

Photocatalytic Degradation of Methylene Blue by ACF/TiO₂ and ACF/ZnO Composites under UV Light

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Abstract Methylene blue (MB) was degraded by TiO₂ and ZnO deposited on an activated carbon fiber (ACF) surface under UV light. The ACF/TiO₂ and ACF/ZnO composites were characterized by BET, SEM, XRD, and EDX. The BET surface area was related to the adsorption capacity for composites. The SEM results showed that titanium dioxide and zinc oxide are distributed on the ACF surface. The XRD results showed that the ACF/TiO₂ and ACF/ZnO composites contained a unique anatase structure for TiO₂ and a typical hexagonal phase for ZnO respectively. These EDX spectra showed the presence of peaks of Ti element on ACF/TiO₂ composite and peaks of Zn element on the ACF/ZnO composite. The blank experiments for either illuminating the MB solution or the suspension containing ACF/TiO₂ or ACF/ZnO in the dark showed that both illumination and the catalyst were necessary for the mineralization of organic dye. Additionally, the ACF/TiO₂ composites proved to be efficient photocatalysts due to degradation of MB at higher reaction rates. The addition of an oxidant ([NH₄]₂S₂O₈) led to an increase of the degradation rate of MB for ACF/TiO₂ and ACF/ZnO composites.

Key words ACF/TiO₂, ACF/ZnO, (NH₄)₂S₂O₈, photocatalytic activity.

1. Introduction

The removal of organic pollutants in waste water is an important measure in environmental protection. Organic dyes and other commercial colorants have been emerged as a focus of environmental remediation efforts.¹⁻³⁾ Over the past few decades, semiconductor photocatalysis is becoming more and more attractive due to its great potential to solve such environmental problems.⁴⁻⁶⁾

Heterogeneous semiconductors photocatalysis is a very promising technique, it has already been applied with success on the degradation of different categories of organic compounds combining the low cost, the mild conditions and the possibility of using sunlight as the source of irradiation.⁷⁾ This technique is based on the illumination of semiconductor particles usually suspended in aqueous solutions. The illumination of these particles with light energy greater than the band gap energy leads to the production of high energy electron/hole pairs (e⁻/h⁺), which can migrate to the surface of the photocatalyst and can either recombine producing thermal energy or participate in redox reactions with the compounds that are adsorbed on the photocatalyst's surface, thus, leading to complete mineralization of the

organic compounds.⁸⁾ Among the various semiconductors employed, titanium dioxide (TiO₂) is known to be good photocatalyst for the degradation of environmental contaminants due to its high photocatalytic activity.⁹⁻¹⁰⁾ Zinc oxide (ZnO) is also an important semiconductor for photocatalytic degradation of environmental pollutants because its photodegradation mechanism has been proven to be similar to that of TiO₂.¹¹⁻¹³⁾

However, because the electron and hole represents high recombine rate which is commonly in nanometer size as we known, the problem of separation and recovery of photocatalyst from the reaction medium exists. An alternative method is immobilization of nano-particles on an inert and suitable supporting matrix.¹⁴⁻¹⁶⁾

Activated carbon (AC) is widely used as a support in gas and water remediation because of its good adsorption, and supported semiconductor nano-particles exhibits a cooperative effect on the kinetics of disappearance of pollutants.¹⁷⁻²⁰⁾ However, AC is commonly used in the forms of granules and powder, and there remain some difficulties in filtering and recovery from water. Activated carbon fiber (ACF), a new formulation of activated carbon, has received increasing attention in recent years as an adsorbent. Compared with AC, ACF is produced in the form of felt or cloth, with high BET surface area and micropore volume.²¹⁾

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In this study, the photocatalytic degradation of methylene blue (MB) was investigated using ACF/TiO₂ and ACF/ZnO under UV light. The objectives of this study were to compare the degradation ability of ACF/TiO₂ and ACF/ZnO composites, to examine the influence of the addition of an oxidant and finally to evaluate their ability.

