.0133 min^{-1}). The samples containing less than 0.3% Fe were more active than bare TiO_2 under UV light. This work asserts that only Fe_2O_3 clusters in small-size and at low coverage on TiO_2 are beneficial to the photocatalytic reaction, while excess iron oxide is detrimental [18].

Y. Zhang & Q. Li utilized the cathodic electrophoretic deposition method to prepare Fe-doped TiO_2 films to enhance the photocatalytic activity toward decolorization of methyl orange. They concluded that the photocatalytic degradation of MO could be described as pseudo-first order reactions [19]. *B. Palanisamy et al.* concluded that mesoporous Fe_2O_3/TiO_2 could be an active catalyst for pollutant degradation, as TiO_2 with framework Fe^{3+} and photosensitization with free Fe_2O_3 were involved in the activity. Mesoporous mixed Fe_2O_3/TiO_2 photocatalyst was applied for degradation of 4-chlorophenol. The reaction was carried out for 180 min with all the catalysts, and the progress of the reaction was monitored by determining the Total Organic Carbon (TOC) at different time intervals to examine the photocatalytic activity [20]. Photocatalytic reactions using TiO_2 or ZnO particles have been shown to be useful for destroying a wide range of environmental pollutants. *Simin Janitabar Darzi & Maryam Movahedi* impregnated ZnO and TiO_2 nanoparticles with merbromin dye and used it as modified photocatalysts for degradation of phenol. Dye-modified ZnO and TiO_2 showed significantly higher photocatalytic activity than neat ZnO and TiO_2 under visible light illumination. In a period of 4 hours, dye-modified ZnO removed phenol almost completely while dye-modified TiO_2 degraded it only to 47% [21].

In this study, the role of iron in improving photocatalytic activity of titanium dioxide was

investigated. The effect of Fe-loading and calcination temperature as two important structural properties of Fe/TiO$_2$ was highlighted. In order to determine the optimum loading of the dopant FT-IR and XRF characterization techniques were used. Thermal behavior of the catalyst was analyzed by TGA. This paper suggests that prior to any optimizations for enhancing the catalytic activity of a doped catalyst; the first step to be taken is optimizing the dopant concentration and calcination temperature.

EXPERIMENTAL SECTION
Material and method

Titanium isopropoxide (98%) and Fe (NO$_3$)$_3$.9H$_2$O (98%) were used as the precursors for the titanium and iron, respectively. Moreover, ethanol (96%), nitric acid (65%), H$_2$O$_2$ (30 %) and phenol (99%) were used in the experiments. All the materials were purchased from Merck Company. The materials were of analytical grade and were used without further purifications.
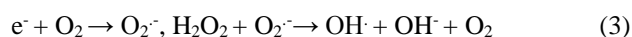
Following *Yoldas* method [22], titanium isopropoxide was added to double-distilled water. The molar ratio of titanium isopropoxide to water was 1:100. The mixture was stirred at a constant rate and heated until the temperature reached 85°C. Then nitric acid was added. The molar ratio of titanium isopropoxide to nitric acid was 1:0.07. Fe was added to the mixture through the solution, which is obtained by dissolving Fe (NO$_3$)$_3$.9H$_2$O in ethanol .The mixture was under reflux at 85°C for 24 h. The obtained gel was dried at 100°C in an oven. Afterwards, the calcination process had been taken place in a furnace for 2 h [5]. Finally, Fe/TiO$_2$ was crushed and sieved into 60-90 μm.

Characterization techniques

Almost any compound having covalent bands absorbs various frequencies of infrared irradiation; this can be considered like a fingerprint of the sample. Fourier transform infrared spectrum (FT-IR) of Fe/TiO$_2$ is recorded by a VECTOR22 (Bruker, Germany) FT-IR spectrophotometer. Iron content of the catalyst was measured by Spectro X-Ray Fluorescence (XRF) spectrometer. The TGA analysis of the Fe/TiO$_2$ catalyst was carried out in a TGA analyzer ATA PT1000 model of the Linseis Company under static air atmosphere in the temperature range of 33.5-650°C.

