



Effects of TiO₂ coating dosage and operational parameters on a TiO₂/Ag photocatalysis system for decolorizing Procion red MX-5B

Yu-Chih Lin*, Ho-Shan Lee

Department of Environmental Engineering and Health, Yuanpei University, 306 Yuan-pei St., Hsinchu City 300, Taiwan

ARTICLE INFO

Article history:

Received 11 August 2009

Received in revised form

19 November 2009

Accepted 4 March 2010

Available online 15 March 2010

Keywords:

Titanium dioxide (TiO₂)

Silver (Ag)

Dye

Decolorization

Photocatalysis

ABSTRACT

In this study, titanium dioxide (TiO₂) powder was coated onto the surface of a dendritic silver (Ag) carrier to synthesize TiO₂/Ag for decolorizing Procion red MX-5B (MX-5B), and related operation factors were also studied. The results showed that even without ultraviolet-A (UVA) irradiation, the Ag carrier from the TiO₂/Ag catalyst had oxidizing ability, which could effectively degrade MX-5B color, but TiO₂ was ineffective. In addition, TiO₂ from TiO₂/Ag demonstrated photocatalysis performance when irradiated, and the Ag carrier further showed an electron-scavenging ability to mitigate electron–hole pair recombination, which can improve the photocatalytic efficacy. With the oxidization and electron-scavenging ability of Ag and the photocatalysis ability of TiO₂, TiO₂/Ag can decolor MX-5B more efficiently than TiO₂. The heavier Ag carrier also improves the solid–liquid separation of nano-TiO₂, making TiO₂/Ag more suitable for application in slurry systems of photocatalytic water treatment.

When the TiO₂/Ag coating ratio was 50% by weight, there was a sufficient amount of TiO₂ on Ag's surface with a good distribution, and it exhibited a good photocatalysis decolorizing effect. In a study of how operational factors impact the decolorizing of MX-5B in the TiO₂/Ag photocatalysis system with UVA irradiation (UVA-TiO₂/Ag), the decolorization efficiency was optimal when the solution was maintained at pH 6.35. The addition of 0.01 M hydrogen peroxide (H₂O₂) aided the photocatalysis decolorization efficiency, although excessive H₂O₂ reacted with hydroxyl free radicals and decreased the active groups in the system, thereby reducing the photocatalysis activity. An operating temperature of 40 °C was conducive to MX-5B decolorization, which was better than operating at room temperature.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

With increasing environment protection awareness in recent years, environment pollution issues have become major concerns; among these issues, wastewater color is very important. Besides causing color contamination as well as affecting waterbody clarity and transmittance, some toxic dyes also pose hazards to organisms in water bodies [1]. Common dye wastewater treatment methods include biological (activated sludge) and chemical processes (the Fenton process and coagulation) [2–5]. Coagulation processes and the Fenton process have low equipment costs, but produce large amounts of sludge; thus, additional costs for sludge treatment are required. Using activated carbon to physically adsorb wastewater color showed a significant effect, but it requires frequent replacement, and the treatment expense is so high that its application is not practical [6,7]. The above problems can be solved by using a titanium dioxide (TiO₂) plus ultraviolet (UV) photocatalysis method to

remove dye color. In the presence of UV irradiation, TiO₂ excites electron–hole pairs that can disrupt the molecular structure of target pollutants, breaking the bonds and resulting in inorganic material; thus, the addition of other chemicals is not needed, and sludge formation can be avoided. In ordinary wastewater treatment, TiO₂ powder with UV irradiation can remove dye wastewater color [8–10], but TiO₂ powder is nano-sized, and it is difficult to achieve solid–liquid separation by filtering or centrifuging methods; hence, its application is restricted. In general, TiO₂ is modified so that its surface can carry nanoscale silver (Ag) [11–15]; this study chose micro-sized Ag as the carrier, coated with TiO₂ powder to synthesize a kind of TiO₂/Ag composite photocatalyst, which differs from previous studies. The Ag carrier uses its electron-scavenging function to alleviate recombination of electron–hole pairs, which are produced by TiO₂ under irradiation, thus increasing the photocatalytic effect. With a significant amount of higher density Ag as the carrier, the oxidization ability contributed by Ag is expected to enhance dye decolorization and improve the solid–liquid separation effect, increasing the ease of use.

Therefore, this study utilized TiO₂/Ag with ultraviolet-A (UVA) irradiation (UVA-TiO₂/Ag) to decolor the azo dye, Procion red MX-5B (MX-5B), in order to examine its performance in wastewater

* Corresponding author.

E-mail addresses: yuchihlin@mail.ypu.edu.tw, yuchih.lin0214@msa.hinet.net (Y.-C. Lin).

Table 1
Characteristics and structure of Procion red MX-5B [16].

Formula	Molecular weight (g/mol)	λ_{\max} (nm)
$C_{19}H_{10}Cl_2N_6Na_2O_7S_2$	615	538

color treatment. Besides comparing the decolorization efficiency of a commercial ST-01 TiO₂ and Ag carrier, this study also investigated the effects of the TiO₂ coating ratio on the Ag carrier, operational dye concentration, pH, temperature, and the addition of hydrogen peroxide (H₂O₂) on decolorization in the UVA-TiO₂/Ag system, as well as the factors of decolorization activity of TiO₂/Ag by a material analysis, so that TiO₂/Ag can be widely applied in dye wastewater treatment.

2. Materials and experimental conditions

The dye used in the study was MX-5B purchased by Sigma–Aldrich (St. Louis, MO, USA), and its chemical properties and molecular structure [16] are given in Table 1. MX-5B is a monoazo dye; its chromophoric group is an azo double bond which absorbs light and affects visibility in water bodies.

The Ag carrier formation is based on the oxidation–reduction principle: copper foil is added to a silver nitrate (AgNO₃) solution, and the solution is kept alkaline; then Ag particles are separated onto the copper foil. The ion chemical reaction equation is:



As the electrostatic potential of the reaction is 0.5 V, a spontaneous reaction can begin with no external energy. The Ag particles are washed with deionized water to remove nitric radicals and then allowed to dry. An alkaline solution of TiO₂ (ST01, Ishihara) was prepared in a given weight ratio, put in solution, and stirred for a uniform suspension, and then Ag was also put into the above solution. Then the TiO₂ combines with Ag due to a difference in the surface charges induced by the zeta potential, and the previously suspended TiO₂ coagulates with Ag to form a precipitate. After washing out the alkalinity and drying the precipitate, the synthesized nano-TiO₂/Ag material [17] was obtained. A weight ratio of TiO₂ coated onto the Ag surface of 50:100 was defined as 50 wt% TiO₂/Ag.

