

Preparation of Fe-AC/TiO₂ composites and pH dependence of their photocatalytic activity for methylene blue

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(Received July 21, 2009)

(Revised September 11, 2009)

(Accepted September 30, 2009)

Abstract In this study, activated carbon (AC) was treated with ferric ion by a sol-gel method. The compound (Fe-AC) was employed for the preparation of Fe-activated carbon/TiO₂ (Fe-AC/TiO₂) composites. The prepared Fe-AC/TiO₂ composites were characterized with surface properties, structural crystallinity, elemental identification and photocatalytic activity. The SEM results showed that ferric compounds and titanium dioxide were fixed onto the AC surfaces. The XRD results showed that Fe-AC/TiO₂ composites mostly contained anatase phase. EDX showed the presence of C, O, and Ti with Fe peaks in all samples. Its photocatalytic degradation effect was evaluated with the degradation behavior of the methylene blue (MB) solution. MB degradation could be attributed to the synergetic effects of adsorption, photo-degradation of TiO₂ and photo-Fenton of Fe component. The degradation rate for this photocatalysis was evaluated as a function of the concentration of the dye, the amount of TiO₂ and the pH. Photocatalytic activity is good at activity pH.

Key words Activated carbon, TiO₂, Composite, Methylene blue, pH

1. Introduction

Industrial dyestuffs including textile dyes are recognized as being an important environmental threat. Physical, chemical, and biological methods are available for treatment of such waste; however, they are not sufficient and advantageous. Therefore applying advanced oxidation processes (AOPs) seems to be reasonable. AOPs are attractive in providing a promising and competitive solution for the abatement of numerous hazardous compounds in wastewater including fenton or photo-assisted fenton process, ozone or/and peroxide photolysis, and semiconductor photocatalysis process. [1-6].

The photocatalytic process with using TiO₂ photocatalyst is very promising for application in the water purification, because many hazardous organic compounds can be decomposed and mineralized by the proceeding oxidation and reduction processes on TiO₂ surface [1]. Among the photocatalysts, TiO₂ (in anatase phase) has been most widely used because it is chemistry activity, inexpensive, non-toxic, and shows relative high chemical stability [7-12].

Iron is the most commonly used metal as a Fenton reagent and can be used in the form of iron salt as a homogeneous catalyst or as a heterogeneous catalyst in

the form of a supported metal. Doping of iron to TiO₂ has been widely described by the others, because iron doping can give some benefits such as retarding the inconvenient recombination reaction, which proceeds after photocatalyst excitation and also can extend the photocatalytic ability of the photocatalyst to the visible region [13, 14].

AC was made excellent alternative because it could concentrate pollutants through adsorption around the loaded TiO₂ leading to an increase in the degradation of the pollutants [15]. In addition, the interaction between pollutants and the surface of AC-TiO₂ was also enhanced the degradation [16]. Consequently, TiO₂/AC is considered to be a promising photocatalyst with an industrial application prospect [17-20].

We study the preparation of Fe-AC/TiO₂ composites and their characterizations were determined by employing BET, SEM, XRD and EDX instruments. Furthermore, the photocatalytic activities of Fe-AC/TiO₂ composites which contained different concentration of TiO₂ were studied for the methylene blue degradation under UV light irradiation.

2. Experimental

2.1. Materials

All chemicals were used as received without further

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purification. Active carbon was purchased from coconut. FeNO₃ and TiOSO₄·xH₂O (TOS) were purchased from Solvachim and Merck, respectively. H₂O₂ were purchased from Daejung chemicals metals Co., LTD which were used for dissolve TOS. Methylene blue was supplied by Duksan pure chemical co., ltd.

2.2. Preparation of Fe-AC Compounds

Active carbon was milled for 5 hours, and treated with phosphoric acid (0.1 M 1 L), drying at 373 K for 5 hours, carbon particles were prepared. 12 g carbon particles were mixed with 50 ml FeNO₃ solution (0.1 M). After strring 1 hour and dring at 373 K, the mixture was heat treatment at 773 K. And then Fe-AC compounds were formed.

