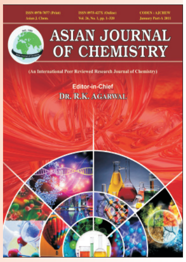
Asian Journal of Chemistry; Vol. 26, No. 22 (2014), 7799-7803

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.17882



Photocatalytic Degradation of Microcystin-LR by Bismuth Tungstate

TINGWEN ZHANG, YANQIU CAO*, AIJUN GONG, YUJIAO WANG and LINA QIU

School of Chemistry and Biology Engineering, University of Science and Technology Beijing, Beijing 100083, P.R. China

*Corresponding author: Fax: +86 10 62333814; Tel: +86 10 62333889; E-mail: yqcaohx@ustb.edu.cn

Received: 24 April 2014; *Accepted*: 25 June 2014; *Published online*: 6 November 2014; AJC-16239

In this study, the photocatalytic degradation of microcystin-LR by bismuth tungstate (Bi_2WO_6) in simulated sunlight process was investigated. The effect of different parameters, such as light intensity, Bi_2WO_6 dosage, reaction temperature, pH and the initial concentration of microcystin-LR were discussed. The degradation rate increased with the increment of light intensity and temperature, due to the increase of number of active cites. The optimal pH was 1.20 and the degradation rate would reduced when the pH increased. Experiments showed that, the ratio of [Bi_2WO_6]/[microcystin-LR] was a constant quantity. Only when the ratio was increased, the degradation rate can be improved. The photocatalytic reaction was also found to follow pseudo-first-order kinetics. Moreover, experiments showed a promising result as for the recycling of Bi_2WO_6.

Keywords: Microcystin-LR, Bismuth tungstate, Photocatalytic degradation.

INTRODUCTION

Microcystin is a kind of cyclic heptapeptide hepatotoxin, which is produced by cyanobacteria blooms. Microcystins can cause adverse effects on bioorganisms and humans by inhibiting protein phosphatases[1]. There are more than 90 kinds of microcystins by now[2]. Microcystins have many variants, such as microcystin-LR, microcystin-RR, microcystin-YR. Amog this, microcystin-LR is the most common and poisonous[3], so WHO rules that the concentration of microcystins should not be higher than 1 μg/L.

Microcystins are very stable in environment because of its cyclic structure and double bond. Microcystins are difficult to lose activity and to volatilize after being boiled and they can not be destroyed at 300 °C. Microcystins can also endure acid and alkaline. Considerable researches of the degradation of microcystin-LR have been made, such as TiO_2 photocatalysis[4-7], Fenton oxidation[8] and other oxidation. TiO_2 is the most widely used due to its high chemical stability and low cost. But TiO_2 can only be activated under UV irridation due to its band gap. Ultra-violet light only represents the 6 % of solar radiation[9], but visible light represents 45 % of sunlight. Therefore, to fully take advantage of sunlight, it is necessary to find new materials that can achieve similar results to TiO_2.

Bismuth tungstate (Bi_2WO_6) is a new kind of photocatalyst and has excellent photocatalytic capacity under simulated solar light[10,11]. Bismuth tungstate as the simplest Aurivillius oxidate consists of bismuth oxide layers (Bi_2O_2) and tungstate oxide layers (WO_6)[12-15]. The energy band gap of Bi_2WO_6 is approximately 2.7 eV. So it can play an important role in photocatalytic degradation under simulated sunlight. It can oxidate many organics which are difficult to biodegrade into inorganic small molecules. For example, the photocatalytic activity of this bismuth tungstate has been demonstrated by the decomposition of water into hydrogen and oxygen and recently in the degradation of organic pollutants such as acetaldehyde, acetic acid, 4-chlorophenol and rhodamine B[16-18]. Many researches have been reported about the photocatalytic capacity of Bi_2WO_6. For example, Tian *et al.* have discussed the photocatalytic performances of Bi_2WO_6 with different morphologies[19]. Chen *et al.* have reported the photocatalytic activity of norfloxacin *via* a simulated solar light by Bi_2WO_6[20]. Tian *et al.* have reported the hydrothermal synthesis of graphitic carbon nitride-Bi_2WO_6 and its degradation of methyl orange was almost 3 and 155 times higher than those of each other[21]. Some researchers have reported that Bi_2WO_6 cannot generate $OH^{\bullet}$ and the main active species were photogenerated holes (h^+), conduction bandelectrons (e_{CB}-) and super oxide radical $(O_2^{\bullet-})$[22-24].