Mechanism

In the photocatalytic degradation process, an organic pollutant is destroyed in the presence of an oxidizing agent and a semiconductor, which was irradiated by an energetic light source. As the result of sufficient illumination with UV lamp, an electron from the valence band migrates to the conduction band leaving behind an electron vacancy (hole) in the valence band. The generated hole in the valence band can produce hydroxyl radicals and subsequently OH radicals oxidize the organic material. The photogenerated e$^-$ and h$^+$ are vigorous oxidizing and reducing agents and their reactions are respectively as follows:

$$H_2O + h^+ \rightarrow OH^\cdot + H^+ \tag{1}$$

$$e^- + H_2O_2 \rightarrow OH^\cdot + OH^- \tag{2}$$

$$e^- + O_2 \rightarrow O_2^{\cdot-}, H_2O_2 + O_2^{\cdot-} \rightarrow OH^\cdot + OH^- + O_2 \tag{3}$$

Eq. (1) expresses the hydroxyl radicals generation by the oxidation step, in which positive holes react with absorbed water. The reduction step leads to the hydroxyl radical generation through direct and indirect routes; the direct way, which is stated in Eq. (2), is the reaction of electrons with H$_2$O$_2$. The indirect way, which is summarized in Eq. (3), composes of two steps, first e$^-$ is transferred to the adsorbed oxygen of the modified catalyst (Fe/TiO$_2$), which produces superoxide anions and then O$_2^{\cdot-}$ reacts with H$_2$O$_2$ resulting in •OH generation. When reduction and oxidation do not advance simultaneously, there would be an electron accumulation in the conduction band. Thereby, this can increase the rate of recombination of e$^-$ and h$^+$. Since the recombination causes energy waste, it should be prevented to ensure efficient photocatalysis. The role of dopant in photocatalysis is in keeping the charges separate through trapping the electrons of TiO$_2$ conduction band and consequently avoiding the recombination of electrons and holes [23, 24]. Fe^{3+} ions, which are absorbed on the TiO$_2$ surface, can act as electron trapping centers. Thus, they increase the electron-hole pair separation efficiency. The mechanism of heterogeneous photocatalytic degradation of phenol by Fe/TiO$_2$ is summarized in Fig. 1.

RESULTS AND DISCUSSION
The FT-IR spectra of Fe/TiO$_2$ and the effect of Fe-loading

Fe/TiO$_2$ photocatalysts which are named A, B, C, D, and E with different loading of Fe were synthesized.
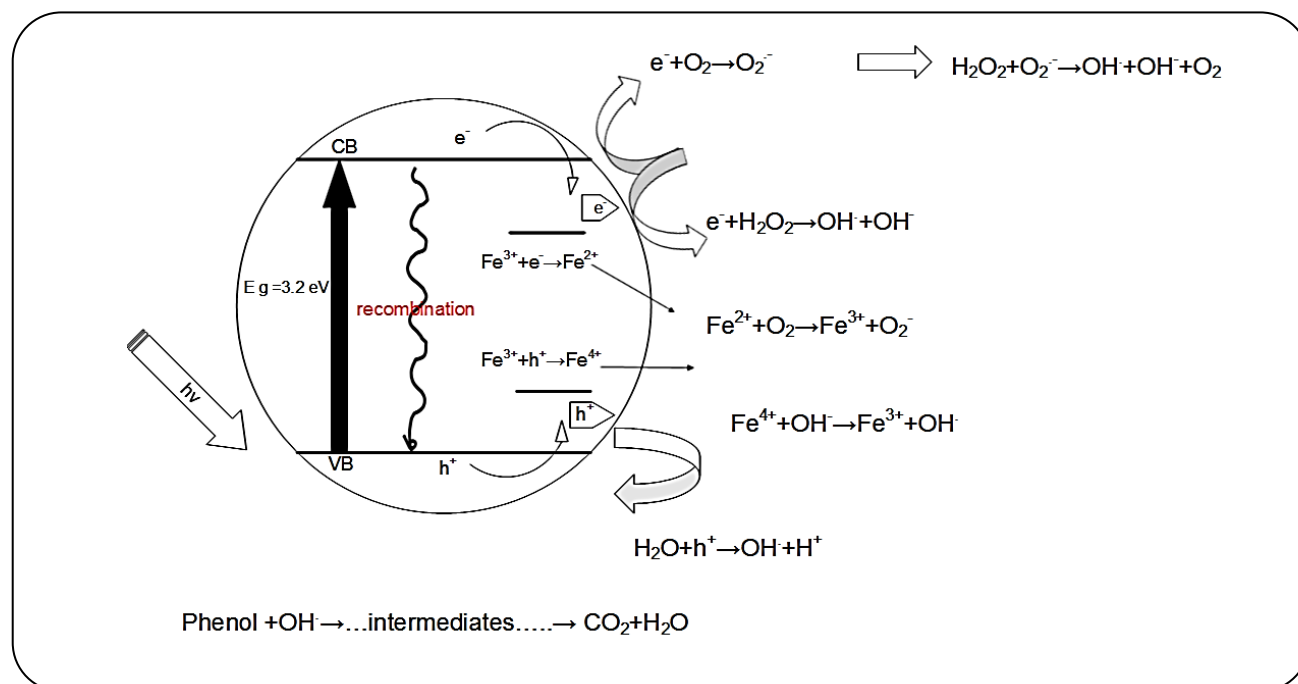
Fig.1: the mechanism of phenol degradation by Fe/ TiO$_2$.
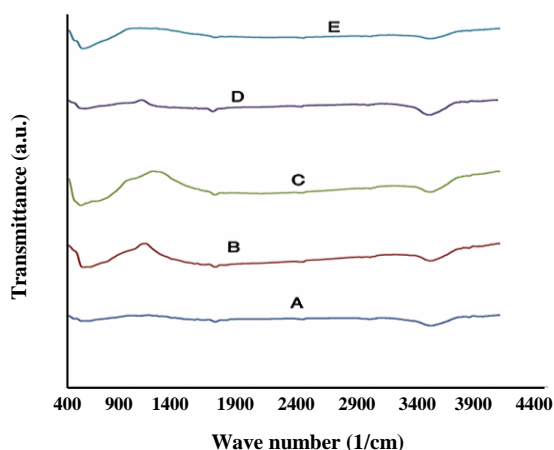