2.3. Preparation of Fe-AC/TiO₂ photocatalysts

The process of preparation of Fe-AC/TiO₂ photocatalysts is used the sol-gel method. A typical procedure is as follows: Due to TOS was easily dissolved by oxydol solution, 3 g, 4 g, 5 g TOS were added to 50 ml of oxydol, respectively. After stirring for 1 h, TOS-H₂O₂ solution was obtained. And then 3 g Fe-AC compounds were added to each TOS-H₂O₂ solution, respectively. Milling the mixture for 1h. Then the supported TiO₂ particles were first dried at 273 K for 6 h and calcined at 773 K for 2 h each. Fe-AC/TiO₂ photocatalyst composites were obtained. The designations for different prepared materials are summarized in Table 1 (FAT1, FAT2, FAT3).

2.4. Characterization of prepared photocatalyst

Several techniques were used for characterization of the Fe-AC/TiO₂ composites. Crystalline phase, particle size and morphology of photocatalysts nanocrystals were investigated by specific surface area (BET), X-ray diffraction analysis (XRD), energy dispersive X-ray spectroscopy (EDX) and scanning electron microscopy (SEM), respectively. The specific surface area (BET) was determined by N₂ adsorption measurements at 77 K

(Micromeritics FlowSorb II 2300). XRD (Shimatz XD-D1, Japan) analysis using CuKα ($\lambda = 1.5418 \text{ \AA}$) radiation was performed assess the crystalline phases. EDX spectra were used for the elemental analysis of the samples. SEM measurements were performed using a Jeol apparatus (model T-330A) operating at 10 kV on specimens upon which a thin layer of gold or carbon had been evaporated. The pH meter (HI8134) was purchased from Hanna instruments of Italy.

2.5. Photocatalytic activity measurements

The photocatalytic test-reaction chosen to characterize the samples which contained different amount of titania was the total degradation of methylene blue solution selected as a model organic pollutant. The static batch photoreactor was a cylindrical flask. Photoactivity of the catalysts was measure for the methylene blue solution decomposition in water. Photocatalysts in the mass of 0.03 g were added to the 50 mL of methylene blue solution with concentration of $1.0 \times 10^{-4} \text{ M}$ and that mixture was lay for at least 2 h in the dark until saturation of adsorption. After adsorption, photodecomposition of MB solution was performed under UV irradiation. UV light (wavelength 365 nm) irradiation the photoreactor for 10 min, 30 min, 60 min, 90 min, 120 min, 150 min, respectively to research the degradation of MB solution. The experiments were performed at room temperature.

2.6. pH examination

HCl and NaOH were used to adjust the pH of photocataytic reactor solution. Adjust the pH to 4 and 8 separately. The sample is 4FAT1, 4FAT2, 4FAT3, 8FAT1, 8FAT2, 8FAT3. UV irradiation the solution like above 2.5 means.

3. Results and Discussion

Table 1 represents the nomenclatures and method of the samples prepared . The surface area calculated using N₂ adsorption measurements at 77 K. As it is evidently

Table 1
Nomenclatures of Fe-AC/TiO₂ compounds

Preparation method	Nomenclatures
[{3gAC + 0.1 M 50 mlFe(NO ₃) ₃ } (773 K) + 3 g TOS/H ₂ O ₂ 50 ml] (923K)	FAT1
[{3gAC + 0.1 M 50 mlFe(NO ₃) ₃ } (773 K) + 4 g TOS/H ₂ O ₂ 50 ml] (923 K)	FAT2
[{3gAC + 0.1 M 50 mlFe(NO ₃) ₃ } (773 K) + 5 g TOS/H ₂ O ₂ 50 ml] (923 K)	FAT3

