The Photocatalytic Decomposition of Different Organic Dyes under UV Irradiation with and without H_2O_2 on Fe-ACF/ TiO_2 Photocatalysts

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ABSTRACT

The Fe-ACF/ TiO_2 composites were prepared by a sol-gel method and were characterized by nitrogen adsorption, Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD), and Energy Dispersive X-ray (EDX). The Fe-ACF/ TiO_2 composites were developed for the decomposition of organic dyes by using a UV lamp. The decomposition effect was investigated under various conditions, such as three selected non-biodegradable organic dyes like Methylene Blue (MB), Methyl Orange (MO), Rhodamine B (Rh.B), and in the presence of Fe and hydrogen peroxide (H_2O_2). The photocatalytic activity was derived from possible combination effects, such as (1) adsorption of ACF, (2) generation of electron/hole by TiO_2 , (3) photo-Fenton reaction of Fe, and (4) oxidation of Fe^{2+} to Fe^{3+} by H_2O_2 .

Key words : Fe-ACF/ TiO_2 composites, Photocatalytic, H_2O_2 , Photo-Fenton, Organic dyes

1. Introduction

The industrial and textile wastewaters is a considerable source of non-aesthetic pollution in the environment and can create dangerous byproducts through oxidation, hydrolysis, or other chemical reactions that take place in the wastewater phase.¹⁻⁴ Therefore, removing such contaminants is a major focus in reducing environmental pollution. In recent years, the photocatalytic decomposition of organic pollutants in water by suspending TiO_2 as a catalyst has been widely studied.^{5,6} When TiO_2 absorbs a photon of energy that is equal to or greater than its band gap width, an electron may travel from the valence band to the conduction band (e_{cb}^-) where a photohole will be generated, as well as electrons in the valence band (h_{vb}^+). In particular, h_{vb}^+ may react with surface-bound H_2O or OH^- to produce the hydroxyl radical ($\text{OH}^\bullet$) and e_{cb}^- is picked up by oxygen to generate superoxide radical anion ($\text{O}_2^{\bullet-}$). It has been suggested that the hydroxyl radicals ($\text{OH}^\bullet$) and superoxide radical anions ($\text{O}_2^{\bullet-}$) have a powerful capability in removing organic functional groups from the photocatalytic decomposition processes. Moreover, the decomposition effect for different organic dyes molecules is different.

Since the suspended TiO_2 powders present some drawbacks, the powders not being able to be easily precipitated and recovered from the water. And, these drawbacks can be harmful to the powders' regeneration and reuse. Therefore, many studies have been devoted to immobilizing TiO_2 on

different substrate materials.^{7,8} Activated Carbon Fiber (ACF), which has good adsorption and a uniform pore structure, has been widely used as a catalyst support for different purposes.⁹⁻¹³ In addition, ACF can attract more water molecules and/or organic binder on the TiO_2 surface. Therefore, ACF is an ideal substrate for TiO_2 immobilization.

Moreover, for TiO_2 itself, there are some limitations due to the capability of electron/hole pairs to recombine within nanoseconds,¹⁴ which can only happen with a light illumination of a suitable wavelength ($\lambda < 390 \text{ nm}$ or $E_{bg} = 3.2 \text{ eV}$)¹⁵⁻¹⁹ and with low photon utilization efficiency. In order to surmount these demerits, incorporating transition metal ions like Cr,²⁰ Mn,²¹ Co,²² Cu,²³ Zr,^{24,25} Fe,²⁶⁻²⁹ into the TiO_2 lattice host could remarkably increase photocatalytic activity. This is especially true when Fe could act as both hole and electron traps that can enhance the photocatalytic activity of TiO_2 ³⁰ and produce photo-Fenton reactions by reducing Fe^{3+} to Fe^{2+} . From the above points, combining ACF and TiO_2 with Fe was considered reliable behavior for increasing photocatalytic activity.

