



## Investigation of Photocatalytic Activity and Kinetics of TiO<sub>2</sub> Sensitized by Benzidine Yellow G

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Received: 27 February 2014;

Accepted: 19 May 2014;

Published online: 6 November 2014;

AJC-16205

A new TiO<sub>2</sub> photocatalyst was sensitized with benzidine yellow G by solvothermal synthesis method and characterized by SEM, XRD and FT-IR. The photocatalytic activity and kinetics of the composite were investigated by the photocatalytic degradation of methylene blue, neutral red and xylenol orange under the visible light irradiation. The results show that the photoresponse of TiO<sub>2</sub> has been extended from ultraviolet to visible region. The degradation rate of the three dyes reached to 72-96%. The kinetics of the photocatalytic degradation process of methylene blue was also been discussed and well conformed to the Langmuir-Hinshelwood kinetics model.

**Keywords:** Photocatalytic activity, Kinetics, Benzidine yellow G, TiO<sub>2</sub>.

### INTRODUCTION

TiO<sub>2</sub> is a well-known and efficient photocatalyst due to its strong oxidation capability, non-toxicity and long term photostability<sup>1</sup>. More interests have been focused on the photocatalytic properties of TiO<sub>2</sub> for its complete mineralization of organic pollutants<sup>2-6</sup>. However, TiO<sub>2</sub> is only effective to ultraviolet light ( $\lambda \leq 380$  nm) which is less than 5% of the sun energy<sup>7,8</sup>. So the large band-gap energy (3.2 eV) of TiO<sub>2</sub> obviously limits the utilization of solar light or artificial visible light<sup>7,8</sup>. Many methods, such as rare earth metal ion and transition metal ion modification, non-metal doping and noble metal deposition are applied to enhance the photocatalytic activities of TiO<sub>2</sub><sup>9-12</sup>. Besides, dye sensitization technique is also a general means to broaden the photoresponse properties of TiO<sub>2</sub><sup>13,14</sup>. The dyes adsorbed on TiO<sub>2</sub> are excited under the irradiation of visible light and transferred the electrons to the conduction band of TiO<sub>2</sub> (3.2 eV)<sup>10, 15-23</sup>. Titanium dioxide acts as an electron carrier that dyes collected and conducted. Then the light responds of TiO<sub>2</sub> are extended to visible region.

It is found that dyes sensitized TiO<sub>2</sub> will easily lose visible light activity in the aqueous solution for solubility and instability of the dyes<sup>24,25</sup>. In this work, benzidine yellow G (BYG) was first used to composite with TiO<sub>2</sub>, which is not only for its solvent and light resistance, but also for its absorption of solar lights. The photocatalytic activities and the kinetics of benzidine yellow G/TiO<sub>2</sub> were also investigated on the degradation of methylene blue, neutral red and xylenol orange. The molecular structure of benzidine yellow and the three dyes are illustrated in Fig. 1.

### EXPERIMENTAL

TiO<sub>2</sub>(P25), BYG (Shandong sunshine pigment co., China). All of the materials were used as received. BYG/TiO<sub>2</sub> composite was prepared with solvothermal synthesis method<sup>26</sup>. 0.43 g of BYG was dispersed in 70 mL DMF. 4.5 g TiO<sub>2</sub> and 0.70 mL Span 80 were stirred with above-mentioned mixture till formed a uniform suspension. Then the suspension was sealed and heated at 150 °C in 100 mL Teflon lined reactor for 3.5 h and naturally cooled to room temperature. After several times of centrifugal separation and distilled deionized water wash, the resultant was dried in the oven at 100 °C. Finally the BYG/TiO<sub>2</sub> composites were obtained by careful grinding.

X-ray diffraction (XRD) was recorded by an X'pert pro X-ray diffractometer (PAN Analytical, Holland) with CuK $\alpha$  radiation and the step scan range was from 10° to 80° (2 $\theta$ ) at intervals of 0.017°. Scanning electron microscopy (SEM, JEOL, X-650, Japan) was used to observe the surface physical morphology of BYG and TiO<sub>2</sub>. FT-IR spectra was carried out with Nicolet 380 (Thermo, America) Spectrometer.