Table 2
Value of surface area for samples

Sample name	Surface area
FAT1	533.333 m ² /g
FAT2	456.923 m ² /g
FAT3	399.830 m ² /g

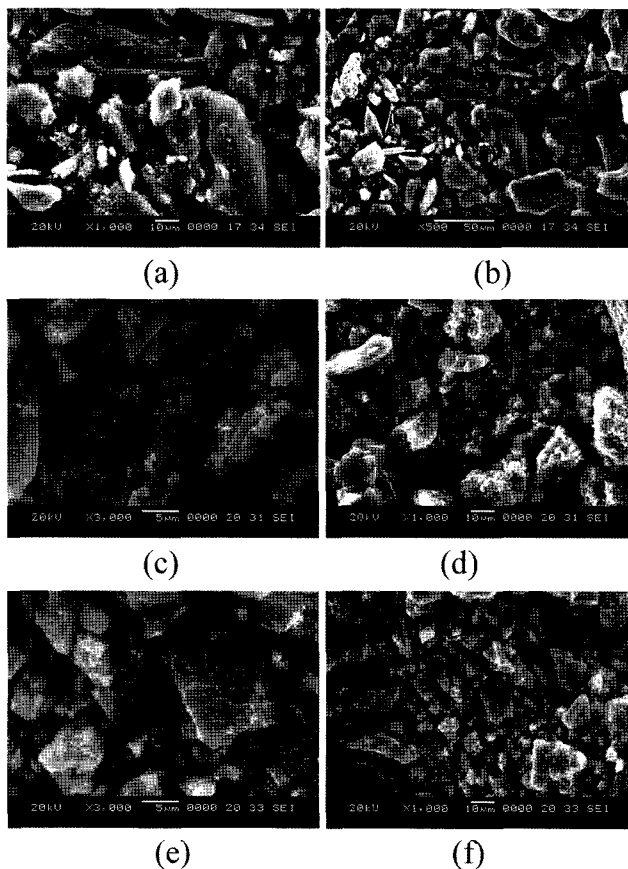


Fig. 1. SEM images of Fe-AC/TiO₂ compounds (a), (c), (e), 1000 magnifications for AFT1, AFT2, AFT3. (b), (d), (f), 500 magnifications for AFT1, AFT2, AFT3.

showed in Table 2, by increase the introduction mass of TiO₂ units into Fe-AC structure via our sol-gel procedure, the surface areas decreased. The smaller crystalline size caused the larger the specific surface areas. The Fe-doping usually inhibits the growth of TiO₂ crystallite and heat-treatment of the samples at 773 K cause the aggregation and sintering of TiO₂ particles [21, 22].

Fig. 1 shows the catalyst surface morphologies observed by Scanning electron microscopy (SEM) at different magnifications and the Fe-AC/TiO₂ compounds surface with iron oxide and TiO₂ units. The morphological evidences of TiO₂ units onto Fe-AC structure which seem to cover the polymer surface were represented in Fig. 1. As shown in Fig. 1, we can see TiO₂ units evenly distributing on Fe-AC structure, and continuous TiO₂ units