In this work, we report the degradation of microcystin-LR with bismuth tungstate (Bi_2WO_6) as photocatalyst under simulated solar light. There are many factors that can affect degradation rate, such as intensity of light, reaction temperature, the concentration of Bi_2WO_6, pH, reaction time and the initial concentration of microcystin-LR. At last, we do some study on the reaction kinetics and the recycling of Bi_2WO_6.

EXPERIMENTAL

Microcystin-LR standards were purchased from Alexis Company. Methanol, ethanol, acetic acid and acetone (analytical grade), trifluoro-acetic acid (HPLC grade), were all purchased from Beijing Chemical Works, China. Bismuth tungstate (analytical grade) was purchased from Alfa Aesar Chemical, Ltd, Tianjin, China. Rotary evaporator was purchased from Ya rong Biochemical Instrument Works, Shanghai, China. Ultrasonic cleaner was purchased from Ultrasonic Instrument, Ltd, Kunshan, China. Ultra-pure water system was purchased from Millipore Company, USA. Circulating water vacuum pump was purchased from Yuhua Instrument, Ltd, Henan, China. Shimadzu High performance liquid chromatography (HPLC) was purchased from Dikma Company, Japan. Xenon lamp was purchased from Nbet Science and Technology, Ltd, Beijing, China. Acidity meter (PHS-3B) was purchased from Ray Magnetic Instrument Works, Shanghai, China. Constant temperature magnetic stirring instrument was purchased from Ronghua Instrument, Ltd, Jiangsu, China.

Dark adsorption test: 20 mL of 6.22 mg/L microcystin-LR solution was added into a quartz conical flask. The Bi_2WO_6 dosage was 8 g/L. the flask was encased with aluminium foil (For all the dark reactions, without any involvement of light irridation). Then the mixture was stirred magnetically in the dark for 60 min to ensure adsorption-desorption equilibrium of microcystin-LR on the surface of Bi_2WO_6.

Photocatalytic reaction: After the dark adsorption test, the quartz conical flask was put under the xenon lamp. (200-2500 nm, 500 W). Before the photodegradation, the xenon lamp was kept warm for 15 min. Then, the xenon lamp was turned on to initiate the photodegradation. The quartz conical flask was put under constant temperature magnetic stirring instrument to maintain the reaction temperature at 40 ± 1 °C. The magnetic stirring was used to maintain a homogeneous Bi_2WO_6 suspension. About 1 mL of the reaction solution was withdrawn from the flask per 2 h and the reaction solution was centrifuged for 5 min under 12000 rpm, 10 °C before HPLC analysis.

Analysis of microcystin-LR by HPLC: The concentration of microcystin-LR in the reaction solution was measured by HPLC with UV detector at 239 nm wavelength. The detection conditions were as follows: column was 250 × 4.6 mm (Agilent, C18 column); the mobile phase was methanol and water (0.1 % TFA) 62:38 (v/v). The flow rate was 1 mL/min. The column temperature was 25 °C, while the sample volume was 20 μL.