2. Experimental Procedure

2.1 Materials

Activated Carbon Fiber (ACF) was purchased from EAST ASIS Carbon Fibers Co., Ltd, (Anshan, China). Zinc nitrate (Zn(NO₃)₂) as a zinc source was purchased from Duksan Pure Chemical Co., Ltd, (Korea). Ammonium hydroxide (NH₄OH) was purchased from Daejung Chemicals & metals Co., Ltd, (Korea). Ammonium persulfate ((NH₄)₂S₂O₈) as an oxidant was purchased from Daejung Chemicals & metals Co., Ltd, (Korea). methylene blue (MB) as analytical grade was purchased from Duksan Pure Chemical Co., Ltd, (Korea).

2.2 Preparation of samples

In this experimental, an original sample of ACF/TiO₂ was quoted from former experiment.²²⁾ ACF/ZnO composites were prepared by a sol-gel route as detailed following: 2 g ACF power was added into to 50 ml 0.1M Zn (NO₃)₂ solution and the mixtures were stirred at room temperature, 5 ml NH₄OH (25%~28%) was slowly added into mixtures. The reaction vessel was sealed and vigorously stirred for 5h. The homogeneous mixtures were heat treated at 773 K for 1h, and then the ACF/ZnO composites were obtained. The nomenclatures and method of the samples prepared are listed in Table 1.

2.3 Characteristics and investigations of the samples

The BET surface area by N₂ adsorption method was measured at 77 K using a BET analyzer (Monosorb, Quantachrome Instruments Ltd., USA). XRD (XD-D1 Shimadzu Ltd., Japan) result used to identify the crystallinity by Cu K α radiation. SEM used to observe the surface state and

structure of ACF/TiO₂ and ACF/ZnO composites using an electron microscope (JSM-5200 JOEL Ltd., Japan). EDX (JSM-5200 JOEL Ltd., Japan) spectra were also obtained for determining the elemental information of ACF/TiO₂ and ACF/ZnO composites. UV-vis absorption parameters for the MB solution decomposed by ACF/TiO₂ and ACF/ZnO composites under UV lamp irradiation with and without (NH₄)₂S₂O₈ were recorded using a UV-vis (Optizen Pop Mecasys Co., Ltd., Korean) spectrophotometer.

2.4 Photocatalytic activity of the samples

The photochemical data presented as behaviors of MB decomposed by ACF/TiO₂ and ACF/ZnO composites in a 100 mL glass container and irradiation system by UV with (NH₄)₂S₂O₈ and without (NH₄)₂S₂O₈, respectively. The sample powder of 0.05 g was suspended in the 50 ml of MB solution with a concentration of 1.0×10^{-5} M. Then, the mixed solution was emplaced in the dark for at least 2 h, in order to establish an adsorption-desorption equilibrium, which was hereafter considered as the initial concentration (c_0) after dark adsorption. Then, experiments were carried out under UV only and under UV with addition of 1×10^{-4} mol (NH₄)₂S₂O₈ to the MB solution. 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 was taken out and immediately centrifuged to separate any suspended solid. The clean transparent solution was immediately analyzed by using a UV-vis spectrophotometer. And then the concentration of MB in the solution was determined as a function of irradiation time from the absorbance change at a wavelength of 660 nm.

3. Results and Discussion

3.1 The surface characteristics

The BET data of pristine ACF, ACF/TiO₂ and ACF/ZnO samples are summarized in Table 2. The BET surface area of the as-received ACF was 1842 m²/g. The BET specific surface areas of ACF/TiO₂ and ACF/ZnO were 1268 m²/g and 762 m²/g, respectively, both of them are smaller than

Table 1. Nomenclatures of ACF/TiO₂ and ACF/ZnO composites.

Preparation method	Nomenclatures
ACF + Titanium iso propoxide	AT
ACF + Zn(NO ₃) ₂ + NH ₄ OH	AZ

Table 2. Specific BET surface areas of pristine ACF, ACF/TiO₂ and ACF/ZnO composites.