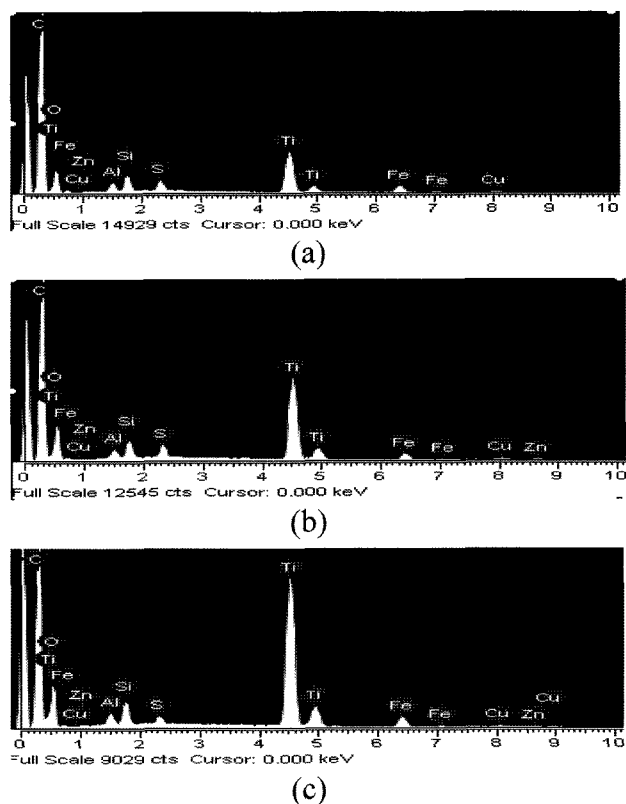


Fig. 2. EDX elemental microanalysis of Fe-AC/TiO₂ compounds (a) AFT1, (b) AFT2, (c) AFT3.

was immobilized on almost every grain of AC. Fig. 1 shows FAT3 have largest TiO₂ units onto Fe-AC structure. The white point is Fe ion which is accreted with AC grain.

Energy Dispersive X-ray (EDX) detector observation (Fig. 2) revealed the inclusive element of the prepared samples. FAT3 have the most TiO₂ units due to the largest TOS was added in the process of sample preparation. The other elements like Si, Cu, Zn were found in Fig. 2, which these element would be content in phosphoric acid.

X-ray diffraction patterns of Fe-AC/TiO₂ samples are shown in Fig. 3. The characteristics diffraction peaks for anatase and rutile structure of TiO₂ and iron diffraction peaks has been verified by inspection of XRD patterns [40] J. Liqiang, S. b, C. Xiaojuna, X. Weimina, D. Zilic, F. Yaoguoc and Honggangb, The preparation and characterization of nanoparticle TiO₂/Ti films and their photocatalytic activity, *J. Phys. Chem. Solids* **64** (2003), pp. 615-623 [23]. The main XRD peak for anatase appears at $2\theta = 25.3^\circ$ with others indexed shown in Fig. 3. It could be observed that all the samples were present in the anatase phases when annealed at 500°C for 1 h. There is not any peak assigned to iron oxide or Fe_xTiO_{2y}

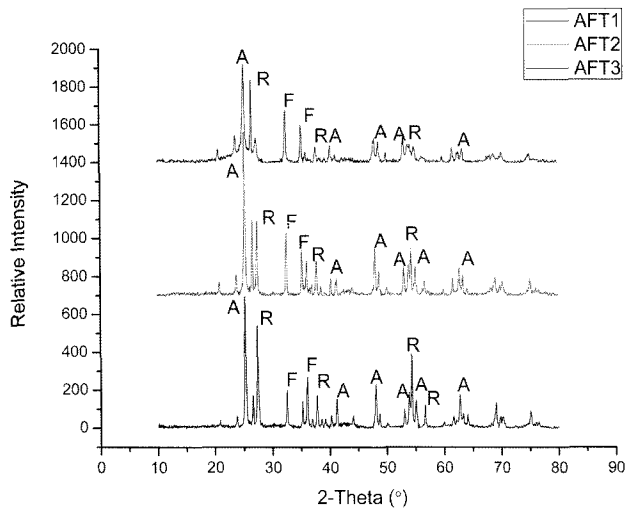


Fig. 3. XRD patterns for Fe-AC/TiO₂ compounds. A: anatase, R: rutile, F: Fe and titanium oxide.

to be observed. One possible reason for this might be that the amount of Fe is too low to be detected by XRD; another reason might be that most iron ions were inserted into the structures of TiO₂ and located at interstices or occupied some of the titanium lattice sites, forming an iron-titanium solid particles. Therefore, TiO₂ units are successfully introduced into Fe-AC structure rather than existing in separate free solid phase. The molecular distribution of TiO₂ units into Fe-AC compound and forming a stable composite could be occurred during the process of hydrolysis of TOS in the presence of oxydol solution (0.1 M).