RESULTS AND DISCUSSION

Effects of light intensity: Photocatalytic activities of Bi_2WO_6 were evaluated by degradation of microcystin-LR under simulated solar light irradiation of a xenon lamp. Before irradiation, microcystin-LR was allowed to adsorb on the surface of Bi_2WO_6 in the dark for 60 min to ensure adsorption-desorption equilibrium. To investigate the effects of light intensity, 6.22 mg/L microcystin-LR was photocatalytic degraded by Bi_2WO_6 at dark, 350 and 500 W light intensity, respectively. The Bi_2WO_6 dosage was 8 g/L. 1 mL of the reaction solution was withdrawn from the reactor and centrifuged before HPLC analysis. As shown in Fig. 1(a), nearly 81 % microcystin-LR was degraded in 12 h at 500 W light intensity, while only 42 % microcystin-LR was degraded in 12 h at 350 W light intensity. At 500 W light intensity, microcystin-LR were degraded quickly for 10 h and at the last 2 h, degradation rate was very slow. In addition, as shown in Fig. 1(b), all the reactions were found to follow pseudo-first-order kinetics. The experimental data obviously showed the reaction rate constant were 0.04340 and 0.1427 h^{-1} for 350 and 500 W light intensity, respectively. In other words, the photocatalytic activity of 500 W light intensity was three times that of 350 W. The main reason is the effect of light intensity. It will produce more photoelectrons and then the active sites on the surface of Bi_2WO_6 increase. So more microcystin-LR can be absorbed on the surface of Bi_2WO_6. Therefore, 500 W light intensity was selected as the optimal light intensity and was used in the following experiments.

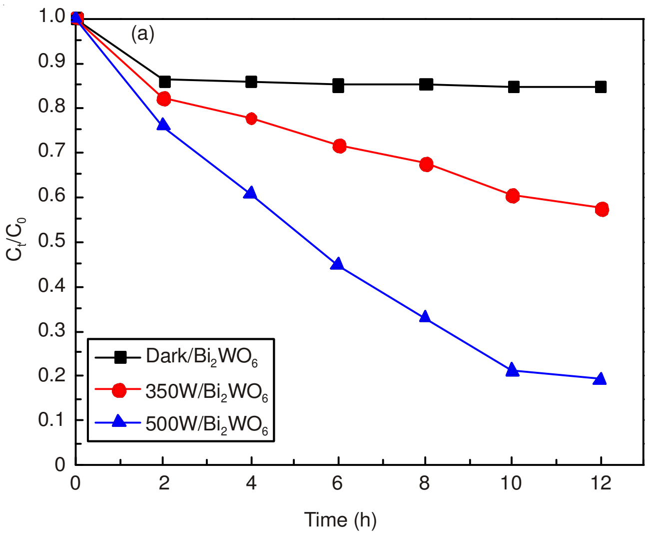


Fig. 1. (a) Effects of light intensity

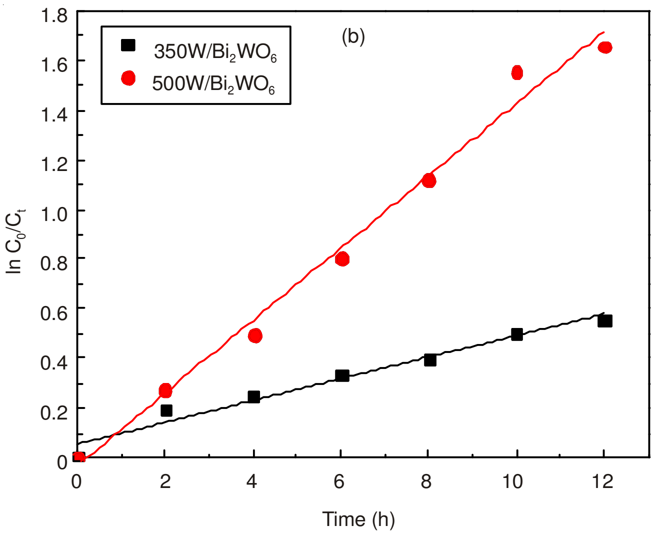


Fig. 1. (b) Reaction kinetics curves of microcystin-LR at 350 and 500 W light intensity, respectively. (Experiment conditions: $[Bi_2WO_6]$ = 8 g/L; $[\text{microcystin-LR}]_0$ = 6.22 mg/L; T = 40 °C; reaction time = 12 h, C_t is the residual concentration of microcystin-LR, C_0 is the initial concentration of microcystin-LR)