**Photocatalytic activity experiment:** The photocatalytic degradation experiment was evaluated by the degradation of methylene blue, xylenol orange and neutral red and carried out by XPA (XuJiang Electromechanical Plant, Nanjing) photochemical reactor. Ultraviolet lights were supplied by a 500 w mercury lamp. And visible lights were provided by 500 w metal halide with an optical filter to get rid of light of wavelength less than 420 nm. The reaction temperature was controlled at about 20 °C with circulating water during the whole experiment. The reaction suspensions were stirred in

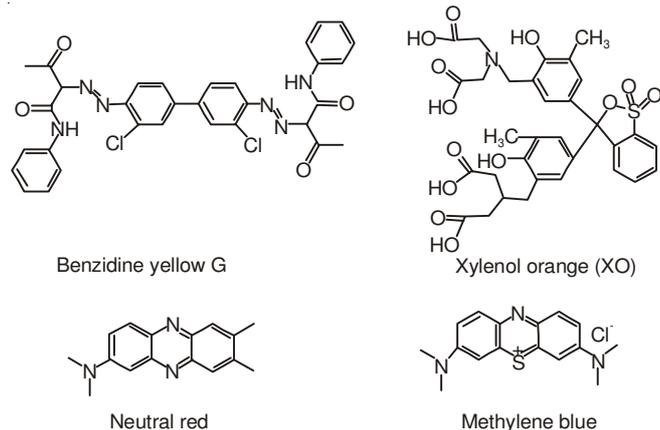


Fig. 1. Molecular structure of benzidine yellow G, methylene blue, neutral red and xylenol orange

the dark to reach adsorption-desorption equilibrium. The photodegradation samples were collected at well-regulated intervals of time and measured by Agilent 8453 UV-visible spectrometer to evaluate the photoactivity of the new catalyst in the irradiation process. The concentration of dye was calculated by its standard curves.

**Dynamic analysis of the degradation process:** The photocatalytic degradation of dye can be described by Langmuir-Hinshelwood kinetics model<sup>27,28</sup>. For relative low concentrations, the Langmuir-Hinshelwood equation can be simplified to a pseudo-first-order kinetic equation<sup>27,28</sup> form as follows:

$$\ln\left(\frac{C_0}{C}\right) = kt$$

In the equation,  $C_0$ ,  $C$  is the initial and the the reaction time concentration of dye molecule, respectively.  $k$  is the pseudo-first-order rate constant and  $t$  is the reaction time.

## RESULTS AND DISCUSSION

**Characteristics of BYG/TiO<sub>2</sub> composites:** The SEM images of TiO<sub>2</sub> and BYG/TiO<sub>2</sub> are shown in Fig. 2. The morphology and size of BYG/TiO<sub>2</sub> are similar to TiO<sub>2</sub> through solvothermal treatment. Fig. 3 is the XRD patterns of TiO<sub>2</sub> and BYG/TiO<sub>2</sub>. The TiO<sub>2</sub> exhibits the typical patterns of anatase and rutile. The peak shapes and positions of BYG/TiO<sub>2</sub> pattern is basically in accordance with original TiO<sub>2</sub>. It is just indicated that the crystalline structure of TiO<sub>2</sub> had no obvious changes after the preparation of BYG/TiO<sub>2</sub>.

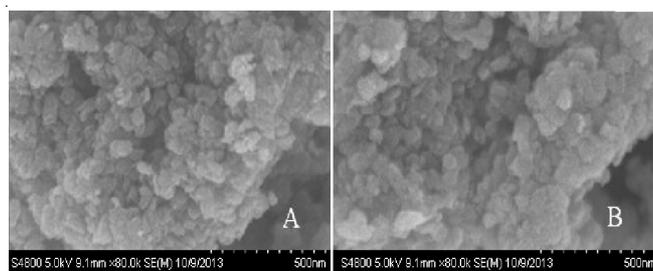


Fig. 2. SEM images of SEM (A)TiO<sub>2</sub> (B) BYG/TiO<sub>2</sub>

The FT-IR spectra of TiO<sub>2</sub>, BYG/TiO<sub>2</sub> and BYG are shown in Fig. 4, which were recorded on a KBr beam splitter. It is