Initially, control tests on degradation of MB solution (ca. 1×10^{-4} M) were carried out in specified conditions described below: the data are obtained following a two step experiments. The first step is placed in dark to adsorb dye, and the second step is exposed to UV light to degrade MB in solution. It is interesting to note that the surface area for FAT3 is much lower than FAT1, FAT2, so its adsorptive property is lower than other samples at our experiment condition. The time of adsorption of the dye onto all the adsorbents (catalysts) for 120 min was resulted in rise of the adsorption of MB onto Fe-AC/TiO₂ compounds. From Fig. 4, a mass of the initial amounts of the dye are adsorbed onto Fe-AC/TiO₂ compounds following a 120 min adsorption in the dark. Photocatalytic ability of our prepared catalysts degradation of MB has been shown in Fig. 4. The reduction of the dye concentration is continued with an oppositely gentle slope which is due to photodegradation. This indicates that the higher surface area and adsorption capacity for Fe-AC/TiO₂ compounds com-

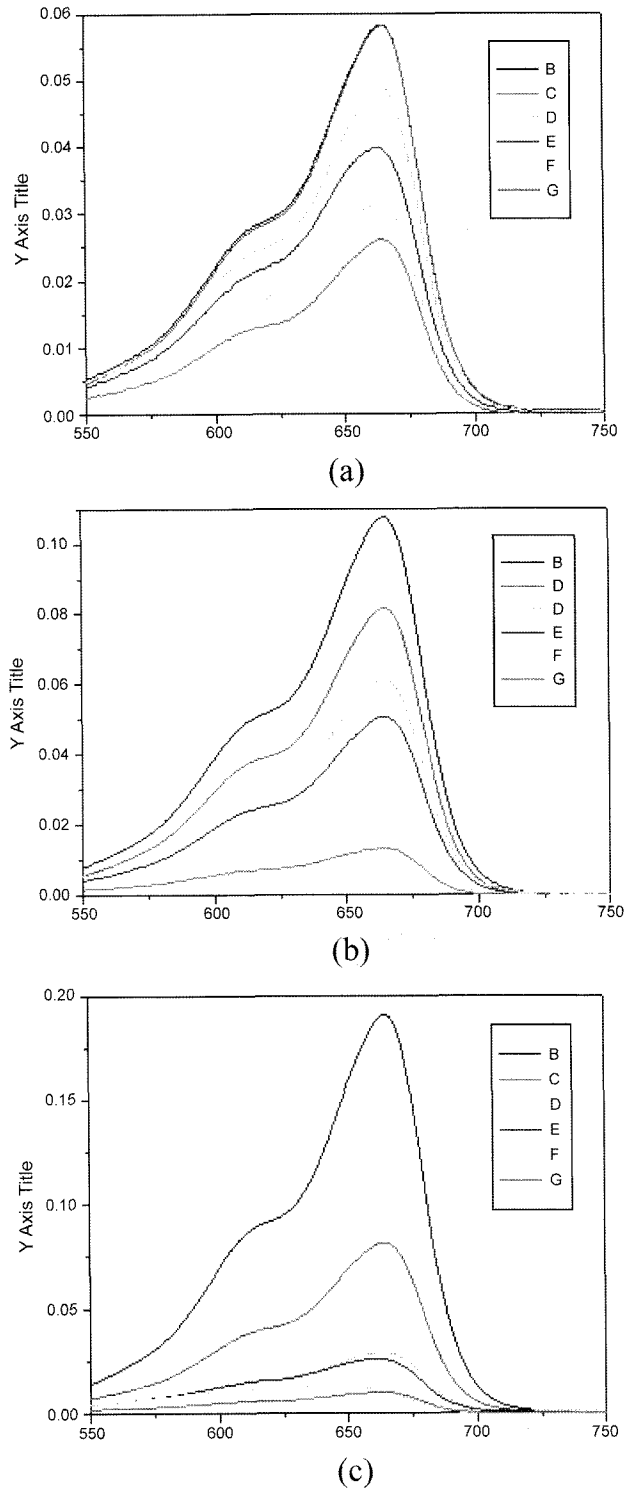


Fig. 4. MB solution on time of UV for Fe-AC/TiO₂ compounds (a) AFT1, (b) AFT2, (c) AFT3. 10, 30, 60, 90, 120, 150 min respectively to research the degradation of MB solution.