According to previous studies,³¹ it is well-known that the photo-Fenton process is governed by the amount and ratio of $\text{Fe}^{2+}/\text{Fe}^{3+}$, because the yield of photo-Fenton reactions is lower when there is an excess of Fe^{2+} ions. Many authors used oxygen gas to oxidate Fe^{2+} to Fe^{3+} as Fenton's reagent.³²⁻³⁴ O_2 is a more environmentally-friendly oxidant, but it still offers low conversion. Some homogeneous and heterogeneous catalytic systems that consisted of Fenton's reagent have been investigated for oxidating Fe^{2+} to Fe^{3+} by using H_2O_2 .³⁵⁻³⁷ The use of H_2O_2 oxidation catalysts with Fenton catalysts proves that they can form more OH radicals and can be reused in the following processes:

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Table 1. The Properties of ACFs

Physical properties	Units
Density	1.23 ~ 1.91 g/mL
Electrical Resistivity	$5.2 \times 10^{-3} \sim 6.8 \times 10^{-3} \Omega \cdot \text{cm}$
Diameter	12 ~ 15 μ
Tensile Strength	$4 \sim 6 \times 10^8 \text{ Pa}$
Tensile Modulus	$3 \times 10^{10} \sim 4 \times 10^{10} \text{ Pa}$
Elemental carbon	$\geq 95 \text{ wt\%}$

The reaction (1) and (2) showed the powerful recuperation of Fe^{3+} and the reuse of the catalyst, which proves that the yield of photo-Fenton reactions is higher when there is an excess of Fe^{2+} ions.

In this paper, Fe-ACF/ TiO_2 composites were synthesized and the decomposition of different dyes, like MB, Rh.B, and MO dyes were studied under UV irradiation both with and without H_2O_2 . The synthesized catalyst was characterized as being BET, SEM, XRD and EDX.

2. Experimental Procedure

2.1. Materials

Activated Carbon Fiber (ACF) was purchased from EAST ASIS Carbon Fibers Co., Ltd, (Anshan, China). Their properties are shown in Table 1. Hydrogen peroxide (H_2O_2 , 35%) was purchased from Daejung Chemicals & Metals Co., Ltd, (Korea). Titanium (IV) oxysulfate hydrate ($\text{TiOSO}_4 \cdot x\text{H}_2\text{O}$ (TOS) 99.99%) was used as a titanium source, which was purchased from Sigma-Aldrich, (Germany), while $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99+%) as the ferric source was purchased from Duksan Pure Chemical Co., Ltd, (Korea). The MB (99.99+%) was used as an analytical grade, which was purchased from Duksan Pure Chemical Co., Ltd, (Korea). The Rh.B (99.99+%) was purchased from Samchun Pure Chemical Co., Ltd, (Korea). The MO (99.99+%) was purchased from Daejung Chemicals & metals Co., Ltd, (Korea).

2.2. Preparation of samples

For this experimental process, 10 g ACF power was first added into to a 50 ml 0.25 M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution and the mixtures were stirred for 24 h by a non-magnetic stirrer at room temperature. After being heated at 773 K, the Fe-ACF was obtained. The Fe-ACF was put into the mixture of TOS and ethanol. Then, the mixed solution was stirred for 5 h in an air atmosphere. After the stirring solution was transformed to a gel state, these gels were heat treated at 923 K for 1h. Then, the Fe-treated ACF/ TiO_2 composites were also obtained. The nomenclatures of the prepared samples are listed in Table 2. At the same time, an original sample of ACF/ TiO_2 was cited from the former experiment⁽³⁸⁾ and compared with that of the Fe-ACF/ TiO_2 composites that were obtained.

Table 2. Nomenclatures of ACF/ TiO_2 and Fe-ACF/ TiO_2 Composites

Sample	Nomenclatures
ACF+Titanium iso propoxide	AT
ACF+ $\text{Fe}(\text{NO}_3)_3$ (0.25 M)+TOS	FAT

Table 3. Structural Representation of Some Selected Organic Dyes

Name of dyes	Molecular structure of dyes
MB $\lambda_{\text{max}} = 660 \text{ nm}$
Rh.B $\lambda_{\text{max}} = 550 \text{ nm}$
MO $\lambda_{\text{max}} = 476 \text{ nm}$

2.3. Characteristics and investigations of the samples

The BET surface area by N_2 adsorption method was measured at 77 K by a BET analyzer (Monosorb, Quantachrome Instruments Ltd., USA). The XRD (XD-D1 Shimadzu Ltd., Japan) result was used to identify the crystallinity from the Cu $\text{K}\alpha$ radiation. SEM was used to observe the surface state and structure of Fe-ACF/ TiO_2 composites by SEM (JSM-5200 JOEL Ltd., Japan). EDX (JSM-5200 JOEL Ltd., Japan) spectra were also obtained for determining the elemental information of the ACF/ TiO_2 and Fe-ACF/ TiO_2 composites. UV-vis absorption parameters for the MB solution were decomposed by ACF/ TiO_2 and Fe-ACF/ TiO_2 composites under UV lamp irradiation (both with H_2O_2 and without H_2O_2) and they were recorded by using a (Spectronic 21 Bausch & Lomb Ltd, USA) spectrophotometer.