In this study, decolorization of MX-5B in UVA-TiO₂/Ag was carried out in a batch reaction. The reactor volume was 0.5 L; the reactor was entirely covered with a black curtain to exclude all light. A 10-W UVA light was set on top of the reactor, about 20 cm from the reactant solution meniscus; the luminance of the light

source over the reactant solution was 0.7 μ W/cm²; and the total irradiation time was 2 h. A 100-mL solution of 30 ppm MX-5B was injected into the reaction system, while 0.3 g of the catalyst was added. After photocatalytic decolorization, the supernatant of the solution was obtained via centrifugation, and injected into an ultraviolet–visible (UV–vis) spectrophotometer (UV-2102, Unico, USA) to obtain the absorbance values of the characteristic wave peaks of MX-5B. Assuming Abs_0 is the absorbance at the initial concentration and Abs_1 is absorbance after photocatalysis reaction, then the decolorization efficiency can be calculated by Eq. (2):

$$\text{decolorization efficiency(\%)} = \frac{Abs_0 - Abs_1}{Abs_0} \times 100\% \quad (2)$$

In the material analysis, this study employed high-resolution scanning electron microscopy (HRSEM, S-4700I, Hitachi, Japan) and X-ray powder diffractometry (XRD, MXP18, MAC Science, Japan) to inspect the surfaces of the prepared composite photocatalyst and determine its crystal structure. High-resolution surface area and porosimetry analysis (ASAP2020 Micromeritics, USA) and transmission electron microscopy (TEM, TECNAI 20, Philips, the Netherlands) were used to analyze the porous structure of the TiO₂/Ag catalyst. X-ray photoelectron spectroscopy (XPS, ULVAC-PHI Quantera, Japan) was used to verify the surface oxidation state of the Ag carrier before and after MX-5B decolorization.

3. Results and discussion

3.1. Material analysis

Fig. 1a illustrates the surface of 50wt% TiO₂/Ag as observed by HRSEM. The prepared Ag carrier had a dendritic fern-leaf structure, with TiO₂ on the top. After magnification to 20,000 \times , it was observed that fine TiO₂ particles were evenly distributed over the Ag carrier surface (Fig. 1b). The material specific surface area is given in Table 2. The specific surface area of the Ag carrier was about 0.0182 m²/g, and its surface had no significant porosity; the specific surface area of TiO₂ was 300 m²/g, while the specific surface area of 50 wt% TiO₂/Ag was 15.24 m²/g, and the porosity was presumed to be from the TiO₂.

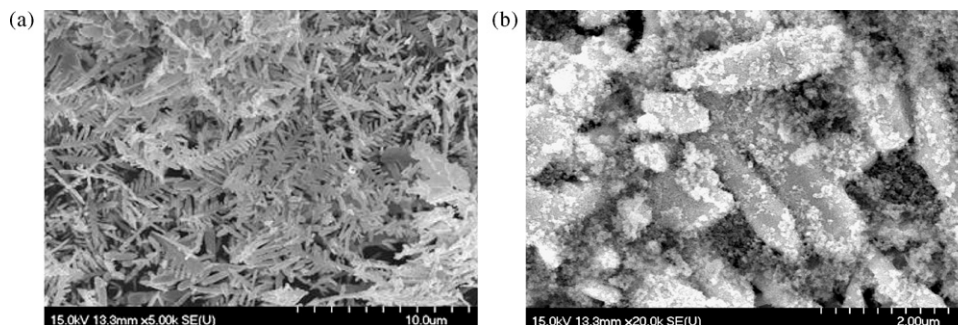


Fig. 1. Surface observation of 50 wt% TiO₂/Ag by HRSEM.

Table 2
Material specific surface area analysis.

Material	Ag	TiO ₂	50 wt% TiO ₂ /Ag
Surface area (m ² /g)	0.0182	300	15.24

Fig. 2 gives the TEM transmittance observations of Ag, TiO₂, and TiO₂/Ag. The Ag surface was smooth without distinct porosity as illustrated in Fig. 2a and b, consistent with the results of the specific surface area. TiO₂ (Fig. 2c) showed a distinct porous structure. As to 50 wt% TiO₂/Ag (Fig. 2d), the porous structure on the left is TiO₂, while the right part is the Ag surface without porosity, thereby proving that the porosity of the 50 wt% TiO₂/Ag was due to TiO₂'s contribution. The XRD spectra are shown in Fig. 3. The Ag carrier produced signal peaks at 38.24°, 44.5°, 64.8°, 77.68°, and 81.96°, indicative of pure metallic Ag; TiO₂ produced signal peaks at 25.84°, 38.48°, 48.44°, 54.98°, and 63.62°, indicating that this is 100% anatase TiO₂, without the presence of other crystalline forms such as rutile or brookite [18]. The XRD spectrum of 50 wt% TiO₂/Ag showed a combined waveform of metallic Ag and TiO₂, proving that the synthesis process did not disrupt their structures, weaken the TiO₂ photocatalytic properties, or produce other chemical changes to form other compounds.

3.2. Comparison among decolorization efficiencies of MX-5B by TiO₂, Ag, and TiO₂/Ag

Fig. 4 gives the UV–vis spectra at different operation times of MX-5B by 50 wt% TiO₂/Ag, TiO₂, and the Ag carrier with or without UVA irradiation. The main absorption peak of MX-5B in the UV–vis spectra appeared at 538 nm. The main absorption peak diminishing at longer operating times indicates dye decolorization, and larger differences between the original peak at 0 min and peaks at longer operating times indicate better decolorization efficiencies. The 50 wt% TiO₂/Ag with and without UVA irradiation showed an MX-5B decolorization effect, and UVA irradiation enhanced the decolorization performance of 50 wt% TiO₂/Ag. TiO₂ with UVA irra-

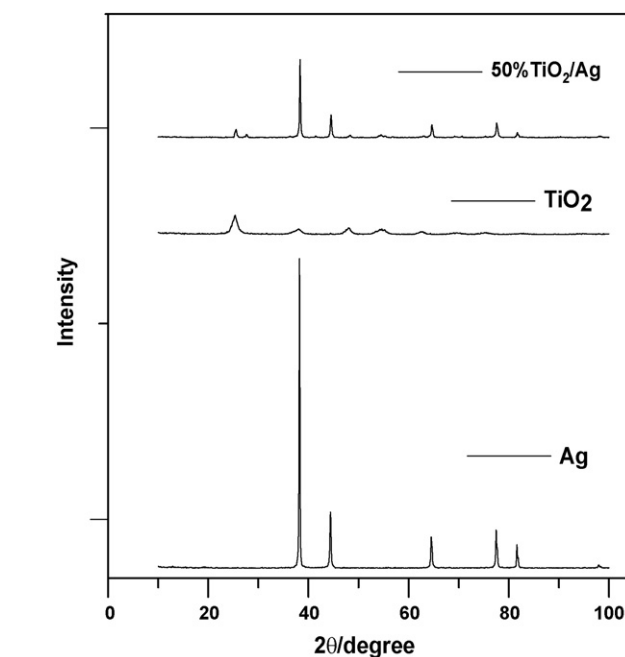


Fig. 3. XRD spectra of Ag, TiO₂, and TiO₂/Ag.

diation also decolorized MX-5B, but TiO₂ without UVA irradiation was ineffective in degrading MX-5B. Without UVA irradiation, Ag still showed the ability to remove MX-5B color, yet UVA irradiation did not improve MX-5B decolorization by Ag. Some intermediates may have been produced during MX-5B decolorization, but they are not further discussed in this study.