Sample	S _{BET} (m ² /g)
Pristine ACF	1842
AT	1268
AZ	762

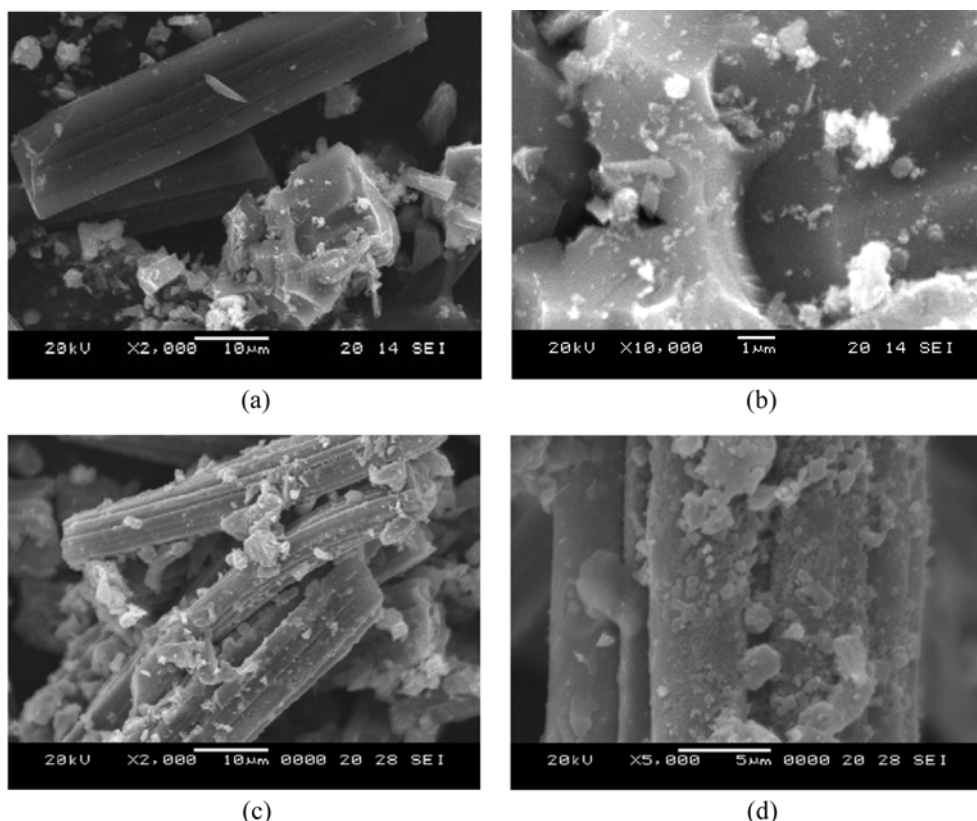


Fig. 1. SEM images of ACF/TiO₂ and ACF/ZnO composites: AT: (a) $\times 2000$, (b) $\times 10000$; AZ: (c) $\times 2000$, (d) $\times 5000$.

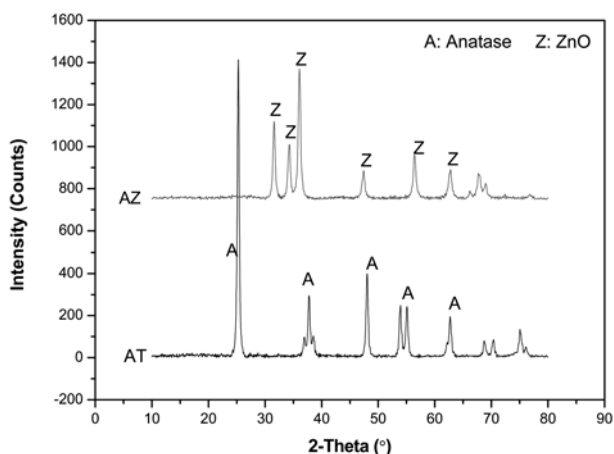


Fig. 2. XRD patterns of powdered ACF/TiO₂ and ACF/ZnO composites.

that of pure ACF, which was ascribed to the partly blocking of micropores by the formation of TiO₂ or ZnO on the ACF surface. It was also noteworthy that decreases of surface area among the composites were related to removal efficiency of MB by adsorption capability.