2.4. Photocatalytic activity of Fe-ACF/ TiO_2

The photochemical data that were presented as behaviors of the organic dyes (MB, Rh.B and MO) were decomposed by ACF/ TiO_2 and Fe-ACF/ TiO_2 composites in a 100 mL glass container, and in an irradiation system by UV, both with H_2O_2 and without H_2O_2 , respectively. The sample powder of 0.03 g was suspended in the 50 ml of organic dye (MB, Rh.B and MO) solution with a concentration of $1.0 \times 10^{-5} \text{ M}$. Then, the mixed solution was emplaced in the dark for at least 2 h in order to establish an adsorption-desorption equilibrium, which is hereafter known as the initial concentration (c_0) after dark adsorption. Then, the experiments were carried out under two conditions: 1) UV only and 2) under UV with an addition of $1.5 \times 10^{-3} \text{ mol H}_2\text{O}_2$ to the organic dye solution (ex, UV and UV + H_2O_2 , respectively). The solution was then withdrawn regularly from the reactor by an order of 30 min, 60 min, 90 min, and 120 min. Afterwards, 10 mL of solution

Table 4. Specific BET Surface Areas of Pristine ACF, ACF/TiO₂ and Fe-ACF/TiO₂ Composite Samples.

Sample	S _{BET} (m ² /g)
Pristine ACF	1842
AT	1268
FAT	745

Table 5. EDX Elemental Microanalysis (wt%) of ACF/TiO₂ and Fe-ACF/TiO₂ Composites

Samples	Elements (wt%)			
	C	O	Ti	Fe
AT	65.5	15.4	18.9	0
FAT	67.14	17.63	6.52	5.18

was taken out and immediately centrifuged in order to separate any suspended solid. The clean transparent solution was immediately analyzed by using a UV-vis spectrophotometer in order to decrease the continual oxidation of H₂O₂ for organic compounds residue. The extent of dye decomposition was estimated by a spectrophotometer at the absorption maximum ($\lambda_{\max}$) of the concerned dye. The molecular structures of the dyes are shown in Table 3.

3. Results and Discussion

3.1. The surface characteristics

The value of the BET surface area of pristine ACF, ACF/TiO₂ and Fe-ACF/TiO₂ samples are shown in Table 4. According to the results of Table 4, the BET surface area of the as-received ACF is 1842 m²/g, while the BET surface area of the ACF/TiO₂ and Fe-ACF/TiO₂ composites decreased to 1268 m²/g and 745 m²/g. It is evident that there was a large change of the micropore size distribution for the ACF/TiO₂ and Fe-ACF/TiO₂ composites, compared with that of the corresponding ACF. This may have been due to the partial blocking of micropores that were formed by TiO₂ on the ACF surface from the heat treatment. This was especially true for the Fe-ACF/TiO₂ composites, where the variation of surface parameters was probably caused by the TiO₂ and Fe compounds. The similar phenomena were also observed in previous studies.^{39,40}

The SEM micrographs of ACF/TiO₂ and Fe-ACF/TiO₂ composites are shown in Fig. 1. It can be observed in Fig. 1 (a) and (b) that the TiO₂ particles were immobilized on the surface of ACF. Some adjacent fibers were connected to each other by the TiO₂ particles that were deposited. Fig. 1(c) and (d) show that the TiO₂ particles were deposited on the ACF as small clusters. Although the TiO₂ particles were deposited on fibers at such a large scale, the Fe-ACF/TiO₂ still retained the same spatial distribution of non-treated ACF/TiO₂. Therefore, adequate UV irradiation was not able to penetrate into the connect-form photocatalyst up to a certain depth in order to form a three dimensional environment for photocatalytic reactions. The rough surface of the TiO₂ layer may have contributed in the increase of the

Fig. 1. SEM images of non-treated ACF/TiO₂ and Fe-ACF/TiO₂ composites: AT: (a)× 500, (b)× 3000; FAT: (c)× 500, (d)× 3000. **Fig. 2.** XRD patterns of the powdered ACF/TiO₂ and Fe-ACF/TiO₂ composites.

surface area of loaded TiO₂, which may have offered a greater chance of substrate adsorption onto the TiO₂ surface. In addition, these small clusters of TiO₂ crystals were spread over the ACF surface in an irregular shape, where the interstices among the crystalline particles provided an ideal path for the transport and adsorption of organic molecules.