Effects of Bi_2WO_6 dosage: The effect of Bi_2WO_6 dosage was studied. As shown in Fig. 2(a), the degradation rate increased with the increase of Bi_2WO_6 dosage. All the reaction data were found to follow pseudo-first-order kinetics. 6.22 mg/L microcystin-LR can be degraded largely with 12 g/L. However, the degradation rate of microcystin-LR by 12 g/L Bi_2WO_6 (83.60 %) was a little higher than 8 g/L Bi_2WO_6 (80.87 %). As shown in Fig. 2(b), the trend of the pseudo-first-order degradation rates can be divided into two stages, in which the rate increased linearly from1 to 8 g/L, then breaked over a Bi_2WO_6 dosage of 8 g/L. This agrees with the result reported by Chen *et al*[25]. The main reason was a result of increment of Bi_2WO_6 dosage, which concurrently produces more electron-hole pairs that can accelerate photocatalytic reactions. But in a heterogeneous system, when the Bi_2WO_6 dosages were overdosed, the reaction system became more muddy, which leaded to a blockage of light penetration. So, the degradation rate became slowly. Therefore, 8 g/L was selected as the optimal Bi_2WO_6 dosage when the concentration of microcystin-LR was 6.22 mg/L.

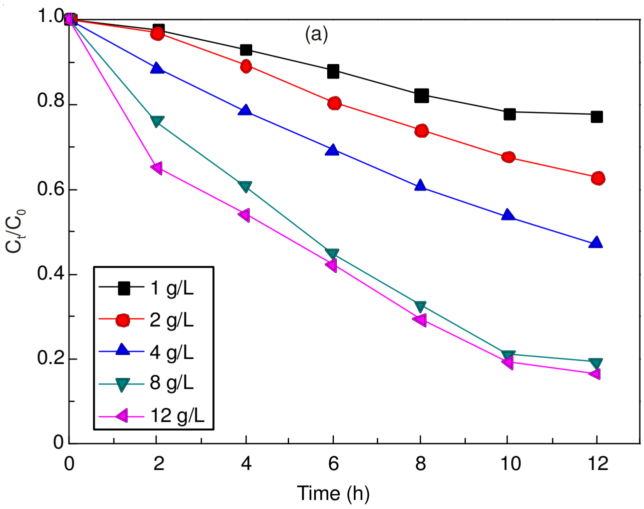


Fig. 2. (a) Effects of Bi_2WO_6 dosages

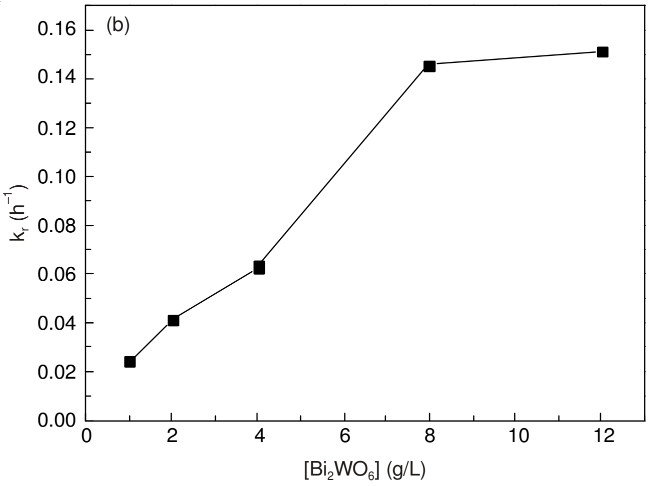


Fig. 2. (b) Reaction rate constant of different Bi_2WO_6 dosages. (Experiment conditons: [microcystin-LR]$_0$ = 6.22 mg/L; T = 40 °C; reaction time = 12 h, K_r is the constant of reaction rate)