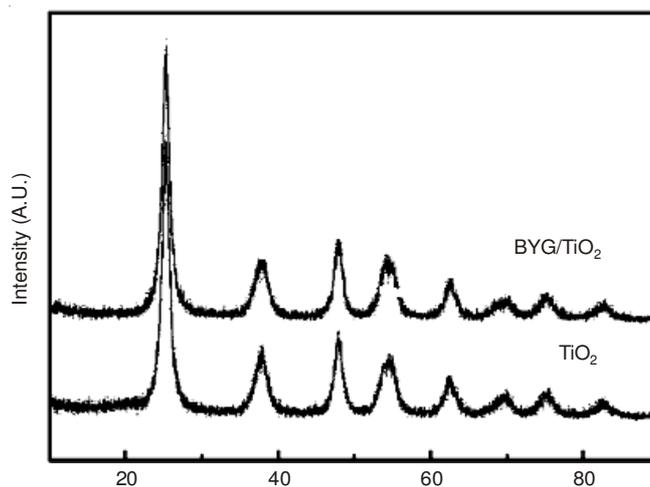


Fig. 3. XRD spectrogram of BYG/TiO<sub>2</sub> and TiO<sub>2</sub>

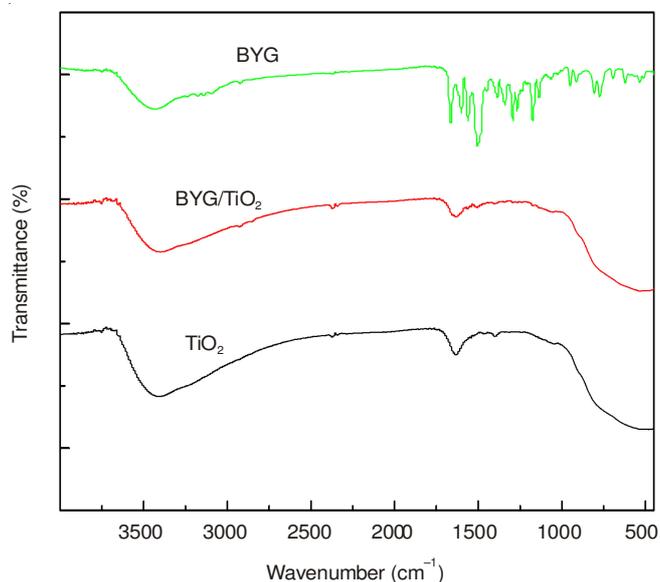


Fig. 4. FT-IR spectra of BYG/TiO<sub>2</sub>, BYG and TiO<sub>2</sub>

known that the characteristic stretching vibration region of TiO<sub>2</sub> is located<sup>27</sup> at 850-400 cm<sup>-1</sup>. By contrast, it can also be concluded that the structure of TiO<sub>2</sub> has not been changed through the synthesis process.

### Photocatalytic activity of BYG/TiO<sub>2</sub>

**Photodegradation of methylene blue:** BYG/TiO<sub>2</sub> (0.4 gL<sup>-1</sup>) and TiO<sub>2</sub> (0.4 gL<sup>-1</sup>) was mixed with methylene blue (2 × 10<sup>-5</sup> molL<sup>-1</sup>) aqueous solution of methylene blue, respectively. The pH of the reaction suspension was measured at 4.6. UV-visible absorption spectra of methylene blue under ultraviolet and visible light irradiation in the presence of BYG/TiO<sub>2</sub> are illustrated in Fig. 5a and 5b. Ahead of irradiation, the above suspensions were kept in dark for 50 min to reach adsorption equilibrium. As Fig. 5c illustrated, the adsorption rate of methylene blue on BYG/TiO<sub>2</sub> and TiO<sub>2</sub> were 45.3 and 8.2 %, respectively. This results indicate that BYG/TiO<sub>2</sub> has stronger adsorption ability than TiO<sub>2</sub>, which indicated that the adsorption capability of BYG/TiO<sub>2</sub> is larger than TiO<sub>2</sub>, which can enhance the degradation of methylene blue at low concentration.