3.2. The composition of non-treated ACF/TiO₂ and Fe-ACF/TiO₂

The XRD spectra of ACF/TiO₂ and Fe-ACF/TiO₂ composites are shown in Fig. 2. The XRD patterns of ACF/TiO₂ and Fe-ACF/TiO₂ photocatalysts show that all of the photocatalysts have developed unique anatase-type TiO₂, where the peaks of all the samples at 25.4°, 38.2°, 47.9°, 54.8° and 62.6° are related to the diffractions of the (101),

Fig. 3. EDX elemental microanalysis of ACF/TiO₂ and Fe-ACF/TiO₂ composites: (a) AT and (b) FAT.

Fig. 4. Adsorption capability of Fe-ACF/TiO₂ for different organic dyes under dark condition.

(112), (200), (211), and (204) planes of anatase. No significant diffraction peaks of rutile-phase TiO₂ were detected in the XRD spectra. The phenomena mentioned above can be attributed to the two following facts that 1) thin TiO₂ layers are tightly connected to the carbon fibers surfaces, and 2) the carbon surfaces that are located under the TiO₂ layers can suppress the phase transformation of TiO₂ from an anatase to a rutile structure at a high temperature.^{41,42)} According to previous studies,^{43,44)} pure anatase nanocrystallites are very efficient photocatalysts, which is the result of their excellent photocatalytic properties. Moreover, in the curve of Fe-ACF/TiO₂, one can clearly find the peaks of Fe, which was further supported by observation via EDX elemental microanalysis of Fe-ACF/TiO₂.

For the elemental analysis of non-treated ACF/TiO₂ and Fe-ACF/TiO₂ composites after heat treatment, samples were analyzed by the EDX. The EDX spectra of samples are

Fig. 5. Dependence of relative concentration of MB, Rh.B, and MO in the aqueous solution $\ln \text{Abs}(\text{max})_t / \text{Abs}(\text{max})_{t_0}$ on UV irradiation time for the non-treated ACF/TiO₂ and Fe-ACF/TiO₂ composites.

shown in Fig. 4. The rustles of typical EDX elemental microanalysis of ACF/TiO₂ and Fe-ACF/TiO₂ composites are shown in Table 3. The results show the main presence of C, O, and Ti. One can also see the peaks of Fe element in the Fe-ACF/TiO₂ composites.

3.3. Degradation of organic dyes

In order to evaluate the absorption ability of Fe-ACF/TiO₂ composites, degradation of different dyes were run under a dark condition, which is shown in Fig. 4. From the figure, it is clear that strong adsorption ability was observed in organic dyes, which can be attributed to the high porosity of ACF. The adsorptive efficiency of ACF to dye molecules was determined by two factors: the pore diameter of ACF and the molecular size of the dye molecule.⁴⁵⁾ The degradation of MB is faster than that of MO and Rh.B, which can be explained by the fact that the MB molecules were close to a strip shape, so they were easier to be adsorbed in the same direction as the pore path. The side tropism adsorption also occurred with that of MO and Rh.B. It was considered that the sorption of the dye is an important parameter in determining the photocatalytic degradation rate.⁴⁶⁾ However, adsorption had little effect on the degradation of the Rh.B. This may have resulted from the molecule structure of Rh.B, which is larger than the pore diameter of ACF.