Effects of reaction temperature: To investigate the influence of the reaction temperature, microcystin-LR was degraded at 30, 40 and 50 °C. The result was shown in Fig. 3. The degradation rate increased with the increase of reaction temperature. Raise reaction temperature can help accelerate reaction. All the reaction data were found to follow pseudo-first-order reaction kinetics. More than 81 % of microcystin-LR was decomposed within 12 h at 40 °C, compared to that observed at 30 °C (76 %) and nearly 83 % microcystin-LR was degraded at 50 °C. The reaction rate constant of 50 °C (0.1530 h^{-1}) was higher than that of 40 °C (0.1454 h^{-1}). The increase of reaction temperature can accelerate photodegradation rate. Therefore, 50 °C was selected as the optimal temperature and was used in the following experiments.

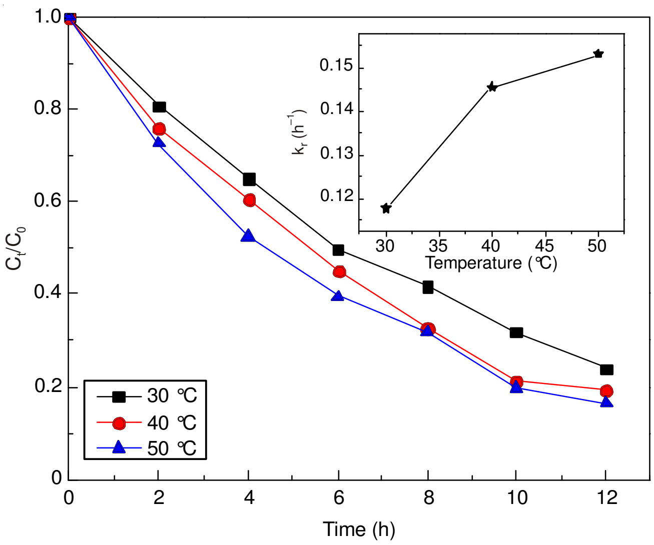


Fig. 3. Effects of reaction temperature. (Experiment conditons: [microcystin-LR]$_0$ = 6.22 mg/L; [Bi_2WO_6] = 8g/L; reaction time = 12 h)

Effects of the pH of reaction solution: Fig. 4 demonstrates the influence of the initail pH of reaction solution, where the degradation rate increased with the reduction of pH and reached an optimal at pH = 1.2. Theoretically, pH of the reaction solution may significantly affect the degradation activity of photocatalyst. For most heterogeneous reacion, the degradation rate was mostly dependent on the concentration of

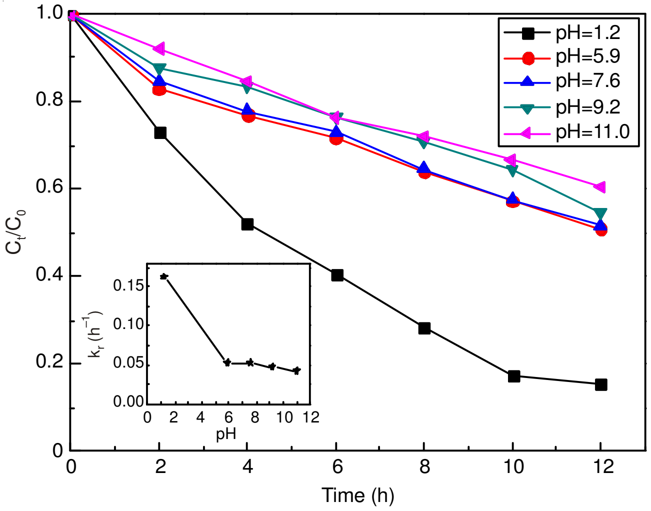


Fig. 4. Effects of pH of reaction solution (Experiment conditions: [microcystin-LR]$_0$ = 6.22 mg/L, [Bi_2WO_6] = 8 g/L, reaction time = 12 h, t = 50 °C, using HCl and NaOH for pH adjust)