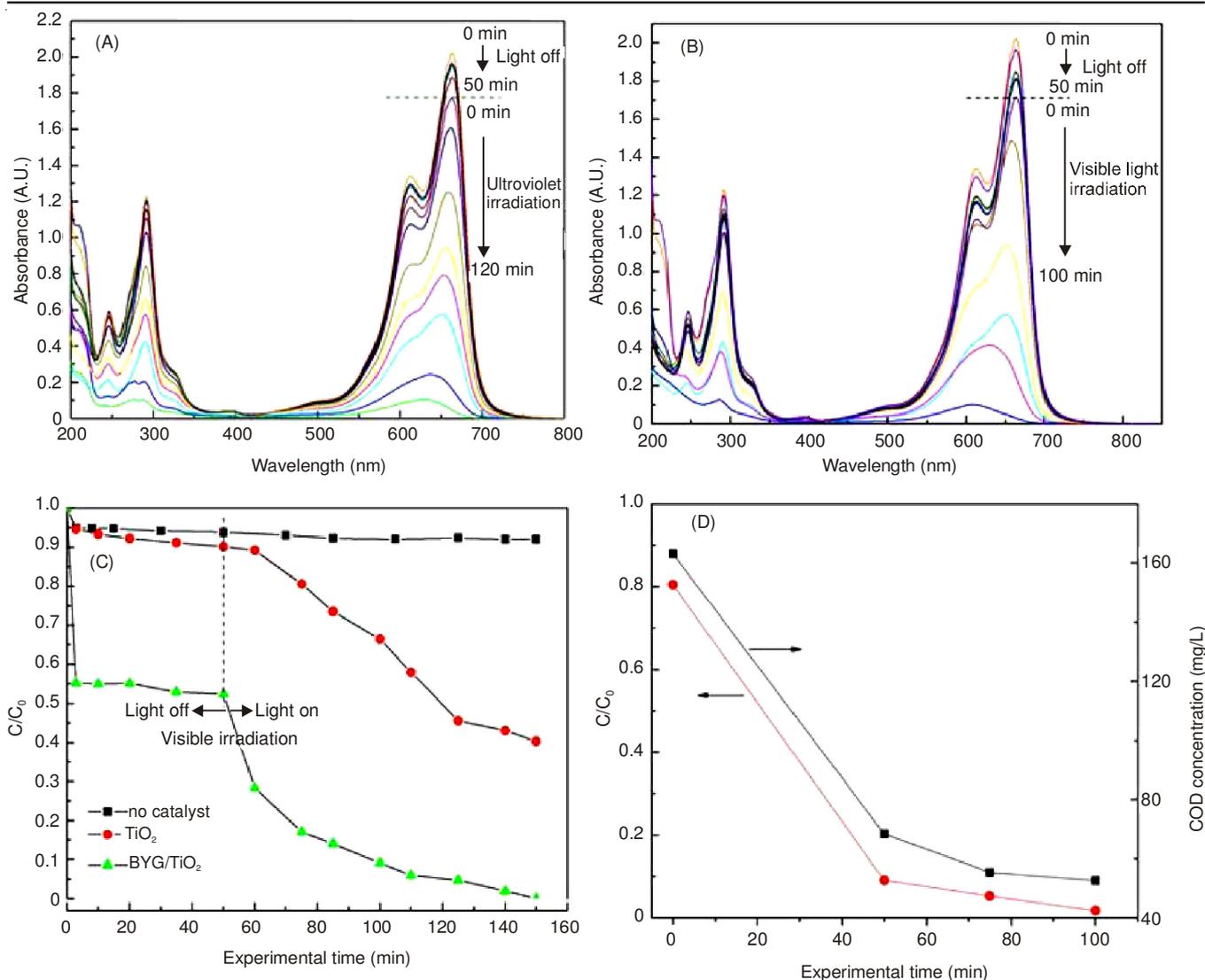


Fig. 5. UV-visible spectral of methylene blue photodegraded by BYG/TiO<sub>2</sub> under (A) ultraviolet irradiation; (B) under visible light irradiation; (C) Photodegradation of methylene blue under visible light irradiation with different catalysts; (D) Variation of chemical oxygen demand (COD) and concentration of methylene blue photodegraded by BYG/TiO<sub>2</sub> in aqueous solutions

In order to compare the photocatalytic activity of BYG/TiO<sub>2</sub> and TiO<sub>2</sub>, the photodegradation experiments were also done under visible light irradiation. The photocatalytic activity was evaluated according to photocatalytic degradation rate to methylene blue in aqueous solution. It is shown that methylene blue did not degrade without photocatalyst and the pure BYG has no photocatalytic activity in the degradation of methylene blue. BYG/TiO<sub>2</sub> performs better photocatalytic activity than the pure TiO<sub>2</sub> under the same experimental conditions.