The decolorization efficiencies of MX-5B by the Ag carrier and 50 wt% TiO₂/Ag with or without UVA irradiation are illustrated in Fig. 5. Without UVA irradiation, decolorization efficiencies of MX-5B by Ag and TiO₂/Ag were higher than that by TiO₂; MX-5B

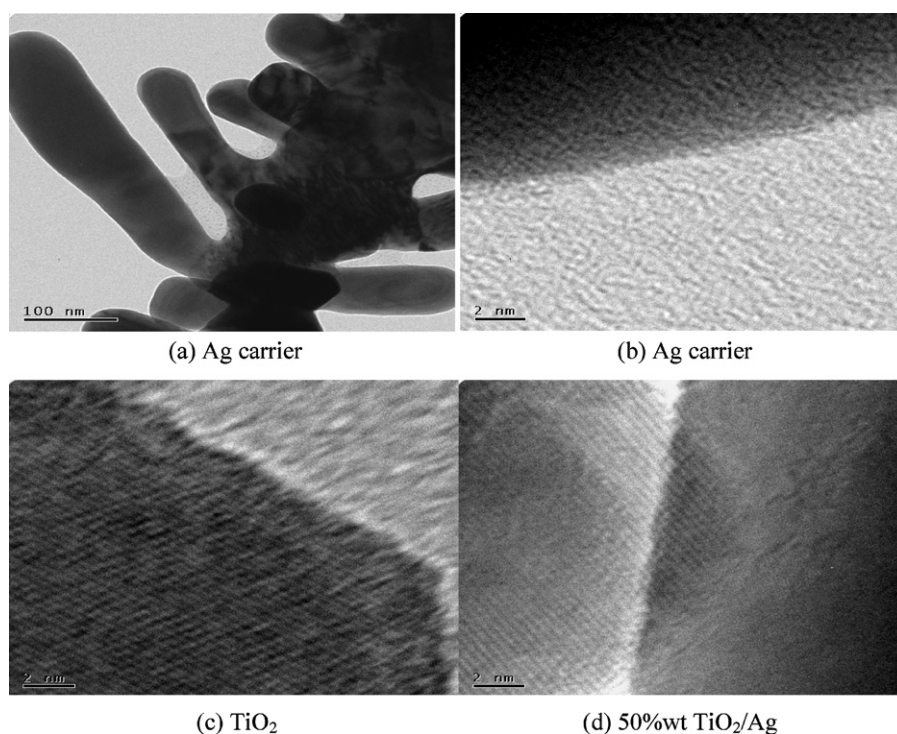


Fig. 2. TEM observations of Ag, TiO₂, and TiO₂/Ag.

showed 40% decolorization efficiency by Ag and TiO₂/Ag, however the adsorption by TiO₂ was ineffective. Although TiO₂ has a porous and crystal structure, as determined by the material specific surface area measurement and TEM observations, those structures did not enhance adsorption of the dye by TiO₂. As the Ag carrier has no porous structure, the dye could not be removed by an adsorption mechanism, and the decolorization activity of Ag and TiO₂/Ag without irradiation was provided by Ag's oxidizing ability, which was

verified by the XPS analysis of Ag surface states before and after the decolorization process without irradiation. Fig. 6 indicates that the Ag surface state was metallic Ag (368 nm) before the reaction, and after reacting with the dye, the surface state became Ag₂O; thus, the decolorization phenomenon was a result of an oxidative reaction between Ag and the dye.

Fig. 5 shows that the Ag catalyst with UVA irradiation did not enhance the MX-5B decolorization effect, which was comparable