pared to that of bare TiO₂ plays the major role for elimination of MB. Obviously, achieving greater adsorption for MB is mainly related to the presence of Fe in AC/TiO₂ compounds. As known, a large surface area may be an important factor in certain photocatalytic degrada-

tion reactions, as a large amount of adsorbed organic molecules promotes the reaction rate. However, powders with a large surface area are usually associated with large amounts of crystalline defects, which favor the recombination of photo-generated electrons and holes leading to a poor photoactivity. Therefore, a reasonable explanation for the enhanced photoactivity of Fe-AC/TiO₂ compounds was that the acceptance of photo-gen-

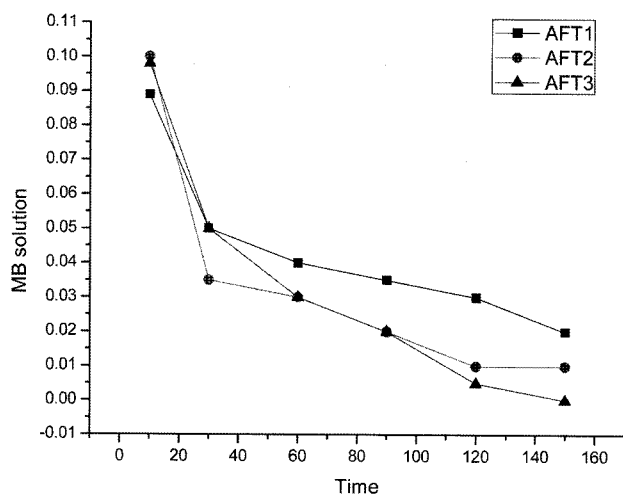


Fig. 5. MB solution on time of adsorption and UV for Fe-AC/TiO₂ compounds.

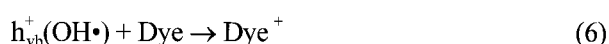
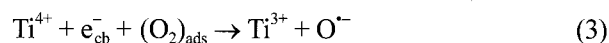
erated as shown in Fig. 5. Time series of MB (Methylene blue) photodegradation using Fe-AC/TiO₂ compounds under UV light irradiation. A possible reaction mechanism for the photooxidation of organism by Fe-AC/TiO₂ compounds shine by UV light. The iron dopant in the titania crystalline matrix can prevent the recombination which promotes the efficiency of TiO₂. In the mean time, TiO₂ with large specific surface area retards the formation of the oxide layer on the surface of the Fe²⁺, Fe³⁺. Because iron Fe²⁺ can be easily oxidized to Fe³⁺ (by dissolved oxygen in the solution), giving some reactive O radicals, which can oxidize MB solution, as it is presented in reaction (1)



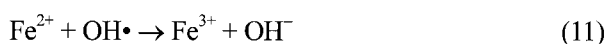
OH• radicals formation on the catalysts surface during UV irradiation.

Iron ions can introduce energy levels into the band-gap, which are responsible for the red shift of intrinsic absorption edge of TiO₂ and of the enhancement of visible light adsorption, but there is no direct correlation between the light absorption ability and photocatalytic rate [24-37]. Factors related to the electronic structure

seem to be more important, associated to the fact that dopant ions influence charge separation, charge-carrier recombination and interfacial charge transfer rates, acting as mediators and affecting the quantum efficiencies. Under irradiation, electron-hole pairs are produced in the conduction and valence bands of TiO₂, and successive events take place.