As the reduction of chemical oxygen demand (COD) reflects the extent of degradation or mineralization of organic species<sup>26</sup>, the chemical oxygen demand during the course of photodegradation was investigated (Fig. 5D). The initial COD of the aqueous solutions of methylene blue ( $2 \times 10^{-4} \text{ mol L}^{-1}$ , catalyst  $0.6 \text{ gL}^{-1}$ )  $173.2 \text{ mg/L}$ . Under the irradiation of visible light for 50 min, the COD value reduced to  $72.6 \text{ mg/L}$  and at the same time the value of  $C/C_0$  is 9.65 %. The reduction of COD and the decrease of the  $C/C_0$  further verified that methylene blue is indeed photodegraded by BYG/TiO<sub>2</sub>. Adsorption is a precondition for heterogeneous catalytic reactions<sup>26</sup>, so methylene blue was better degraded as adsorbed

on BYG/TiO<sub>2</sub>. The BYG/TiO<sub>2</sub> presents its initial yellow shade and does not present obvious red of methylene blue after it has been used. In addition methylene blue was not detected in the washing solvent in recycling experiments. Therefore, the COD concentration did not deduct part of initial adsorption.

#### Photodegradation of neutral red and xylenol orange:

Neutral red and xylenol orange are two common dyes which are often used as titration indicators and staining agents for their good stability. We also investigated the photocatalytic activity of BYG/TiO<sub>2</sub> on the degradation of neutral red and xylenol orange to demonstrate the potential applicability of BYG/TiO<sub>2</sub>. UV-visible absorption spectra of aqueous solution of neutral red and xylenol orange under visible light irradiation in the presence of BYG/TiO<sub>2</sub> are illustrated in Fig. 6A and 7A. Neutral red and xylenol orange were subjected to BYG/TiO<sub>2</sub> and TiO<sub>2</sub> under respective conditions to investigate the catalytic activities. Their initial pH value was 5.2 and 4.0, respectively. The photocatalytic results are illustrated in Fig. 6b and 7b.

Photocatalytic reaction of neutral red after 50 min of adsorption in the dark to establish the equilibrium. It takes

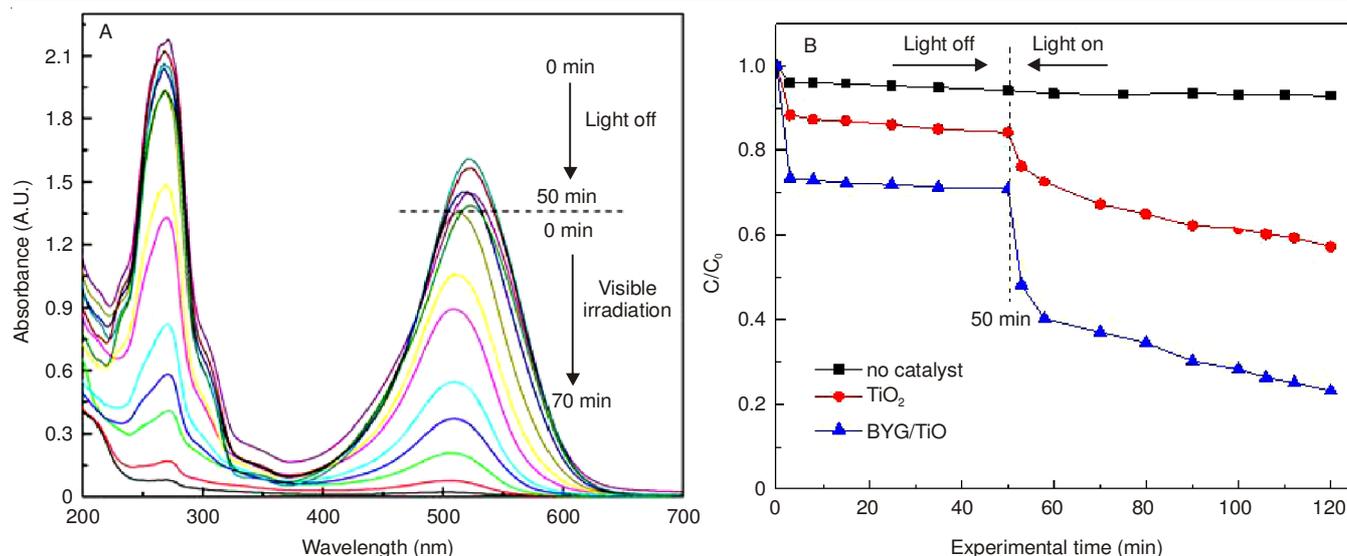


Fig. 6. (A) UV-visible absorption spectra of neutral red (NR) aqueous solution under visible light irradiation in the presence of BYG/TiO<sub>2</sub> at pH = 5.2. (B) Photodegradation of neutral red with BYG/TiO<sub>2</sub> and TiO<sub>2</sub> under visible light irradiation (Initial neutral red concentration was  $4.1 \times 10^{-5}$  mol/L; catalyst dosage was  $0.6$  g/L)