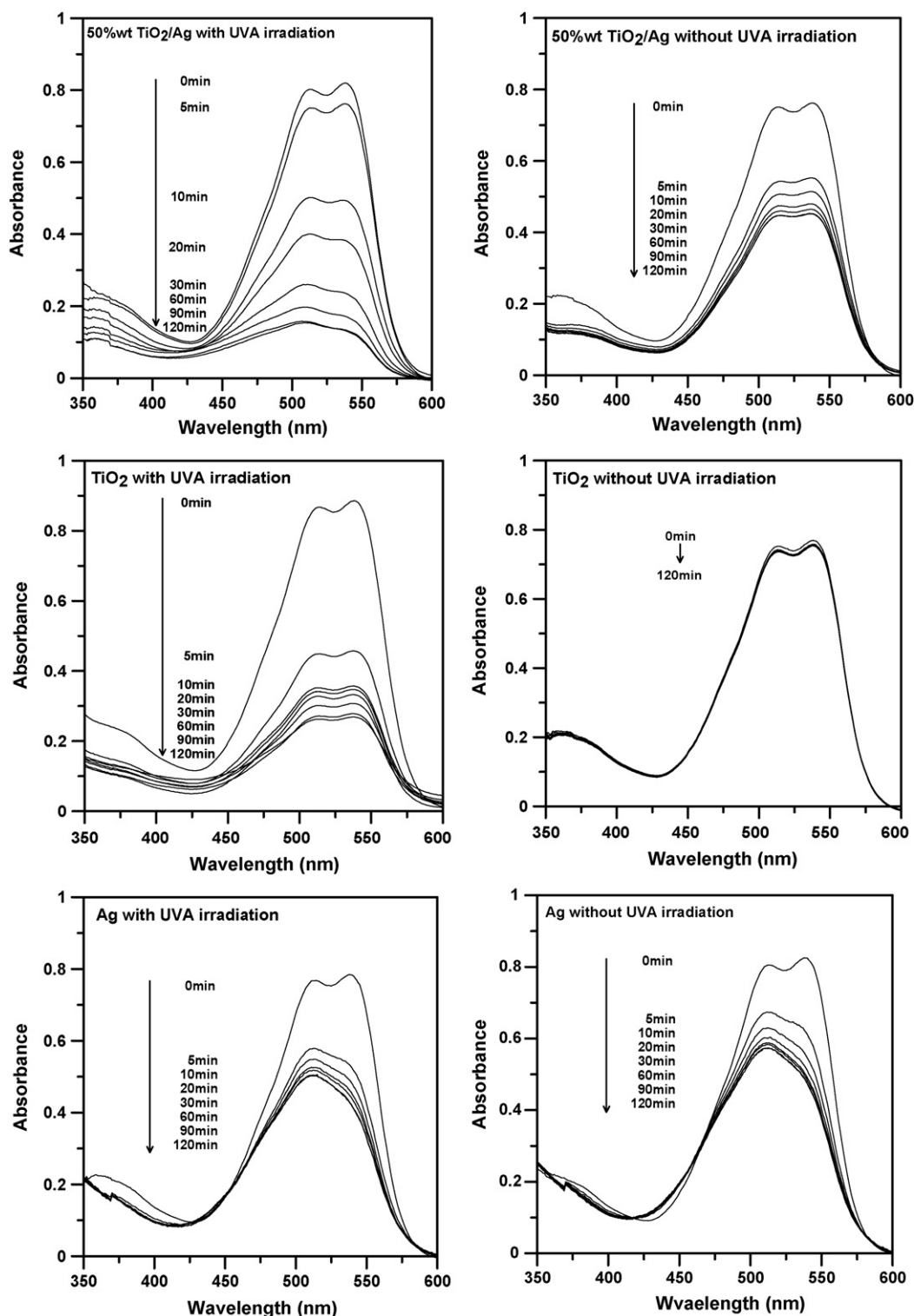


Fig. 4. UV-vis spectra at different operation times of Procione MX-5B by 50 wt% TiO₂/Ag, TiO₂, and the Ag carrier with or without UVA irradiation.

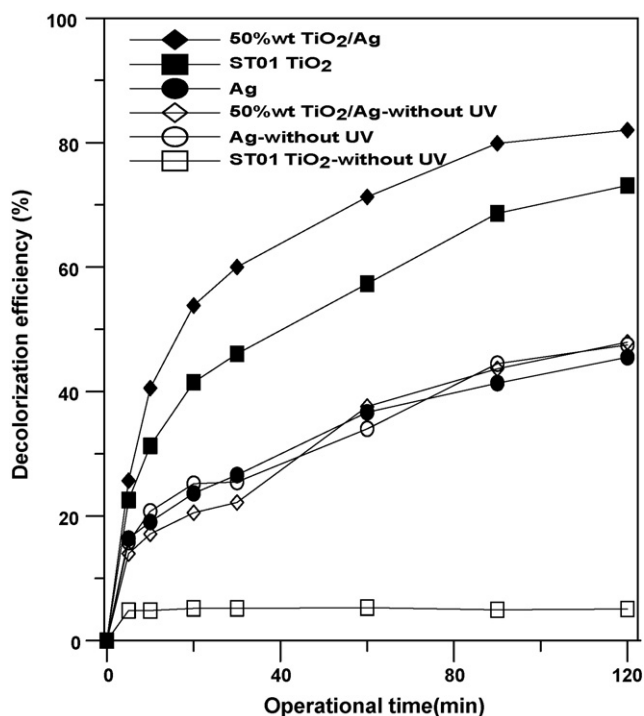


Fig. 5. Comparison of the decolorization efficiencies of Procion red MX-5B by TiO_2 , Ag, and TiO_2/Ag with or without UVA irradiation.

to the efficiency without irradiation. UVA irradiation improved the MX-5B decolorization efficiency of both TiO_2/Ag and TiO_2 . The MX-5B decolorization efficiency of TiO_2/Ag was obviously greater than that of TiO_2 , because TiO_2/Ag itself has both photocatalysis and oxidization activities provided by TiO_2 and Ag, respectively, to decolorize MX-5B. Furthermore, Ag in TiO_2/Ag acted as an electron scavenger, and delayed electron-hole pair recombination derived from excitation of irradiated TiO_2 , thus promoting photocatalytic

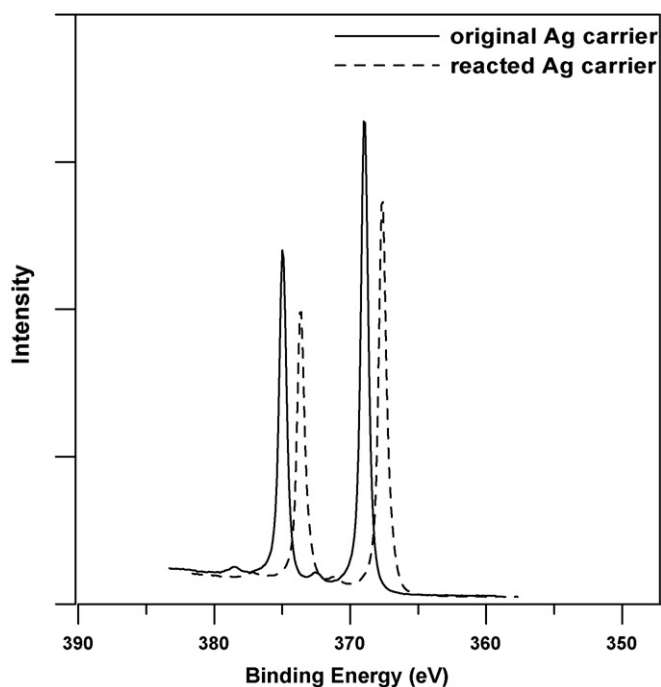


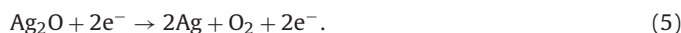
Fig. 6. XPS analysis of Ag before and after the decolorization process without UVA irradiation.

Table 3

Pseudo-first-order decolorization rate constants of the TiO_2/Ag , TiO_2 and Ag systems under UVA irradiation.

Type	TiO_2/Ag	TiO_2	Ag
k (min^{-1})	0.0195	0.0129	0.0051
R^2	0.950	0.958	0.903

decolorization. In addition, the reason for the good performance of Ag/TiO_2 was that part of the electrons excited from the irradiated TiO_2 may also transform the oxidation state of Ag to metallic Ag, and restore the oxidation activity for MX-5B decolorization; the reaction mechanism can be inferred as follows:



Sahel et al. [19] and Wu and Yu [20] reported that the photocatalytic decolorization of MX-5B approximates pseudo-first-order kinetics. According to this equation, the rate constants of the photocatalytic decolorization of MX-5B by TiO_2 , the Ag carrier, and TiO_2/Ag were calculated and the results are given in Table 3, indicating that the reaction constant of TiO_2/Ag was obviously better than that of TiO_2 .