Fig. 2: FT-IR spectra of A, B, C, D, and E catalysts.

The following order showed the increasing amount of the Fe: (A<B<C<D<E), Where catalyst E has the highest amount of Fe and catalyst A is pure titania.

Fig. 2 shows the FT-IR spectra of the catalysts A-E in the range of 400–4000cm^{-1}. It is obvious that for all the catalysts, there is a stretching vibration at 500 cm^{-1} but with different intensity, which can be attributed to Ti-O-Ti vibrations, which are affected by the introduction of iron in to the lattice. Moreover, in the range of 1100-1200 cm^{-1} one other peak appears for all the catalysts except A,

which is pure titania. The intensity of this peak is increased as the Fe-loading increased up to catalyst C, further increase in Fe loading does not result in increase the intensity of the peaks. This result indicates that at these concentrations of Fe, the dopant does not incorporate into the TiO$_2$ lattice properly. In fact, when doping exceeds a certain level, due to the decrease of the distance between trapping sites, Fe^{3+} may also act as the recombination centers of the photogenerated electrons and holes, which is not favorable and it does not lead to improve the catalytic activity.

The FT-IR results confirm that the optimum Fe-loading is ascribed to catalyst C. In addition experimental results in Fig. 3 show that the best performance is assigned to catalyst C. A synthetic wastewater of phenol (150 ppm) was irradiated by the UV lamp (757.38 mW/cm^3). Fe/TiO$_2$ containing different loadings of Fe with the same dosage of 0.5 g/L was applied as the catalyst. H$_2$O$_2$ (12.5 mL, 30% wt. /wt.) was added as an oxidizing agent. The optimum value for catalyst dosage and H$_2$O$_2$ was determined through our previous work [5]. After 2 hours of reaction, highest efficiency is attained by catalyst C. Fig. 3 shows that proper amount of dopant has a synergetic effect with the activity of the catalyst. The optimum loading of iron retards the recombination of
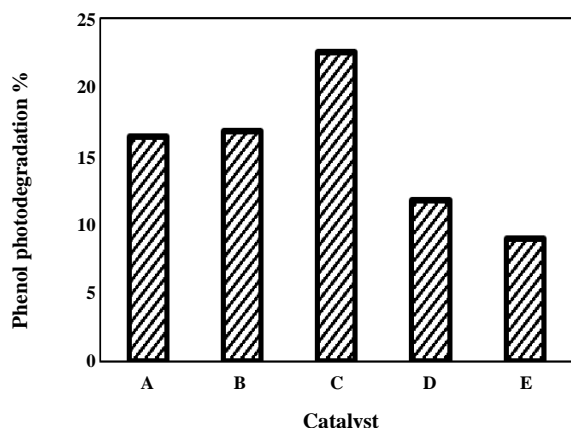
Fig. 3: The effect of Fe-Loading on the activity of Fe/TiO$_2$.