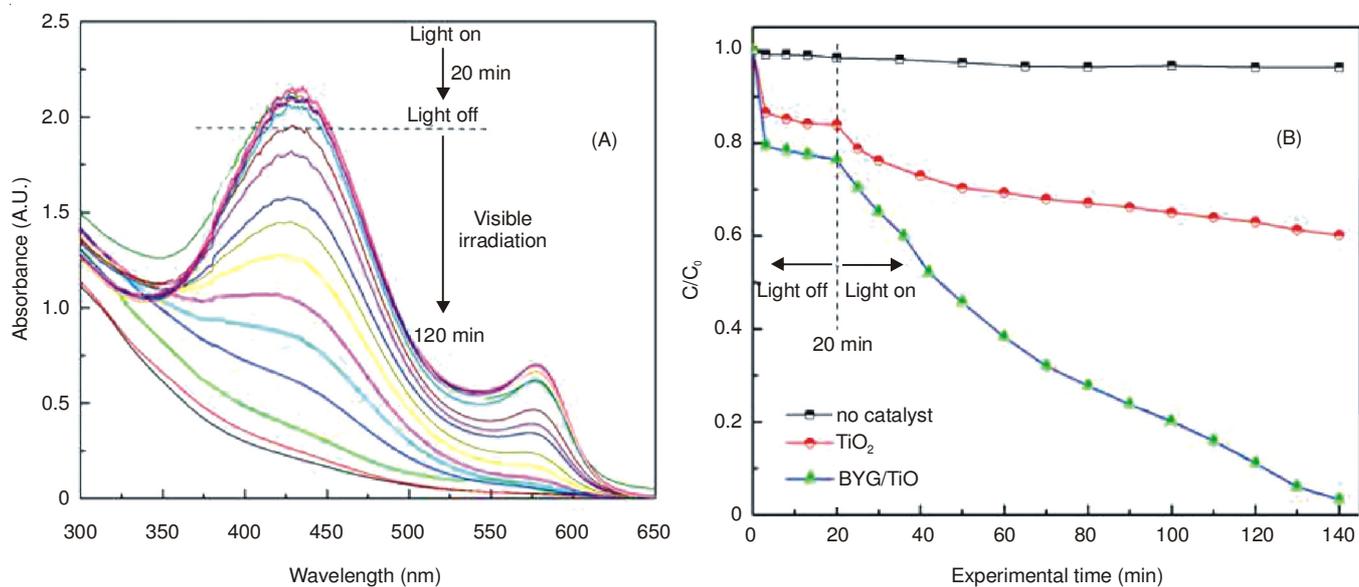


Fig. 7. (A) UV-visible absorption spectra of xylenol orange (XO) aqueous solution under visible light irradiation in the presence of BYG/TiO<sub>2</sub> at pH = 4. (B) Photodegradation of xylenol orange with BYG/TiO<sub>2</sub> and TiO<sub>2</sub> under visible light irradiation (Initial xylenol orange concentration was  $3.6 \times 10^{-5}$  mol/L; catalyst dosage was  $0.6$  g/L)

about 20 min for the equilibrium between the xylenol orange and catalysts. It is indicated that the dyes could reach an equilibrium state on the catalyst in a short time. And the concentration of neutral red and xylenol orange did not decrease obviously in the absence of BYG/TiO<sub>2</sub> and TiO<sub>2</sub> in the dark, which was similar to that of methylene blue and could be explained by the adsorption of the dyes. The photocatalytic efficiency of BYG/TiO<sub>2</sub> to degrade neutral red and xylenol orange is better than that of pure TiO<sub>2</sub> under identical conditions with exposure to visible light. The decolourization ratio of neutral red were 72.6 and 33.8 % with BYG/TiO<sub>2</sub> and TiO<sub>2</sub>. The photodegradation rate of xylenol orange were 93.5 and 35.7 % under the irradiation of visible lights for 120 min. However, pure benzidine yellow-G has no photocatalytic activity in the degradation of neutral red and xylenol orange and the photodegradation ability of TiO<sub>2</sub> is still less than that of BYG/TiO<sub>2</sub>.