3.3. Effects of TiO_2/Ag at various TiO_2 coating ratios on the decolorization efficiency of MX-5B

This study coated TiO_2 onto Ag particles at weight percentages of 10, 30, 50, 70, and 90 wt% TiO_2/Ag to examine the effects of the TiO_2 coating ratio on the decolorization efficiency of MX-5B by the UVA- TiO_2/Ag system. As shown in Fig. 7, the decolorization efficiency of 50 wt% TiO_2/Ag was better than those of other ratios of

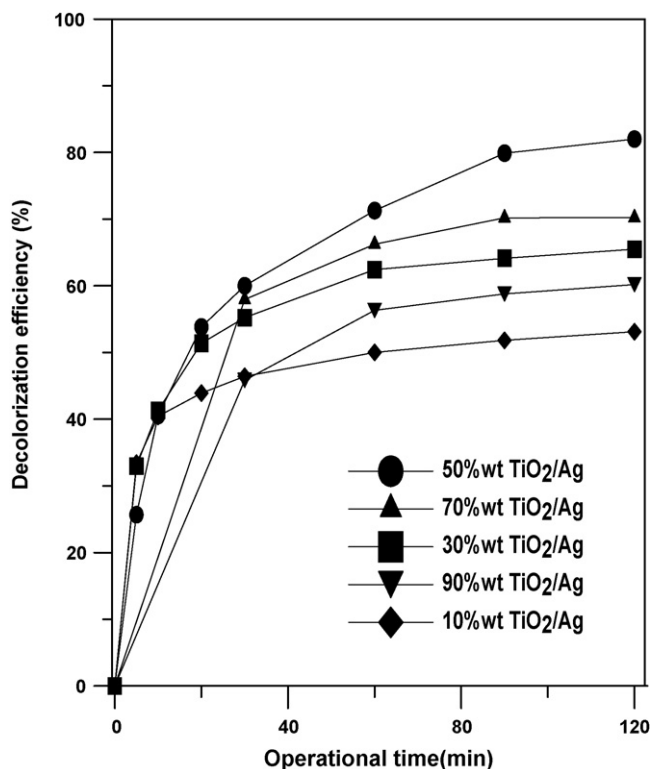


Fig. 7. Comparison of the decolorization efficiency of Procion red MX-5B by TiO_2/Ag with various TiO_2 coating ratios.

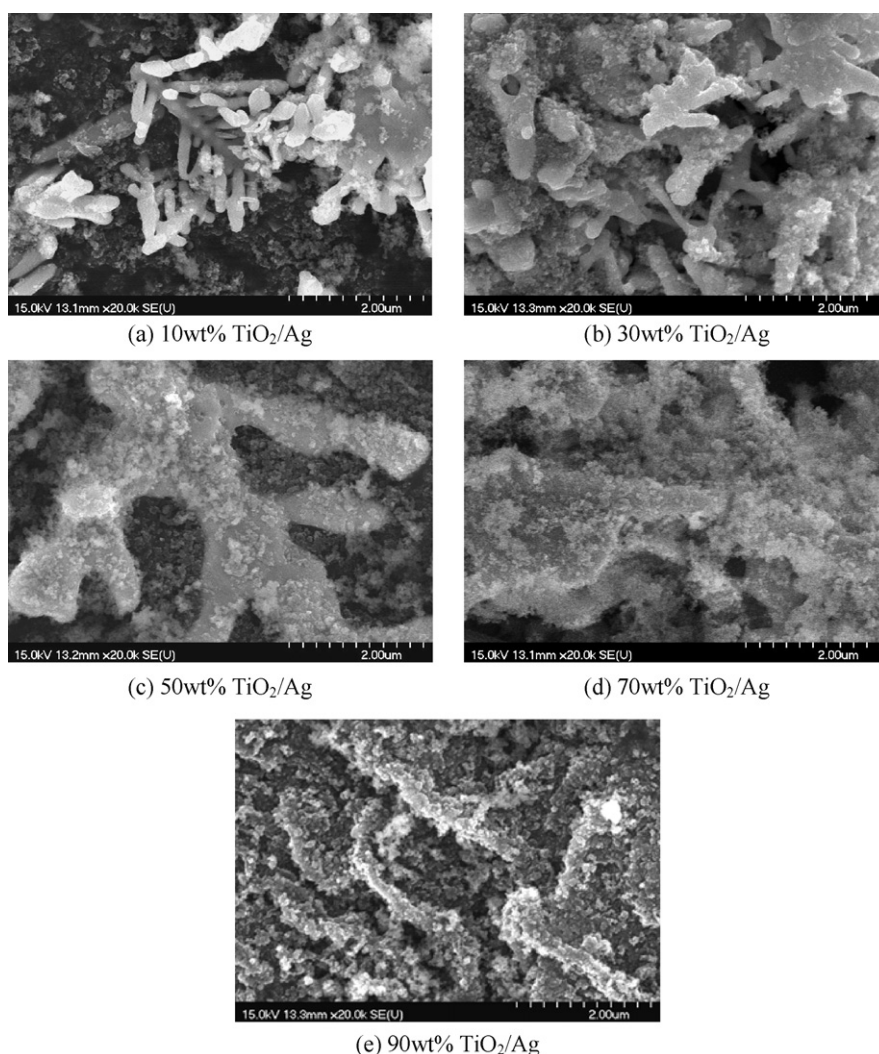


Fig. 8. Surface observations of TiO_2/Ag with various TiO_2 coating ratios.

TiO_2/Ag . When the coating percentage was 10–50 wt%, the decolorization efficiency improved with the TiO_2 coating ratio. However, when the coating percentage was >50, 70 and 90 wt% TiO_2/Ag were inferior to 50 wt% TiO_2/Ag in terms of the decolorization efficiency. The reason can be explained by SEM, shown in Fig. 8. At 10–50 wt% TiO_2/Ag , TiO_2 particles carried on the Ag surface increased with the ratio and were evenly distributed; but at 70–90 wt% TiO_2/Ag , excessive TiO_2 particles on Ag surface began to form particle stacks, thereby reducing the photocatalysis surface area. As a result, the photocatalytic effect fell in proportion to TiO_2 addition [21].

3.4. Effects of various initial concentrations of MX-5B on the decolorization efficiency and TOC removal by UVA- TiO_2/Ag

Fig. 9 shows the effects of various initial concentrations of MX-5B on the decolorization efficiency and total organic carbon (TOC) removal by UVA- TiO_2/Ag . To measure TOC, hydrochloric acid was used as an acidifier to decrease the solution pH to 2, then the solution was injected into a TOC analyzer (TOC-5000, Shimadzu, Japan) for analysis. TOC represents the content of organic carbon in a water sample that cannot be detected by means of biological oxygen demand or chemical oxygen demand determinations. These organic carbons can cause bad odors in water bodies, and are used by microorganisms as nutrient salts, thereby leading to microbial breeding. When using TiO_2/Ag to process high-concentration

MX-5B, both the decolorization efficiency and TOC removal were lower; at a concentration of 100 mg/L, the TOC removal rate was even <20%. The TOC removal rate was better when decolorizing low concentrations of the dye. In general, with higher MX-5B concentrations, the decolorization efficiency by UVA- TiO_2/Ag was worse. This is because in addition to the concentration exceeding the loading of the catalyst, when the treatment solution contained high MX-5B concentrations, the solution color was darker and more dye molecules blocked light access to the solution, thus causing UV light-energy loss. Accordingly, TiO_2 's photocatalytic activity deteriorated, leading to decreases in decolorization and the TOC removal efficiency [15].