In order to evaluate the actual photocatalytic activity of the ACF/TiO₂ and Fe-ACF/TiO₂ photocatalysts, a comparison of the decomposition processes of three organic dyes, namely, photolysis and photo-Fenton reaction, were carried out, and the results are shown in Fig. 5. It was found that MB, a widely used organic color in dyeing and textile industries, can be decomposed at a higher degree than that of MO and Rh.B under UV irradiation, as shown by the curves of the photolysis. According to previous studies,^{47,48)} -CH₃ elimination and C-N scission can positively occur on the MB

Fig. 6. Dependence of relative concentration of MB, Rh.B, and MO in the aqueous solution $\text{Abs}(\text{max})_t / \text{Abs}(\text{max})_{c_0}$ on UV irradiation time with H_2O_2 for the Fe-ACF/ TiO_2 composites.

molecules via formation of a hydroxyl radical ($\text{OH}^\bullet$).

In order to degrade MB, Rh.B, and MO by using ACF/ TiO_2 and Fe-ACF/ TiO_2 composites, Fe-ACF/ TiO_2 composites were found to be more photoactive towards the three dyes solutions than ACF/ TiO_2 . It is noteworthy that the Fe modified ACF- TiO_2 enhanced the photocatalytic activity greatly, which was proposed to be enhanced via photo-Fenton reaction and by reducing the recombination rate of the h^+/e^- pairs. As mentioned above the photo-Fenton reduction of Fe^{3+} to Fe^{2+} in the OH^- solution under UV light gave rise to $\text{OH}^\bullet$ radicals. Moreover, Fe species operated an additional electron accepting species to enhance the photocatalytic activity of TiO_2 , according to the following reactions:

The reactivity of the Fe^{3+} with the electrons was photo-generated at the conduction band of TiO_2 could be beneficial or detrimental factors to the oxidative processes depending on the iron species that is present in the medium. Thus, the active degradation was strongly influenced by the presence of $\text{Fe}^{3+}/\text{Fe}^{2+}$ in the TiO_2 suspension.

3.4. H_2O_2 -assisted Fenton processes

H_2O_2 -assisted Fenton processes were also done by testing the decomposition of the above three organic dyes on the Fe-ACF/ TiO_2 composites, which is shown in Fig. 6. When comparing Fig. 5 and Fig. 6, one can see that the rates and efficiencies in the degradation of dyes were found to significantly improve in the presence of peroxides. The high decomposition rate of organic dyes when H_2O_2 was used under UV irradiation can also be observed. However, it was reported in previous studies that the amount of $\text{OH}^\bullet$ generated directly by the photolysis of H_2O_2 under UV is very small.⁴⁹⁾ Therefore, higher photocatalytic activity can be attributed to the increase of the formation of $\text{OH}^\bullet$

radicals, which were caused by the oxidation of Fe^{2+} after addition of H_2O_2 into the reaction solutions. The reaction of Fe^{2+} with H_2O_2 represents a supplementary source of $\text{OH}^\bullet$ radicals, which resulted in the increase in the decomposition rate of the irradiated systems.

4. Conclusion

The results of these studies clearly indicate that organic dyes can be efficiently decomposed in the presence of photocatalysts. The results also indicate that the decomposition rate could be influenced by a number of conditions, such as the type of organic dye being used and the presence of Fe and H_2O_2 . The rate of decomposition of MB was found to be the best among all the dyes. The rate of decomposition could be enhanced when there is a production of photo-Fenton reactions. The presence of H_2O_2 further enhanced the rate of decomposition due to the improved photo-Fenton reactions.