Fig. 4: The TGA curve of Fe/TiO.

e$^-$ and h$^+$. The catalysts were analyzed by an X-Ray Fluorescence (XRF), and their chemical analysis were determined as the following: The catalysts A, is pure titanium dioxide, and Fe$_2$O$_3$/TiO$_2$ ratio for B, C, D, and E is 0.2%, 0.27%, 0.41%, and 0.5%, respectively. Accordingly, the optimum loading of Fe is ascribed to catalyst C with the ratio of Fe$_2$O$_3$/TiO$_2$: 0.27%.

The peak at 1650 cm^{-1} corresponds to the bending vibrations of O–H, and the broad bands at around 3400cm^{-1} are attributed to the surface adsorbed water and hydroxyl groups. The results are in good agreement with [20, 25].

It has been shown that iron as dopant in the Fe/TiO$_2$ contributes to the separation of photogenerated electron-hole pairs and it inhibits the recombination of electrons and holes. Accordingly, doping TiO$_2$ with iron results in enhancing its activity. However, it is remarkable that there is an optimum amount (Fe$_2$O$_3$/TiO$_2$: 0.27%) for it.

Thermal Gravimetric Analysis (TGA)

Fig. 4 shows the Thermal Gravimetric Analysis (TGA) of Fe/TiO$_2$ (catalyst C). In the TGA curve, three regions with different slopes are recognized. These regions are 33.5-200.6°C, 200.6-416.5°C and 416.5-650°C, respectively. In the first region, 35.64% of the total weight loss has occurred. In 33.5-100°C, weight loss is attributed to vaporization of water. In 100-200°C, the weight loss is attributed to the degradation of volatile organic materials. In the second region, 200.6-416.5°C, decomposition of organic material with strong bound has occurred. Weight loss in the third region, 416.5-600°C, is negligible and insignificant [26].
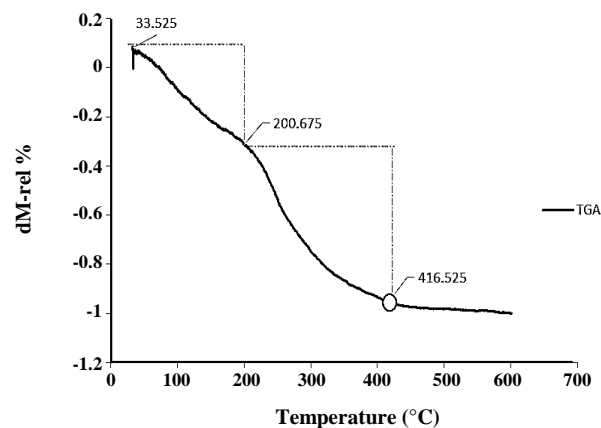
Calcination temperature

The catalytic activity is significantly dependent on calcination temperature of the catalyst. Thermal treatment of TiO$_2$ gels at higher temperatures promotes phase transformation from thermodynamically metastable anatase to the more stable rutile phase [23].

In order to make clear the effect of calcination temperature, Fe/TiO$_2$ catalysts were synthesized at different calcination temperatures including 400°C, 500°C, and 600°C . A synthetic wastewater of phenol (200 ppm) was irradiated by the UV lamp (757.38 mW/cm^3). Fe/TiO$_2$ (catalyst C) with the dosage of 0.5 g/L was applied as the catalyst. H$_2$O$_2$ (12.5 mL, 30% wt. /wt.) was added as an oxidizing agent. Fig.4 shows the effect of calcination temperature of Fe/TiO$_2$ photocatalyst on phenol degradation, which shows that up to the investigated temperature, the higher calcination temperature, the higher the catalytic activity. After 2 hours of reaction, highest efficiency was achieved by the catalyst with calcination temperature of 600°C. The increased photocatalytic degradation efficiency was attributed to the crystallinity. Crystallization process is depicted in the TGA curve of fig.4, the smooth line where almost no mass changes occur. Below 400°C, most of the titania is amorphous and crystallization starts with transformation of amorphous to the anatase phase. Subsequently, the rutile phase forms with increasing the temperature [27].