3.5. Effects of various pH values on the decolorization efficiency of MX-5B by UVA- TiO_2/Ag

The decolorization efficiencies of MX-5B by UVA- TiO_2/Ag at various pH values are shown in Fig. 10. The initial pH of the 30 ppm MX-5B dye solution was about 6.35, and 50 wt% of the TiO_2/Ag photocatalyst irradiated by UVA for 2 h had an 80% decolorization efficiency of MX-5B; as seen, the decolorization efficiency was the best when the pH was not adjusted.

Before the photocatalysis process, when adjusting the solution to pH 3–5, the solution color change decreased to 1–2%, which would not affect the photocatalysis decolorization efficiency.

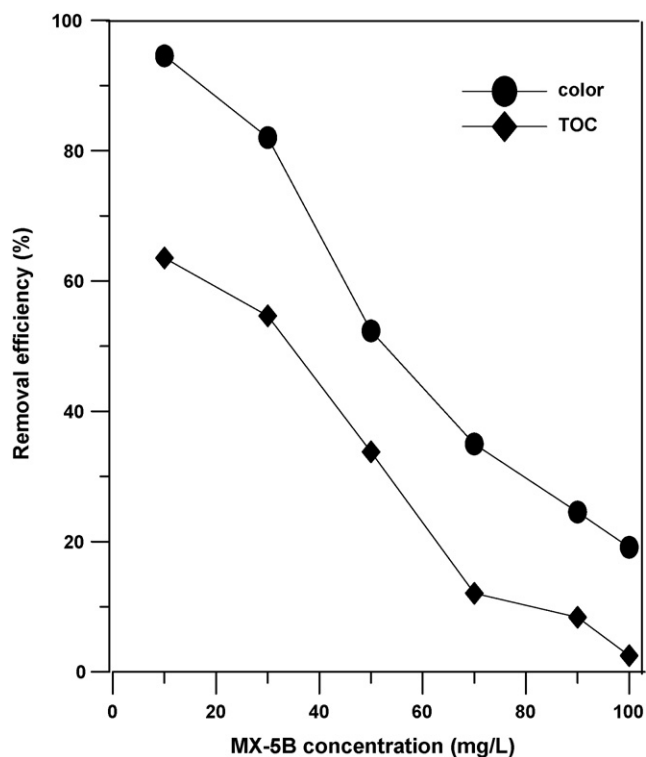


Fig. 9. Effects of various initial concentrations of Procion red MX-5B on the decolorization efficiency and TOC removal by UVA-TiO₂/Ag.

The photocatalytic decolorization efficiency at acidic conditions with UVA-TiO₂/Ag was 70%. The decolorization efficiency in an acidic condition was slightly lower than that in a neutral condition because H⁺ increases in solution in an acidic condition, so that the positive charge in solution rises (Eq. (6)), delaying the tendency

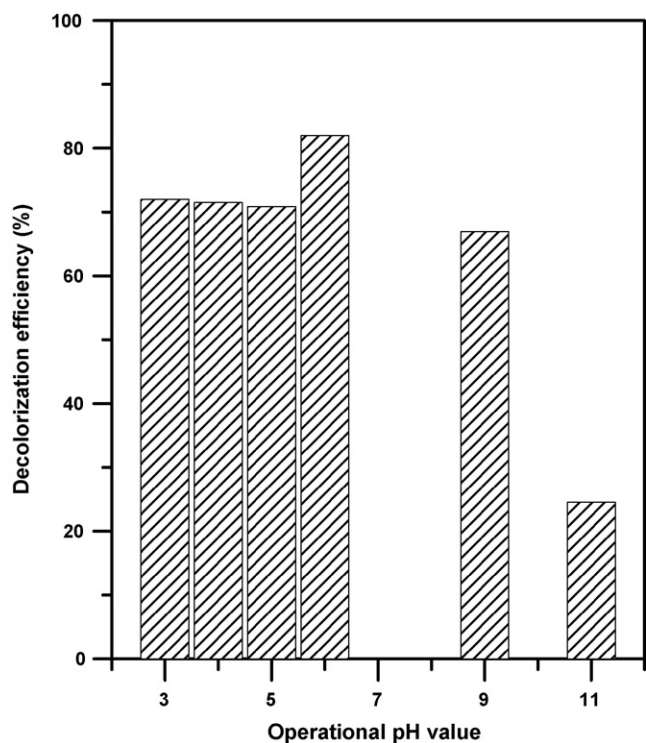


Fig. 10. Effects of various pH values on the decolorization efficiency of Procion red MX-5B by UVA-TiO₂/Ag.

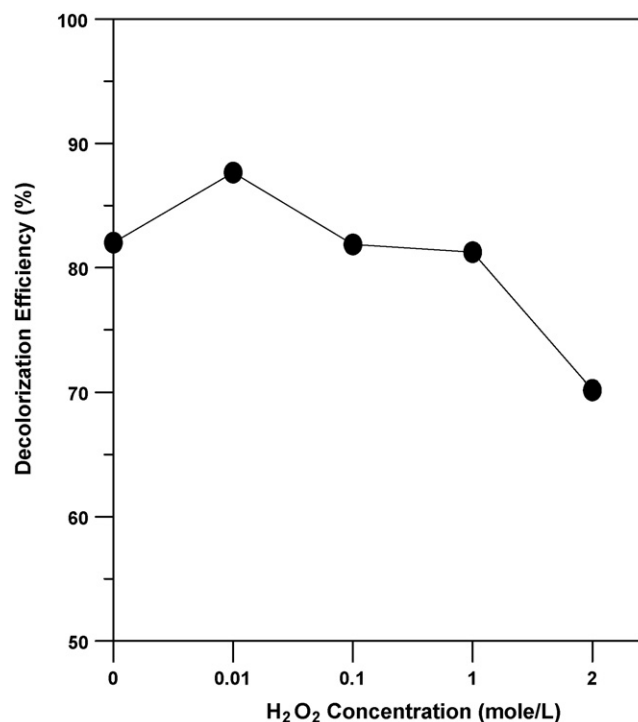


Fig. 11. Effects of H₂O₂ addition on the decolorization efficiency of Procion red MX-5B by UVA-TiO₂/Ag.

of Ag to form an oxidized state [22] (Eq. (7)), and further decreasing the oxidation–decolorization activity of Ag. As a result, the general decolorization efficiency fell.