hydrogen ion (H^+) or hydroxide (OH^-) in aqueous solution. The initial pH of reaction solution was prepared at 1.2, 5.9, 7.6, 9.2 and 11. Obviously, The degradation rate decreased as the pH levels increased from 1.2 to 11. When the pH was higher than 5.9, the difference between neutral and alkaline conditions was very weak. Therefore, the degradation rate decreased may due to the electrostatic repulsion between microcystin-LR and the surface of Bi_2WO_6.

Effects of the initial concentration of microcystin-LR: To investigate the consequences of microcystin-LR concentration on the kinetics of microcystin-LR degradation, 6.22, 12.13, 24.73 and 53.93 mg/L microcystin-LR was photodegraded by 8 g/L Bi_2WO_6 at pH = 1.2. As shown in Fig. 5(a), the photodegradation rate continuously decreased as $[\text{microcystin-LR}]_0$ increased from 6.22 to 53.93 mg/L. Nearly 84 % micro-cystin-LR was degraded at $[\text{microcystin-LR}]_0$ = 6.22 mg/L for 12 h, while only 39 % microcystin-LR was degraded at $[\text{microcystin-LR}]_0$ = 53.93 mg/L. As shown in Fig. 5(b), in which the pseudo first-order reaction rate constants of micro-cystin-LR degradation were found to be reduced when the concentration of microcystin-LR increased. The main reason is that the ratio of [catalyst dosage]/$[\text{microcystin-LR}]_0$ decreased, where Bi_2WO_6 dosage was kept as a constant when the $[\text{microcystin-LR}]_0$ increased[26].

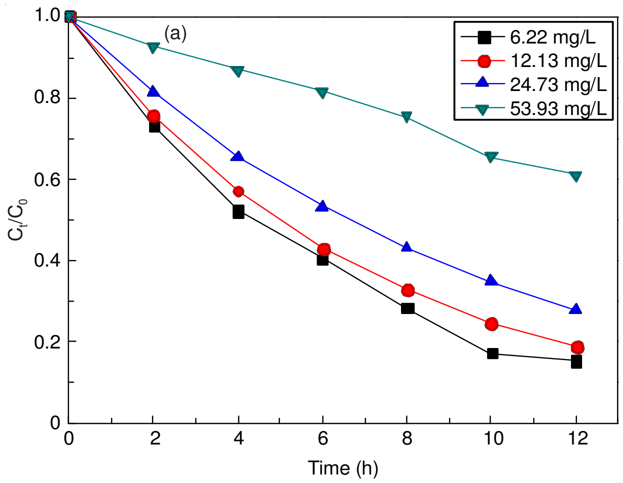


Fig. 5. (a) Effects of initial concentration of microcystin-LR

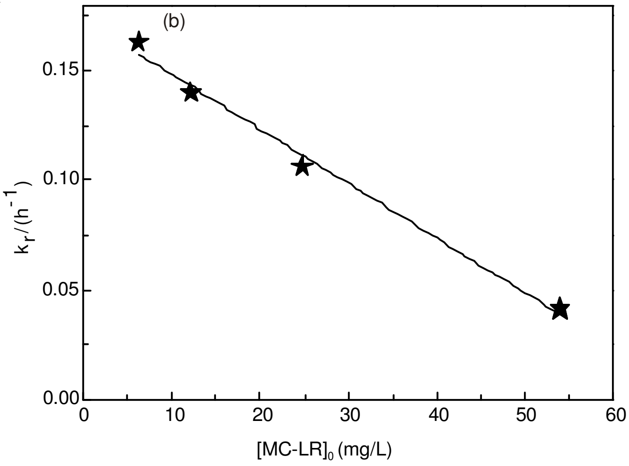


Fig. 5. (b) Reaction rate constant of different initial concentrations of microcystin-LR. (Experiment conditions: [Bi_2WO_6] = 8 g/L; reaction time = 12 h; pH = 1, t = 50 °C)