REFERENCES

1. U. Pagga and D. Bruan, "Behavior of Dye Stuffs in Aerobic Biodegradation Tests," *Chemosphere*, **15** 479-84 (1986).
2. A. Bianco-Prevot, C. Baiocchi, M. C. Brussino, E. Pramauro, P. Savarino, V. Augugliaro, G. Marci, and L. Palmisano, "Photocatalytic Degradation of Acid Blue 80 in Aqueous Solutions Containing TiO_2 Suspensions," *Environ. Sci. Technol.*, **35** 971-76 (2001).
3. B. Neppolian, H. C. Choi, S. Sakthivel, B. Arabindoo, and V. Murugesan, "Solar Light Induced and TiO_2 Assisted Degradation of Textile Dye Reactive Blue 4," *Chemosphere*, **46** [8] 1173-81 (2002).
4. M. Saquib and M. Muneer, " TiO_2 -mediated Photocatalytic Degradation of a Triphenylmethane Dye (gentian violet), in Aqueous Suspensions," *Dyes Pigments*, **56** 37-49 (2003).
5. B. Zielinska, J. Grzechulska, and A. W. Morawski, "Photocatalytic Decomposition of Textile Dyes on TiO_2 -Tytanpol A11 and TiO_2 -Degussa P25," *J. Photochem. Photobiol. A: Chem.*, **157** 65-70 (2003).
6. E. Vulliet, J. M. Chovelon, C. Guillard, and J. M. Herrmann, "Factors Influencing the Photocatalytic Degradation of Sulfonyleurea Herbicides by TiO_2 Aqueous Suspension," *J. Photochem. Photobiol. A: Chem.*, **159** 71-9 (2003).
7. P. F. Fu, Y. Luan, and X. G. Dai, "Preparation of Activated Carbon Fibers Supported TiO_2 Photocatalyst and Evaluation of its Photocatalytic Reactivity," *J. Mole. Catal. A: Chem.*, **221** 81-8 (2004).
8. S. Gelover, P. Mondragon, and A. Jimenez, "Titanium Dioxide Sol-Gel Deposited Over Glass and its Application as Photocatalyst for Water Decontamination," *J. Photochem. Photobiol. A: Chem.*, **165** 241-46 (2004).
9. M. L. Chen, C. S. Lim, and W. C. Oh, "Photocatalytic Effect for TiO_2 /ACF Composite Electrochemically Prepared with TNB Electrolyte," *Carbon Letter*, **8** 177-83 (2007).
10. Y. N. Hou, J. H. Qu, X. Zhao, P. J. Lei, D. J. Wan, and C. P. Huang "Electro-photocatalytic Degradation of Acid Orange II Using a Novel TiO_2 /ACF Photoanode," *Sci. of the Total*