When adjusting the pH to 9–11 without irradiation, the color of the MX-5B solution decreased as the pH rose; when the pH reached 11, the color fell 20% compared to the case with no adjustment. When adjusting the pH of the solution to 9, the decolorization efficiency of MX-5B by the photocatalytic process was lower than that without adjustment; when the pH was raised to 11, the photocatalytic decolorization efficiency dropped to 30%. It did not benefit from alkalinity degrading the color, which differs from the results of So et al., who suggested that alkaline conditions are conducive in the UV-TiO₂ system to decolorize the MX-5B dye. In this study, the decolorization efficiency by UVA-TiO₂/Ag fell in alkaline conditions because the Ag reacted with hydroxyl ions to form silver hydroxide (AgOH), thus lowering the activities of Ag as it was functioning as an electron scavenger and dye oxidizer. As a result, the decolorization efficiency fell; and the amount of TiO₂ was insufficient to exert an advantage of an excellent decolorization ability in alkaline conditions, thus failing to improve the decolorization efficiency.

3.6. Effects of H₂O₂ addition on the decolorization efficiency of MX-5B by UVA-TiO₂/Ag

This study added various H₂O₂ concentrations, and studied the effects of TiO₂/Ag combined with H₂O₂ on the MX-5B decolorization efficiency, as illustrated in Fig. 11. The background experiment with 0.01 M H₂O₂ with UV irradiation indicated no decolorization effect. As shown in Fig. 11, there was about 80% decolorization efficiency when H₂O₂ was not added. After adding 0.01 M H₂O₂ to the dye, the decolorization efficiency increased by nearly 10%; when the H₂O₂ concentration was increased to 0.1 and 1 M, decolorization efficiencies were lower than that with 0.01 M H₂O₂. If the

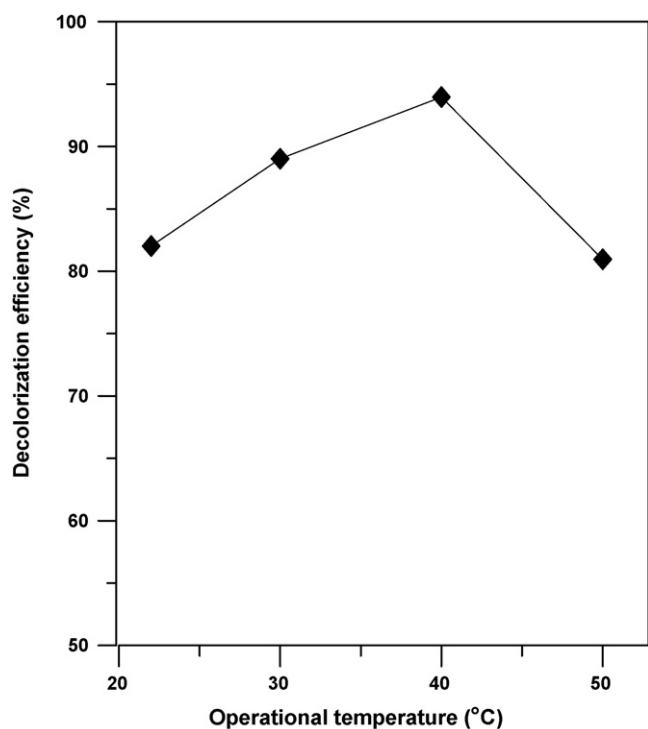


Fig. 12. Effects of various operating temperatures on the decolorization efficiency of Procion red MX-5B by UVA-TiO₂/Ag.

H₂O₂ concentration was raised to 2 M, the decolorization efficiency remained at only 70%. Therefore, the addition of 0.01 M H₂O₂ promoted degradation and decolorization by the UVA-TiO₂/Ag system, but excessive H₂O₂ concentrations decreased the decolorization efficiency. Daneshvar et al. [23] found that with photocatalysis systems combining TiO₂ and H₂O₂, in addition to more hydroxyl free radicals, H₂O₂ also played a role as an electron scavenger to reduce the electron–hole recombination rate, thereby increasing the photocatalytic efficiency. However, overly high concentrations (>0.01 M) of H₂O₂ reacted with hydroxyl free radicals, and the resultant again reacted with hydroxyl free radicals and decreased hydroxyl free radicals in the system, thereby leading to a fall in the photocatalytic efficiency. Similar results were obtained in this study, the UVA-TiO₂/Ag system; thus, an appropriate concentration H₂O₂ should be chosen to enhance the photocatalytic efficiency.

3.7. Effects of various operating temperatures on the decolorization efficiency of MX-5B by UVA-TiO₂/Ag

As shown in Fig. 12, when the operating temperature was increased from a room temperature of 22 to 40 °C, the decolorization efficiency of MX-5B rose accordingly; an increase in the solution temperature implied an increase in the system reaction activation energy, facilitating a rise of the decolorization efficiency. However, when the reaction temperature reached 50 °C, the decolorization efficiency decreased because overly high temperatures accelerate the recombination rate of electron–hole pairs excited from the irradiated TiO₂, thus lowering the photocatalytic decolorization efficiency, which is consistent with the results of Wu and Yu [20], and Rauf and Ashraf [24].

4. Conclusions

This study coated TiO₂ onto an Ag carrier to synthesize a TiO₂/Ag photocatalyst. In the absence of UV irradiation, Ag from the TiO₂/Ag could effectively decolorize Procion red MX-5B due

to its own oxidizing activity. TiO₂ showed photocatalysis properties in the presence of UV irradiation, and Ag from the TiO₂/Ag also played a role as an electron scavenger, delaying the combination of electron–hole pairs. In the photocatalytic process, part of the electrons excited from the irradiated TiO₂ transformed the oxidation state of Ag to metallic Ag, which revived the oxidation activity. Thus these described characteristics enhanced the photocatalytic activity of TiO₂/Ag on MX-5B decolorization to a higher level than with commercial TiO₂. In addition, the heavier Ag carrier improved the solid–liquid separation of nano-TiO₂, thus contributing to TiO₂/Ag being more suitable for application in slurry systems for photocatalytic water treatment.