Reaction kinetics: Most of the heterogeneous photocatalysis reaction are accorded with Langmuir-Hinshel-wood (LH) kinetics model:

$$r = -\frac{dC}{dt} = \frac{kKC}{1+KC} \tag{1}$$

where r is the photodegradation rate of microcystin-LR, C is the initial concentration of microcystin-LR, t is reaction time, k is reaction rate constant, K is adsorption equilibrium constant. In this study, $[\text{microcystin-LR}]_0 <<10^{-3}$ mol/L, KC << 1, so eqn. 1 can be transformed to eqn. 2:

$$r = -\frac{dC}{dt} = kKC = K_{app}C \tag{2}$$

the linear expression of equation 2 is:

$$\ln\left(\frac{C_0}{C_r}\right) = K_{app}t \tag{3}$$

In eqn. 3, C_0 and C_t are the concentration of microcystin-LR when the reaction time are 0 and *t* min.

K_{app} is the apparent rate constant. After plotting $\ln(C_0/C_t)$ *vs.* time, a good linear correlation with a correlation coefficient of $R^2 = 0.9885$ was obtained (Fig. 6). The slope is K_{app}, $K_{app} = 0.1633\ h^{-1}$. $R^2 = 0.9885 > 0.95$, so the photo-degradation reaction was followed to pseudo-first-order kinetics.

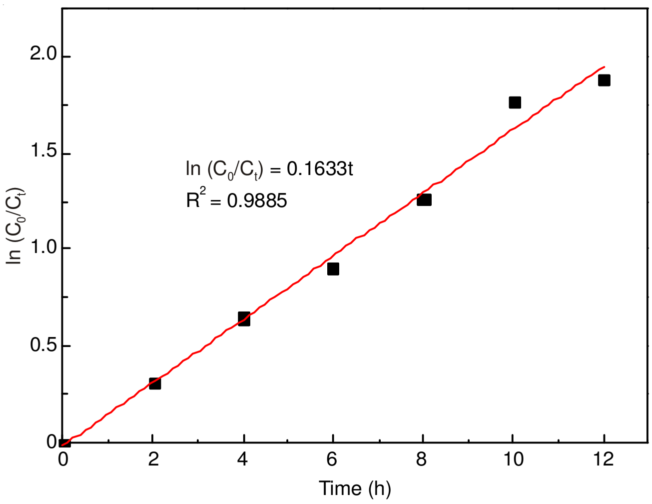


Fig. 6. Kinetics curves of microcystin-LR photodegraded by Bi_2WO_6 (experiment conditions:$[\text{microcystin-LR}]_0$ = 6.22 mg/L, [Bi_2WO_6] = 8 g/L, pH = 1.2, T = 50°C)

Reuse of Bi_2WO_6: In order to realize the maximization of Bi_2WO_6 utilization, the reuse of Bi_2WO_6 was investigated. The initial concentration of microcystin-LR was 6.22 μg/mL, the reaction solution was 9 mL. 0.072 g Bi_2WO_6 was used for the first time. After photodegradation, Bi_2WO_6 was used again through filtration, seperation and drying. The result was shown in Fig. 7. Bi_2WO_6 was used for three times successively. The result showed that Bi_2WO_6 had a good photodegradation on microcystin-LR every time. Because of the loss during filtration and separation (Table-1, nearly 16 % Bi_2WO_6 was lost each time) photodegradation rate was decreased in the same time period. The difference between the first time and the second time was negligible. But at the third time, the photodegradation rate was decreased obviously, nearly 69 % microcystin-LR was degraded at the third time, while almost 83 % microcystin-LR was degraded at the first and second time.