Where Ox is an electron acceptor and dye is electron donor. Irradiation of iron-doped TiO₂ can lead to the following addition steps.



In this study, the photocatalytic activity of the TiO₂ powders doped by Fe evenly with lower dopant level is better than that of undoped TiO₂. In iron-doped titania, Fe³⁺ can improve the photocatalytic efficiency by enhancing processes such as separation of photogenerated charges (by hole or electron trapping), detrapping and/or transfer of trapped charges to interface and to adsorbed substrates, reducing consequently recombination [37-50]. However, dopants can act as recombination centers.

We change pH to investigate the photocatalytic of Fe-AC/TiO₂ compounds to methylene blue. In examination use the pH meter to measure the pH of dye solution at 10 min, 30 min, 60 min, 90 min, 120 min, 150 min separately. Fig. 6 shows the pH variation of dyes in the aqueous solution on time with photocatalytic reaction. It is clear that the change trends of pH value for methylene blue solution. The MB solution rapidly decomposed to acidic species, and the most TiO₂ exist the best

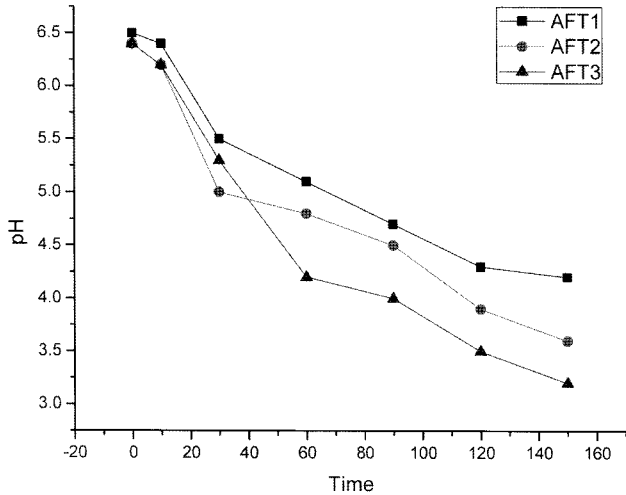
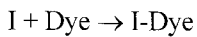


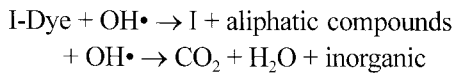
Fig. 6. pH variation of MB in the aqueous solution on time with photocatalytic reaction.

MB degrading rate have.

In the photocatalytic applications have larger amount of OH• radicals, which possess high oxidative potential, it can oxidize most organic pollutants into inorganic materials. These oxidizing agents can nonselectively attack the adsorbed organic molecules or those close to the catalyst surface. The reaction occurs at those TiO₂/solution interfaces.[51]



(I: adsorption site)



From hereinbefore expressions the OH• reduced in the reaction process, which induce the pH reduced. Larger amounts of TiO₂ in catalytic compounds cause larger amounts of OH• produce, and oxidize more organic pollutants into inorganic materials.

Since dyes to be degraded can be at different pH in colored effluents, comparative experiments were performed at two pH values: 4 and 8. The pH had a little influence upon the kinetics of disappearance (Fig. 7). It was observed that when pH=8 the rate is a litter batter. dye is quickly decomposed at only 30 minutes may be the concentration of MB solution is low and MB will decomposed at high temperature. In this case we measured the temperature during the experiment, the MB solution's temperature is only about 15°C. So we can remove the ingredient of temperature. As stated above, the amount of MB adsorbed increased by changing the pH to 4 and 8. The increased adsorption amounts should result in the enhancement of the photodecomposition of