- Environ.*, **407** 2431-39 (2009).
11. D. Q. Mo and D. Q. Ye, "Surface Study of Composite Photocatalyst Based on Plasma Modified Activated Carbon Fibers with TiO_2 ," *Surf. Coat. Technol.*, **203** 1154-60 (2009).
 12. W. C. Oh, F. J. Zhang, M. L. Chen, Y. M. Lee, and W. B. Ko, "Characterization and Relative Photonic Efficiencies of a New Fe-ACF/ TiO_2 Composite Photocatalysts Designed for Organic Dye Decomposition," *J. Indust. Engin. Chem.*, **15** 190-5 (2009).
 13. W. C. Oh and M. L. Chen, "Electrochemical Preparation of TiO_2 /ACF Composites With TNB Electrolyte and Their Photocatalytic Effect," *J. Ceram. Process. Res.*, **9** 100-6 (2008).
 14. N. Serpone and D. Lawless, "Spectroscopic, Photoconductivity, and Photocatalytic Studies of TiO_2 Colloids: Naked and with the Lattice Doped with Cr^{3+} , Fe^{3+} , and V^{5+} Cations," *Langmuir*, **10** 643-52 (1994).
 15. T. Sauer, G. C. Neto, H. J. Jose, and R. F. P. M. Moreira, "Kinetics of Photocatalytic Degradation of Reactive Dyes in a TiO_2 Slurry Reactor," *J. Photochem. Photobiol. A: Chem.*, **149** 147-54 (2002).
 16. C. Galindo, P. Jacques, and A. Kalt, "Photochemical and Photocatalytic Degradation of an Indigoid Dye: a Case Study of Acid Blue 74 (AB74)," *J. Photochem. Photobiol. A: Chem.*, **141** 47-56 (2001).
 17. F. Zhang, J. Zhao, T. Shen, H. Hidaka, E. Pelizzetti, and N. Serpone, " TiO_2 -assisted Photodegradation of Dye Pollutants II. Adsorption and Degradation Kinetics of Eosin in TiO_2 Dispersions under Visible Light Irradiation," *Appl. Catal. B: Environ.*, **15** 147-56 (1998).
 18. M. A. Hasnat, I. A. Siddiquy, and A. Nuruddin, "Comparative Photocatalytic Studies of Degradation of a Cationic and an Anionic Dye," *Dyes Pigments*, **66**, 185-8 (2005).
 19. R. W. Matthews, "Photooxidation of Organic Impurities in Water Using Thin Film of TiO_2 ," *J. Phys. Chem.*, **91** 3328-33 (1987).
 20. C. G. Wu, C. C. Chao, and F. T. Kuo, "Enhancement of the Photo Catalytic Performance of TiO_2 Catalysts via Transition Metal Modification," *Catal. Today*, **97** 103-12 (2004).
 21. D. Dvoranova, V. Brezova, M. Mazura, and M. A. Malati, "Investigations of Metal-doped Titanium Dioxide Photocatalysts," *Appl. Catal. B: Environ.*, **37** 91-105 (2002).
 22. M. A. Barakat, H. Schaeffer, G. Hayes and S. Ismat-Shah, "Photocatalytic Degradation of 2-chlorophenol by Co-doped TiO_2 Nanoparticles," *Appl. Catal. B: Environ.*, **57** 23-30 (2004).
 23. D. Beydoun, H. Tse, R. Amal, G. Low, and S. McEvoy, "Effect of Copper (II) on the Photocatalytic Degradation of Sucrose," *J. Mol. Catal. A: Chem.*, **177** 265-72 (2002).
 24. P. A. Gay, P. Berçot, and J. Pagetti, "Electrodeposition and Characterisation of Ag-ZrO₂ Electroplated Coatings," *Surf. Coat. Technol.*, **140** 147-54 (2001).
 25. F. Hou, W. Wang, and H. Guo, "Effect of the Dispersibility of ZrO₂ Nanoparticles in Ni-ZrO₂ Electroplated Nanocomposite Coatings on the Mechanical Properties of Nanocomposite Coatings," *Appl. Surf. Sci.*, **252** 3812-17 (2006).
 26. Z. Zhang, C. Wang, R. Zakria, and J. Y. Ying, "Role of Particle Size in Nanocrystalline TiO_2 -based Photocatalysts," *J. Phys. Chem. B.*, **102** 10871-78 (1998).
 27. W. F. Yao, H. Wang, X. H. Xu, X. F. Cheng, J. Huang, S. X. Shang, X. N. Yang, and M. Wang, "Photocatalytic Property of Bismuth Titanate $\text{Bi}_{12}\text{TiO}_{20}$ Crystals," *Appl. Catal. A: Gen.*, **243** [1] 185-90 (2003).
 28. J. Feng, R. S. K. Wong, X. Hu, and P. L. Yue, "Discoloration and Mineralization of Orange II by Using Fe^{3+} -doped TiO_2 and Bentonite Clay-based Fe Nanocatalysts," *Catal. Today*, **98** 441-46 (2004).
 29. J. A. Navia, J. J. Testab, P. Djedjeianb, J. R. Padron, D. Rodriguez, and M. I. Litter, "Iron-doped Titania Powders Prepared by a Sol-Gel Method: Part II: Photocatalytic Properties," *Appl. Catal. A: Gen.*, **178** 191-203 (1999).
 30. J. Zhua, W. Zheng, B. Hea, J. Zhang, and M. Anpob, "Characterization of Fe- TiO_2 Photocatalysts Synthesized by Hydrothermal Method and their Photocatalytic Reactivity for Photodegradation of XRG Dye Diluted in Water," *J. Mol. Catal. A: Chem.*, **216** 35-43 (2004).
 31. I. Sirés, J. A. Garrido, R. M. Rodríguez, E. Brillas, N. Oturan, and M. A. Oturan, "Catalytic Behavior of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ System in the Electro-Fenton Degradation of the Antimicrobial Chlorophene," *Appl. Catal. B: Environ.*, **72** 382-94 (2007).
 32. Y. K. Masumoto, R. Hamada, K. Yokota, S. Nishiyama, and S. Tsuruya, "Liquid-phase Oxidation of Benzene to Phenol by Vanadium Catalysts in Aqueous Solvent with High Acetic Acid Concentration," *J. Mol. Catal. A.*, **184** 215-22 (2002).
 33. T. Miyahara, H. Kanzaki, R. Hamada, S. Kuroiwa, S. Nishiyama, and S. Tsuruya, "Liquid-phase Oxidation of Benzene to Phenol by $\text{CuO-Al}_2\text{O}_3$ Catalysts Prepared by Co-precipitation Method," *J. Mol. Catal. A.*, **176** 141-50 (2001).
 34. H. Kanzaki, T. Kitamura, R. Hamada, S. Nishiyama and S. Tsuruya, "Activities for Phenol Formation Using Cu Catalysts Supported on Al_2O_3 in the Liquid-phase Oxidation of Benzene in Aqueous Solvent with High Acetic Acid Concentration," *J. Mol. Catal. A.*, **208** 203-11 (2004).
 35. M. Pera-Titus, V. Garcia-Molina, M. A. Ban'os, J. Giménez, and S. Espluga, "Degradation of Chlorophenols by Means of Advanced Oxidation Processes: a General Review," *Appl. Catal. B: Environ.*, **47** 219-56 (2004).
 36. N. Quici, M. Morgada, R. Gettar, M. Bolte, and M. Litter, "Photocatalytic Degradation of Citric Acid under Different Conditions: TiO_2 Heterogeneous Photocatalysis Against Homogeneous Photolytic Processes Promoted by Fe(III) and H_2O_2 ," *Appl. Catal. B: Environ.*, **71** 117-24 (2007).
 37. B. Tryba, "Immobilization of TiO_2 and Fe-C- TiO_2 Photocatalysts on the Cotton Material for Application in a Flow Photocatalytic Reactor for Decomposition of Phenol in Water," *J. Hazar. Mat.*, **151** 623-27 (2008).
 38. Y. G. Go, F. J. Zhang, M. L. Chen, and W. C. Oh, "Fabrication of Zn-treated ACF/ TiO_2 Composites and Their Photocatalytic Activity for Degradation of Methylene Blue," *J. Mater. Res.*, **19** [3] 142-50 (2009).
 39. F. J. Zhang, M. L. Chen, and W. C. Oh, "Synthesis and Characterization of CNT/ TiO_2 Photoelectrocatalytic Electrodes for Methlene Blue Degradation," *Kor. J. Mater. Res.*, **18** 583-91 (2008).
 40. W. D Wang, P. Serp, P. Kalck, and J. L. Faria, "Visible Light Photodegradation of Phenol on MWNT- TiO_2 Composite Catalysts Prepared by a Modified Sol-Gel Method," *J. Mole. Catal. A: Chem.*, **235** 194-99 (2005).