When the TiO₂ coating ratio of TiO₂/Ag was 50 wt%, a sufficient amount of TiO₂ particles was evenly distributed on the Ag carrier surface, and its photocatalytic decolorization activity was optimal. However, coating excessive TiO₂ led to particle stacking, which decreased photocatalytic decolorization. When TiO₂/Ag was used at various pH values, the decolorization efficiency was optimum at the initial solution pH (6.35). Acidic conditions inhibit Ag's oxidization activity for MX-5B decolorization; while alkaline conditions enable Ag to form AgOH, and also lower the electron-scavenging function and decolorization efficiency. The addition of 0.01 M H₂O₂ aided the photocatalytic decolorization efficiency of UVA-TiO₂/Ag, but excessive H₂O₂ (>0.01 M) in the solution reacted with hydroxyl free radicals to decrease active groups in the system, thereby reducing photocatalytic decolorization. When the operating temperature rose from 20 to 40 °C, the temperature rise facilitated TiO₂/Ag photocatalysis to decolorize MX-5B. Overly high temperatures caused an increase in the electron–hole pair recombination rate and decreased the photocatalysis effect.

Due to the characteristics of the TiO₂/Ag catalyst developed in this study, its decolorization efficiency is present with or without UV irradiation. In addition, preparation of the photocatalyst is very simple, and the cost is economical, too. The results of this study illustrate a new photocatalytic treatment method for dyed wastewater and other pollutants, and further, can act as a basis for developing effective photocatalysts in the absence/presence of light irradiation.

References

- [1] A.S. Kabil, Chlorotriazine reactive azo red 120 textile dye induces micronuclei in fish, *Ecotox. Environ. Saf.* 47 (2000) 149–155.
- [2] S.H. Lin, M.L. Chen, Treatment of textile wastewater by chemical methods for reuse, *Water Res.* 31 (1997) 868–876.
- [3] S. Sirianuntapiboon, P. Srisornsak, Removal of disperse dyes from textile wastewater using bio-sludge, *Bioresour. Technol.* 98 (2007) 1057–1066.
- [4] A.L. Ahmad, S.W. Puasa, Reactive dyes decolorization from an aqueous solution by combined coagulation/micellar-enhanced ultrafiltration process, *Chem. Eng. J.* 132 (2007) 257–265.
- [5] J.H. Mo, Y.H. Lee, J. Kim, J.Y. Jeong, J. Jegal, Treatment of dye aqueous solutions using nanofiltration polyamide composite membranes for the dye wastewater reuse, *Dyes Pigm.* 76 (2008) 429–434.
- [6] R. Gong, Y. Sun, J. Chen, H. Liu, C. Yang, Effect of chemical modification on dye adsorption capacity of peanut hulls, *Dyes Pigm.* 67 (2005) 175–181.
- [7] M. Ahmaruzzaman, Adsorption of phenolic compounds on low-cost adsorbents: a review, *Adv. Colloid Interface Sci.* 143 (2008) 48–67.
- [8] N. Manouchehr, G. Khodayar, M. Kazem, Photocatalytic degradation of azo dye acid Red 114 in water with TiO₂ supported on clinoptilolite as a catalyst, *Desalination* 219 (2008) 293–300.
- [9] M. Saquiba, M.A. Tariqa, M. Faisala, M. Muneerb, Photocatalytic degradation of two selected dye derivatives in aqueous suspensions of titanium dioxide, *Desalination* 219 (2008) 301–311.
- [10] M. Abu Tariq, M. Faisal, M. Saquib, M. Muneer, Heterogeneous photocatalytic degradation of an anthraquinone and a triphenylmethane dye derivative in aqueous suspensions of semiconductor, *Dyes Pigm.* 76 (2008) 358–365.
- [11] N. Sobana, M. Muruganandham, M. Swaminathan, Nano-Ag particles doped TiO₂ for efficient photodegradation of direct azo dyes, *J. Mol. Catal.* 258 (2006) 124–132.
- [12] N. Sobana, K. Selvam, M. Swaminathan, Optimization of photocatalytic degradation conditions of direct red 23 using nano-Ag doped TiO₂, *Sep. Purif. Technol.* 62 (2008) 648–653.

- [13] A.K. Gupta, A. Pal, C. Sahoo, Photocatalytic degradation of a mixture of crystal violet (basic violet 3) and methyl red dye in aqueous suspensions using Ag⁺ doped TiO₂, *Dyes Pigm.* 69 (2006) 224–232.
- [14] C.H. Li, Y.H. Hsieh, W.T. Chiu, C.C. Liu, C.L. Kao, Study on preparation and photocatalytic performance of Ag/TiO₂ and Pt/TiO₂ photocatalysts, *Sep. Purif. Technol.* 58 (2007) 148–151.
- [15] A.V. Rupa, D. Manikandan, D. Divakar, T. Sivakumar, Effect of deposition of Ag on TiO₂ nanoparticles on the photodegradation of reactive yellow-17, *J. Hazard. Mater.* 147 (2007) 906–913.
- [16] C.M. So, M.Y. Cheng, J.C. Yu, P.K. Wong, Degradation of azo dye Procion red MX-5B by photocatalytic oxidation, *Chemosphere* 46 (2002) 905–912.
- [17] C.H. Lin, Y.C. Lin, C.L. Chang, W.C. Chen, S.Y. Cheng, Y.H. Wang, S.C. Lin, S.H. Lee, Photodecomposition of methylene-blue by highly-dispersed nano TiO₂/Ag catalyst, *React. Kinet. Catal. Lett.* 90 (2007) 267–273.
- [18] S. Yamabi, H. Imai, Synthesis of rutile and anatase films with high surface areas in aqueous solutions containing urea, *Thin Solid Films* 434 (2003) 86–93.
- [19] K. Sahel, N. Perol, H. Chermette, C. Bordes, Z. Derriche, C. Guillard, Photocatalytic decolorization of removal black 5 (RB5) and Procion red MX-5B—isortherm of adsorption, kinetic of decolorization and mineralization, *Appl. Catal. B Environ.* 77 (2007) 100–109.
- [20] C.H. Wu, C.H. Yu, Effects of TiO₂ dosage, pH and temperature on decolorization of C.I. reactive red 2 in a UV/US/TiO₂ system, *J. Hazard. Mater.* 169 (2009) 1179–1183.
- [21] A.R. Malagutti, H.A.J.L. Mourão, J.R. Garbin, C. Ribeiro, Deposition of TiO₂ and Ag: TiO₂ thin films by the polymeric precursor method and their application in the photodegradation of textile dyes, *Appl. Catal. B Environ.* 90 (2009) 205–212.
- [22] H. Huo, H. Su, W. Jiang, T. Tan, Effect of trace Ag⁺ adsorption on degradation of organic dye wastes, *Biochem. Eng. J.* 43 (2009) 2–7.
- [23] N. Daneshvar, D. Salari, A.R. Khataee, Photocatalytic degradation of azo dye acid red 14 in water: investigation of the effect of operational parameters, *J. Photochem. Photobiol. A Chem.* 157 (2003) 111–116.
- [24] M.A. Rauf, S.S. Ashraf, Fundamental principles and application of heterogeneous photocatalytic degradation of dyes in solution, *Chem. Eng. J.* 151 (2009) 10–18.