According to *Ruey-Shin Juang*, the samples annealed below 400 °C become crystalline with dominantly anatase structure and upon annealing at 500–600 °C, the samples possess both anatase and rutile structures, whereas the samples
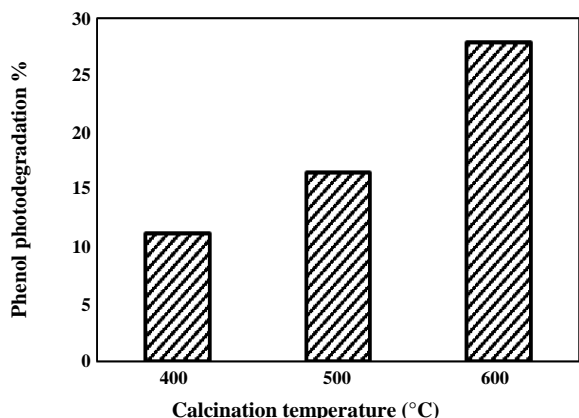
Fig. 5: The effect of calcination temperature on the catalytic activity of TiO.

Fig. 6: The effect of UV irradiation time on the phenol degradation over Fe/TiO₂ photocatalyst.

annealed at 800 °C are completely transformed to the rutile structure[28]. The result is consistent with that of *Ruey-Shin Juang's*, which says that the highest photocatalytic activity is observed at 600°C, which can be attributed to crystalline structure containing both anatase and rutile, the co-existence of the two phases leads to a synergistic effect, indicating that it is the most appropriate calcination temperature [28, 29].

The effect of UV irradiation time on the activity of the Fe/TiO2 photocatalyst

Increasing UV irradiation time will result in increasing the efficiency of the photocatalyst, due to the increase in the electron-hole generation [30]. At a specified phenol concentration (200 ppm), it is observed in Fig.6 that time has enhanced phenol degradation. This is because of the fact, that when more time is devoted to the reaction, the catalyst surface will be exposed to the UV light for a longer time and thus, more sites will be activated. It was completely explained in the mechanism section that, as the result of sufficient illumination with UV lamp, an electron from the valence band migrates to the conduction band leaving behind an electron vacancy (hole) in the valence band. The generated hole in the valence band can produce hydroxyl radicals and subsequently, OH radicals oxidize the organic material. Accordingly, the more the catalyst is exposed to UV irradiation, the more OH radicals are formed and, the higher efficiencies can be attained for the catalyst. The highest phenol degradation efficiency for Fe/TiO₂ photocatalyst after irradiation time of 600 min was attained.
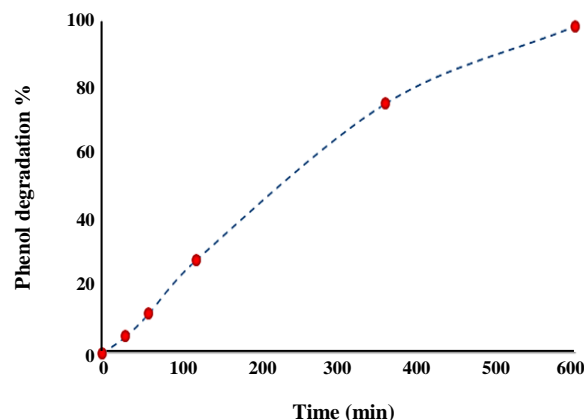
Therefore, the optimum condition for phenol degradation process is as follows: Fe loading in the TiO₂ lattice: Fe_2O_3/TiO_2 is 0.27%, calcination temperature: 600°C, and irradiation time of 600 min. Under this circumstance, 98.26% of the phenol in water was decomposed.

CONCLUSIONS

In this study, the effect of Fe-loading and calcination temperature as two important structural properties of Fe/TiO₂ was highlighted. This paper suggests that prior to any optimizations for enhancing the catalytic activity of a doped catalyst; the first step to be taken is optimizing the dopant concentration and calcination temperature.

The findings of this paper consist of the followings:

1- The catalytic activity of Fe/TiO₂ is drastically affected by the concentration of the Fe.

2- There is an optimum amount for iron as the dopant in Fe/TiO₂.

3- FT-IR results are consistent with experimental results. The intensity of the corresponded peak to Ti-O-Fe bonds confirms the obtained experimental data.

4- The catalytic activity is significantly dependent on calcination temperature of the catalyst.

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