The SEM microphotographs of TiO₂/ACF and ACF/ZnO composites prepared are shown in Fig. 1. It was observed that TiO₂ and ZnO particles are finely agglomerated on

the surface of ACF as regular distribution. Generally, it was considered that good particle dispersions can produce high photocatalytic activity. In comparison of TiO₂/ACF and ACF/ZnO, it was observed that there is little difference, the some TiO₂ particles were removed from ACF as shown in Fig. 1(a), the ZnO particles were evenly distributed in ACF/ZnO composites, which was beneficial for the photocatalytic reaction because the photocatalytic reaction was carried out on the external surfaces of the ACF/ZnO composites catalysts by existing reactants using UV light and the nano-size structured catalyst could provide a more effective surface for MB adsorption and UV light absorption.²³⁾

The XRD patterns of TiO₂/ACF and ACF/ZnO are shown in Fig. 2, The XRD pattern of TiO₂ showed peaks corresponding to unique anatase phases. the peaks at 25.4°, 38.2°, 47.9°, 54.8° and 62.6° are related to the diffractions of the (101), (112), (200), (211), and (204) planes, No significant diffraction peaks of rutile-phase TiO₂ were detected in the XRD spectra. The phenomena mentioned above can be attributed to two following facts that thin TiO₂ layers were tightly contacted to the carbon fibers surfaces, and carbon surfaces located under TiO₂ layers can suppress phase transformation of TiO₂ from anatase to rutile structure

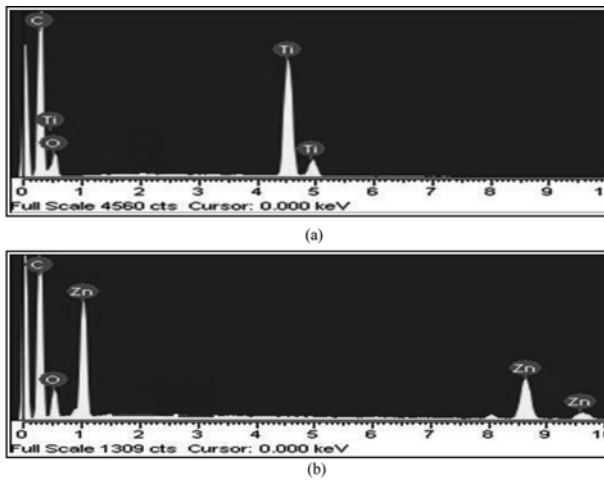


Fig. 3. EDX elemental microanalysis of ACF/TiO₂ and ACF/ZnO composites: (a) AT and (b) AZ.

Table 3. EDX elemental microanalysis (wt.%) of ACF/TiO₂ and ACF/ZnO composites.

Sample	C	O	Ti	Zn
AT	53.84	21.79	23.90	0
AZ	60.19	13.59	0	25.70

at high temperature.²⁴⁻²⁵ According to the former studies,²⁶⁻²⁷ Pure anatase nanocrystallites are very efficient photocatalysts, can cause their superior photocatalytic properties. It was also observed that ZnO has hexagonal phase relative to (100), (002), (101), (102), (110), and (103) planes²⁸ and the corresponding peaks are shown in Fig. 2.

Fig. 3 shows the EDX spectra of ACF/TiO₂ and ACF/ZnO composites. These spectra show the presence of peaks from the C and O elements. For the ACF/TiO₂ composites, we observed the strongly peaks of the Ti element, and the strongly peaks of the Zn element was detected in the ACF/ZnO composites. The results of elemental composition analysis of the composite series are listed in Table 3.