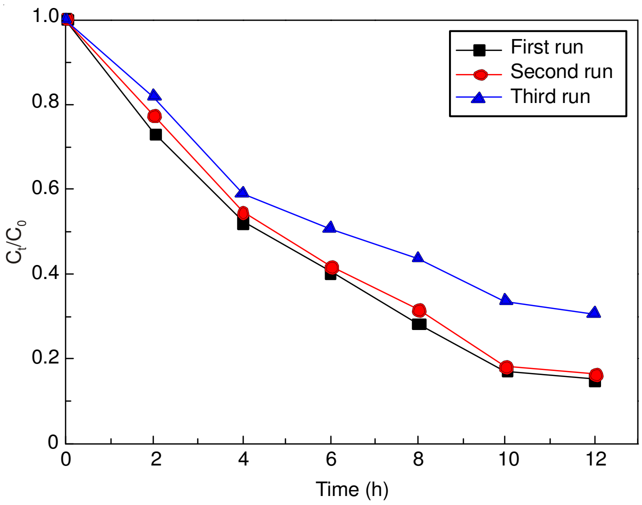


Fig. 7. Reuse of Bi_2WO_6. (Experiment conditons: [microcystin-LR]$_0$ = 6.22 mg/L; [Bi_2WO_6] = 8 g/L; reaction time = 12 h; pH = 1; t = 50 °C)

TABLE-1
REPEATED USE OF CATALYST

Use times	First	Second	Third
Bi_2WO_6 dosage/(g)	0.0720	0.0612	0.0498

Verification experiments: According to the optimal photodegradation conditions, we had a verification experiment. We test the photodegradation of microcystin-LR by Bi_2WO_6 for three times. The photodegradation of microcystin-LR by Bi_2WO_6 was determined. As shown in Table-2, the degradation rate was greater than 83 % and the average photodegradation rate was 84.57 %, so the method of microcystin-LR photodegraded by Bi_2WO_6 was stable and practicable.

TABLE-2
RESULTS OF MICROCYSTIN-LR
PHOTODEGRADATION BY Bi_2WO_6

Times	[MC-LR]$_0$ (mg/L)	[MC-LR]$_t$ (mg/L)	Degradation rate (%)
1	6.22	0.95	84.7
2	6.22	1.02	83.6
3	6.22	0.92	85.2
Average	6.22	0.96	84.5

Conclusion

In this study, the simulated solar light/Bi_2WO_6 photocatalytic method showed a good performance in microcystin-LR degradation. More than 84 % microcystin-LR can be degraded by Bi_2WO_6. The effect of different parameters, such an light intensity, Bi_2WO_6 dosage, reaction temperature, pH and the initial concentration of microcystin-LR was investigated. The results showed that the photocatalytic activity of 500 W light intensity was three times that of 350 W. The degradation rate increased with the increment of Bi_2WO_6 dosage, but leveled off at 8 g/L. The main reason was that more Bi_2WO_6 can produce more electron-hole pairs, but when Bi_2WO_6 was overdosed, the system became more muddy, so the degradation rate became slowly.The effect of pH made a big difference. It had a higher removal at pH = 1.2. The reaction temperature also made a difference on the degradation rate. The photo-degradation process was conformed to Langmuir-Hinshelwood (LH) kinetics model. The process was found to follow pseudo-first-order kinetics. The reuse of Bi_2WO_6 showed a promising result, after the third time of catalyst recycling, the microcystin-LR still remained 69 % degradation rate. So we can realize a maximum of Bi_2WO_6 utilization.

ACKNOWLEDGEMENTS

This study was financially supported by Project of Engineering Research Institute of University of Science and Technology Beijing (YJ2009-016).

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