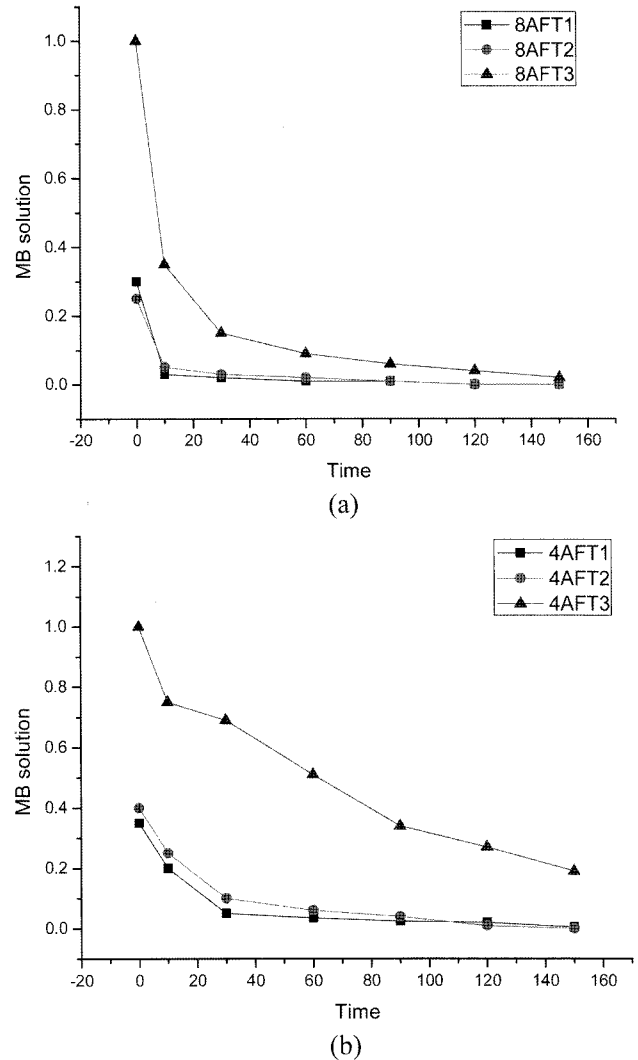
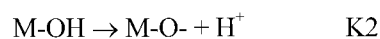
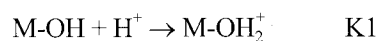


Fig. 7. Photocatalytic activity for Fe-AC/TiO₂ compounds at different pH environment. (a) compounds at alkaline pH, (b) compounds at acidic pH.

MB, because the photoactivated catalytic active site decomposes the MB adsorbed on or near it. This is indicative of the significant role of the surface property of the photocatalyst TiO₂; the acid-base property of the metal oxide surface has a considerable influence on the photocatalytic activity with varying pH. The pH effect can be explained on the basis of the zero point of charge of TiO₂. The adsorption of H₂O molecules at surface metal sites is followed by the dissociation of OH groups leading to a coverage [52] with chemically equivalent metal hydroxyl groups (M-OH). Due to the amphoteric behaviour of most metal hydroxides, the following two equilibria must be considered.



So when the pH of photocatalytic reactor solution is 8, the photocatalytic activity is better than that is 4.

4. Conclusions

Fe ion and TiO₂ units were covered on the AC surface and were developed through a deposition process of sol-gel method in this paper. SEM image represents Fe-AC/TiO₂ composites were synthesized by immobilizing TiO₂ particles on the surface of AC and Fe studded on the composites. XRD image represents Fe-AC/TiO₂ composites have a single crystal structure which is anatase; C and O with Ti, Fe peaks were found from EDX results. The MB decomposition processes confirmed the adsorption and photocatalytic reaction on the composites. The Fe-AC/TiO₂ photocatalyst was found to engender the principal beneficial effects: The Fe-AC/TiO₂ samples show a strong absorption and can efficiently decompose the methylene blue (MB) solution under UV light. Iron ion acted as a photoactivator can enhance the degradation reaction rate for MB solution. Fe-AC/TiO₂ enhanced the photocatalytic activity due to TiO₂ increased. The pH is reduced along with dye degradation, and photocatalytic activity at alkaline pH is better than at acidic pH.

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