41. T. Tsumura, N. Kojitani, H. Umemura, M. Toyoda, and M. Inagaki, "Composites between Photoactive Anatase-type TiO_2 and Adsorptive Carbon," *Appl. Surf. Sci.*, **196** 429-36 (2002).
42. T. Tsumura, N. Kojitani, I. Izumi, N. Iwashita, M. Toyoda, and M. Inagaki, "Carbon Coating of Anatase-type TiO_2 and Photoactivity," *J. Mater. Chem.*, **12** 1391-96 (2002).
43. M. L. Chen, J. S. Bae, and W. C. Oh, "Photocatalytic Effect for the Carbon-coated TiO_2 Prepared from Different Heat Treatment Temperature," *Anal. Sci. & Technol.*, **19** [6] 460-67 (2006).
44. M. L. Chen, J. S. Bae, and W. C. Oh, "Preparation of Carbon-Coated TiO_2 at Different Heat Treatment temperature and Their Photoactivity," *Carbon Sci.*, **7** 259-65 (2006).
45. S. Kasaoka, Y. Sakata, E. Tanaka and R. Naitch, "Studies on the Adsorption of Various Dyes in the Liquid Phase," *Int. Chem. Eng.*, **29** 734-42 (1989).
46. N. Barka, S. Qourzal, A. Assabbane, A. Nounah and Y. Ait-Ichou, "Factors Influencing the Photocatalytic Degradation of Rhodamine B by TiO_2 -coated Non-woven Paper," *J. Photochem. Photobiol. A.*, **195** 346-51(2008).
47. Z. Q. Yu and S. C. Chuang, "The Effect of Pt on the Photocatalytic Degradation Pathway of Methylene Blue Over TiO_2 under Ambient Conditions," *Appl. Catal. B: Environ.*, **83** 277-85 (2008).
48. A. Houas, H. Lachheb, M. Ksibi, E. Elaloui, C. Guillard and J.M. Herrmann, "Photocatalytic Degradation Pathway of Methylene blue in Water," *Appl. Catal. B: Environ.*, **31** 145-57 (2001).
49. C. L. Hsueh, Y. H. Huang and C. Y. Chen, "Novel Activated Alumina-supported Iron Oxide-Composite as a Heterogeneous Catalyst for Photooxidative Degradation of Reactive Black 5," *J. Hazard. Mater. B*, **129** 228-33 (2006).