3.2 Photocatalytic activity

The remove of MB in the presence or in the absence of the photocatalysts (ACF/TiO₂ or ACF/ZnO) is presented in Fig. 4. it was observed that ACF/TiO₂ is more effective than ACF/ZnO since more rapid decomposition is achieved, On the other hand, low degradation of MB achieved after 2 h of irradiation only and addition of pristine ACF only indicated that the rapid decomposition was achieved in the presence of the photocatalyst which can be clearly ascribed to the TiO₂ and ZnO activity. Moreover, the addition of the pristine ACF or photocatalyst in the absence

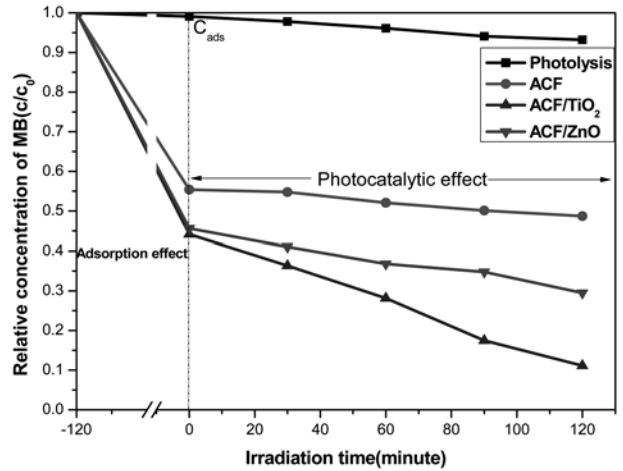


Fig. 4. Photodegradation of MB in the presence of UV light only, ACF, ACF/TiO₂, or ACF/ZnO.

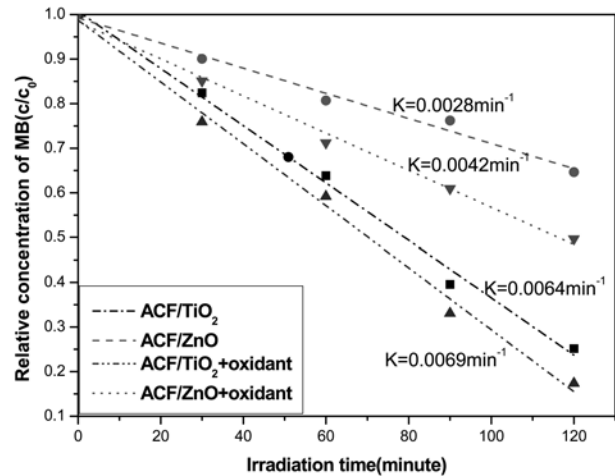


Fig. 5. Apparent first order kinetics of MB degradation for ACF/TiO₂ and ACF/ZnO composites in present of oxidant ((NH₄)₂S₂O₈).

of irradiation condition had a significant effect on the concentration of MB due to higher absorption capability of ACF. In addition, the ACF can fleetly transfer electron to reduce electronic accumulation on TiO₂ or ZnO particles, which is in agreement with previous study.²⁹

3.3 Kinetics

MB solution degradation behaviors under UV irradiation in present of (NH₄)₂S₂O₈ on ACF/TiO₂ and ACF/ZnO samples are shown in Fig. 5 and the photocatalytic reaction can be simply described by pseudo-first order kinetics, the representation for the rates of degradation of MB is given by:

$$C/C_0 = kT \quad (1)$$

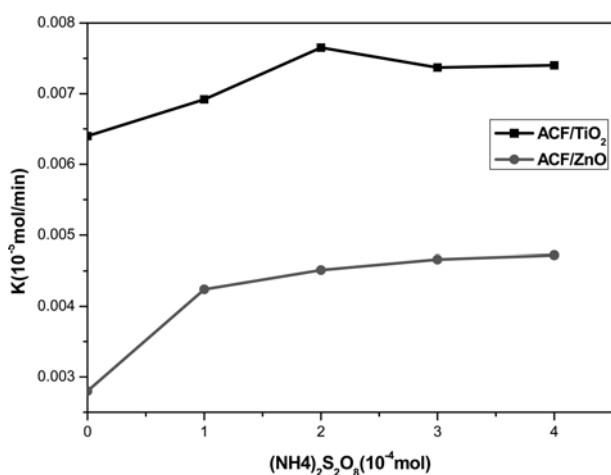
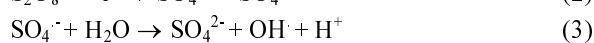


Fig. 6. Effect of the (NH₄)₂S₂O₈ on the photocatalytic degradation rate of MB in the presence of ACF/TiO₂ and ACF/ZnO.

Where C and C_0 are the initial concentration of MB, T is the irradiation time and k denotes the overall degradation rate constant. Experiments were carried out using lower initial concentrations of (NH₄)₂S₂O₈ (1×10^{-4} mol). By plotting C/C_0 as a function of time through regression, we obtained for each sample the k (min^{-1}) constant from the slopes of the simulated straight lines.

As indicated in Fig. 5, the linear transform of this expression yields $K = 0.0064 \text{ min}^{-1}$ for the ACF/TiO₂ and $K = 0.0028 \text{ min}^{-1}$ for the ACF/ZnO by the linear fit using the above experimental data within 120min of illumination. The addition of (NH₄)₂S₂O₈ to a photocatalytic system enhances the reaction rate, $K = 0.0069 \text{ min}^{-1}$ and $K = 0.0042 \text{ min}^{-1}$, respectively. This phenomenon is attributed to the prevention of the recombination between electrons and holes by the entrapment of the photogenerated electron. Generally, hydrogen peroxide is selected as the oxidant and it has been used with success for the increase of the photodegradation rate of many organic compounds.³⁰⁻³¹ In this study, the effect of (NH₄)₂S₂O₈ is investigated. It affects an increase of the reaction rate. This ability of (NH₄)₂S₂O₈ is attributed to not only the promotion of charge separation but also the production of sulfate radicals which are very strong oxidizing agents, which generated by the following Eq((2)-(3)):



3.4 Effect of the addition of an oxidant

The effect of (NH₄)₂S₂O₈ on the photocatalytic degradation rate of MB is presented in Fig. 6. It is obvious that

increase of degradation rate of MB was caused with increase of the concentration of (NH₄)₂S₂O₈. Especially, increase of degradation rate was kept at high concentration of the (NH₄)₂S₂O₈ in the presence of ACF/ZnO, but slightly declined in the presence of ACF/TiO₂. It is attributed that the sulfate radicals can be reduced by entrapment of the electrons again. The reaction is showed in Eq (4):



It is suggested that high concentration of SO_4^{2-} is detrimental to the reaction rate. Unlike hydrogen peroxide, high concentrations are not detrimental to the reaction rate and no dependence on the oxidant/contaminant molar ration is observed.³²⁾

4. Conclusions

The ACF/TiO₂ and ACF/ZnO composites were prepared by a same sol-gel method. The BET surface area of ACF was decreased with introduction of TiO₂ and ZnO particles. The SEM images showed that the TiO₂ and ZnO particles were irregularly dispersed on ACF surface. The XRD results showed that a unique anatase structure and typical hexagonal phase for ZnO was detected respectively. According to the photocatalytic results, it has been shown that ACF/TiO₂ and ACF/ZnO can efficiently degrade MB solution due to adsorption and photolysis, and it is obvious that ACF/TiO₂ was better than ACF/ZnO on degradation rate of MB. With the addition of an oxidant effect was observed that leads to an enhancement and improvement of the efficiency of the ACF/TiO₂ and ACF/ZnO.

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