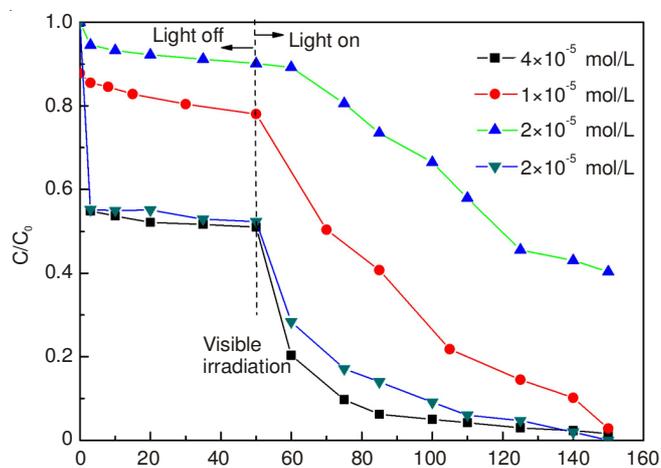


Fig. 8. Photodegradation of different concentration of methylene blue with BYG/TiO<sub>2</sub>

TABLE-1  
RESULTS OF PHOTOCATALYTIC DEGRADATION KINETICS OF METHYLENE BLUE (MB)

Degradation condition	Initial concentration (mol L <sup>-1</sup> )	ln(C <sub>0</sub> /C) ~ t	Related coefficient
TiO <sub>2</sub>	2 × 10 <sup>-5</sup> mol L <sup>-1</sup>	ln(C <sub>0</sub> /C) = 0.00373t	0.975
BYG/TiO <sub>2</sub>	1 × 10 <sup>-5</sup> mol L <sup>-1</sup>	ln(C <sub>0</sub> /C) = 0.00825t	0.965
BYG/TiO <sub>2</sub>	2 × 10 <sup>-5</sup> mol L <sup>-1</sup>	ln(C <sub>0</sub> /C) = 0.00681t	0.983
BYG/TiO <sub>2</sub>	4 × 10 <sup>-5</sup> mol L <sup>-1</sup>	ln(C <sub>0</sub> /C) = 0.00464t	0.952

**Stability of BYG/TiO<sub>2</sub>:** To explore the stability of BYG/TiO<sub>2</sub>, recycling experiments were also conducted under the same reaction conditions. The renewed BYG/TiO<sub>2</sub> was collected after each experiment. The photocatalyst was centrifuged, washed and dried in oven at 100 °C for 0.5 h, then used directly in the next run. The photodegradation rate of methylene blue reached 96.3, 96, 95.9 and 95.8 %. The BYG/TiO<sub>2</sub> composite exhibited better stability.

**Kinetics models of the photodegradation of methylene blue with BYG/TiO<sub>2</sub>:** In the photocatalytic degradation process, the organic dyes in the reaction system absorbs visible lights and lowers its intensity, so the initial concentration of the dye plays an important part on the photocatalytic degradation efficiency<sup>29,30</sup>. From the results of Fig. 8, the photodegradation activity of BYG/TiO<sub>2</sub> (0.4 gL<sup>-1</sup>) with methylene blue decreases as the initial concentration of methylene blue increases. So the increase concentration of methylene blue in the reaction system hinders the lights adsorption and decreased photocatalytic degradation rate of methylene blue. Table-1 shows that the value of constant k increases greatly with the addition of BYG/TiO<sub>2</sub> and decreases smoothly with the concentration increase of methylene blue. The related coefficient values with different initial content of methylene blue are greater than 0.95, which indicates that the photodegradation kinetics of methylene blue with BYG/TiO<sub>2</sub> is in agreement with Langmuir-Hinshelwood kinetics model.

## Conclusion

In this work, a new photocatalyst TiO<sub>2</sub> sensitized with BYG was firstly synthesized and characterized by SEM, XRD. It is found that the modification of TiO<sub>2</sub> with benzidine yellow-G did not change the molecular structure and crystallization performance of TiO<sub>2</sub>. BYG/TiO<sub>2</sub> has more efficient photoactivity and photodegradation ability of dye pollutions than pure TiO<sub>2</sub> under visible lights. The degradation kinetics of BYG/TiO<sub>2</sub> composites corresponds to Langmuir-Hinshelwood kinetics model.

## ACKNOWLEDGEMENTS

This work is supported by Science Development and Project Programs No. 2013ZC1603; Doctor Funds of Binzhou University No. 2009Y02.

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